



FATİH UNIVERSITY

The Graduate School of Sciences and Engineering

**Doctor of Philosophy in
Chemistry**

**THE PRODUCTION OF AZOLE FUNCTIONAL
NOVEL PROTON CONDUCTIVE MEMBRANES FOR
POLYMER ELECTROLYTE MEMBRANE FUEL
CELL (PEMFC) APPLICATIONS**

by

Deniz SİNİRLİOĞLU

**Ph.D.
2016**

January 2016



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A thesis submitted to

the Graduate School of Sciences and Engineering

of

Fatih University

in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

Chemistry

January 2016
Istanbul, Turkey

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Ph.D. Thesis – Chemistry
January 2016

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ABSTRACT

Proton exchange membrane (PEM) is the critical component for the operation of a fuel cell. It serves as an electrolyte for transporting protons from the anode to the cathode and as a separator to prevent mixing of the fuel gases. DuPont's Nafion and its analogues are the most widely used PEMs since they have high chemical stability, excellent mechanical properties and provide high proton conductivity in the fully hydrated state. However, at elevated temperatures due to loss of humidity, conductivity falls down dramatically, which is a barrier to the development of high performance fuel cells. The present thesis is dedicated to the development of anhydrous PEMs, which can be successful alternatives to Nafion providing comparable conductivities at low temperatures and enhanced conductivities at high temperatures.

In this context, several novel anhydrous PEMs consisting of various types of homopolymers, random copolymers, and blends as well as distinct graft structures have been successfully prepared and characterized fully. These are reported under different headings in a reasonable order focusing primarily on the functional moieties responsible for proton transport in the anhydrous systems. In the first part, synthesis of methacrylate/ methacrylamide based azole functional homopolymers, denoted as PMA-Tri-(TA)_x; PMA-ATri-(TA)_x; PMA-ATet-(TA)_x, was carried out via a post-polymerization functionalization of poly(methacryloyl chloride) with triazole, amino-triazole, and aminotetrazole. These were then doped with triflic acid to obtain the desired membranes. In the succeeding sections, a novel monomer, 5-(methacrylamido)tetrazole was synthesized and further employed in the preparation of a series of methacrylate based PEMs. These studies partly involve production of PEMs

by blending the homopolymer of the afore-mentioned methacrylic monomer with sulfonated polysulfone (SPSU-PMTeX blend) and poly(vinyl phosphonic acid) separately. This simple approach eliminated the addition of acid dopants, resulting in better film formabilities in cases where relatively higher acid contents were used. In the remaining sections, 5-(methacrylamido)tetrazole was copolymerized with 1-vinyl-1,2,4-triazole and with several other monomers containing different types of acid functionalities, such as sulphonic acid, phosphonic acid, and boronic acid. Some of these copolymers were also doped with phosphoric acid to facilitate the proton transport.

In the final parts, PVDF based anhydrous PEMs were prepared via a simple “grafting through” strategy. The PVDF powder was treated with potassium hydroxide (KOH) yielding $-\text{CH}=\text{CF}-$ double bonds in the main chain. Upon respective usage of the alkaline treated PVDF as a macromonomer in conjunction with vinyltriazole (VTri) and glycidyl methacrylate (GMA) in the graft copolymerization, anhydrous PEMs were obtained. In the former, doping with triflic acid afforded (PVDF-*g*-PVTri-(TA)_x), whereby in the latter, poly(vinyl phosphonic acid) was reacted with poly(glycidyl methacrylate) grafts and (PVDF-*g*-PGMA-*g*-PVPA(x)) was obtained. Besides, synthesized PVDF-*g*-PGMA copolymers were functionalized with 5-aminotetrazole (ATet), and subsequently doped with triflic acid (TA) at several mole ratios with respect to tetrazole units. Finally PVDF-*g*-PGMA-ATet-(TA)_x membranes were fabricated. All membranes were characterized with Fourier Transform Infrared Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (¹H-NMR, ¹³C-NMR, ³¹P-NMR, and ¹⁹F-NMR), Elemental Analysis (EA), and Energy-Dispersive X-ray Spectroscopy (EDS). The thermal properties of the samples were analyzed via Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). The surface roughness, crystallinity, and morphology of the membranes were studied using Atomic Force Microscopy (AFM), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The electrochemical stability of the materials was tested by Cyclic Voltammetry (CV). The proton conductivity of the membranes was studied using impedance spectroscopy.

Keywords: Fuel cell, proton conductivity, 5-(methacrylamido)tetrazole (MTet), vinyl triazole (VTri), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), glycidyl methacrylate (GMA), 5-aminotetrazole (ATet), vinyl phosphonic acid (VPA), vinyl benzene boronic acid (VBBA), graft copolymer, PVDF, alkaline treated method.

POLİMER ELEKTROLİT MEMBRAN YAKIT HÜCRESİ UYGULAMALARI İÇİN AZOL FONKSİYONLU YENİ PROTON İLETKEN MEMBRANLARIN HAZIRLANMASI

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Doktora Tezi – Kimya
Ocak 2016

Tez Danışmanı: Doç. Dr. Ali Ekrem MÜFTÜOĞLU

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ÖZ

Proton değişim membran (PEM), yakıt pilinin çalışması için önemli bir bileşendir. Proton değişim membran, yakıt pillerinde anot ve katot arasında proton iletimini sağlayan ve bu bölgedeki yakıt gazlarının karışmasını engellemek amacıyla, ayırıcı ve elektrolit olarak kullanılır. DuPont firması tarafından üretilen Nafyon ve türevleri en yaygın olarak kullanılan proton geçirgen membranlardır. Nafyon'un yüksek termal ve kimyasal dayanıklılığının yanında, iletkenliğinin neme bağlı olması ve nemli olan membranın kuruması nedeniyle, yakıt pili performansı ve membran ömrü azalmaktadır. Bu tezde, yüksek sıcaklıklarda yüksek iletkenliğe ve düşük sıcaklıklarda Nafyon ile kıyaslanabilir iletkenlik değerlerine sahip ve Nafyon'a alternatif olabilecek nemsiz (susuz) proton geçirgen membranlar geliştirilmiştir.

Bu kapsamda, çeşitli homopolimerleri, rasgele kopolimerleri ve farklı aşırı yapılarını içeren bazı yeni nemsiz (susuz) proton geçirgen membranlar başarılı bir şekilde hazırlandı ve tamamen karakterize edildi. Nemsiz sistemlerde proton iletimini sağlayan ve yapısında fonksiyonel grupları bulunduran bu membranlar farklı başlıklar altında rapor edildi. Birinci bölümde, poli (metakriloil klorür) polimeri sentezlenip triazol, aminotriazol ve aminotetrazol bileşikleriyle fonksiyonlandırılarak “PMA-Tri-(TA)_x; PMA-ATri-(TA)_x; ve PMA-ATet-(TA)_x” olarak adlandırılan metakrilat / metakrilamit bazlı azol fonksiyonel homopolimerlerin sentezi gerçekleştirildi. İstenilen membranları elde etmek için, azol fonksiyonel homopolimerler trifilik asit ile dop edildi. Diğer bölümde, yeni bir monomer olan 5-(metakrilamido)tetrazol monomeri sentezlendi ve bazı metakrilat bazlı proton geçirgen membranların hazırlanmasında kul-

lanıldı. Bu çalışmalar, kısmen yukarıda bahsedilen metakrilik monomerin homopolimeri ile ayrı ayrı sülfonatlı polisülfon (SPSU-PM TetX) ve poli (vinil fosfonik asit) homopolimerlerinin harmanlanmasıyla proton geçirgen membranların üretimini içerir. Bu basit yaklaşım, nispeten daha yüksek asit içeriği kullanılan sistemlerde daha iyi bir membran oluşturmak için kullanılan asit dopanların eklenmesini ortadan kaldırmıştır. Geri kalan bölümlerde, 5-(metakrilamido) tetrazol monomerinin 1-vinil-1,2,4-triazol ve sülfonik asit, fosfonik asit ve borik asit içeren asit fonksiyonel gruba sahip farklı monomerler ile kopolimerleri hazırlandı. Bu kopolimerlerin bazıları, proton iletimini kolaylaştırmak için, fosforik asit ile dop edilmiştir.

Son bölümde, basit bir yöntem olan “aşılama” yoluyla PVDF esaslı susuz proton değişim membranlar hazırlandı. PVDF tozu, ana zincirde -CH=CF- çift bağı oluşturmak için potasyum hidroksit (KOH) ile muamele edildi. Alkalınasyon yöntemiyle elde edilen PVDF makromonomer olarak kullanılarak, vinyltriazole (VTri) ve glisidil metakrilat (GMA) monomerlerinin PVDF üzerine aşılama ile susuz proton değişim membranlar elde edildi. İlk elde edilen aşı kopolimer trifilik asit ile dop edilerek (PVDF-*g*-PVTri-(TA)_x) aşı kopolimer membranları; diğer aşı kopolimer ise (PVDF-*g*-PGMA) poli (vinil fosfonik asit) ile tepkimeye sokularak (PVDF-*g*-PGMA-*g*-PVPA(x)) aşı kopolimer membranları elde edildi. Ayrıca, elde edilen PVDF-*g*-PGMA aşı kopolimerleri 5-aminotetrazol (ATet) ile modifiye edilip trifilik asit ile dop edilerek PVDF-*g*-PGMA-ATet-(TA)_x membranları elde edildi. Bu çalışmalarda sentezlenen membranlar, Fourier Dönüşümlü Kızılötesi Spektroskopisi (FTIR), Nükleer Manyetik Rezonans Spektroskopisi (¹H-NMR, ¹³C-NMR, ³¹P-NMR ve ¹⁹F-NMR), elementel analiz (EA) ve Enerji Dağılımlı X-ışını spektroskopisi (EDS) yöntemleri kullanılarak karakterize edildi. Numunelerin ısısal özellikleri termogravimetrik analiz (TGA) ve diferansiyel taramalı kalorimetri (DSC) ile analiz edildi. Membranların yüzey kalınlığı, kristalinitesi ve morfolojisi, Atomik Kuvvet Mikroskobu (AFM), X-ışını kırınımı (XRD) ve Taramalı Elektron Mikroskobu (SEM) kullanılarak incelendi. Maddelerin elektrokimyasal kararlılığı döngüsel voltametri (CV) ile test edildi. Membranların proton iletkenliği empedans spektroskopisi ile incelendi.

Anahtar Kelimeler: Yakıt pili, proton iletkenlik, 5-(metakrilamido)tetrazol (MTet), vinil triazol (VTri), 2-akrilamido-2-metil-1-propansülfonik asit (AMPS), glisidil metakrilat (GMA), 5-aminotetrazol (ATet), vinil fosfonik asit (VPA), vinil benzen boronik asit (VBBA), aşı kopolimer, PVDF, alkalınasyon yöntemi.

To my parents

ACKNOWLEDGEMENT

First and foremost, I would like to express my gratitude to my supervisor Assoc. Prof. Dr. Ali Ekrem MÜFTÜOĞLU for his motivation, helpful discussion, stimulating and incentive suggestions at every stage of the research and in the preparation of this thesis. In addition, his valuable times of consultation and editing that went into the completion of this dissertation were unbelievable.

I thank to my co-supervisor, Prof. Dr. Ayhan BOZKURT, for his generous assistance and insightful discussions during my study. Besides, I specially thank to him for opening his lab and research facilities for my use.

I would like to thank Prof. Dr. Hanifi SARAÇ and Assoc. Prof. Dr. Kurtuluş GÖLCÜK for serving on my thesis supervisory committee. I am grateful to them for their careful and critical reading of my thesis and invaluable suggestions.

I want to thank to Head of the Chemistry Department, Prof. Dr. Abdulhadi BAYKAL, for his motivation and support during my thesis.

I would like to thank to Mr. İbrahim ŞAŞMAZ for measuring the NMR spectra, and for helpful discussions. I am grateful to Fatih University-BINATAM center for the SEM, EDS, XRD and AFM measurements. Also, my special thanks go to Dr. Mehmet ŞENEL, Res. Assist. Sümeyye Bahçeci SERTKOL, and Res. Assist. Emre ÇEVİK, for helping me measure and obtaining the cyclic voltammetry (CV) data. My special thanks go to Dr. Sevim ÜNÜGÜR ÇELİK, with whom I shared numerous memorable and valuable experiences at the university. Also, my special thanks go to Dr. Serhat GÜNDÜZ for his heartfelt helps and valuable advices.

I would like to thank to Fatih University for kindly providing financial support and scholarship throughout this research.

I express my thanks and appreciation to my all family for their understanding, motivation and patience. Finally, I want to express my gratitude to my dear wife Zeynep for her heartfelt encouragements and patience during I prepare my PhD thesis.

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LIST OF SYMBOLS AND ABBREVIATIONS

SYMBOL/ABBREVIATION

AFC	Alkaline Fuel Cell
AFM	Atomic Force Microscopy
AIBADC	α,α' -Azodiisobutyramidine dihydrochloride
AIBN	α,α' -azobisisobutyronitrile
AMPS	2-acrylamido-2-methyl-1-propanesulfonic acid
ATet	5-Aminotetrazole
ATri	3-Amino-1,2,4-triazole
ATRP	Atom Transfer Radical Polymerization
BnIm	Benzimidazole
^{13}C -NMR	^{13}C -Nuclear Magnetic Resonance Spectroscopy
CV	Cyclic Voltammetry
DCE	1,2-dichloroethane
DG	Degree of Grafting
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DS	Degree of Sulfonation
DSC	Differential Scanning Calorimeter
EA	Elemental Analysis
EDS	Energy-Dispersive X-ray Spectroscopy
ETFE	Poly(ethylene- <i>alt</i> -tetrafluoroethylene)
FC	Fuel Cell
FEP	poly(tetrafluoroethylene- <i>co</i> -hexafluoropropylene)
FTIR	Fourier Transform Infrared Radiation
GMA	Glycidyl methacrylate
^1H -NMR	^1H -Nuclear Magnetic Resonance Spectroscopy

HETCOR	Two-dimensional heteronuclear ^{13}C - ^1H NMR methods
Im	Imidazole
MCFC	Molten Carbonate Fuel Cells
MEA	Membrane Electrode Assembly
MeIm	1-Methylimidazole
MTet	5-(methacrylamido)tetrazole
NMP	<i>N</i> -methylpyrrolidone
NMR	Nuclear Magnetic Resonance
PA	Phosphoric acid
PAFC	Phosphoric acid fuel cells
PAMPS	Poly(2-acrylamido-2-methyl-1-propane sulfonic acid)
PBI	Polybenzimidazole
PEEK	Poly(ether ether ketone)
PEM	Proton Exchange Membrane or Polymer Electrolyte Membrane
PEMFCs	Polymer Electrolyte Membrane Fuel Cells
PFA	Poly(tetrafluoroethylene-co-perfluoropropylvinylether)
PFSA	Perfluorosulfonic acid
PMAC	Poly(methacryloyl chloride)
PMTet	Poly(5-(methacrylamido)tetrazole)
PSSA	Poly(styrene sulfonic acid)
PSU	Polysulfone
PTFE	Poly(tetrafluoroethylene)
PVDF	Poly(vinylidene fluoride)
PVBBA	Poly (vinyl benzene boronic acid)
PVPA	Poly(vinylphosphonic acid)
PVTri	Poly(vinyl triazole)
Py	Pyrazole
RH	Relative Humidity
SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cells
SPEEK	Sulfonated poly(ether ether ketone)
SPSU	Sulfonated polysulfone
TA	Trifluoromethanesulfonic acid or Triflic acid
TEA	Triethylamine

Tet	Tetrazole
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
TMSCS	Trimethylsilyl chlorosulfonate
ToF-SIMS	Time-of-flight secondary ion mass spectroscopy
Tri	Triazole
VBBA	4-vinyl benzene boronic acid
VIm	1-vinylimidazole
VP	4-vinylpyridine
VPA	Vinyl phosphonic acid
VTri	1-vinyl-1,2,4-triazole
WSP	Water soluble polymer
WU	Water Uptake
XPS	X-ray photoelectron spectroscopy
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Fuel cell systems have been alternative energy sources which convert the chemical energy directly into electrical energy. They are regarded as key components for exploitation of the energy stored in hydrogen molecules. Fuel cells, in general, are attractive because they provide an innovative alternative to current power sources with higher efficiencies, renewable fuels, and a lower environmental cost. These attractive features have led to numerous initiatives toward the realization of fuel cell technology for practical applications (Celik, 2012a).

Among various types of fuel cells, particularly proton exchange membrane fuel cells (PEMFCs), also referred to as polymer electrolyte membrane fuel cells (PEMFCs), have garnered a great deal of attention due to their high energy conversion efficiency and their ability to address the environmental concerns related to current energy production (Sezgin et al., 2014; Celik et al., 2012b). Proton exchange membranes (PEMs) are the key components in fuel cell systems, and serve as an electrolyte for transporting protons from the anode to the cathode and as a separator to prevent mixing of the fuel gases (Sasa et al., 2013). Perfluorosulfonic acid (PFSA) membranes, the best known example of which is DuPont's Nafion, are the most widely used PEMs. These membranes have high chemical stability, excellent mechanical properties and provide high proton conductivity in the fully hydrated state (Abdel-Hady et al., 2013; Golcuk et al., 2013; Celik et al., 2012b). They have hydrophilic and hydrophobic regions and the proton transfer occurs via water molecules present in their hydrophilic channels. These acidic polymers have high water uptake and in humidified conditions their usage are limited to 100 °C. Furthermore, high price, low stability at high temperatures, low

conductivity at low humidity or high temperature and high methanol permeability of Nafion are barriers to the development of high performance fuel cells (Li et al., 2010).

As alternatives to Nafion, sulfonic acid and phosphonic acid functional polymers were most commonly used. For this purpose, sulfonic acid functional aliphatic and aromatic polymers such as poly(styrene sulfonic acid), polysulfone, and phosphonic acid functional polymers such as poly(vinylphosphonic acid) (PVPA) were used as proton conductive material. Although these acidic polymers have high proton conductivity, they could not be used above 100 °C which the conductivity tends to decrease due to humidity loss (Celik et al., 2012b; Parvole et al., 2008; Goktepe et al., 2008; Kaltbeitzel et al., 2007; Lufrano et al., 2000). Therefore, alternative systems should be prepared that are cheaper than Nafion and with high proton conductivities at elevated temperatures.

A principal approach for enabling operation of PEMs at higher temperature is the replacement of water with alternative proton solvents having higher boiling points (Celik, 2012a; Celik et al., 2012b). These solvents may be strong acids like H_3PO_4 (Li et al., 2013; Ye et al., 2012; Pu et al., 2008) or especially heterocyclic molecules such as imidazole (Liu et al., 2007; Pu et al., 2001; Yamada et al., 2005), benzimidazole (Kim et al., 2007), triazole (Sasa et al., 2013; Ozden et al., 2010a; Sen et al., 2010; Guhathakurta et al., 2009; Gunday et al., 2006) and tetrazole (Boroglu et al., 2011; Ozden et al., 2010b; Celik et al., 2008) since they have high boiling points which makes them attractive for synthesis of more temperature tolerant proton conductive membranes that can be applicable to various electrochemical devices such as fuel cells at elevated temperatures. The proton transfer in those systems are provided via hydrogen bonding between acid or heterocyclic molecules.

Although these molecules can be intercalated into the polymer membrane, their leaching out problem lead the scientists to prepare matrices that have heterocyclic compounds attached to the polymer backbone. For example, poly(vinyl imidazole), poly(vinyl triazole) and poly(vinyl tetrazole) were synthesized and used as proton conductive polymers after doping with phosphoric or triflic acid (Pu et al., 2008; Celik et al., 2008d; Li et al., 2005; Pu et al., 2001). In these systems, the aliphatic chain improves its fabrication property, and the triazole or tetrazole side groups may act as

proton donors and acceptors in the presence of acid dopants. The proton transport occurs between hydrogen bonds of neighboring heterocyclic units through structure diffusion (Celik et al., 2012b; Sinirlioglu et al., 2013).

However, acid dopants may also present similar “leaching out” problems. So as to eliminate the addition of acid dopants, an alternate approach is to synthesize copolymers comprising both *N*-heterocyclic monomers such as vinyl imidazole, vinyl tetrazole, vinyl triazole and acidic monomers such as vinyl phosphonic acid (VPA), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) (Celik et al., 2010; Celik et al., 2008b; Celik et al., 2008c; Martwiset et al., 2007; Erdemi and Bozkurt, 2004; Bozkurt, 2003). High proton conductivity was obtained in these studies in anhydrous conditions and with no dopant. Another facile and established approach to serve this goal is blending acid functional polymers such as poly(styrene sulfonic acid) (PSSA), sulfonated polysulfone (SPSU), and poly(vinyl phosphonic acid) (PVPA) with azole containing polymers such as poly(vinyl triazole) (PVTri) and polybenzimidazole (PBI) with high proton conductivities (Boroglu et al., 2013; Lufrano et al., 2012; Aslan and Bozkurt, 2011; Celik and Bozkurt, 2011; Pu et al., 2010; Aslan and Bozkurt, 2009; Bingol et al., 2008; Goktepe et al., 2008).

Sufficient proton conductivities at elevated temperatures can be maintained via the above-mentioned methods. However, it is not only the increased proton conductivities of membranes that must be considered for the operation and effectiveness of a fuel cell, it is also the mechanical and thermal stability of the PEMs that must be enhanced in these studies. For this purpose, use of engineering plastics as the main membrane material have been successfully achieved. Usually, the reported works involve polytetrafluoroethylene (PTFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(tetrafluoroethylene-co-perfluoropropylvinylether) (PFA), poly(ethylene-*alt*-tetrafluoroethylene) (ETFE), poly(ether ether ketone) (PEEK), and poly(vinylidene fluoride) (PVDF) films. Among them, PVDF has attracted continuous interest due to its relatively lower cost, high chemical resistance, and enhanced thermal and mechanical properties (Sezgin et al., 2013; Arslantas et al., 2014; Liu et al., 2013; Golcuk et al., 2013; Lepit et al., 2012; Sui et al., 2012; Roh et al., 2010). In most of these works, PVDF was modified to impart new functionalities via a number of grafting technologies using UV-light (Golcuk et al., 2013; Sasa et al., 2013),

X-ray and gamma radiation (Lepit et al., 2012; Liu et al., 2011; Fei et al., 2010), the ozone method (Chiang et al., 2009; Chang et al. 2009, Chang et al. 2008), atom transfer radical polymerization (ATRP) (Sui et al., 2012; Meng et al., 2011; Liu et al., 2010; Roh et al., 2010; Kim et al., 2008) and alkaline treatment (Liu et al., 2013; Tang et al., 2009). However, there are almost no reports in literature regarding the production of PVDF based anhydrous PEMs, and therefore, it is quite novel to explore the potential of anhydrous PEMs in fuel cell research.

In the present thesis, methacrylate/methacrylamide based triazole and tetrazole functional polymer electrolyte membranes were produced via post-polymerization functionalization. Then, 5-(methacrylamido)tetrazole (MTet) monomer was prepared by the reaction of methacryloyl chloride with 5-aminotetrazole. Novel copolymer electrolyte membranes based on MTet and 4-vinyl benzene boronic acid (VBBA), 1-vinyl-1,2,4-triazole (VTri), vinyl phosphonic acid (VPA), and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), respectively, were synthesized by conventional free-radical polymerization at several monomer feed ratios. Some of these copolymers were doped with phosphoric acid to facilitate the proton transport. Then, novel composite membranes were produced by blending poly(5-(methacrylamido)tetrazole) (PMTet) with sulfonated polysulfone (SPSU) and poly(vinylphosphonic acid) (PVPA), respectively. In the final part, a simple “grafting through” approach was employed in the preparation of PVDF based anhydrous PEMs. Alkaline treated PVDF was used as a macromonomer in combination with vinyltriazole (VTri) and glycidyl methacrylate (GMA) in the graft copolymerization, respectively, and anhydrous PEMs were obtained. The obtained membranes were characterized with FTIR, ^1H -NMR, ^{13}C -NMR, ^{19}F -NMR, ^{31}P -NMR, elemental analysis, and EDS. The thermal properties of the samples were analyzed with TGA and DSC. The surface roughness and morphology of the membranes were studied using Atomic Force Microscopy (AFM), X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). The electrochemical stability of the materials was tested by cyclic voltammetry. The proton conductivity of the membranes was studied using impedance spectroscopy.

1.2 FUEL CELLS

In the 21st century, energy shortages and environmental pollution are priority global concerns. Fuel cell (FC) technology is a promising solution to these challenges, because fuel cells can generate energy efficiently without pollutant release (the final product is water if hydrogen is applied as the fuel) since they are highly efficient and do not emit pollutants such as SO_x, NO_x, and CO₂, compared to the coal combustion engines (Song et al., 2013; Celik et al., 2012b).

Fuel cells (FCs) are electrochemical devices that can directly convert the chemical energy from a fuel into electricity through a chemical reaction with oxygen or another oxidizing agent (Song et al., 2013, Zaidi et al., 2008). They are different from batteries in that they require a constant source of fuel and oxygen to run, but they can produce electricity continually for as long as these inputs are supplied. Instead of burning fossil fuels, a fuel cell is kind of battery that produce energy by electrochemical reaction of fuel and oxygen. Hydrogen is generally used as fuel source in fuel cell applications. Methane, natural gas, ethanol, methanol are also other fuels are used. Product of reaction of oxygen and hydrogen is just water and heat, so there is no polluting staff. Global warming, clean environment and decreasing of existing fuel resources are most important reasons of interests in fuel cells. In concept of works about clean transportation and environment, fuel cells are thought to be very good candidate as fuel for automobiles and stationary systems. Portable power applications are another area that fuel cells are widely being used as alternative device for batteries. Mobile phones, laptop computers and other personal digital assistant applications are all in concept of this area (Song et al., 2013; Celik, 2012a).

The principle of the first crude fuel cell was first discovered by William Grove in 1839. After years, NASA demonstrated some potential applications in providing power and drinking water in space flights. As a result of this, industry started to recognize potential commercial applications of fuel cell driven by technical, economic, and social forces such as high performance reliability, durability, characteristics, and environmental feasibility. They are used to power fuel cell vehicles, including automobiles, buses, forklifts, airplanes, boats, motorcycles and submarines. Commercial applications of fuel cells gradually became more attractive over the past five decades. This acceptance was primarily driven by the growing demand for environmentally

friendly power plants, for vehicle and stationary energy applications (see Fig. 1.1) (Fuel Cell Today: London, U.K. 2012), zero-emission power sources for confined environments, and high energy density power sources for mobile devices (Kraytsberg et al., 2014).

Fuel cells consist of three main parts are anode (negative electrode), cathode (positive electrode) and between these two electrodes, the electrolyte (membrane). Hydrogen gas is sent to the anode electrode and oxygen is sent to the Cathode electrode. When hydrogen molecules passes through the tubes are separated molecular ions (electrons and protons) from molecular structure. Electrolyte does not allow electron transfer but just hydrogen ions can pass and achieve the cathode electrode. Electrons are transferred to the cathode by external circuit. At the cathode hydrogen ions, electrons and oxygen combine and complete the cycle. Pure water and heat are by products of the cycle. Catalysts have been using in fuel cells to improve the efficiency of the process (Celik et al., 2012b, Zaidi et al., 2008). Fuel cells may be classified based on the used criteria to different methods which typically depend on the different parameters related to operating conditions and fuel cell structure. Fuel cell systems have different variables such as type of the electrolyte used in fuel cell, type of the exchanged ion through the electrolyte, type of the reactants (e.g. primary fuels and oxidants), operating temperature and pressure, direct and indirect usage of the primary fuels in fuel cell system, and finally the primary and regenerative systems. It is common that fuel cells are generally classified and nominated based on the nature of used electrolyte in the fuel cell (Kim et al., 2015, Lin et al., 2000). Therefore, based on this classification, fuel cells include the following different types: (1) alkaline fuel cells (AFC) with the alkaline solution electrolyte (such as potassium hydroxide KOH), (2) phosphoric acid fuel cells (PAFC) with acidic solution electrolyte (such as phosphoric acid), (3) solid proton exchange membrane (PEMFC) which are known to polymer electrolyte membrane fuel cells and their electrolyte consist of the proton exchange membrane, (4) molten carbonate fuel cells (MCFC) with molten carbonate salt electrolyte, and (5) solid oxide fuel cells (SOFC) with ceramic ion conducting electrolyte in solid oxide form (Kim et al., 2015; Celik, 2012a; Celik et al., 2012b; Kraytsberg et al., 2014). Table 1.1 and Figure 1.2 demonstrate the typical characteristics of these various fuel cell systems. Fuel cells can be used as highly efficient and non-polluting power sources.

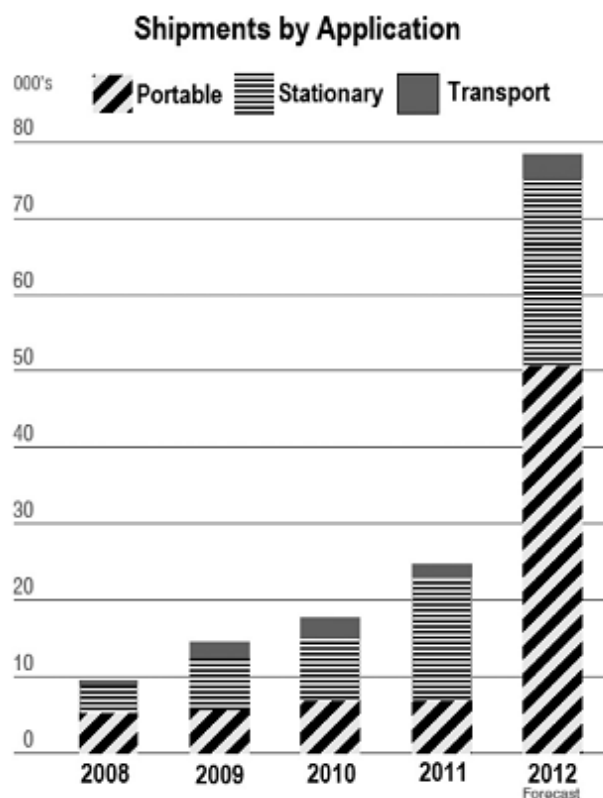


Figure 1.1 Annual fuel cell system shipments worldwide (Fuel Cell Today: London, U.K., 2012).

Table 1.1 Summary of major differences of the fuel cell types (Kim et al., 2015, Golcuk 2011; Peighambardoust et al., 2010). (A: Anode; C: Cathode)

Fuel Cell	Electrolyte	Temperature (°C)	Electrochemical reaction	Applications
Alkaline (AFC)	Potassium Hydroxide	90-100	A: $\text{H}_2 + 2\text{OH}^- \rightarrow 2\text{H}_2\text{O} + 2\text{e}^-$ C: $1/2\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$	Military Space Flight
Phosphoric Acid (PAFC)	Phosphoric Acid	175-200	A: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ C: $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	Electric Utility Transportation
Molten Carbonate (MCFC)	Lithium, Sodium and/or Potassium Carbonate	600-800	A: $\text{H}_2 + \text{CO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{CO}_2 + 2\text{e}^-$ C: $1/2\text{O}_2 + \text{CO}_2 + 2\text{e}^- \rightarrow \text{CO}_3^{2-}$	Electric Utility
Solid Oxide (SOFC)	Zirconium Oxide doped by Yttrium	600-1000	A: $\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^-$ C: $1/2\text{O}_2 + 2\text{e}^- \rightarrow \text{O}^{2-}$	Electric Utility
Proton Exchange Membrane (PEM)	Solid Organic Polymer (poly-perfluorosulfonic acid)	60-100	A: $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$ C: $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$	Electric Utility Portable Power Transportation

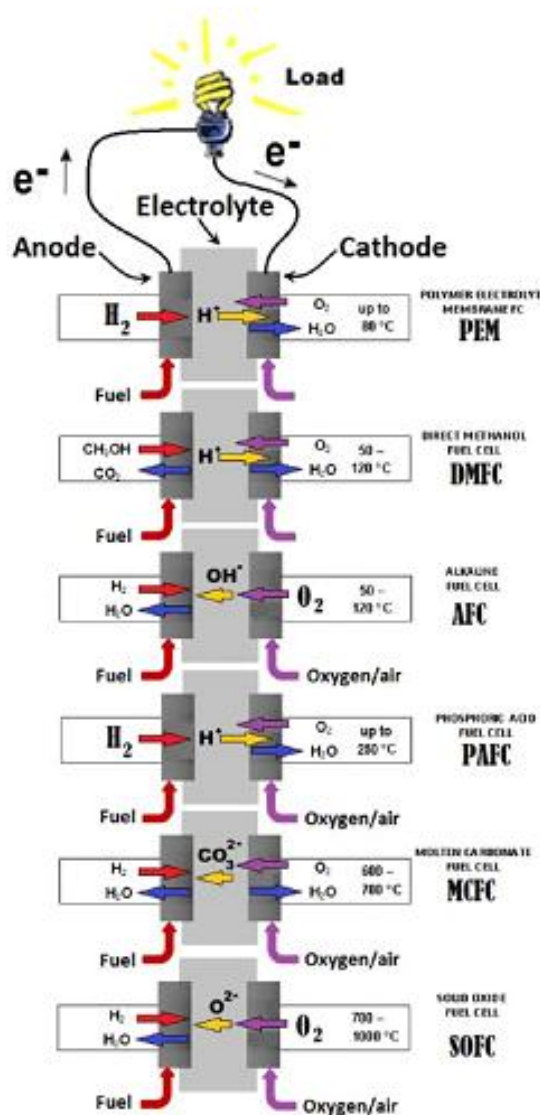


Figure 1.2 Summary of fuel cell types (Kraytsberg et al., 2014).

1.2.1 Polymer electrolyte membrane fuel cell (PEMFC)

PEMFC is the most likely candidate for transportation applications which has a high power density and a relatively low operating temperature. It is self-starting without the need of external warm up and readily generating electricity which makes it particularly promising. A hydrogen-powered PEMFC consists of two electrodes and a separator polymer membrane as shown in Figure 1.3. It converts the chemical energy stored in hydrogen fuel directly and efficiently to electrical energy with water as the only by product, have the potential to reduce our energy use, pollutant emissions, and dependence on fossil fuels (Kim et al., 2015).

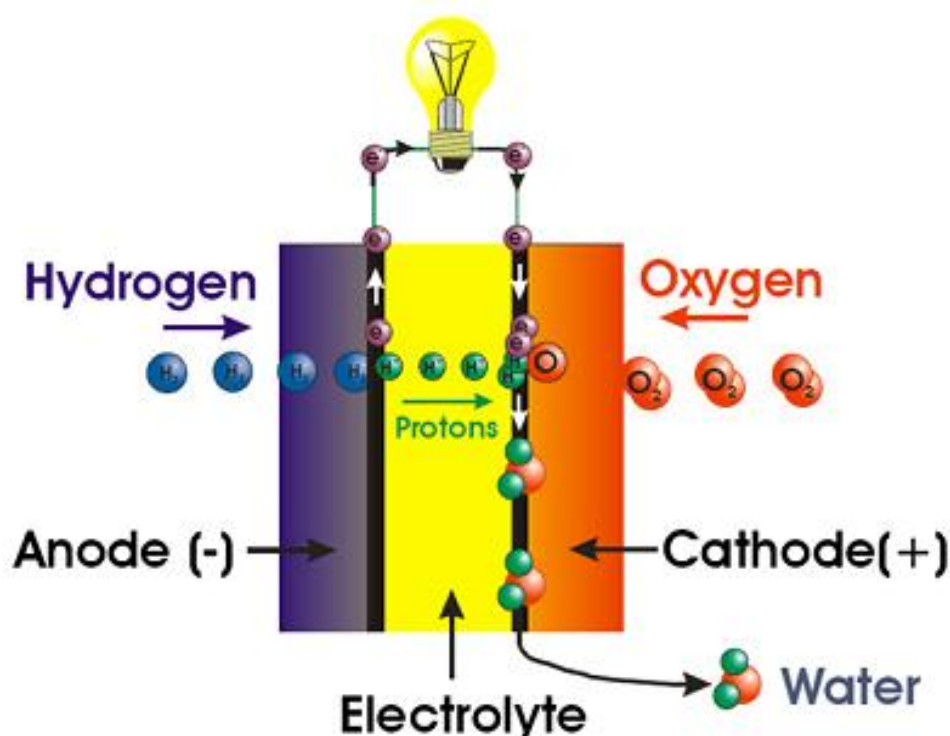
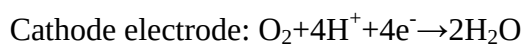


Figure 1.3 Schematic design of the polymer electrolyte membrane fuel cell (Peighambardoust et al., 2010).

Hydrogen is supplied to the anode and air is channeled to the cathode. At the anode, a platinum catalyst causes the hydrogen to split into positive hydrogen ions (protons) and negatively charged electrons. The polymer electrolyte membrane (PEM) permits only the transfer of proton to the cathode. The electrons travel along an external circuit to the cathode and create an electrical current. At the cathode, the electrons and protons combine with oxygen to form water which is the only waste product of hydrogen fueled PEMFCs (Peighambardoust et al., 2010). Anodic and cathodic reactions have been done in the PEM fuel cell with H_2 gas in anode in following:



the two above reactions will be change the following general reaction after the combination:



1.2.2 Solid Oxide Fuel Cell (SOFC)

Solid oxide fuel cells are considered as the best useful fuel cell for stationary power generators that could provide electricity and heat for houses, factories or towns (Singhal et al., 2008). The operation temperature is very high (700-1000 °C) for this type of fuel cell. This high temperature results a reliability problem, since parts of the fuel cell can break down after cycling on and off repeatedly. However, solid oxide fuel cells are very stable under continuous use. The SOFC has demonstrated the longest operating life of any fuel cell under certain operating conditions. The high temperature may also be an advantage: the steam produced by the fuel cell can be channeled into turbines to generate more electricity and the heat can be used for heating purposes. This process is called co-generation of heat and power and it improves the overall efficiency of the system (Celik, 2012a; Celik et al., 2012b; Golcuk 2011).

1.2.3 Alkaline Fuel Cell (AFC)

Alkaline fuel cell is one of the oldest designs for fuel cells; the United States space program has used them since the 1960s (Van den Broeck 1993). The AFC is very susceptible to contamination, so it requires pure hydrogen and oxygen. Alkaline fuel cells use an aqueous solution of potassium hydroxide in a porous stabilized matrix as an electrolyte. The operating temperature ranges from 65 to 200 °C. It is also very expensive, so this type of fuel cell is unlikely to be commercialized, but research has revisited this type of fuel cells recently again (Jiang et al., 2009; Celik, 2012a; Celik et al., 2012b; Golcuk 2011).

1.2.4 Molten Carbonate Fuel Cell (MCFC)

Like the SOFC, molten-carbonate fuel cells are also useful for large stationary power generators (Bischoff 2006). The fuel cells use molten alkaline carbonate (e.g., sodium bicarbonate NaHCO_3) as electrolyte. Since the operation temperature is 600 °C they can generate useful steam and improve the overall efficiency.

1.2.5 Phosphoric-acid fuel cell (PAFC)

The phosphoric-acid fuel cell has its potential use in small stationary power-generation systems (Kumura et al., 2004). Molten phosphoric acid (H_3PO_4) is used as

electrolyte. The optimum operating temperature range is 150-200 °C. It operates at a higher temperature than polymer electrolyte membrane fuel cells, so it has a longer warm-up time. Therefore, it is not possible to use them in cars (Celik, 2012a; Golcuk 2011).

1.2.6 Direct-methanol fuel cell (DMFC)

Direct methanol fuel cells are subcategory of proton exchange membrane fuel cells (PEMFCs) and their working principle is also similar to them. In anode electrode, methanol-water mixture is fed directly to anode electrode. In anode electrochemical reaction, methanol is breakdown and protons, electrons and carbon dioxide become products of the reaction. Protons separated from other products pass through polymer electrolyte membrane and migrate to cathode electrode. Then the protons combine with oxygen that fed from air and form water. As a result of these reactions thermodynamical potentials are generated and produced electricity is gotten by using an external circuit. Direct methanol fuel cells are comprised by anode, cathode, electrolyte and transparent membrane. According to researches have been made up to this time , most effective issues that affect efficiency of DMFCs are transparency of the membrane, stucture of electrolyte and choosing most suitable catalyst for electrodes. Researchers have been done a great deal of experiments about to increase electro oxidation performance of methanol in anode electrode and get more current density. Platinum, ruthenium and mixture of these metals have been used as catalyst material in these applications, which makes these fuel cells expensive. In addition to that durability, high efficiency and low cost are other important parameters for catalyst materials (Jiang et al., 2009). Researchers use a polymer membrane as electrolyte in DMFC. Methanol as fuel must be reformed to yield H_2 prior to the electrochemical processes. This is also true for the use of natural gas. Yet, the PEMs are not sufficiently tight, methanol crossover is a problem (Celik, 2012a).

1.3 POLYMER ELECTROLYTE MEMBRANE (PEM) FOR FUEL CELLS

The proton exchange membrane fuel cell, also called polymer electrolyte membrane fuel cell, uses a polymer to conduct mobile ions (H^+) through the system.

This low temperature fuel cell boasts a rapid start time as well as a compact unit design, no specific orientation requirements, and no corrosive fluid hazards, all of which make it ideal for use in vehicles and portable devices. The operating conditions vary with purpose; however PEM fuel cells generally operate at temperatures ranging from 85 to 105 °C and at ambient pressure or higher (Kim et al., 2015, Celik et al., 2012b, Jiang et al., 2009, Peighambardoust et al., 2010).

The main functioning unit of a PEM fuel cell is the membrane electrode assembly (MEA). The MEA is comprised of a very thin membrane, a polymer electrolyte which serves to facilitate proton transport from the anode to the cathode, sandwiched between a two electrodes. The electrodes are carbon-supported catalyst fixed to porous carbon cloth or paper. This assembly of anodic diffusion layer, catalyst layer, membrane, catalyst layer, cathodic diffusion layer is perfectly aligned and hot pressed until it is one inseparable unit (Celik, 2012a; Celik et al., 2012b; Larminie, 2003).

The MEA is the electrochemical heart of any fuel cell. The anode and cathode gases or liquids need to be effectively separated by the PEM. A PEM needs to be a good electronic isolator and a proton conductor. Different applications have different requirements for PEMs. General issues which are critical to a high performance of the PEM include high proton conductivity, low water diffusion and electro-osmosis, low permeability of fuel and oxidant, reduced thermally or impurity induced instability, good mechanical properties, the membrane in a fuel cell suffers from the stress which caused by the swelling and deswelling of the membrane in humidity, low cost and environmental friendly (Jiang et al., 2009).

Within a PEM fuel cell, the primary reactions taking place are that the hydrogen gas enters through the field flow plates of the anode and diffuses through the carbon cloth or paper. It reacts with the platinum catalyst, losing two electrons which are conducted by the carbon out to the external circuit as the remaining protons are transported through the membrane. Meanwhile, air enters the cathode side of the assembly. The oxygen molecule is broken and the ions react with the protons from the membrane and electrons arriving through the external circuit to make water. The overall system of a PEM fuel cell is shown in Figure 1.4.

The PEMFC is an attractive power source for vehicles and portable electronic devices due to its high power density and relatively low operating temperature. Other advantages of PEMFCs over other types of fuel cells are their nonvolatile electrolytes and efficient energy conversion. To achieve high performance in fuel cell applications, the polymer electrolyte as membrane must possess the following desirable properties: high proton conductivity to support high currents with minimal resistive losses, zero electron conductivity, adequate mechanical strength and stability, chemical and electrochemical stability under operating conditions, moisture control in stack extremely low permeability to fuel or oxidant, low production cost and the capability for easy fabrication (Kim et al., 2015, Celik, 2012a, Jiang et al., 2009).

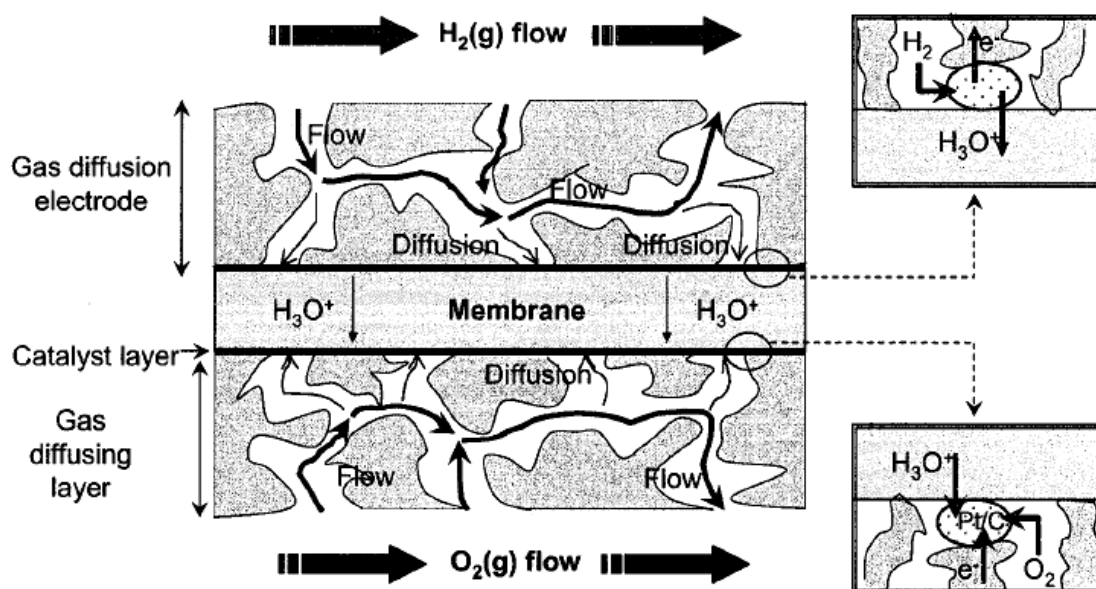


Figure 1.4 Schematic illustration of an individual PEM Fuel Cell (Sui et al., 2000).

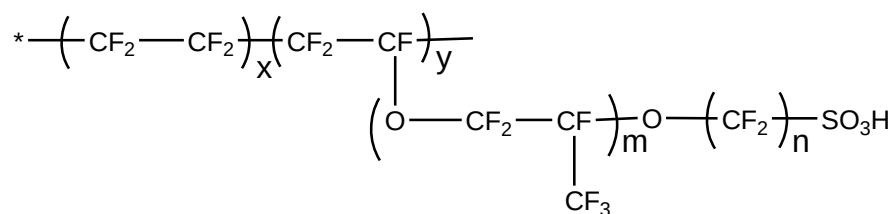
A polymer electrolyte membrane or proton exchange membrane (PEM) connecting the anode and cathode is a fundamental part of PEMFC systems (see Fig. 1.3). Furthermore, the PEM must possess properties that make it compatible with the environments in both the anode and cathode chambers, which is a relatively difficult requirement. For PEMFCs, the PEM is a key component, which needs to have the

following properties such as, high proton conductivity under the operating conditions, high chemical and mechanical stability, low permeability of fuels, and low cost, respectively (Zuo et al., 2012; Celik, 2012a; Celik et al., 2012b).

1.3.1 Perfluorosulfonic Acid Membranes

Development of PEMs for fuel cells has undergone a number of technological transformations since their inception. PEMFCs were originally introduced in early 1960's, based on using Gemini Space's (GE) sulfonated polystyrene as the electrolyte. Proton exchange membranes (PEMs) are generally based on hydrated sulfonated polymers. Among these, perfluorosulfonic acid membranes, such as Nafion[®], have drawn much interest because of their chemical and electrochemical stability, which proved to be superior in both performance and durability. Nafion was first developed in the late 1960s by DuPont (structure shown in Figure 1.5). It has a structure of copolymer from fluoro 3,6-dioxo-4,6-octane sulfonic acid with poly(tetrafluoroethylene) (PTFE) that Teflon backbone of this structure gives the hydrophobic nature for membrane and hydrophilic sulfonic acid groups ($-\text{SO}_3\text{H}$) have been grafted chemically into backbone by the free radical initiated copolymerization (Rikukawa et al., 2000; Celik, 2012a; Celik et al., 2012b; Golcuk 2011). These ionic groups have caused the absorption of the large amount of water by polymer and therefore, lead to hydration of polymer. Thus, the factors affecting the performance of the suitable proton exchange membrane are the level of hydration and thickness of the membrane which is playing an important role in deciding their suitability for application in fuel cell (Celik, 2012a; Kraytsberg et al., 2014).

Nafion was developed by modifying another DuPont product, Teflon, which was the first synthetic polymer with ionic properties (ionomers) ever developed. Ionic properties are imparted to Nafion by adding a pendant sulfonic acid group into the polymer backbone. The exemplified structure of Nafion is shown in Figure 1.5, where the sulfonic acid group is shown in its anhydrous form, $-\text{SO}_3\text{H}$. When exposed to water, the hydrolyzed form (SO_3^- , H_3O^+) appears, allowing for proton transport across the material (Martwiset et al., 2009; Kraytsberg et al., 2014). There are three common types of Nafion such as, 112, 115, and 117. The designation 117 refers to a film having 1100 equivalent weight, the number of grams of dry Nafion per mole of sulfonic acid groups when the material is in the acid form (Martwiset et al., 2009).



Nafion 117	$m \geq 1, n=2, x=5-13.5, y=1000$
Flemion	$m=0, n=1-5$
Aciplex	$m=0, n=2-5, x=1.5-14$
Dow membrane	$m=0, n=2, x=3.6-10$

Figure 1.5 Chemical structures of perfluorinated polymer electrolyte membranes (Rikukawa and Sanui, 2000).

Several models have been proposed for the morphology of Nafion[®] (Mauritz and Moore 2004, Schmidt-Rohrand Chen et al., 2008). For instance, Fig. 1.6 shows the Yeager 3-Phase Model, which is based on a three-phase clustered system with interconnecting channels within the polymer. The three regions consist of (A) a fluorocarbon backbone, some of which is microcrystalline, (B) an interfacial regions of relatively large fractional void volume containing some pendant side chains, some water, and those sulfate or carboxylic groups and counter ions which are not in clusters, and (C) clustered regions in which the majority of the ionic exchange sites, counter ions, and absorbed water exist (Celik, 2012a; Celik et al., 2012b; Brookman and Nicholson 1986).

Hydrophilic sulfonic groups, which are side-attached to the fluorinated hydrophobic backbone of Nafion, may be subjected to hydration; i.e., water molecules may accumulate around these groups. Water affects the Nafion proton conductivity by controlling the formation, dimensions, and connectivity of proton pathways in Nafion. As more water molecules become available, these water clusters grow in size and the Nafion material separates into hydrophobic regions and water-filled hydrophilic domains (Kim et al., 2015, Kraysberg et al., 2014, Celik, 2012a, Celik et al., 2012b, Peighambardoust et al., 2010).

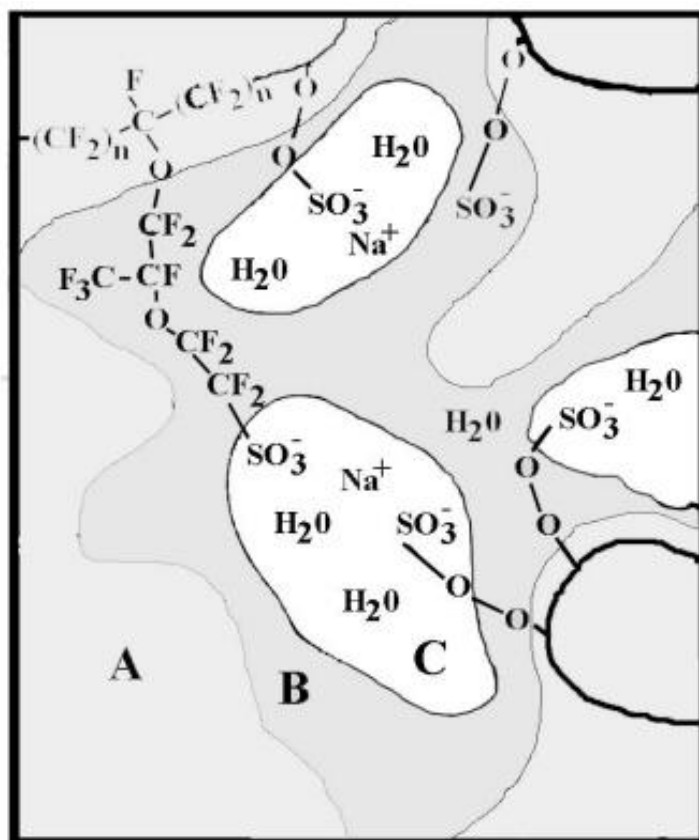


Figure 1.6 The Yeager 3 Phase Model of Nafion[®] Clusters (Yeager and Eisenberg, 1982).

Nafion with a low water content contains only small isolated water clusters and behaves as an insulator. Eventually, a percolation threshold of proton conductivity is passed. At this point, the water clusters are connected in a random network embedded in a continuous, sponge-like fluorocarbon phase. However, most of the water molecules are still located at the borders of the clusters, and thus, most of the water molecules inside the percolation channels accumulate in sulfonate group solvation shells. This leads to a high activation energy for proton transfer, which impedes a “hop-turn” (i.e., Grotthuss-type) proton conductivity and results in a primarily proton-diffusion-based conductivity. At the same time, the low proton mobility results in small proton conductivity. As the water content increases, the channels become broader and more free water molecules become available. However, the strong electrostatic interaction between the hydronium ions and multiple sulfonate groups still impedes Grotthuss-type proton conductivity and results in a predominantly diffusion-based proton conductivity. Under this hydration state, proton mobility is a key factor that determines the proton

conductivity (Kim et al., 2015; Kraytsberg et al., 2014; Celik, 2012a; Celik et al., 2012b; Golcuk 2011; Peighambardoust et al., 2010). As the water content increases, the water clusters and channels increase in size and the amount of available free water inside the aqueous phase increases. This results in an increasing dominance of the Grotthuss-type conductivity, which increases proton transport capabilities. Once Nafion becomes fully saturated with water, its structure is patterned with highly interconnected water channels and nearly spherical small hydrophilic domains containing water drops. These nearly spherical domains are surrounded by the hydrophobic polymer backbone chains, with the hydrophilic ionic groups located at the interface. A well-developed percolated network is formed, with the network comprising channels filled with free water. Thus, a saturated Nafion membrane resembles a phase separated system containing hydrophobic main chain agglomerates and hydrophilic water/acid segments (Golcuk 2011; Peighambardoust et al., 2010).

Perfluorosulfonic acid based materials are widely used as the PEM in fuel cell systems. The transport properties in these materials largely depend on the water content. Thus, in order to be practical, such systems must be operated at temperatures below the dew point of water (Celik, 2012a; Celik et al., 2012b; Golcuk 2011). Other shortcomings and limitations, such as high cost, high susceptibility of proton conductivity to low humidity and temperatures above 80 °C have motivated research toward finding alternative PEMs with higher efficiency and performance at desired conditions.

1.3.2 Proton Conduction Mechanisms in Proton Exchange Membranes

Proton conduction is fundamental for proton exchange membrane fuel cells and is usually the first characteristic considered when evaluating membranes for potential fuel cell use. Resistive loss is proportional to the ionic resistance of the membrane and high conductivity is essential for the required performance especially at high current density. At a molecular level, the proton transport in hydrated polymeric matrices is in general described on the basis of either of the two principal mechanisms: “proton hopping” or “Grotthuss mechanism”, and “diffusion mechanism” which water is as vehicle or “vehicular mechanism” (Kreuer 2004; Peighambardoust et al., 2010; Golcuk 2011; Celik, 2012a). The proton transport based on the “Grotthuss mechanism” (also called the “hopping mechanism”, “chain mechanism” or “structure diffusion”) comprises rapid

intermolecular proton transfers (hopping) down a chain of hydrogen bonds, for which the transfer events are assumed to be highly correlated, with reorientation of water dipoles to produce a configuration which allows for the next hopping event. In proton hopping mechanism protons hop from one hydrolyzed ionic site (SO_3^- , H_3O^+) to another across the membrane (see Figure 1.7). The produced proton by oxidation of hydrogen in anode adheres to water molecule than the provisional hydronium ion is formed and one different proton from same hydronium ion hops on the other water molecule. In this mechanism, ionic clusters were swelled in presence of water and formed the percolation mechanism for proton transferring. A fast Grotthuss-type mechanism must enable the formation of protonic defects, and provide strongly fluctuating proton donor and acceptor functions in an otherwise non-polar environment. The latter avoids strong solvent effects that tend to suppress proton transfer reactions (Kreuer 2004, Celik, 2012a; Golcuk 2011).

However, this mechanism can not explain all abnormal proton conductive systems. Based on NMR spectra and self-diffusion coefficients, Kreuer et al., proposed a “Vehicle mechanism”, also called molecular diffusion, for the interpretation of the conductivity of fast proton conductors, such as Nafion (Kreuer, 1982). According to this model the proton does not migrate as H^+ but as H_3O^+ , NH_4^+ , etc., bonded to a “vehicle” such as H_2O , NH_3 , etc. The “unloaded” vehicles move in the opposite direction shown in Figure 1.8. Sequential hydrogen bonds are not necessary for proton transport with this model. In this mechanism, hydrated proton (H_3O^+) diffuses through the aqueous medium in response to the electrochemical difference. In vehicular mechanism, the water connected protons ($\text{H}^+(\text{H}_2\text{O})_x$) in the result of the electroosmotic drag carry the one or more molecules of water through the membrane and itself are transferred with them. The major function of the formation of the vehicular mechanism is the existence of the free volumes within polymeric chains in proton exchange membrane which allow the transferring of the hydrated protons through the membrane (Golcuk 2011; Celik, 2012a).

The two mechanisms essentially differ from the nature of the hydrogen bonds formed between the protonated species and their environments. The Grotthuss mechanism is preferred in media which support strong hydrogen bonding, while vehicle mechanism is preferred in species with weaker hydrogen bonding (Golcuk 2011).

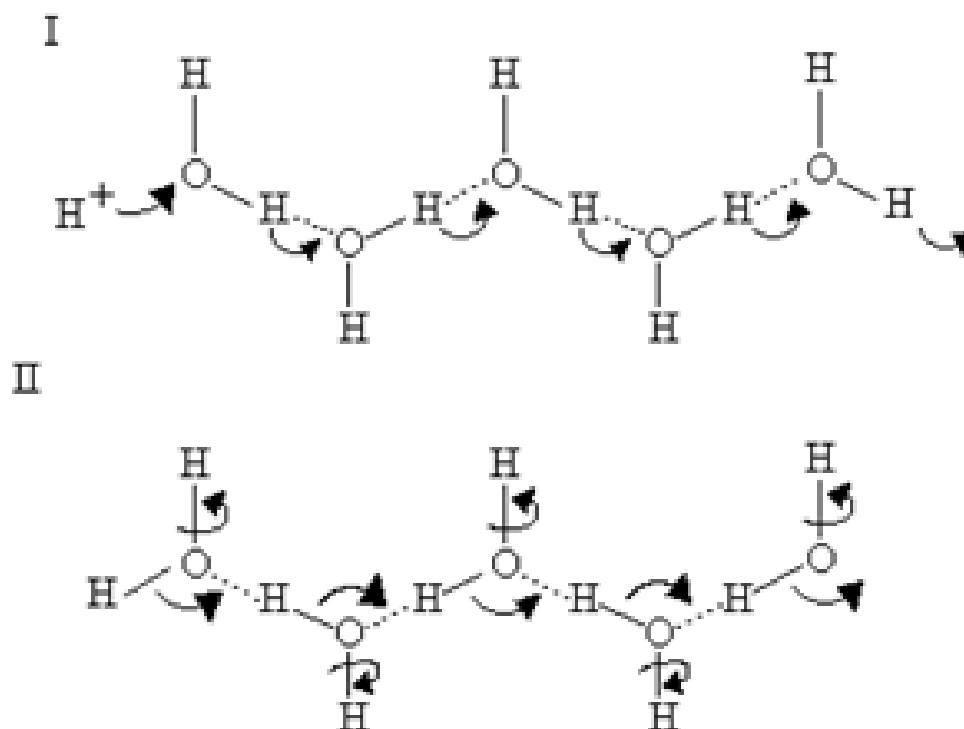


Figure 1.7 Grotthuss mechanism.

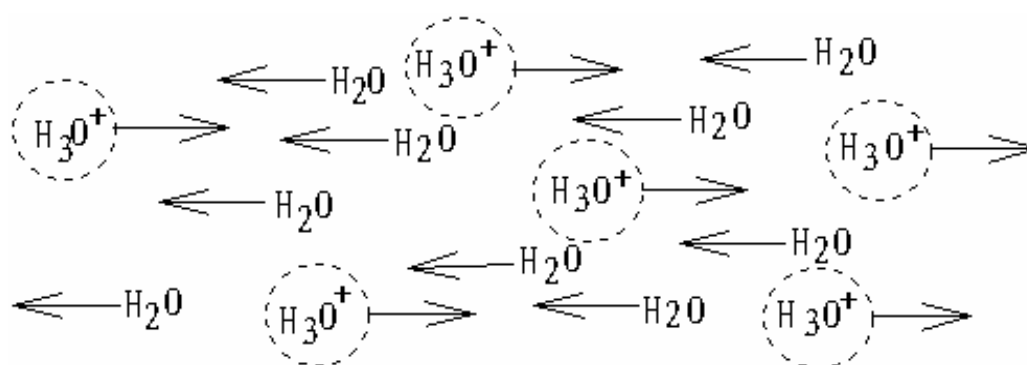


Figure 1.8 Vehicular mechanism (Kreuer 1982).

1.3.3 Anhydrous Proton Conductive Membranes

Proton exchange membrane fuel cells (PEMFCs) have gained prominence after they become applicable to various technological areas particularly on portable power

generating systems. In general, polymer based proton conducting materials can be categorized according to the temperature range in which they exhibit high proton conductivity (Sinirlioglu et al., 2013).

Problems associated with the PEMs present major obstacles for widespread acceptance of PEMFCs. First, the existing PEMs are expensive and mechanically unstable, especially for operation at moderate and elevated temperatures. Second, these materials typically require the continuous presence of humidity in order to perform their function in electrode reactions and conducting protons, not only limiting the operating condition of fuel cells to temperatures below about 80 °C, but also with a negative impact on the performance of PEMFCs, through slowing the process kinetics in electrodes, combined with decrease in CO tolerance. In addition, existing membranes are highly susceptible to elevated temperatures due to the shrinkage of electrolyte within the catalyst layer, which consequently reduces the electrochemical surface area in electrodes. Therefore, one of the key directions in development of PEMs is to implement novel designs in producing materials with sufficiently high chemical and mechanical stability with effective operation at intermediate temperatures (100-200 °C) and relatively low humidity (RH~25-30 %) levels (Kreuer, 2002).

Essentially, the development of PEMFCs capable of operating at temperatures approaching 200 °C can result in several key improvements in widespread use of fuel cells. For example, systems operating at elevated temperatures are more efficient and reduce the overall cell cost by decreasing the required platinum loading. In addition, the overall heat management of the device is simplified (Li et al., 2003, Lecolley et al., 2003). This also will eliminate some of the water management issues such as membrane swelling and water dynamics (Perrin et al., 2006). In addition, operating at high temperatures would play an important role in improving the overall performance of fuel cell operating with fuel containing impurities (e.g., carbon monoxide) and issues related to the efficiency of the heat rejection and water management (Celik, 2012a; Li et al., 2009, Pu et al., 2005). Progresses on these criteria would have major contributions in cutting the costs associated with the PEMs.

A principal approaches for enabling operation of PEMs at higher temperature is the replacement of water with alternative proton solvents possessing higher boiling points. Investigations over the past few years have resulted in the development of

several kinds of anhydrous proton conducting membranes. Preparation of polymer-acid blends was among the early trials in which basic or neutral polymers and copolymers (often containing functional groups such as imide, imine, ether, etc.) were blended with strong acids (Alberti and Casciola, 2001, Bozkurt and Meyer, 2001, Kreuer, 2001). In these blend systems, acids such as H_3PO_4 or H_2SO_4 act as proton donor and plasticizer, and the transport is carried out mainly through the exchange of protons between the ions derived from the acid. A number of polymer electrolytes have been examined extensively, exhibiting high proton conductivity in the anhydrous state. However, one of the major drawbacks is that the acidic units are susceptible to self-condensation at high temperatures (Celik et al., 2012, Bozkurt and Meyer, 2001). Only a few systems, mainly those based on polybenzimidazole (PBI) membranes, have been reported demonstrating efficient operation at temperatures above 100 °C (Celik, 2012a, Celik et al., 2012b; Hazarika et al., 2012, Wei et al., 1995). Li et al., revealed that operation of acid-doped polymer electrolytes in fuel cell at temperatures below 100 °C could result in washing the proton solvent away from the system. This indicates that special attention must be paid to the operation of such systems in a defined temperature range (Li et al., 2004). Schuster et al., provided a comprehensive review on the various types of protogenic groups as PEM separator materials for intermediate temperature and low humidity conditions) (Schuster et al., 2005; Celik, 2012a).

Aiming to overcome the challenges faced in the exploitation of polymer-acid systems, an alternative kind of proton conducting electrolytes was introduced by Kreuer (Kreuer, 1997, Kreuer et al., 1998) operating with acidic polymers in combination with amphoteric nitrogen-containing heterocyclic structures as a proton solvent. As speculated, the performance of these systems did not depend on the humidity. In fact, heterocycles behave similar to water but are able to form hydrogen bond networks that undergo auto-protolysis at much higher extent leading to high proton conductivity (Kreuer et al., 1998). On the other hand, the host polymer improves the mechanical properties enabling fabrication of thin free-standing films with higher stability in the presence of electrode materials (Bermudez et al., 1992). In addition, the host polymer functions as a source of protons by supplying protons to heterocyclic protogenic solvents. This results in enhanced defect-type proton conductivity. Despite progress made in the development of high temperature electrolytes and replacement of water with alternative protons solvents, the volatility of these low molecular weight solvents

remains as one of the key shortcomings hampering their widespread acceptance. This has led to new research avenues in order to address this issue. For instance, researchers have tried to immobilize these heterocyclic compounds on the polymer structure (Celik, 2012a). Based on the findings, this must be achieved carefully by using flexible spacers to avoid sacrificing the high local mobility of proton solvent molecules and protonic charge carriers. Due to the immobilization of the proton solvent molecules, proton transfer is anticipated to rely on the structural diffusion mechanism based on dynamic hydrogen bonds networks. The prevalence of this mechanism is well investigated in case of Im immobilized systems (Munch et al., 2001, Iannuzzi et al., 2004, Schuster et al., 2001). Simulation studies have shown that the structural diffusion is much more complex than the single jump of an excess proton from one molecule to another. Also, the proton transfer requires extensive reorientation of adjacent heterocycles and reorganization of the hydrogen bond coordination sphere of the migrating protons. In this respect, an ideal tethering should be constructed of flexible and sufficiently long spacers to enable high local mobility. In addition, it must possess sufficiently high concentrations of proton solvents to maximize the charge carriers and enable sufficient percolation (Scharfenberger et al., 2006). Another approach in the development of proton conducting electrolytes is to combine the functions of the protogenic group and the proton solvent in a single molecule. Such molecules must be amphoteric in the sense that they behave as both a proton donor (acid) and proton acceptor (base) and they must form dynamical hydrogen bond networks. Therefore, briefly, scientists summarized that there are generally three different approaches (Celik, 2012a) toward anhydrous PEMs in terms of their chemical structure and conductivity mechanisms:

- a) Polymer-acid complexes. These are based on polymer networks which contain ether, amide, amine or imino groups are doped with strong acids such as H_3PO_4 or H_2SO_4 .
- b) Intrinsic proton conductors based on homopolymers, copolymers, and polymer networks produced by tethering the heterocyclic proton solvent.
- c) Polymer / heterocycle hybrid electrolytes. In principle, these materials consist of acidic host matrix that forms complexes with amphoteric heterocycles and conduction occurs through protonic defects.

1.3.3.1 Azole-based heterocyclic compounds as proton solvents

The concept of using heterocycles was first introduced by Kreuer et al., who suggested exploitation of nitrogen-containing heterocycles as protogenic solvents for proton conduction (Kreuer et al., 1998). Most heterocyclic groups have high boiling points which makes them attractive for the development of more temperature-tolerant proton conductive membranes. In addition, unlike water, they can be incorporated into the polymer structure to further reduce their volatility during operation (Celik, 2012a).

In these heterocycles, the basic nitrogen sites act as strong proton acceptors with respect to strong acid groups such as sulfonic acid and phosphonic acid group (Jannasch 2003, Kreuer 2007, Steininger et al., 2007). The rather isometric molecules are advantageous for extended local dynamics and their protonated and unprotonated nitrogen functions may act as donors and acceptors in proton transfer reactions while the ring itself is non-polar and avoids strong solvent effects. Furthermore, pure heterocycles in the liquid state show higher conductivity than pure water due to the high degree of self-dissociation indicating small solvent effects, which is also advantageous for high proton mobility (Celik, 2012a). The pK_a values of various heterocycles are provided in Table 1.2.

Table 1.2 Melting points, boiling points and pK_a of the heterocycles.

Heterocycle Compound	Melting point (°C)	Boiling point (°C)	pK _a
Imidazole	90	257	7.2
Benzimidazole	170	-----	12.9
Methyl imidazole	-60	198	7.4
Pyrazole	68	187	2.5
1H-1,2,3-Triazole	23	203	1.17
1H-1,2,4-Triazole	120	256	2.39
1H-Tetrazole	157	220	4.89
5-Aminotetrazole	202	-----	8.1

1.3.3.1.1 Imidazole (Im)

Imidazole (Im) is one of the most simple and widely used heterocycles (Fig. 1.9). Im has also found other applications such as in blends with ionic liquids (Sun et al., 2001, Noda et al., 2003). In physical aspects, Im is a solid material at standard condition with a boiling point of ~ 257 °C. Its proton conductivity at its melting point (90 °C) is approximately 10^{-3} S/cm (Kreuer 1997). The pK_a for Im is reported to be approximately 14.9 while the pK_a for imidazolium is about 7 (Munch et al., 2001; Celik, 2012a).

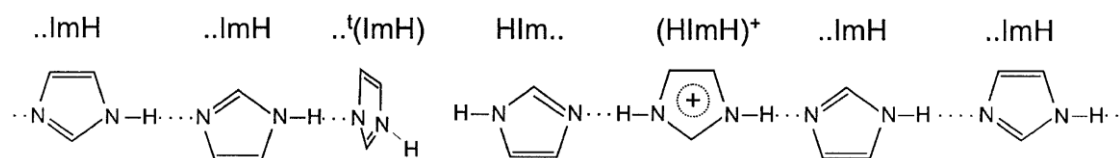


Figure 1.9 Proton conduction in imidazole through the Grotthuss mechanism, schematically showing the reorientation of the Im moiety (Munch et al., 2001).

The proposed mechanism for the proton conduction in Im-based systems involves proton transfer between the neighboring protonated and unprotonated guest molecules (Grotthuss mechanism) (Kreuer 1997, Casciola et al., 1991). This occurs as a result of aggregation of Im moieties in hydrogen-bonded chains (Bozkurt et al., 2003, Yamada and Honma, 2005; Sevil and Bozkurt, 2004). Investigations using quantum chemical calculations on nitrogen atoms as mediator for proton conduction have indicated the possibility for hydrogen bond between nitrogen and lower proton transfer barriers (Zhou et al., 2006, He et al., 2003). The schematic representation of the Grotthuss mechanism along the neighboring imidazole molecules is illustrated in Fig. 1.9. According to this schematic, the proton transfer between the adjacent Im molecules involves reorientation of the Im moiety. While high proton mobility has been observed in Im-based materials, this reorientation step in Im molecules is regarded as a rate limiting factor for the long range proton transfer across membranes based on Im. As a result, the overall proton conductivity of Im-based membrane electrolytes, such as in ionic liquids, oligomers and polymers is relatively low. In addition, the electrochemical stability of Im appears to be inadequate for fuel cell applications, largely due to the high electronic density of the Im

ring and also due to the diffusion and absorption of Im on the surface of the catalytic electrodes (Schuster et al., 2005; Noda et al., 2003; Yang et al., 2001; Li et al., 2005).

1-Methylimidazole (MeIm) (Fig. 1.10a) is a heterocycle from among the Im derivatives. Although the pK_{a1} value of MeIm molecule is much higher than that of Im, the conductivity of the complexes made from MeIm is not as high as those complexes made from Im (Schechter et al., 2002; Celik, 2012a).

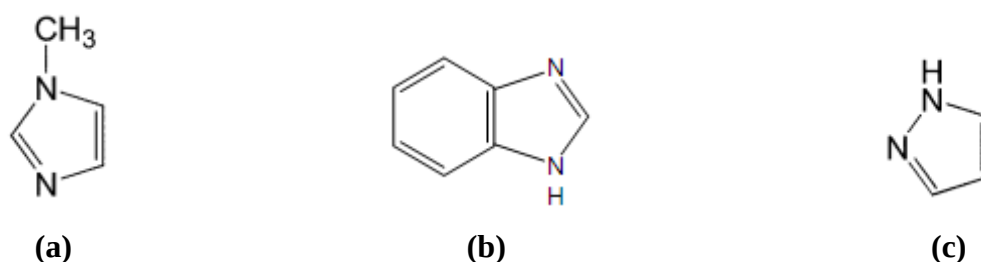


Figure 1.10 The structures of **(a)** 1-methyl imidazole, **(b)** benzimidazole (BnIm), and **(c)** pyrazole(Py).

1.3.3.1.2 Benzimidazole (BnIm)

Benzimidazole (BnIm) (Fig. 1.10b) is a heterocyclic compound comprised of the fusion of benzene and Im with a melting point of 170 °C. Similar to Im, the neighboring protonated and non-protonated nitrogens in BnIm act as donor and acceptor in proton transfer reactions. It should be noted that this is in contrast to acidic molecules such as phosphoric and sulfuric acids described as proton donors and acceptors with the formation of protonic defects (e.g., $H_2PO_4^-$; HSO_4^-) and intermolecular proton transfer reactions (Dippel et al., 1993). The reported pK_a for BnIm and benzimidazolium are 12.9 and 5.3, respectively (Munch et al., 2001). Although these values are slightly less than those for Im, benzimidazole can be used as a dopant in acidic polymers to facilitate the proton transfer via Grotthuss mechanism. In addition unlike Im, BnIm does not have electrochemical stability problem in fuel cell applications (Celik, 2012a).

1.3.3.1.3 Pyrazole (Py)

According to Kreuer et al., molecular diffusion coefficients for pyrazole (Py) (Fig. 1.10c) are generally higher than those for Im. This is in accordance with the lower melting and boiling points (b.p.=186 °C) of Py and also less tendency to form hydrogen bonded structures. Py possesses a lower rate of proton conduction compared to Im. This is ascribed to the weaker tendency for molecular association by hydrogen bonding and also lower basicity of Py (Kreuer et al., 1998). The proton conductivity of Py is 1.4×10^{-6} S/cm (at 120 °C) (Casciola et al., 1991). Based on the findings, proton diffusion for Py and Im is similar, occurring through a chain of suitably oriented molecules, without rotation of the protonated molecule (Casciola et al., 1991). This is attributed to the presence of the hydrogen bonded to the nitrogen in the neutral molecule. Once the proton has been transferred through the chain, the neutral molecules can rotate so as to be ready for a new proton transfer. Fig. 1.11 shows the proposed Grotthuss type transport mechanism in pyrazole. It is reported that pyrazole molecules possess low basicity ($pK_a=2.61$) and thus do not act as proton donor and acceptor in composite material largely due to the fact that non-protonated ($-N=$) group of pyrazole ring cannot strongly interact with the free protons from the host material in complexes (Yamada and Honma, 2005). Therefore, pyrazole has not been preferred as a proton source in the composite membranes of polyacids in PEM synthesis.

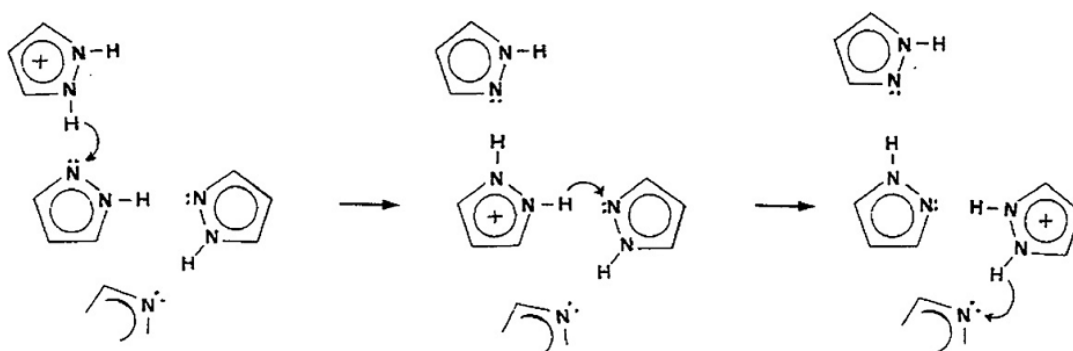


Figure 1.11 Proton conduction in pyrazole through Grotthuss mechanism (Casciola et al., 1991).

1.3.3.1.4 Triazole (Tri)

Triazoles are another class of heterocyclic protogenic solvents exhibiting promising results. Several triazoles are of interest: 1H-1,2,4-triazole (Fig. 1.12a) is a crystalline solid at standard condition with melting and boiling points of 120 °C and 260 °C, respectively. 1H-1,2,3-triazole (Fig. 1.12b) is a liquid at room temperature, with melting and boiling points of 23 °C and 203 °C, respectively (Zhou et al., 2005). As shown in Fig. 1.12, the molecular structure of Tri resembles that of other heterocyclic structures such as Im and Py, with the difference that Tri comprises three nitrogen atoms in the five-membered ring. In this regard, the prevalent proton conduction mechanism in Tri has been expected to be similar in nature to that of other heterocyclic compounds (Celik, 2012a).

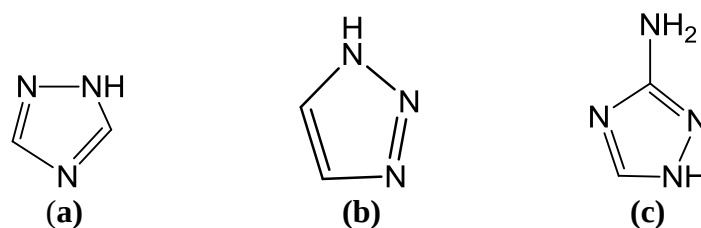


Figure 1.12 The molecular structures of **(a)** 1H-1,2,4-triazole, **(b)** 1H-1,2,3-triazole, **(c)** 3-amino-1,2,4-triazole (as also called aminotriazole) (ATri).

Neutral Tri (Fig. 1.12b) has two tautomers, 1H-1,2,3-triazole and 2H-1,2,3-triazole, and so does protonated Tri, 1,3-diH-1,2,3-triazolium and 1,2-diH-1,2,3-triazolium cations (Zhou et al., 2006). These isomers inter-convert by tautomerisation, which may occur through intra- or inter-molecular proton transfer (Rauhut, 2003). Although 2H-1,2,3-triazole is more stable in the gas phase, 1H-1,2,3-triazole becomes more stable in solution because of its larger dipole moment (Minkin et al., 2000). The presence of these tautomers and their interactions has made a detailed study of the systems very complex. Zhou et al., employed quantum mechanical calculations and conducted a study on the intra- and intermolecular proton transfer in 1H(2H)-1,2,3-triazole based systems in order to gain an understanding on the interactions between the neutral Tri and triazolium cations, and its effect on the short and long range proton conduction (Zhou et al., 2006). Their findings indicated the formation of stable

complexes between a -NH group on the protonated Tri as the proton donor and a nitrogen atom on the neutral Tri as the proton acceptor. The ionic conductivity of pure 1H-1,2,3-triazole is about 1.3×10^{-4} S/cm (at room temperature) which implies its considerable proton conductivity in liquid state and also produces protonic charge carriers upon self-dissociation of 1H-1,2,3-triazole molecules (Zhou et al., 2005; Celik, 2012a).

The proton conductivity of pure 1H-1,2,4-triazole is reported to be 1.5×10^{-4} S/cm (at 115 °C) and about 1.2×10^{-3} S/cm (at the melting point) (Li et al., 2005). This can be related to the low pK_{a1} where self dissociation of 1H-1,2,4-triazole produces highly mobile proton charge carriers (Li et al., 2005; Gunday et al., 2006). Zhou et al., suggested the proton conduction for triazole-based systems to be different from that for Im largely due to the presence of several proton-carrying isomers for triazoles (Zhou et al., 2006). Therefore, Tri can be doped into acidic host polymers and may improve the anhydrous conductivity of the materials in the dry state. Based on the reports, in polyelectrolyte / Tri systems the heterocyclic groups form a hydrogen bonding networks and promote long-range proton transport that is far better than that with Im (Zhou et al., 2005). Results of an investigation using computational methods on the reactions paths for different proton transfer reactions in 1,2,3-triazole suggested that Tri forms clusters that favor intermolecular proton transfer reactions (Rauhut, 2003). Therefore, blending of Tri with an acidic polyelectrolyte can be useful for the development of high temperature resistive free-standing films due to the possibility of long-range proton transport via structural diffusion (Celik, 2012a).

1.3.3.1.5 Tetrazole (Tet)

As an aromatic heterocyclic compound, tetrazole (Fig. 1.13a) with formula CH_2N_4 consists of a five-membered ring of four nitrogen atoms and one carbon atom. Having a ring structure similar to that of imidazole (Figure 1.9), it may conduct protons through either an inter- or intra- molecular proton transfer mechanism, as does imidazole. However, there are multiple advantages in using tetrazole versus imidazole. As previously reported, once a proton is transferred from one imidazole ring to another, the imidazole ring must flip before subsequent inter-molecular proton transfer can occur in the same direction. This reorientation was presumed to be the rate-determining step for long-range motion of protons in imidazole-based membranes (Munch et al., 2001). In

contrast, adjacent nitrogen atoms between tetrazole rings may act as additional proton acceptors, thus effectively promoting inter-molecular proton transfer. Intra-molecular proton transfer (tautomerization by migration of protons via a switch of a single bond with an adjacent double bond) within each tetrazole ring may also play an important role in proton transport (Song et al., 2013; Celik, 2012a). The difference in Pauling electronegativity between N and H is 0.8, while only 0.3 for C and H, implying protons are more loosely bound to N than to C. This leads one to expect higher intra-molecular proton transport within a tetrazole ring containing four closely located nitrogen atoms compared to an imidazole ring containing only two sparsely located nitrogen atoms. The interactions between H and each N atom along the ring are believed to be nearly the same, although there might be some differences in lengths of single and double bonds. All of these proton transfer processes may occur in a coordinated fashion. As a consequence, protons can hop from one tetrazole ring to another more effectively without flipping of rings (Song et al., 2013; Celik et al., 2012b).

1H-tetrazole is solid at room temperature and has melting and boiling points of 157 °C (Mihina et al., 1950) and 220 °C, respectively. It has a pK_a of 4.9 and several forms such as 5-aminotetrazole (Fig. 1.13b), 1-methyl 5-aminotetrazole and 1,5-diaminotetrazole (Satchell and Smith, 2002). Tetrazoles are thermally stable compounds and 5-aminotetrazole shows tautomerization as imino and amino forms (Lesnikovich et al., 2002; Levchik et al., 1992). Since it has higher nitrogen units in its ring, Tet is expected to perform easier proton transfer when used as a proton solvent in PEM materials.



Figure 1.13 The molecular structure of (a) 1H-tetrazole (b) 5-aminotetrazole.

1.3.3.2 PVDF Based Proton Conductive Membranes

PVDF based proton-conducting membranes are one of the most important components for a polymer electrolyte membrane fuel cell (PEMFC), serving as a separator to prevent mixing of the reactant gases and as an electrolyte for transporting protons from the anode to the cathode. PVDF is a partially fluorinated polymer with excellent thermal, mechanical and chemical stability along with lower cost compared to perfluorinated membrane such as the Nafion series from DuPont, which is the most common polymer electrolyte membranes used in fuel cells applications (Sezgin et al., 2014; Liu et al., 2013; Golcuk et al., 2013; Lepit et al., 2012; Sui et al., 2012; Golcuk 2011; Roh et al., 2010). Recently, many researchers have tried to employ very different methods such as UV-light (Golcuk et al., 2013; Sasa et al., 2013), X-ray and gamma irradiation (Lepit et al., 2012; Liu et al., 2011; Fei et al., 2010), the ozone method (Chiang et al., 2009; Chang et al. 2009; Chang et al. 2008), ATRP (Sui et al., 2012; Meng et al., 2011; Liu et al., 2010; Roh et al., 2010; and Kim et al., 2008), and alkaline treatment method (Liu et al., 2013; Tang et al., 2009) to prepare polymer electrolyte membranes that consist of PVDF since it is cheaper than Nafion while similar in chemical nature to Nafion. Poly(vinylidene fluoride)-*g*-poly(styrenes ulfonic acid) (PVDF-*g*-PSSA) copolymers with either linear or arborescent PSSA side chains were prepared via an ozone-treatment method by Su et al. (Su et al., 2010). The effect of the PSSA side chain structures on the membrane morphology, methanol crossovers, and proton conductivities of the graft copolymers-based PEMs were examined. At 90 °C, PEMs with linear and arborescent PSSA grafts yielded a maximum proton conductivity of 3.60×10^{-3} S/cm and 7.32×10^{-3} S/cm, respectively. Li et al. reported the preparation of nanofiber reinforced Nafion-based composite membranes via a novel three-step reaction route involving ozone-treatment. The resulting composite membranes showed high proton conductivity, good mechanical properties, low methanol permeability, and high dimensional stability, for application in fuel cells (Li and Liu, 2014). The proton conductivity in these studies are based on the humidity content and consequently these membranes were not suitable for high temperature applications.

So far, very few studies of PVDF and azole based anhydrous PEM designs were reported (Arslantas et al., 2014; Sezgin et al., 2014; Golcuk et al., 2013; Sasa et al., 2013; Lepit et al., 2012). In these studies, moderate to high proton conductivities were

obtained. For example, a novel UV induced polymerization method was employed in the grafting of styrene and 4-(chloromethyl)styrene onto partially fluorinated poly(vinylidene difluoride) (PVDF) (Golcuk et al., 2013; Sasa et al., 2013). Golcuk et al. reported the preparation of triazole doped poly(styrenesulfonic acid) grafted PVDF, PVDF-*g*-PSSA(Tri)₂, with a maximum proton conductivity of 5×10^{-5} S/cm at 150 °C and anhydrous conditions. In another work reported by Sasa et al., a maximum proton conductivity of 0.02 S/cm at 150 °C was found for triflic acid doped triazole-functional poly(chloromethyl styrene) grafted PVDF, PVDF-*g*-PCMS-Tri-1TA. Abdel-Hady et al. reported the grafting of glycidyl methacrylate/styrene onto PVDF membranes via gamma irradiation (Abdel-Hady et al., 2013). Sezgin et al. studied the synthesis of a graft copolymer consisting of 1-vinyl-1,2,4-triazole (VTri) and a PVDF base matrix under UV light in one step to achieve, PVDF-*g*-PVTri-(TA)_x, anhydrous PEMs. Arslantas et al. reported the preparation of triflic acid doped aminotetrazole-functional PVDF-*g*-PGMA-ATet anhydrous membranes, with a maximum proton conductivity of 0.011 S/cm at 150 °C and anhydrous conditions. Besides, Lepit et al. reported a maximum proton conductivity of 1×10^{-3} S/cm at 100 °C for 1-vinylimidazole and PVDF based PEMs prepared via radiation-induced grafting.

CHAPTER 2

EXPERIMENTAL

2.1 SYNTHESIS OF METHACRYLATE / METHACRYLAMIDE BASED AZOLE FUNCTIONAL MEMBRANES

Methacryloyl chloride (>97%) was purchased from Alfa Aesar and distilled prior to use. Azobisisobutyronitrile (AIBN; Merck) was recrystallized in THF prior to use. 5-aminotetrazole (ATet) (>98%, Alfa Aesar), 1H-1,2,4-triazole (Tri) (>97%), and 3-amino-1,2,4-triazole (ATri) (95%) were obtained from Aldrich Chemical Company. 1,4-dioxane (Merck), trifluoromethanesulfonic acid (TA) (>98, Fluka), *N,N*-dimethylformamide (Merck), triethylamine (Merck) and hexane (Merck) were used without further purification (Sinirlioglu et al., 2014c).

Poly(methacryloyl chloride) (PMAC) was prepared via conventional free radical polymerization of methacryloyl chloride in 1,4-dioxane using azobisisobutyronitrile, AIBN (1% mol) as initiator (yield: 65%). The mixture was purged with nitrogen and the polymerization reaction was performed at 60 °C for 32 h (Strohriegl, 1993). The synthesis of homopolymer and reaction of PMAC with 5-aminotetrazole (ATet), 3-amino-1,2,4-triazole (ATri) and 1H-1,2,4-triazole (Tri) were carried out. A typical procedure was given as the following: 1.3 g of PMAC was dissolved in 10 mL DMF, and triazole solutions (1.03 g Tri or 1.25 g ATri in 10 mL DMF) were added to PMAC solution together with 1.3 mL triethylamine (TEA). And in another vessel, 1.3 g PMAC and 1.27 g 5-aminotetrazole (ATet) were dissolved in 10 mL DMF separately and the solution was mixed after adding 2 mL triethylamine (Ozden et al., 2010). The reaction mixture was purged with nitrogen and the polymerization reaction was performed at 60°C for 24 h, separately. The resulting polymers were dialyzed against water to remove unreacted ATet, ATri and Tri and then dried under vacuum (Sinirlioglu et al., 2014c).

Polymer membranes were obtained by doping with trifilic acid (TA) of the triazole and tetrazole functional polymers at stoichiometric ratios of 1.0, 2.0 and 4.0 (TA/ATri, TA/Tri, TA/ATet). A stoichiometric amount of PMA-ATet, PMA-ATri, PMA-Tri was admixed with TA in DMF, and homogeneous solutions of PMA-ATet-(TA)_x, PMA-ATri-(TA)_x and PMA-Tri-(TA)_x were produced, respectively. The solutions were cast in polished polytetrafluoroethylene (PTFE) plates, and the solvent was evaporated in vacuum oven for several days at 50 °C. The films were stored in glove box for characterizations (Sinirlioglu et al., 2014c).

2.2 SYNTHESIS OF NOVEL MEMBRANES BASED ON POLY(5-(METHACRYLAMIDO)TETRAZOLE) AND SULFONATED POLYSULFONE

The commercial polysulfone (PSU) (Sigma-Aldrich), trimethylsilyl chlorosulfonate (TMSCS; Sigma-Aldrich), 1,2-dichloroethane (DCE; Merck), methanol (Sigma-Aldrich), 5-aminotetrazole (Alfa Aesar), 1,4-dioxane (Merck) and dimethylformamide (DMF; Merck) were used without further purification. Methacryloyl chloride was purchased from Alfa Aesar and distilled prior to use. Azobisisobutyronitrile (AIBN; Merck) was recrystallized in THF prior to use (Sinirlioglu et al., 2014d).

Tetrazole functional monomer (MTet) was synthesized according to literature (Taden et al., 2002). Methacryloyl chloride (10.7 g, 10.0 mL, 102 mmol) was added dropwise to a suspension of 5-aminotetrazole monohydrate (10.0 g, 97.0 mmol) in THF (250 mL) and H₂O (12 mL) at room temperature. The solid dissolved during the addition of the first 3 mL of methacryloyl chloride. After 15 min of stirring, the product started to precipitate, and the reaction mixture was diluted with distilled water (250 mL), and stored overnight in a refrigerator. The white solid was collected by filtration, washed with distilled water (4x20 mL) and dried in vacuo at 20 °C. ¹H-NMR (400 MHz, DMSO-d₆, δ): 1.97 (s, 3H, CH₃), 5.74 (s, 1H, =CH), 6.09 (s, 1H, =CH), 11.97 (s, 1H, CONH), 15.90 (br s, 1H, tetrazole-NH). ¹³C-NMR (400 MHz, DMSO-d₆, δ): 18.2 (CH₃), 123.9 (CH₂), 137.6, 150.1, 166.7 (ipso-C, C=O) (Sinirlioglu et al., 2014d).

Then, azole functional methacrylic homopolymer was prepared using conventional free radical polymerization. A solution of 5-(methacrylamido)tetrazole

(2.00 g, 13.1 mmol) and azobisisobutyronitrile (AIBN; 20 mg, 0.12 mmol) in dimethylformamide (DMF, 20 mL) was degassed and stirred overnight at 65 °C. The reaction mixture was then added dropwise to methanol (250 mL) / concentrated hydrochloric acid (5 mL). The colorless solid was collected by filtration, washed with methanol (4x20 mL), and dried in vacuo at 80 °C (Taden et al., 2002; Sinirlioglu et al., 2014d).

Sulfonated polysulfone (SPSU) was prepared according to literature (Devrim et al., 2009). The commercial PSU was dissolved in 1,2-dichloroethane (DCE) at 25 °C for 4 h under nitrogen atmosphere. Trimethylsilyl chlorosulfonate (TMSCS) was added at room temperature as the sulfonation agent. PSU/TMSCS mole ratio was set as 1:2. During the reaction, N₂ was purged continuously through the reaction solution and HCl was constantly produced and released out of the reactor with N₂. After about 36 h, methanol was added to quench the reaction and to cleave the silyl sulfonate moieties yielding SPSU. Silicon containing compounds, methyl sulfate, dichloroethane, methanol, and water were removed through evaporation and then the polymer was dried in vacuum (400 mmHg) at 55 °C (Sinirlioglu et al., 2014d).

The degree of sulfonation (DS) of SPSU was determined by acid-base titration with standard NaOH solution. Initially, the SPSU was dissolved in DMF. The solution of polymer was then titrated by an aqueous solution of 0.0147 N NaOH using phenolphthalein as the indicator. The titration gave a sulfonation ratio of 140 % [(mol SO₃H/repeat unit) x100], which was higher than those reported for this sulfonation method (127 %) (Gustian et al., 2012; Chen et al., 2005).

Proton conducting composite membranes were prepared by doping of SPSU with poly(5-(methacrylamido)tetrazole) (PMTet). A stoichiometric amount of SPSU and PMTet was admixed in DMF with the following mol ratios: SPSU / PMTet, 1:0.5, 1:1, 1:2. The dissolution was completed with mechanical stirring at ambient temperature overnight. The membrane was prepared by casting of the SPSU-PMTet solution on a polished poly(tetrafluoroethylene) dish, and the solvent was slowly evaporated at 50 °C for 24 h. To ensure complete solvent removal, the membranes were placed under vacuum at 50 °C. Homogeneous and semi-transparent membranes were obtained (Sinirlioglu et al., 2014d).

2.3 SYNTHESIS OF COPOLYMERS BASED ON 5-(METHACRYLAMIDO) TETRAZOLE AND 1-VINYL-1,2,4-TRIAZOLE

Methacryloyl chloride (>97%) was purchased from Alfa Aesar and distilled prior to use. Azobisisobutyronitrile (AIBN; Merck) was recrystallized in THF prior to use. 5-Aminotetrazole (>98%, Alfa Aesar), 1-vinyl-1,2,4-triazole (>97%, Fluka), N,N-dimethylformamide (DMF; Merck), tetrahydrofuran (THF; Merck), orthophosphoric acid (>99%, Merck) and methanol (Sigma-Aldrich) were used as received (Sinirlioglu et al., 2013).

Tetrazole functional monomer (MTet) was synthesized according to literature (Taden et al., 2002; Sinirlioglu et al., 2013). 5-(methacrylamido)tetrazole (MTet) was copolymerized with vinyl triazole (VTri) in DMF at 65 °C for 24 h. MTet was dissolved in DMF (5 mL) and VTri was added along with α,α' -azobisisobutyronitrile (AIBN) (1% mol). After the polymerization, the polymer solution was added dropwise to a mixture of methanol (250 mL) and concentrated hydrochloric acid (5 mL). White precipitate formed was collected by filtration, washed with methanol (4x20 mL), and dried in vacuo at 40°C for 48 h (Sinirlioglu et al., 2013).

Azole functional copolymer electrolytes were obtained by doping of the triazole and tetrazole functional copolymers with ortho-phosphoric acid (H_3PO_4) at stoichiometric ratios of 1.0 and 2.0. A stoichiometric amount of P(VTri-co-MTet) was admixed with H_3PO_4 in DMF, and a homogeneous solution of $\text{P}(\text{VTri-co-MTet})_x\text{H}_3\text{PO}_4$ ($x=1.0$ and 2.0) was produced. The solution was cast in a polished Teflon plate and the solvent was slowly evaporated at 50 °C for 24 h. To ensure complete solvent removal, the sample was placed in a vacuum oven for several days at 50 °C. The samples were stored in a glove box for characterization.

2.4 SYNTHESIS OF COPOLYMERS BASED ON VINYL PHOSPHONIC ACID AND 5-(METHACRYLAMIDO) TETRAZOLE

Tetrazole functional monomer (MTet) was synthesized according to literature (Taden et al., 2002). 5-(methacrylamido)tetrazole (MTet) was copolymerized with vinyl phosphonic acid (VPA) in DMF at 80 °C for 24 h. MTet was dissolved in DMF (7 mL)

and VPA was added along with α,α' -Azodiisobutyramidine dihydrochloride (AIBADC) (1% mol) (Celik et al., 2008). Copolymerization was not achieved with AIBN. After the polymerization, the polymer solution was added dropwise to a mixture of methanol (250 mL) and concentrated hydrochloric acid (5 mL). White precipitate formed was collected by filtration, washed with methanol (4x20 mL), and dried in vacuo at 40 °C for 48 h, and then stored in a glove box in order to determine proton conductivity and other characterizations (Sinirlioglu et al., 2013).

For MTet monomer, ^1H -NMR (400MHz, DMSO- d_6 , δ): 1.97 (s, 3H, CH_3), 5.74 (s, 1H, =CH), 6.09 (s, 1H, =CH), 11.97 (s, 1H, CONH), 15.90 (br, s, 1H, tetrazole-NH).

^{13}C -NMR (400 MHz, DMSO- d_6 , δ): 18.2 (CH_3), 123.9 (CH_2), 137.6, 150.1, 166.7 (ipso-C, C=O).

For P(MTet-co-VPA) (S1), ^{13}C -NMR (400 MHz, DMSO- d_6 , δ , ppm): 16.8, 30.7, 33.9, 35.8, 45.3, 48.9, 130, 132, 149.9, 162.4, 176.2

^{31}P (decoupled) NMR (400 MHz, DMSO- d_6 , δ , ppm): 11.93, 20.87, 23.4, 25.5, 27.8, 28.5, 29, 33.9

For P(MTet-co-VPA) (S2), ^{13}C -NMR (400 MHz, DMSO- d_6 , δ , ppm): 16.8, 31.0, 33.9, 35.8, 45.3, 48.6, 130.3, 132.5, 149.9, 162.4, 176.2

^{31}P (decoupled) NMR (400 MHz, DMSO- d_6 , δ , ppm): 11.80, 23.04, 25.9, 27.06, 27.6, 28.4, 34.07

For P(MTet-co-VPA) (S3), ^{13}C -NMR (400 MHz, DMSO- d_6 , δ , ppm): 16.7, 30.8, 34.07, 35.8, 45.5, 48.5, 130.4, 132, 150.0, 162.3, 176.1

^{31}P (decoupled) NMR (400 MHz, DMSO- d_6 , δ , ppm): 11.85, 21.0, 23.4, 25.4, 26.02, 27.6, 28.9, 34.02

2.5 SYNTHESIS OF NOVEL COMPOSITE MEMBRANES BASED ON POLY(VINYL PHOSPHONIC ACID) AND POLY(5-(METHACRYLAMIDO)TETRAZOLE)

Poly(vinyl phosphonic acid) (PVPA) was synthesized by free radical polymerization of vinyl phosphonic acid according to the literature (Steininger et al., 2007). Tetrazole functional monomer (MTet) was synthesized according to literature (Taden et al., 2002). Then, azole functional methacrylamide based homopolymer was prepared using conventional free radical polymerization. A solution of MTet (2.00 g, 13.1 mmol) and azobisisobutyronitrile (AIBN; 20 mg, 0.12 mmol) in dimethylformamide (DMF, 20 mL) was degassed and stirred overnight at 65 °C. The reaction mixture was then added dropwise to methanol (250 mL) / concentrated hydrochloric acid (5 mL). The colorless solid was collected by filtration, washed with methanol (4x20 mL), and dried in vacuo at 80 °C (Taden et al., 2002). ¹H-NMR (400MHz, DMSO-d₆, δ): 0.85 (br m, 3H, CH₃), 2.09, 2.34 (br s, 2H, CH₂), 11.65 (br s, 1H, CONH), 15.90 (br s, 1H, tetrazole-NH) (Sinirlioglu et al., 2013).

Proton conducting composite membranes were prepared by incorporating PVPA into PMTet at the different ratios to obtain PMTet(PVPA)_x (x= 0.5, 1.0, 2.0 and 4.0), where x assigns the molar ratio of the polymer repeating units. A stoichiometric amount of PVPA and PMTet was admixed in DMF. The dissolution was completed with mechanical stirring at ambient temperature overnight. The membrane was prepared by casting of the PMTet-PVPA solution on a polished polytetrafluoroethylene dish, and the solvent was slowly evaporated at 50 °C for 24 h. To ensure complete solvent removal, the membranes were placed under vacuum at 50 °C and stored in a glove box in order to determine proton conductivity and other characterizations (Sinirlioglu et al., 2015a).

2.6 PREPARATION OF THIN FILMS FROM NEW AZOLIC COPOLYMERS

MTet monomer was synthesized according to literature (Taden et al., 2002). The synthesis of copolymers with various monomer feed ratios of MTet and AMPS (MTet : AMPS (mol/mol)=1:0.5, 1:1 and 1:2) was carried out in DMF solution (20 mL) at 75 °C with AIBN (1% mol) as initiator for 24 h.

PAMPS was produced by free radical polymerization of 2-acrylamido-2-methyl-1-propanesulfonic acid in 1,4-dioxane / deionized water (2:1) using potassium persulfate as initiator (Aslan and Bozkurt, 2011). The reaction mixture was purged with nitrogen, and the polymerization reaction was performed at 70 °C for 36 h.

For the synthesis of P(MTet-*co*-AMPS) (S2) copolymer, 1.5 g (9.80 mmol) MTet and 2.03 g (9.80 mmol) AMPS were added into 20 mL DMF and 0.032 g (0.196 mmol) AIBN was used to initiate the copolymerization. The reaction mixtures were purged with nitrogen before polymerization started. The copolymer was obtained as a white sticky product. The sample was filtrated and dried in vacuum and stored in a glove box. For conductivity measurements, aqueous solutions of the copolymers in DMF were cast onto polished poly(tetrafluoroethylene) (PTFE) plates, dried under vacuum at 50 °C and then stored in a glove box. Transparent, hygroscopic and free-standing films (~200 µm) were obtained for all the samples (Sinirlioglu et al., 2014e).

For MTet monomer, ¹H-NMR (400MHz, DMSO-d₆, δ): 1.97 (s, 3H, CH₃), 5.74 (s, 1H, =CH), 6.09 (s, 1H, =CH), 11.97 (s, 1H, CONH), 15.90 (br, s, 1H, tetrazole-NH).

¹³C-NMR (400 MHz, DMSO-d₆, δ): 18.2 (CH₃), 123.9 (CH₂), 137.6, 150.1, 166.7 (ipso-C, C=O).

For PMTet homopolymer: ¹H-NMR (400MHz, DMSO-d₆, δ): 0.85 (br m, 3H, CH₃), 2.09, 2.34 (br s, 2H, CH₂), 11.65 (br s, 1H, CONH), 15.90 (br s, 1H, tetrazole-NH).

For PAMPS homopolymer: ¹H-NMR (400MHz, D₂O, δ): 7.45 ppm (-NH-), 4.4 ppm (-CH₂-SO₃H), 3.06 ppm (-SO₃H), 2.70 ppm (-CH-CO), 2.0 ppm (-CH₂-CH-), and 1.42 ppm (-CH₃).

For P(MTet-*co*-AMPS) (S3) copolymer, ¹H-NMR (400 MHz, DMSO-d₆, δ, ppm): 1.35 (-CH₃), 2.34 (-CH₂-CH-, backbone), 2.68 (-CH-CO), 5.07 (CH₂-SO₃H), 7.26-8.63 (-NH- from AMPS and MTet), 11.20 (1H, CONH, MTet), 15.50 (br, s, 1H, tetrazole-NH).

2.7 SYNTHESIS OF INORGANIC-ORGANIC HYBRID MEMBRANES BASED ON BORONIC ACID AND TETRAZOLE

Methacryloyl chloride (>97%, Alfa Aesar) was purchased from Alfa Aesar and distilled prior to use. 4-Vinyl benzene boronic acid (VBBA) (>98 %, Alfa Aesar) was purified by recrystallization from anhydrous ethanol. 5-Aminotetrazole (>98%, Alpha Aesar), N,N-dimethylformamide (DMF; Merck), tetrahydrofuran (THF; Merck), hydrochloric acid (HCl; Merck), methanol (Sigma-Aldrich), α,α' -azodiisobutyramidine dihydrochloride (AIBADC) (Aldrich), and orthophosphoric acid (>99 %, Merck) were used without further purification.

5-(methacrylamido) tetrazole (MTet) monomer was synthesized according to literature (Taden et al., 2002). 4-vinyl benzene boronic acid (VBBA) was copolymerized with MTet using free radical copolymerization in DMF at 85 °C for 24 h. A typical procedure is as follows: MTet (0.0017 mol) and 4-vinyl benzene boronic acid (VBBA) (0.0034 mol) were dissolved in DMF (5mL). α,α' -Azodiisobutyramidine dihydrochloride (AIBADC) (1% by mol) was added and the solution was purged with N₂ gas. After polymerization, the resulting copolymer was obtained as a yellowish solid upon precipitation in excess methanol, followed by filtration. The solid was then washed with excess cold DMF to remove unreacted monomers and dried in vacuo for use in analysis (Sinirlioglu et al., 2013).

P(VBBA-co-MTet) was doped with phosphoric acid (H₃PO₄) at molar ratios of 1.0 and 2.0 with respect to tetrazole units. The copolymer and acid were admixed in DMF, stirred for several hours at room temperature to produce a homogeneous solution of P(VBBA-co-MTet)-xH₃PO₄. The solution was spread over a polished Teflon plate and kept at 50 °C for 24 h under a hood for solvent removal. Transparent and free-standing films were thus obtained. The samples were stored in a glove box for characterization (Sinirlioglu et al., 2014f).

2.8 SYNTHESIS OF ANHYDROUS PROTON EXCHANGE MEMBRANES VIA GRAFTING VINYLTRIAZOLE ONTO ALKALINE TREATED PVDF

Polyvinylidene fluoride (PVDF, average $M_w \sim 534,000$, powder) was purchased from Fluka. Azobisisobutyronitrile (AIBN; Merck) was recrystallized in THF prior to use. Diethyl ether ($\geq 99.9\%$) was purchased from Merck. Potassium hydroxide (KOH, $> 85\%$), 1-Vinyl-1,2,4-triazole ($>97\%$), *N,N*-Dimethylformamide (DMF, $\geq 99.9\%$), and trifluoromethanesulfonic acid (triflic acid, TA) were supplied from Aldrich. They were all reagent grade and used as received.

The PVDF powder was first treated with potassium hydroxide (KOH). Briefly, PVDF was immersed in a 10 wt % KOH solution containing 0.05 wt % ethanol, and then the solution was stirred for 10 min at 60 °C. The precipitate was collected by filtration and then washed with distilled water. A 4 g sample of alkaline-treated PVDF powder was dissolved in 60 mL of *N,N*-dimethylformamide (DMF) at 70 °C. After the complete dissolution, the monomer VTri and 0.0380 g of AIBN (2 % mol) were added to the system under a N_2 atmosphere with continuous magnetic stirring. Three types of copolymers (C1, C2, C3) with different weight ratios of alkaline-treated PVDF powder and VTri in the reaction system were synthesized. The graft polymerization proceeded in an oil bath for 24 h at 70 °C. The copolymer was precipitated by excess diethyl ether, filtrated, and washed thoroughly with excess distilled water to remove the residue solvent, monomers and homopolymers. All samples were dried in vacuum oven for 2 days at 70 °C (Sinirlioglu et al., 2014b).

A stoichiometric amount of PVDF-*g*-PVTri films was admixed with TA in DMF, and homogeneous solutions of PVDF-*g*-PVTri-(TA)_x were produced. Solutions with, $x=1.0, 2.0$ and 3.0 moles, were prepared, where x is the number of moles of $-SO_3H$ per mole of triazole. The solutions were cast in polished polytetrafluoroethylene (PTFE) plates, and the solvent was evaporated and dried in vacuum oven for several days at 50 °C. The films were stored in glove box for characterizations.

2.9 SYNTHESIS OF PERFLUORINATED PROTON EXCHANGE MEMBRANES PREPARED BY CHEMICALLY COMBINING POLY(VINYL PHOSPHONIC ACID) WITH PVDF BY MEANS OF POLY(GLYCIDYL METHACRYLATE) GRAFTS

Polyvinylidene fluoride (PVDF, average $M_w \sim 534,000$) was purchased from Fluka. Glycidyl methacrylate (>99 %, Merck) was passed through basic alumina column to remove the inhibitor and stored at $-20\text{ }^{\circ}\text{C}$. Azobisisobutyronitrile (AIBN; Merck) was recrystallized in THF prior to use. *N,N*-Dimethylformamide (DMF, $\geq 99.9\%$), methanol (99.9 %, Aldrich), potassium hydroxide (KOH, >85%), vinylphosphonic acid (>95% Fluka) and toluene (> 99 % Merck) were used as received.

The PVDF powder was first treated with potassium hydroxide (KOH). Briefly, PVDF was immersed in a 10 wt % KOH solution containing 0.05 wt % ethanol, and then the solution was stirred for 10 min at $60\text{ }^{\circ}\text{C}$. The precipitate was collected by filtration and then washed with distilled water (Sinirlioglu et al., 2014; Liu et al., 2013). A 5 g sample of alkaline-treated PVDF powder was dissolved in 60 mL of *N,N*-dimethylformamide (DMF) at $70\text{ }^{\circ}\text{C}$. After the complete dissolution, the monomer GMA (5 mL, 5.35 g) and 0.1235 g of AIBN (2 % mol) were added to the system under a N_2 atmosphere with continuous magnetic stirring. The graft polymerization proceeded in an oil bath for 24 h at $70\text{ }^{\circ}\text{C}$. The copolymer was precipitated by excess methanol, then filtrated, and washed thoroughly with excess chloroform for 24 h to remove the PGMA homopolymers. All samples were dried in vacuum oven for 2 days at $70\text{ }^{\circ}\text{C}$ (Sinirlioglu et al., 2015b).

Poly(vinyl phosphonic acid) (PVPA) was produced by free radical polymerization of vinyl phosphonic acid in an earlier study (Bingol et al., 2007). PVDF-*g*-PGMA and PVPA were dissolved in DMF and water, separately. A stoichiometric amounts of PVDF-*g*-PGMA and PVPA solutions were admixed. For instance, to obtain PVDF-*g*-PGMA-*g*-PVPA(20) membrane, 0.5 g PVDF-*g*-PGMA in 40 mL DMF and 0.1 g PVPA in 0.4 mL water were mixed and stirred for 24 h at $70\text{ }^{\circ}\text{C}$. The graft copolymers, PVDF-*g*-PGMA-*g*-PVPA(*x*), were precipitated in diethyl ether and purified by washing with methanol to remove unreacted PVPA. The obtained graft copolymers are soluble in DMF and the solutions of the samples were emitted in polished poly(tetrafluoroethylene) (PTFE) plates. The solvent was evaporated in vacuum oven at

60 °C. Hygroscopic and free-standing films were obtained and stored in the glove box during characterizations (Sinirlioglu et al., 2015b).

2.10 SYNTHESIS OF PVDF BASED ANHYDROUS PROTON EXCHANGE MEMBRANES PREPARED VIA A FACILE “GRAFTING THROUGH” STRATEGY

Polyvinylidene fluoride (PVDF, average $M_w \sim 534,000$) was purchased from Fluka. Glycidyl methacrylate (> 99 %, Merck) was passed through basic alumina column to remove the inhibitor and stored at -20 °C. Azobisisobutyronitrile (AIBN; Merck) was recrystallized in THF prior to use. *N,N*-Dimethylformamide (DMF, ≥ 99.9 %), methanol (99.9 %, Aldrich), potassium hydroxide (KOH, > 85 %), 5-aminotetrazole monohydrate (97 %, Aldrich) and trifluoromethanesulfonic acid (TA) (Alfa Aesar, 98 %) were supplied from Aldrich and used as received.

The PVDF powder was first treated with potassium hydroxide (KOH). Briefly, PVDF was immersed in a 10 wt % KOH solution containing 0.05 wt % ethanol, and then the solution was stirred for 10 min at 60 °C. The precipitate was collected by filtration and then washed with distilled water (Sinirlioglu et al., 2014; Liu et al., 2013). A 5 g sample of alkaline-treated PVDF powder was dissolved in 60 mL of *N,N*-dimethylformamide (DMF) at 70 °C. After the complete dissolution, the monomer GMA (5 mL, 5.35 g) and 0.1235 g of AIBN (2 % mol) were added to the system under a N_2 atmosphere with continuous magnetic stirring. Three types of copolymers (C1-C3) with different weight ratios of alkaline-treated PVDF powder and GMA in the reaction system were produced (please see Table 3.26). The graft polymerization proceeded in an oil bath for 24 h at 70 °C. The obtained graft copolymer (PVDF-*g*-PGMA) was precipitated by excess methanol, then filtrated, and washed thoroughly with excess chloroform for 24 h to remove the PGMA homopolymers. All samples were dried in vacuum oven for 2 days at 70 °C (Sinirlioglu et al., 2015a; Sinirlioglu et al., 2015b).

Then, PVDF-*g*-PGMA (C3) was dissolved in DMF at 80 °C, and then, ATet with a stoichiometric ratio of 1:5 (PGMA / ATet) was added into the solution. After being purged with $N_{2(g)}$, the solution was stirred for 24 h at 100 °C. The polymer was

precipitated in methanol, then filtered, and washed with excess distilled water to remove unreacted 5-aminotetrazole (Arslantas et al., 2014). The above purification procedure was repeated three times. After drying in a vacuum oven at room temperature overnight, the membrane was obtained. EDS results: C: 41.25; F: 9.35; O: 18.17; N: 29.74 (theoretical: C: 40.40; F: 10.09; O: 17.65; N: 30.71) (Sinirlioglu et al., 2015b).

A stoichiometric amount of PVDF-*g*-PGMA-ATet was admixed with TA in DMF at room temperature and homogeneous solutions of PVDF-*g*-PGMA-ATet-(TA)_x were produced. Solutions with x= 1.0, 2.0 and 3.0 moles were prepared, where x is the number of moles of -SO₃H per mole of tetrazole units. The solutions were cast in polished polytetrafluoroethylene plates, and the solvent was left to evaporate under hood and dried completely in a vacuum oven for 48 h. The obtained graft copolymer membranes were stored in a glove box for characterizations.

2.11 CHARACTERIZATIONS

Fourier Transform Infrared Spectroscopy (FTIR) is most useful for identifying chemicals that are either organic or inorganic. It can be utilized to quantitate some components of an unknown mixture. It can be applied to the analysis of solids, liquids, and gasses. The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a fairly recent development in the manner in which the data is collected and converted from an interference pattern to a spectrum. FTIR can be used to identify chemicals from spills, paints, polymers, coatings, drugs, and contaminants. FTIR is perhaps the most powerful tool for identifying types of chemical bonds (functional groups). The wavelength of light absorbed is characteristic of the chemical bond as can be seen in this annotated spectrum. FT-IR spectra were recorded on a Bruker Alpha-P in ATR in range of 4000 cm⁻¹- 400 cm⁻¹.

Nuclear magnetic resonance spectroscopy (NMR spectroscopy) is a research technique that exploits the magnetic properties of certain atomic nuclei to determine physical and chemical properties of atoms or the molecules in which they are contained. It relies on the phenomenon of nuclear magnetic resonance and can provide detailed information about the structure, dynamics, reaction state, and chemical environment of

molecules. When placed in a magnetic field, NMR active nuclei (such as ^1H or ^{13}C) absorb electromagnetic radiation at a frequency characteristic of the isotope. The resonant frequency, energy of the absorption, and the intensity of the signal are proportional to the strength of the magnetic field. ^1H -NMR, ^{13}C -NMR, ^{19}F -NMR, ^{31}P -NMR, two-dimensional heteronuclear ^{13}C - ^1H NMR (HETCOR) measurements were performed with Bruker Avance 400 MHz in d_6 -DMSO or D_2O . Chemical shifts are reported in ppm relative to TMS as internal standard.

A scanning electron microscope (SEM) is a type of electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. For conventional imaging in the SEM, specimens must be electrically conductive, at least at the surface, and electrically grounded to prevent the accumulation of electrostatic charge at the surface. Non-conductive materials are therefore usually coated with an ultra thin coating of electrically conducting material (e.g. gold), deposited on the sample either by low-vacuum sputter coating or by high-vacuum evaporation. The morphology of the membranes was observed by scanning electron microscopy (SEM) type JEOL 7001 FESEM. The samples were previously coated with gold in a sputtering device.

The bulk composition of the samples was determined by the Energy Dispersive X-ray Spectrometry (EDS) method using a SEM type JEOL-7001 FESEM (Tokyo, Japan) instrument. All of the samples were previously coated with gold for 150 s in a sputtering device. The carbon, oxygen, phosphorous, and nitrogen were measured from three different regions in the samples and the average value is used.

The composition of carbon, hydrogen and nitrogen in the polymers was measured by using Thermo Scientific Flash 2000 Organic Elemental Analyzer. The measurements were repeated three times for a sample to determine carbon, hydrogen, and nitrogen. And the average value was taken.

Thermogravimetry analysis (TGA) is based on the measurement of the weight loss of the material as a function of temperature, or isothermally as a function of time,

in an atmosphere of nitrogen, helium, air, other gas, or in vacuum. TGA curve provides information concerning the thermal stability of the initial sample, intermediate compounds that may be formed and of the residue if any. In addition to thermal stability, the weight losses observed in TGA can be quantified to predict the pathway of degradation or to obtain compositional information. The ability to vary atmosphere during the TGA evaluation, particularly from an inert to a reactive gas, provides additional information about a material composition and its stability. The experimental data offer more sophisticated understanding of reactions occurring at materials heating. Thermal stabilities of the polymer electrolytes were examined by a Perkin Elmer STA 6000 Thermal Analyzer. The samples (~10 mg) were heated from room temperature to 750 °C under N₂ atmosphere at a scanning rate of 10 °C/min.

DSC measures the temperatures and heat flow associated with transitions in materials as a function of time and temperature. It determines transition temperatures, melting and crystallization, and heat capacity. In heat flux instruments, the sample and reference are heated from the same source and the temperature difference is measured. In amorphous polymers, DSC shows the glass transition temperature (T_g) and presence of single T_g verifies the homogeneity of the polymer. Perkin Elmer JADE Differential Scanning Calorimetry (DSC) was used to investigate the thermal transitions of the samples. The samples (~10 mg) were put into aluminum pans and then heated to the desired temperature at a rate of 10 °C/min under nitrogen atmosphere and heating-cooling curves were recorded at a rate of 10 °C/min. The second heating curves were evaluated (Celik, 2012a).

X-ray powder diffraction (XRD) patterns of the samples were conducted by X-ray diffraction instrument, Rigaku Smart Lab Diffractometer operated at 40 kV and 35 mA using Cu Ka radiation.

Water uptake (WU) measurement was determined by the weight difference between the fully hydrated membranes and dried membranes. The dried membranes (W_{dry}) were weighed and then wetted until the weight remained constant. The wet or saturated weights of the membranes (W_{wet}) were measured quickly after removing or wiping out any remaining surface water with a paper. The water uptake was calculated according to the equation (2.1):

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (2.1)$$

Methanol permeability was measured using our homemade diaphragm diffusion cell with a volume of 4 mL. The cell was filled with a pure methanol. Methanol vapor in equilibrium with the liquid diffused along the concentration gradient through the membrane, which was clamped between the mouth of glass and the cap. The cap has a hole with a 0.82 cm diameter so that the methanol diffused through the membrane could escape. The weight loss is recorded as a function of time and the data were used for permeability calculations. Molar methanol flux (J) through the membranes was calculated using Eq. (2.2). Methanol permeability of the membranes may be calculated using molar flux (J) shown in Eq. (2.3).

$$J = \frac{W}{M_w \times A \times t} \quad (2.2)$$

$$\frac{J_1 l_1}{J_2 l_2} = \frac{P_1}{P_2} \quad (2.3)$$

where J : flux, MW : molecular weight, W : weight loss (g), P : permeability, l : thickness (cm), A : area (cm²), t : time (s).

The tapping mode AFM images of the copolymers were acquired using a Park AFM (XE-100, Park AFM, Korea), supported on a Minus-K (25BM-6, Minus-K, Inglewood, CA) vibration isolation base. The AFM parameters to obtain the images were carefully set to minimize the pressure of tip on the copolymers. Different sizes of images (such as 13×13 μm, 10×10 μm, 20×20 μm, etc.) were acquired at a resolution of 512 x 512 points within the range of 0.5-0.8 Hz scan rate and were subjected to first-order flattening. Surface roughness was calculated by using the Root Mean Square (RMS), that is, the standard deviation of the Z values within a given area, defined by,

$$RMS = \sqrt{\frac{\sum_{i=1}^N (Z_i - Z_{ave})^2}{N}} \quad (2.4)$$

where Z_{ave} is the average, Z_i is the current Z value, and N is the number of points within the analyzed area. It was noted that the surface roughness depends on the curvature and size of the AFM tip and on the image processing. The RMS mean values and the standard deviations were obtained by analyzing at least 6 AFM images.

Cyclic voltammograms were obtained with a potentiostat CHI instrument Model 842B. Voltammograms of the samples were recorded in a three electrode CV system, using a polymer electrolyte modified Pt working electrode and a Pt counter electrode. The reference electrode was silver/silver chloride (Ag/AgCl) calibrated by a ferrocene/ferricinium redox system. Cyclic voltammetry studies were carried out in 0.1 M tetraethylammonium tetrafluoroborate (TBATFB)/acetonitrile.

The proton conductivity measurements were performed using a Novocontrol dielectric-impedance analyzer. The samples were sandwiched between platinum blocking electrodes and the conductivities were measured in the frequency range 1 Hz and 3 MHz at 10 °C intervals. The temperature was controlled with a Novocontrol cryosystem, which is applicable between -150 and 250 °C. The AC conductivities, σ_{ac} (ω) of the polymers were measured at several temperatures using impedance spectroscopy. Frequency dependent AC conductivities (σ_{ac} (ω)) were measured using eq. (2.5):

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \epsilon''(\omega) \omega \epsilon_0 \quad (2.5)$$

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, ϵ_0 is the vacuum permittivity ($\epsilon_0 = 8.852 \times 10^{-14}$ F/cm), and ϵ'' is the imaginary part of complex dielectric permittivity (ϵ^*).

The DC conductivity (σ_{dc}) of the samples was determined from the plateaus of $\log \sigma_{ac}$ versus $\log F$ by linear fitting of the data. A marked curvature is observed for all samples and the curves are interpreted with Arrhenius equation:

$$\ln \sigma = \ln \sigma_0 - E_{dc} / kT \quad (2.6)$$

where σ_0 is the pre-exponential terms, E_{dc} is the activation energy and k is the Boltzmann constant.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 SYNTHESIS AND PROTON CONDUCTIVITY STUDIES OF METHACRYLATE / METHACRYLAMIDE BASED AZOLE FUNCTIONAL MEMBRANES

Polymers bearing triazole and tetrazole moieties have been the focus of much attention because of their powerful energetic usage, biological activity and high thermal stability (Shin et al., 2011; Pu et al., 2007; Igrunova et al., 2001). In both poly(vinyl tetrazole) and poly(vinyl triazole), the aliphatic chain improves its fabrication property, and the triazole and tetrazole side groups may act as proton donors and acceptors. The proton transport occurs between hydrogen bonds of neighboring heterocyclic units through structure diffusion (Sinirlioglu et al., 2014c).

Herein, anhydrous polymer electrolytes based on azole functional methacrylates and methacrylamides have been produced for use in proton exchange membrane fuel cells (PEMFCs). To the best of our knowledge, this contribution is the first to report on the preparation of methacrylate/methacrylamide based triazole and tetrazole functional polymer electrolytes via post-polymerization functionalization. Poly(methacryloyl chloride) (PMAC) was synthesized by free radical polymerization of methacryloyl chloride, followed by covalent attachment of 5-aminotetrazole (ATet), 3-amino-1,2,4-triazole (ATri) and 1H-1,2,4-triazole (Tri) distinctly onto PMAC as depicted in Fig. 3.1. Then, functional polymers were doped with triflic acid (TA) at several stoichiometric ratios (Sinirlioglu et al., 2014c).

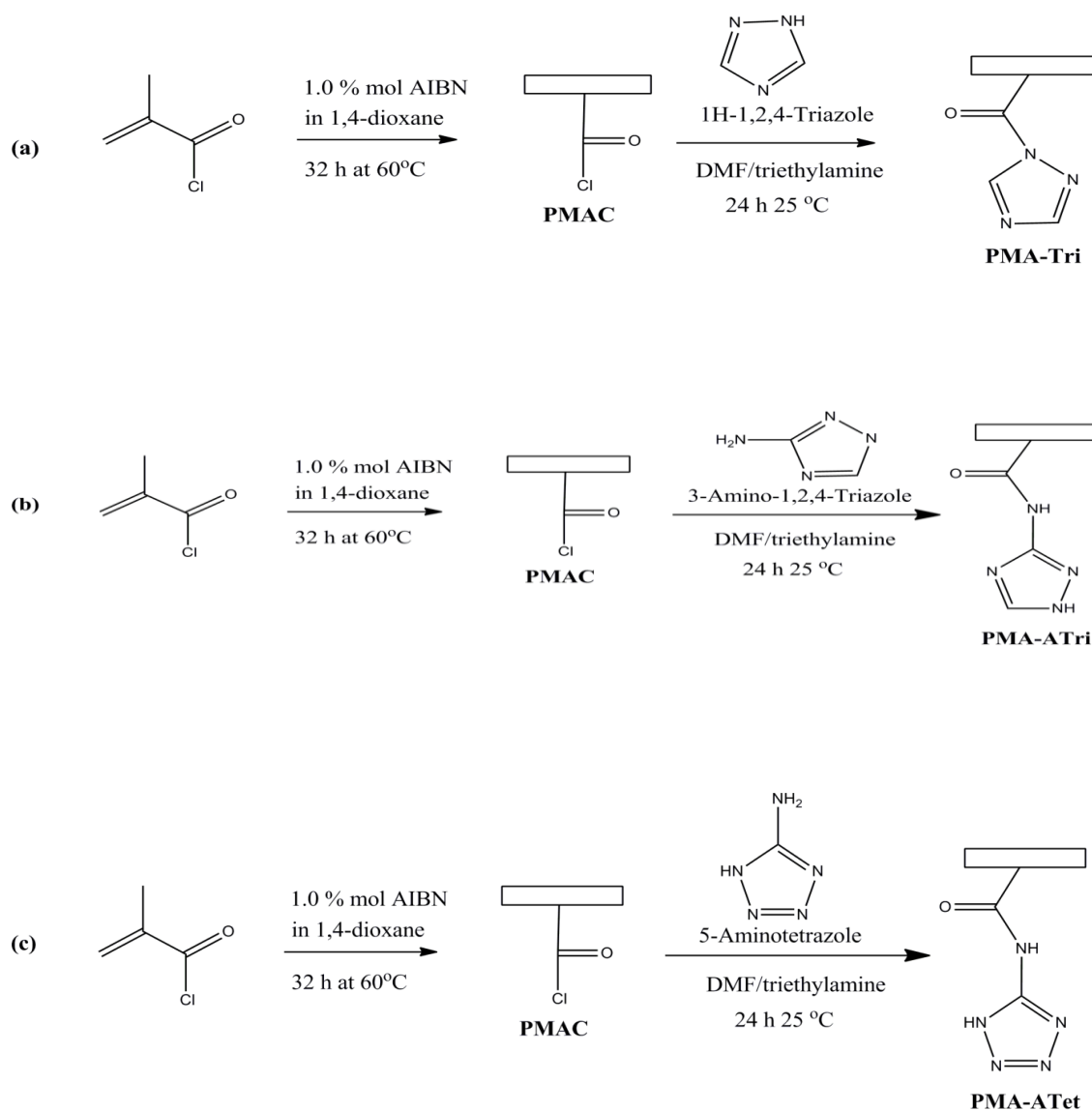


Figure 3.1 (a) Synthesis scheme of triazole functional poly(methacryloyl chloride), (b) Synthesis scheme of aminotriazole functional poly(methacryloyl chloride), (c) Synthesis scheme of tetrazole functional poly(methacryloyl chloride).

The composition of the polymer was verified by elemental analysis. Aminotetrazole, triazole and aminotriazole contents of the samples were calculated through nitrogen analysis, and the results are summarized in Table 3.1. It is verified that 5-aminotetrazole, 3-amino-1,2,4-triazole and 1H-1,2,4-triazole are about 41 %, 48 % and 38 % accessible to PMAC, respectively.

Table 3.1 Azole content of PMA-ATet, PMA-ATri and PMA-Tri calculated from elemental analysis results.

Sample	C (%)	H (%)	N (%)	Azole (%)
PMA-ATet	41.35	6.94	23.30	41
PMA-ATri	40.73	6.88	21.20	48
PMA-Tri	42.06	6.92	20.86	38

Methacryloyl chloride is a clear liquid that is miscible in methanol, water, and 1,4-dioxane. ATri is soluble in water, methanol, ethanol and chloroform, and sparingly soluble in ethyl acetate. It is insoluble in ether and acetone. ATet has good solubility in water and ethanol. Tri is soluble in formamide, water and alcohols such as ethanol, butanol and propanol. The homopolymer, PMAC, is a colorless solid that can be dissolved in water, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and *N*-methylpyrrolidone (NMP). Modification of PMAC with Tri, ATri and ATet yields brownish membranes that are soluble in solvents such as DMF, DMSO, and NMP.

3.1.1 NMR studies

The ^{13}C -NMR spectra of PMA-ATri, PMA-ATet, and PMA-Tri are shown in Fig. 3.2, Fig. 3.3 and Fig. 3.4 together with spectral assignment, respectively. Carbon atoms of the aliphatic chain groups appear at around 18 and 44 ppm. The peaks between 155 and 162 ppm belong to carbon of the triazole rings and triazole rings attached to NH sites in the PMA-ATri, respectively (Fig. 3.2). The peak located at around 180 ppm belongs to carbon of the carbonyl group (Sinirlioglu et al., 2014c).

The ^{13}C -NMR spectra of PMA-ATet is shown in Fig. 3.3. Signals corresponding to the methyl and methylene groups appear between 18 and 44 ppm, respectively. The peak located at around 180 ppm belongs to carbon of the carbonyl group. Additionally, the azole ring carbon gives a peak around 155 ppm of the NH sites in the aminotetrazole ring (Sinirlioglu et al., 2014c).

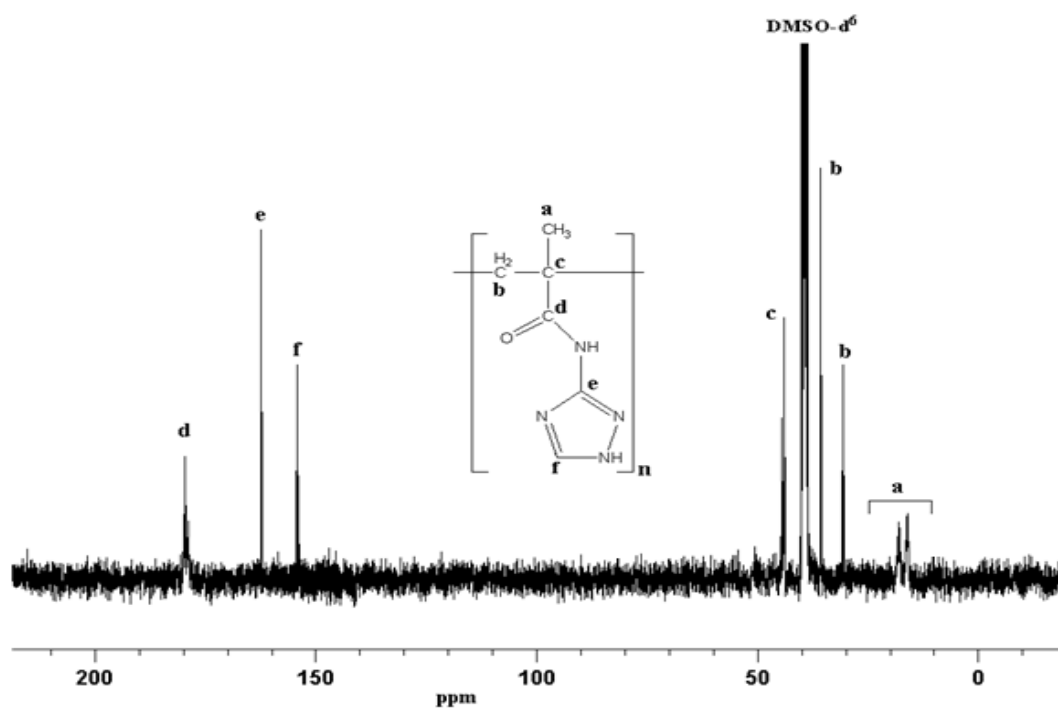


Figure 3.2 ^{13}C -NMR spectrum of PMA-ATri recorded in $\text{DMSO}-d_6$.

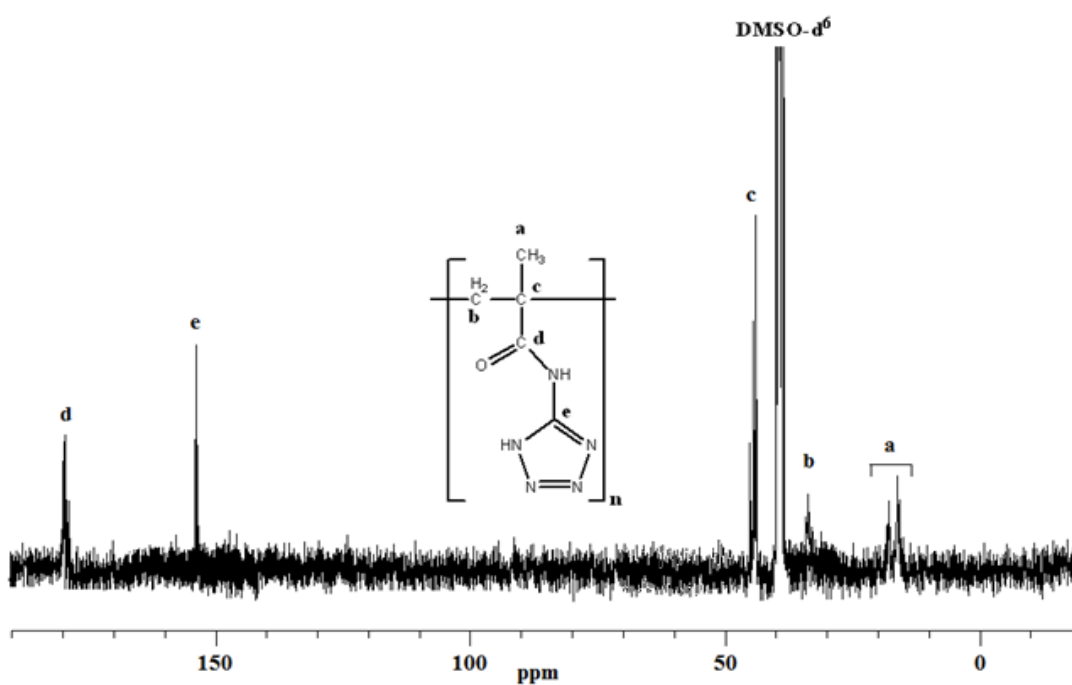


Figure 3.3 ^{13}C -NMR spectrum of PMA-ATet recorded in $\text{DMSO}-d_6$.

The ^{13}C -NMR spectra of PMA-Tri is represented in Fig. 3.4. Carbon atoms of the aliphatic chain groups (methyl and methylene carbons) appear between 17 and 45 ppm region, respectively. The peak located at around 180 ppm belongs to carbon of the carbonyl group. In addition, the azole ring carbons give a peak around 150 ppm in triazole ring (Sinirlioglu et al., 2014c).

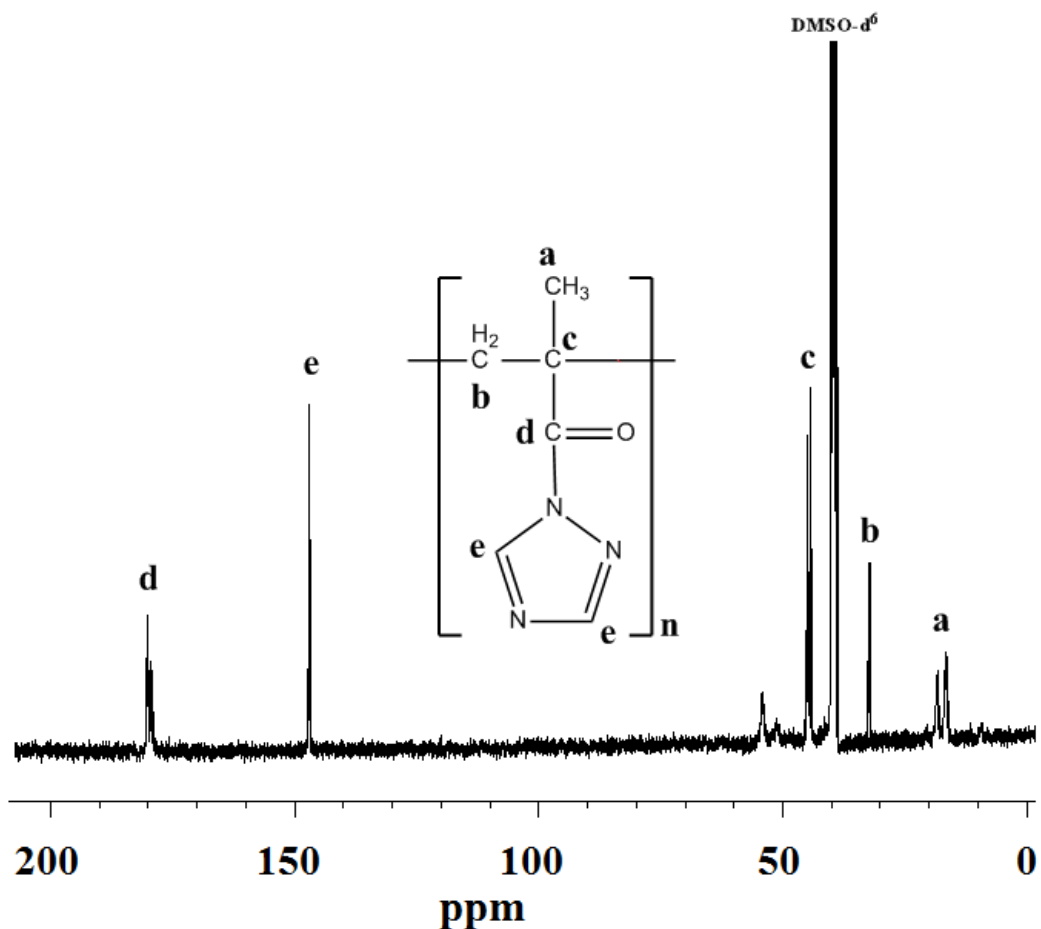


Figure 3.4 ^{13}C -NMR spectrum of PMA-Tri recorded in DMSO-d_6 .

3.1.2 FTIR studies

In the IR spectrum of PMAC, there is a strong band due to the stretching vibration of halide attached to $\text{C}=\text{O}$ groups at 1698 cm^{-1} . The aliphatic C-H stretchings were observed at $2800\text{--}3000\text{ cm}^{-1}$ regions. There is a broad band due to the stretching vibration of carbonyl group attached to C-Cl groups at 760 cm^{-1} (Fig. 3.5). PMA-ATet

exhibited several medium or strong peaks at 1689 cm^{-1} and 1465 cm^{-1} due to amide bond and tetrazole ring vibrations, respectively (Ozden et al., 2010; Celik and Bozkurt, 2008; Levchik 1992). The triazole units show several medium or strong peaks at 1692 cm^{-1} and $1445\text{--}1550\text{ cm}^{-1}$ range due to the amide bond and $\text{C}=\text{N}$, $\text{C}-\text{N}$ ring vibrations, respectively. The aliphatic $\text{C}-\text{H}$ stretchings were observed at $1380\text{--}1470\text{ cm}^{-1}$ and $2800\text{--}3000\text{ cm}^{-1}$ regions (Sinirlioglu et al., 2014c).

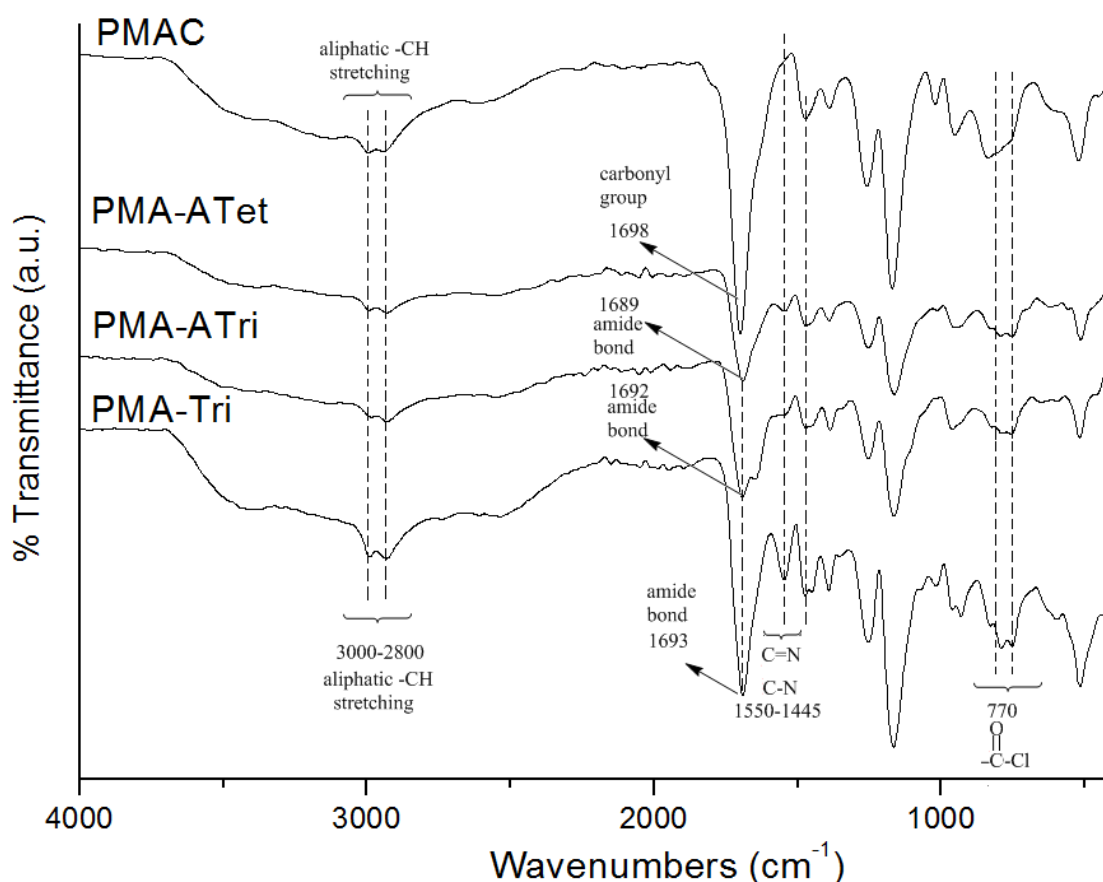


Figure 3.5 FTIR spectra of PMAC, PMA-ATet, PMA-ATri and PMA-Tri.

Fig. 3.6, Fig. 3.7, and Fig. 3.8 show the FTIR spectrum of acid-doped PMA-ATet, PMA-ATri and PMA-Tri. Triflic acid gives several absorptions between 1000 cm^{-1} and 1250 cm^{-1} . The strong bands at 1155 and 1229 cm^{-1} are attributed to SO_2 , and a strong absorption peak at 1026 cm^{-1} most probably belongs to $-\text{SO}_3^-[\text{H}^+]$. The formation of a peak at around 3170 cm^{-1} shows the protonation of the triazole and tetrazole rings, in addition to the broad peaks around 3480 cm^{-1} (Sinirlioglu et al., 2014c).

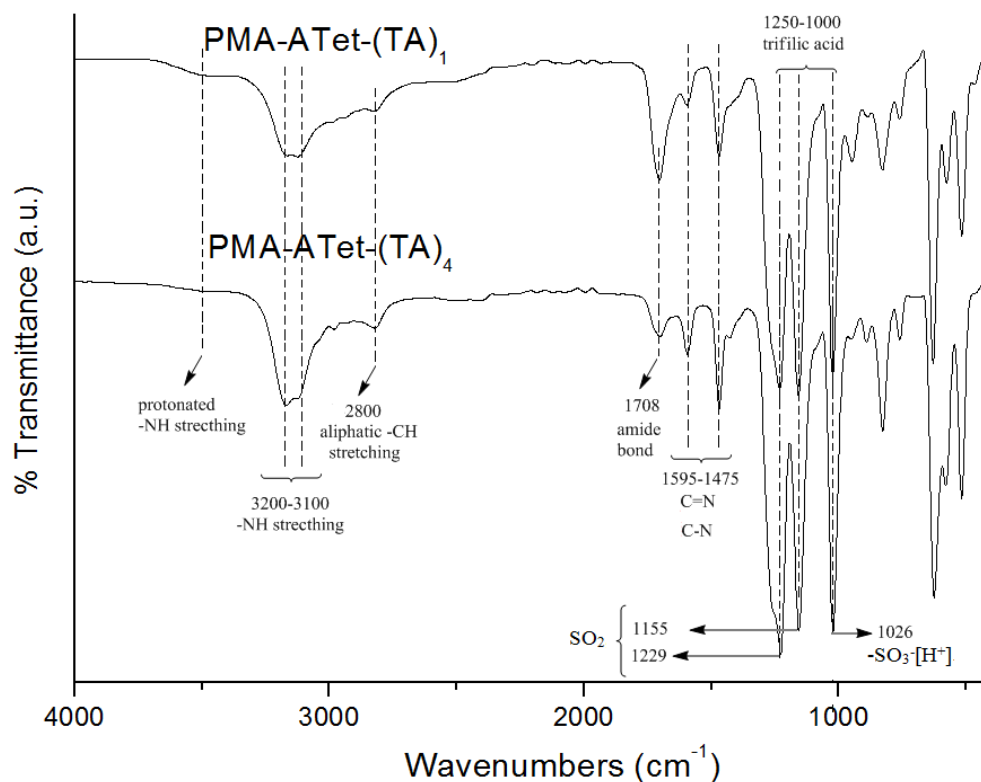


Figure 3.6 FTIR spectra of PMA-ATet-(TA)₁ and PMA-ATet-(TA)₄.

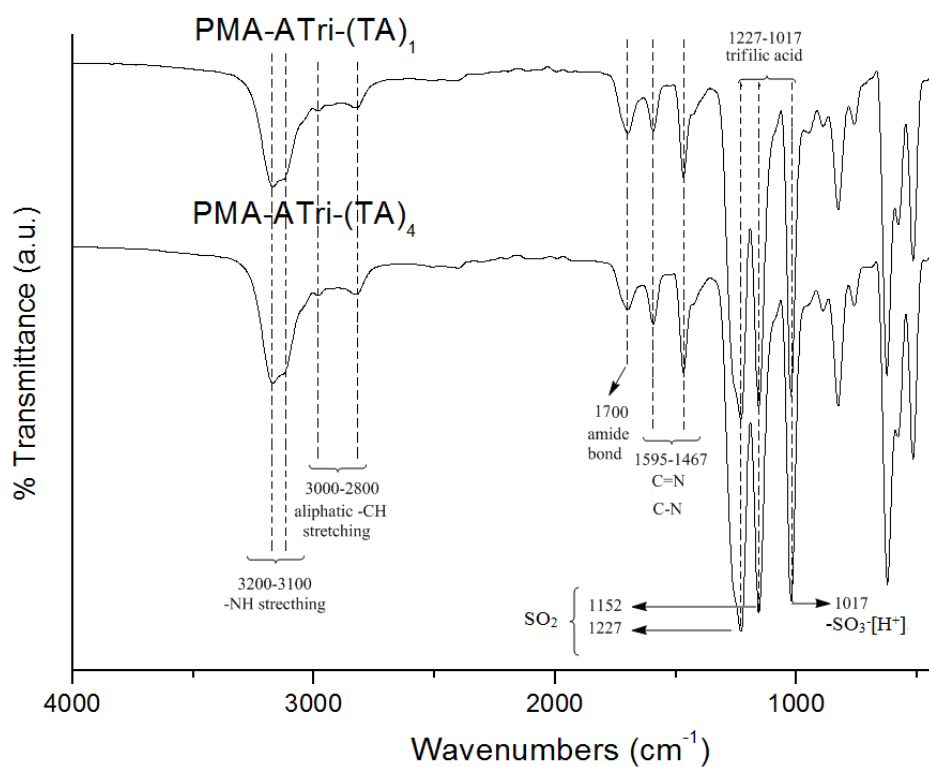


Figure 3.7 FTIR spectra of PMA-ATri-(TA)₁ and PMA-ATri-(TA)₄.

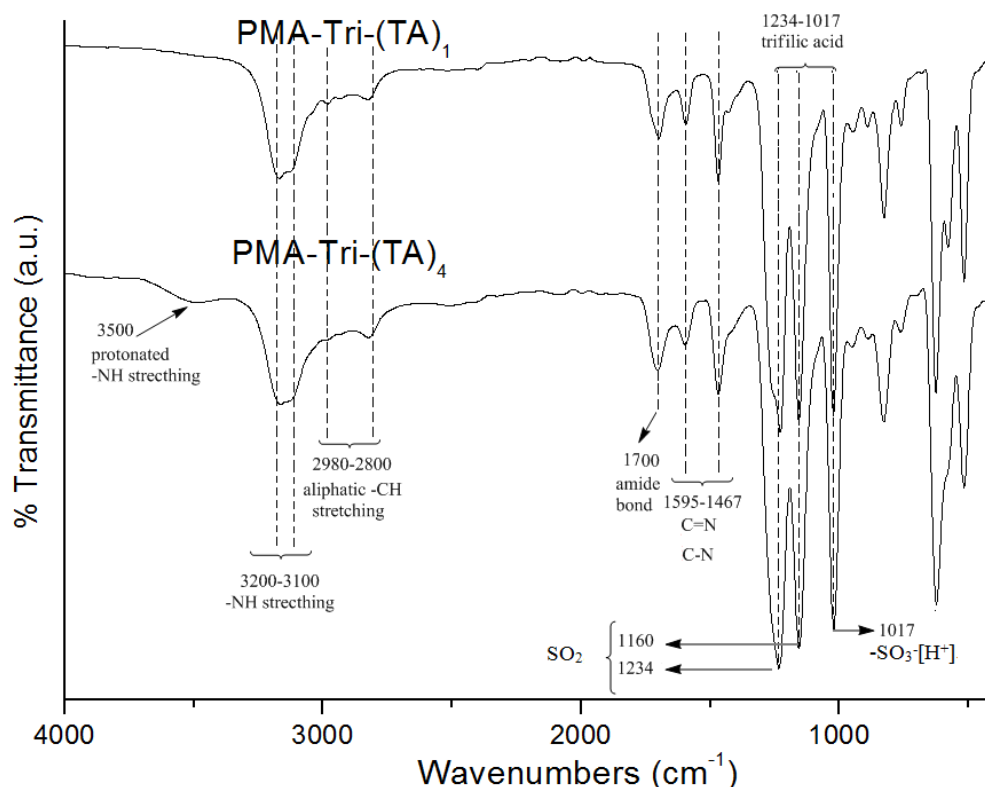


Figure 3.8 FTIR spectra of PMA-Tri-(TA)₁ and PMA-Tri-(TA)₄.

3.1.3 Thermal analysis

The thermal stability of PMA-ATri-(TA)_x and PMA-Tri-(TA)_x ($x=1$ and 4) electrolytes were studied by TGA and depicted in Fig. 3.9 and Fig. 3.10, respectively. The homopolymer, PMAC, is thermally stable up to 210°C beyond which it degrades via two stages. Decomposition of PMAC is represented at 210°C and 365°C (Fig. 3.9). After the modification of PMAC with 3-aminotriazole, the thermal stability decreases to 195°C as depicted in Fig. 3.9. About 30 % of the PMA-ATri decomposes between 195 and 350°C because of degradation of aminotriazole units and after 360°C , second weight loss region occurs because of decomposition of the polymer backbone. Since the functional polymers were doped with triflic acid (TA), the thermal stability shifts to 300°C (Sinirlioglu et al., 2014c).

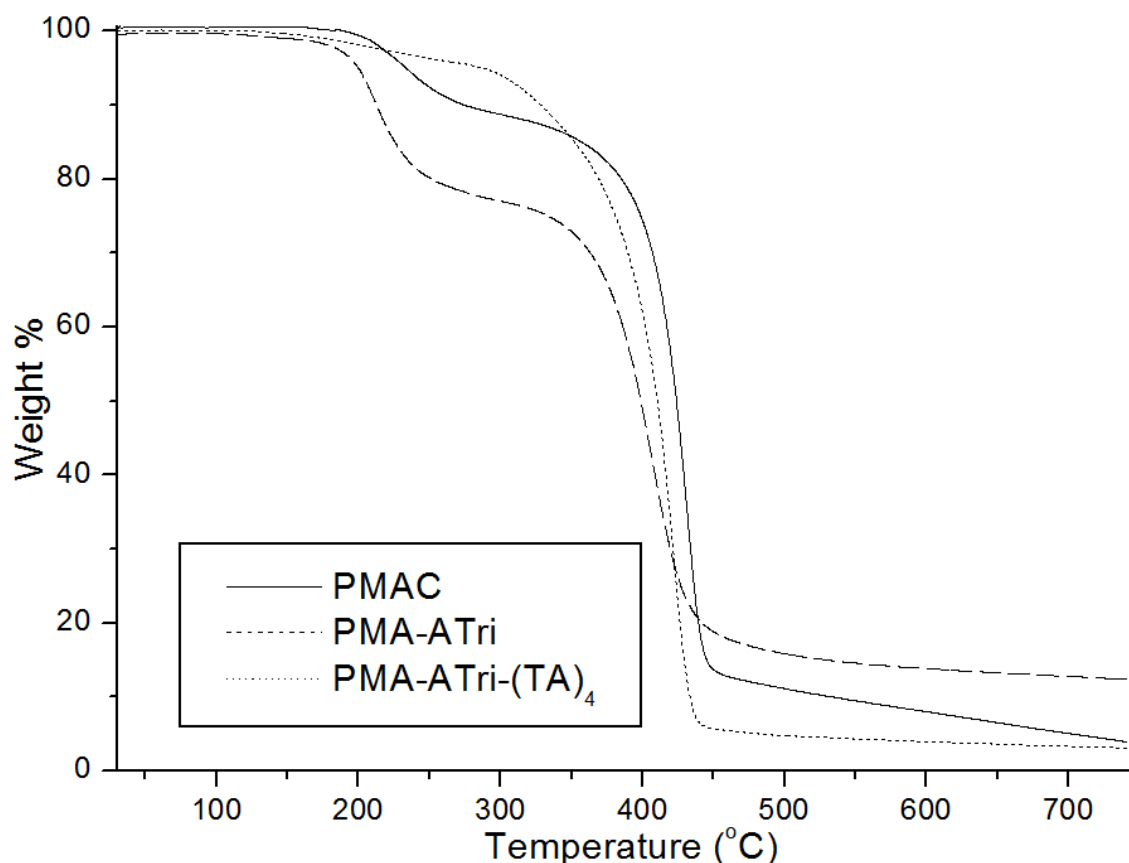


Figure 3.9 TG thermograms of PMAC, PMA-ATri and PMA-ATri-(TA)₄ recorded at a heating rate of 10 °C/min under nitrogen atmosphere.

Figure 3.10 shows the TGA of triazole functional samples. The sample PMA-Tri is thermally stable up to 200 °C. Approximately, 30 % of the PMA-Tri decomposes between 200 and 350 °C because of degradation of triazole units, and after 360 °C, second weight loss region occurs because of decomposition of the polymer backbone. As the functional polymer was doped with triflic acid, the thermal stability increases. All of these doped samples are thermally stable up around 325 °C. In these doped samples, the weight loss starts at higher temperatures compared with pure polymer as nearly single step. This may be due to the hydrogen bonding between triflic acid and triazole units, which delays the triazole unit degradation (Sinirlioglu et al., 2014c).

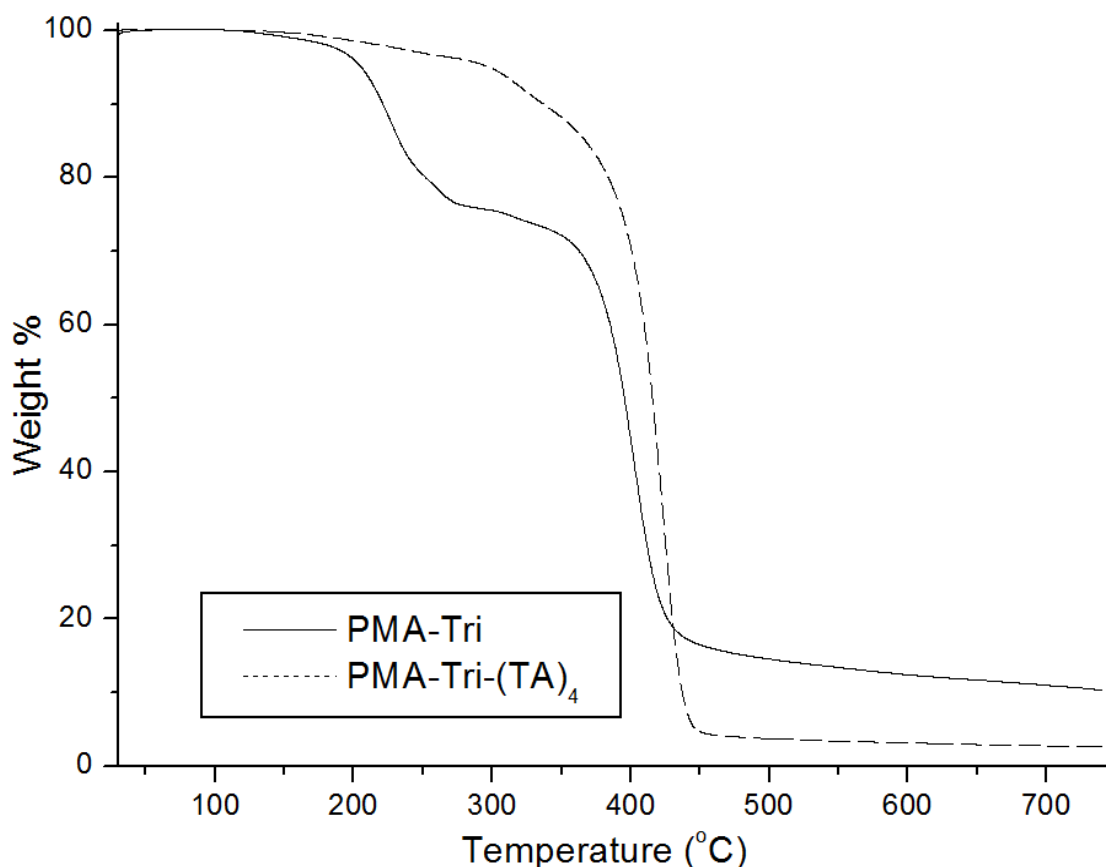


Figure 3.10 TG thermograms of PMA-Tri and PMA-Tri-(TA)₄ recorded at a heating rate of 10 °C/min under nitrogen atmosphere.

The thermal stability of PMA-ATet and PMA-ATet-(TA)_x ($x=1$ and 4) electrolytes were studied by thermogravimetric analysis (TGA) and depicted in Figure 3.11. PMA-ATet functional polymer exhibited a thermal stability up to 196 °C. The doped samples are also thermally stable up to at least 210 °C. 25 % of PMA-ATet decomposes between 210 and 340 °C because of degradation of aminotetrazole units and after 365 °C, second weight loss region occurs because of decomposition of the polymer backbone. After doping the polymer, 10% of the samples, PMA-ATet-(TA)_x ($x= 1.0, 2.0$ and 4.0), decompose up to 250 °C and major weight loss occurs between 250 and 440 °C which presumably derives from the decomposition of the polymer electrolyte main chain (Strohriegl, 1993; Sinirlioglu et al., 2014c).

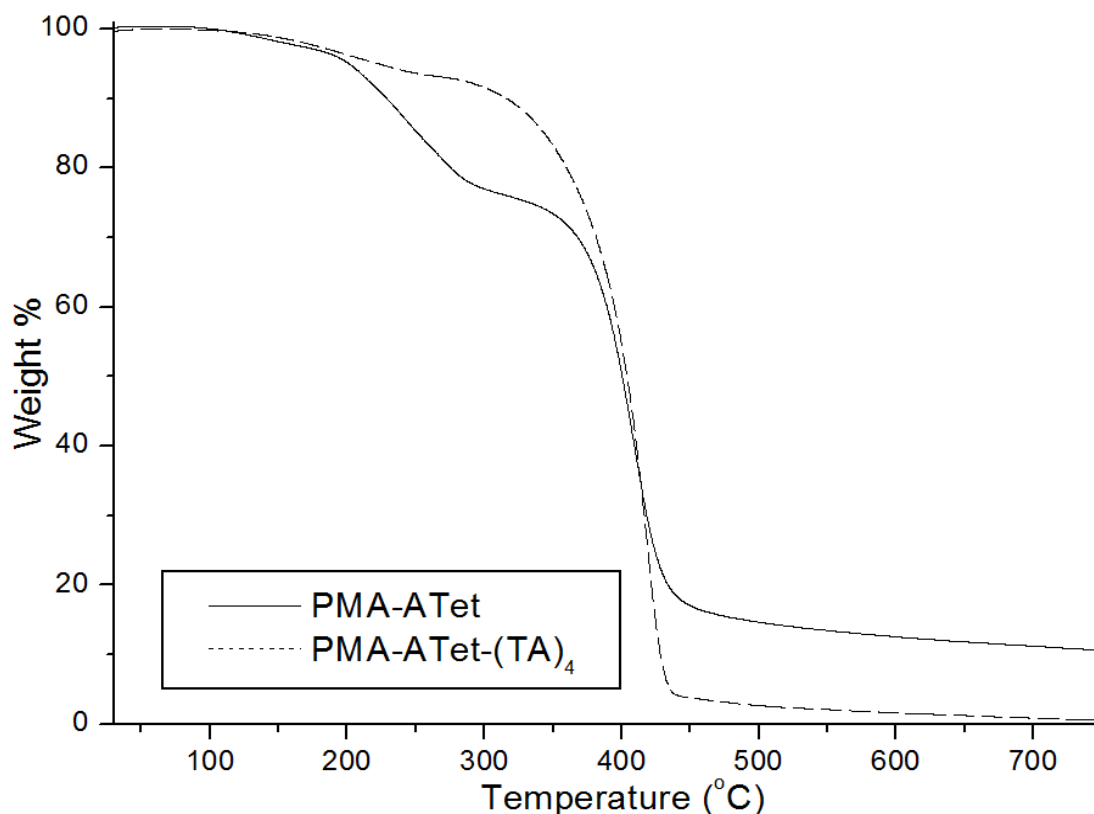


Figure 3.11 TG thermograms of PMA-ATet and PMA-ATet-(TA)₄ recorded at a heating rate of 10 °C/min under nitrogen atmosphere.

Table 3.2 shows the glass transition temperature, T_g , of PMA-ATet, PMA-ATri, PMA-Tri and triflic acid-doped samples, PMA-ATet-(TA)_x, PMA-ATri-(TA)_x, PMA-Tri-(TA)_x ($x=1.0, 2.0$ and 4.0) under inert atmosphere at a scan rate of 10 °C/min, respectively. The second heating curves were evaluated. The glass transition temperature, T_g of the homopolymer is measured at approximately 120 °C. While the tetrazole functional polymer, PMA-ATet, has a T_g of 98 °C. The glass transition temperatures of PMA-ATet-(TA)₁, PMA-ATet-(TA)₂ and PMA-ATet-(TA)₄ were shifted to 79 °C, 67 °C and 56 °C, respectively. While the aminotriazole functional polymer, PMA-ATri, has a T_g of 107 °C. The glass transition temperatures of PMA-ATri-(TA)₁, PMA-ATri-(TA)₂ and PMA-ATri-(TA)₄ were shifted to 78 °C, 74 °C and 66 °C, respectively. Also, triazole functional polymer has a T_g of 112 °C. The glass transition temperatures of PMA-Tri-(TA)₁, PMA-Tri-(TA)₂ and PMA-Tri-(TA)₄ were shifted to 96 °C, 91 °C and 84 °C, respectively (Sinirlioglu et al., 2014c). Clearly, the T_g values indicate a pronounced effect of the TA content on the softening behavior of the materials. The presence of single T_g confirms the homogeneity of the materials.

Table 3.2 T_g and proton conductivities of azole containing polymers.

Sample Name	Polymer-(TA) ratio	T _g (°C)	Max. Proton Conductivity at 150 °C (S/cm)
PMAC	-----	120	-----
PMA-Tri	-----	112	-----
PMA-ATri	-----	107	-----
PMA-ATet	-----	98	-----
PMA-Tri-(TA) ₁	1:1	96	0.004
PMA-Tri-(TA) ₂	1:2	91	0.007
PMA-Tri-(TA) ₄	1:4	84	0.02
PMA-ATri-(TA) ₁	1:1	78	1.5 x 10 ⁻⁴
PMA-ATri-(TA) ₂	1:2	74	4.8 x 10 ⁻⁴
PMA-ATri-(TA) ₄	1:4	66	8.7 x 10 ⁻⁴
PMA-ATet-(TA) ₁	1:1	79	0.008
PMA-ATet-(TA) ₂	1:2	67	0.009
PMA-ATet-(TA) ₄	1:4	56	0.01

3.1.4 Proton conductivity measurements

The proton conductivity studies of the samples were performed using a Novocontrol dielectric-impedance analyzer. For conductivity measurements, the samples were sandwiched between platinum blocking electrodes and measurements were performed at 20-150 °C temperature range and in the frequency range 1-3 MHz at 10 °C intervals. The AC conductivities, $\sigma_{ac}(\omega)$ of the polymers were measured at several temperatures using impedance spectroscopy. Frequency dependent AC conductivities ($\sigma_{ac}(\omega)$) were measured using the equation (2.5):

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \varepsilon''(\omega) \omega \varepsilon_0 \quad (2.5)$$

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, ε_0 is the vacuum permittivity ($\varepsilon_0 = 8.852 \times 10^{-14}$ F/cm), and ε'' is the imaginary part of complex

dielectric permittivity (ϵ^*). The proton conductivities of anhydrous nanocomposite polymer electrolytes were measured from 20 °C to 150 °C (Celik et al., 2012b).

The DC conductivity (σ_{dc}) of the samples was derived from the plateaus of log scale σ_{ac} versus frequency (F) curves by linear fitting plateau regions and extrapolating to zero frequency of the data. A marked curvature is observed for all samples and the curves are interpreted with the Vogel-Tamman-Fulcher (VTF) equation (2.6):

$$\log \sigma = \log \sigma_0 - E_v/[k(T-T_0)] \quad (2.6)$$

where σ_0 is the conductivity at infinite temperature, E_v is the Vogel activation energy and T_0 is the Vogel temperature.

The direct current (DC) conductivities of the triflic acid-doped PMA-ATri, PMA-Tri and PMA-ATet which were derived from impedance plots are compared in Fig. 3.12, Fig. 3.13 and Fig. 3.14. The conductivity isotherm illustrates that the DC conductivity strongly depends on temperature and the doping ratio of triflic acid. In the anhydrous conditions, the highest proton conductivities were obtained for TA ratio of 4. PMA-Tri-(TA)₄, PMA-ATri-(TA)₄ and PMA-ATet-(TA)₄ membranes gave maximum conductivities of 0.02 S/cm, 8.7×10^{-4} S/cm, and 0.01 S/cm at 150 °C, respectively (Sinirlioglu et al., 2014c). In the azole functional polymer/acid systems, acid ratio plays a crucial role in proton conductivity. Çelik et al showed that the proton conductivity decreased as the triflic acid (TA) ratio became lower, which was explained with an aggregation scheme of the azole units in the polymer matrix (Celik and Bozkurt, 2008). In a similar work, Aslan et al. investigated effect of the TA ratio on azole functional polymers and the proton conductivity reached to 0.012 S/cm at 80 °C (Aslan and Bozkurt, 2009). Triazole and tetrazole units are promising heterocycles whose molecular structures are similar to imidazole and therefore may conduct protons via structure diffusion mechanism (Celik et al., 2012b; Celik et al., 2011; Li et al., 2005). The high conductivities attained for highly doped PMA-Tri, PMA-ATri and PMA-ATet host matrices imply that conductivity in such systems occurs predominantly via the Grotthuss mechanism. Also tetrazole and triazole are promising in that respect where their basic nitrogen sites act as strong proton acceptors with respect to the acid group in the membranes, thus forming proton charge carriers (Kreuer, 1998). The proton could travel between protonated azole units and sulfonic acid units of TA.

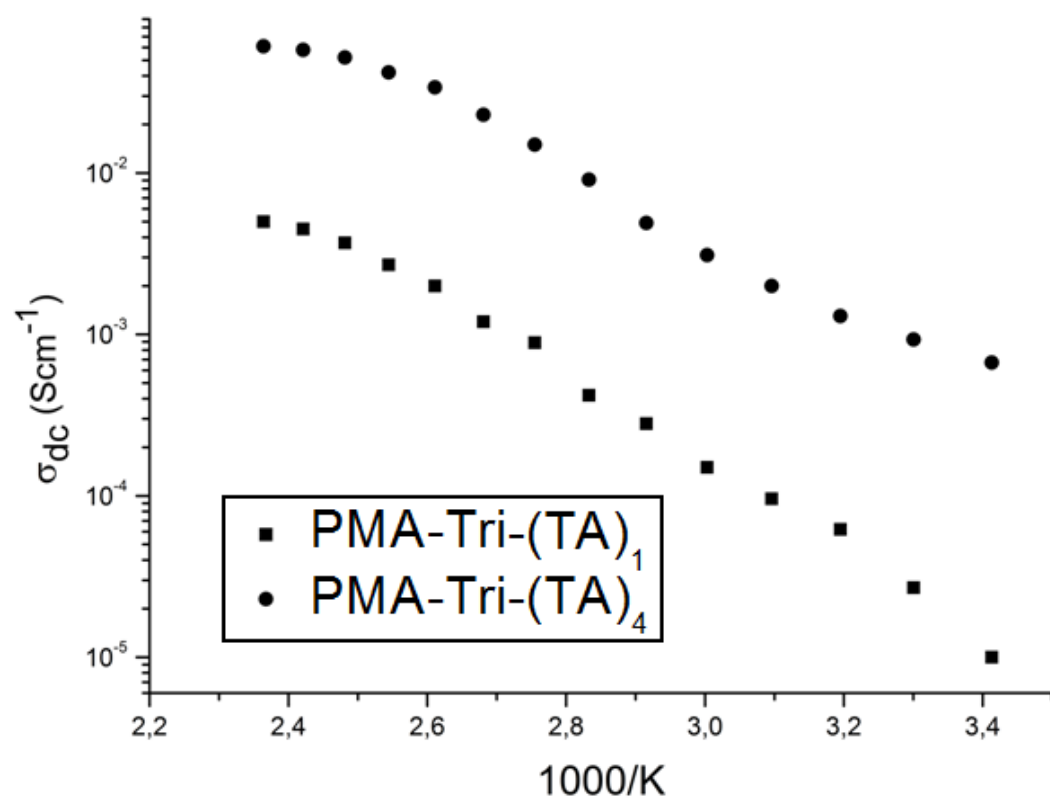


Figure 3.12 DC conductivities of PMA-Tri-(TA)_x (x=1 and 4) as a function of reciprocal temperature.

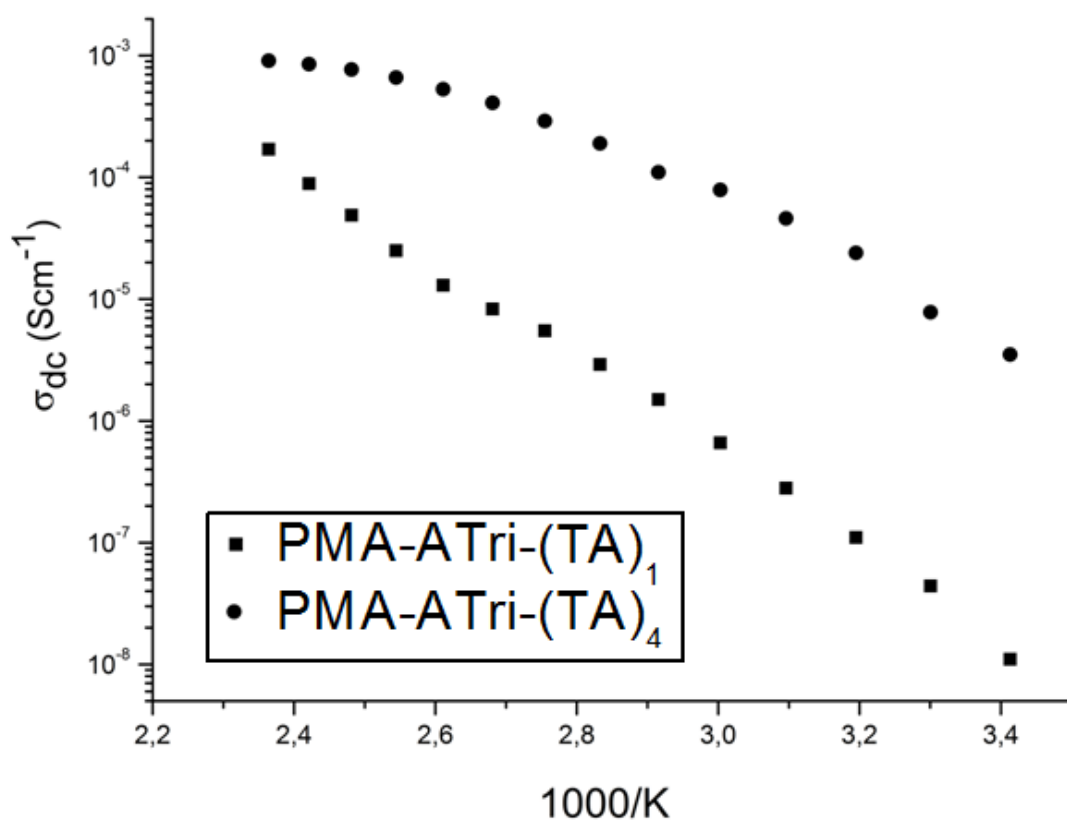


Figure 3.13 DC conductivities of PMA-ATri-(TA)_x (x=1 and 4) as a function of reciprocal temperature.

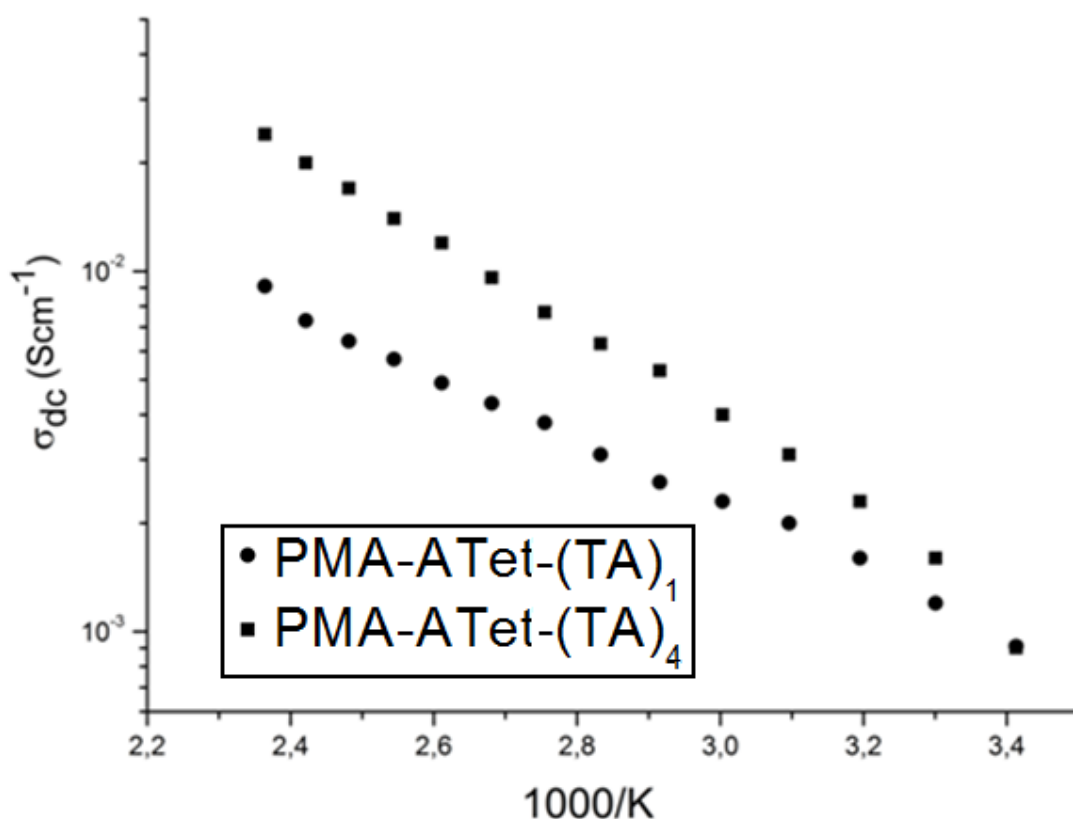


Figure 3.14 DC conductivities of PMA-ATet-(TA)_x (x=1 and 4) as a function of reciprocal temperature.

3.2 SYNTHESIS OF NOVEL MEMBRANES BASED ON POLY(5-(METHACRYLAMIDO)TETRAZOLE) AND SULFONATED POLYSULFONE

Blending two or more polymers is a simple approach to develop polymer electrolyte membranes with the advantage of combining superior features of each component (Di Vona et al., 2006; Wu et al., 2006). In particular, molecules or polymers bearing azole heterocycles with high proton conductivity can be suitably incorporated into stable polymers showing good mechanical and thermal properties such as Nafion, sulfonated polysulfone (SPSU), and sulfonated poly(ether ether ketone) (SPEEK) (Gustian et al., 2012; Fu et al., 2008; Kerres et al., 2007; Daletou et al., 2005; Hasiotis et al., 2001).

The sulfonated polysulfone (SPSU) is a good candidate for producing proton exchange membranes due to its low cost and commercial availability. Furthermore,

polysulfones (PSUs) show high thermal, chemical, and mechanical stability due to their phenyl rings on the polymer backbone. These aromatic polymers can be sulfonated by treatment with various sulfonating agents (Lufrano et al., 2000; Hasiotis et al., 2001). The proton conductivity of the sulfonated polysulfone (SPSU) membranes depends on the sulfonation ratio and the studies about SPSU are mostly based on humidity control (Devrim et al., 2009; Smitha et al., 2008; Chen et al., 2005; Lufrano et al., 2000), however, there are only few reports (Gustian et al., 2012; Fu et al., 2008; Li et al., 2005) regarding its use in anhydrous proton conducting systems (Sinirlioglu et al., 2014d).

In this study, 5-(methacrylamido)tetrazole (MTet) monomer was prepared by the reaction of methacryloyl chloride with 5-aminotetrazole. It was subsequently polymerized via conventional free radical mechanism to obtain poly(5-(methacrylamido)tetrazole) (PMTet). Azole functional methacrylic homopolymer was prepared using conventional free radical polymerization as depicted in Figure 3.15.

SPSU (Fig. 3.16) was prepared according to literature (Chen et al., 2005). The commercial PSU was dissolved in 1,2-dichloroethane (DCE) at 25 °C for 4 h under nitrogen atmosphere. Trimethylsilyl chlorosulfonate (TMSCS) was added at room temperature as the sulfonation agent. PSU / TMSCS mole ratio was set as 1:2. Silicon containing compounds, methyl sulfate, dichloroethane, methanol, and water were removed through evaporation and then the polymer was dried in vacuum (400 mmHg) at 55 °C (Sinirlioglu et al., 2014d).

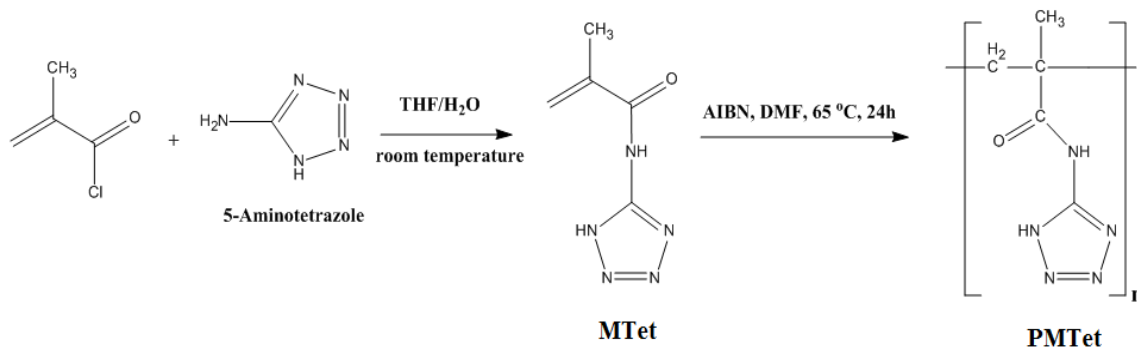


Figure 3.15 Synthesis and polymerization of tetrazole functional methacrylamide based monomer.

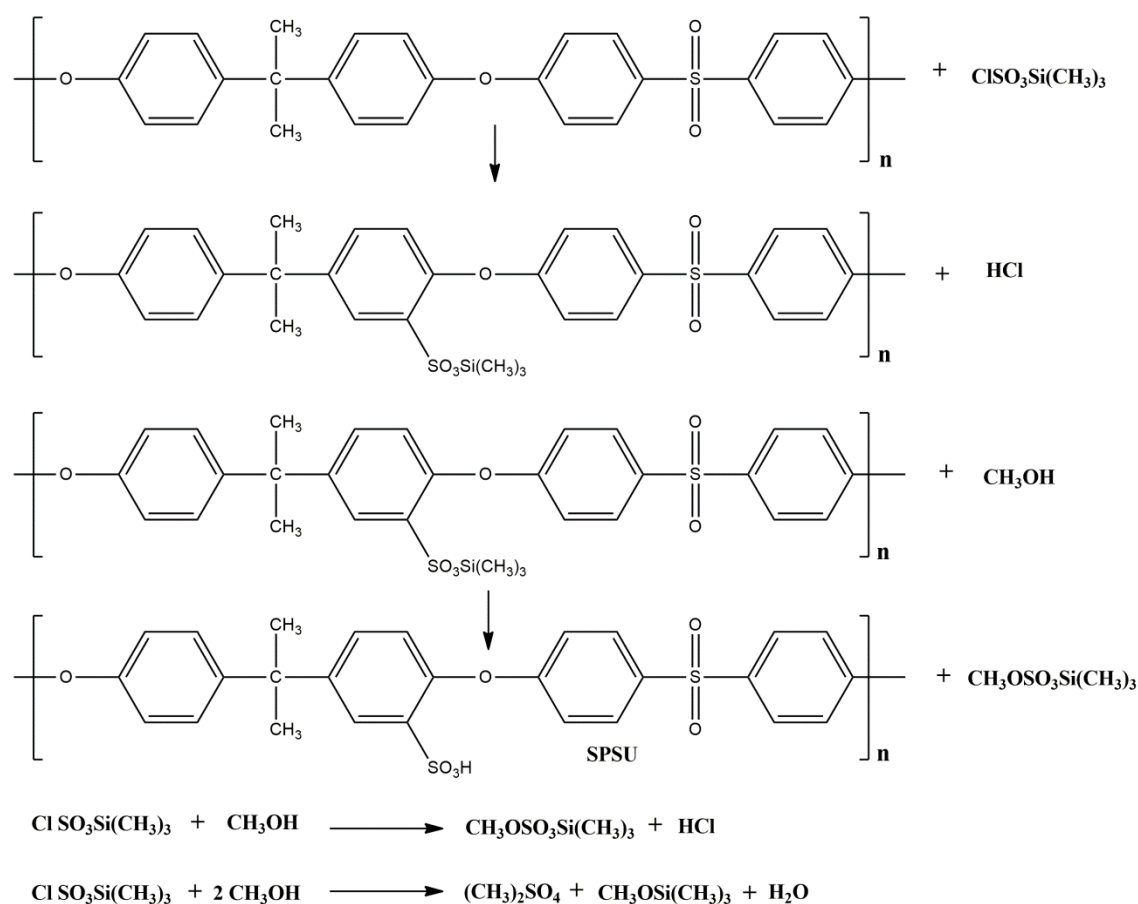


Figure 3.16 The reactions involved in the sulfonation process of PSU. $(\text{CH}_3)_2\text{SO}_4$ and $\text{CH}_3\text{OSi}(\text{CH}_3)_3$ are volatile under vacuum at high temperature (Devrim et al., 2009).

The degree of sulfonation (DS) of SPSU was determined by acid-base titration with standard NaOH solution. Initially, the SPSU was dissolved in DMF. The solution of polymer was then titrated by an aqueous solution of 0.0147 N NaOH using phenolphthalein as the end point indicator. The titration method indicated a sulfonation ratio of 140% [(mol SO_3H /repeat unit) $\times 100$], which is higher than the reported maximum sulfonation level for this method (127 %) (Harrison et al., 2005).

Proton conducting composite membranes were prepared by doping of SPSU with poly(5-(methacrylamido)tetrazole) (PMTet). Homogeneous and semi-transparent membranes were obtained (Figure 3.17).

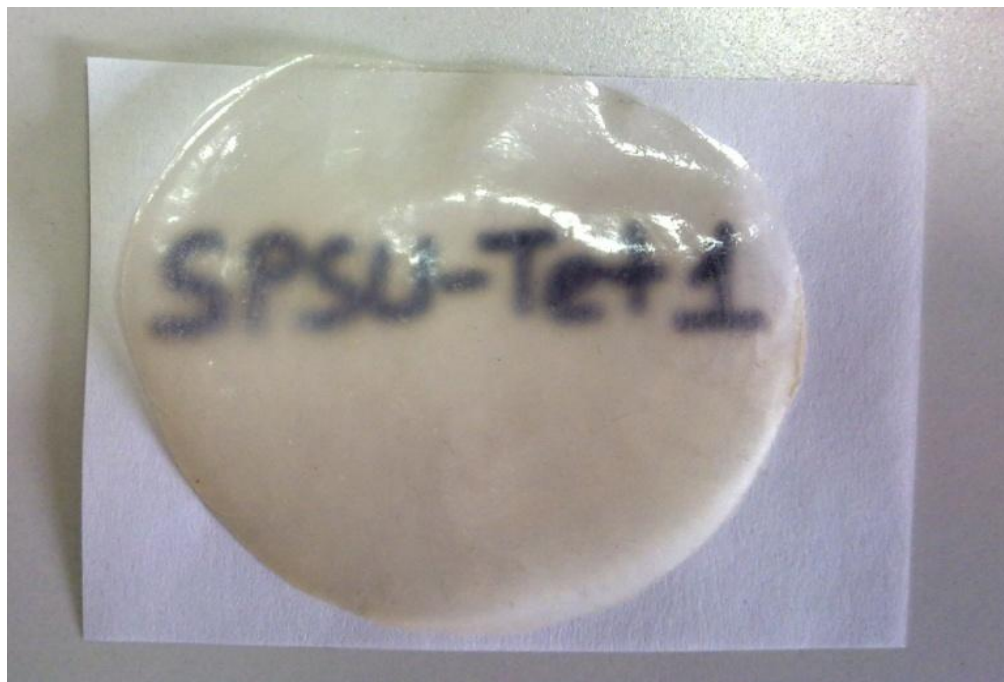


Figure 3.17 Picture of homogeneous and semi-transparent SPSU-PM Tet1 membrane.

3.2.1 FTIR studies

Figure 3.18 shows the FTIR spectra of pure PSU, SPSU and PMTet. PMTet exhibited several medium or strong peaks between 1689 cm^{-1} and 1475 cm^{-1} due to amide bond and tetrazole ring vibrations, respectively (Celik et al., 2008a). And also, PMTet has N-N stretching at 1245 cm^{-1} . The peaks at $735\text{--}1160\text{ cm}^{-1}$ correspond to C-H stretching bands and the formation of a slightly broad peak at around 3200 cm^{-1} shows the protonation of tetrazole rings. SPSU has peaks at $686, 1010, 1090, 1143, 1236, 1480, 2940, 3100, 3400\text{ cm}^{-1}$, which correspond to C-S, SO_3 , C-O, R- SO_2 -R, C-O, C=C (aromatic), C-H (aliphatic), C-H (aromatic), and -OH stretching bonds, respectively. In FTIR of SPSU, the presence of OH peaks at 3400 cm^{-1} and O=S=O stretching vibration of $-\text{SO}_3$ groups near 1010 cm^{-1} confirms the sulfonation of PSU (Gustian et al., 2012; Sinirlioglu et al., 2014d). Figure 3.19 shows FTIR spectra of SPSU-PM TetX blends. The intensities of the bands corresponding to the azole ring stretchings at 1475 and 1650 cm^{-1} have changed. SPSU-PM TetX blends have a peak at 3180 cm^{-1} that corresponds to N-H stretching. Furthermore, between 3500 and 2000 cm^{-1} , a broadening of the band can be related to hydrogen bonding network formation N-H between heterocyclic PMTet homopolymer and SPSU ($-\text{SO}_3\text{H}$) (Sinirlioglu et al., 2014d).

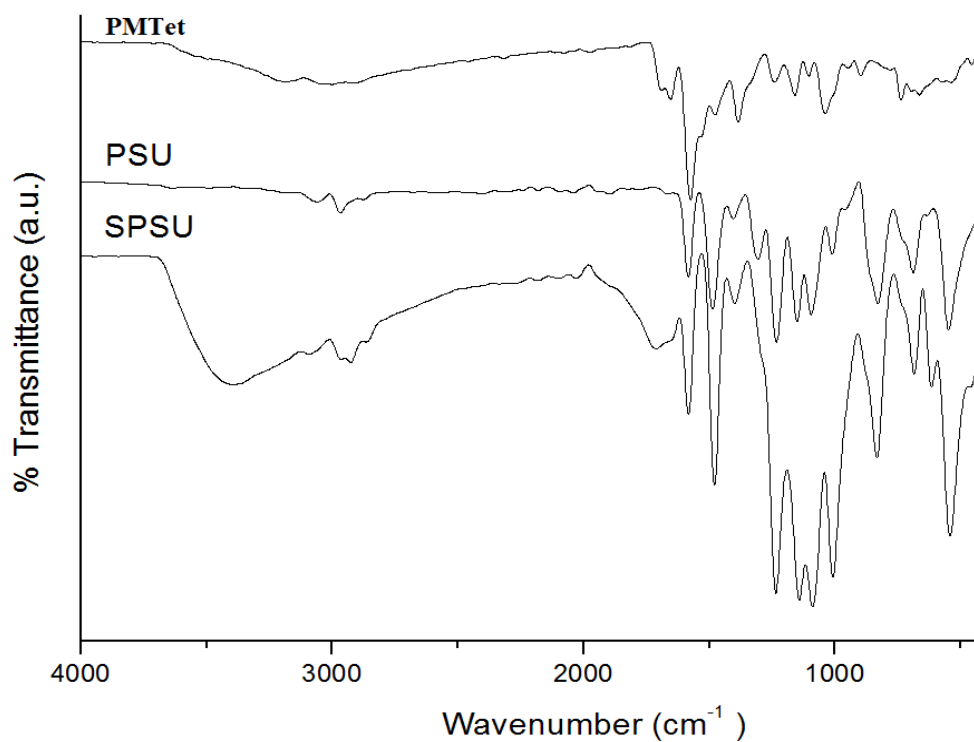


Figure 3.18 FTIR spectra of polysulfone (PSU), sulfonated polysulfone (SPSU) and poly(5-(methacrylamido)tetrazole, (PMTet).

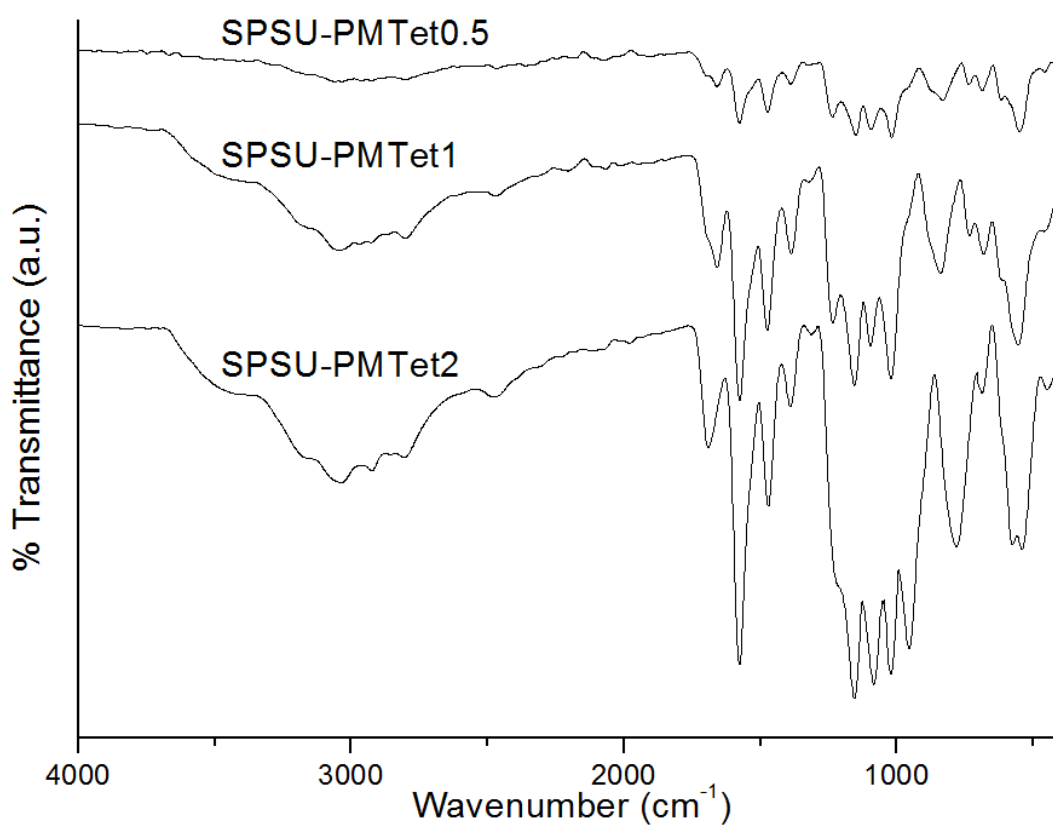


Figure 3.19 FTIR spectra of SPSU-PMTet0.5, SPSU-PMTet1 and SPSU-PMTet2.

3.2.2 NMR studies

Fig. 3.20 and Fig. 3.21 show ^1H -NMR and ^{13}C -NMR spectra of tetrazole functional monomer (MTet), respectively. The appearance of the peaks belonging to -NH proton of the tetrazole ring and amide bond proton at 15.90 and 11.97 ppm are a typical indication for the successful modification of methacryloylchloride monomer as depicted in Fig. 3.20 (Andreas et al., 2002). Also, the signals at 6.09 ppm and 5.74 ppm are assigned to the methine proton (1H , $=\text{CH}$) which indicates in vinyl group.

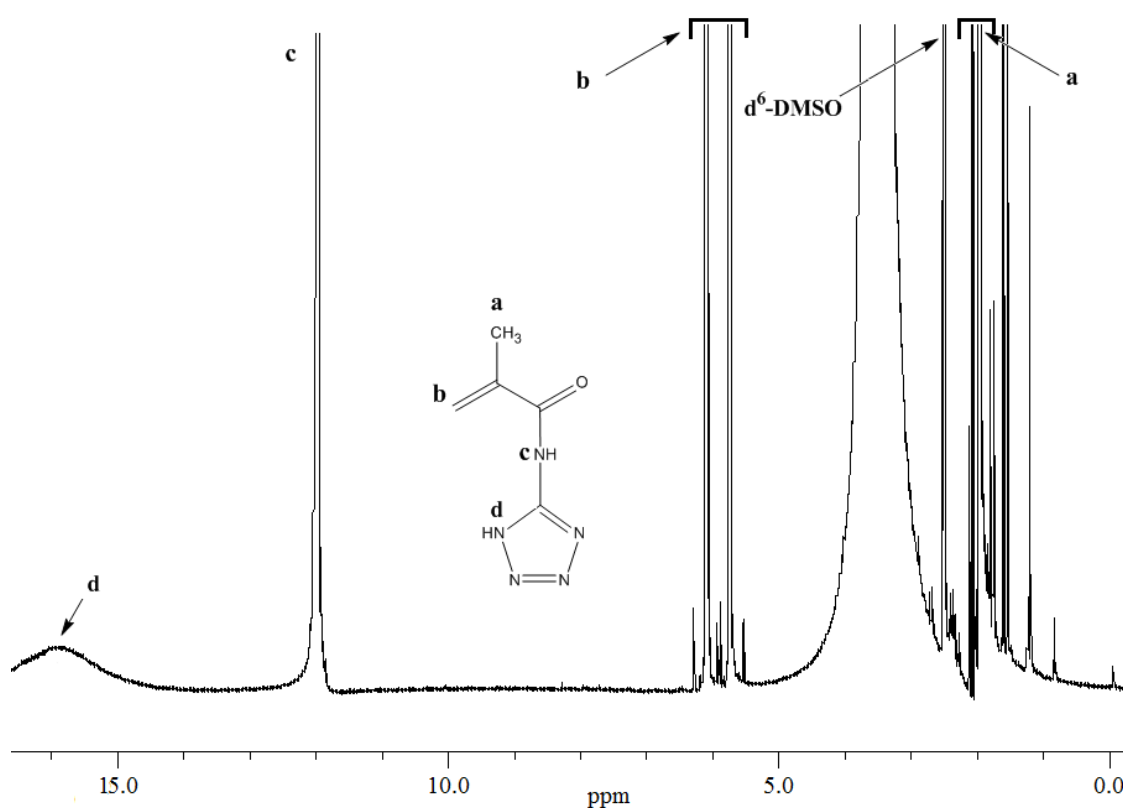


Figure 3.20 ^1H -NMR spectra of MTet monomer recorded in DMSO-d_6 .

^{13}C -NMR spectra of MTet monomer is given Fig. 3.21. Signals corresponding to the methyl group appeared around 18 ppm. The peak located at around 167 ppm belongs to carbon of the carbonyl group. Additionally, the tetrazole ring carbon gave a peak around 150 ppm in the aminotetrazole ring (Andreas et al., 2002). ^{13}C -NMR (400 MHz, DMSO-d_6 , δ): 18.2 (CH_3), 123.9 (CH_2), 137.6, 150.1, 166.7 (ipso-C, $\text{C}=\text{O}$).

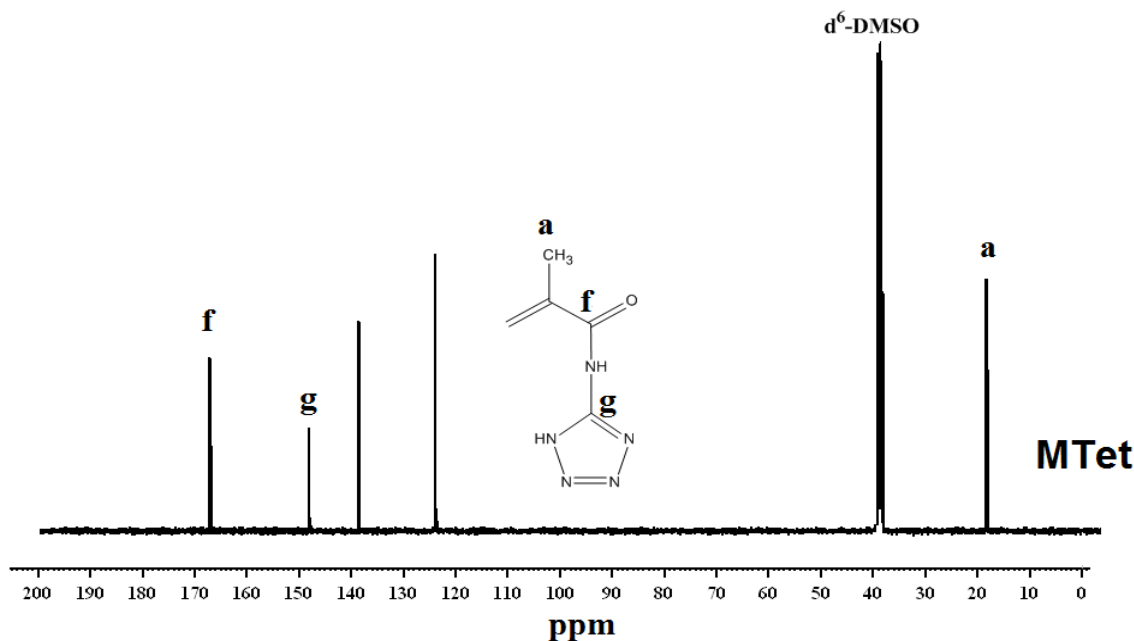


Figure 3.21 ^{13}C -NMR spectra of MTet monomer recorded in DMSO-d_6 .

Fig. 3.22 shows ^1H -NMR spectra of tetrazole functional polymer, abbreviated as Poly(5-methacrylamidotetrazole) (PMTet). The appearance of the peaks belonging to -NH proton of the tetrazole ring and amide bond proton at 15.90 and 11.65 ppm are a typical indication for the successful polymerization of tetrazole functional monomer, respectively. The disappearance of peaks at 6.09 and 5.74 ppm from vinylic protons of MTet monomer, depicted in Fig. 3.22, supports that the monomer has been polymerized completely (Sinirlioglu et al., 2014d). In addition, the signals at 2.34 ppm and 2.09 ppm are assigned to the methylene proton (2H, -CH_2) which indicates polymer backbone. (Andreas et al., 2002). The signals at 2.51 and 3.40 ppm belong to solvent (DMSO) and water, respectively. In addition, the signals at 2.75, 2.89 and 7.99 ppm belong to the DMF (Sinirlioglu et al., 2014d).

Fig. 3.23 illustrates the representative ^1H -NMR spectrum of PSU (a) and SPSU (b). The proton resonance at around 7.70 ppm is assigned to the proton adjacent to the new pendant sulfonic acid. Also, the aromatic -CH protons are depicted with numerical numbers. Consequently, FTIR and ^1H -NMR analysis confirmed the successful electrophilic substitution of trimethylsilyl chlorosulfonate and chlorosulfonic onto PSU (Devrim et al., 2009; Sinirlioglu et al., 2014d).

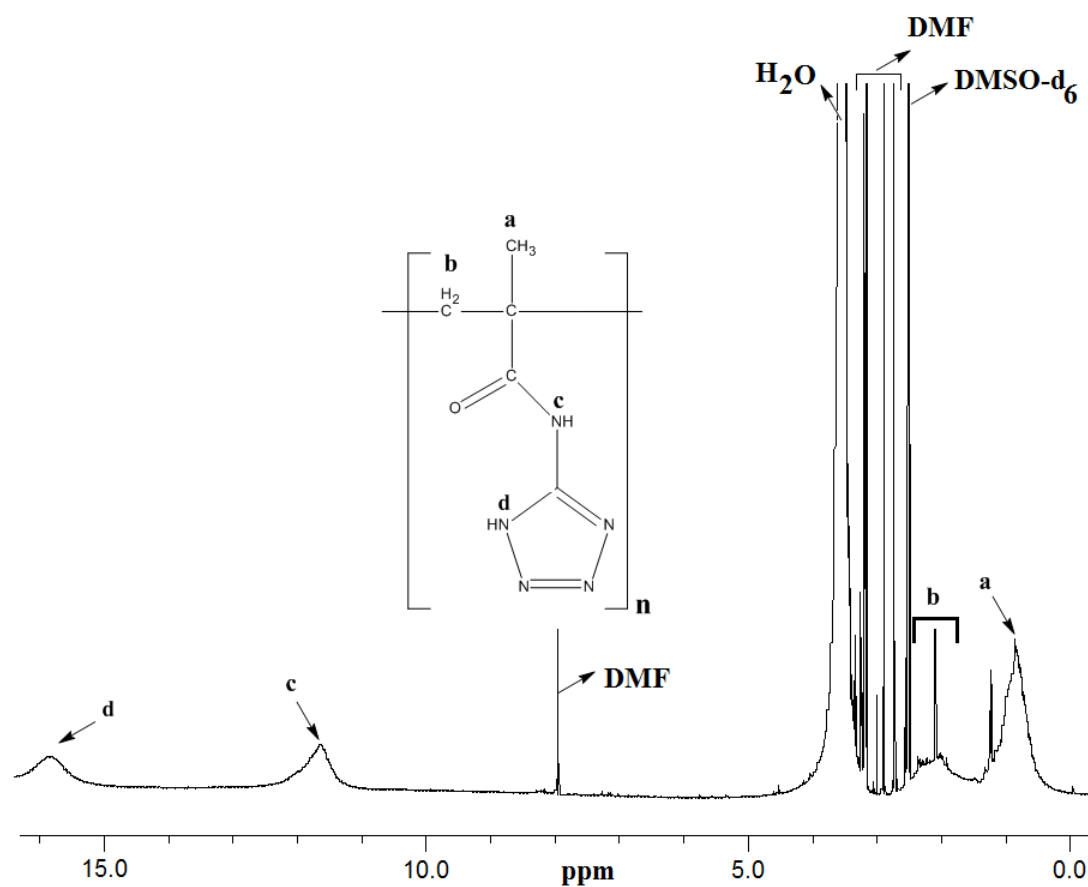


Figure 3.22 ^1H -NMR spectra of poly(5-(methacrylamido)tetrazole) recorded in DMSO-d_6 .

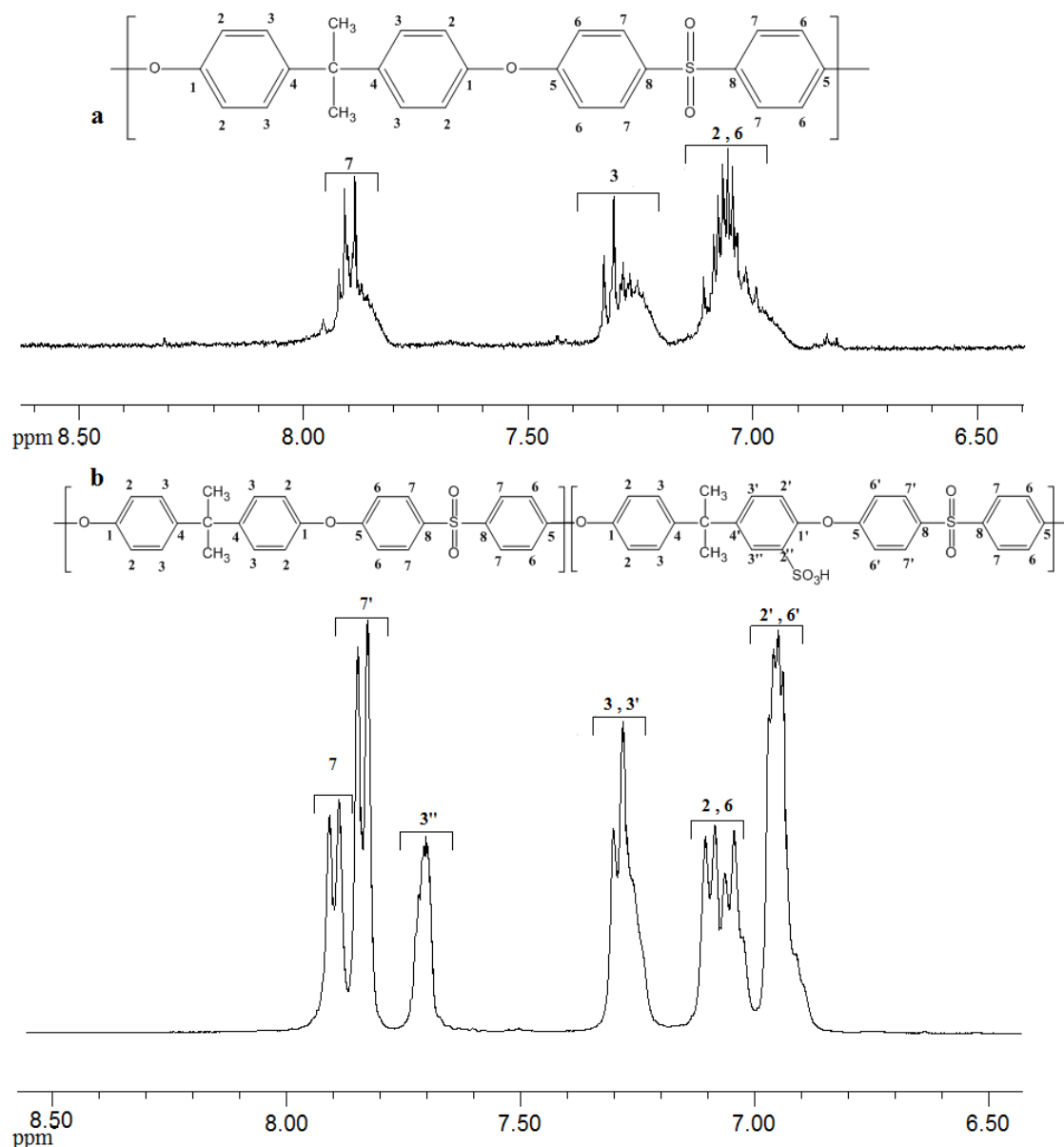


Figure 3.23 (a) ^1H -NMR spectra of polysulfone (PSU) recorded in DMSO-d_6 , (b) ^1H -NMR spectra of sulfonated polysulfone (SPSU) recorded in DMSO-d_6 .

3.2.3 Thermal analysis

Thermogravimetric analysis (TGA) of PMTet, PSU, SPSU and SPSU-PMTet(x) ($x = 0.5, 1.0$ and 2.0) membranes was reported in Fig. 3.24. PMTet exhibited a thermal stability up to 220°C . 40 % of PMTet decomposes between 220 and 380°C because of degradation of tetrazole units and after 380°C , second weight loss region occurs because of decomposition of the polymer backbone.

Pure PSU is thermally stable up to around 500 °C and there is only one weight loss step that is ascribed to the decomposition of the polymeric backbone (Lufrano et al., 2008). For the SPSU, there are three transitions of weight loss in three separate temperature ranges can be separated in the Figure 7. The first step around 100 °C is related to the loss of the absorbed water. The second one, SPSU has weight loss region where 40% weight loss occurs between 200 °C and 370 °C, can be assigned to the degradation of sulfonic acid groups. The third thermal degradation of SPSU after 460 °C is attributed to the degradation of polymer backbone (Devrim et al., 2009; Smitha et al., 2008). This distinct change in TGA curve also verifies the sulfonation of PSU. As SPSU was blended with PMTet, the degradation temperature decreased a little but all blends can be said to be thermally stable at least 190 °C (Sinirlioglu et al., 2014d).

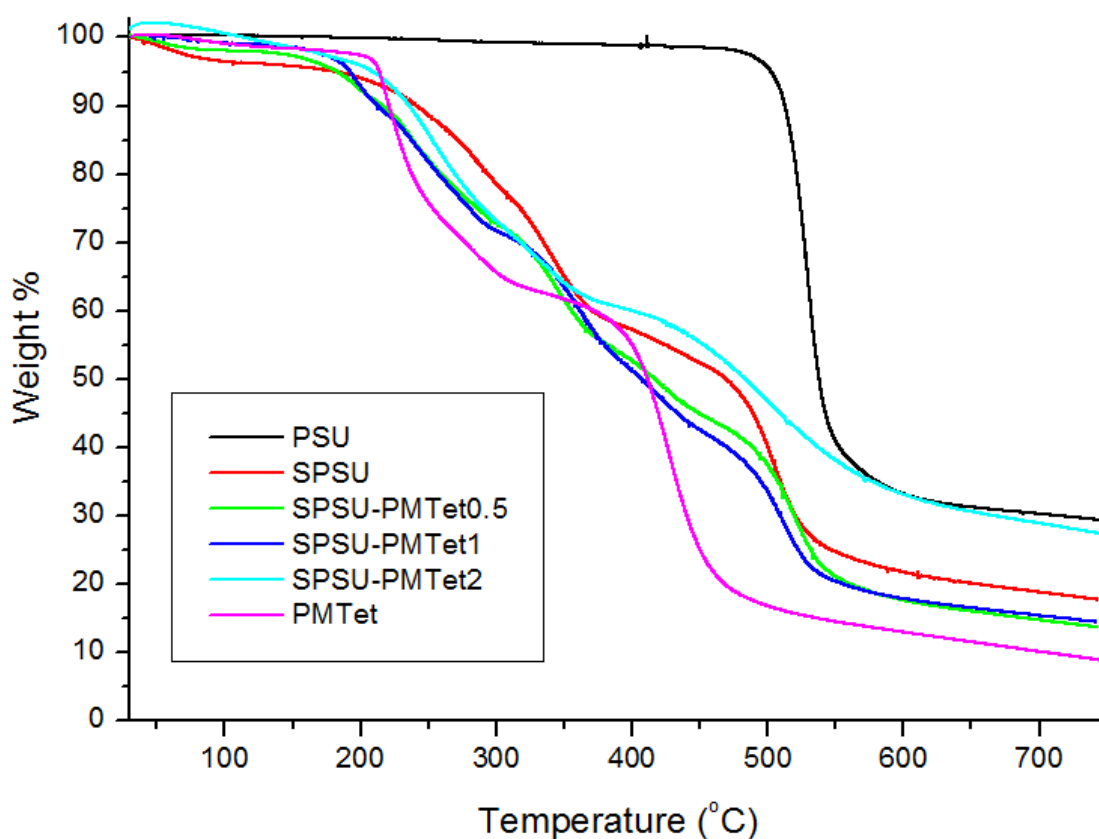


Figure 3.24 TGA curves of PMTet, PSU, SPSU, SPSU-PMTet0.5, SPSU-PMTet1, and SPSU-PMTet2 at a heating rate of 10°C min⁻¹.

Table 3.3 shows the glass transition temperature, T_g , of PSU, SPSU, SPSU-PMTetX under inert atmosphere at a scan rate of 10 °C/min, respectively. Differential scanning calorimeter (DSC) curves of PSU, SPSU, PMTet, and SPSU-PMTetX (X= 0.5, 1 and 2) composite membranes are given in Fig. 3.25. In DSC measurements, the second heating curves were evaluated. The T_g of pure PSU was measured as 190 °C. After sulfonation, the T_g decreased to 128 °C. T_g of PMTet is measured at approximately 93 °C. When PMTet is incorporated into the sulfonated polysulfone, the glass transition temperatures of blend membranes, SPSU-PMTet0.5, SPSU-PMTet1 and SPSU-PMTet2 were shifted to 183 °C, 176 °C and 185 °C, respectively (Fig. 3.25). In the composite membranes, the presence of single T_g confirms the homogeneity of the materials. The composite membranes have higher T_g points than pure SPSU and PMTet which also confirms the formation of ionic interaction between tetrazole and sulfonic acid groups (Sinirlioglu et al., 2014d).

Table 3.3 T_g of PSU, SPSU, PMTet and blend membranes.

Sample Name	Polymer/polymer ratio	T_g (°C)
PSU	-----	190 °C
SPSU	-----	128 °C
PMTet	-----	93 °C
SPSU-PMTet0.5	1:0.5	183 °C
SPSU-PMTet1	1 : 1	176 °C
SPSU-PMTet2	1 : 2	185 °C

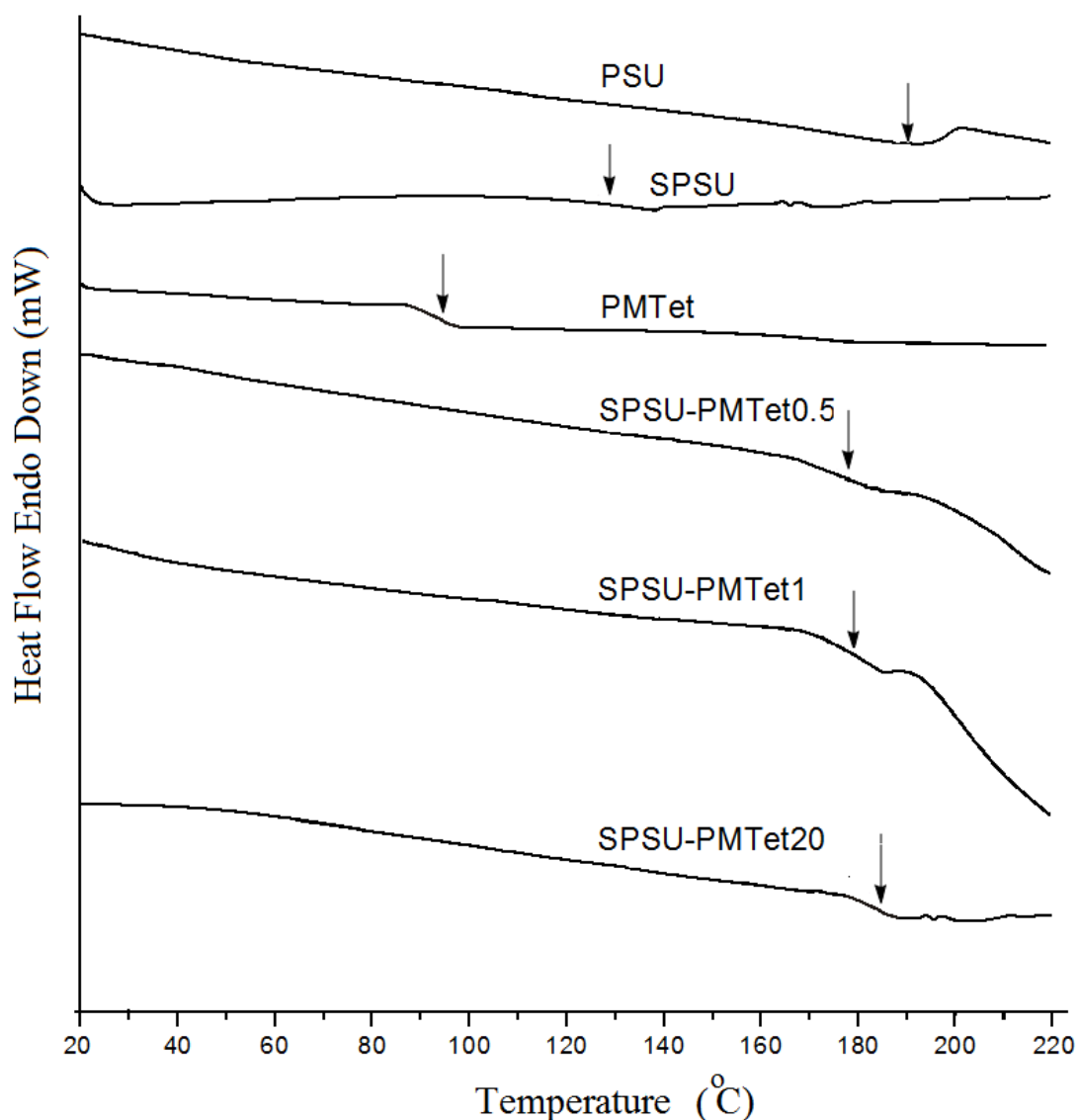
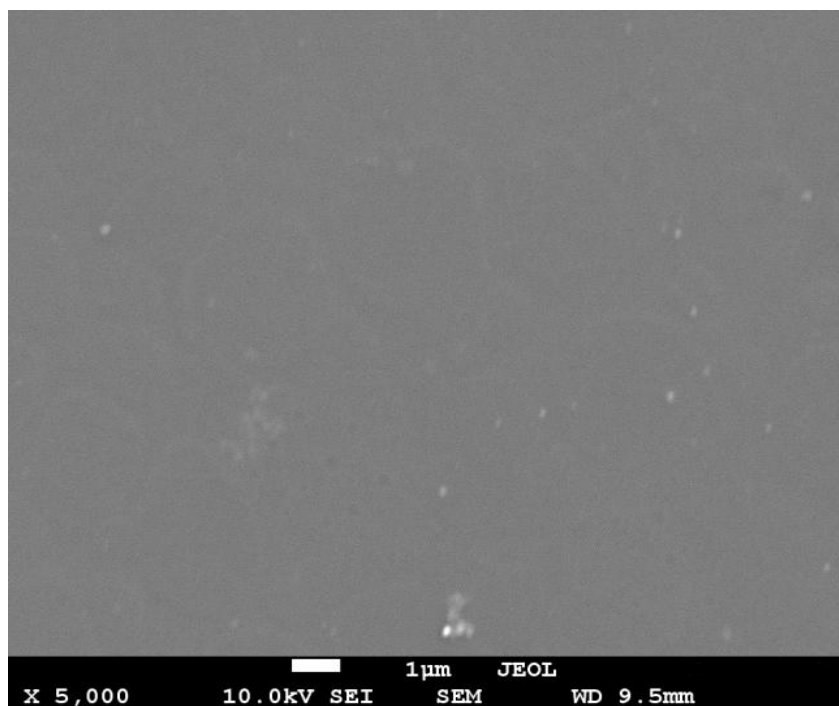


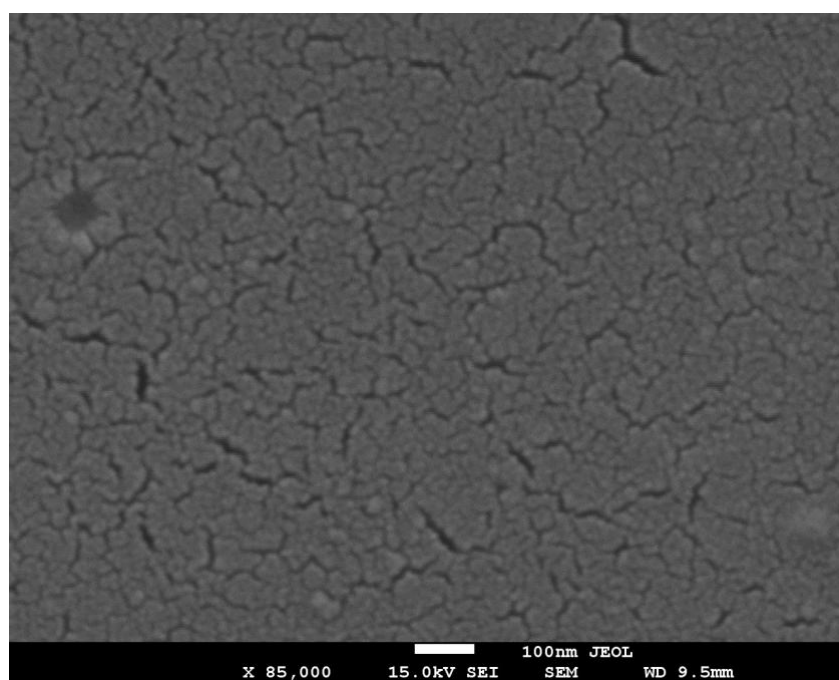
Figure 3.25 DSC thermograms of PSU, SPSU, PMTet, and SPSU-PMTetX composite membranes recorded under N₂ atmosphere at a heating rate of 10 °C/min.

3.2.4 Morphology

Surface morphologies of the blend membranes were investigated by SEM and depicted in Fig.3.26a and Fig. 3.26b. For all the samples, the images show single phase formation due to strong interaction between the sulfonic acid groups of SPSU and the tetrazole units of PMTet and the membranes seem homogeneous. This shows that the PMTet homopolymer uniformly distributed into the PSU matrix, and there is no agglomeration or phase separation at nanoscale and micrometer-scale level.



(a)



(b)

Figure 3.26 (a) SEM micrographs of the surface of SPSU-PMTet0.5, (b) SEM micrographs of the surface of SPSU-PMTet1.

3.2.5 Water Uptake

The water uptake of the membranes is a major parameter influencing proton conductivity, mechanical property and stability. The water uptake measurements were made according to the literature (Tsai et al., 2007). Water uptakes of the SPSU-PMTetX membranes are given in Fig. 3.27. As can be seen, water uptake with increasing sulfonic acid content due to swelling of SPSU in the blend. This is due to the fact that the sulfonic acid groups are hydrophilic and hence in order to obtain the membranes which have high degree of sulfonation polysulfone can absorb more water (Tsai et al., 2007). The swelling character of the samples reasonably decreased when there is equimolar of sulfonated polysulfone and tetrazole containing polymer. This finding is assigned to ionic interaction between SPSU and tetrazole containing polymer where the material becomes more rigid when $x=1$. The sample with (1:0.5) composition has the highest water uptake value (350 %). Clearly, the results showed that the increase in the sulfonic groups content in the composites improved the water uptake, and brought about better hydrophilicity (Sinirlioglu et al., 2014d).

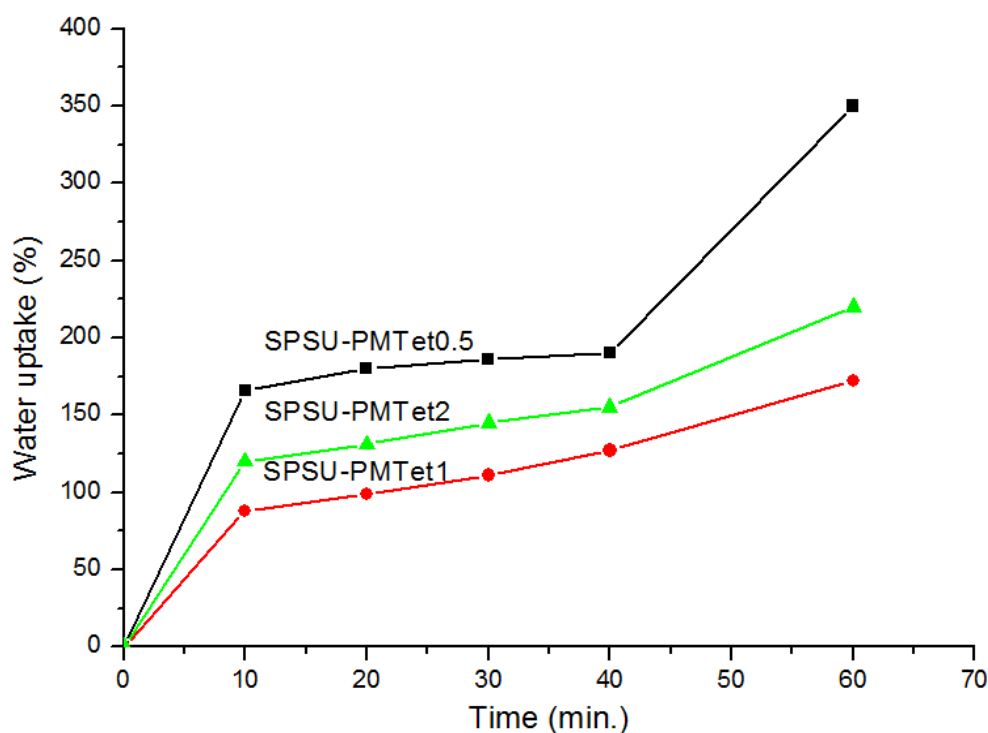


Figure 3.27 Water uptakes of SPSU-PMTetX ($X=0.5, 1$ and 2) at the time of 10-60 min in deionized water at 25 °C.

3.2.6 Methanol Permeability

Methanol permeability is a possible problem in the application of the membranes in direct methanol fuel cells. At high methanol concentrations its permeability from anode side to the cathode side results polarization losses. In this work, methanol permeability of the composite membranes was measured by simple homemade diaphragm diffusion cell similar to the previous Works (Gasa et al., 2007; Gasa et al., 2006). The cell is filled with 2 mL methanol and the mass flow is recorded as a function of time (Fig. 3.28). Molar methanol flux (J) through SPSU-PMTet(x) composite membranes was calculated using Eq. (2.2). Methanol permeability of blend membranes may be calculated using molar flux (J) shown in Eq. (2.3) (Boroglu et al., 2011b; Sen et al., 2008).

$$J = \frac{W}{M_w \times A \times t} \quad (2.2)$$

$$\frac{J_1 l_1}{J_2 l_2} = \frac{P_1}{P_2} \quad (2.3)$$

where J : flux, MW : molecular weight, W : weight loss (g), P : permeability, l : thickness (cm), A : area (cm²), t : time (s).

As seen in the equations the permeability is directly proportional to the molar flux. The molar flux of the SPSU-PMTetX composite membranes are shown in Fig. 3.28. The values are $3.66 \times 10^{-9} \text{ molcm}^{-2}\text{s}^{-1}$, $3.04 \times 10^{-9} \text{ molcm}^{-2}\text{s}^{-1}$ and $1.91 \times 10^{-9} \text{ molcm}^{-2}\text{s}^{-1}$ for SPSU-PMTet0.5, SPSU-PMTet1 and SPSU-PMTet2, respectively. Previously, the methanol permeability of Nafion 112 in the same conditions was measured and reported as $1.89 \times 10^{-9} \text{ molcm}^{-2}\text{s}^{-1}$ (Sen et al., 2008). As seen in Fig. 3.28, the methanol permeability of the composite membranes are very close to Nafion 112 (Sinirlioglu et al., 2014d).

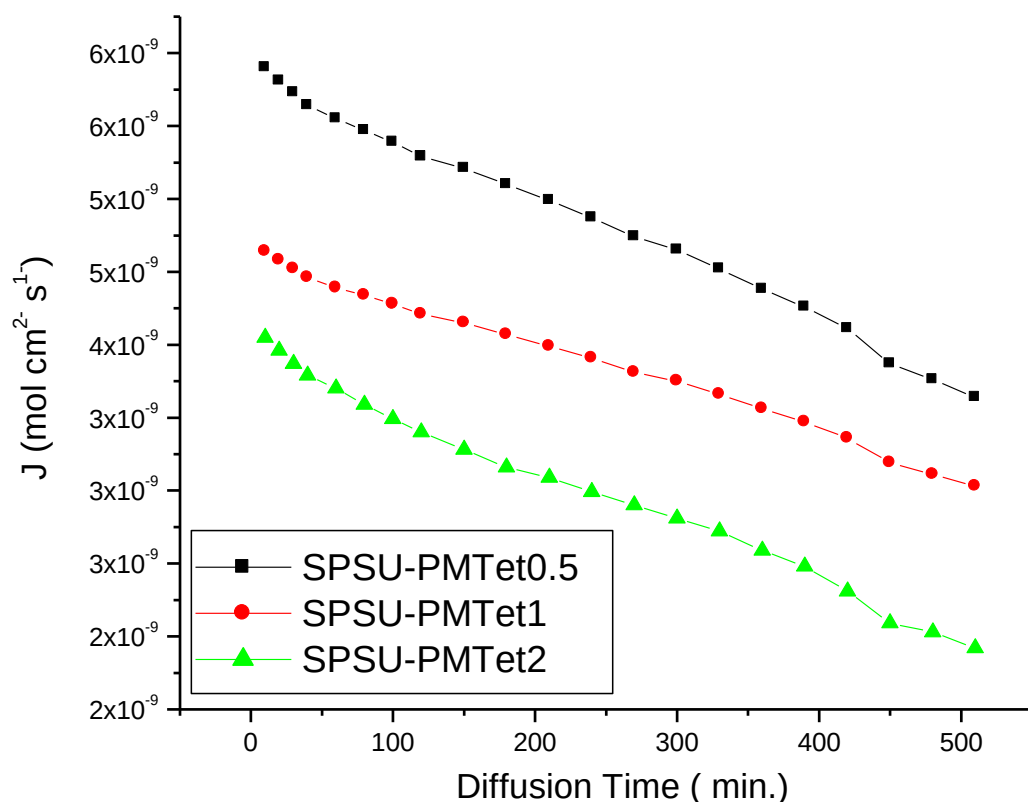


Figure 3.28 Methanol permeability of SPSU-PMTetX (X= 0.5, 1 and 2) composite membranes.

3.2.7 Atomic Force Microscopy (AFM)

The selected AFM images of the SPSU-PMTetX (X= 0.5, 1 and 2) membranes are illustrated in Fig. 3.29. Herein, AFM was used for determination of phase morphology and homogeneity of the blend membranes. 5×5 μm, 10×10 μm, and 20×20 μm images were taken at a resolution of 512 x 512 points within the range of 0.5-0.8 Hz scan rate and were subjected to first-order flattening (Sedin, 2001). For all the samples in Fig. 3.29, the images exhibit a single phase formation and the membranes seem homogeneous at nanometer-scale level. This shows that the heterocyclic PMTet homopolymer uniformly distributed into the SPSU matrix when the PMTet mol ratio was increased from 0.50 to 2.0. However, the surface image (in Fig. 3.29B and Fig.3.29C) might be due to salt formation of between acid-base (azole groups) units. In Fig. 3.29A, we observe a hole in nm scale which is related with the drying procedure for

SPSU-PMTe0.5 and has no effect on the proton conductivity or thermal properties. We can say that the membranes seem to be homogeneous (Sinirlioglu et al., 2014d).

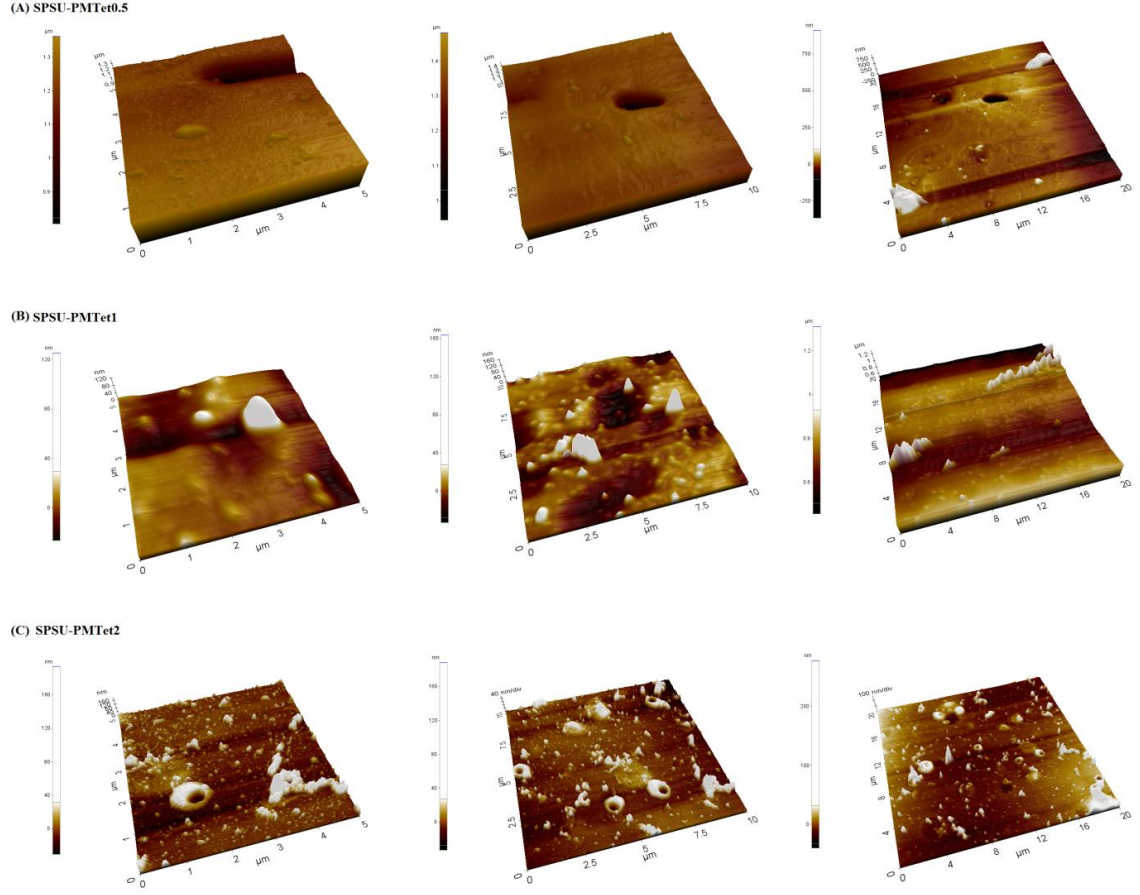


Figure 3.29 AFM pictures (3d) of SPSU-PMTeX (X= 0.5, 1 and 2) composite membranes. (a) $5 \times 5 \mu\text{m}$, (b) $10 \times 10 \mu\text{m}$, and (c) $20 \times 20 \mu\text{m}$.

3.2.8 Proton conductivity measurements

The AC conductivities, $\sigma_{ac}(\omega)$ of the polymers were measured at several temperatures using impedance spectroscopy. Frequency dependent AC conductivities ($\sigma_{ac}(\omega)$) were measured using the equation (2.5) (please see the previous section):

$$\sigma'(\omega) = \sigma_{ac}(\omega) = \epsilon''(\omega) \omega \epsilon_0 \quad (2.5)$$

where $\sigma'(\omega)$ is the real part of conductivity, $\omega = 2\pi f$ is the angular frequency, ϵ_0 is the vacuum permittivity ($\epsilon_0 = 8.852 \times 10^{-14}$ F/cm), and ϵ'' is the imaginary part of complex dielectric permittivity (ϵ^*). The proton conductivities of anhydrous nanocomposite polymer electrolytes were measured from 20 °C to 150 °C.

Fig. 3.30, Fig. 3.31, and Fig. 3.32 show the AC conductivities of SPSU-PMTEt0.5, SPSU-PMTEt1 and SPSU-PMTEt2 versus log frequency at several temperatures. The conductivity increases with the temperature and the DC conductivity (σ_{dc}) of the samples was derived from the plateaus of σ_{ac} versus log frequency by linear fitting of the data (10^2 - 10^4 Hz at 110-150 °C) (Sinirlioglu et al., 2014d).

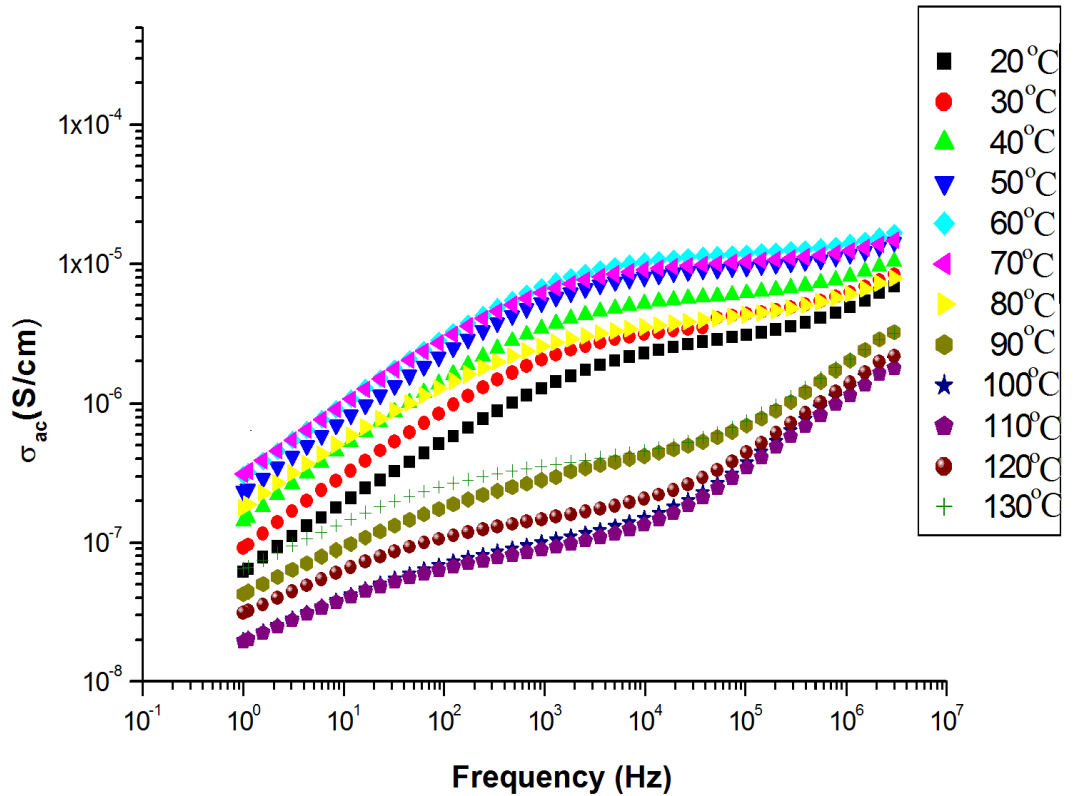


Figure 3.30 AC conductivity versus frequency of SPSU-PMTEt0.5 at several temperatures.

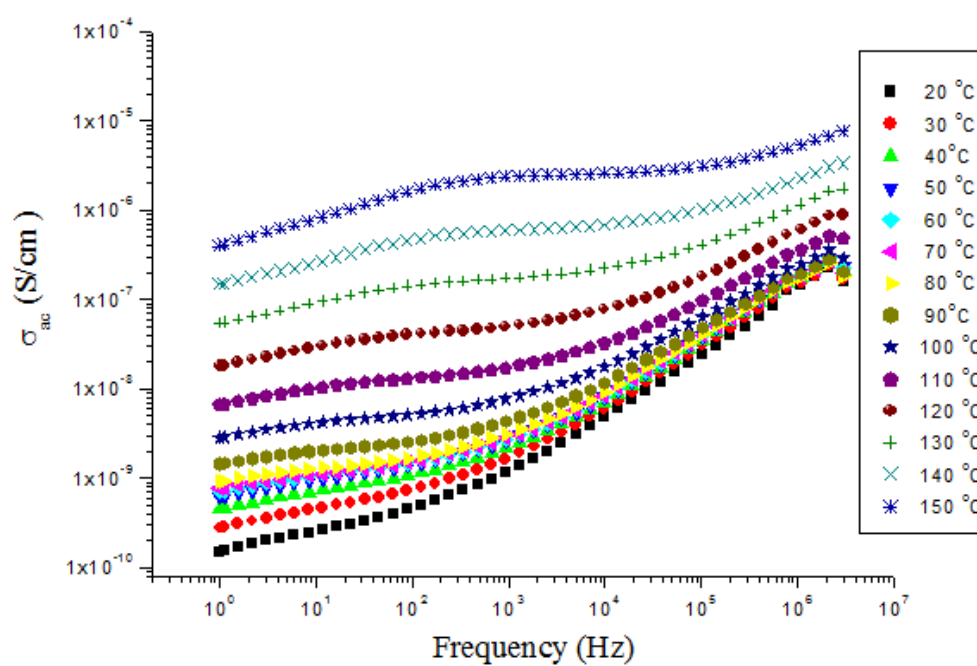


Figure 3.31 AC conductivity versus frequency of SPSU-PMTet1 at several temperatures.

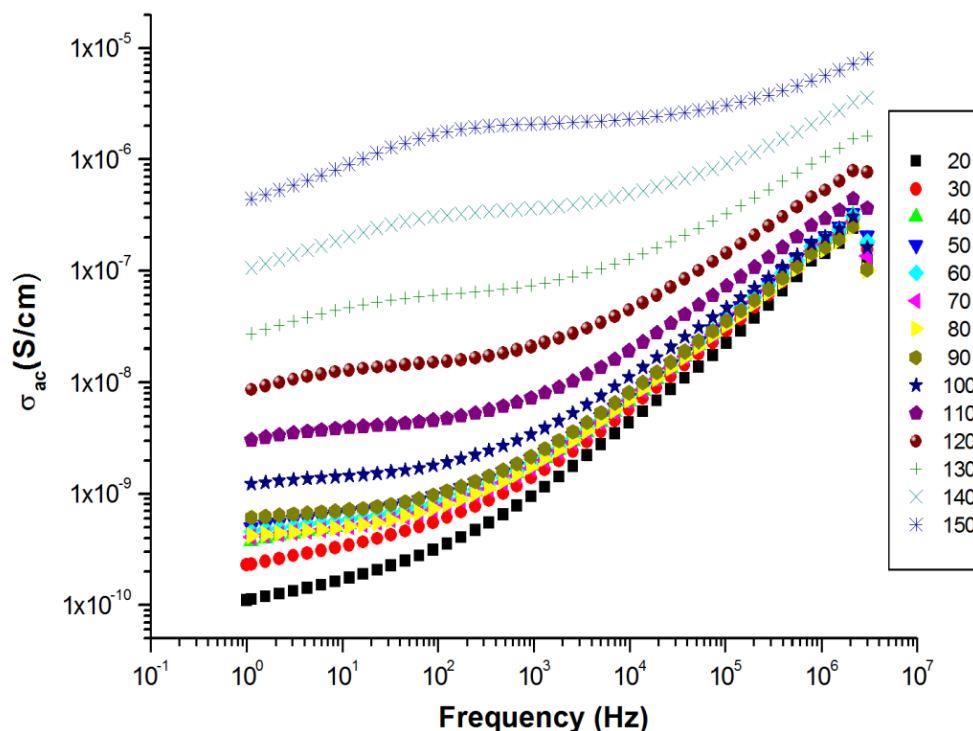


Figure 3.32 AC conductivity versus frequency of SPSU-PMTet2 at several temperatures.

The DC conductivities of SPSU-PMTetX ($x=0.5, 1, 2$) were compared in Fig.3.33. It is clear that the DC conductivity strongly depends on the temperature and SPSU ratio. The maximum proton conductivity was obtained as $2.2 \times 10^{-6} \text{ S.cm}^{-1}$ for all samples at 150 °C (Sinirlioglu et al., 2014d).

SPSU/1*H*-1,2,3-triazole composite membranes were reported as anhydrous system but the system produced considerable proton conductivity at high dopant ratios (Li et al., 2005). Manthiram et al. attached 5-aminobenzotriazole to polysulfone backbone and after blending with sulfonated poly(ether ether ketone) they investigated the proton conductivity and reported values around 10^{-4} S/cm in anhydrous conditions (Manthiram et al., 2010). In another study, phosphatoantimonic acid was doped into SPSU and they investigated the proton conductivity in humidified state (Genova-Dimitrova et al., 2001). Previously, SPSU / benzotriazole system was reported which resulted high proton conductivity at lower dopant ratios (Gustian et al., 2012). In order to be used in both humidified and anhydrous conditions, SPSU may be blended with

azole containing polymer so that there is a proton transfer path between sulfonic acid and azole units. In addition, the absence of small molecules in the system prevents leaching and it is possible to use the membrane in low or high humidified states also.

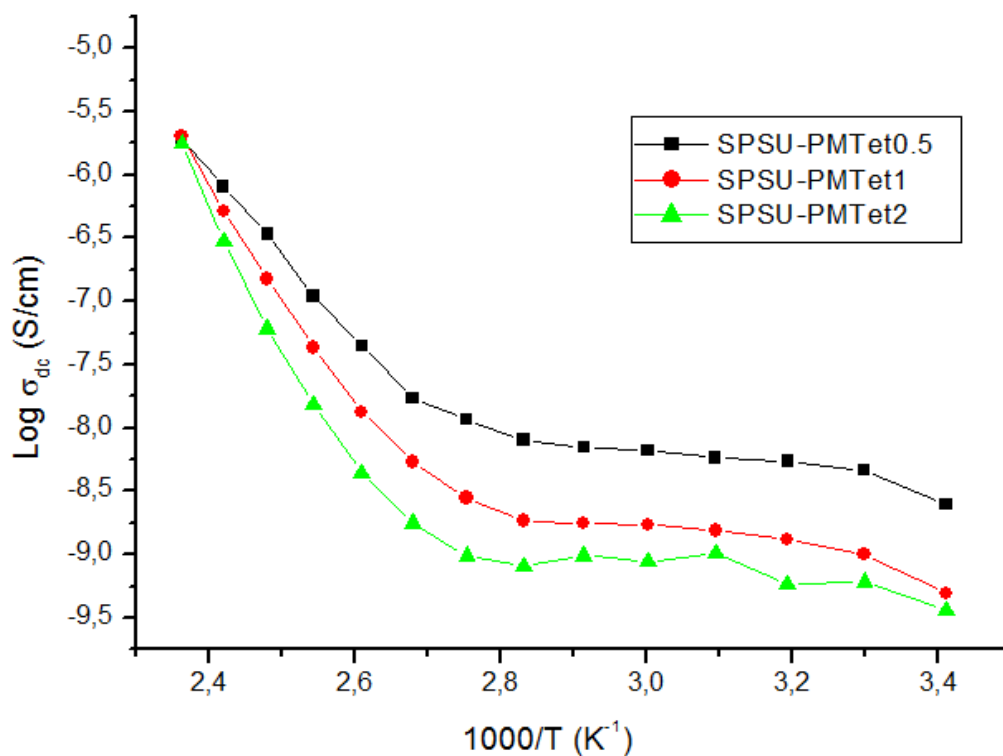


Figure 3.33 Variation of the DC proton conductivity of SPSU-PMTet0.5, SPSU-PMTet1 and SPSU-PMTet2 as a function of reciprocal temperature.

5-aminotetrazole is a heterocyclic molecule and previously used as proton source by immobilization into several polymer backbones (Ozden et al., 2010a; Celik et al., 2008a). In these studies the tetrazole units provided high proton conductivity after doping with triflic and phosphoric acids. However these azole functional polymers have low film forming property and this makes them unsuitable for PEMFC applications. In this work, poly(5-(methacrylamido)tetrazole) (PMTet) is considered to make ionic interaction with sulfonic acid units of SPSU. As seen in SEM images, the composite membranes are homogeneous but low proton conductivity may be due to ionic crosslink between PMTet and SPSU which limits the proton transfer in the matrix (Aslan and Bozkurt, 2009). Therefore, the proton conductivity was investigated also in humidified

condition and depicted in Fig. 3.34. The proton conductivity values decreases with temperature due to the loss of water with temperature. The proton conductivity of our samples are close to Nafion in the humidified condition. The membranes with higher SPSU ratio resulted higher proton conductivity values (6×10^{-3} S/cm). Possible mechanism of proton transport in the composite membranes is tentatively depicted in Fig. 3.35 (Sinirlioglu et al., 2014d).

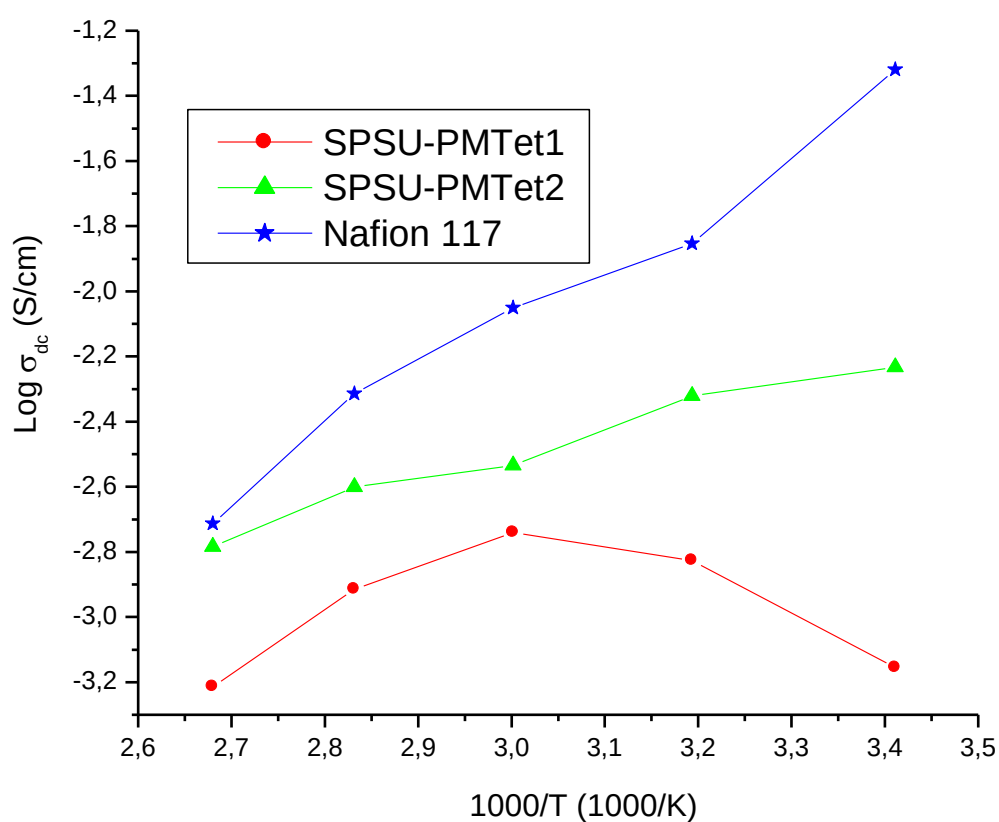


Figure 3.34 DC proton conductivity of fully humidified (100 % humidity) Nafion 117, SPSU-PMTet1 and SPSU-PMTet2 as a function of reciprocal temperature.

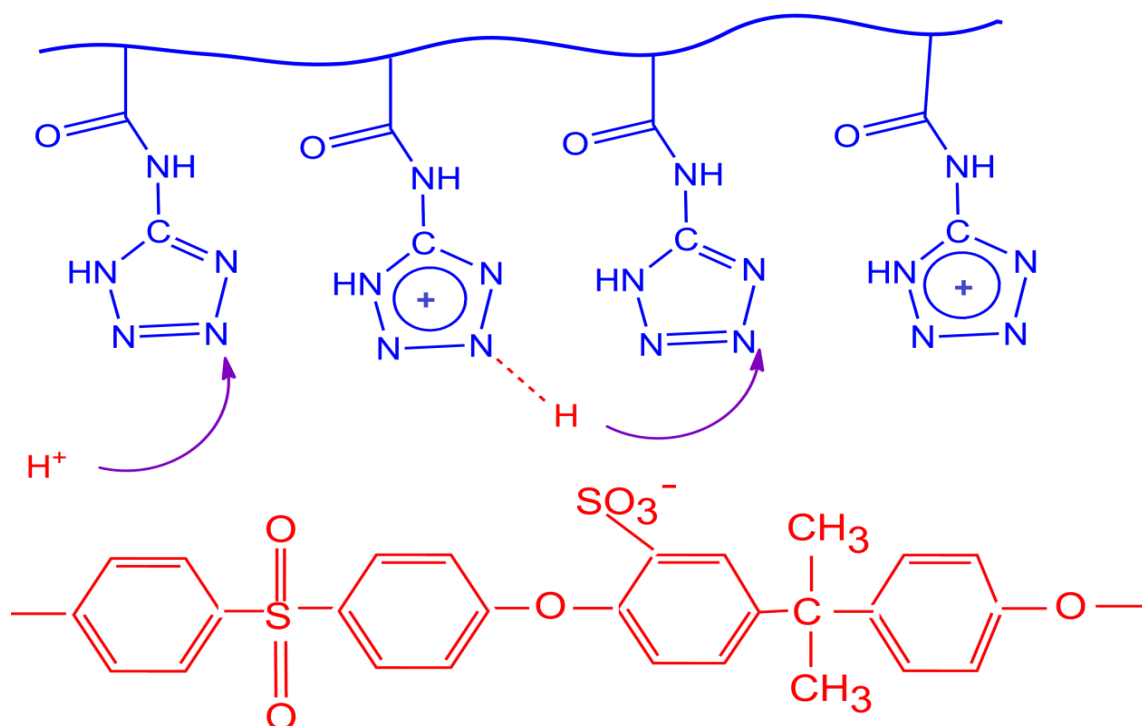


Figure 3.35 Possible mechanism of proton transport in SPSU-PMTet(x) composite membranes.

3.3 SYNTHESIS OF COPOLYMERS BASED ON 5-(METHACRYLAMIDO) TETRAZOLE AND 1-VINYL-1,2,4-TRIAZOLE

Copolymerization of *N*-heterocyclic monomers and acidic monomers has been employed for the development of anhydrous PEMs since *N*-heterocycles may act as proton solvents whereby acidic groups serve as proton-donating sites. These copolymer membranes display high proton conductivity at elevated temperatures and in anhydrous conditions (Celik and Bozkurt, 2010; Celik et al., 2008; Woudenberg et al., 2007; Martwiset et al., 2007; Pu et al., 2006; Erdemi and Bozkurt, 2004; Tsarevsky et al., 2004; Bozkurt et al., 2003). In an effort to achieve relatively higher proton conductivities, we have decided to explore the potential of novel copolymers with chemically different repeating units in the preparation of PEMs. Reports regarding copolymers with both triazole and tetrazole groups on the same side chain are very rare (Pu et al., 2007). Therefore, it is remarkable that a copolymer consisting of vinylic and acrylic repeating units with triazole and tetrazole moieties be prepared. Upon doping

with H_3PO_4 , the obtained membrane displayed higher proton conductivities as compared to their homopolymer analogues (Sinirlioglu et al., 2013).

In this study, several copolymers were prepared by free radical copolymerization of 1-vinyl-1,2,4-triazole (VTri) and 5-(methacrylamido)tetrazole (MTet) with various molar feed ratios (see Fig. 3.36, and Table 3.4). The copolymers were doped with H_3PO_4 at several stoichiometric ratios to obtain proton conductive copolymer electrolytes. The composition of the copolymers (S1-S3) was analyzed by ^1H -NMR spectra using the integral ratios of the peaks (Table 3.5) (Sinirlioglu et al., 2013).

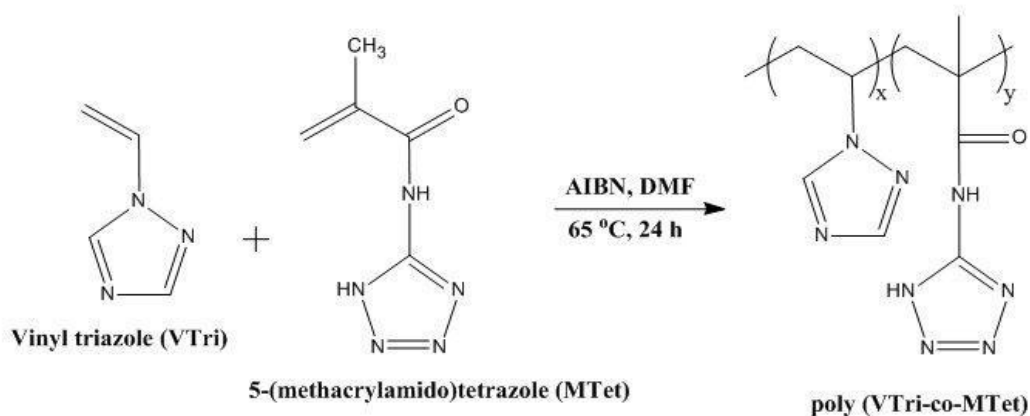


Figure 3.36 The synthesis of P(VTri-co-MTet) copolymers

Table 3.4 Conditions and results in the synthesis of P(VTri-co-MTet) copolymers.

Sample	VTri	MTet	Conversion
P(VTri-co-MTet), S1	0.62 g, 6.54 mmol	0.50 g, 3.27 mmol	0.82 g, 73 %
P(VTri-co-MTet), S2	0,31 g, 3.27 mmol	0.50 g, 3.27 mmol	0.72 g, 89 %
P(VTri-co-MTet), S3	0.16 g, 1.63 mmol	0.50 g, 3.27 mmol	0.56 g, 85 %

Table 3.5 Feed mol ratio of the monomers and compositions of the copolymers.

Sample Name	[Feed mol ratio] VTri:MTet	[Sample mol ratio] *
		VTri:MTet
S1	2: 1	0.67:0.33
S2	1: 1	0.56:0.44
S3	1: 2	0.30:0.70

* calculated from $^1\text{H-NMR}$

3.3.1 FTIR studies

The FTIR spectra of PVTri and PMTet homopolymers, the copolymers with various molar feed ratios of the monomers, and phosphoric acid doped copolymers are presented in Fig. 3.37, Fig. 3.38 and Fig. 3.39. In PVTri homopolymer, the triazole units exhibited several medium or strong peaks in the $1430\text{-}1650\text{ cm}^{-1}$ range due to ring stretching (C-N, C=N) vibrations. The peak at 1270 cm^{-1} is due to the ring N-N stretching (Aslan and Bozkurt, 2009; Celik et al., 2008b). PMTet homopolymer exhibited several medium or strong peaks between 1689 cm^{-1} and 1475 cm^{-1} due to amide bond and tetrazole ring vibrations, respectively. PMTet also showed N-N stretching at 1245 cm^{-1} . The peaks at $735\text{-}1160\text{ cm}^{-1}$ correspond to C-H stretching bands and the formation of a slightly broad peak at around 3200 cm^{-1} shows the protonation of tetrazole rings (Sinirlioglu et al., 2013). S1 copolymer exhibited several medium or strong peaks at 1690 cm^{-1} , 1657 cm^{-1} and 1435 cm^{-1} , which were due to amide bond, triazole (C-N, C=N) and tetrazole (C-N, C=N) ring vibrations, respectively. The peak at 1265 cm^{-1} is due to the ring N-N stretching (Aslan and Bozkurt, 2009; Sinirlioglu et al., 2013). The aliphatic C-H stretchings were observed at $1387\text{-}1435\text{ cm}^{-1}$ and $2800\text{-}3000\text{ cm}^{-1}$ regions. The broad and strong band at $2200\text{-}3250\text{ cm}^{-1}$ belongs to the stretching vibration of N-H of characteristic tetrazole ring. This broad band confirmed the hydrogen bonding network, which is necessary for proton conduction (Sinirlioglu et al., 2013; Aslan and Bozkurt, 2009).

After doping of S1 copolymer with H_3PO_4 , the intensities of the bands at 1435 cm^{-1} and 1657 cm^{-1} changed. Two strong peaks appeared near 500 cm^{-1} and 1000 cm^{-1} , which can be attributed to PO_2 bending vibration and P-O symmetric stretching of H_3PO_4 . The intensity of P-OH stretching at around 1000 cm^{-1} increased with increasing acid ratio. The strong peak shifted from 962 cm^{-1} to a lower wavenumber of 948 cm^{-1} , which are the characteristic peaks for H_2PO_4^- and HPO_4^{2-} , respectively. This change is due to partial self-ionization of phosphoric acid. There was a significant change in the shape of the carbonyl peak at 1690 cm^{-1} due to protonation (Sinirlioglu et al., 2013). In addition, the decrease in the intensity of the tetrazole ring stretching at 1570 cm^{-1} indicates the ring protonation. Furthermore, a broadening of the band between 3500 and 2200 cm^{-1} can be attributed to hydrogen bonding network formation. These results indicated that the interaction between copolymer and phosphoric acid occurred both on carbonyl and tetrazole units and this interaction was improved with increasing content of phosphoric acid (Fig. 3.37) (Sinirlioglu et al., 2013; Celik et al., 2008b). Similar absorption bands were also present in FTIR spectra as shown in Fig. 3.38 and Fig. 3.39.

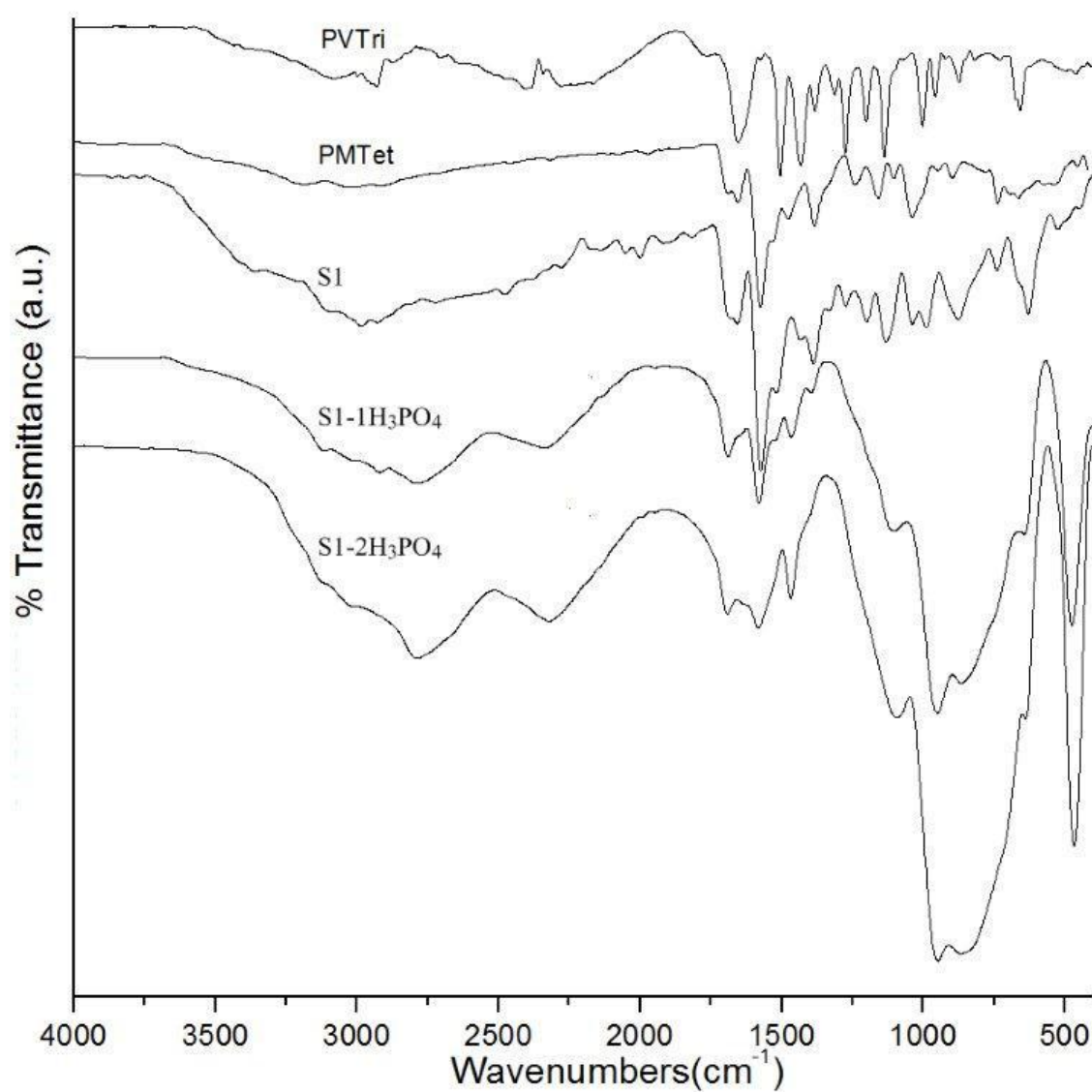


Figure 3.37 FTIR spectra of PVTri, PMTet, S1, S1-1H₃PO₄ and S1-2H₃PO₄ copolymers.

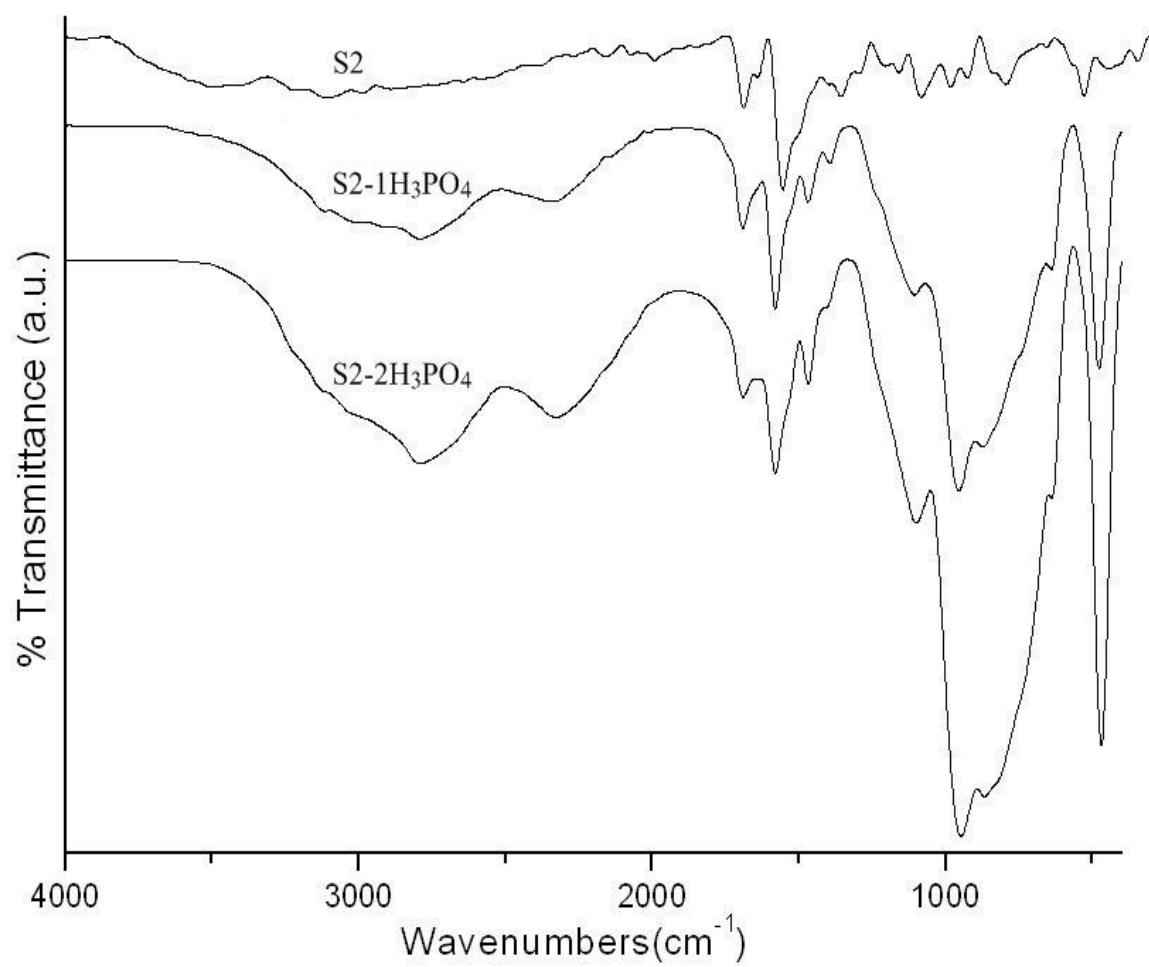


Figure 3.38 FTIR spectra of S2, S2-1H₃PO₄ and S2-2H₃PO₄ copolymers

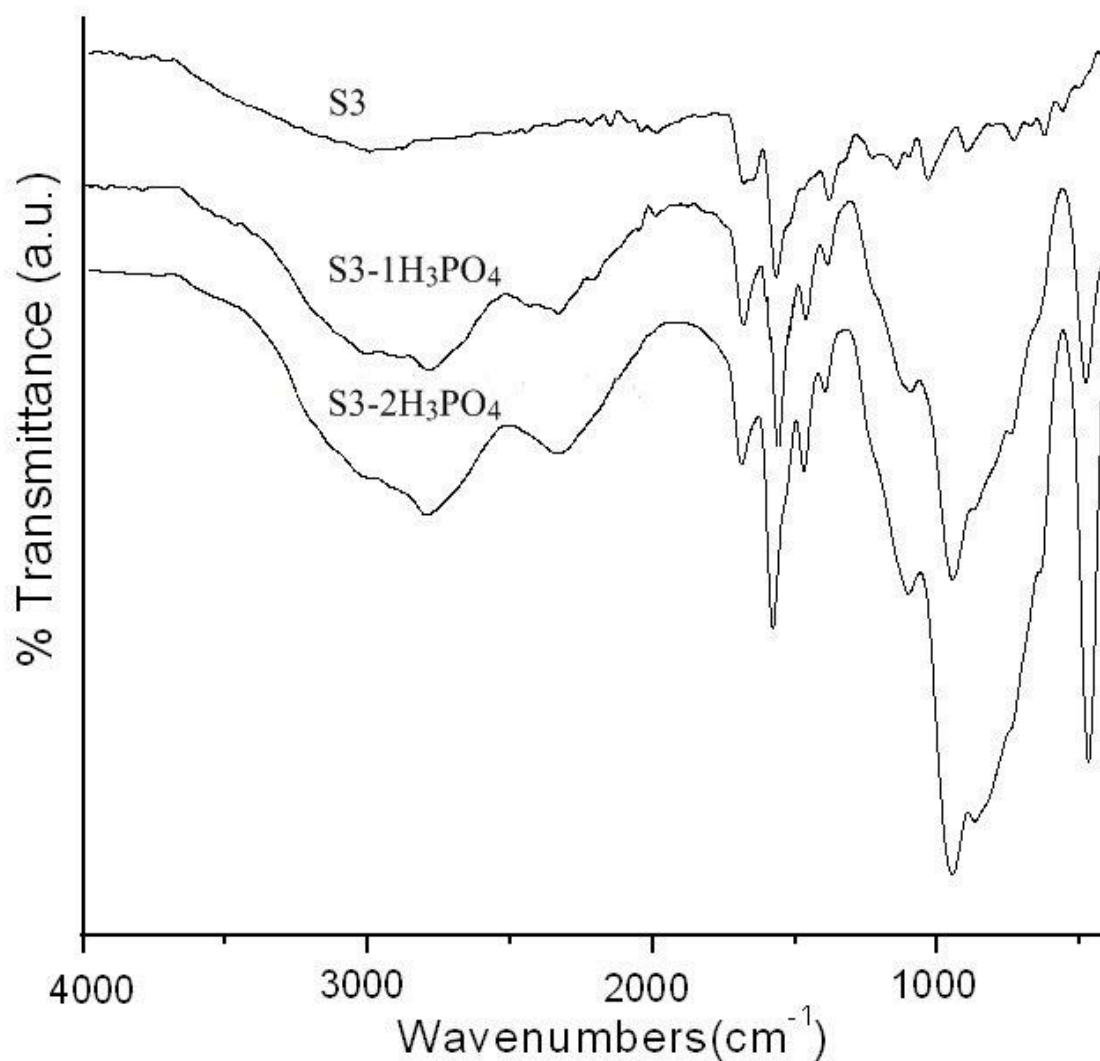


Figure 3.39 FTIR spectra of S3, S3-1H₃PO₄ and S3-2H₃PO₄ copolymers.

3.3.2 NMR studies

¹H-NMR spectra of S1, S2 and S3 copolymers are presented in Fig. 3.40. The single broad peak at around 15.78 ppm is assigned to the N-H proton of tetrazole groups. The appearance of the peaks between 11 and 12 ppm can be attributed to NH proton which indicates amide bond proton. And also, the signals between 8.50 ppm and 7.0 ppm belong to the methine proton of the triazole rings. These results clearly showed the successful preparation of P(VTri-co-MTet) copolymer. For S1; ¹H-NMR (400 MHz, DMSO-d₆, δ): 7.95 (br, 1H, =CH, triazole ring), 8.10 (br, 1H, =CH, triazole ring), 11.33-11.65 (br, 1H, CONH), 15.78 (br, s, 1H, tetrazole-NH) (Sinirlioglu et al., 2013).

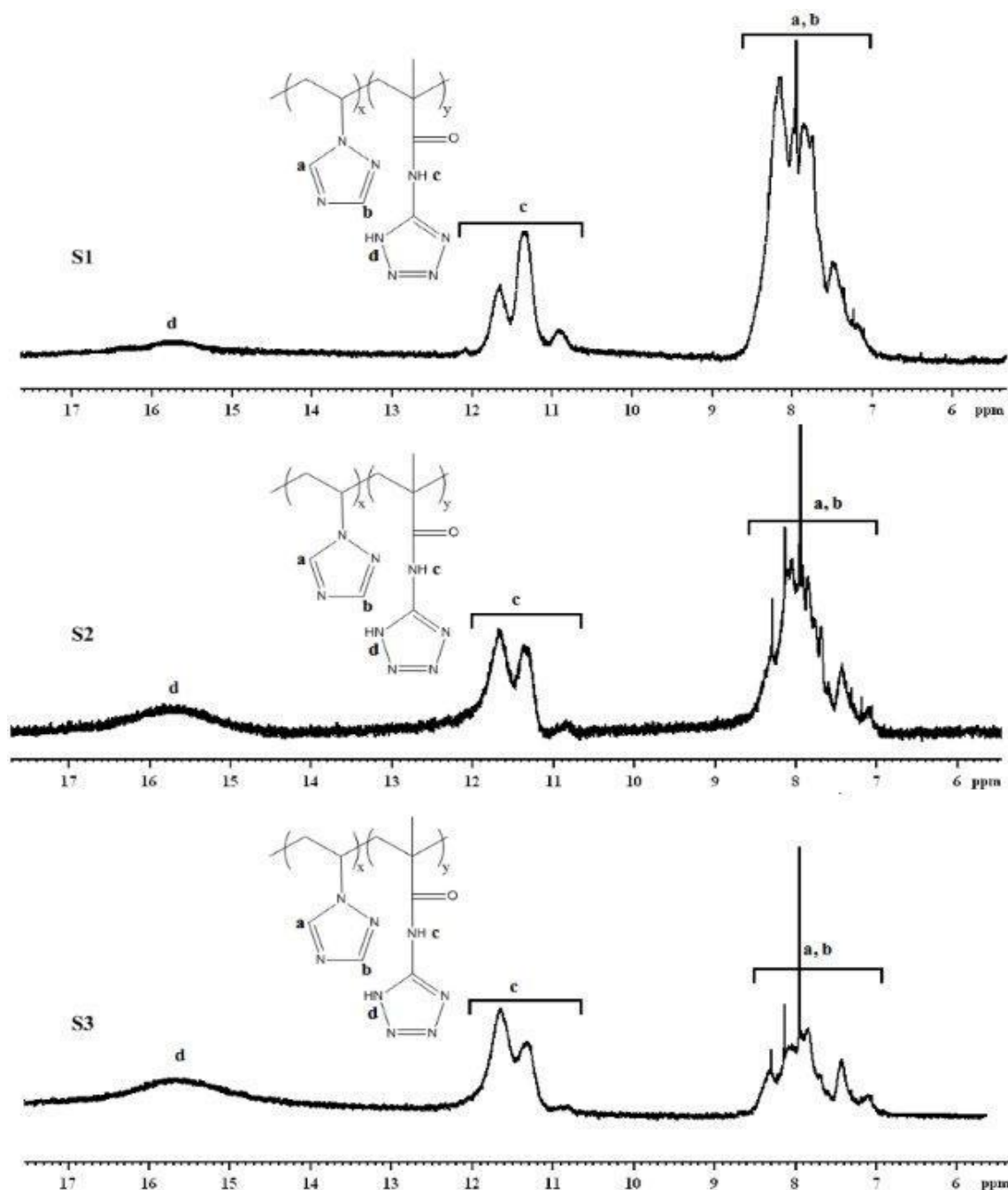


Figure 3.40 ¹H-NMR spectra of S1, S2 and S3 copolymers recorded in DMSO-d₆ in the range of 5-18 ppm).

3.3.3 Thermal Properties

The samples were dried under vacuum at 90 °C for 24 h. TGA curves of PVTri, PMTet, and P(VTri-co-MTet) are shown in Fig. 3.41, Fig. 3.42 and Fig.3.43. PVTri was stable at least 350 °C. After 350 °C, a remarkable weight loss in a single step originated from the thermal decomposition of triazole groups and the polymer backbone. PMTet

homopolymer exhibited a thermal stability up to 215 °C. 30 % of PMTet decomposed between 215 and 350 °C because of degradation of aminotetrazole units and after 400 °C, a second weight loss occurred because of degradation of the polymer backbone. S1 copolymer exhibited a thermal stability up to 215 °C. 30 % of S1 copolymer breaks down between 215 and 300 °C because of degradation of aminotetrazole and triazole units and, second weight loss occurs after 350 °C because of decomposition of the copolymer backbone. Upon doping of S1 with H_3PO_4 , it exhibited a thermal stability up to 220 °C, after which it began to degrade (Sinirlioglu et al., 2013).

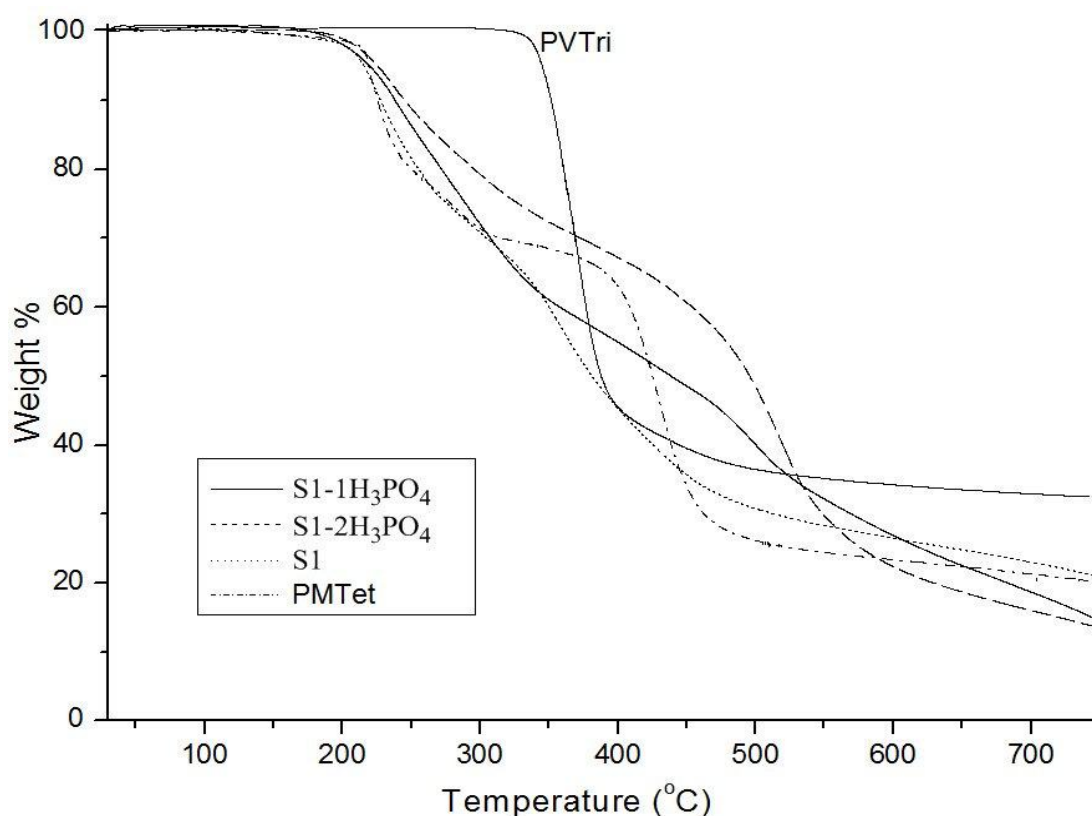


Figure 3.41 TG thermograms of PVTri, PMTet, S1, S1-1H₃PO₄ and S1-2H₃PO₄ copolymers at a heating rate of 10 °C/min in inert atmosphere.

Although the initial degradation temperatures of S1 and S1-xH₃PO₄ (x=1.0 and 2.0) copolymers were almost the same, the temperature of the maximum degradation of S1-xH₃PO₄ was a little higher than that of S1, which might be a result of hydrogen bond formation between S1 and phosphoric acid groups. This result indicates that S1-xH₃PO₄

copolymer electrolyte shows a relatively higher thermal stability than S1. In general, all acid doped copolymer electrolyte materials were thermally stable up to 220 °C due to hydrogen bond formation. For all samples (S1-S3) there was a little decomposition up to 220 °C while the major decomposition occurred above 350 °C (Sinirlioglu et al., 2013).

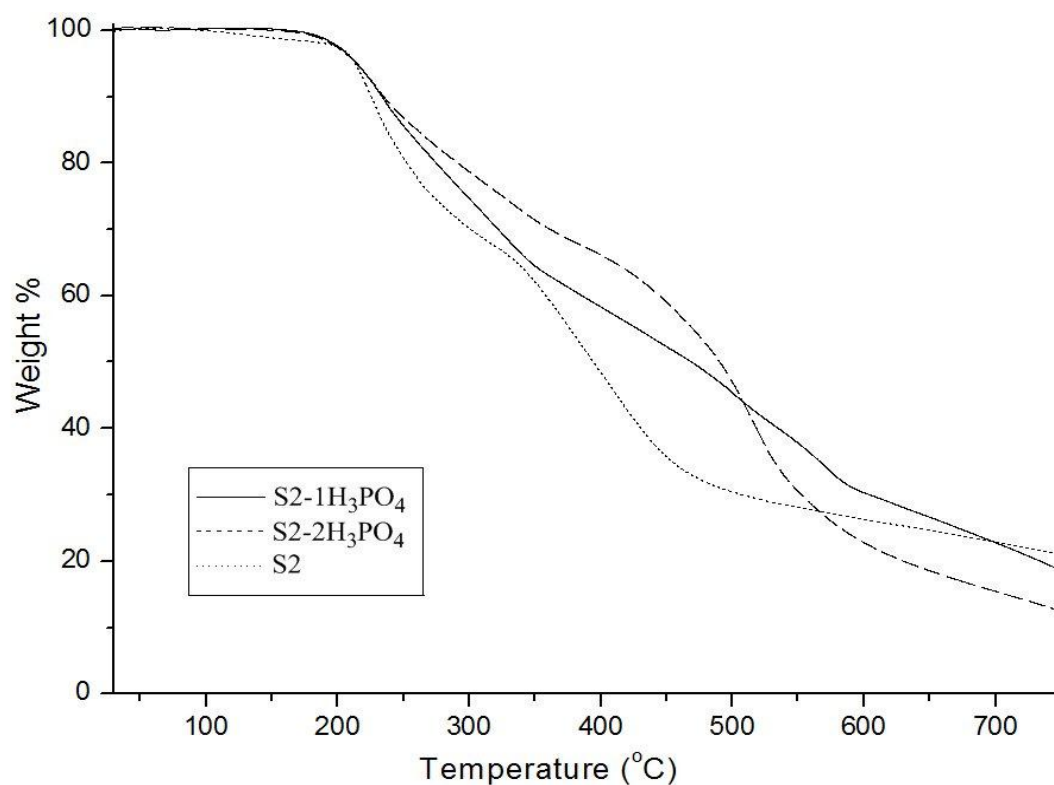


Figure 3.42 TG thermograms of S2, S2-1H₃PO₄ and S2-2H₃PO₄ copolymers at a heating rate of 10 °C/min in inert atmosphere.

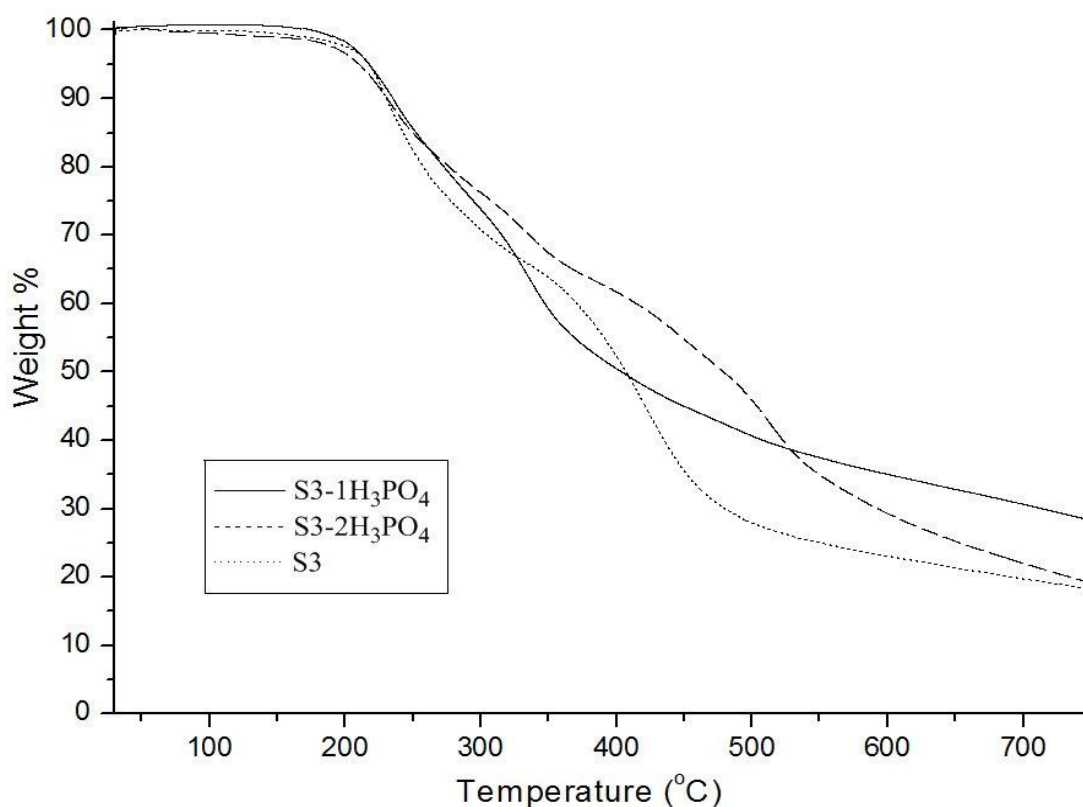
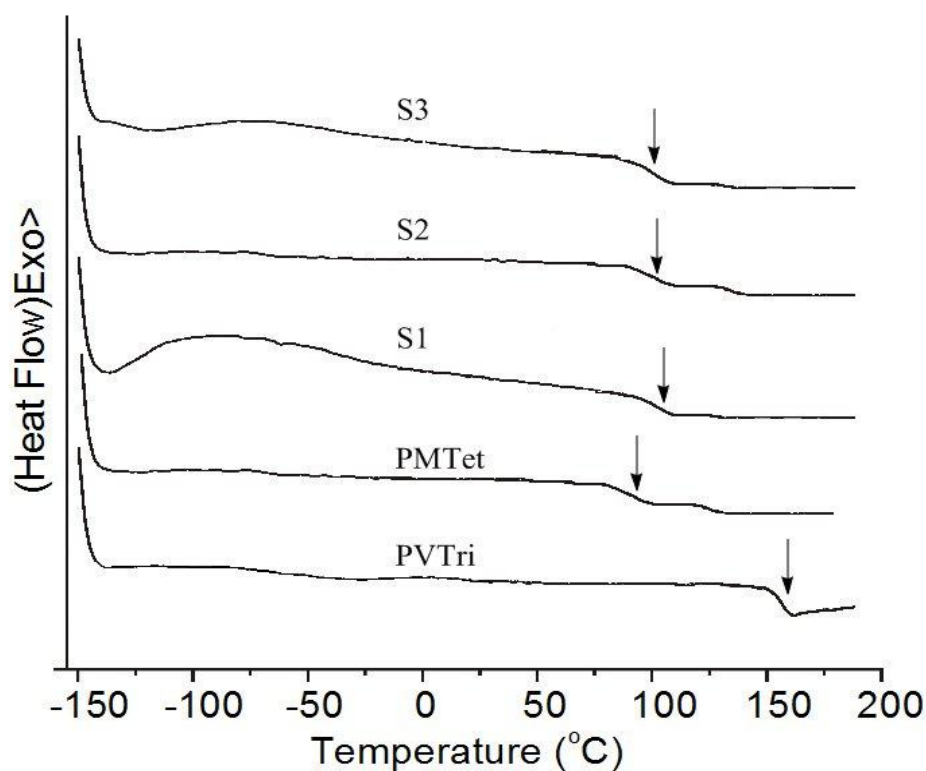


Figure 3.43 TG thermograms of S3, S3-1H₃PO₄ and S3-2H₃PO₄ copolymers at a heating rate of 10°C/min in inert atmosphere.

Table 3.6 shows the glass transition temperature, T_g of P(VTri-co-MTet) copolymers and phosphoric acid doped copolymer electrolytes under inert atmosphere at a scan rate of 10 °C/min, respectively. In DSC measurements, the second heating curves were evaluated. Characteristic DSC curves of PVTri, PMTet, S1, S2 and S3 copolymers are shown in Fig. 3.44. T_g of PVTri was measured at around 165 °C (Celik et al., 2008c) and PMTet exhibited a glass transition at approximately 93°C (Sinirlioglu et al., 2013). The T_g of S1, S2 and S3 copolymers were measured around 105 °C, 103 °C and 101 °C, respectively. After doping the copolymers with H₃PO₄, the glass transition temperatures of copolymers shift to lower temperatures. Clearly, the T_g values show a pronounced effect of increasing both tetrazole functional monomer (MTet) and phosphoric acid content on the softening behavior of the copolymers. The presence of single T_g confirms the homogeneity of the materials. Similar plasticizing effect was reported in the previous works (Hongting et al., 2008; Celik and Bozkurt, 2008).

Table 3.6 T_g and maximum proton conductivity values of copolymers.

Sample Name	[Feed mol ratio] VTri : MTet	Doping ratio with H_3PO_4	T_g ($^{\circ}C$)	Max. Proton Conductivity at 150 $^{\circ}C$ (S/cm)
S1	2:1	-----	105	-----
S2	1:1	-----	103	-----
S3	1:2	-----	101	-----
S1-1 H_3PO_4	2:1	1:1	95	0.007
S1-2 H_3PO_4	2:1	1:2	84	0.012
S2-1 H_3PO_4	1:1	1:1	89	0.002
S2-2 H_3PO_4	1:1	1:2	86	0.014
S3-1 H_3PO_4	1:2	1:1	94	0.004
S3-2 H_3PO_4	1:2	1:2	86	0.016

Figure 3.44 DSC thermograms of PVTri, PMTet, S1, S2 and S3 copolymers recorded under N_2 atmosphere at a heating rate of 10 $^{\circ}C/min$.

3.3.4 Morphology

Surface morphologies of the copolymer electrolyte membranes were investigated by scanning electron microscopy (SEM) and depicted in Fig. 3.45. The images of the SEM (Fig.3.45b-d) do not show clear-cut phase separation. Image (c) showed formation of a smooth surface while in image (d) at the nanometer scale, formation of a highly porous surface was observed. This is the expected morphology due to strong interactions between phosphoric acid groups and the tetrazole and triazole units. This observation is also consistent with the DSC results, in which a single T_g was observed (Hazarika et al., 2012). However, the heterogeneous surface image at the 10 μm scale (image (b)) might be due to a complexation between acid-base (azole groups) units, which created some extent of agglomeration (Sinirlioglu et al., 2013).

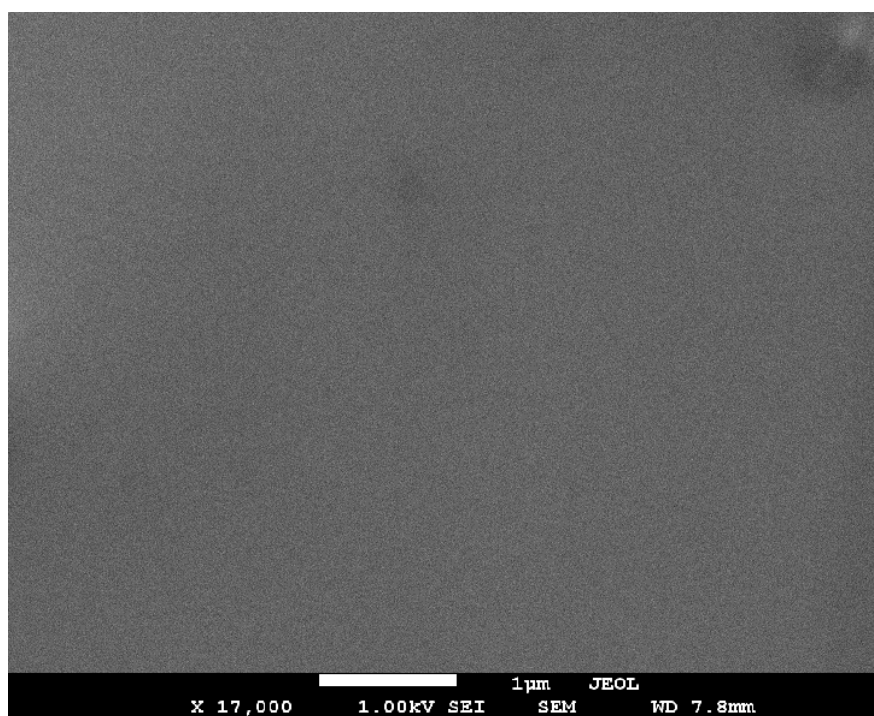


Figure 3.45 (a) SEM image of the surface of S3-2H₃PO₄ copolymer at 1 μm .

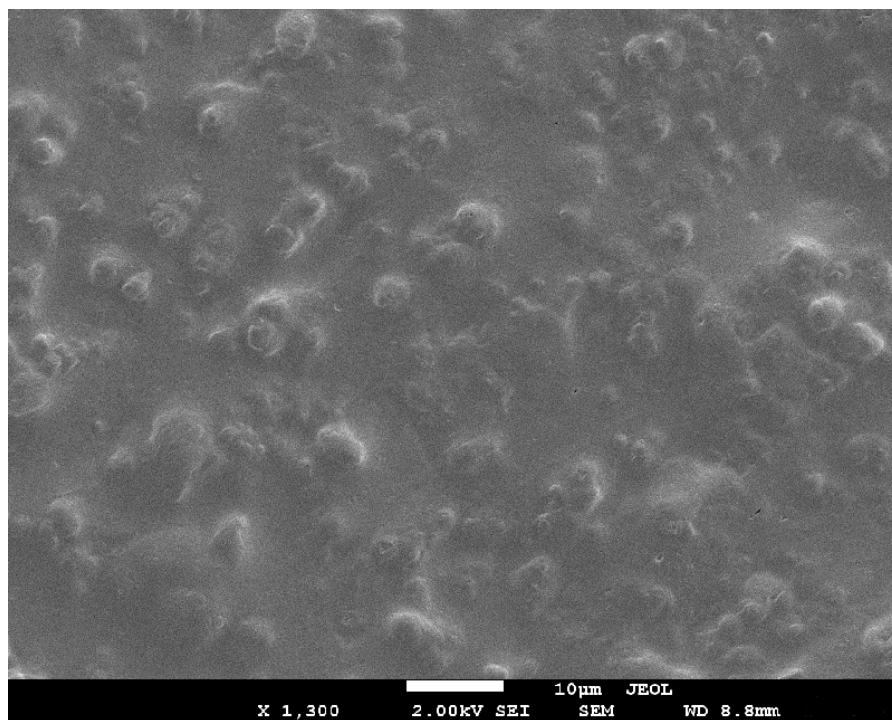


Figure 3.45 (b) SEM image of the surface of S3-2H₃PO₄ copolymer at 10 μm.

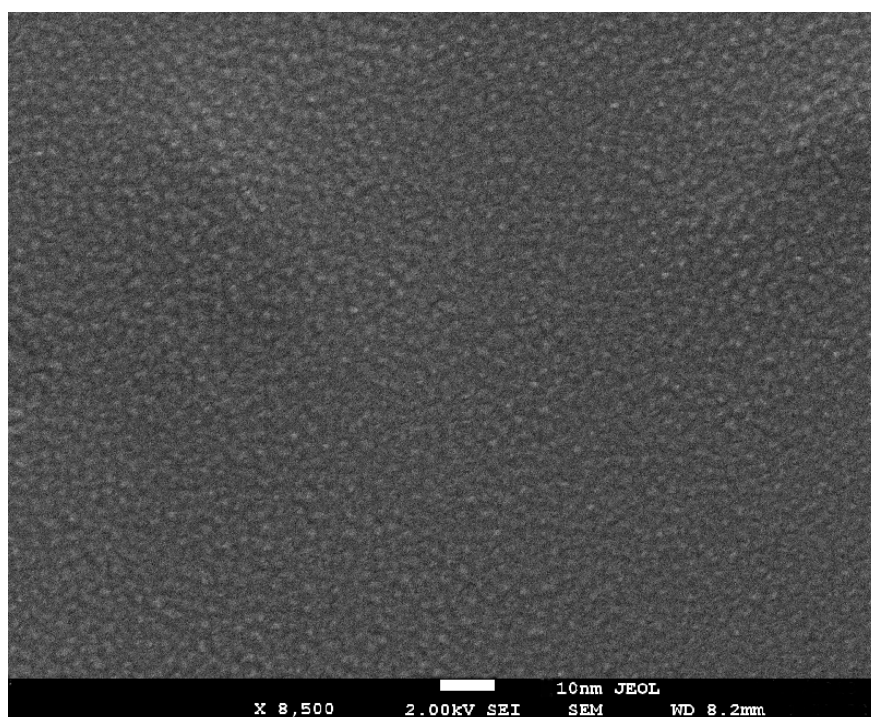


Figure 3.45 (c) SEM image of the surface of S3-2H₃PO₄ copolymer at 10 nm.

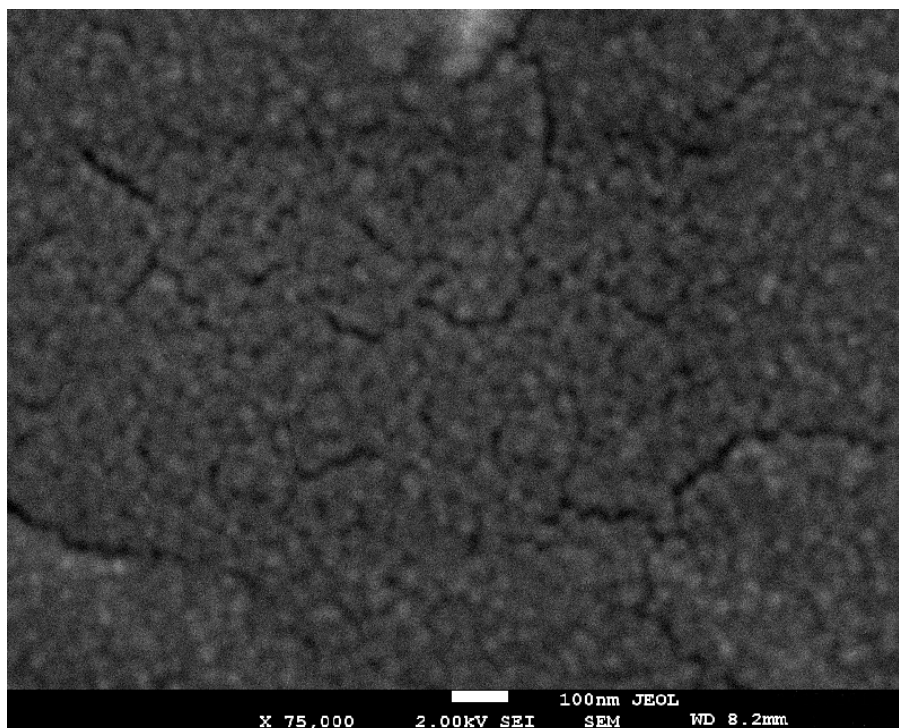


Figure 3.45 (d) SEM image of the surface of S3-2H₃PO₄ copolymer at 100 nm.

3.3.5 Proton conductivity Measurements

The AC proton conductivities of anhydrous membranes were measured from 20 °C to 150 °C. The AC conductivity versus frequency plots at several temperatures are presented in Fig. 3.46, Fig. 3.47, Fig. 3.48, Fig. 3.49 and Fig.3.50. As expected, higher proton conductivities were observed as temperature was increased. Several regions in the plots are characteristic for proton conducting polymers. At low frequencies, the conductivity increases with log frequency, which was then leveled off as a result of electrode polarizations. The irregularities at the low frequency regions can be attributed to polarization, which blocks the electrode-electrolyte interface (Celik et al., 2012b). Among the conductivity measurements listed in Table 3.6, the maximum values were obtained for higher dopant ratios. In the anhydrous conditions, the proton conductivity of S1-2H₃PO₄, S2-2H₃PO₄ and S3-2H₃PO₄ copolymer membranes were measured as 0.012 S/cm, 0.014 S/cm and 0.016 S/cm at 150 °C, respectively (Sinirlioglu et al., 2013). Previously, Pu et al. prepared poly(5-vinyl tetrazole)/H₃PO₄ blends and obtained a maximum proton conductivity of 3×10^{-3} S/cm at 110 °C. They indicated the presence of proton transfer between tetrazole units (Pu et al., 2006). Celik et al. synthesized

poly(vinyl triazole)/H₃PO₄ blends and reported a maximum proton conductivity of 5×10^{-3} S/cm at 150 °C (Celik et al., 2008c). Several copolymers containing 5-vinyl tetrazole were produced by ‘click chemistry’ from polyacrylonitrile (PAN) due to the unavailability of 5-vinyl tetrazole monomer (Pu et al., 2006). Pu et al. reported the proton conductivity of phosphoric acid doped poly(1,2,4-vinyl triazole-co-5-vinyl tetrazole-co-acrylonitrile) as about 10^{-5} S/cm at 60 °C under dry conditions (Pu et al., 2007). Further studies concerning vinyl phosphonic acid (VPA) copolymerized with vinyl triazole (VTri) (Celik et al., 2008b) or vinyl imidazole (VIm) (Bozkurt et al., 2003) were carried out. The proton conductivity of P(VPA-co-VIm) copolymer was (1×10^{-6} S/cm) while it was higher ($\sim 1 \times 10^{-3}$ S/cm) in P(VPA-co-VTri). It can be clearly stated that the anhydrous proton conductivities obtained in our study (0.012 S/cm, 0.014 S/cm and 0.016 S/cm) at 150 °C were higher than the above-mentioned ones (Sinirlioglu et al., 2013).

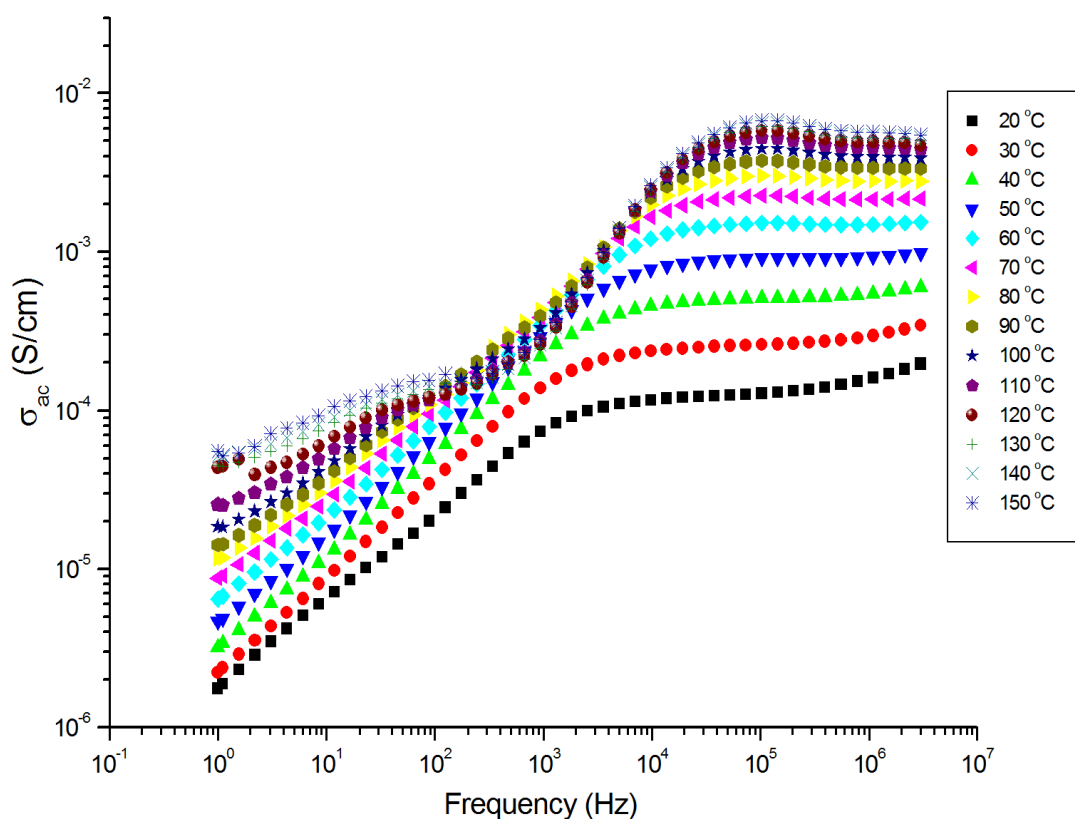


Figure 3.46 AC conductivity versus frequency of S1-1H₃PO₄ at several temperatures.

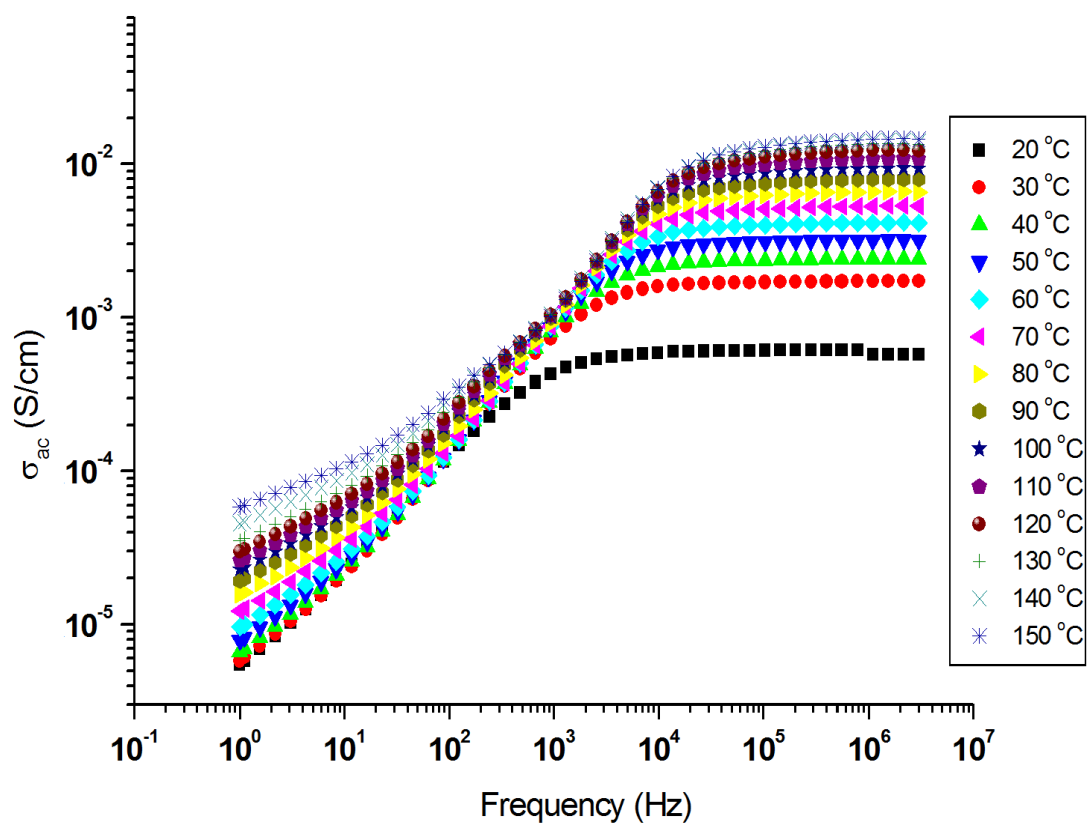


Figure 3.47 AC conductivity versus frequency of S1-2H₃PO₄ at several temperatures.

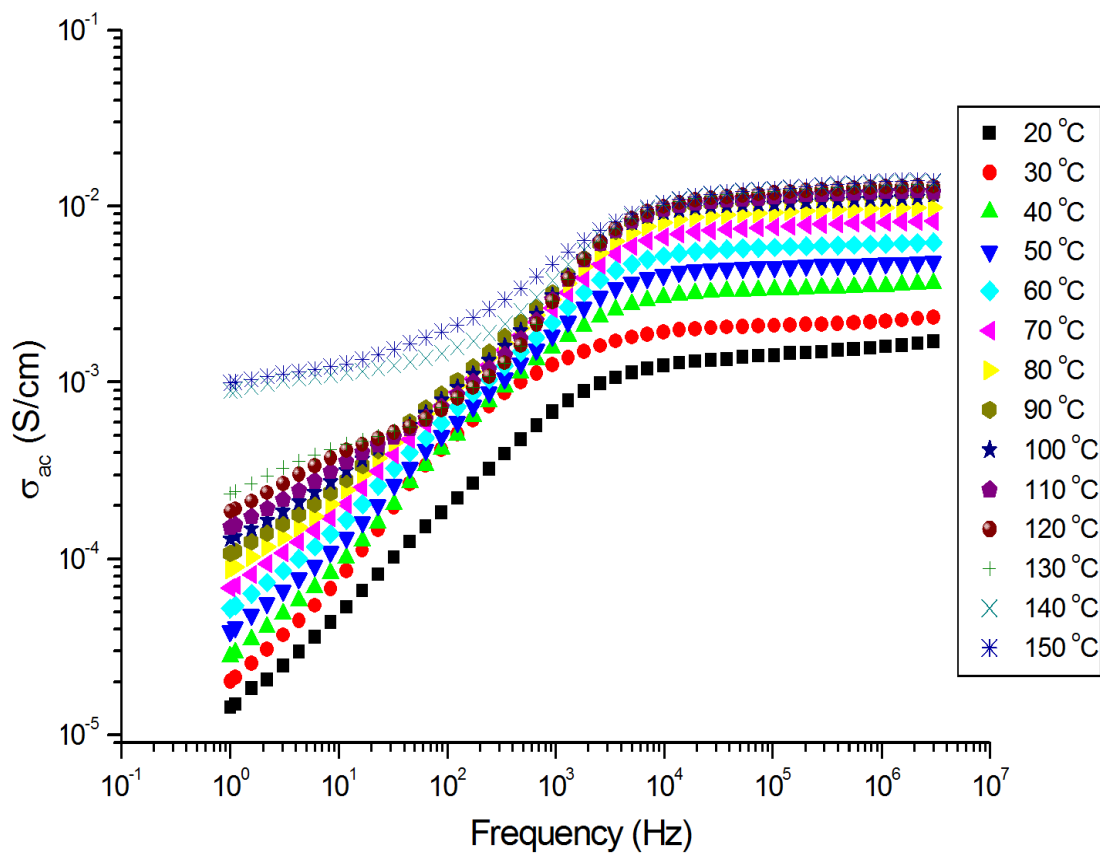


Figure 3.48 AC conductivity versus frequency of S2-2H₃PO₄ at several temperatures.

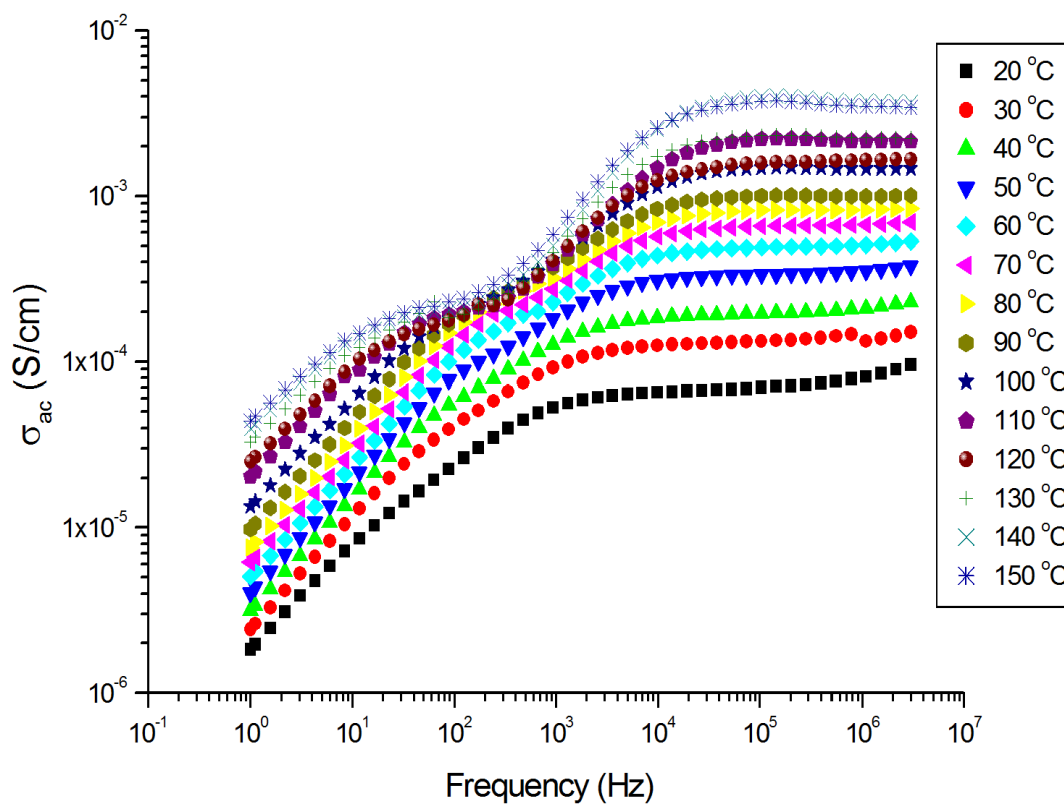


Figure 3.49 AC conductivity versus frequency of S3-1H₃PO₄ at several temperatures.

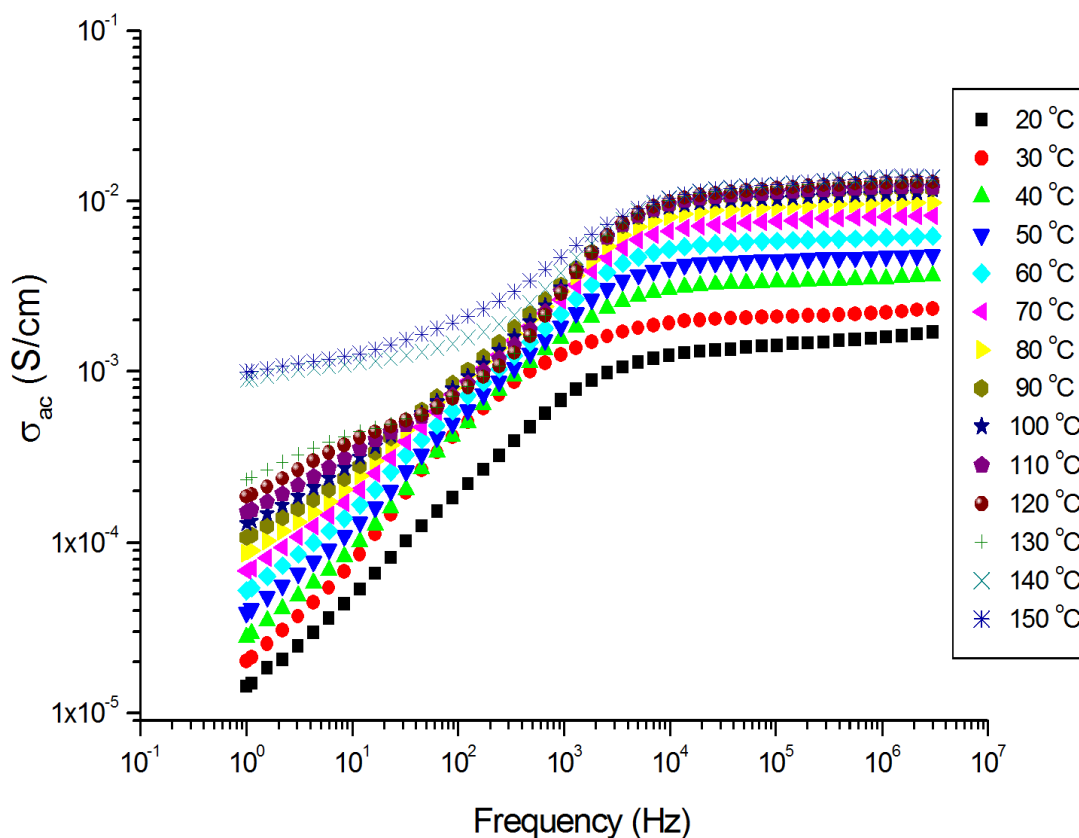


Figure 3.50 AC conductivity versus frequency of S3-2H₃PO₄ at several temperatures.

The DC conductivity (σ_{dc}) of the samples was determined from the plateaus of log σ_{ac} versus log F by linear fitting of the data. In Fig. 3.51, the DC conductivities of all the acid doped copolymers were compared. It can be seen from the conductivity isotherm that the DC conductivity is directly proportional to both the temperature and doping ratio of phosphoric acid.

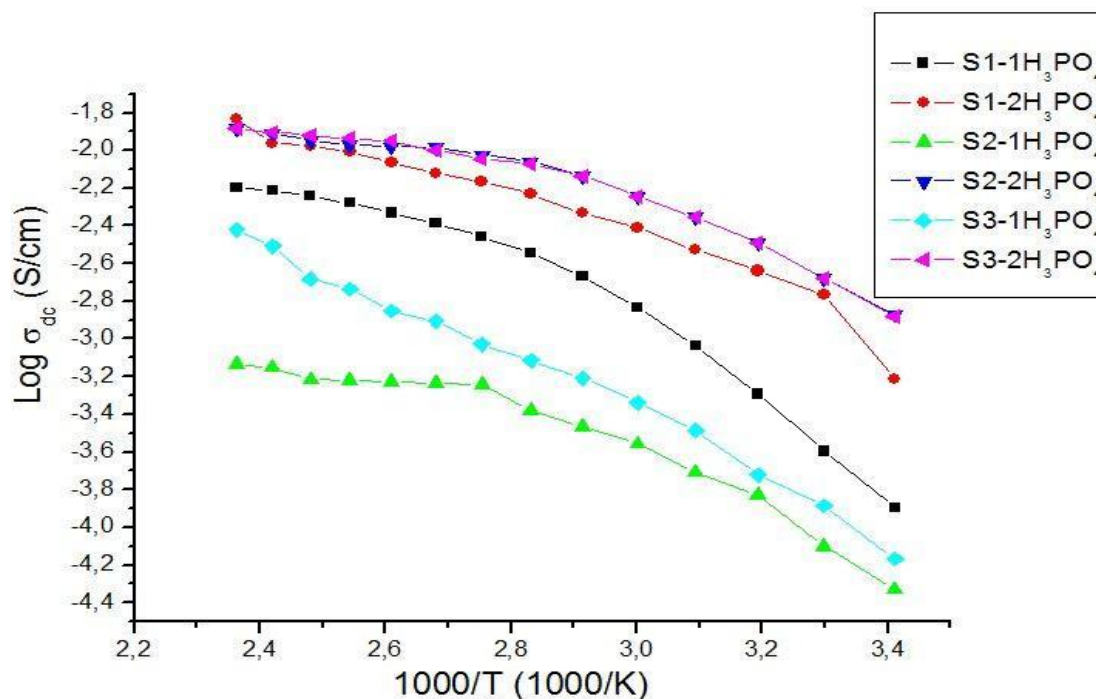


Figure 3.51 Variation of the DC proton conductivity of H₃PO₄ doped P(VTri-co-MTet) copolymers as a function of reciprocal temperature.

Generally, there are two different proton transport mechanisms that contribute to the proton conductivity in polymer electrolytes. The first is the vehicle mechanism where the protons move along the conductive substrate on a neutral or charged “vehicle” (Celik et al., 2012b). The second is the Grotthuss mechanism, in which the conductivity is primarily controlled by proton transport involving phosphate ions, such as H_4PO_4^+ , and H_2PO_4^- . In the current system, since the copolymers were doped with phosphoric acid, the proton diffusion occurs mainly by Grotthuss mechanism. However, it should be noted that the proton hopping from one N-H site to a free nitrogen also contributes to the conductivity as in the previously reported azole-based systems where the long-range proton transfer occurs throughout the protonic defects (Ozden et al., 2010a). In other words, protons are transported between protonated and unprotonated heterocyclic units. On the other hand, it is well established that undoped polymers have low proton conductivities due to the lack of proton defect formation and continuous path for proton transfer (Pu et al., 2007). Therefore, only the results of doped copolymers have been outlined in this work. Furthermore, as discussed in the FTIR analysis section, phosphoric acid plays a role in the formation of dynamic hydrogen

bonded chains and, consequently, provides better proton transport in the long range (Hongting et al., 2008; Sinirlioglu et al., 2013). Possible mechanism of proton transport in $P(VTri-co-MTet)-xH_3PO_4$, in which phosphoric acid is coordinated with triazole and tetrazole groups is tentatively depicted in Fig. 3.52.

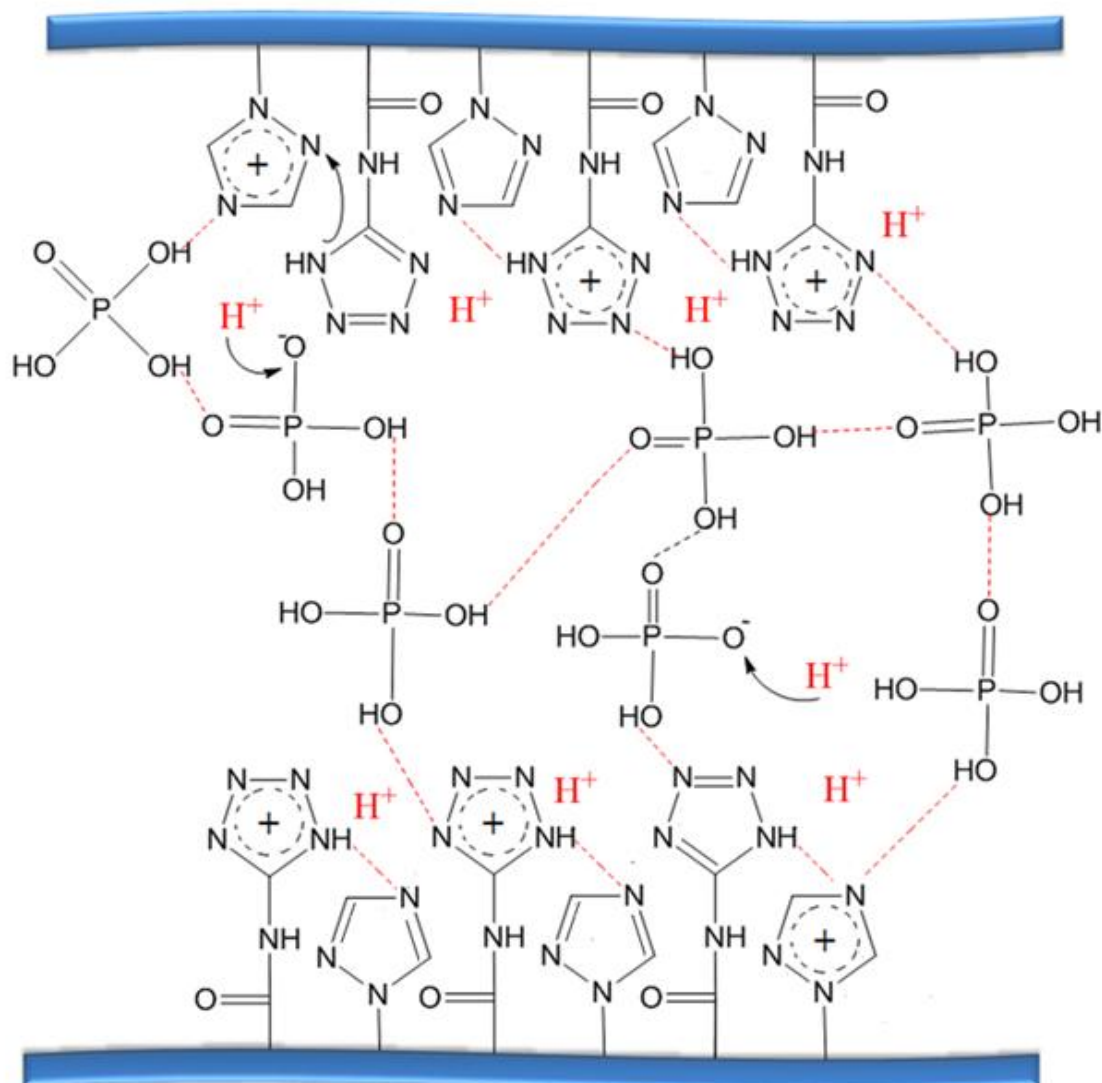


Figure 3.52 Possible mechanism of proton transport in $P(VTri-co-MTet)-xH_3PO_4$ ($x=1.0$ and 2.0) copolymer electrolytes.

3.3.6 Cyclic Voltammetry

Cyclic voltammogram of S3-2H₃PO₄ was given in Fig. 3.53. The measurement was performed in a typical three electrode cell containing 0.1 mol dm⁻³ CH₃CN solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) using a platinum work electrode, a platinum auxiliary electrode, and an Ag/Ag⁺ reference electrode. It was clearly observed that the CV of S3-2H₃PO₄ comprised no peak within the anodic sweep (-0.5 to 1.5 V potential range). In the cathodic sweep, formation of gaseous hydrogen was developed which localized near the electrode and was subsequently reoxidized toward the anodic cycle. Thus the electrochemical stability window was at least 3 V. These results implied that the copolymer had adequate electrochemical stability under fuel cell conditions (Sinirlioglu et al., 2013).

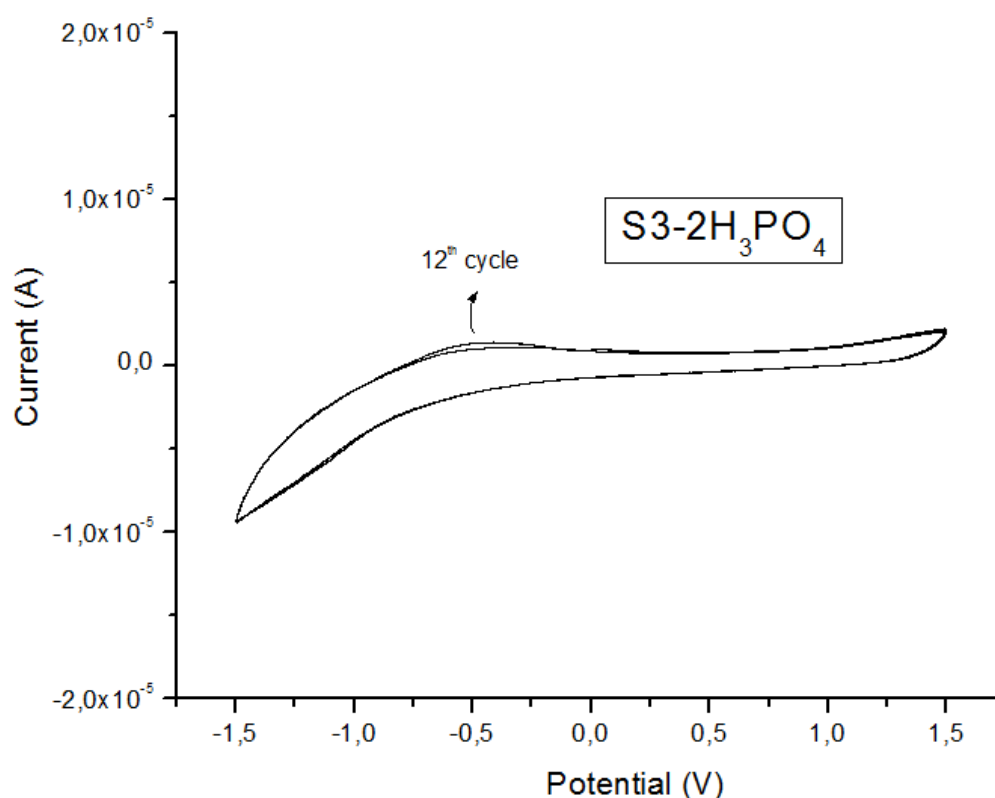


Figure 3.53 Cyclic voltammograms of S3-2H₃PO₄ in 0.1 M TBATFB/acetonitrile. Curves were obtained with a scan rate of 50 mV/s.

3.4 SYNTHESIS OF COPOLYMERS BASED ON VINYL PHOSPHONIC ACID AND 5-(METHACRYLAMIDO)TETRAZOLE

Recently, the phosphate-functional polymers and their derivatives have attracted considerable attention for fuel cell applications. Vinylphosphonic acid is an acidic monomer which can be polymerized with high yield by free radical polymerization. Generally, vinyl phosphonic acid monomer was selected as a model system to study the structure and the proton-conducting mechanism in a phosphonic acid functional polymers, since it contains a high concentration of acid groups. Phosphonic acid is considered to form a strong hydrogen-bonding network involving both P=O and P-OH as proton acceptor and proton donor groups (Sinirlioglu et al., 2014a). In this contribution, 5-(methacrylamido)tetrazole monomer, prepared by the reaction of methacryloyl chloride with 5-aminotetrazole (see Fig. 3.54), was copolymerized with vinyl phosphonic acid via conventional free radical mechanism to achieve poly(MTet-co-VPA) copolymer (see Fig. 3.55 and Table 3.7). The compositions of the copolymers are analyzed by elemental analysis (EA) and energy dispersive X-ray spectrometry (EDS) to determine especially nitrogen and phosphorous, respectively (see Table 3.8 and Table 3.9). EDS results confirmed the elemental analysis (EA) results, successfully. The copolymer, poly(MTet-co-VPA), the colorless copolymer, is found to show little or no solubility in most solvents without exception of DMF, DMSO, and NMP upon warming (Sinirlioglu et al., 2014a).

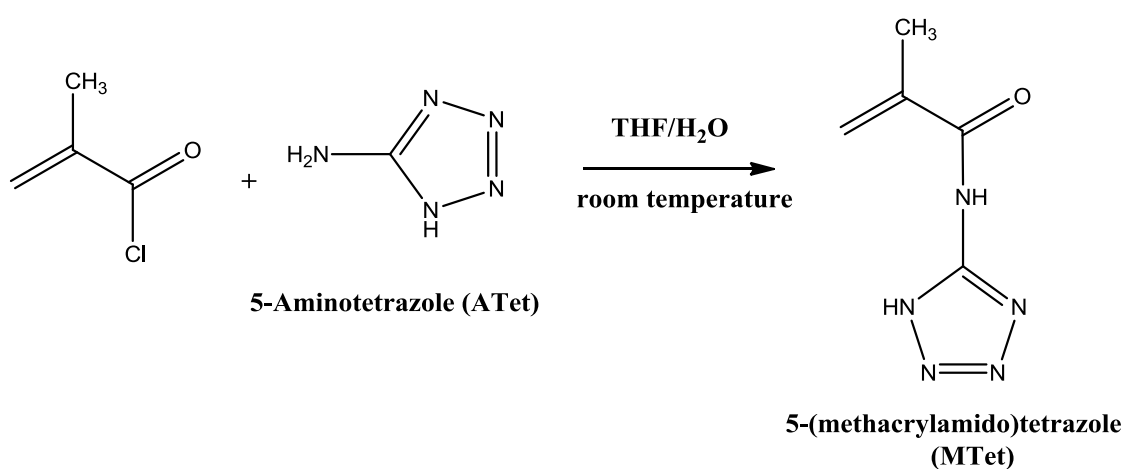


Figure 3.54 The synthesis of 5-(methacrylamido)tetrazole (MTet) monomer.

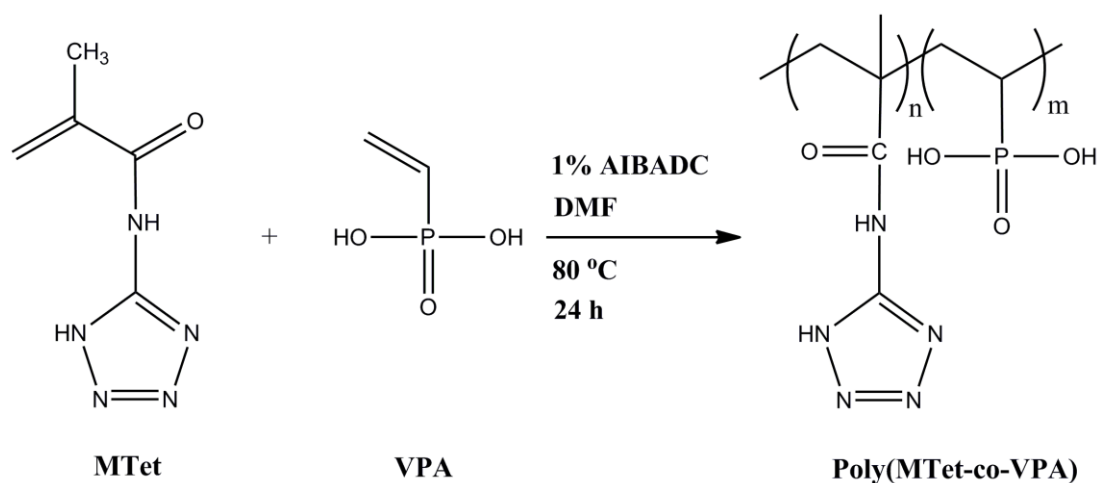


Figure 3.55 The synthesis of Poly(MTet-co-VPA) copolymers.

Table 3.7 Conditions and results in the synthesis of Poly(MTet-co-VPA) copolymers.

Sample	MTet	VPA	Conversion
P(MTet-co-VPA), S1	1.00 g, 6.54 mmol	1.410 g, 13.08 mmol	2.02 g, 84%
P(MTet-co-VPA), S2	1.00 g, 6.54 mmol	0.706 g, 6.54 mmol	1.48 g, 87 %
P(MTet-co-VPA), S3	1.00 g, 6.54 mmol	0.353 g, 3.27 mmol	1.28 g, 95 %

Table 3.8 Composition of poly(MTet-co-VPA) copolymers.

Sample	Feed mol ratio MTet:VPA	Elemental Analysis			Copolymer mol ratio MTet:VPA
		C (%)	H (%)	N (%)	
P(MTet-co-VPA), S1	1: 2	33.3	4.67	19.3	1:1.89
P(MTet-co-VPA), S2	1: 1	34.6	4.59	27.9	1:0.9
P(MTet-co-VPA), S3	1: 0.5	35.4	4.60	34.5	1:0.45

Table 3.9 The synthesis and SEM-EDS analysis of poly(MTet-co-VPA) copolymers.

Sample	MTet:VPA [Feed mol ratio]	Conversion	% P in samples [w/w]	MTet:VPA [Sample mol ratio]
S1	1: 2	84 %	16.09	1:1.81
S2	1: 1	87 %	10.74	1:0.84
S3	1: 0.5	95 %	6.07	1:0.38

3.4.1 FTIR Studies

The FTIR spectra of PVPA and PMTet homopolymers, the copolymers with various molar feed ratios of the monomers (S1-S3) are presented in Fig. 3.56. PVPA has strong bands at 990 and 910 cm^{-1} that belong to asymmetric stretching vibrations of the P-OH group and at 1150 cm^{-1} that corresponds to P=O stretching (Aslan and Bozkurt, 2012). Peaks associated with -CH stretchings were observed in the vinyl phosphonic acid between 2800 and 3000 cm^{-1} . PMTet homopolymer exhibited several medium or strong peaks between 1689 cm^{-1} and 1475 cm^{-1} due to amide bond and tetrazole ring vibrations, respectively. PMTet also showed N-N stretching at 1245 cm^{-1} . The peaks at 725-1160 cm^{-1} correspond to C-H stretching bands and the formation of a slightly broad peak at around 3200 cm^{-1} shows the protonation of tetrazole rings. S3 copolymer (c) exhibited several medium or strong peaks at 1657 cm^{-1} and 1474 cm^{-1} , which were due to amide bond and tetrazole (C-N, C=N) ring vibrations, respectively. The peak at 1265 cm^{-1} is due to the ring N-N stretching. The aliphatic C-H stretchings were observed at between 1250-1400 cm^{-1} and around 2800 cm^{-1} regions. In the copolymers, a very strong interaction between phosphonic acid and 5-(methacrylamido)tetrazole units can be observed in the fingerprint region. The protonation of the ‘free’ nitrogens of the 5-(methacrylamido)tetrazole units can be observed with the large change of the intensity of the band at 1657 cm^{-1} . Additionally, at higher VPA ratio (d and e), the P-O-H vibration at 930 cm^{-1} becomes stronger, indicating the existence of excess acidic protons. The intensity of these peaks increased in parallel with the concentration of VPA into the copolymers. Furthermore, the band broadening between 3500 cm^{-1} and

2500 cm^{-1} is due to the hydrogen bonding network which is necessary for proton conduction (Sinirlioglu et al., 2014a; Celik and Bozkurt, 2008b). The FT-IR data confirms that protonation occurs through transfer of protons from phosphonic acid units to heterocyclic rings.

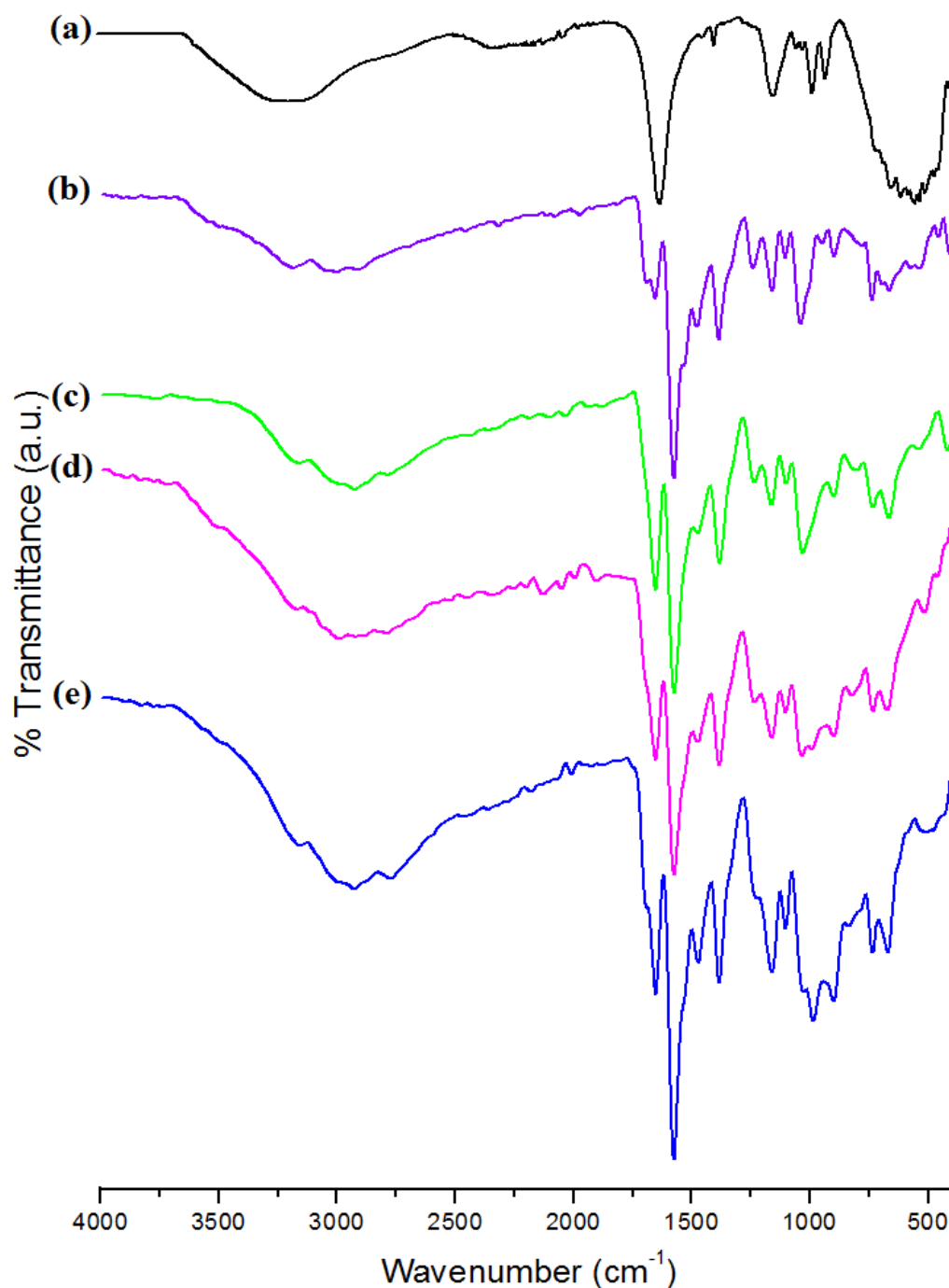


Figure 3.56 FTIR spectra of (a) PVPA, (b) PMTet, (c) P(MTet-co-VPA), S3; (d) P(MTet-co-VPA), S2; (e) P(MTet-co-VPA), S1 copolymers.

3.4.2 NMR Studies

All copolymers contain several types of hydrogen which have three different functional groups such as amide, tetrazole ring (-NH) and phosphonic acid groups. These -NH and -OH hydrogens are mobile due to formation of hydrogen bonding network between 5-(methacrylamido)tetrazole groups and phosphonic acid units of VPA, so we can not only determine the structure with using ^1H -NMR spectra (see Fig. 3.57) (Sinirlioglu et al., 2014a). Previously, especially solid-state NMR was studied and reported to elucidate the structure and the local proton diffusion of the PVPA homopolymers (Bibent et al., 2013; Komber et al., 2008; Lee et al., 2007; Bingol et al., 2006) and copolymers (Wagner et al., 2009; Millaruello et al., 2008).

^{13}C -NMR spectra of S1, S2 and S3 copolymers are presented in Fig. 3.58. Copolymerization of VPA with MTet generates new resonances. The backbone carbons of PVPA appear between at 31 and 36 ppm as sharper resonances, indicating higher mobility of the PVPA backbone compared to the PMTet backbone. Also, upon introduction of PVPA into the copolymer, a new resonance appears ~ 162 ppm as depicted in Fig. 3.58 (Sinirlioglu et al., 2014a). This resonance could be assigned to crosslinking of the PMTet ring with a PVPA side group via a C-O-P bond. The intensity of the ~ 162 ppm resonance increases with addition of PVPA (Celik and Bozkurt, 2008b). This observation gives an additional hint to the possible crosslinking between the side groups. The P-O of PVPA is somehow connected to the methacrylamidotetrazole by the carbonyl group (C=O) which is shifted to higher chemical shift values in the spectra. After the copolymerization of MTet with VPA, the ring carbon resonance of PMTet has less intensity with increased amount of PVPA in the copolymers (Sinirlioglu et al., 2014a). This is an indication of reduced mobility of the heterocycle due to the crosslinking of the side groups and/or hydrogen bonding interactions between MTet and VPA (Sinirlioglu et al., 2014a; Celik and Bozkurt, 2008b). In addition to the signals of the regular structures, the ^{13}C NMR spectra provide evidence that also radical VPA polymerization results in regioirregular H-H (head to head) and T-T (tail to tail) structures represented by methylene carbon signals at 31-36 ppm and methine carbon signals at around 45-49 ppm (Wagner et al., 2009; Millaruello et al., 2008; Komber et al., 2008; Lee et al., 2007; Bingol et al., 2006; Bozkurt et al., 2001).

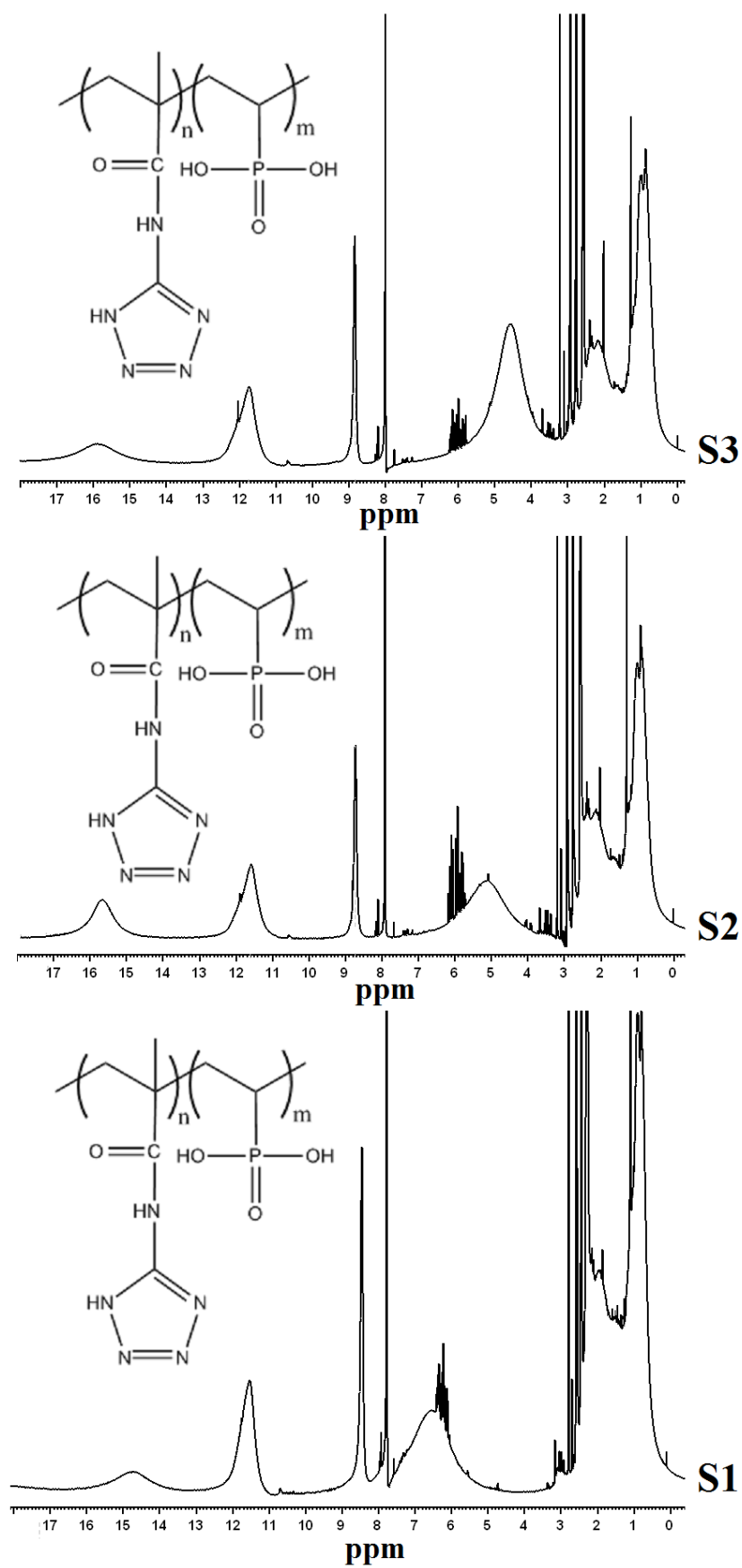


Figure 3.57 ^1H -NMR spectra of P(MTet-co-VPA) copolymers recorded in DMSO-d_6 .

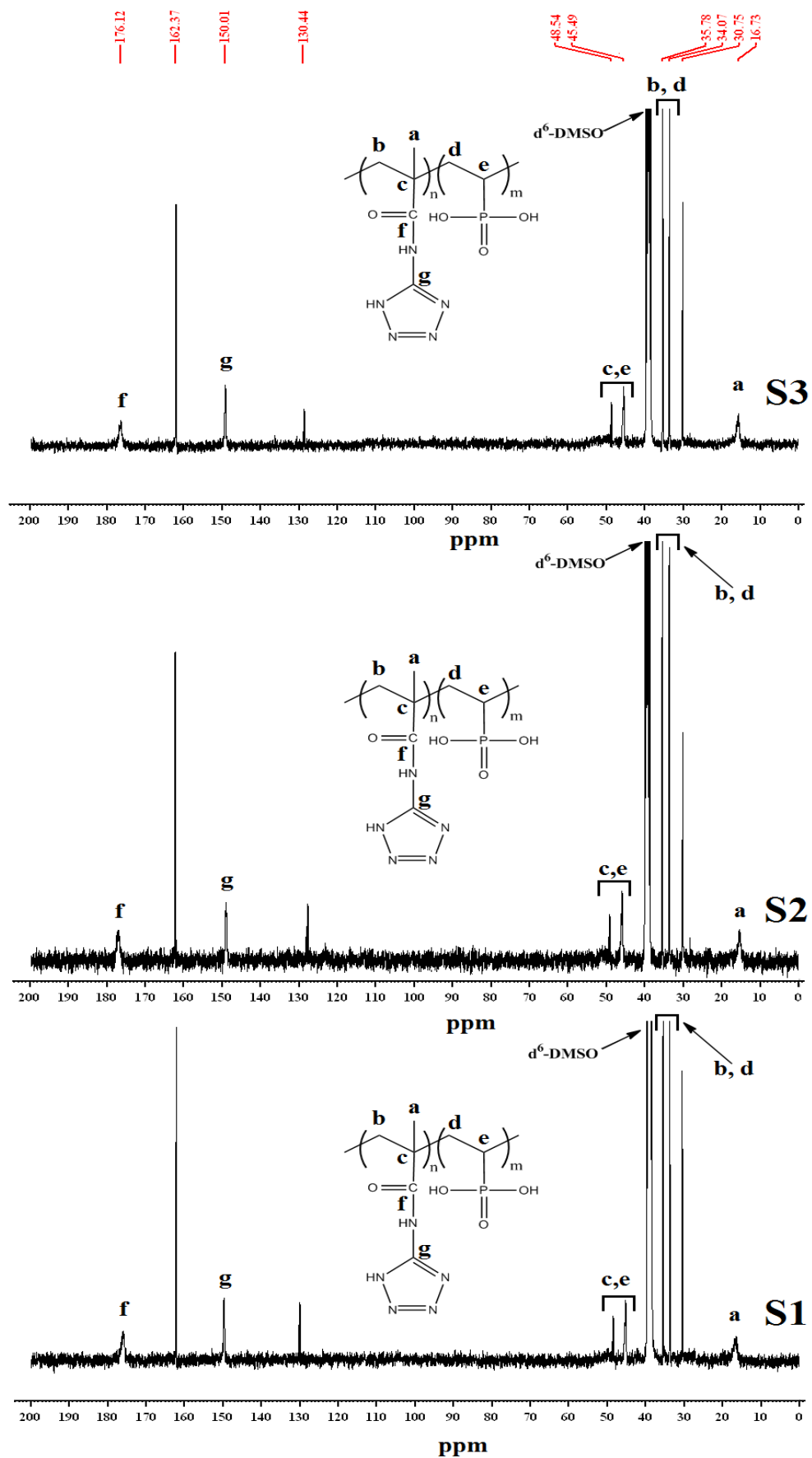


Figure 3.58 ^{13}C -NMR spectra of P(MTet-co-VPA) copolymers recorded in DMSO-d_6 .

^{31}P (decoupled) NMR spectra of P(MTet-*co*-VPA), (S3-S1) copolymers is dominated by a broad shoulder resonance between 34 and 27 ppm, resulting from the phosphonic acid groups as shown in Fig. 3.59. A weak shoulder is observed at around ~ 22 ppm and it is tentatively assigned to the phosphoric acid anhydride. In addition, a sharp peak is remarkable at around ~ 12 ppm which is assigned to the P=O groups (Sinirlioglu et al., 2014a).

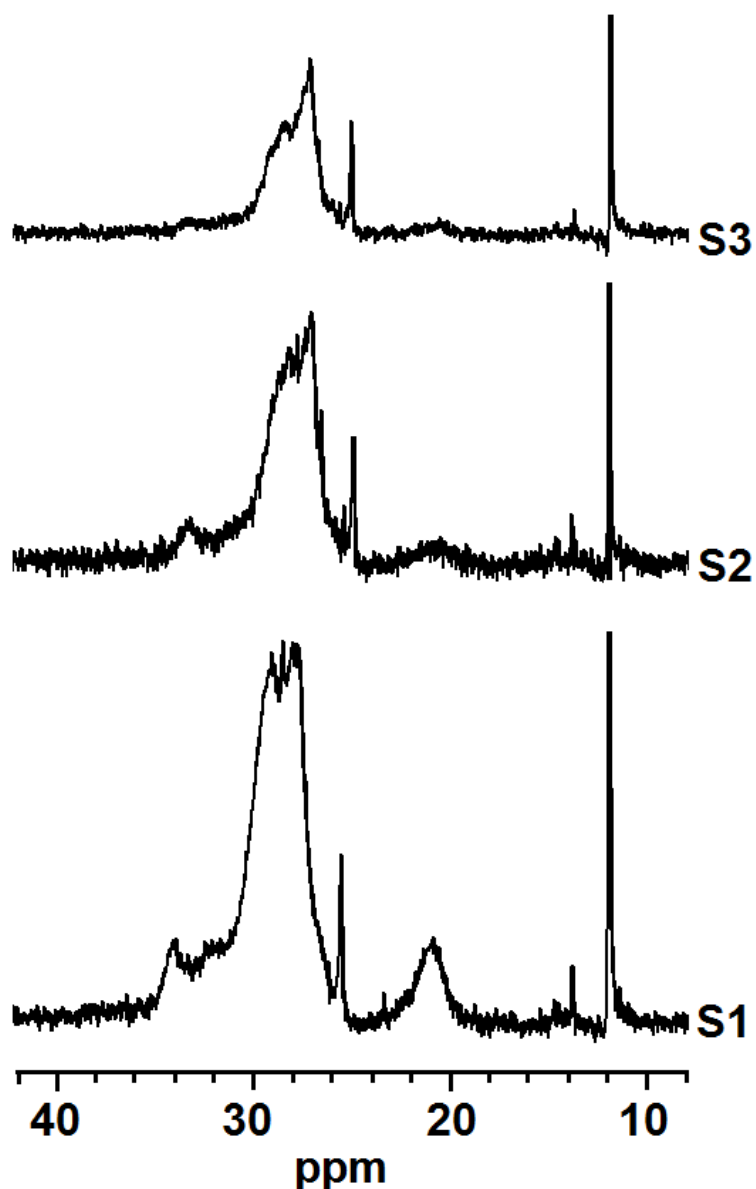


Figure 3.59 ^{31}P (decoupled) NMR spectra of P(MTet-*co*-VPA) copolymers recorded in DMSO- d_6 .

Two-dimensional heteronuclear ^{13}C - ^1H NMR methods (HETCOR) have been used successfully to assign spectra and characterize the structure of macromolecules or polymers in solution (Bielecki and Burum, 1991; Mirau and Bovey, 1986). It is shown here that these data provide evidence supporting the normal ^{13}C NMR for poly(MTet-co-VPA) copolymers. Fig. 3.60, Fig. 3.61 and Fig. 3.62 show a two-dimensional ^{13}C - ^1H heteronuclear correlation spectrum of S1, S2, and S3 copolymers. The horizontal axis of Fig. 3.60, Fig. 3.61 and Fig. 3.62 correspond to the ^{13}C chemical shift range (0 to 180 ppm), and the vertical axis corresponds to the proton shift range (0 to 9 ppm). Horizontal (^{13}C) and vertical (^1H) projections of the two-dimensional spectrum are shown above and left, respectively. Data from Fig. 3.60, Fig. 3.61 and Fig. 3.62 allow for the (^{13}C) and (^1H) NMR assignment of S1, S2, and S3 copolymers, respectively. The individual (^{13}C) and (^1H) chemical shifts of S1, S2, and S3 copolymers are shown in Table 3.10, along with the assignment. Peak values are illustrated with dash line in the heteronuclear (^{13}C) and (^1H) (HETCOR) NMR spectra. After copolymerization of VPA with MTet generates new resonances. The backbone carbons of PVPA appear between at 31 and 36 ppm as sharper resonances and their associated protons are (between around 2.53 and 2.88 ppm) clearly distinguishable. These C and H atoms correlated to each other. In addition, upon introduction of PVPA into the copolymer, a new resonance appears ~162 ppm as depicted in Fig. 3.60, Fig. 3.61, Fig. 3.62 and this C atom is connected with the proton with the chemical shift at around 7.95 ppm as shown with dash line in Fig. 3.60, Fig. 3.61 and Fig. 3.62, respectively (Sinirlioglu et al., 2014a).

Table 3.10 ^{13}C and ^1H Correlations of poly(MTet-co-VPA; S1, S2, and S3) copolymers.

S1		S2		S3	
Chemical shift (ppm)		Chemical shift (ppm)		Chemical shift (ppm)	
^{13}C peaks	^1H peaks	^{13}C peaks	^1H peaks	^{13}C peaks	^1H peaks
162.5	7.95	162.9	7.92	163	7.94
35.8	2.88	36.2	2.83	36.2	2.86
34.4	2.73	34.6	2.73	34.2	2.72
31.1	2.53	31.3	2.56	31.1	2.62

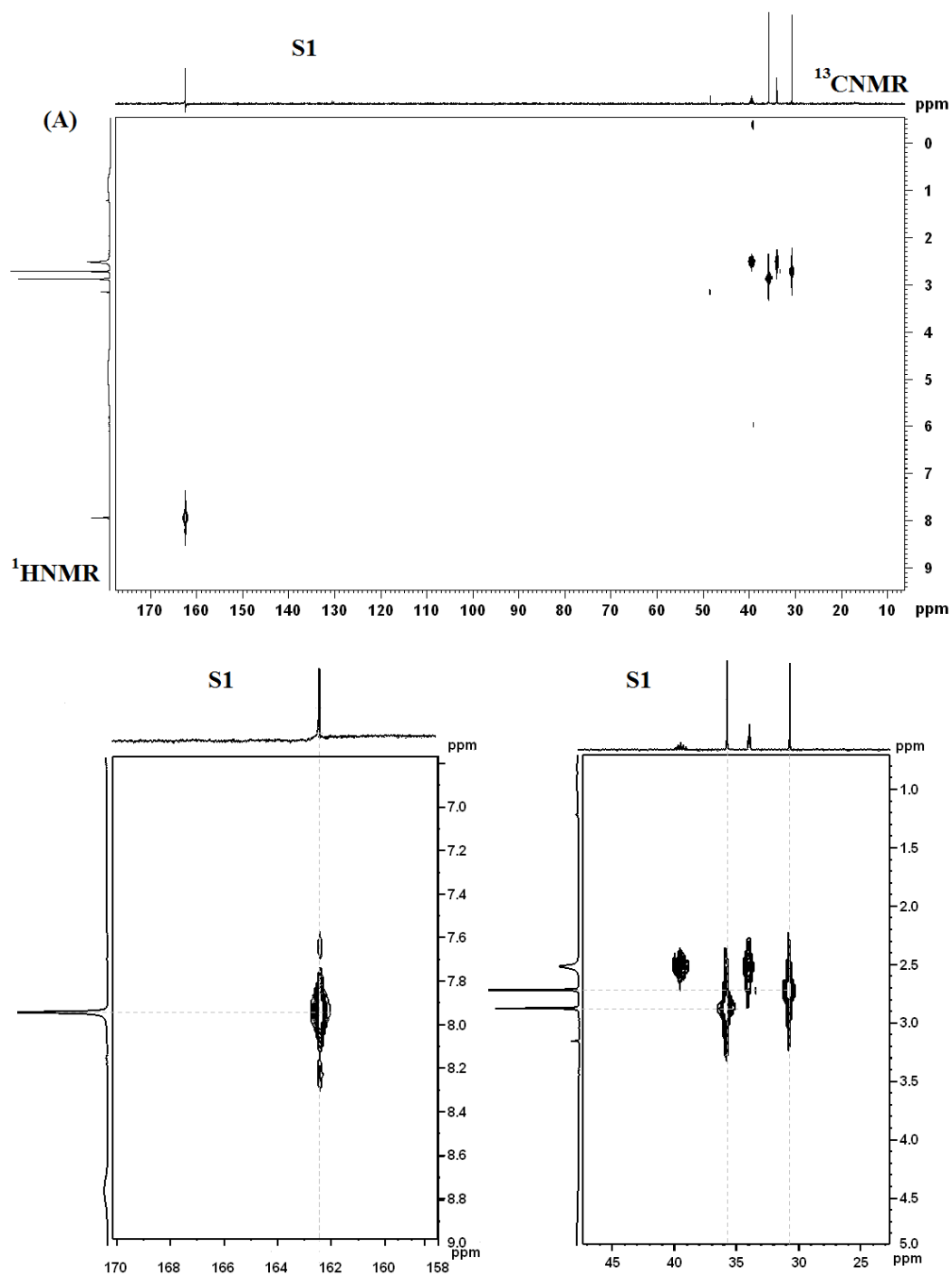


Figure 3.60 Two dimensional ^{13}C - ^1H HETCOR spectra of P(MTet-co-VPA), (S1) copolymer recorded in DMSO-d_6 . ^{13}C and ^1H projections are shown above and to the left of the plot.

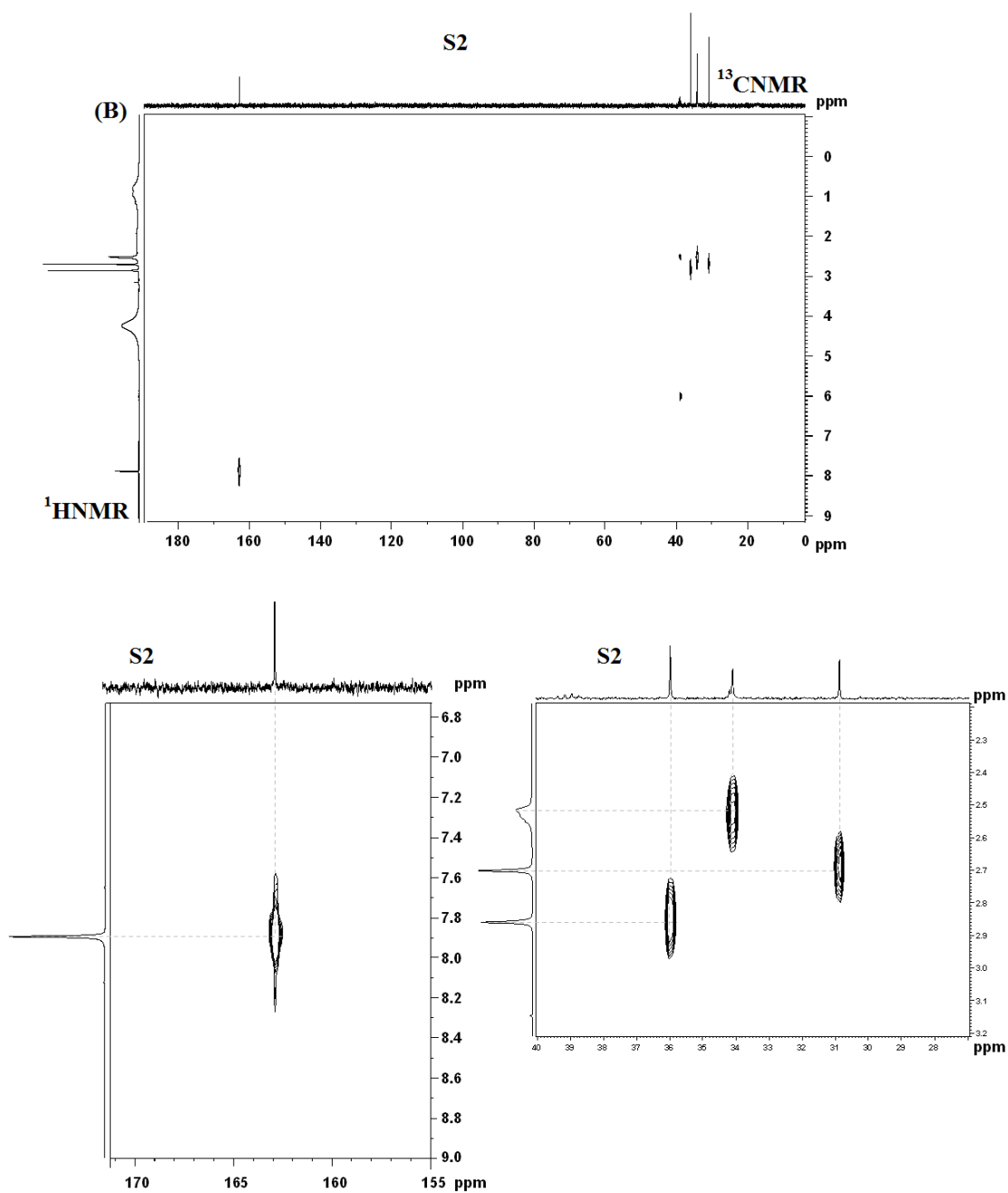


Figure 3.61 Two dimensional ^{13}C - ^1H HETCOR spectra of P(MTet-co-VPA), (S2) copolymer recorded in DMSO-d_6 . ^{13}C and ^1H projections are shown above and to the left of the plot.

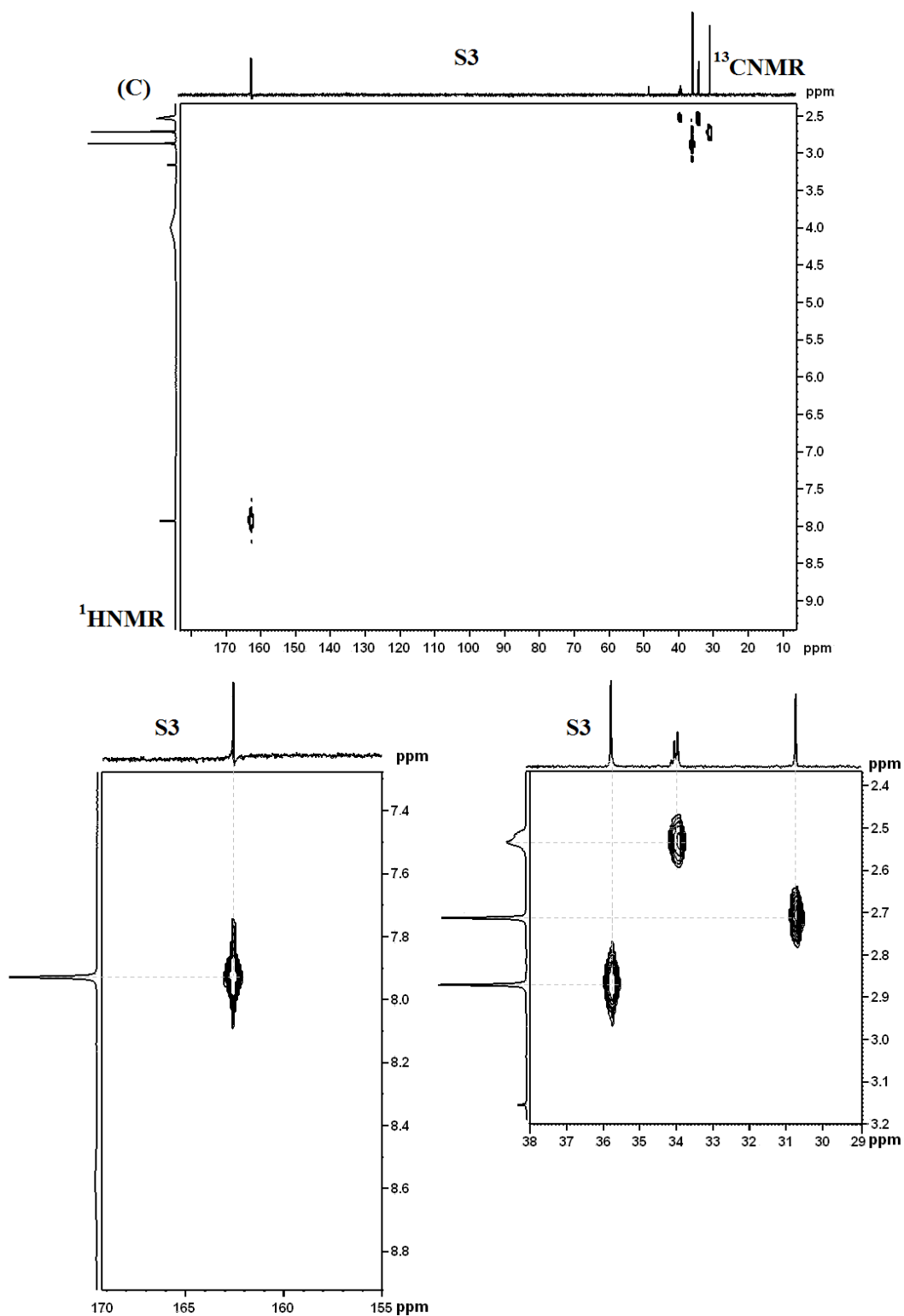


Figure 3.62 Two dimensional ^{13}C - ^1H HETCOR spectra of P(MTet-co-VPA), (S3) copolymer recorded in DMSO- d_6 . ^{13}C and ^1H projections are shown above and to the left of the plot.

3.4.3 Thermal Properties

The samples were dried under vacuum at 90 °C for 24 h. Table 3.11 lists the glass transition temperatures of the PVPA, PMTet, poly(MTet-co-VPA) copolymer electrolytes under inert atmosphere at a scan rate of 10 °C/min, respectively. In DSC measurements, the second heating curves were evaluated. PVPA exhibits a glass transition at around -23 °C (Celik and Bozkurt, 2008b; Sevil and Bozkurt, 2004), and PMTet exhibited a glass transition at approximately 93 °C (Sinirlioglu et al., 2013). The poly(MTet-co-VPA), (S1-S3) copolymers have definite glass transition temperatures were measured around 39 °C, 46 °C and 49 °C, respectively. The presence of single T_g confirms the homogeneity of the materials and the presence of a glass transition in the copolymers illustrated that the presence of ionic interactions does not prevent cooperative relaxations of the copolymers (Sinirlioglu et al., 2014a).

Table 3.11 T_g and maximum proton conductivity values of PVPA, PMTet, S1, S2, and S3 copolymer electrolyte membranes.

Sample Name	Feed mol ratio MTet:VPA	T_g (°C)	Max. Proton Conductivity (S/cm) at 150 °C
PVPA	-----	-23	10^{-3}
PMTet	-----	93	2×10^{-6}
P(MTet-co-VPA), S1	1: 2	39	0.01
P(MTet-co-VPA), S2	1: 1	46	0.004
P(MTet-co-VPA), S3	1: 0.5	49	8×10^{-4}

TGA curves of PMTet, and P(MTet-co-VPA) (S1-S3) copolymers are shown in Fig. 3.63. PVPA is thermally stable until 200 °C but there is a little weight loss between 100-200 °C due to condensation of phosphonic acid units (Sevil and Bozkurt, 2004; Jiang et al., 1999). PMTet homopolymer exhibited a thermal stability up to 215 °C. 30 % of PMTet decomposed between 215 and 350 °C because of degradation of aminotetrazole units and after 400 °C, a second weight loss occurred because of

degradation of the polymer backbone. After copolymerization of the corresponding monomers, the degradation temperature decreased a little but all copolymers can be said to be thermally stable at least 185 °C, there is a little weight loss between 100-160 °C due to condensation of phosphonic acid units. 35 % of all copolymers break down between 185 and 270 °C because of degradation of aminotetrazole groups and, second weight loss occurs after 320 °C due to the decomposition of the copolymer backbone (Sinirlioglu et al., 2014a).

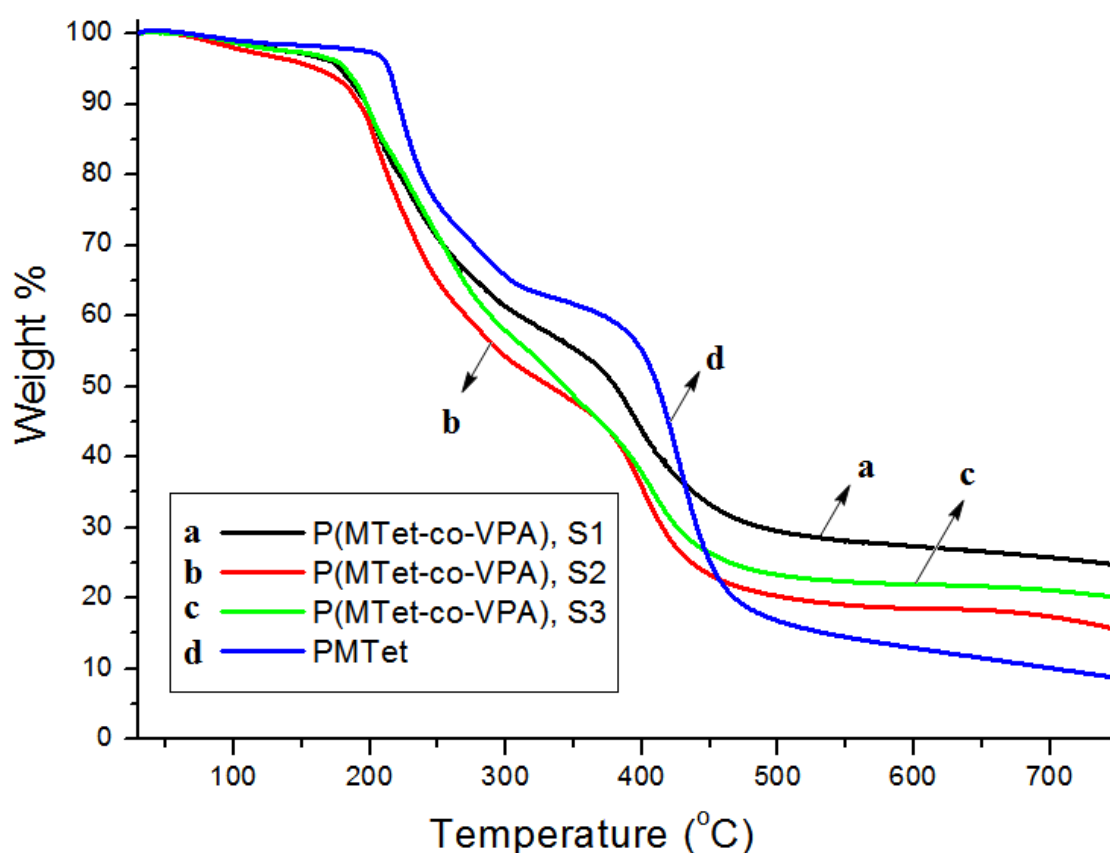


Figure 3.63 TGA curves of PMTet, and P(MTet-co-VPA; S1, S2, and S3) copolymers at a heating rate of 10 °C/ min.

3.4.4 X-ray Diffraction (XRD)

XRD patterns of PMTet homopolymer, S1, S2 and S3 copolymers are given in Fig. 3.64. There are two strong peaks in the diffractograms of pure PMTet at 2θ values

of 18° and 24° , this indicated the high degree of crystallinity of PMTet. For P(MTet-co-VPA) (S1-S3), the characteristic peak at around 18° almost disappeared immediately (Sinirlioglu et al., 2014a). This result revealed that the original crystalline structure of pure PMTet homopolymer was seriously destroyed. The crystallinity of the membranes decreases when the VPA mol content was increased from 0.50 to 2.0. This behavior was described as the elimination of hydrogen bonding network between tetrazole groups of MTet and phosphonic acid units of VPA at higher acid compositions (Sinirlioglu et al., 2014a; Goktepe et al., 2008).

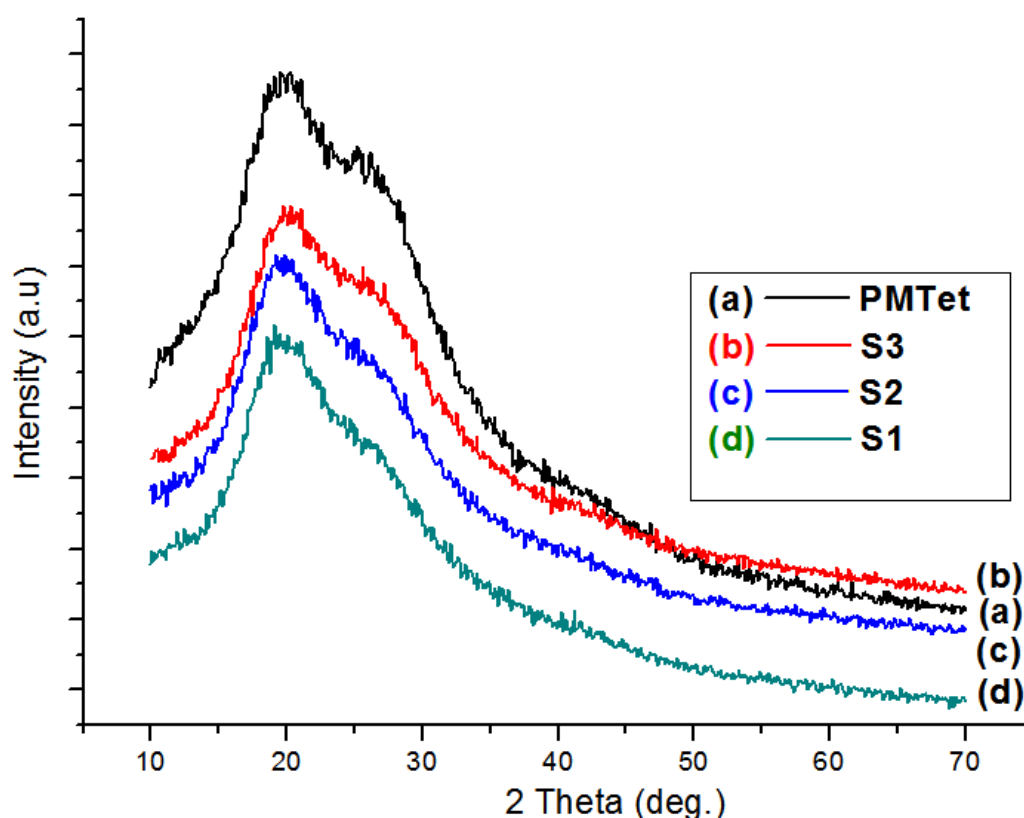


Figure 3.64 XRD patterns of (a) PMTet, (b) P(MTet-co-VPA; S3), (c) P(MTet-co-VPA; S2) and (d) P(MTet-co-VPA; S1).

3.4.5 Scanning Electron Microscopy (SEM)

Surface morphologies of the copolymer electrolyte membranes were investigated by SEM and depicted in Fig. 3.65. From the figures, it was observed that all samples

were homogeneously dispersed and the images showed single phase formation due to strong interaction between phosphonic acid groups and the tetrazole units. This showed that there was no agglomeration or phase separation at the micrometer or nanometer level. This observation was also consistent with the DSC results, in which a single T_g was observed (Sinirlioglu et al., 2014a).

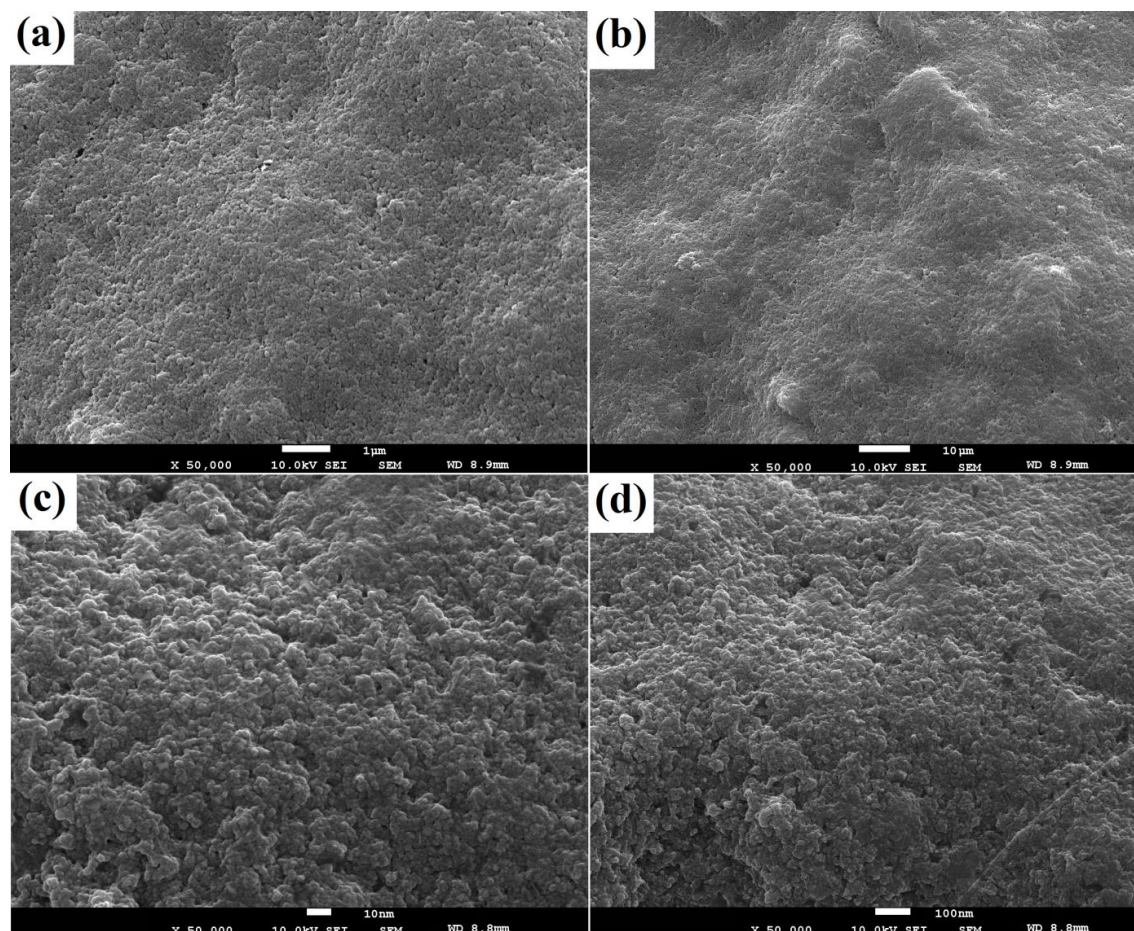


Figure 3.65 SEM images of the surface of poly(MTet-co-VPA) (S1) copolymer electrolytes at different micrometer- and nanometer-scale level by 50,000X magnification, (a) 1 μm, (b) 10 μm, (c) 10 nm and (d) 100 nm.

3.4.6 Atomic Force Microscopy (AFM)

The selected AFM images of copolymer electrolytes are illustrated in Fig. 3.66. The mean values of surface roughness of copolymers and PVPA homopolymer are listed in Table 3.12. Surface roughness was calculated by using the Root Mean Square

(RMS), that is, the standard deviation of the Z values within a given area, defined by where Z_{ave} is the average, Z_i is the current Z value, and N is the number of points within the analyzed area (please see equation 2.4 in the previous section). It was noted that the surface roughness depends on the curvature and size of the AFM tip and on the image processing. The RMS mean values and the standard deviations were obtained by analyzing at least 6 AFM images. The RMS roughness drastically increased from 200 nm to 341 nm when the VPA content was increased from 33 % to 67 % (Sinirlioglu et al., 2014a).

Table 3.12 The mean RMS roughness values with the standard deviations.

Samples	Roughness (nm)
PVPA	2.4 $\pm$ 0.1
P(MTet-co-VPA; S1)	341 $\pm$ 187
P(MTet-co-VPA; S2)	242 $\pm$ 199
P(MTet-co-VPA; S3)	200 $\pm$ 113

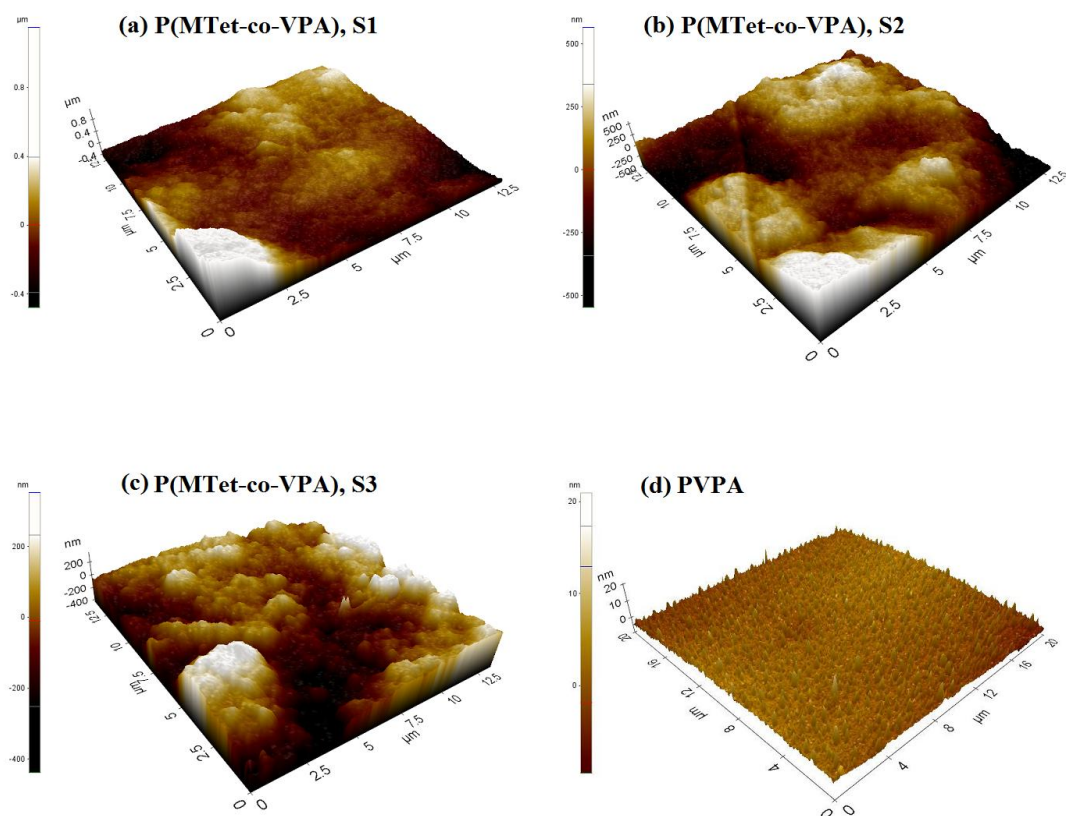


Figure 3.66 AFM pictures (3d) of PVPA (20×20 μm), and P(MTet-co-VPA) (S1-S3) (12.5×12.5 μm) copolymer electrolytes.

3.4.7 Proton Conductivity Measurements

The proton conductivities of anhydrous membranes were measured from 20 °C to 150 °C. The AC conductivity versus frequency plots at several temperatures are presented in Fig. 3.67, Fig. 3.68, Fig. 3.69 and Fig. 3.70. As expected, higher proton conductivities were observed as temperature was increased (Sinirlioglu et al., 2014a).

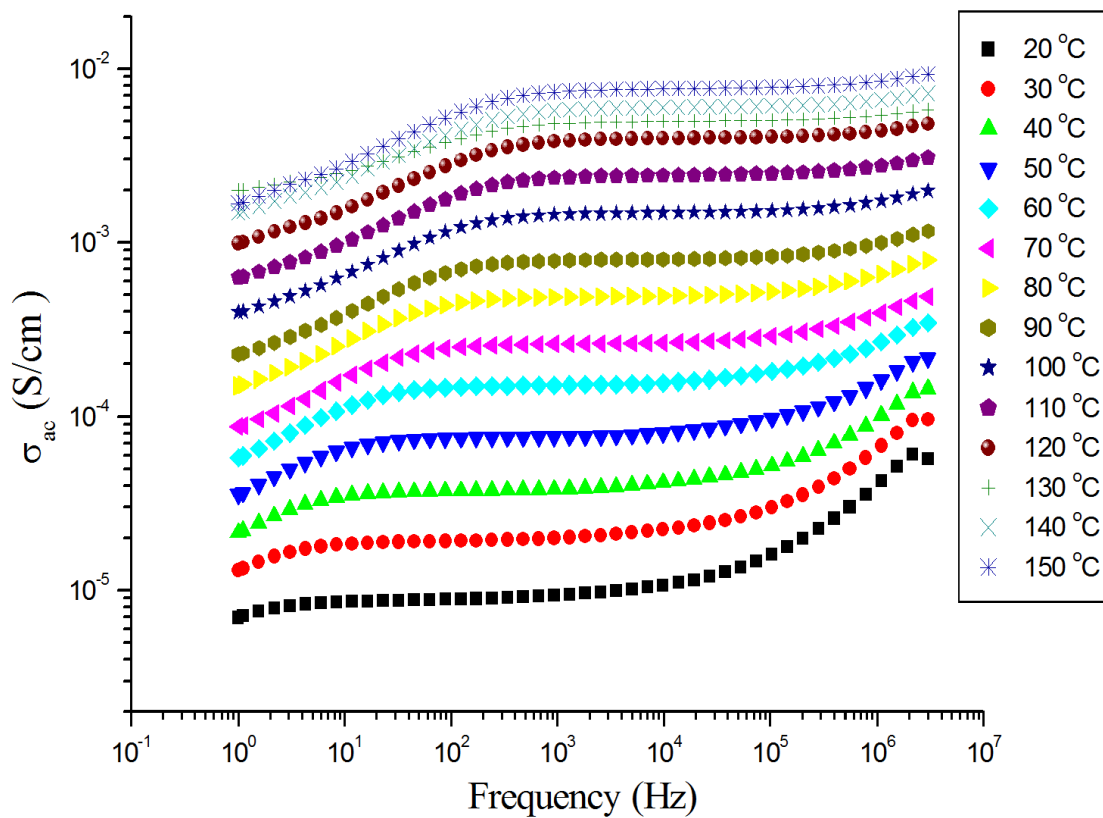


Figure 3.67 AC conductivity versus frequency of Poly(MTet-co-VPA, S1) copolymer at several temperatures.

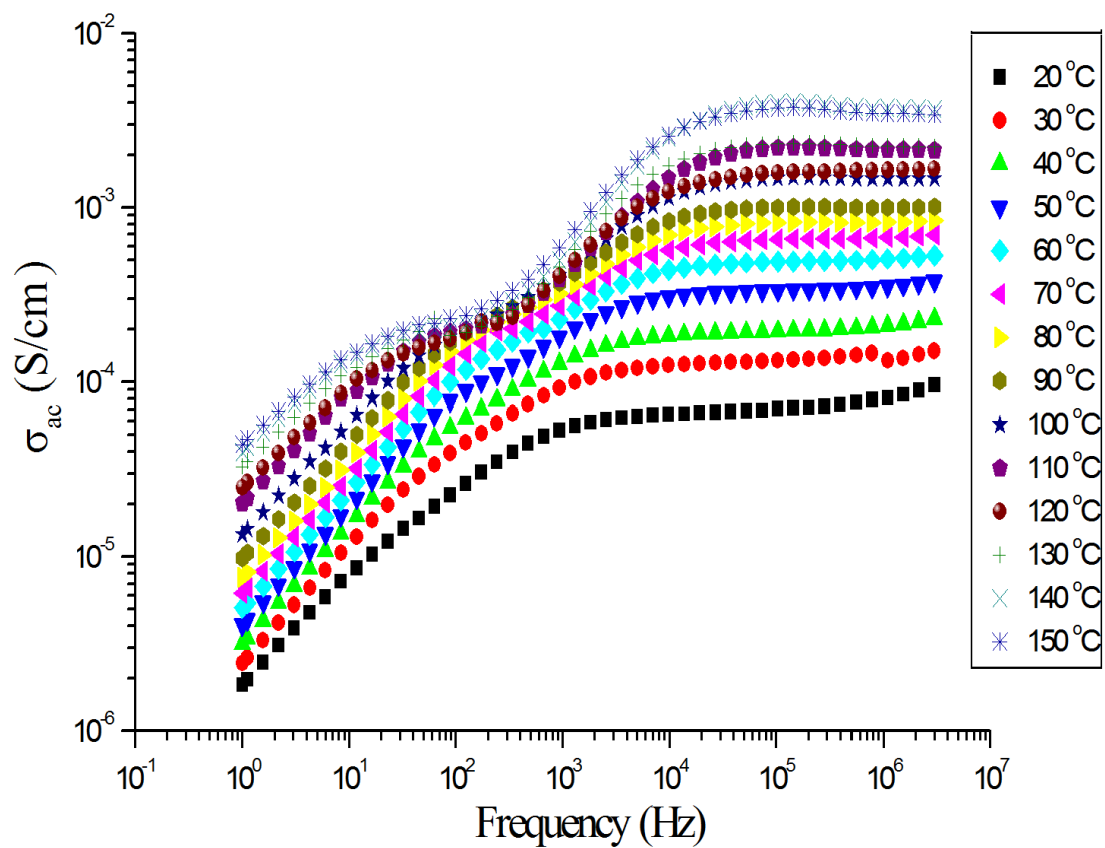


Figure 3.68 AC conductivity versus frequency of Poly(MTet-co-VPA, S2) copolymer at several temperatures.

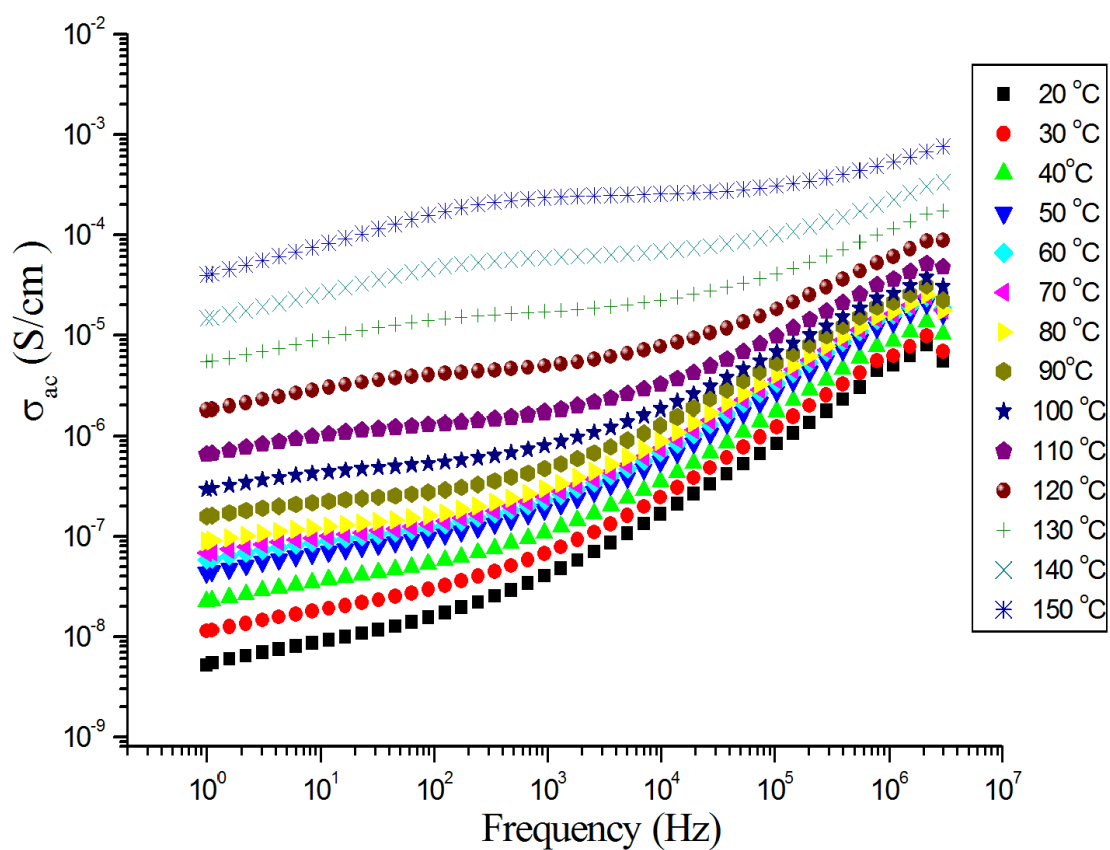


Figure 3.69 AC conductivity versus frequency of Poly(MTet-co-VPA, S3) copolymer at several temperatures.

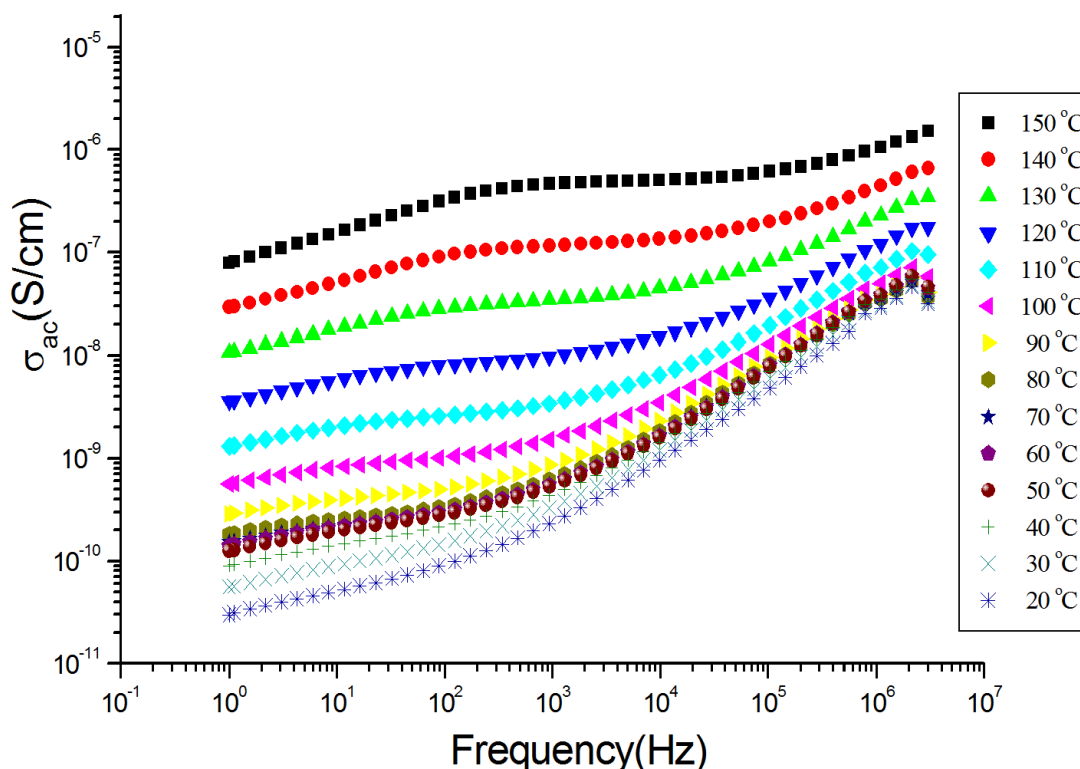


Figure 3.70 AC conductivity versus frequency of PMTet homopolymer at several temperatures.

The DC conductivity (σ_{dc}) of the samples was determined from the plateaus of $\log \sigma_{ac}$ versus $\log F$ by linear fitting of the data. In Fig. 3.71, the DC conductivities of all copolymers and PMTet homopolymer were compared. It can be seen from the conductivity isotherm that the DC conductivity is directly proportional to both the temperature and vinyl phosphonic acid (VPA) content. In the anhydrous conditions, the proton conductivity of poly(MTet-co-VPA; S1, S2 and S3) copolymer electrolytes were measured as 0.01 S/cm, 0.004 S/cm, and 8×10^{-4} S/cm at 150 °C, respectively. There is a deviation from linearity above 60 °C which may be due to the increase in the segmental motions and its positive contribution to the proton conductivity (Sinirlioglu et al., 2014a).

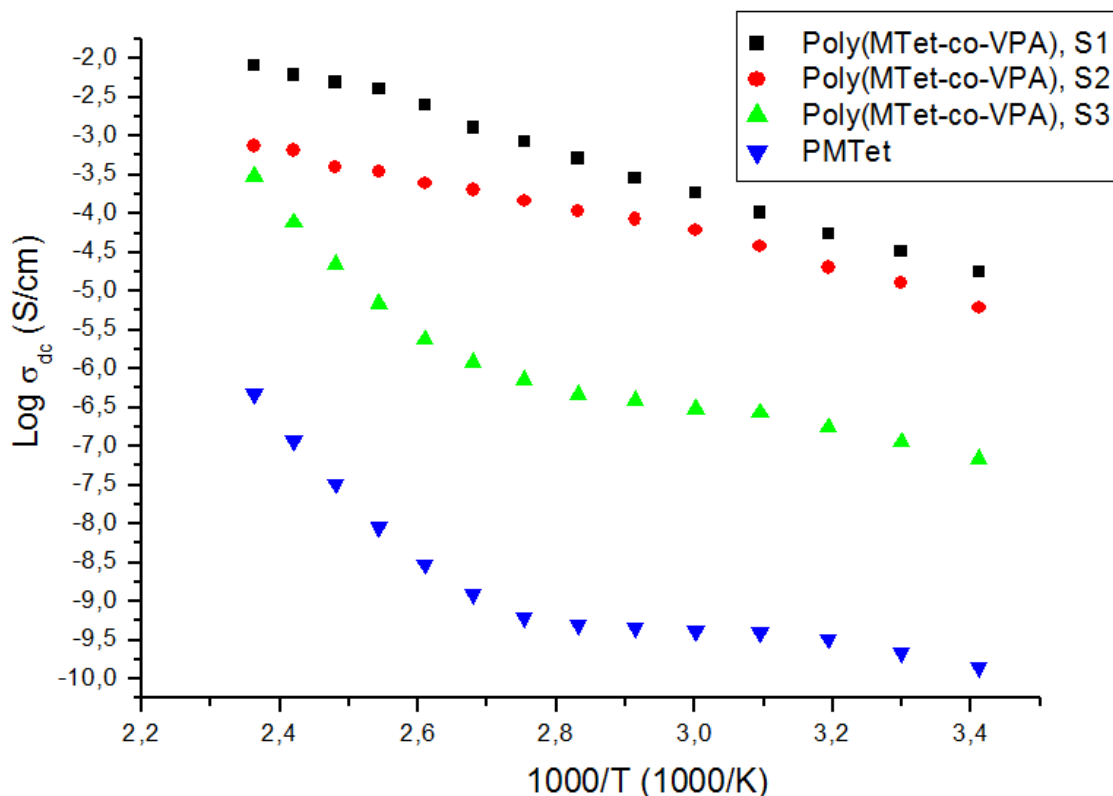


Figure 3.71 Variation of the DC proton conductivity of Poly(MTet-co-VPA) copolymers and PMTet homopolymers as a function of reciprocal temperature.

Previously, VPA was copolymerized with heterocyclic monomers such as vinyl imidazole (Bozkurt et al., 2003) and vinyl triazole (Celik et al., 2008b). The proton conductivity of P(VPA-co-VIm) copolymer was low (1×10^{-6} S/cm) while it was higher ($\sim 1 \times 10^{-3}$ S/cm) in P(VPA-co-VTri) copolymers. In particular, the proton conductivity increased with the content of phosphonic acid units in the polymer chain and VPA containing poly(VPA-co-VTri) copolymers, ($\sim 70\%$ PVPA mole ratio) showed a conductivity of $\sim 10^{-3}$ S/cm at 120°C in the anhydrous state. The low proton conductivity in P(VPA-co-VIm) was attributed to the restrictions in the segmental motions of copolymer chains by ionic cross-linking (Bozkurt, 2003). In the current system, the major part of proton transport is provided over both phosphonic acid coordinated with tetrazole units. Herein, MTet is considered to make hydrogen bonding network with phosphonic acid units of VPA. As seen in FTIR spectrum, copolymer electrolytes as well as conductivity data, it can be concluded that a Grotthuss mechanism (structural diffusion) is the possible pathway for the total proton diffusion. This

continuous pathway may convey proton transport over the -POH groups and tetrazole groups. The proton could travel along the hydrogen bonds from one functional group to another (Celik et al., 2012; Celik and Bozkurt, 2008; Ramirez-Salgado, 2007; Smitha et al., 2004).

3.4.8 Cyclic Voltammetry

Cyclic voltammogram of Poly(MTet-co-VPA; S2) copolymer was given in Fig. 3.72. It was clearly observed that the CV of S2 copolymer comprised no peak within the anodic sweep (-1.5 to 1.5 V potential range). In the cathodic sweep, formation of gaseous hydrogen was developed which localized near the electrode and was subsequently reoxidized toward the anodic cycle. Thus the electrochemical stability window was at least 3 V. These results implied that the copolymer has adequate electrochemical stability under fuel cell conditions (Sinirlioglu et al., 2014a).

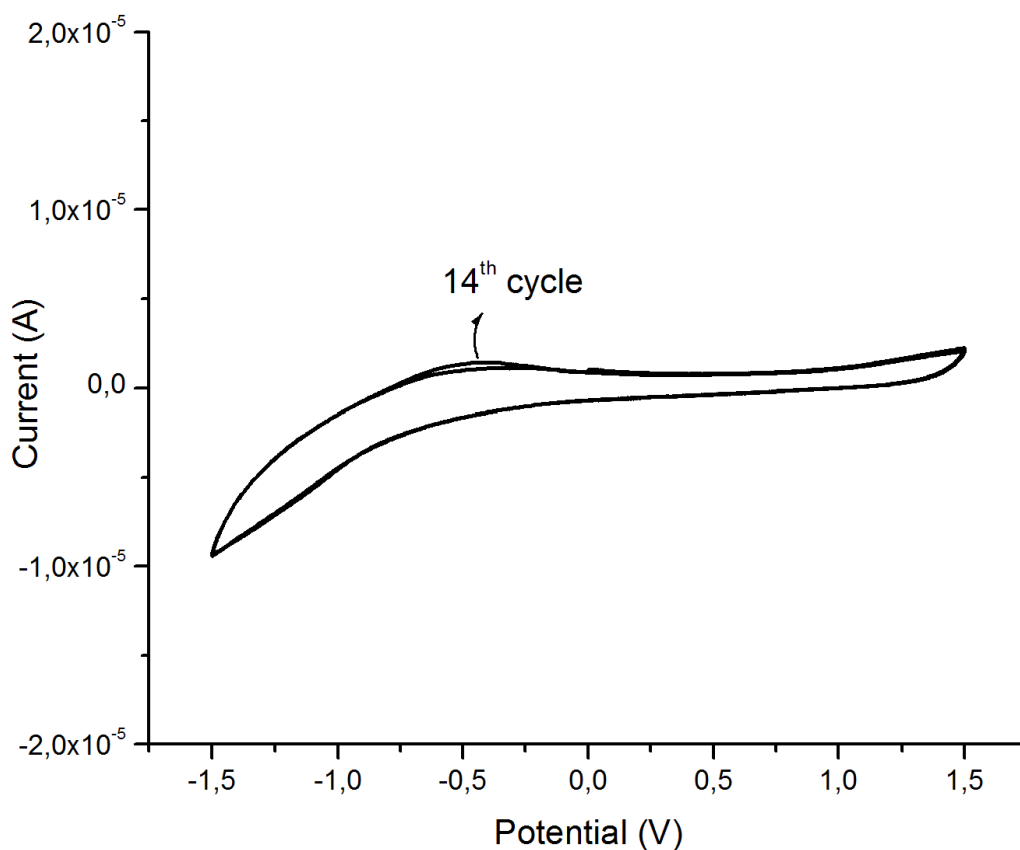


Figure 3.72 Cyclic voltammograms of Poly(MTet-co-VPA; S2) in 0.1 M TBATFB/acetonitrile. Curves were obtained with a scan rate of 50 mV/s.

3.5 SYNTHESIS OF NOVEL COMPOSITE MEMBRANES BASED ON POLY(VINYL PHOSPHONIC ACID) AND POLY(5-(METHACRYLAMIDO)TETRAZOLE)

In this part of thesis, MTet monomer, prepared by the reaction of methacryloyl chloride with 5-aminotetrazole, was polymerized via conventional free radical polymerization to attain poly(5-(methacrylamido)tetrazole) (PMTet) (see Fig. 3.15 and Fig. 3.73). Poly(vinyl phosphonic acid) (PVPA) was produced by free radical polymerization of vinyl phosphonic acid as discussed in an earlier study (see Fig. 3.73). The composite membranes were prepared by intercalated PVPA into PMTet at the different ratios to obtain PMTetP(VPA) $_x$ ($x = 0.5, 1.0, 2.0$ and 4.0) where x assigns the molar ratio of the polymer repeating units. In the present blend system, tetrazole molecules were immobilized into a polymer to eliminate the leaching of the azole molecules and PVPA is blended with this tetrazole functional polymer to facilitate the proton transport via Grotthus mechanism. On the other hand, since PVPA is a water soluble polymer, its usage as PEM membrane is limited. Therefore, it may be useful to blend it with a water insoluble polymer (Sinirlioglu et al., 2015a).

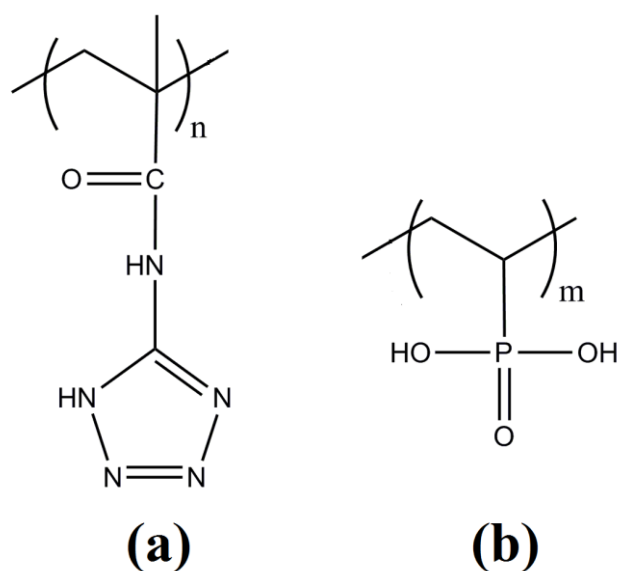


Figure 3.73 Structure of (a) PMTet, and (b) PVPA.

Also, the solubility of the samples were studied. The monomer is a colorless solid that dissolves in methanol, DMF, or DMSO upon warming. Its solubility in water is negligible. The colorless PMTet homopolymer was found to show little or no solubility in most solvents. Except DMF, dimethyl sulfoxide (DMSO), and *N*-methylpyrrolidinone (NMP), it has no solubility in other solvents such as water, methanol, ethanol, THF and acetone. A high degree of hydrogen bonding between the amide and tetrazole groups was thought to be responsible for the low solubility of the materials for common organic solvents (Sinirlioglu et al., 2015a).

3.5.1 NMR Studies

^1H -NMR spectrum of PMTet homopolymer was given in the previous section (see Fig. 3.22). The disappearance of peaks at 6.09 and 5.74 ppm from vinylic protons of MTet monomer supports that the MTet monomer has been polymerized completely. The appearance of the peaks belonging to -NH proton of the tetrazole ring and amide bond proton at 15.90 and 11.65 ppm are a typical indication for the successful polymerization of MTet. Also, the signals at 2.34 ppm and 2.09 ppm are assigned to the methylene proton ($2\text{H}, -\text{CH}_2$) which indicates polymer backbone (Sinirlioglu et al., 2014d; Sinirlioglu et al., 2015a).

3.5.2 FTIR Studies

The FTIR spectra of PVPA and PMTet homopolymers, and PMTetP(VPA)_x ($x=0.5, 1.0, 2.0$, and 4.0) composite membranes are presented in Fig. 3.74. Pure PVPA has strong bands at 990 and 910 cm^{-1} that belong to asymmetric stretching vibrations of the P-OH group and at 1150 cm^{-1} that corresponds to P=O stretching (Aslan and Bozkurt, 2012; Steininger et al., 2007). The C=C band of the vinyl phosphonic acid was evident at 1635 cm^{-1} . Peaks associated with -CH stretchings ($=\text{CH}$, $=\text{CH}_2$) were observed in the vinyl phosphonic acid between 2800 and 3000 cm^{-1} . PMTet homopolymer exhibited several medium or strong peaks between 1689 cm^{-1} , 1657 cm^{-1} and 1475 cm^{-1} due to amide bond and tetrazole (C-N, C=N) ring vibrations, respectively. PMTet also showed N-N stretching at 1245 cm^{-1} . The peaks at 725 - 1160 cm^{-1} correspond to C-H stretching bands and the formation of a slightly broad peak at around 3200 cm^{-1} shows the protonation of tetrazole rings (Sinirlioglu et al., 2013; Taden et al., 2002). PMTetP(VPA)_x ($x=0.5, 1.0, 2.0$, and 4.0) (“c,d,e, and f” spectrum in

Fig. 3.74) exhibited several medium or strong peaks at 1657 cm^{-1} and 1474 cm^{-1} , which were due to amide bond and tetrazole (C-N, C=N) ring vibrations, respectively. The peak at 1265 cm^{-1} is due to the ring N-N stretching. The aliphatic C-H stretchings were observed at between $1250\text{--}1400\text{ cm}^{-1}$ and around $2800\text{--}3000\text{ cm}^{-1}$ regions. In the composite membranes, a very strong interaction between phosphonic acid and 5-(methacrylamido)tetrazole units can be observed in the fingerprint region (Sinirlioglu et al., 2015a). The protonation of the 'free' nitrogens of the 5-(methacrylamido)tetrazole units can be observed with the large change of the intensity of the band at 1657 cm^{-1} . Additionally, at higher VPA ratio (f), the P-O-H vibration at 930 cm^{-1} becomes stronger, indicating the existence of excess acidic protons. The intensity of these peaks increased in parallel with the concentration of PVPA into the composite membranes. These peaks are overlapped with the corresponding peaks of tetrazole units of composite matrix and became broader (Fig. 3.74 (e, f)). Furthermore, the band broadening between 3500 cm^{-1} and 2000 cm^{-1} is due to the hydrogen bonding network between -NH proton of PMTet and phosphonic acid units of PVPA which is necessary for proton conduction (Sinirlioglu et al., 2015a). The FTIR data confirms that protonation occurs through transfer of protons from phosphonic acid units to heterocyclic tetrazole rings.

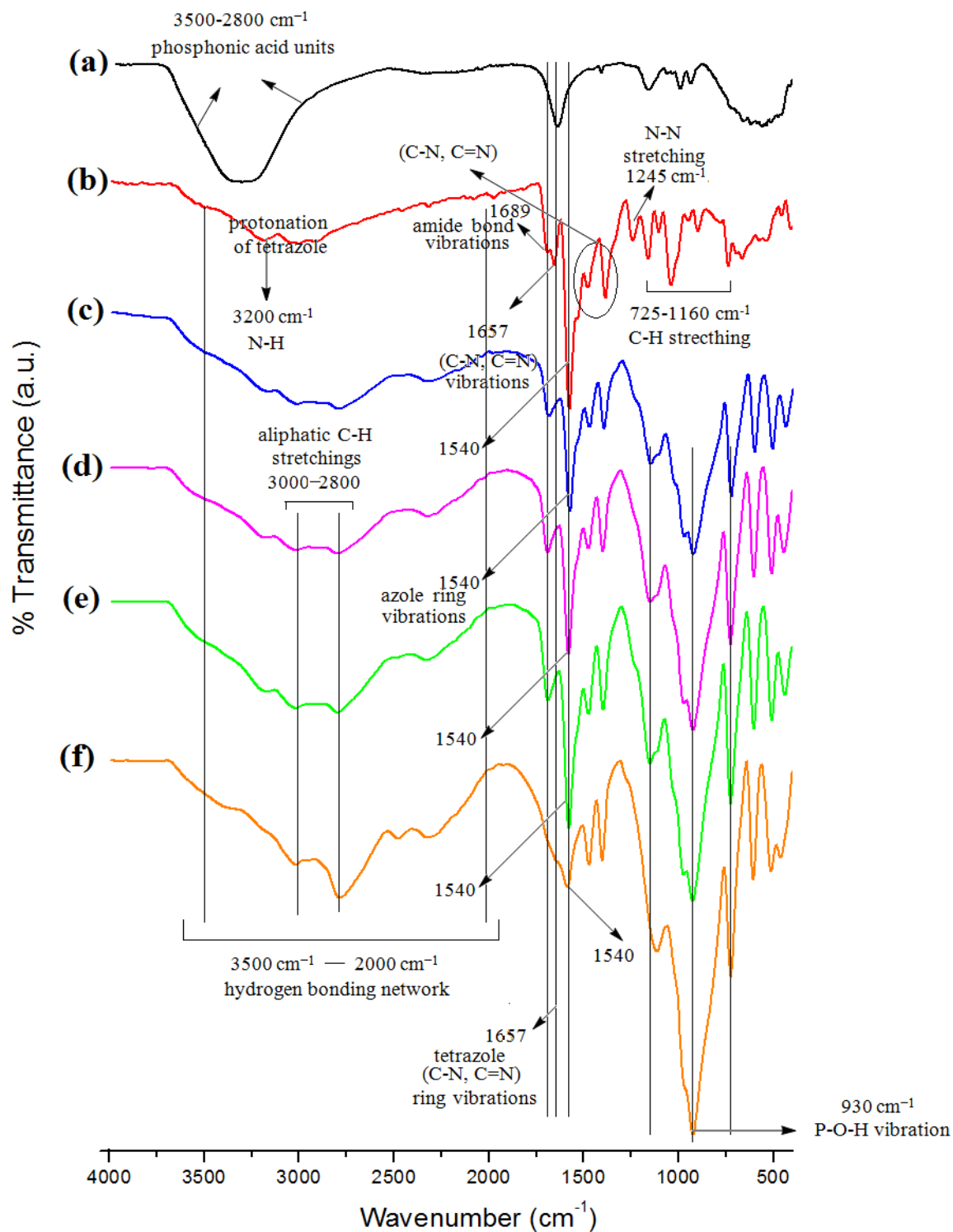


Figure 3.74 FTIR spectra of (a) PVPA, (b) PMTet, (c) PMTetP(VPA)_{0.5}, (d) PMTetP(VPA)₁, (e) PMTetP(VPA)₂, (f) PMTetP(VPA)₄ composite membranes.

3.5.3 Thermal Properties

Prior to the analysis the samples were dried under vacuum at 90 °C for 24 h and stored in a glove box. The DSC measurements were carried out under inert atmosphere at a scan rate of 10 °C/min and the second heating curves were evaluated. Previously, pure PVPA was reported to have a T_g of -23 °C (Goktepe et al., 2008; Sevil and Bozkurt, 2004), and PMTet exhibited a glass transition at approximately 93 °C (Sinirlioglu et al., 2013). Table 3.13 lists the glass transition temperatures of the PVPA, PMTet, and PMTetP(VPA)_x composite membranes. The PMTetP(VPA)_x (x=0.5, 1.0, 2.0, and 4.0) composite membranes have definite glass transition temperatures which were measured around 74 °C, 71 °C, 61 °C and 40 °C, respectively. The results showed that upon increasing incorporated PVPA content in the blend, the glass transition temperature of composite membranes decreased from 74 °C to 40 °C as expected. The presence of single T_g confirms the homogeneity of the materials (Sinirlioglu et al., 2015a).

Table 3.13 T_g and maximum proton conductivity values of PVPA, PMTet, PMTetP(VPA)_x composite membranes.

Sample Name	Feed mol ratio PMTet : PVPA	T_g (°C)	Max. Proton Conductivity (S/cm) at 150 °C
PVPA	-----	-23 °C	10^{-3}
PMTet	-----	93 °C	2×10^{-6}
PMTetP(VPA) _{0.5}	1: 0.5	74°C	2.3×10^{-4}
PMTetP(VPA) ₁	1: 1	71 °C	0.002
PMTetP(VPA) ₂	1: 2	61 °C	0.005
PMTetP(VPA) ₄	1: 4	40 °C	0.06

TGA curves of PVPA, PMTet, and PMTetP(VPA)_x composite membranes are illustrated in Fig. 3.75. PVPA is thermally stable until 200 °C but there is a little weight loss between 100-200 °C due to condensation of phosphonic acid units (Aslan and Bozkurt, 2012; Celik and Bozkurt, 2011; Celik and Bozkurt, 2008). PMTet

homopolymer exhibited a thermal stability up to 215 °C. 30 % of PMTet decomposed between 215 and 350 °C because of degradation of aminotetrazole units and after 400 °C, a second weight loss occurred because of degradation of the polymer backbone. After blending of the corresponding homopolymers, the slightly weight change at about 180 °C can be attributed to condensation of phosphonic acid groups. Clearly, the dried materials are thermally stable at least 210 °C and then, they decompose (Sinirlioglu et al., 2015a).

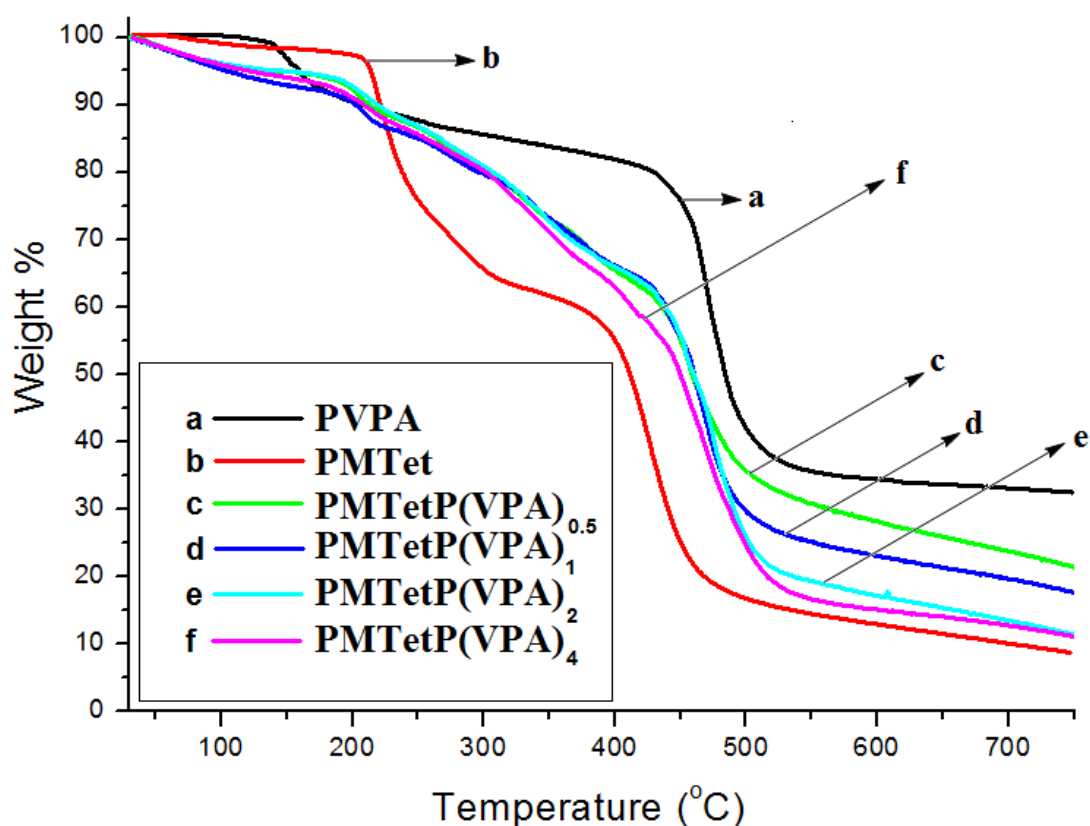


Figure 3.75 TGA curves of (a) PVPA, (b) PMTet, (c) PMTetP(VPA)_{0.5}, (d) PMTetP(VPA)₁, (e) PMTetP(VPA)₂, (f) PMTetP(VPA)₄ composite membranes at a heating rate of 10 °C/min.

3.5.4 XRD Studies

XRD patterns of PMTet, PMTetP(VPA)_x (x=0.5, 1.0, 2.0, and 4.0) composite membranes are presented in Fig. 3.76. There are two strong peaks in the diffractograms of pure PMTet at 2θ values of 18° and 24°, this indicated the high degree of crystallinity

of PMTet. For PMTetP(VPA)_x composite membranes, the characteristic peak at around 24° almost disappeared immediately. This result revealed that the original crystalline structure of pure PMTet homopolymer was seriously destroyed. The crystallinity of the composite membranes decreases when the PVPA mol content was increased from 0.50 to 4.0. That is, the amorphous character of the composite membranes increases with increasing PVPA content. Especially, at the highest acid ratio of PVPA, the crystallinity of the composite membranes (PMTetP(VPA)₄) almost disappeared (Sinirlioglu et al., 2015a). This behavior was described as the elimination of hydrogen bonding network between 5-(methacrylamido)tetrazole groups of PMTet and phosphonic acid units of PVPA at higher acid compositions (Zhang et al., 2013; Sakai et al., 2010; Goktepe et al., 2008).

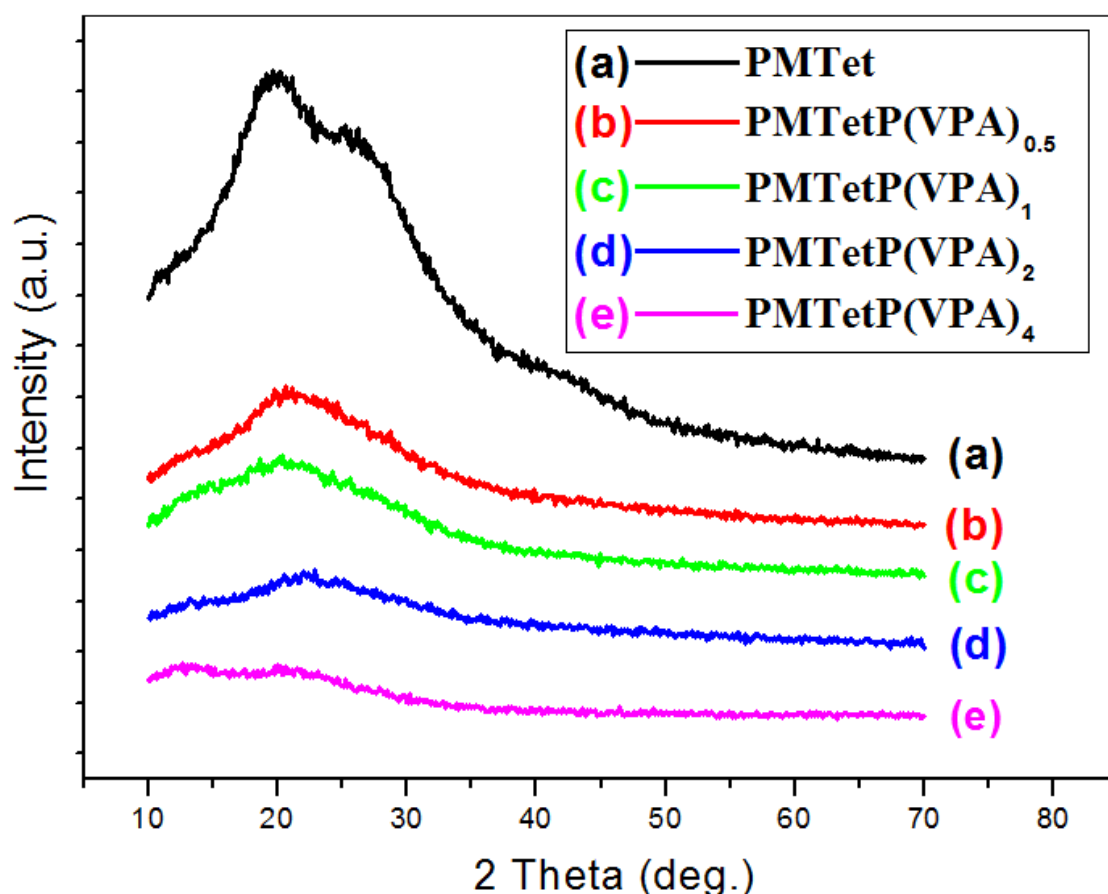


Figure 3.76 XRD patterns of (a) PMTet, (b) PMTetP(VPA)_{0.5}, (c) PMTetP(VPA)₁, (d) PMTetP(VPA)₂, (e) PMTetP(VPA)₄ composite membranes.

3.5.5 Scanning Electron Microscopy (SEM)

Surface topography of the PMTetP(VPA)_x composite membranes was examined by scanning electron microscopy and depicted in Fig. 3.77. After the composite membranes were produced by incorporating PVPA into PMTet at the different ratios, from the figures, it was observed that all samples (except Fig. 3.77 (b)) were homogeneously dispersed with increasing the PVPA content and the images showed single phase formation due to strong interaction between phosphonic acid groups and the tetrazole units. This observation was also consistent with the DSC results, in which a single T_g was observed (Aslan and Bozkurt, 2012). However, the surface image (in Fig. 3.77 (b)) shows heterogeneity, which might be possibly due to salt formation between acid (phosphonic acid group)-base (azole groups) units. The surface image (in Fig. 3.76 (c)) shows several regions attributable to partial salt formation (Sinirlioglu et al., 2015a; Sinirlioglu et al., 2013).

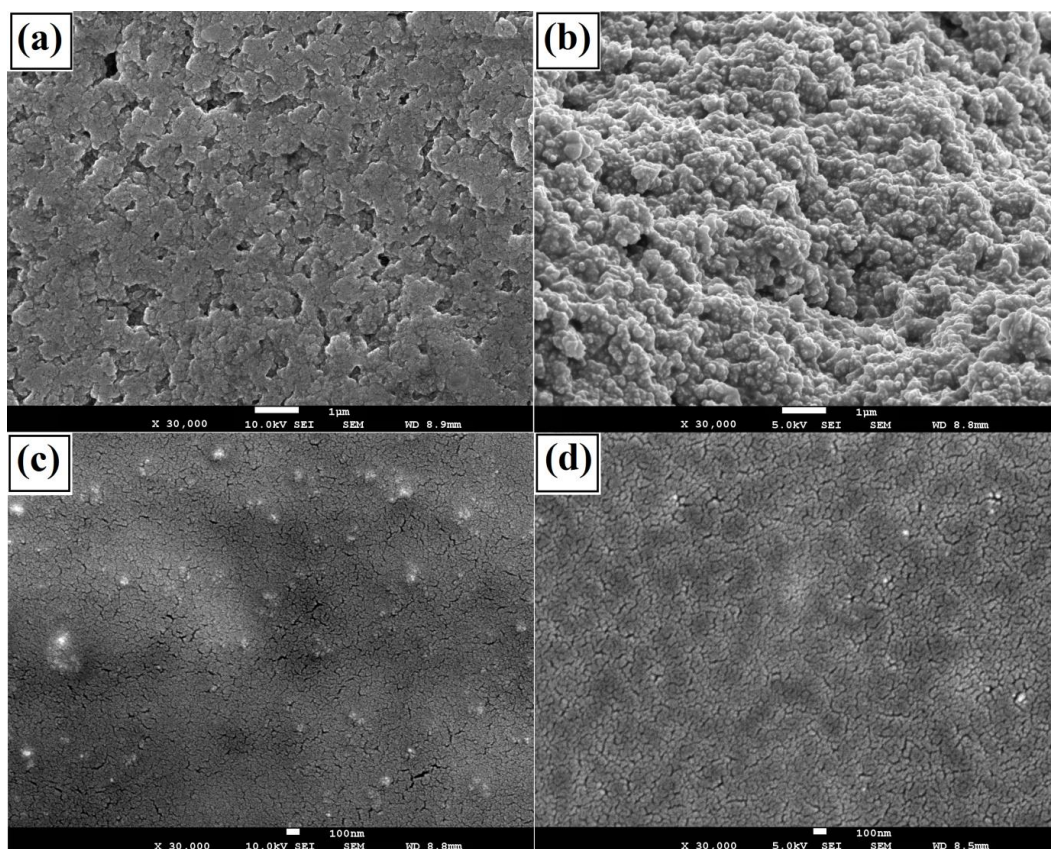


Figure 3.77 SEM images of the surface of (a) PMTetP(VPA)_{0.5}, (b) PMTetP(VPA)₁, (c) PMTetP(VPA)₂, (d) PMTetP(VPA)₄ at different scale level by 30,000X magnification, (a) 1 μ m, (b) 1 μ m, (c) 100 nm and (d) 100 nm.

3.5.6 Atomic Force Microscopy (AFM)

AFM was used for determination of phase morphology and homogeneity of the composite membranes. In addition, the surface roughness of the composite membranes was determined. The selected AFM images of composite membranes are presented in Fig. 3.78. The mean values of surface roughness of PMTetP(VPA)_x composite membranes and PVPA homopolymer are listed in Table 3.14.

10×10 μm images were obtained at a resolution of 512 x 512 points within the range of 0.5-0.8 Hz scan rate and were subjected to first-order flattening. Surface roughness was calculated by using the Root Mean Square (RMS), that is, the standard deviation of the Z values within a given area, defined by where Z_{ave} is the average, Z_i is the current Z value, and N is the number of points within the analyzed area (please see equation 2.4). It was noted that the surface roughness depends on the curvature and size of the AFM tip and on the image processing. The RMS mean values and the standard deviations were obtained by analyzing at least 6 AFM images. The RMS roughness drastically decreased from 15.50 nm to 5.23 nm when the PVPA mol ratio was increased from 0.5 to 4 (Sinirlioglu et al., 2015a). Furthermore, for all the samples in Fig. 3.78, the images exhibit single phase formation and the membranes seem homogeneous at nanometer-scale level. This shows that the heterocyclic PMTet homopolymer uniformly dissipate with PVPA matrix. However, the surface images (in Fig. 3.78 (b,c,d) show several regions which may possibly be a result of salt formation between acid (phosphonic acid groups)-base (azole groups) units (Sinirlioglu et al., 2015a).

Table 3.14 The mean RMS roughness values with the standard deviations.

Sample Name	Roughness (nm)
PVPA	2.4 ± 0.1
PMTetP(VPA) _{0.5}	15.50 ± 0.96
PMTetP(VPA) ₁	7.22 ± 0.37
PMTetP(VPA) ₂	6.63 ± 0.41
PMTetP(VPA) ₄	5.23 ± 0.48

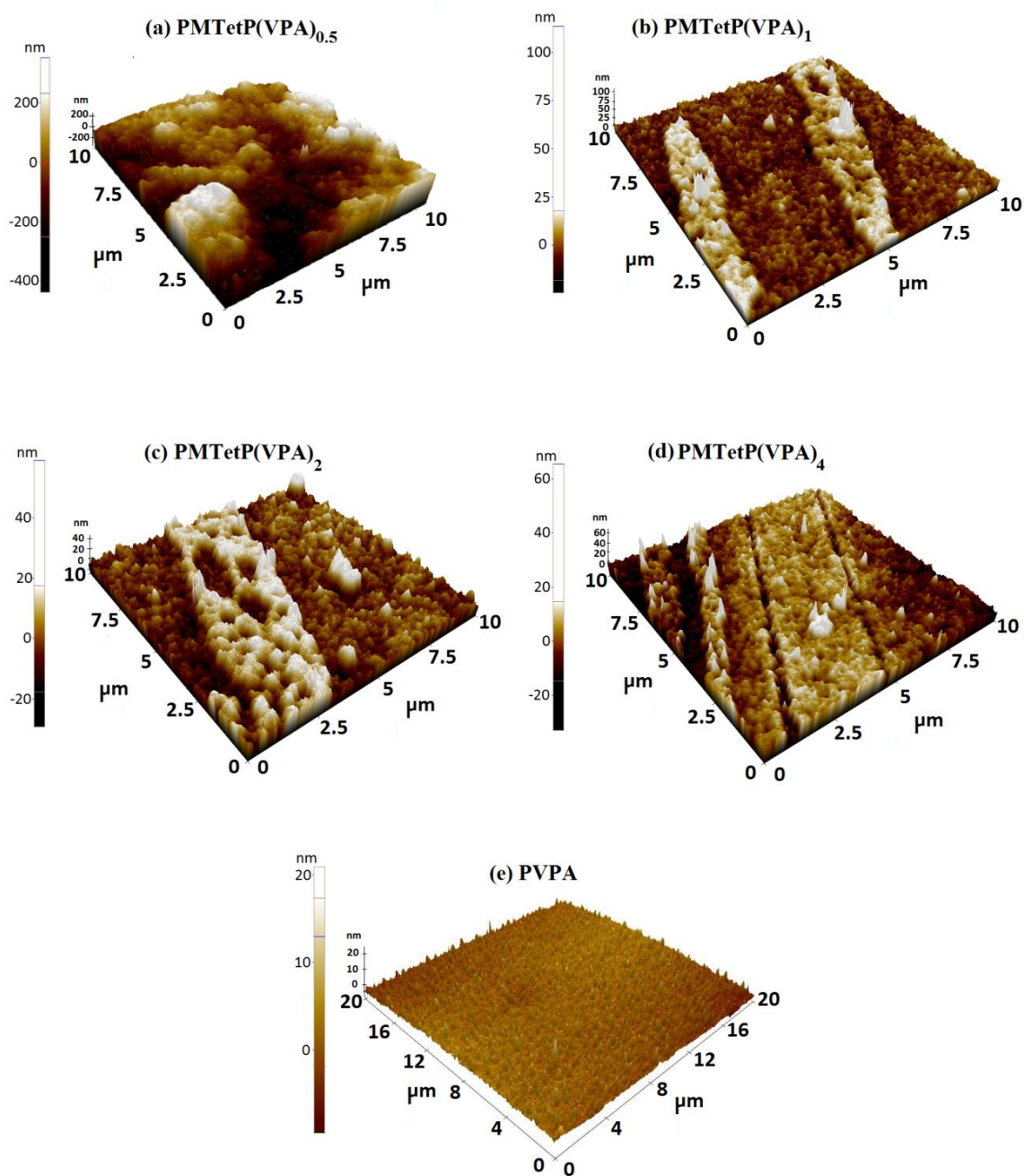


Figure 3.78 AFM pictures (3d) of (a) PMTetP(VPA)_{0.5}, (b) PMTetP(VPA)₁, (c) PMTetP(VPA)₂, (d) PMTetP(VPA)₄, (e) PVPA.

3.5.7 Proton Conductivity Measurements

The AC conductivities (σ_{ac}) of the polymers were measured at several temperatures using impedance spectroscopy at liquid nitrogen atmosphere. The AC conductivity of the composite membranes, PMTetP(VPA)_x, versus frequency plots at several temperatures are presented in Fig. 3.79, Fig. 3.80, Fig. 3.81 and Fig. 3.82. As

expected, proton conductivity increases with the temperature. In the anhydrous conditions, the proton conductivity of PMTetP(VPA)_x (x=0.5, 1, 2 and 4) composite membranes were measured as 2.3×10^{-4} S/cm, 0.002 S/cm, 0.005 S/cm, and 0.06 S/cm at 150 °C, respectively.

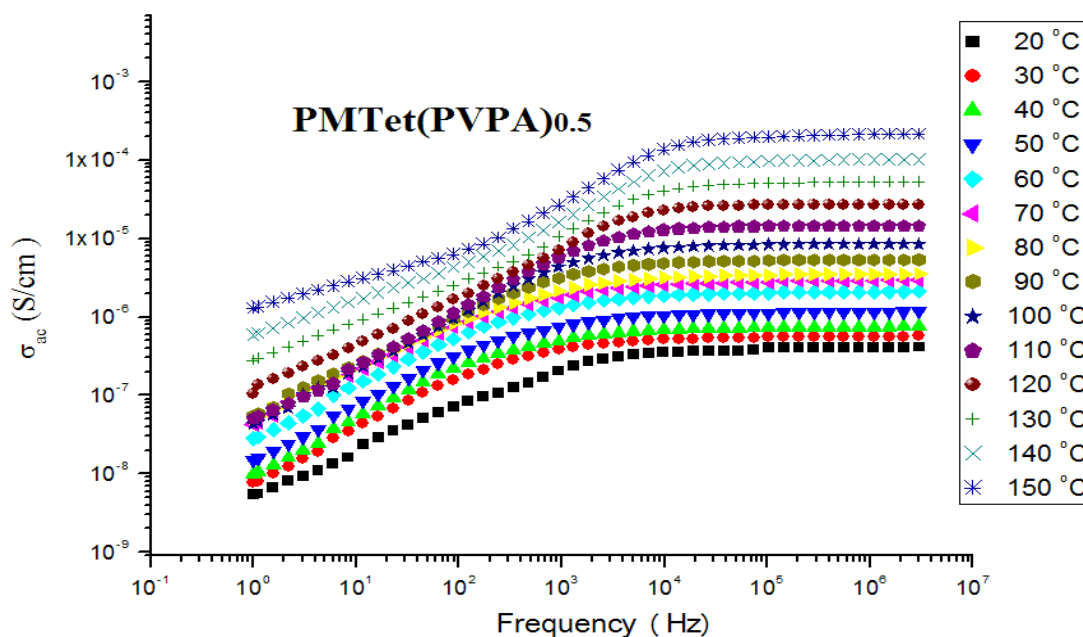


Figure 3.79 AC conductivity versus frequency of PMTetP(VPA)_{0.5} composite membranes at several temperatures.

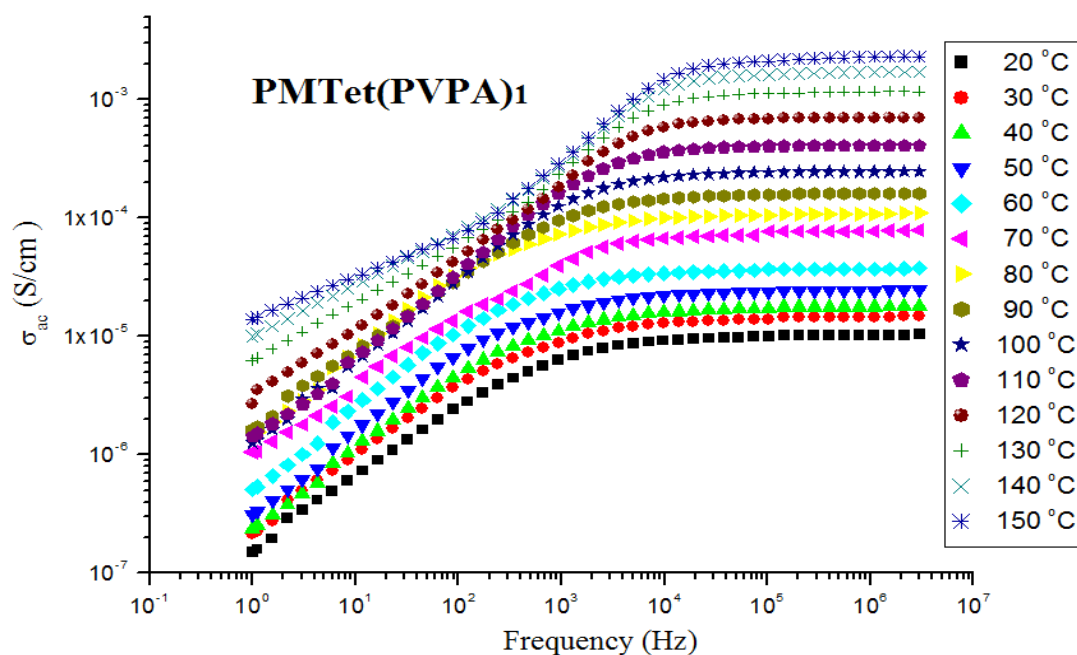


Figure 3.80 AC conductivity versus frequency of PMTetP(VPA)₁ composite membranes at several temperatures.

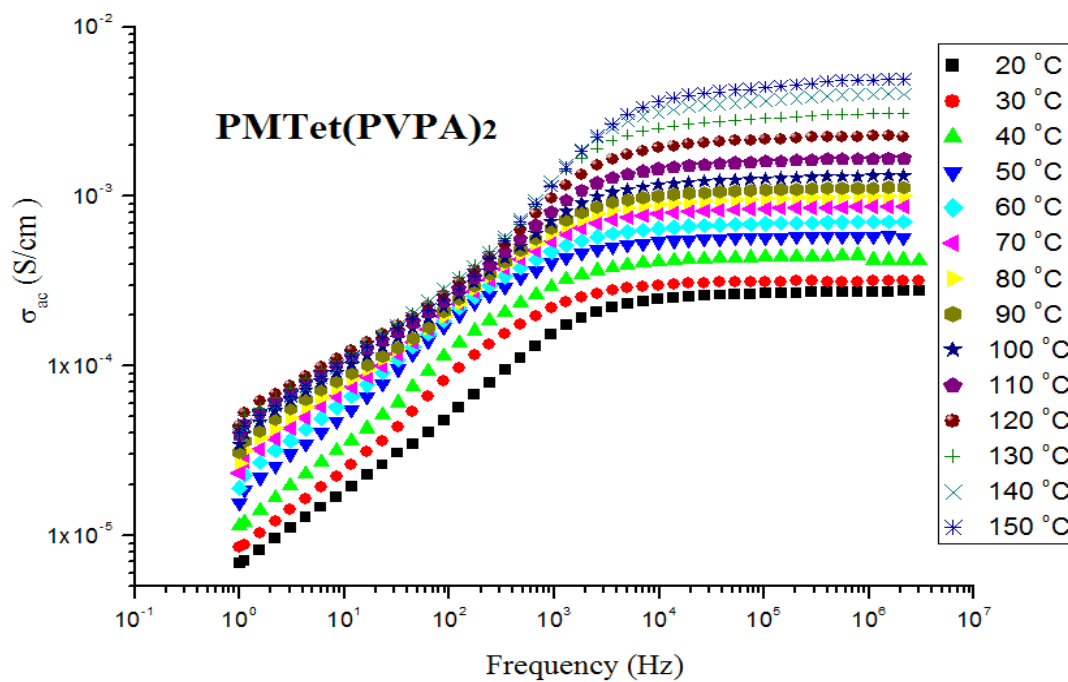


Figure 3.81 AC conductivity versus frequency of PMTetP(VPA)₂ composite membranes at several temperatures.

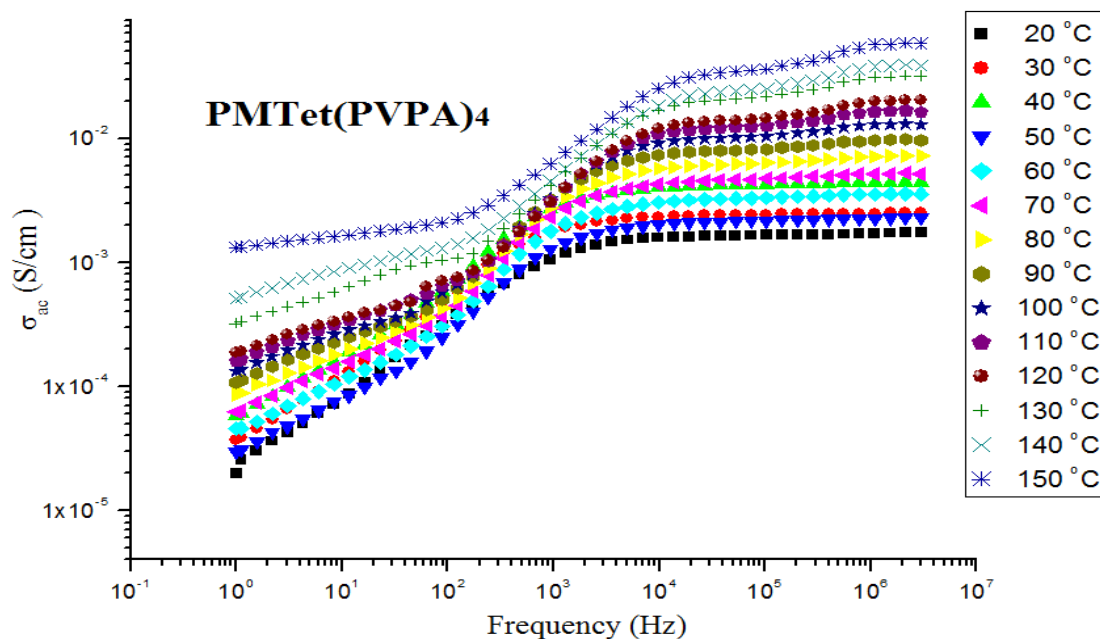


Figure 3.82 AC conductivity versus frequency of PMTetP(VPA)₄ composite membranes at several temperatures.

The DC conductivity (σ_{dc}) of the samples was determined from the plateaus of $\log \sigma_{ac}$ versus $\log F$ by linear fitting of the data (e.g. 10^4 - 3×10^6 Hz). In Fig. 3.83, the DC conductivities of all composite membranes were compared. It can be seen from the conductivity isotherm that the DC conductivity is proportional to both the temperature and PVPA content. Generally, the DC curve can be interpreted with Arrhenius or Vogel-Tamman-Fulcher (VTF) behavior depending on the type of the curve and T_g of the material. Here the curves are close to linearity and although the materials have T_g around 40-70 °C, there is no curvative above these points. Therefore, we can say that the blend system shows Arrhenius behavior in the measurement range (Sinirlioglu et al., 2015a).

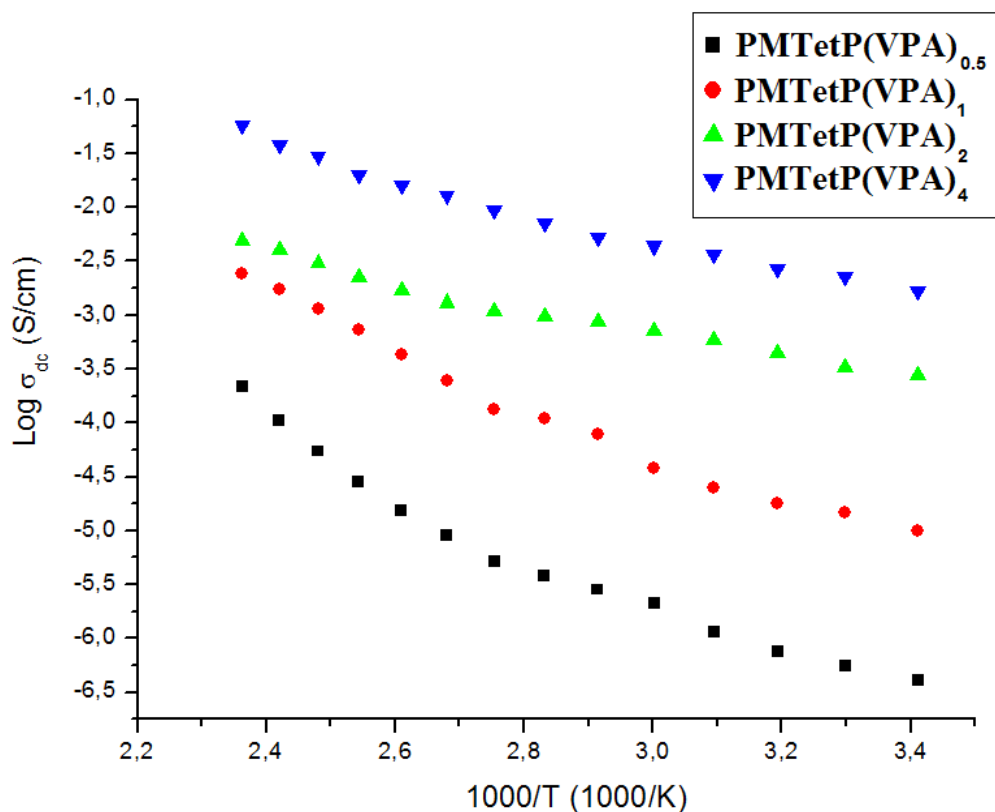


Figure 3.83 Variation of the DC proton conductivity of PMTetP(VPA)_x (x=0.5, 1.0, 2.0, and 4.0) composite membranes as a function of reciprocal temperature.

In the anhydrous polymer electrolyte systems the proton transport are generally provided by acidic protons and heterocyclic molecules. Acid protons can be taken by heterocyclic molecules and this protonated molecule can further give the proton to other acid or azole molecules. This mechanism is called as Grotthus mechanism and there are several parameters affecting the proton transport in a polymer matrix (Sinirlioglu et al., 2015a). PVPA is an acidic polymer and have higher phosphonic acid content compared to other phosphonated polymers. It has high proton conductivity (10^{-3} Scm^{-1}) and good film forming property which are important characteristics of polymer electrolyte membrane (Celik et al., 2012b; Kaltbeitzel et al. 2007). Although pure PVPA has several advantages, its water solubility makes it an improper material for PEMFC applications. Therefore, this polymer is needed to be copolymerized or blended with other structures. In this blending method, the second material should be chosen properly

so that proton transport can be provided in the blend also. In addition the mechanical property of the second polymer is also important. Previously, PVPA was blended with Nafion and poly(vinyl triazole) (PVTri) and the maximum proton conductivity was reported as $\sim 10^{-5}$ S/cm for Nafion-P(VPA)₃ and 2.2×10^{-6} S/cm for PVTriP(VPA)₂ in anhydrous conditions (Sen et al., 2013; Aslan and Bozkurt, 2009).

5-Aminotetrazole is a heterocyclic molecule and previously used as proton source by immobilization into several polymer backbones (Ozden et al., 2010a; Celik and Bozkurt, 2008a). In these studies, the tetrazole units provided high proton conductivity after doping with triflic and phosphoric acids. However these azole functional polymers have low film forming property and this makes them unsuitable for PEMFC applications. In this work, 5-aminotetrazole was immobilized into methacryloyl chloride monomer, then polymerized, and blended with PVPA. As expected we obtained free standing films which are less hygroscopic and stable compared to pure PVPA. In the current system, the major part of proton transport is provided over both phosphonic acid and tetrazole units. Herein, PMTet is considered to make hydrogen bonding network with phosphonic acid units of PVPA. This continuous pathway may convey proton transport over the POH groups and tetrazole groups. The proton could travel along the hydrogen bonds from one functional group to another (Sinirlioglu et al., 2015a). Possible mechanism of proton transport in PMTetP(VPA)_x membranes, in which phosphonic acid units is coordinated with tetrazole groups is tentatively illustrated in Fig. 3.84.

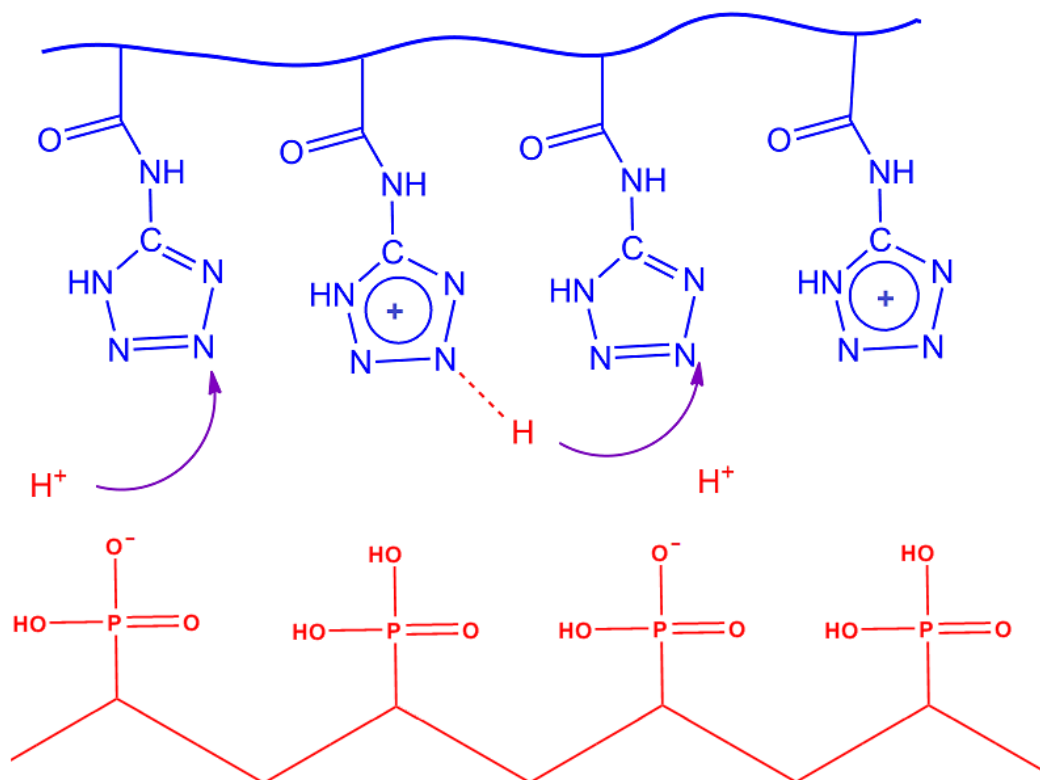


Figure 3.84 Possible mechanism of proton transport in PMTetP(VPA)_x membranes.

3.5.8 Cyclic Voltammetry

Cyclic voltammogram of PMTetP(VPA)₂ composite membrane was illustrated in Fig. 3.85 due to its good film forming property. The measurement was performed in a typical three electrode cell containing 0.1 mol dm⁻³ CH₃CN solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) using a platinum work electrode, a platinum auxiliary electrode, and an Ag/Ag⁺ reference electrode. It was clearly observed that the CV of PMTetP(VPA)₂ composite membrane comprised no peak within both anodic sweep (-0.5 to 1.5 V potential range) and cathodic sweep. Thus, the electrochemical stability window was at least 3V and these results showed that this membrane may be used under fuel cell conditions (Sinirlioglu et al., 2015a).

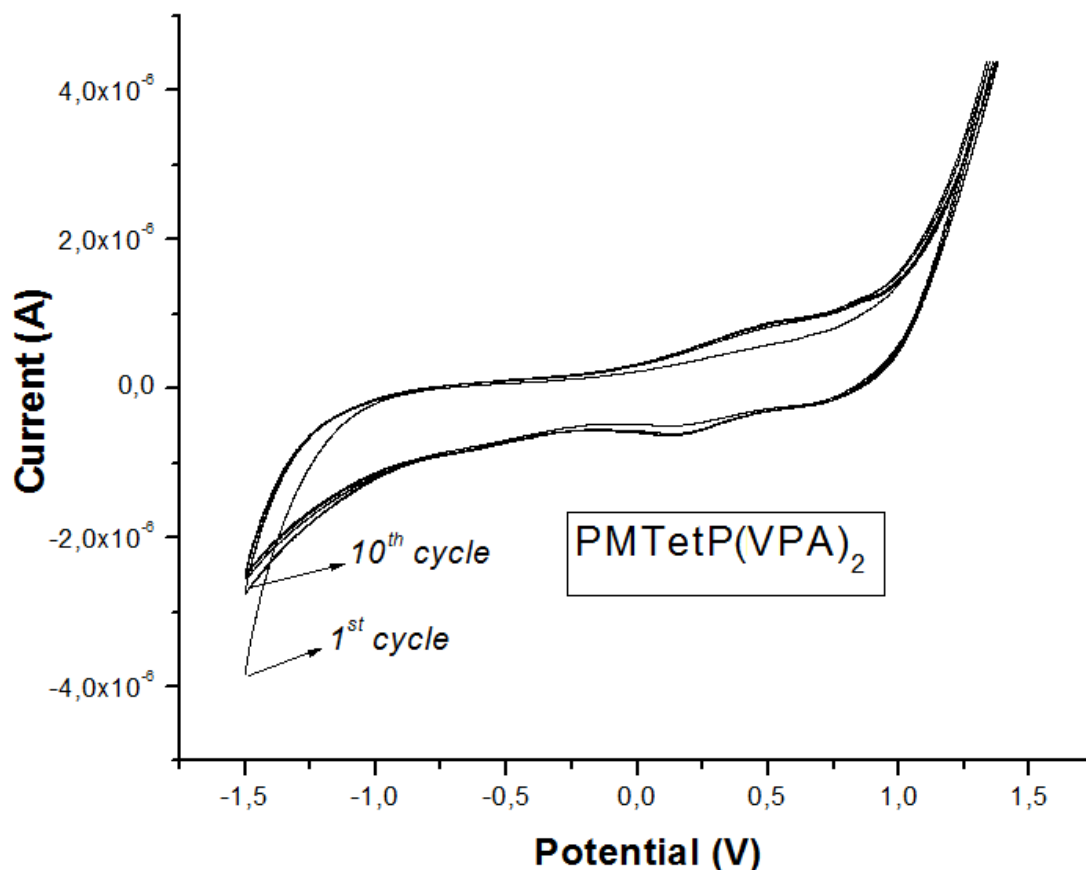


Figure 3.85 Cyclic voltammograms of PMTetP(VPA)₂ composite membrane in 0.1 M TBATFB/acetonitrile. Curves were obtained with a scan rate of 50 mV/s.

3.6 PREPARATION OF THIN FILMS FROM NEW AZOLIC COPOLYMERS

The main aim of this study is to obtain the PEMs with high proton conductivity and low or close methanol permeability for PEMFC applications when compared with Nafion. In an effort to achieve this objective, we have decided to examine the potential of novel copolymer electrolyte membranes with chemically different repeating units in the preparation of PEMs. Therefore, it is remarkable that a copolymer consisting of acidic and methacrylamide based repeating units with AMPS and tetrazole moieties might be prepared. For this purpose, 5-(methacrylamido)tetrazole monomer was prepared by the reaction of methacryloyl chloride with 5-aminotetrazole. Cheap and easily available 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) monomer was chosen due to its good film forming property, making it suitable for PEMFC applications. By introducing AMPS, the proton conductivity of membranes would be improved greatly due to the superior ability of sulfonic acid groups of AMPS in

supporting proton conduction (Sinirlioglu et al., 2014e). In this contribution, 5-(methacrylamido)tetrazole monomer, prepared by the reaction of methacryloyl chloride with 5-aminotetrazole, was copolymerized with 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) via conventional free radical mechanism with various molar feed ratios to achieve poly(MTet-*co*-AMPS) copolymers (Fig. 3.86 and Table 3.15). Homogeneous, transparent and thin film of copolymers were obtained (Fig. 3.87).

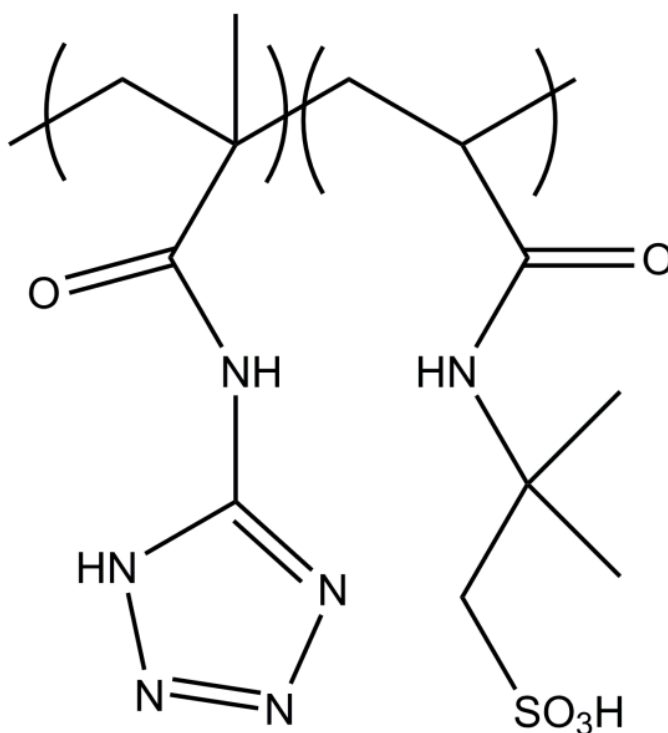


Figure 3.86 Molecular structure of P(MTet-*co*-AMPS) copolymer.

Table 3.15 Conditions and results in the synthesis of poly(MTet-*co*-AMPS) copolymers.

Sample	MTet	AMPS	Conversion
P(MTet- <i>co</i> -AMPS), S1	1.50 g, 9.80 mmol	1.016 g, 4.90 mmol	2.02 g, 80 %
P(MTet- <i>co</i> -AMPS), S2	1.50 g, 9.80 mmol	2.031 g, 9.80 mmol	3.38 g, 96 %
P(MTet- <i>co</i> -AMPS), S3	1.50 g, 9.80 mmol	4.062 g, 19.6 mmol	4.56 g, 82 %

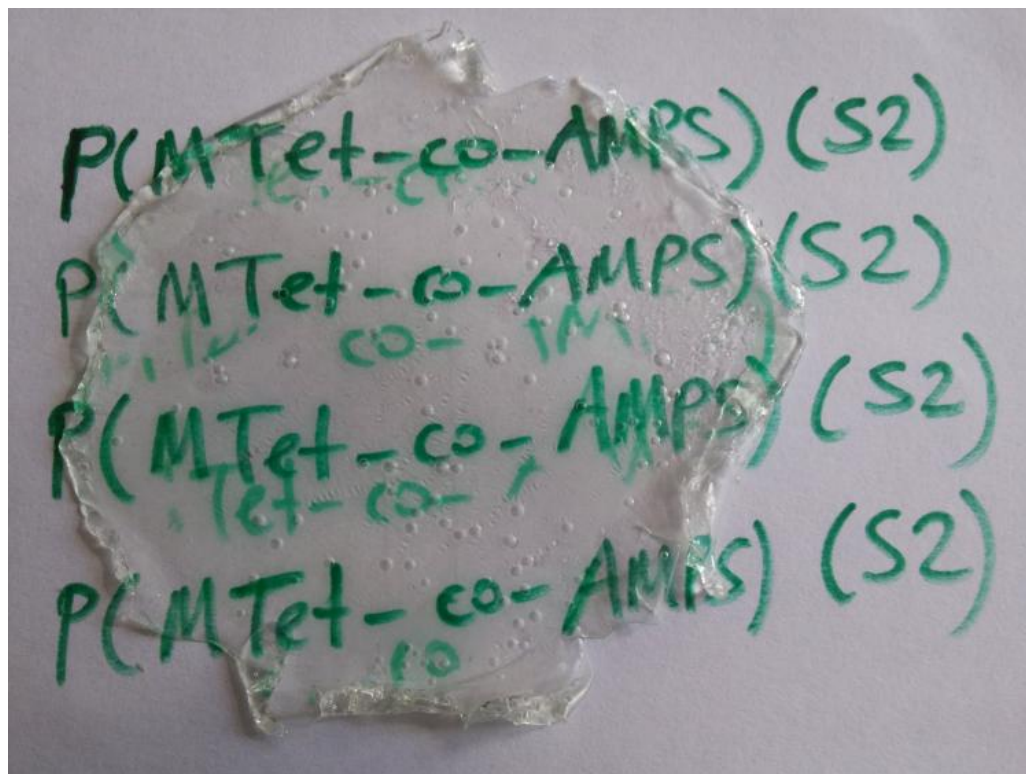


Figure 3.87 Homogeneous, transparent and thin film of poly(MTet-co-AMPS) (S2) copolymer.

Table 3.16 Composition of poly(MTet-co-AMPS) copolymers

Sample	Feed mol ratio MTet:AMPS	Elemental Analysis			Copolymer mol ratio (MTet:AMPS)
		C (%)	H (%)	N (%)	
S1	1: 0.5	39.76	5.26	34.36	1 : 0.44
S2	1: 1	40.01	5.56	23.33	1 : 1.00
S3	1: 2	40.21	5.83	17.17	1 : 1.65

The actual compositions of the copolymers were calculated from the elemental analysis data. The composition of the copolymer is only slightly dependent on the monomer feed ratio (Erdemi and Bozkurt, 2004). When AMPS in the feed mol ratio is varied from 0.5 (S1) to 2.0 (S3), the AMPS mol ratio in the copolymer is changed from 0.44 (S1) to 1.65 (S3) (Table 3.16). The elemental analysis results demonstrated that

composition of the copolymers are consistent with the monomer feed ratios (Sinirlioglu et al., 2014e).

In conventional free radical polymerization, which obeys the terminal model, the composition drift can be explained by the equation (3.1), where r_1 and r_2 are the reactivity ratios, f_1 and f_2 are the molar fractions of monomers 1 and 2 in the monomer feed, and F_1 is the molar fraction of units from monomer 1 in the copolymer.

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \quad (3.1)$$

From the equation (3.1), given the feed ratio of monomers (F_1) and copolymer composition (f_1), the monomer reactivity ratios r_1 (MTet) and r_2 (AMPS) were calculated as $r_1=1.10$ and $r_2=0.85$. The values being close to unity, the monomers form nearly random copolymers. However, deviation from ideal copolymerization is observed and MTet tends to react slightly more with the propagating active site (Sinirlioglu et al., 2014e; Erdemi and Bozkurt, 2004).

The copolymer membranes, P(MTet-co-AMPS) (S1-S3), is found to show little or no solubility in most solvents without exception of DMF and DMSO upon warming. Herein, 5-(methacrylamido)tetrazole (MTet) monomer is a colorless solid that dissolves in methanol, DMF, or DMSO upon warming. PMTet homopolymer was hardly soluble in most solvents, but it especially dissolves in DMF and DMSO upon warming. PAMPS is soluble in water which can only be used in the of form gels. P(MTet-co-AMPS) copolymers are soluble in DMF, so they were dissolved in DMF, then were mixed to get poly(MTet-co-AMPS) copolymer electrolyte membranes for proton conductivity measurements (Fig. 3.87). Furthermore, a high degree of hydrogen bonding between the amide, tetrazole and sulfonic acid groups of AMPS was thought to be responsible for the low or no solubility of the copolymer membranes (Sinirlioglu et al., 2014e).

3.6.1 FTIR Studies

The FTIR spectra of PAMPS, PMTet, P(MTet-co-AMPS) (S1-S3) copolymers are represented in Fig. 3.88. In PAMPS spectrum, a broad band at 3448 cm^{-1} is due to the collapse of -NH and -OH (-SO₃H) stretching frequency. The peaks present at 3039 cm^{-1} and 2924 cm^{-1} represent the C-H stretching frequency of -CH₃ and -CH₂, respectively.

Two bands around 1725 and 1624 cm^{-1} are due to C=O stretching (amide I band) and N-H bending (amide II band), respectively. Two peaks at 1406 and 1317 cm^{-1} are due to asymmetric and symmetrical stretching of (S=O) group. The strong stretching absorption in the region of 1133 to 940 cm^{-1} represent S-O-C group. PMTet homopolymer exhibited several medium or strong peaks between 1689 cm^{-1} and 1475 cm^{-1} due to amide bond and tetrazole ring vibrations, respectively. PMTet also showed N-N stretching at 1245 cm^{-1} . The peaks at 735-1160 cm^{-1} correspond to C-H stretching bands and the formation of a slightly broad peak at around 3200 cm^{-1} shows the protonation of tetrazole rings (Sinirlioglu et al., 2014e).

Copolymers give a strong and broad absorption band at 1028 cm^{-1} corresponding to asymmetric O=S=O stretching vibration and a broad band at 1183 cm^{-1} due to $-\text{SO}_3\text{H}$ units (Celik and Bozkurt, 2010). Furthermore, amide group shows a characteristic peak at about 1652 cm^{-1} (Gunday et al., 2006). The N-H stretching of the same group is observed near 3300 cm^{-1} . C=N and C-N stretching peaks are observed at around 1462 and 1550 cm^{-1} due to tetrazole ring. The peaks present at 3000-2900 cm^{-1} represent the C-H stretching frequency of $-\text{CH}_3$ and $-\text{CH}_2$, respectively. Especially, a broad band at 3300 cm^{-1} is due to the collapse of $-\text{NH}$ and $-\text{OH}$ ($-\text{SO}_3\text{H}$) stretching frequency. The broad absorption in the region of 3400-2500 cm^{-1} shows the formation of hydrogen bonding network between AMPS and tetrazole units which is necessary for proton conduction (Sinirlioglu et al., 2014e).

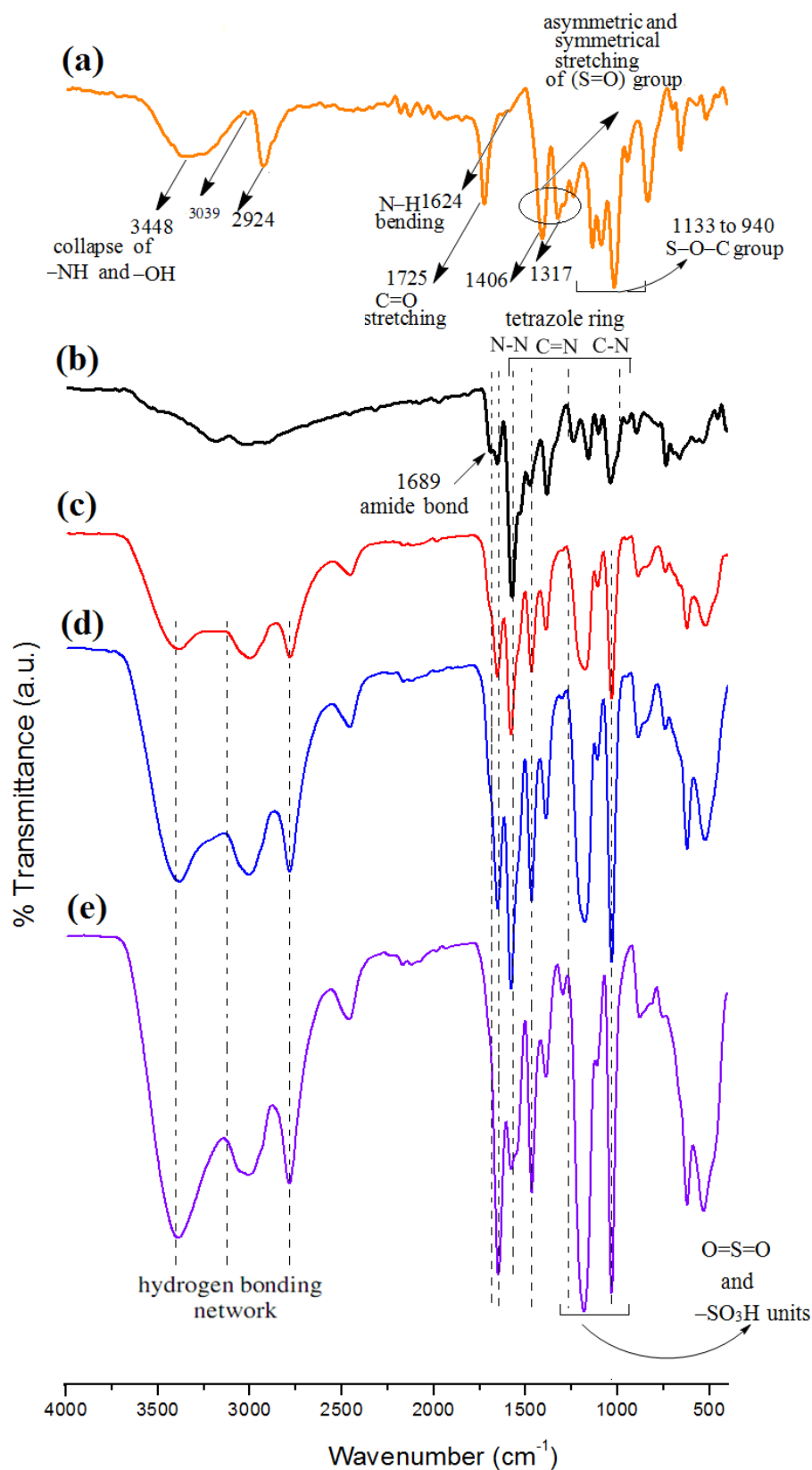


Fig. 3.88 FTIR spectra of (a) PAMPS, (b) PMTet, (c) P(MTet-co-AMPS) (S1), (d) P(MTet-co-AMPS) (S2), (e) P(MTet-co-AMPS) (S3) copolymer membranes.

3.6.2 NMR Studies

^1H -NMR spectrum of PMTet homopolymer was given in the previous section (see Fig. 3.22). The appearance of the peaks belonging to -NH proton of the tetrazole ring and amide bond proton at 15.90 and 11.65 ppm are a typical indication for the successful polymerization of tetrazole functional monomer. Also, the signals at 2.34 ppm and 2.09 ppm are assigned to the methylene proton (2H, -CH₂) which indicates polymer backbone. The signals between 2.5 and 4 ppm belongs to solvent (DMSO-d₆) and water as 2.51 and 3.40 ppm, respectively. In addition, the signals at 2.75, 2.89 and 7.99 ppm belong to the dimethylformamide (DMF) (Sinirlioglu et al., 2014e).

Fig. 3.89 shows ^1H -NMR spectra of PAMPS homopolymer. The resonance peaks are at 7.45 ppm (-NH-), 4.4 ppm (-CH₂-SO₃H), 3.06 ppm (-SO₃H), 2.70 ppm (-CH-CO), 2.0 ppm (-CH₂-CH-), and 1.42 ppm (-CH₃). In addition, the signal at 4.77 ppm belongs to D₂O (Sinirlioglu et al., 2014e).

^1H -NMR spectra of S1, S2 and S3 copolymers are illustrated in Fig. 3.90. The single broad peak at around 15.50 ppm is assigned to the N-H proton of tetrazole ring. The appearance of the peaks at around 11.2 ppm can be attributed to NH proton which indicates amide bond proton in the MTet units. And also, the signals between 8.63 ppm and 7.26 ppm belong to the -NH protons from AMPS and MTet repeating units. In addition, the resonance peaks are 5.07 ppm (-CH₂-SO₃H), 2.86 ppm (-CH-CO), 2.68 ppm (-CH-CO), 2.34 (-CH₂-CH, backbone) and 1.35 ppm (-CH₃) (Sinirlioglu et al., 2014e; Sinirlioglu et al., 2013; Azmeera et al., 2012).

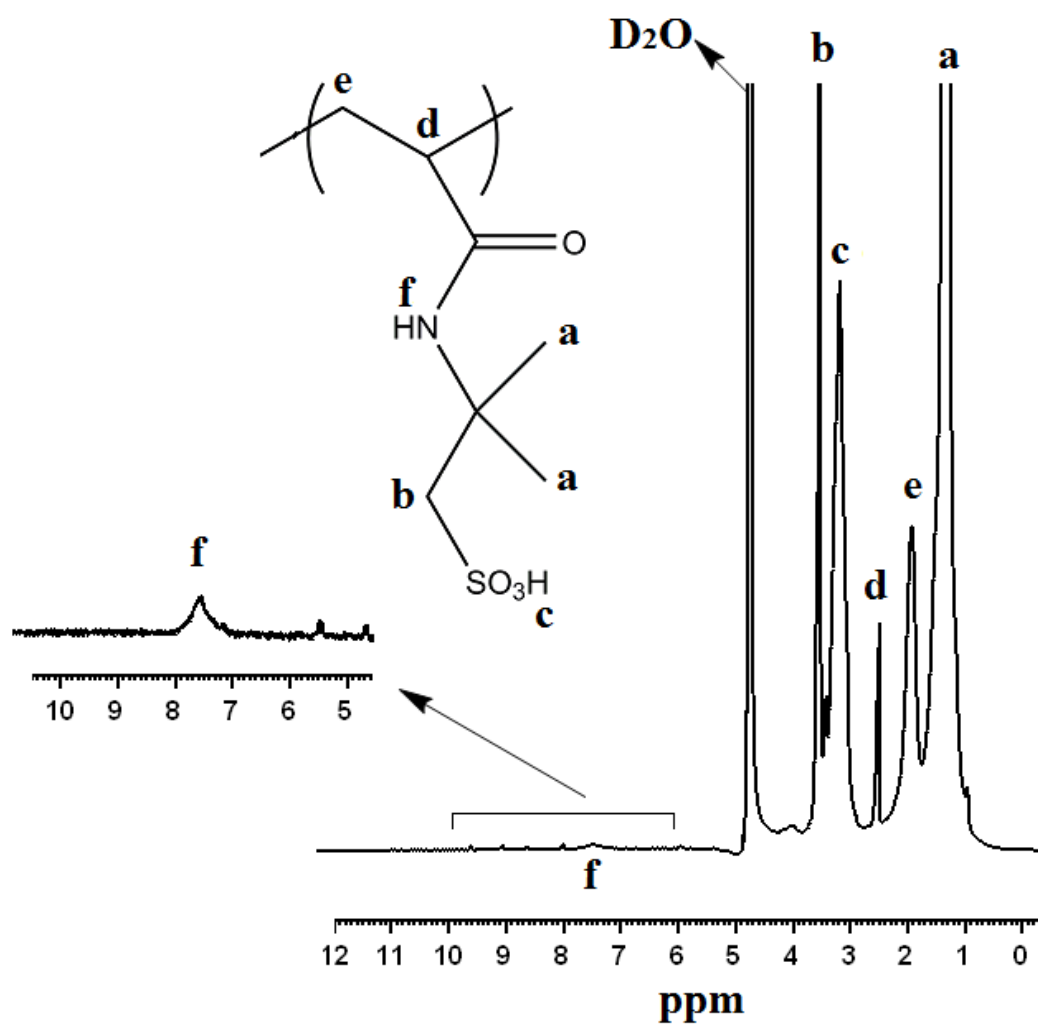


Figure 3.89 ^1H -NMR spectrum of PAMPS recorded in D_2O .

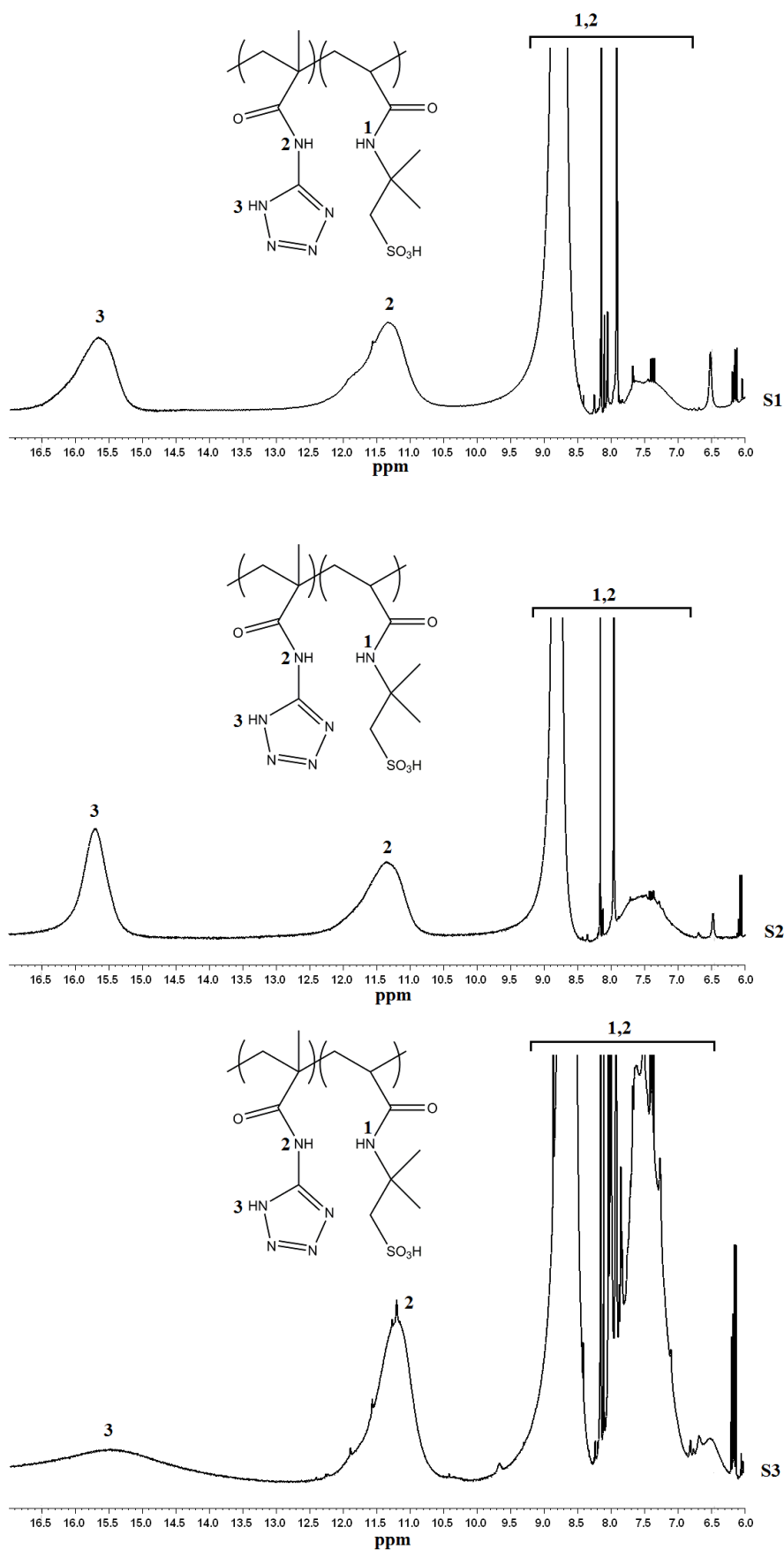


Figure 3.90 ^1H -NMR spectra (in the range of 6-17 ppm) of S1, S2 and S3 copolymers recorded in DMSO-d_6 .

3.6.3 Thermal Properties

The DSC measurements were carried out under inert atmosphere at a scan rate of 10 °C/min and the second heating curves were evaluated. The T_g and T_m values of poly(MTet-co-AMPS) (S1-S3) copolymers, PMTet, and PAMPS homopolymers are summarized in Table 3.17. The T_g of PMTet and PAMPS homopolymers were measured as 93 °C and 108 °C, respectively. The copolymer electrolytes S1, S2, and S3 have definite glass transition temperatures at 96 °C, 101 °C, and 106 °C, respectively (Fig. 3.91). The results demonstrated that as the quantity of AMPS increased, T_g of the samples shifted to higher temperatures when compared with PMTet homopolymer (Sinirlioglu et al., 2014e).

Table 3.17 T_g, T_m, and maximum proton conductivity values of PMTet, PAMPS, S1, S2 and S3 copolymers

Sample	T _g (°C)	T _m (°C)	Max. Proton Conductivity (S/cm) at 150 °C	log σ _o	E _{dc} (eV)
PMTet	93 °C	216 °C	2x10 ⁻⁶	-0.62	0.57
PAMPS	108 °C	198 °C	1.11x10 ⁻⁴	2.99	0.56
S1	96 °C	175 °C	7.09x10 ⁻⁵	-0.67	0.29
S2	101 °C	158 °C	8.88x10 ⁻⁴	0.78	0.32
S3	106 °C	148 °C	0.009	4.76	0.57

Fig. 3.92 shows TGA results of S1, S2 and S3 copolymers, PMTet and PAMPS homopolymers. PMTet exhibited a thermal stability up to 215 °C. 30 % of PMTet decomposed between 215 and 350 °C because of degradation of aminotetrazole units and after 400 °C, a second weight loss occurred because of degradation of the polymer backbone. The PAMPS homopolymer showed a thermal stability up to 220 °C, then it decomposes. As seen in TGA of the electrolytes (Fig. 3.92e), there is a slight weight change between 100 and 200 °C which may be due to evaporation of free water which could not be removed during drying process. The first weight loss was attributed to the splitting-off of the sulfonic acid groups. The second degradation step corresponded to

the decomposition of the polymer backbone (Fig. 3.92e). As seen in the TGA curve of copolymers, there is a minor weight loss until 250 °C which can be attributed to absorbed humidity. Major decomposition occurs between 250 and 300 °C due to the loss of sulfonic acid and tetrazole units and then decomposition of polymer backbones starts (Sinirlioglu et al., 2014e).

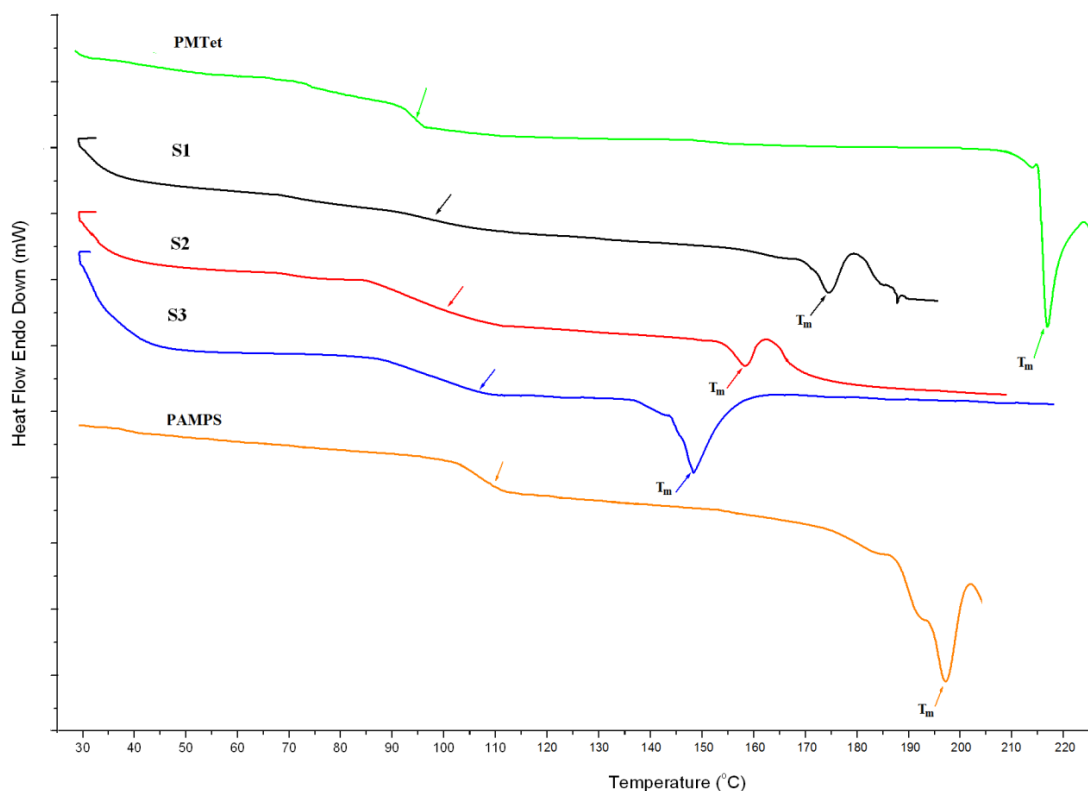


Figure 3.91 DSC thermograms of poly(MTet-co-AMPS) (S1, S2 and S3) copolymers, PMTet and PAMPS homopolymers recorded under N₂ atmosphere at a heating rate of 10 °C/min.

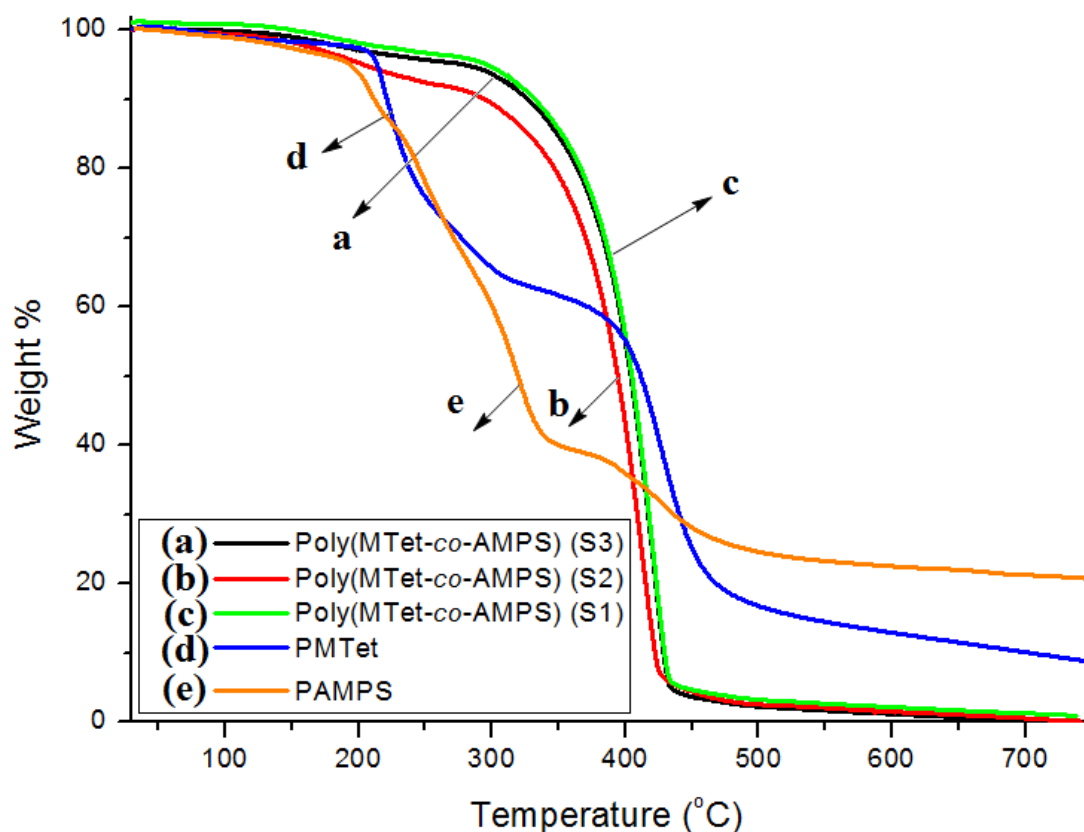


Figure 3.92 TGA curves of (a) S3, (b) S2, (c) S1 copolymers, (d) PMTet, and (e) PAMPS homopolymers at a heating rate of 10 °C/min in inert atmosphere.

3.6.4 Water Uptake

Water uptake measurement was determined by the weight difference between the fully hydrated membranes and dried membranes. The dried membranes (W_{dry}) were weighed and then wetted until the weight remained constant. The wet or saturated weights of the membranes (W_{wet}) were measured quickly after removing or wiping out any remaining surface water with a paper. The water uptake was calculated using the (eq. 2.1). The water uptake of the membranes is a major parameter influencing proton conductivity, mechanical property and stability. The water uptake measurements were made according to the literature. Water uptakes of the copolymer electrolyte membranes (S1-S3) are shown in Fig. 3.93. It can be understood based on the fact that the water uptake of S1, S2, and S3 membranes elevates with the increasing of AMPS content. This is due to the fact that the sulfonic acid groups are hydrophilic which have high amount of AMPS can absorb more water. This result is assigned to the forming of

hydrogen bonding network between AMPS and MTet units where the material becomes more rigid when the sample are with (1:1) composition (Sinirlioglu et al., 2014e).

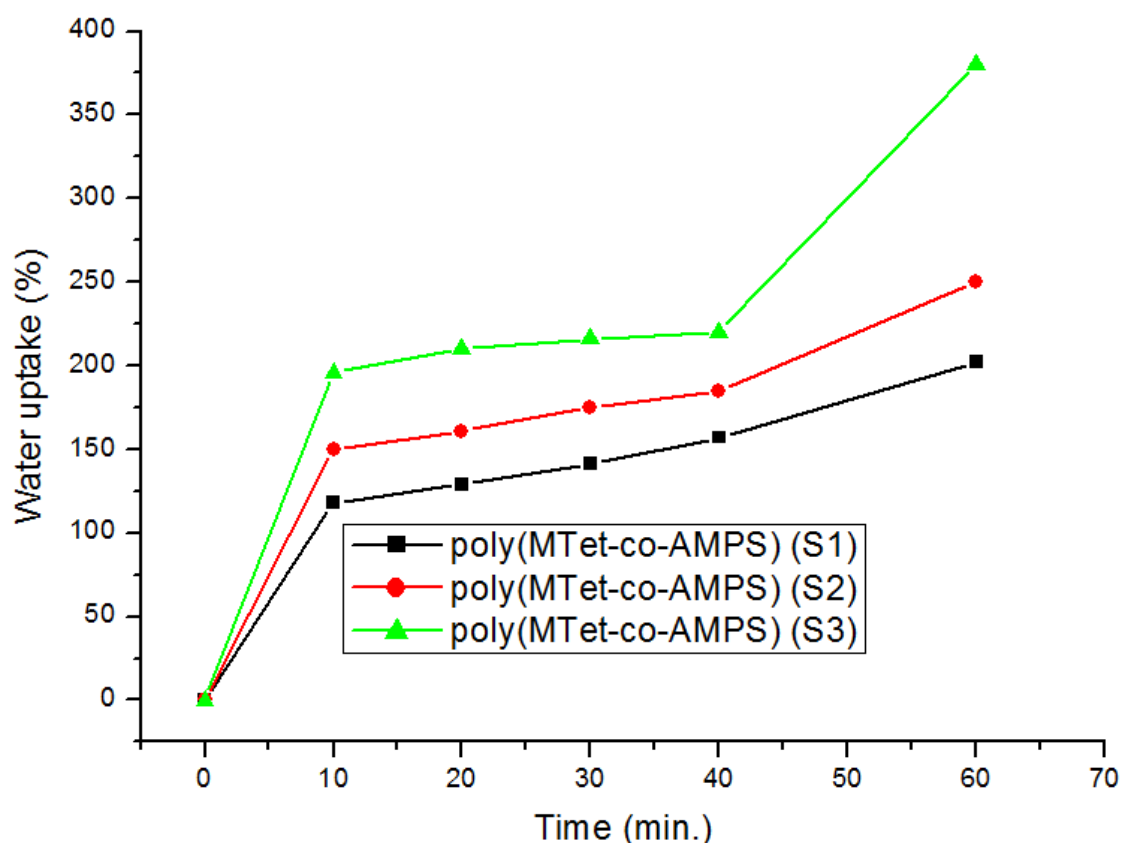


Figure 3.93 Water uptakes of poly(MTet-co-AMPS) (S1, S2 and S3) copolymer electrolyte membranes at the time of 10-60 min in deionized water at 25 °C.

3.6.5 Methanol Permeability

Methanol permeability is a possible problem in the application of the membranes in direct methanol fuel cells. At high methanol concentrations its permeability from anode side to the cathode side results polarization losses. In this study, methanol permeability of the copolymer electrolyte membranes was measured by simple homemade diaphragm diffusion cell similar to the previous works (Gasa et al., 2006). The cell is filled with 2 mL methanol and the mass flow is recorded as a function of time (Fig. 3.94). Molar methanol flux (J) through of S1, S2 and S3 copolymer electrolyte membranes was calculated using eq. (2.2). Methanol permeability of

copolymer electrolyte membranes may be calculated using molar flux (J) shown in eq. (2.3). The PMTet homopolymer is a colorless solid, not a membrane. In addition, PAMPS homopolymer, a water soluble polymer (WSP), was obtained as transparent soft gels, so we cannot measure the methanol permeability of PAMPS using our system. When the mol content of AMPS increased from 0.50 to 2.0, resulting copolymers (S1-S3) formed transparent and soft free-standing thin films. As seen in the equations, the permeability is directly proportional to the molar flux. The molar flux of the S1, S2 and S3 copolymer electrolyte membranes are shown in Fig. 3.94. The values are $1.60 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, $2.71 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ and $3.32 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ for S1, S2, and S3, respectively. Previously, the methanol permeability of Nafion 112 in the same conditions was reported as $1.89 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ (Sen et al., 2008). The methanol permeability of S1 ($1.60 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$) is lower than Nafion 112. When the mol content of AMPS increased from 1.0 to 2.0, the methanol permeability of S2 and S3 membranes gradually increased from $2.71 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ to $3.32 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ when compared with the Nafion 112. This tendency was the same as the results of water uptake. The increase in AMPS content leads to incorporation of more hydrophilic sulfonic acid groups as well as formation of more and larger water absorption channels (Sinirlioglu et al., 2014e).

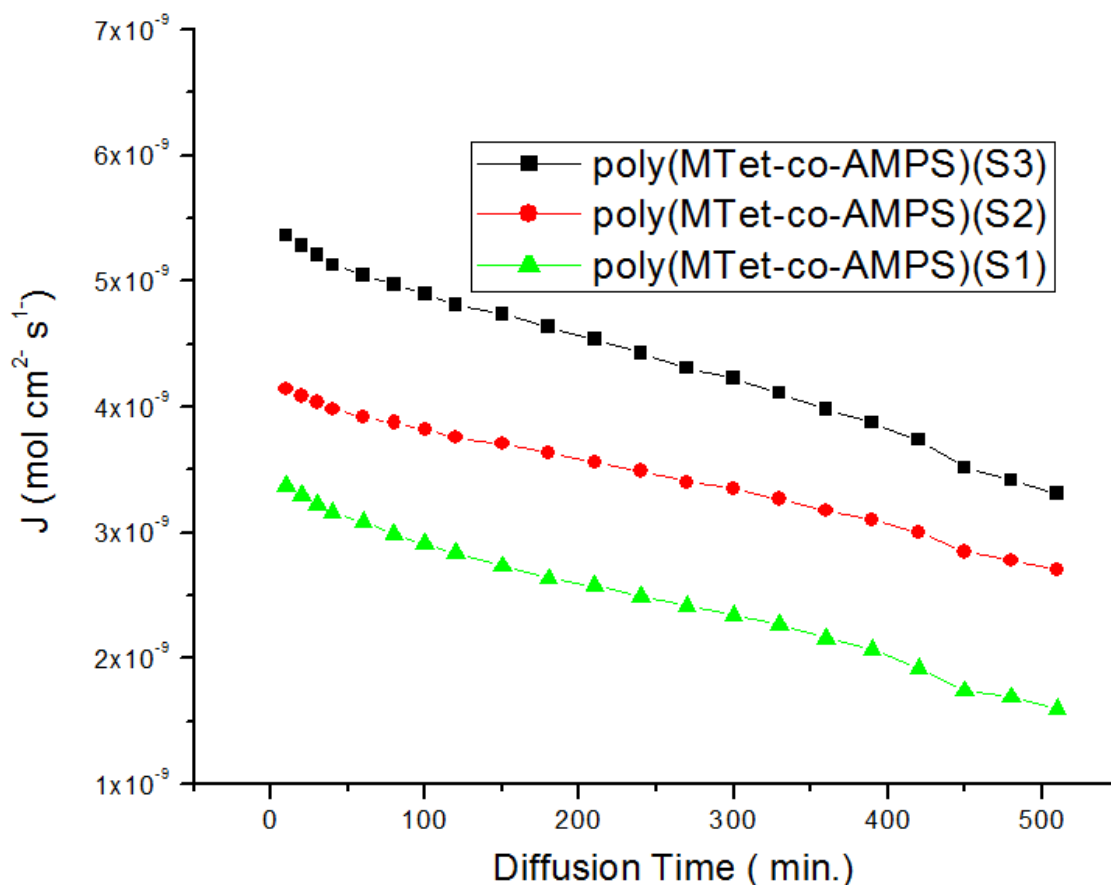


Figure 3.94 Methanol permeability of S1, S2 and S3 copolymer electrolyte membranes.

3.6.6 XRD Results

The XRD patterns of PMTet, PAMPS, and P(MTet-co-AMPS) (S1, S2, and S3) copolymer electrolyte membranes are illustrated in Fig. 3.95. PMTet is a crystalline polymer and has an endotherm around 216 °C (Table 3.17). There are two strong peaks in the diffractograms of pure PMTet at 2θ values of 18° and 24° , this indicated the high degree of crystallinity of PMTet (Sinirlioglu et al., 2014e). In addition, PMTet shows high crystallinity in contrast to PAMPS which exhibits small crystallinity as seen in the Fig. 3.95 (Azmeera et al., 2012). For P(MTet-co-AMPS) (S1, S2, and S3), the characteristic peak at around 18° almost disappeared immediately. This result revealed that the original crystalline structure of pure PMTet homopolymer was seriously destroyed. The crystallinity of the copolymer electrolyte membranes decreases when the AMPS mol content was increased from 0.50 to 2.0 (Sinirlioglu et al., 2014e).

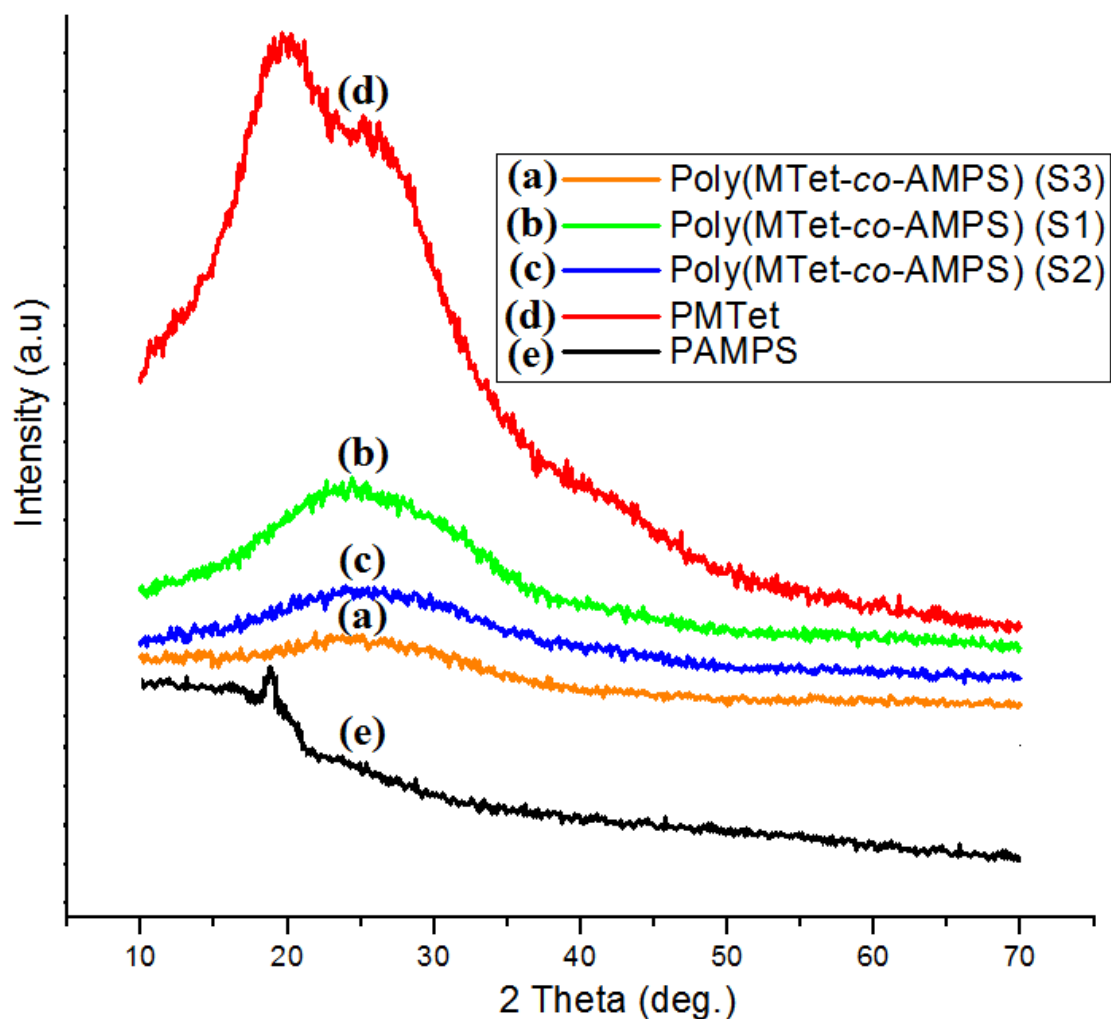


Figure 3.95 XRD patterns of (a) poly(MTet-co-AMPS) (S3), (b) poly(MTet-co-AMPS) (S1), (c) poly(MTet-co-AMPS) (S2), (d) PMTet, and (e) PAMPS.

3.6.7 Morphology

Surface morphology of the copolymer electrolyte membrane P(MTet-co-AMPS) (S2) was investigated by scanning electron microscopy (SEM) and depicted in Fig. 3.96. The images showed single phase formation due to strong interaction between sulfonic acid groups of AMPS and the tetrazole units of PMTet. This showed that the membranes appear to be homogeneous (Sinirlioglu et al., 2014e).

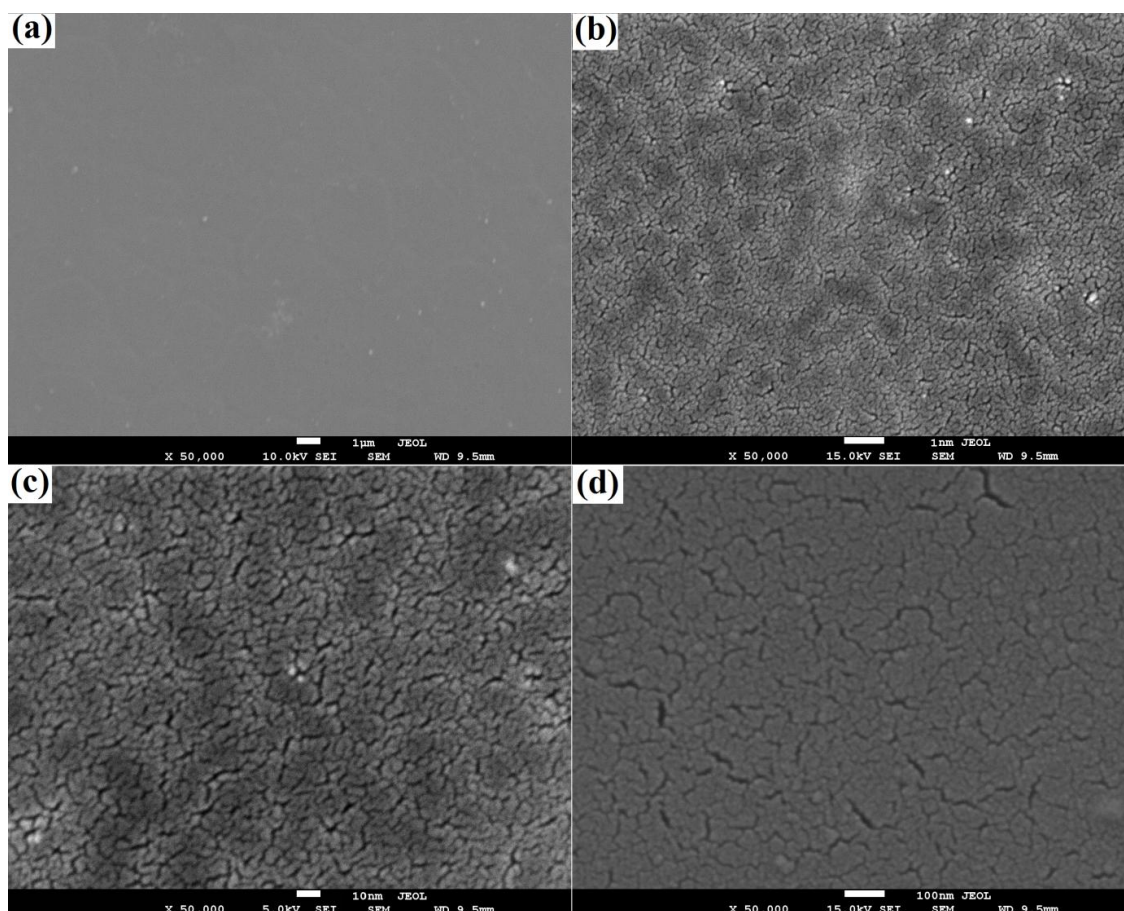


Figure 3.96 SEM images of the surface of poly(MTet-*co*-AMPS) (S2) copolymer electrolyte membrane at different micrometer- and nanometer-scale level by 50,000X magnification, (a) 1 μm , (b) 1 nm, (c) 10 nm and (d) 100 nm.

3.6.8 Proton Conductivity Measurements

The AC conductivities, $\sigma_{ac}(\omega)$, of the polymers were measured at several temperatures using impedance spectroscopy. The proton conductivities of anhydrous membranes were measured from 20 °C to 150 °C. The AC conductivity of all samples versus frequency plots at several temperatures are presented in Fig. 3.97, Fig. 3.98, Fig. 3.99, Fig. 3.100, and Fig. 3.101. As expected, higher proton conductivities were observed as temperature was increased. Several regions in the plots are characteristic for proton conducting polymers. At low frequencies, the conductivity increases with log frequency, which was then leveled off as a result of electrode polarizations. The irregularities at the low frequency regions can be attributed to polarization, which blocks the electrode-electrolyte interface. S2 and S3 showed higher proton

conductivities when compared to the homopolymers. In the anhydrous conditions, the proton conductivity of PMTet, PAMPS homopolymers, and P(MTet-co-AMPS) (S1-S3) copolymer electrolyte membranes were measured as $2 \times 10^{-6} \text{ Scm}^{-1}$, $1.11 \times 10^{-4} \text{ Scm}^{-1}$, $7.09 \times 10^{-5} \text{ S/cm}$, $8.88 \times 10^{-4} \text{ S/cm}$, and 0.009 S/cm , at 150°C , respectively (Sinirlioglu et al., 2014e).

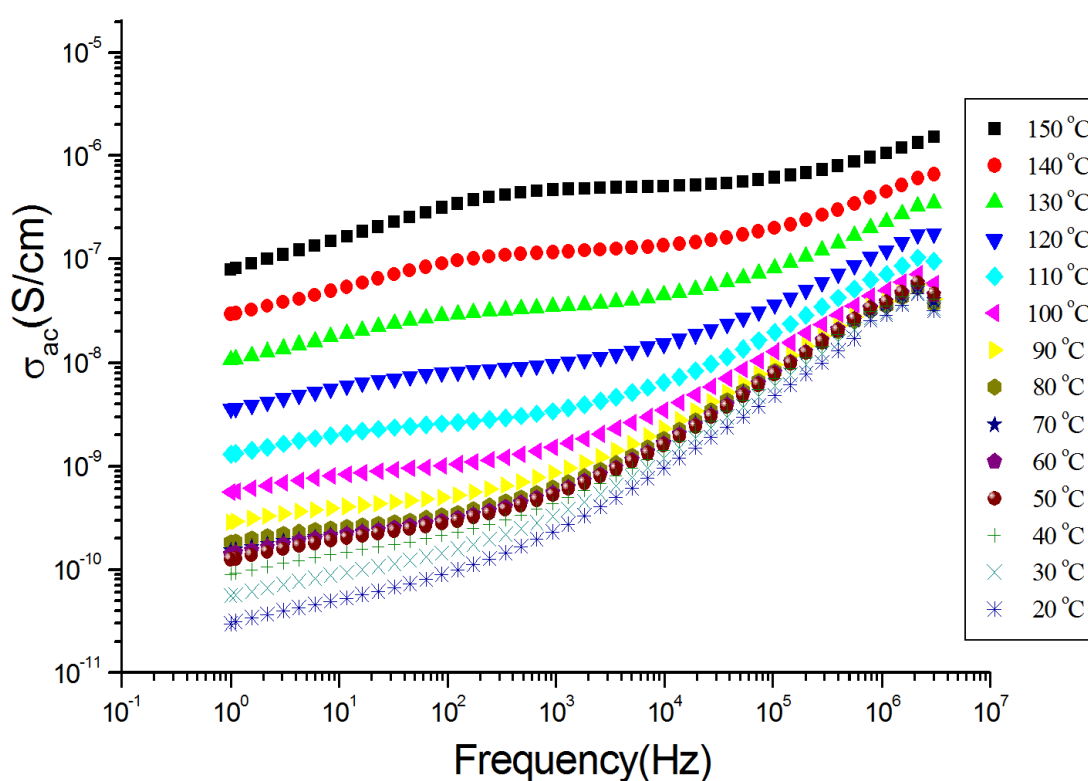


Figure 3.97 AC conductivity versus frequency of PMTet homopolymer at several temperatures.

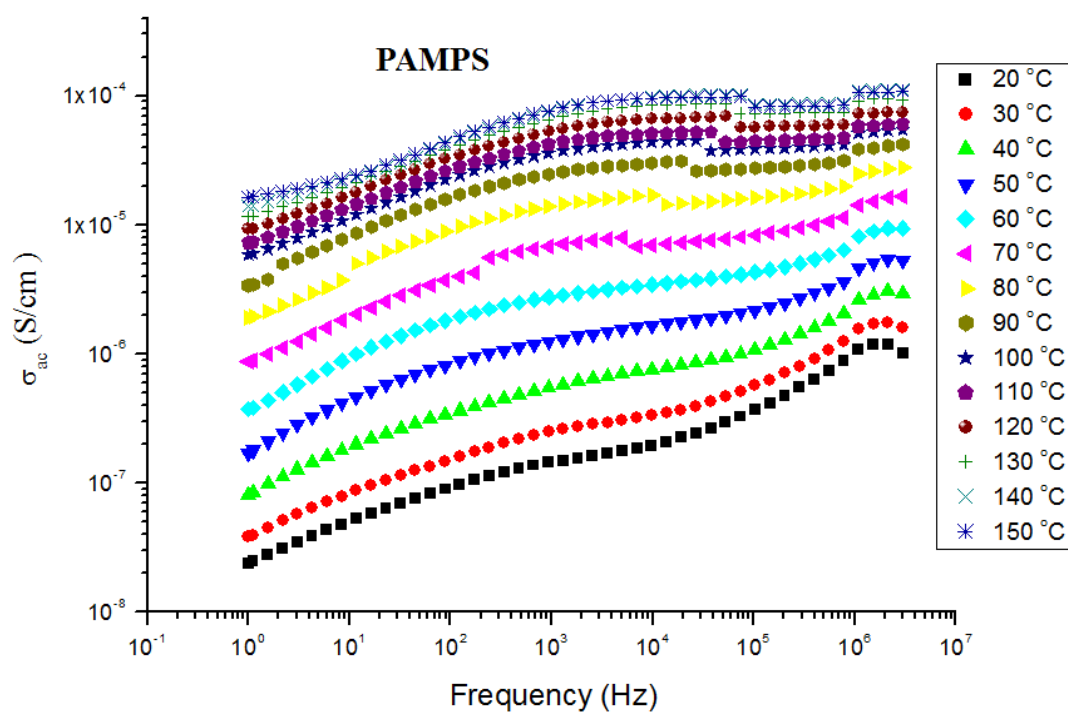


Figure 3.98 AC conductivity versus frequency of PAMPS homopolymer at several temperatures.

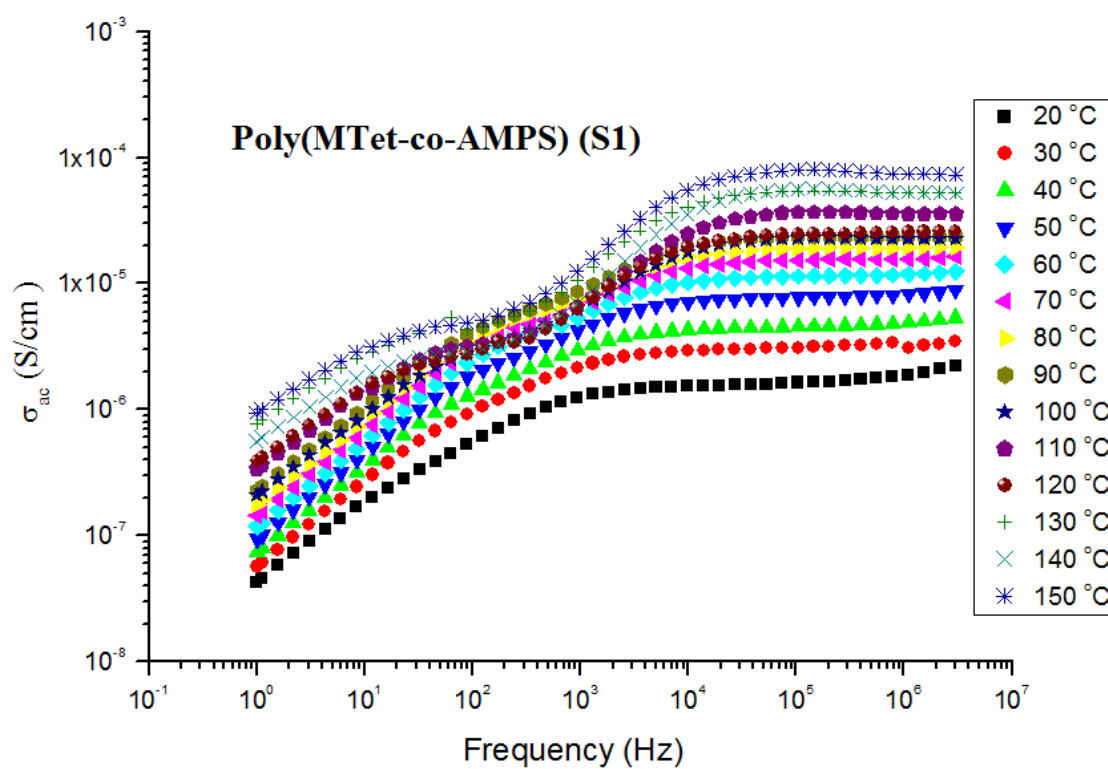


Figure 3.99 AC conductivity versus frequency of poly(MTet-co-AMPS) (S1) copolymer electrolyte membrane at several temperatures.

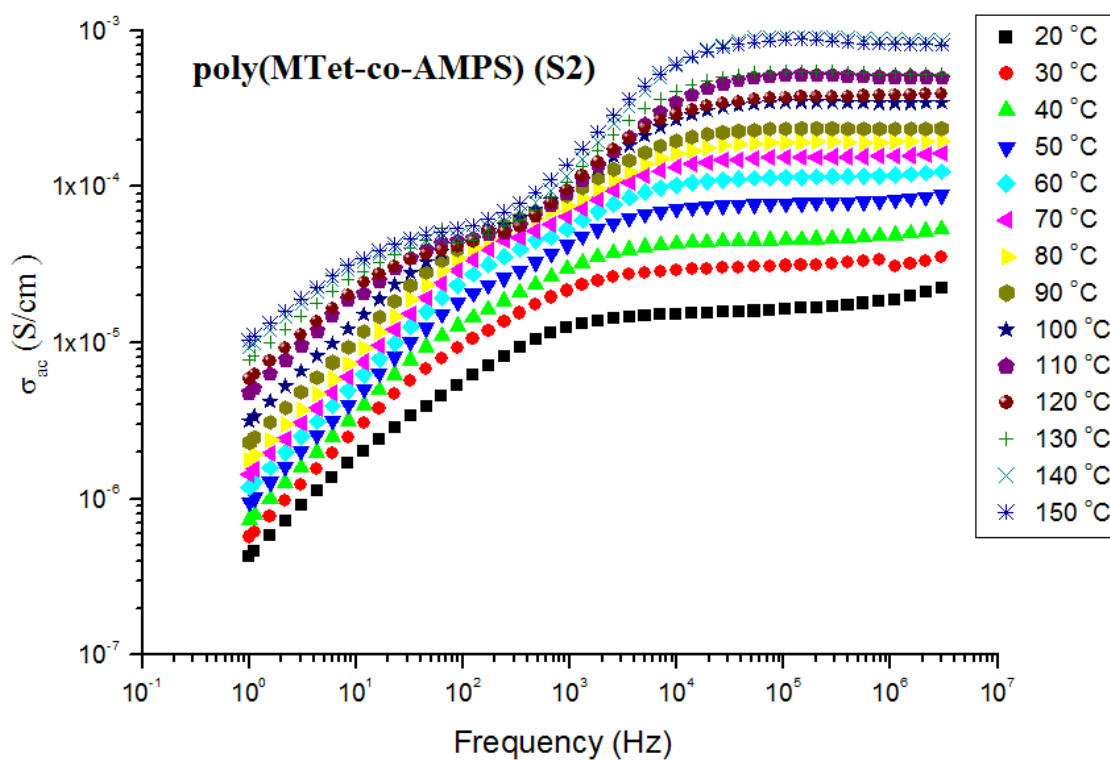


Figure 3.100 AC conductivity versus frequency of poly(MTet-co-AMPS) (S2) copolymer electrolyte membrane at several temperatures.

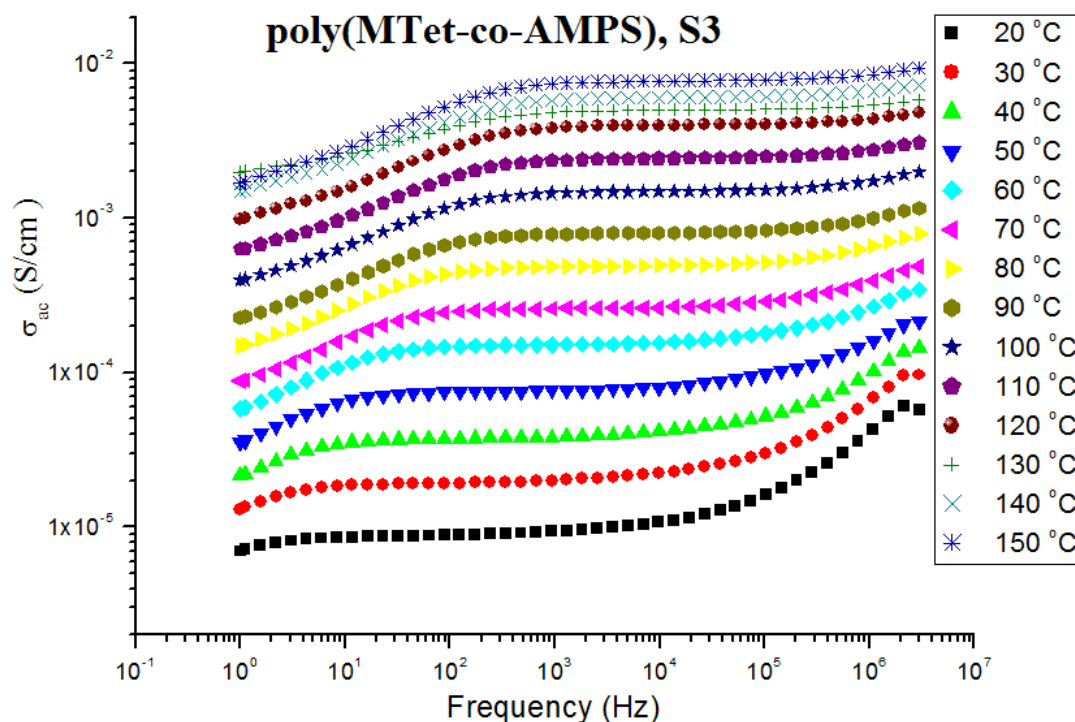


Figure 3.101 AC conductivity versus frequency of poly(MTet-co-AMPS) (S3) copolymer electrolyte membrane at several temperatures.

The DC conductivity (σ_{dc}) of the samples was determined from the plateaus of $\log \sigma_{ac}$ versus $\log F$ by linear fitting of the data. In Fig. 3.102, the DC conductivities of PMTet, PAMPS homopolymers and all copolymer membranes were compared. It can be seen from the conductivity isotherm that the DC conductivity is directly proportional to both the temperature and AMPS content (S1-S3). Since the copolymers have high T_g values, the Arrhenius behaviour is expected in the measurement temperature range which was also reported for the previous AMPS copolymer systems (Sinirlioglu et al., 2014e; Celik and Bozkurt, 2010).

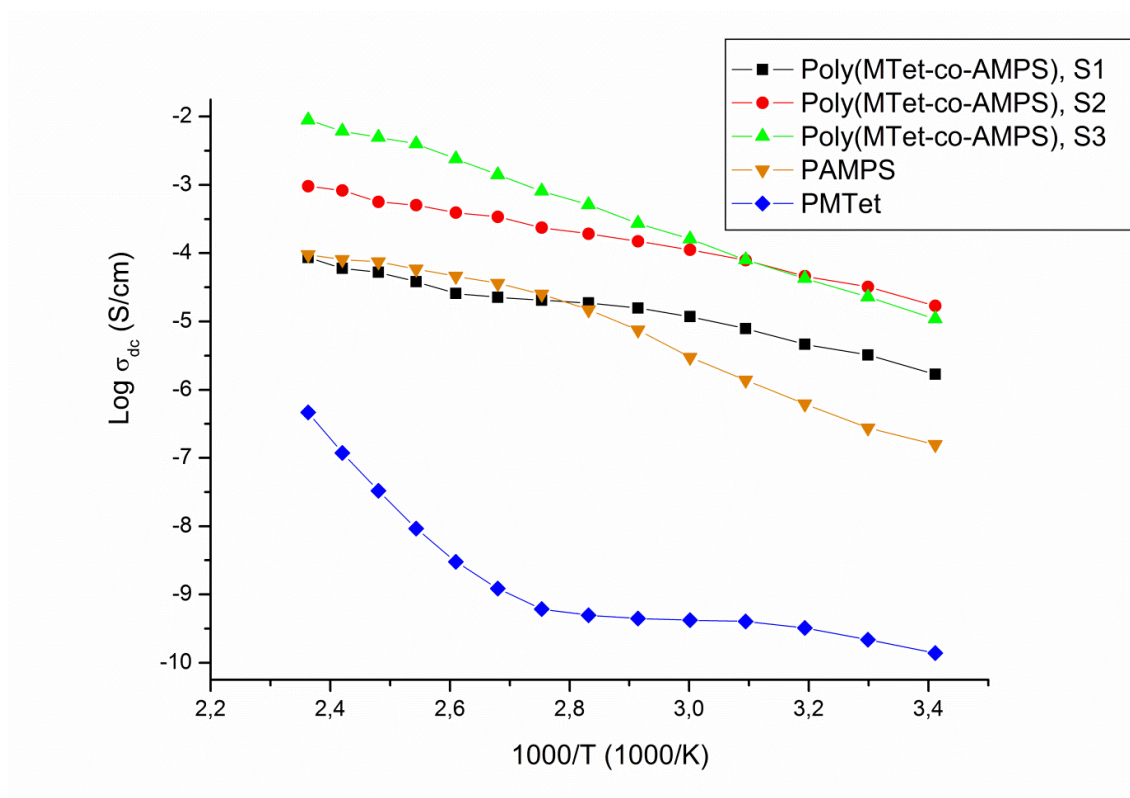


Figure 3.102 Variation of the DC proton conductivity of PMTet, PAMPS homopolymers, and poly(MTet-co-AMPS) (S1-S3) copolymer electrolyte membranes as a function of reciprocal temperature.

Generally, there are two different proton transport mechanisms that contribute to the proton conductivity in polymer electrolytes. The first is the vehicle mechanism where the protons move along the conductive substrate on a neutral or charged “vehicle”. The second is the Grotthuss mechanism. It should be noted that the proton hopping from one N-H site to a free nitrogen also contributes to the conductivity as in the previously reported azole-based systems where the long-range proton transfer occurs throughout the protonic defects (Sinirlioglu et al., 2014e; Celik et al., 2012b).

Triazole doped sulfonic acid systems were previously studied by several groups (Celik and Bozkurt 2010; Gunday et al., 2006). Gunday et al. reported a proton conductivity of 9.3×10^{-4} S/cm at 140 °C for 1H-1,2,4-triazole doped PAMPS system. Previously, several copolymers containing 5-vinyl tetrazole were produced by ‘click chemistry’ from polyacrylonitrile (PAN) due to the unavailability of 5-vinyl tetrazole monomer (Pu et al., 2006). Further studies concerning 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) copolymerized with vinyl triazole (VTri) was carried out.

Celik et al. synthesized a new proton conducting electrolyte membranes based on AMPS and 1-vinyl-1,2,4-triazole (VTri) and investigated different aspects of the properties of poly(VTri-co-AMPS) (Celik and Bozkurt, 2010). In that systems, acidic molecules such as sulfonic acid could also play as proton donors and acceptors in the proton transfer reactions. Celik et al. reported a proton conductivity of 2×10^{-3} S/cm at 130 °C for P(VTri-co-AMPS) (S2) copolymer.

In this study, 5-aminotetrazole was immobilized into methacryloyl chloride monomer. Herein, 5-(methacrylamido)tetrazole is considered to make hydrogen bonding network with sulfonic acid units of AMPS. Protonated and non-protonated nitrogens in heterocyclic group of MTet and sulfonate groups of AMPS serve as proton charge carrier (Sinirlioglu et al., 2014e). As can be seen in Fig. 3.102, the copolymer electrolytes (S2 and S3) have high proton conductivity due to strong interaction between sulfonic acid groups and the tetrazole units when compared to the homopolymers. In addition, as illustrated the FTIR spectrum, copolymer electrolytes as well as conductivity data, it can be concluded that a Grotthus mechanism (structural diffusion) is the possible pathway for the total proton diffusion. This continuous pathway may convey proton transport over the $-\text{SO}_3\text{H}$ groups and tetrazole groups. The proton could travel along the hydrogen bonds from one functional group to another. It can be clearly stated that the anhydrous proton conductivities obtained in our work, P(MTet-co-AMPS) (S3) copolymer, 0.009 S/cm) at 150 °C were higher than the above-mentioned ones (Sinirlioglu et al., 2014e).

3.6.9 Cyclic Voltammetry

Cyclic voltammogram of P(MTet-co-AMPS) (S2) copolymer electrolyte membrane was given in Fig. 3.103. The measurement was performed in a typical three electrode cell containing 0.1 mol/dm^3 CH_3CN solution of tetrabutylammonium hexafluorophosphate (TBAPF6) using a platinum work electrode, a platinum auxiliary electrode, and an Ag/Ag^+ reference electrode. It was clearly observed that the CV of S2 copolymer electrolyte membrane comprised no peak within anodic sweep (-0.5 to 1.5 V potential range). In the cathodic sweep, formation of gaseous hydrogen was developed which localized near the electrode and was subsequently reoxidized toward the anodic cycle. Thus the electrochemical stability window was at least 3 V and these results

demonstrated that this membrane might be used under fuel cell conditions (Sinirlioglu et al., 2014e).

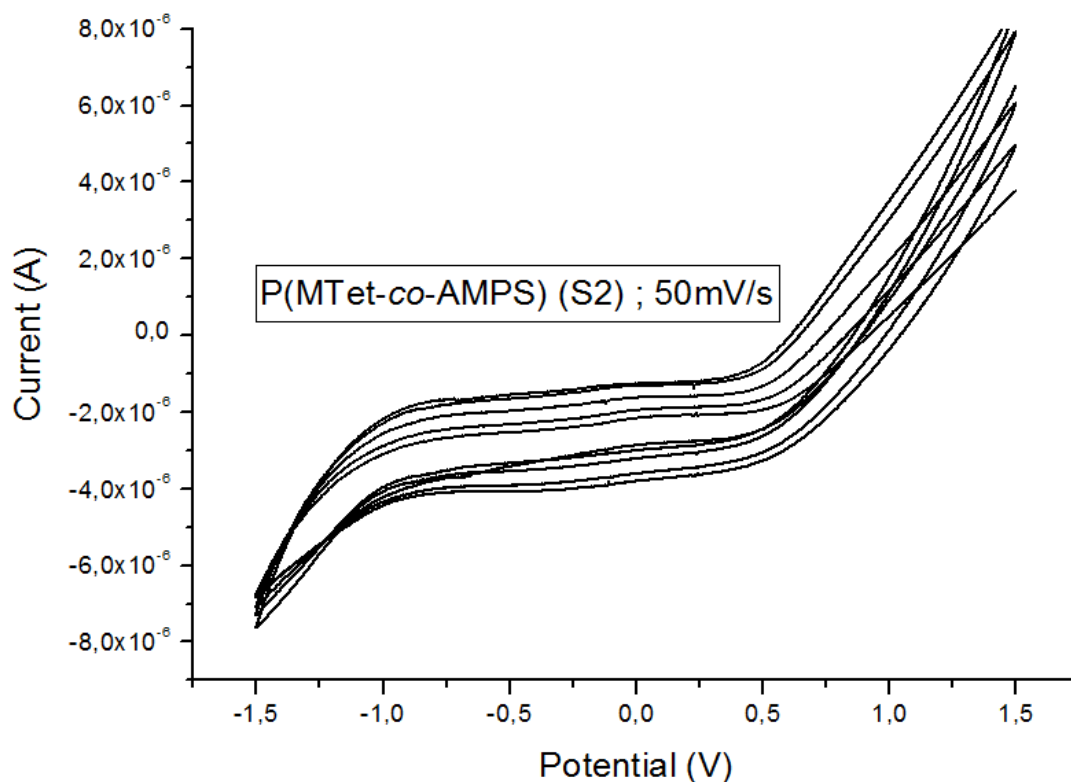


Figure 3.103 Cyclic voltammograms of P(MTet-co-AMPS) (S2) copolymer membrane in 0.1 M TBATFB/acetonitrile. Curves were obtained with a scan rate of 50 mV/s.

3.7 SYNTHESIS OF INORGANIC-ORGANIC HYBRID MEMBRANES BASED ON BORONIC ACID AND TETRAZOLE

Boron-containing polymers have attracted increasing interest due to their flame retardant properties (Jain et al., 2002), and their nontoxic product emission upon combustion (Cheng et al., 2011; Sacristan et al., 2010). An especially interesting class of boron containing polymers are those containing boronic acid functionalities (Cui et al., 2010). The phenyl boronic acid containing polymers are hydrophobic which have no solubility in most organic solvents. Furthermore, aromatic boronic acid based monomers are specially suitable because they are known to improve the flame retardant

behavior of polymers (Sacristan et al., 2010; Cui et al., 2010). It also imparts insolubility in common solvents to the membrane.

We have decided to explore the potential of tetrazole functionality in boronic acid electrolyte membranes, since tetrazole (Tet) heterocycle with four N atoms on the ring provides more configuration than imidazole and triazole rings. Thus, Tet-based polymers may exhibit different proton transport ability from imidazole and triazole-based polymers and might result in higher proton conductivity as compared to the above-mentioned boronic acid/imidazole and boronic acid/triazole copolymers (Sinirlioglu et al., 2014f). In this contribution, 5-(methacrylamido) tetrazole monomer, prepared by the reaction of methacryloyl chloride with ATet, was copolymerized with VBBA by conventional free radical mechanism with various molar feed ratios to attain P(VBBA-co-MTet) copolymers (Fig. 3.104). Homogeneous, transparent, and free-standing films were obtained (Fig. 3.105) (Sinirlioglu et al., 2014f).

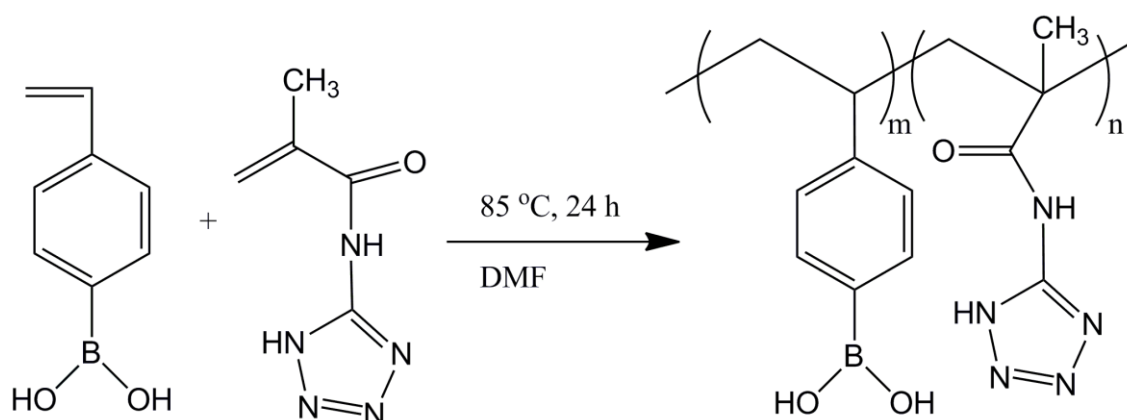


Figure 3.104 The synthesis of P(VBBA-co-MTet) (S1, S2, and S3) copolymers.

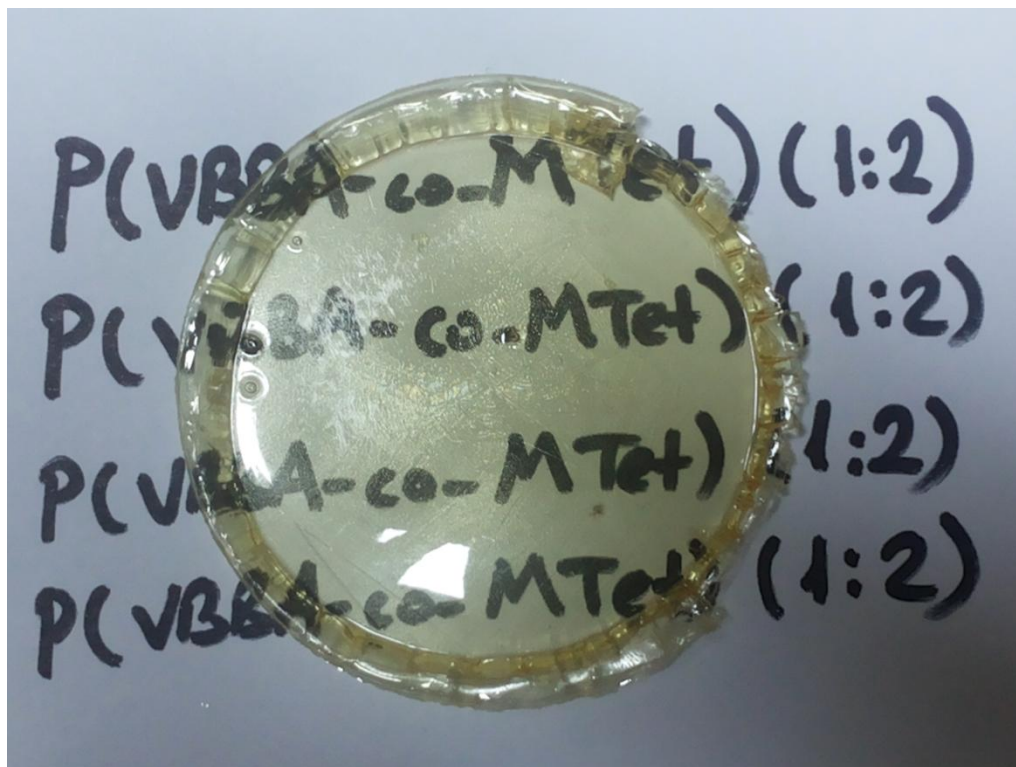


Figure 3.105 Homogeneous, transparent, and free-standing films of poly(VBBA-co-MTet) (S3) copolymer.

The composition of the copolymers was analyzed by elemental analysis and it was listed in Table 3.18. The mol ratio of the S1, S2, and S3 copolymers was calculated using the nitrogen contents. The results demonstrated that copolymer compositions are close to the monomer feed ratios. The actual compositions of the copolymers were calculated from the elemental analysis data. The composition of the copolymer is only slightly dependent on the monomer feed ratio. When MTet in the feed mol ratio is varied from 0.5 (S1) to 2.0 (S3), the MTet mol ratio in the copolymer is changed from 0.46 (S1) to 1.72 (S3) (Sinirlioglu et al., 2014f).

In conventional free radical polymerization, which obeys the terminal model, the composition drift can be explained by the equation (3.1), where r_1 and r_2 are the reactivity ratios, f_1 and f_2 are the molar fractions of monomers 1 and 2 in the monomer feed, and F_1 is the molar fraction of units from monomer 1 in the copolymer. From the equation (3.1), given the feed ratio of monomers (F_1) and copolymer composition (f_1), the monomer reactivity ratios r_1 (VBBA) and r_2 (MTet) were calculated as $r_1=1.02$ and $r_2=0.80$. The values being close to unity, the monomers form nearly random

copolymers. However, deviation from ideal copolymerization is observed and VBBA tends to react slightly more with the propagating active site (Sinirlioglu et al., 2014f).

Herein, 5-(methacrylamido)tetrazole (MTet) monomer is a colorless solid that dissolves in methanol, DMF, or DMSO upon warming. Its solubility in water is negligible. PMTet polymer was hardly soluble in most solvents, but it especially dissolves in DMF and DMSO upon warming. 4-vinyl benzene boronic acid (VBBA) monomer is soluble in most polar organic solvents such as DMF, DMSO, THF and it is poorly soluble in hexane. Poly(vinyl benzene boronic acid) (PVBBA) homopolymer has no solubility in most solvents except for DMF and DMSO. The insolubility of PVBBA is an important advantage for PEM production. The copolymer membranes, P(VBBA-co-MTet), is found to show no solubility in aqueous medium and common organic solvents, except DMF and DMSO which were dissolved in DMF, then were mixed to get poly(VBBA-co-MTet) copolymer membranes for proton conductivity measurements (Sinirlioglu et al., 2014f).

Table 3.18 Composition of poly(vinyl benzene boronic acid-co-5-(methacrylamido)tetrazole) P(VBBA-co-MTet) copolymers.

Sample Name	Feed mol ratio, (VBBA: MTet)	Elemental Analysis			Copolymer mol ratio, (VBBA:MTet)
		C (%)	H (%)	N (%)	
S1	1:0.5	54.81	5.55	14.80	1:0.46
S2	1:1	50.23	5.28	22.34	1:0.92
S3	1:2	46.79	5.02	29.29	1:1.72

3.7.1 FTIR Studies

The FTIR spectra of PVBBA and PMTet homopolymers along with S1-S3 copolymers are illustrated in Fig. 3.106. PMTet showed several medium or strong peaks between 1689 cm^{-1} and 1475 cm^{-1} due to amide bond and tetrazole ring vibrations (Sinirlioglu et al., 2014f). Furthermore, the peaks between $735\text{--}1160\text{ cm}^{-1}$ correspond to

C-H stretching bands and the formation of a slightly broad peak at around 3200 cm^{-1} shows the protonation of tetrazole rings. On the other hand, PVBBA gave a broad peak at around 3380 cm^{-1} and another one at 1420 cm^{-1} due to OH stretching of boronic acid and vibration of phenyl boronic acid linkage, respectively. Additional absorption bands at 1342 cm^{-1} and 1105 cm^{-1} belong to the vibration of B-O and B-OH bonds. The copolymers (S1-S3) also showed the characteristic stretchings and bendings, which were available in the spectra of the homopolymers. This clearly supported that the copolymerization was successful. After doping with H_3PO_4 , the characteristic absorptions of the P-OH, P=O, and P-O⁻ groups for S1-S3 copolymers appeared at $1113\text{-}830\text{ cm}^{-1}$. The intensity of the peak at 1384 cm^{-1} decreased due to possible intramolecular condensation of B-OH forming B-O-B linkages and also intermolecular condensation of B-OH and P-OH forming B-O-P bonds. The band between $2000\text{-}2500\text{ cm}^{-1}$ is attributed to the P-OH bending of the phosphoric acid and this band increased with an increase in H_3PO_4 concentration as depicted in Fig. 3.107 (Sinirlioglu et al., 2014f).

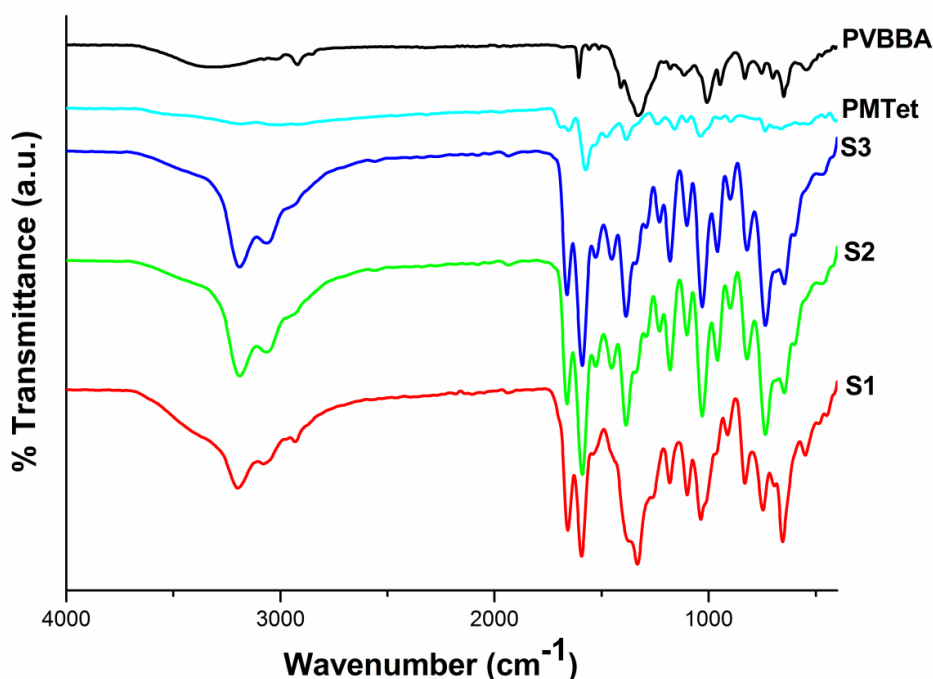


Figure 3.106 FTIR spectra of PVBBA, PMTet, P(VBBA-co-MTet) (S1-S3) copolymers.

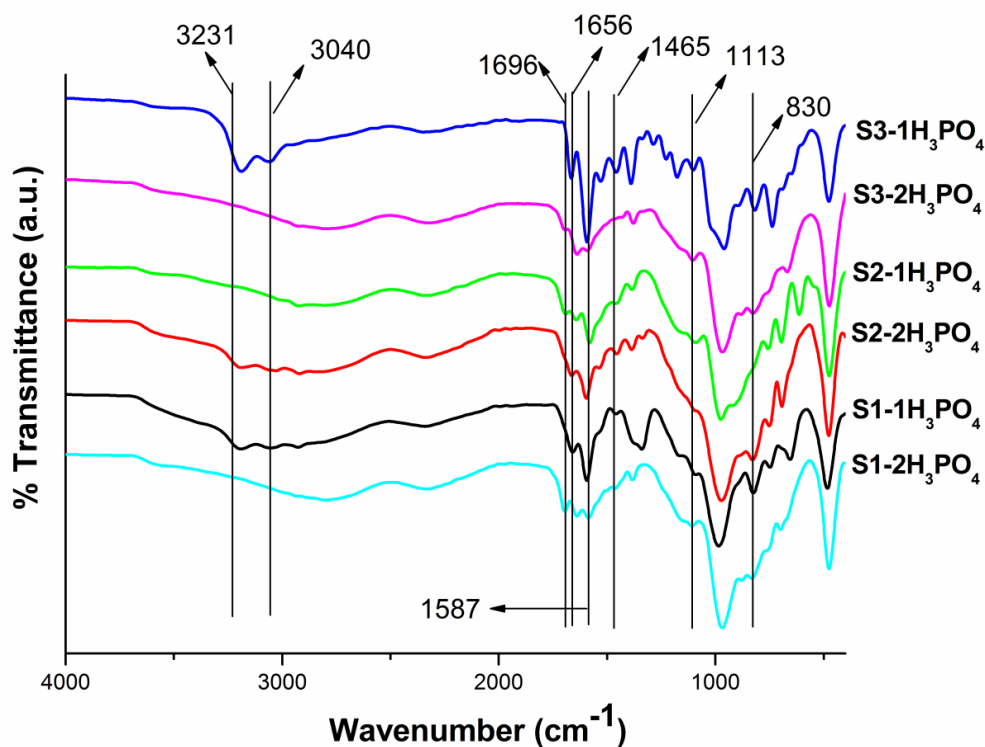


Figure 3.107 FTIR spectra of H_3PO_4 doped P(VBBA-co-MTet) (S1-S3) copolymers.

3.7.2 NMR Studies

^1H -NMR spectrum of MTet monomer was given in the previous section (see Fig. 3.20). The signals at 6.09 ppm and 5.74 ppm are assigned to the methine proton (1H , $=\text{CH}$) of the vinyl group. The appearance of the peaks belonging to $-\text{NH}$ proton of the tetrazole ring and amide proton at 15.90 and 11.97 ppm are a typical indication for the successful modification of methacryloylchloride monomer (Sinirlioglu et al., 2013).

^1H -NMR spectrum of PMTet homopolymer was given in the previous section (see Fig. 3.22). The appearance of the signals at 2.34 ppm and 2.09 ppm, which can be assigned to the methylene protons (2H , $-\text{CH}_2$), indicated the formation of the polymer backbone. Furthermore, the disappearance of the signals at 6.09 ppm and 5.74 ppm from the monomer confirmed complete polymerization of the monomer. The signals between 2.5 and 4 ppm belongs to solvent ($\text{DMSO}-d_6$) and water as 2.51 and 3.40 ppm, respectively. In addition, the signals at 2.75, 2.89 and 7.99 ppm belong to the DMF (Sinirlioglu et al., 2014f; Sinirlioglu et al., 2015a).

¹H-NMR spectra of VBBA and P(VBBA-co-MTet) (S2) copolymer are given in Fig. 3.108. The VBBA is completely dissolved in DMSO-d₆. In Fig. 3.108 (A), the resonance peaks are between at 7.90-7.44 ppm (4H, aromatic phenyl ring protons), 6.78-6.71 ppm (CH=, 1H, multiplet), 5.91(-CH₂=, 2H, two quartet) and 5.31(-CH₂=, 2H, two quartet) (Sinirlioglu et al., 2014f). P(VBBA-co-MTet) (S2) copolymer is slightly dissolved in DMSO-d₆, so two drops of DMF were added to dissolve it completely. The disappearance of peaks at 5.25 (a), 5.90 (a) and 6.78 (b) ppm from vinylic protons of boronic acid monomer, depicted in Fig. 3.108 (B), supports that the monomer has been copolymerized completely (Sinirlioglu et al., 2014f). In addition, the signals between 7.90 (d) and 7.40 (c) ppm belong to aromatic protons of the benzene rings. The appearance of the peaks belonging to -NH proton of the tetrazole ring and amide bond proton at 15.80 and 11.99 ppm are a typical indication for the successful copolymerization of MTet with VBBA as can be illustrated in Fig. 3.108 (B). Also, the signals at around 3.05 ppm and 2.59 ppm are assigned to the methylene and methine protons which indicate polymer backbone (Sinirlioglu et al., 2014f).

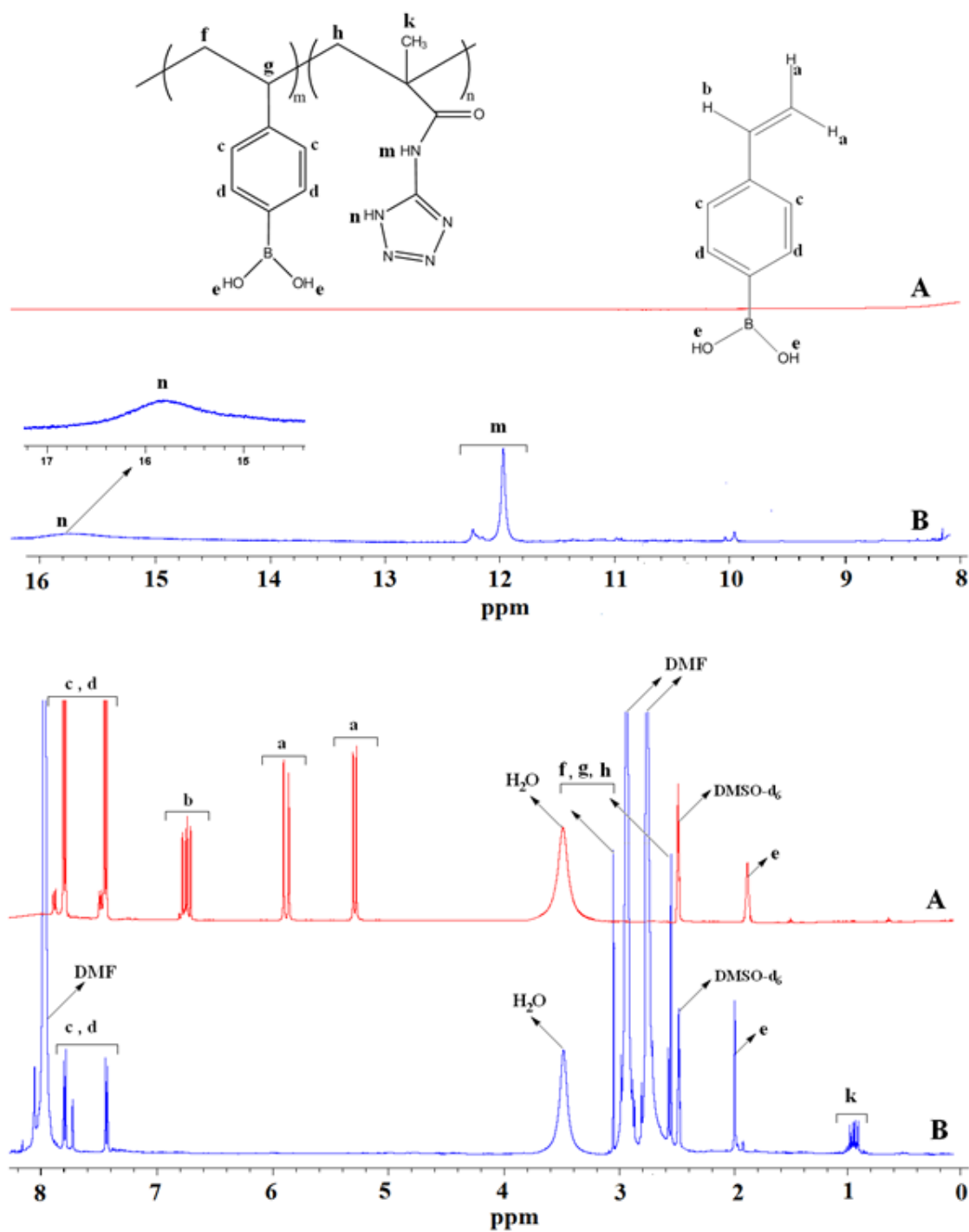


Figure 3.108 ^1H -NMR spectra of (A) VBBA monomer and (B) S2 copolymer recorded in DMSO-d_6 .

In addition, ^{11}B -NMR spectrum confirmed the presence of boron in the boron containing copolymers as depicted in Fig. 3.109. In ^{11}B -NMR spectra, VBBA and (S1-S3) copolymers the peak from boron appears at around 30 ppm, the intensity of which, slightly decreases when the amount of MTet increases from 0.50 to 2.0. The peak at 20 ppm might be a result of a Lewis acid-base interaction between boronic acid and tetrazole nitrogens (Sinirlioglu et al., 2014f).

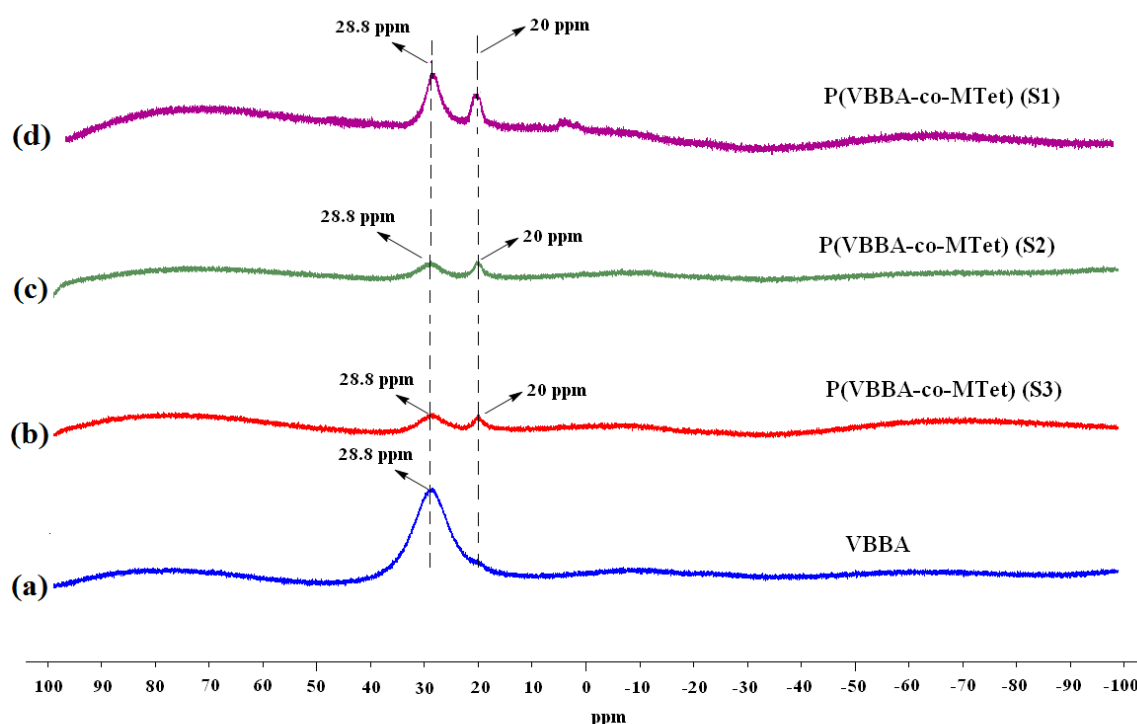


Figure 3.109 The ^{11}B -NMR spectra of (a) VBBA monomer; (b) S3, (c) S2, and (d) S1 copolymers recorded in DMSO-d_6 .

3.7.3 Thermal Properties

Thermal stability is an important property for polymer electrolytes during application in PEMFC. Prior to the analysis, the membranes were dried under vacuum at 100 °C for 24 h and stored in a glove box. The DSC measurements were carried out under inert atmosphere at a scan rate of 10 °C/min. The sample and reference were heated from the same source and the temperature difference was measured. During the measurements, the samples were first heated from -50 °C to 200 °C, and they were then

cooled from 200 °C to 0 °C. The second heating was performed between 0 °C and 250 °C at a scan rate of 10 °C/min and the second heating curves were evaluated (Sinirlioglu et al., 2014f). The glass transition temperature, T_g , of the obtained membranes are listed in Table 3.19. The T_g of PMTet homopolymer was found as approximately 93 °C and no T_g was observed for pure PVBBA homopolymer (Celik and Bozkurt, 2013; Sezgin et al., 2008). The T_g of P(VBBA-co-MTet) (S1-S3) membranes were found as 112 °C, 103 °C, and 95 °C, respectively. When P(VBBA-co-MTet) (S1-S3) membranes were doped with phosphoric acid, the glass transition temperatures decreased (Table 3.19). Clearly, the T_g values show a pronounced effect of increasing phosphoric acid content on the softening behavior of the pure copolymers. The presence of single T_g confirms the homogeneity of the materials (Sinirlioglu et al., 2013; Sinirlioglu et al., 2014f).

Table 3.19 T_g and maximum proton conductivity values of copolymers.

Sample Name	[Feed mol ratio] VBBA:MTet	Doping ratio with H_3PO_4	T_g (°C)	Max. Proton Conductivity at 150 °C (S/cm)	log σ_o	E_{dc} (eV)
S1	1:0.5	-----	112	-----	-----	-----
S2	1:1	-----	103	-----	-----	-----
S3	1:2	-----	95	-----	-----	-----
S1-1 H_3PO_4	1:0.5	1:1	107	1.03×10^{-5}	-0.99	0.359
S1-2 H_3PO_4	1:0.5	1:2	98	6.73×10^{-5}	-0.15	0.362
S2-1 H_3PO_4	1:1	1:1	92	1.12×10^{-4}	-0.07	0.362
S2-2 H_3PO_4	1:1	1:2	87	9.49×10^{-4}	1.06	0.368
S3-1 H_3PO_4	1:2	1:1	91	0.003	-0.07	0.217
S3-2 H_3PO_4	1:2	1:2	80	0.021	0.68	0.197

The thermal stability of the membranes was analyzed by using TGA in comparison with PMTet, PVBBA, and pure copolymers (S1-S3). The obtained TGA curves are presented in Fig. 3.110 and Fig. 3.111. Pure PVBBA was thermally stable up

to approximately 400 °C. There was a small weight loss between 150 and 250 °C due to condensation of the boronic acid units; a major weight loss occurred above 400 °C due to the degradation of the polymer backbone (Sinirlioglu et al., 2014f). Furthermore, boric acid functional molecules have interesting thermal properties since boronic acid can easily form cyclotrimeric anhydrides by simple heating or water loss (Celik and Bozkurt, 2013; Sezgin et al., 2009; Sezgin et al., 2008). PMTet homopolymer showed thermally stability up to 215 °C (Sinirlioglu et al., 2013). 40 % of PMTet decomposed between 220 and 380 °C because of degradation of tetrazole units and after 380 °C, second weight loss region occurs due to the decomposition of the polymer backbone (Sinirlioglu et al., 2014f).

All pure copolymers (S1-S3) showed a two-step degradation pattern at around 200 and 380 °C due to the decomposition of PVBBA units and the copolymer backbone, respectively, as seen in Fig. 3.110 and Fig. 3.111. The initial weight loss in the first stage can be attributed to the loss of loosely bound water that was possibly absorbed during storage. 10 % weight loss between 100-200 °C was due to condensation of boronic acid groups in PVBBA units (Sinirlioglu et al., 2014f). 35 % of P(VBBA-co-MTet) (S1) decomposed between 210 and 370 °C due to the degradation of tetrazole units while a second weight loss region was seen above 370 °C stemming from the decomposition of the copolymer backbone. As the mol ratio of MTet increased in the copolymers (S1-S3), the thermal stability also increased due to lower content of boronic acid condensation product (Sinirlioglu et al., 2014f). Doping with phosphoric acid (PA) caused a slight decrease in the thermal stability of the membranes, however, all membranes were thermally stable up to at least 170 °C. All the acid doped membranes demonstrated an exponential weight change between 150-200 °C due to intermolecular and intramolecular condensation of boronic acid and phosphoric acid units. The weight loss between 200 and 300 °C were attributed to the degradation of tetrazole units and major weight loss region after 360 °C was due to the decomposition of the copolymer backbone. The fact that the membranes were thermally stable up to 170 °C implied that the membranes showed the potential to be tested in high temperature PEMFC operation (Sinirlioglu et al., 2014f).

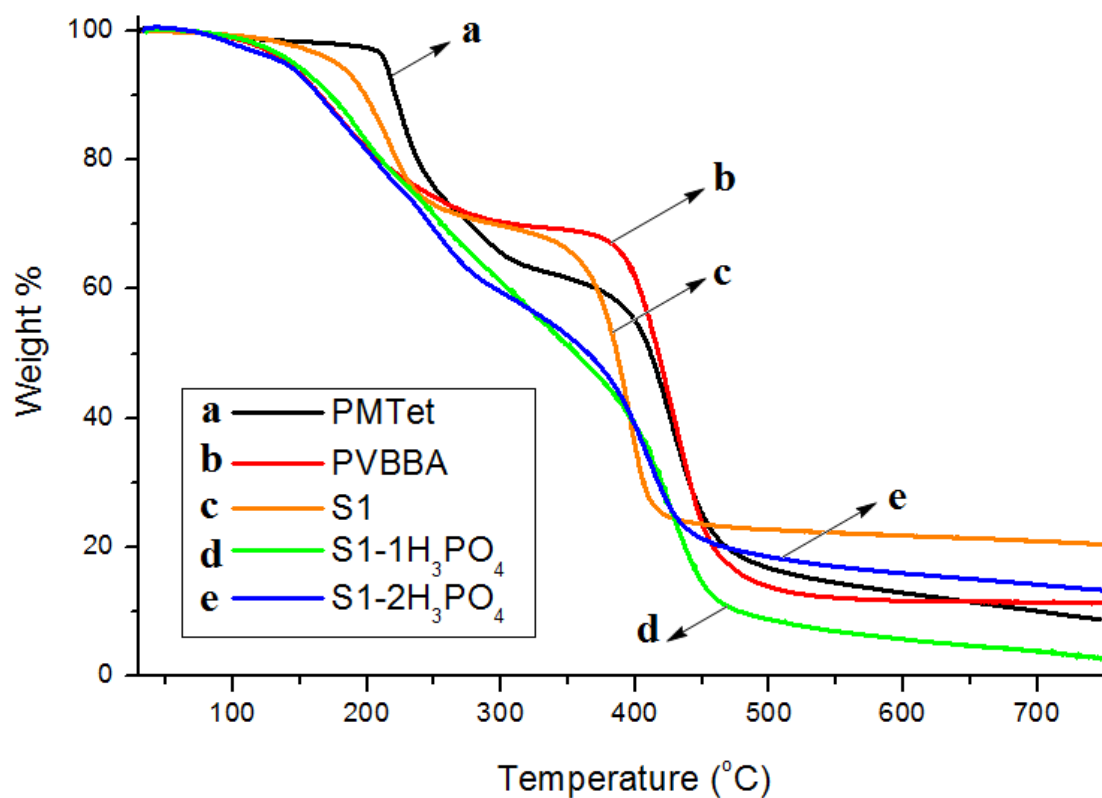


Figure 3.110 TG thermograms of PMTet, PVBBA, S1, S1-1H₃PO₄, and S1-2H₃PO₄ copolymers at a heating rate of 10 °C/min in inert atmosphere.

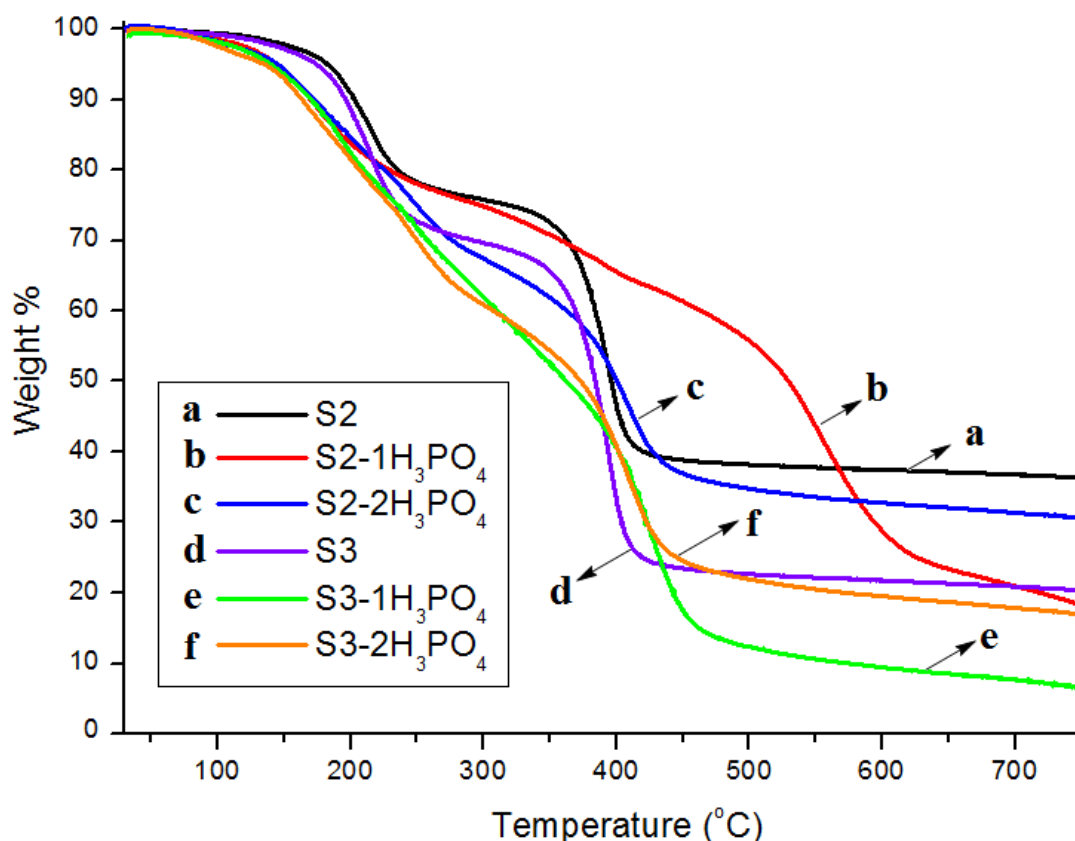


Figure 3.111 TG thermograms of S2, S2-1H₃PO₄, S2-2H₃PO₄, S3, S3-1H₃PO₄, and S3-2H₃PO₄ copolymers at a heating rate of 10 °C/min in inert atmosphere.

3.7.4 Morphology

The morphology study is important to confirm the homogeneity of the polymers. Fig. 3.112 shows SEM micrographs of pure and PA-doped copolymers (S1, S3, S1-xH₃PO₄, and S3-xH₃PO₄) and they seem to be homogeneous. All samples exhibit single phase formation which shows that PVBBA, PMTet and H₃PO₄ units are uniformly distributed in the matrix and there is no agglomeration or phase separation at the nanometer level (100 nm) (Sinirlioglu et al., 2015). In Fig. 3.112 (C-E), there are several small cracks in nanometer scale, which might originate from the drying procedure. However, the presence of cracks is an indication of the extent of brittleness of the membranes. It is also noteworthy that the cracks may result in a substantial increase in the gas crossover at catalyst in PEMFC and limit the operation of the cell. It seems that further modification of the membranes with reinforcement additives would be necessary before they can be applied in fuel cell tests (Sinirlioglu et al., 2014f).

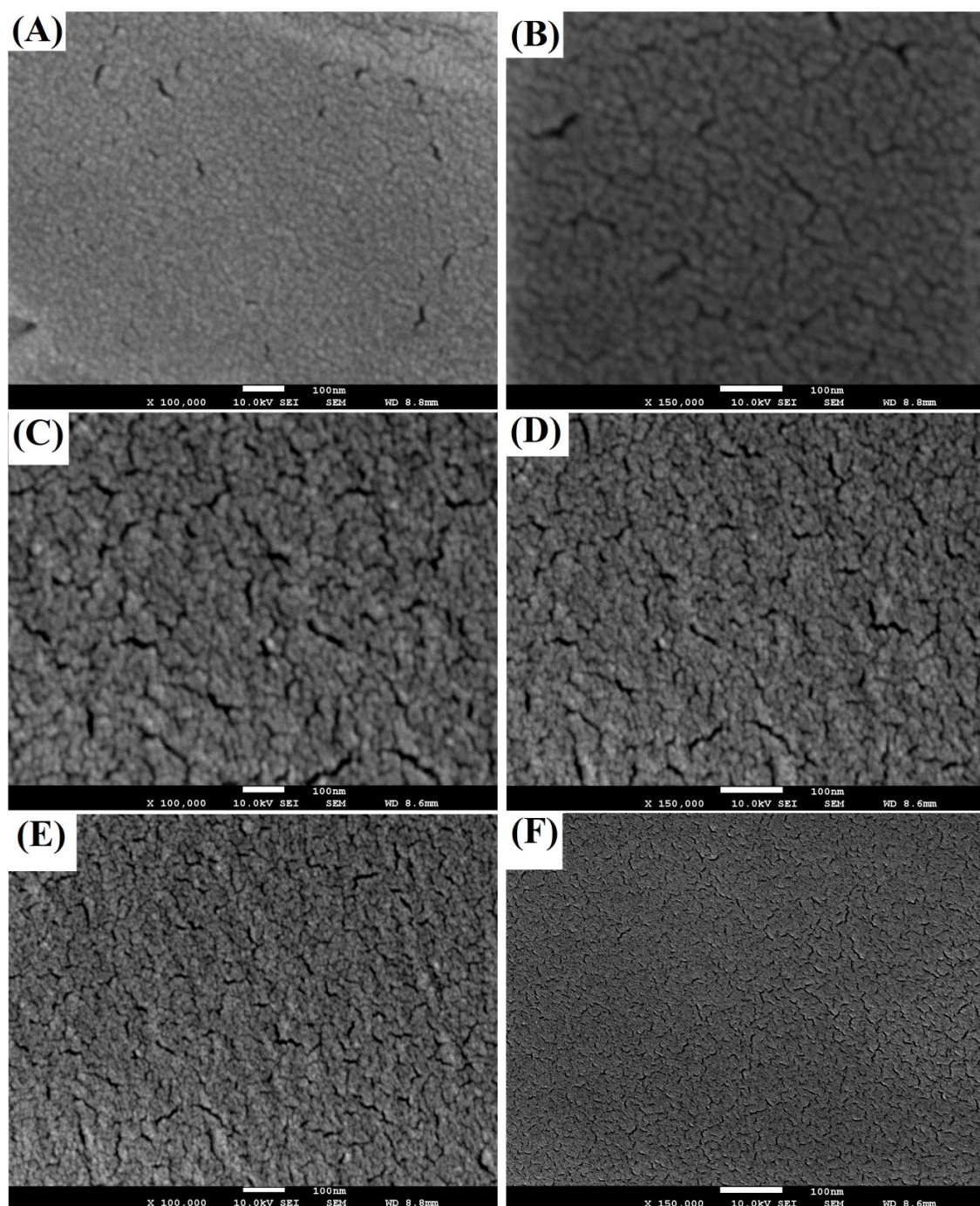


Figure 3.112 SEM images of the surface of (A) P(VBBA-co-MTet) (S1), (B) P(VBBA-co-MTet) (S3), (C) acid doped P(VBBA-co-MTet) (S1-1H₃PO₄), (D) acid doped P(VBBA-co-MTet) (S3-1H₃PO₄), (E) acid doped P(VBBA-co-MTet) (S1-2H₃PO₄), and (F) acid doped P(VBBA-co-MTet) (S3-2H₃PO₄) copolymer electrolytes at 100 nm level by different magnification as 100,000X (A, C, E) and 150,000X (B, D, F), respectively.

3.7.5 XRD Studies

The X-ray diffraction (XRD) measurement is a constructive method to examine the crystallinity of the obtained membranes. The XRD patterns of PMTet and S1-S3 copolymer membranes are illustrated in Fig. 3.113. VBBA monomer has typical crystalline structure, while PVBBA homopolymer showed predominantly amorphous structure (Kahraman et al., 2004). PMTet is a crystalline polymer and has an endotherm around 216 °C. There are two strong broad peaks in the diffractograms of pure PMTet at 2θ values of 18° and 24°, this indicated the high degree of crystallinity of PMTet as seen in the Fig. 3.113 (Sinirlioglu et al., 2014f). The strong peaks at 2θ values of 19.1 and 26.7° slightly reduced in the diffractogram of P(VBBA-co-MTet) (S1 and S2). For S3 copolymer, the original characteristic peak at around 24° totally disappeared, and another original crystalline peak at around 18° was slightly decreased. This result revealed that greater disarray in the chain alignment occurred in all pure copolymers and the original crystalline structure of pure PMTet homopolymer was partially destroyed. It showed that the crystallinity was significantly diminished when the MTet content was decreased from 2.0 to 0.50 (Sinirlioglu et al., 2014f).

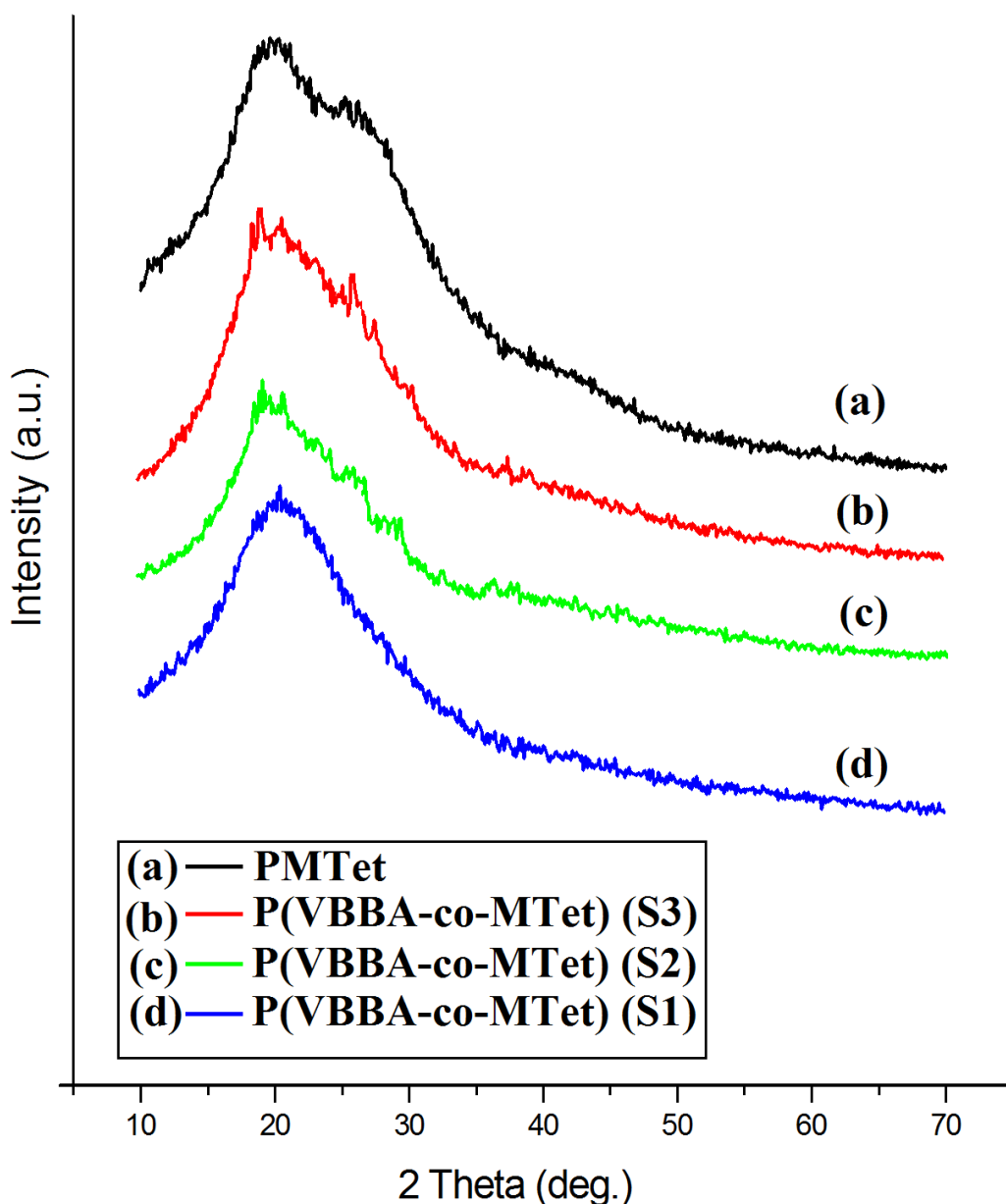


Figure 3.113 XRD patterns of (a) PMTet, (b) P(VBBA-co-MTet) (S3), (c) P(VBBA-co-MTet) (S2), (d) P(VBBA-co-MTet) (S1) copolymers.

3.7.6 Proton conductivity Measurements

The proton conductivity of the copolymer membranes is the most essential properties to be studied for the potential application in high temperature fuel cells. The samples were cut into thin slices with the average thickness of around 300 μm . The proton conductivities of all acid doped membranes were measured in the temperature range of 20 $^{\circ}\text{C}$ to 150 $^{\circ}\text{C}$ (Sinirlioglu et al., 2014f). The phosphoric acid (PA)-doped copolymer membranes were fixed between additional external parallel plate electrodes

(between platinum blocking electrodes) to form a sandwich using the simple two-electrode method and impedance was measured by varying the temperature from 20 °C to 150 °C. Fig. 3.114, Fig. 3.115, Fig. 3.116, Fig. 3.117, Fig. 3.118, and Fig. 3.119 show the AC conductivity of PA-doped copolymer membranes versus log frequency at several temperatures. As expected the conductivity increases with the temperature. Maximum proton conductivities of the obtained PEMs are listed in Table 3.19. It can be seen that as the amounts of PA and MTet increase, the conductivity values increase as expected since both of them have a direct contribution in the conduction mechanism. In the absence of humidity, the maximum proton conductivity was obtained as 0.021 S/cm for P(VBBA-co-MTet)-2H₃PO₄ (S3-2H₃PO₄) at 150 °C (Sinirlioglu et al., 2014f).

Boronic acid is a Lewis acid and instead of giving proton it accepts hydroxides and causes the medium to become acidic. Therefore, pure copolymers have low proton conductivity due to lack of proton defect formation and continuous path for conduction (Sinirlioglu et al., 2014f). After doping the copolymers, tetrazole groups were protonated and the proton conductivity occurs between protonated tetrazole and phosphoric acid units via structure diffusion (Sacristan et al., 2010; Cui et al., 2010). Furthermore, the swelling of the copolymer with acid caused phosphoric acid functional polymers by forming a chemical linkage, that is B-O-P at higher temperatures. Herein, vinyl benzene boronic acid copolymer backbone is very important to obtain an insoluble main matrix hydrophilic units forming a channel for the dopant. Previously, Sezgin et al. prepared PA-doped poly(vinyl benzene boronic acid-co-vinylimidazole) (Sezgin et al., 2009), and obtained a maximum proton conductivity of 3×10^{-3} S/cm while Celik et al. reported a higher maximum proton conductivity, 6×10^{-3} S/cm at 150 °C, for PA-doped poly(4-vinyl benzene boronic acid-co-1-vinyl-1,2,4-triazole) membrane (Celik and Bozkurt, 2013). The anhydrous proton conductivity obtained in our work (0.021 S/cm) at 150 °C was even 3.5 times as much as the latter (Sinirlioglu et al., 2014f).

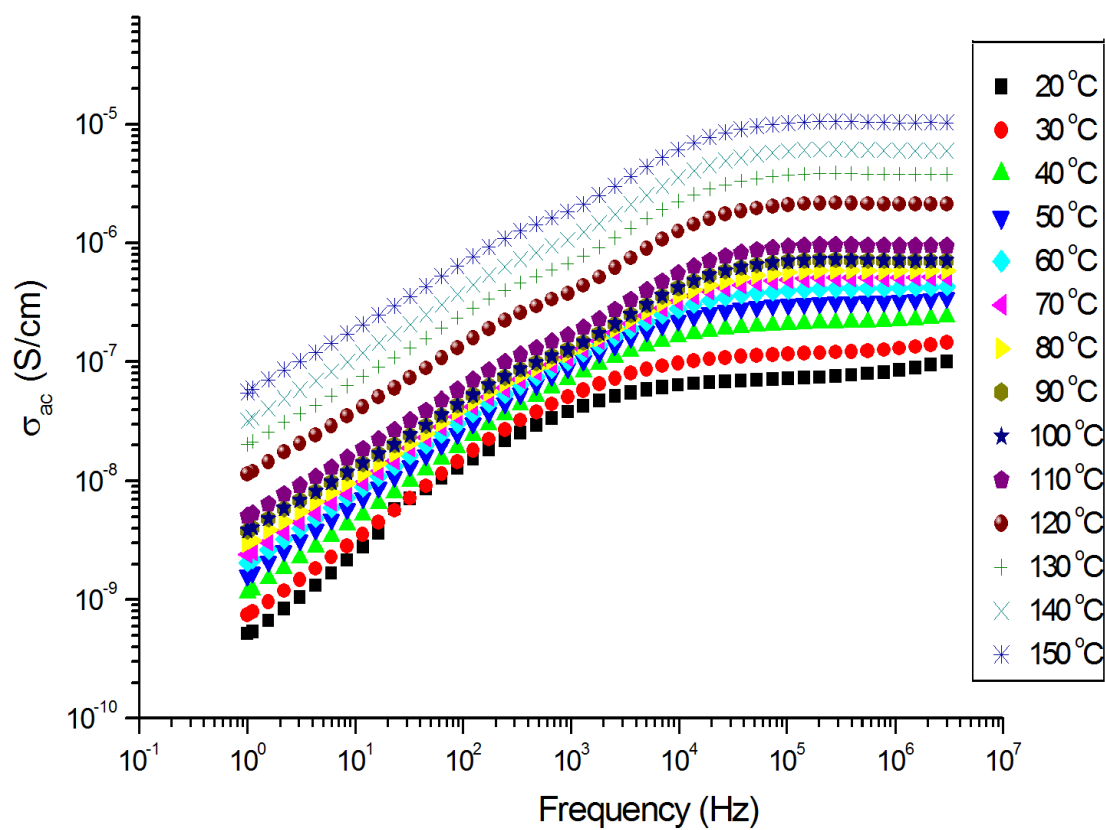


Figure 3.114 AC conductivity versus frequency of S1-1H₃PO₄ copolymer electrolyte membrane at several temperatures.

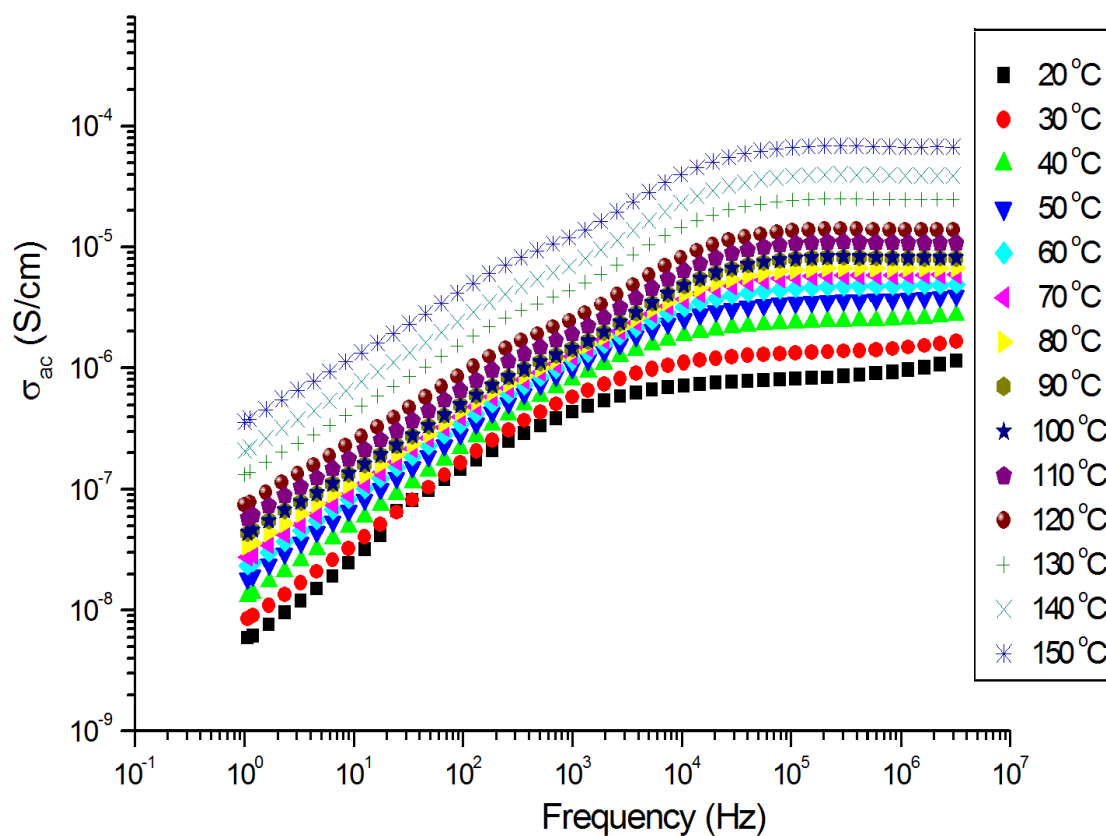


Figure 3.115 AC conductivity versus frequency of S1-2H₃PO₄ copolymer electrolyte membrane at several temperatures.

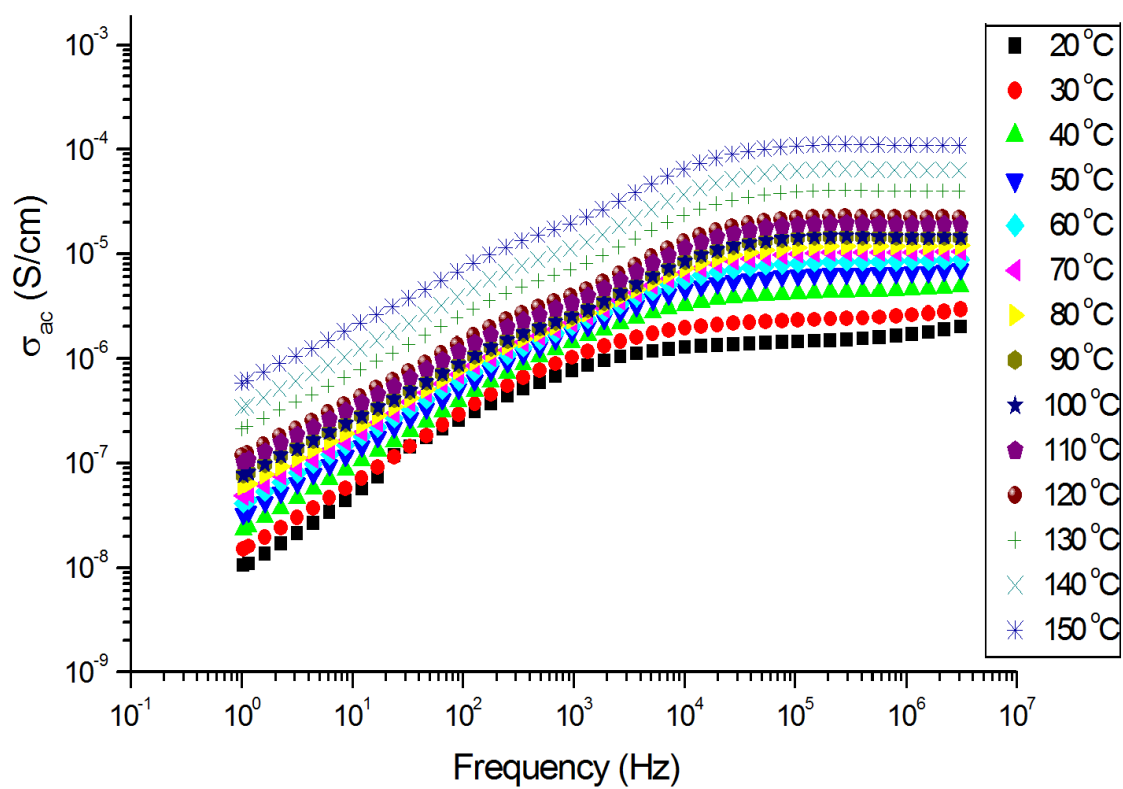


Figure 3.116 AC conductivity versus frequency of S2-1H₃PO₄ copolymer electrolyte membrane at several temperatures.

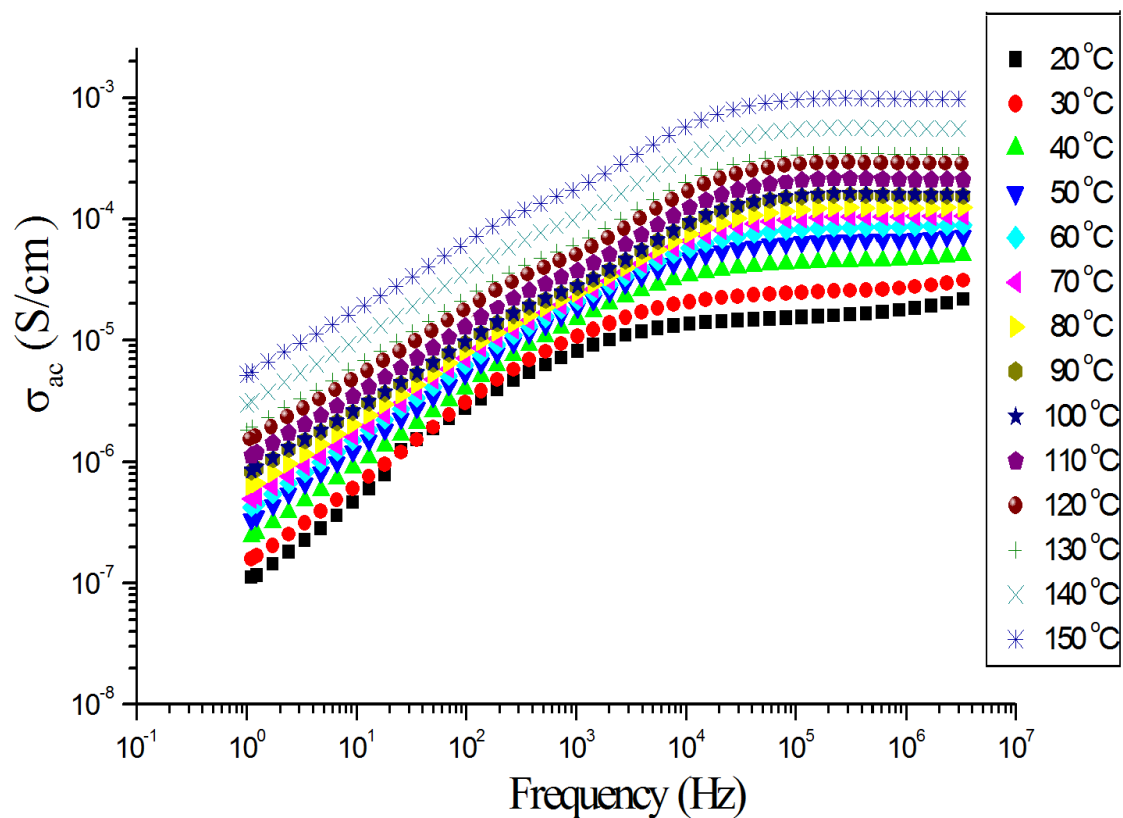


Figure 3.117 AC conductivity versus frequency of S2-2H₃PO₄ copolymer electrolyte membrane at several temperatures.

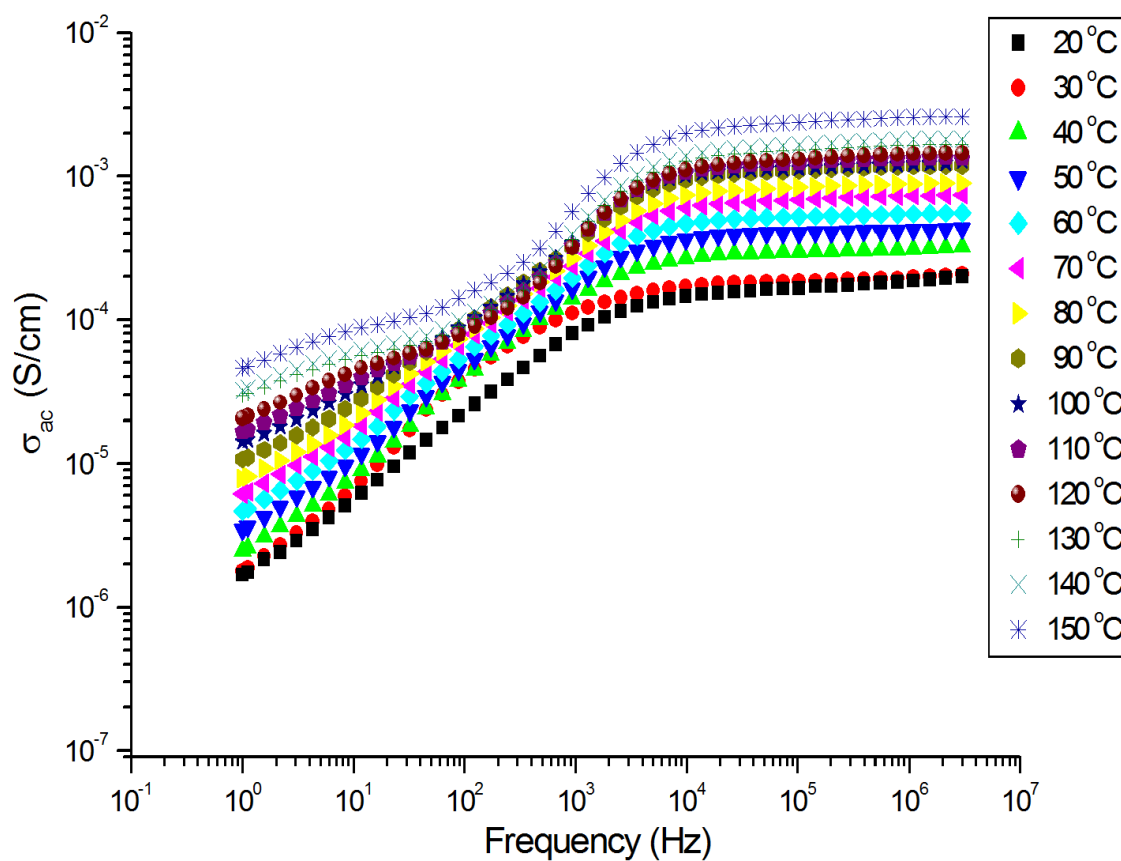


Figure 3.118 AC conductivity versus frequency of S3-1H₃PO₄ copolymer electrolyte membrane at several temperatures.

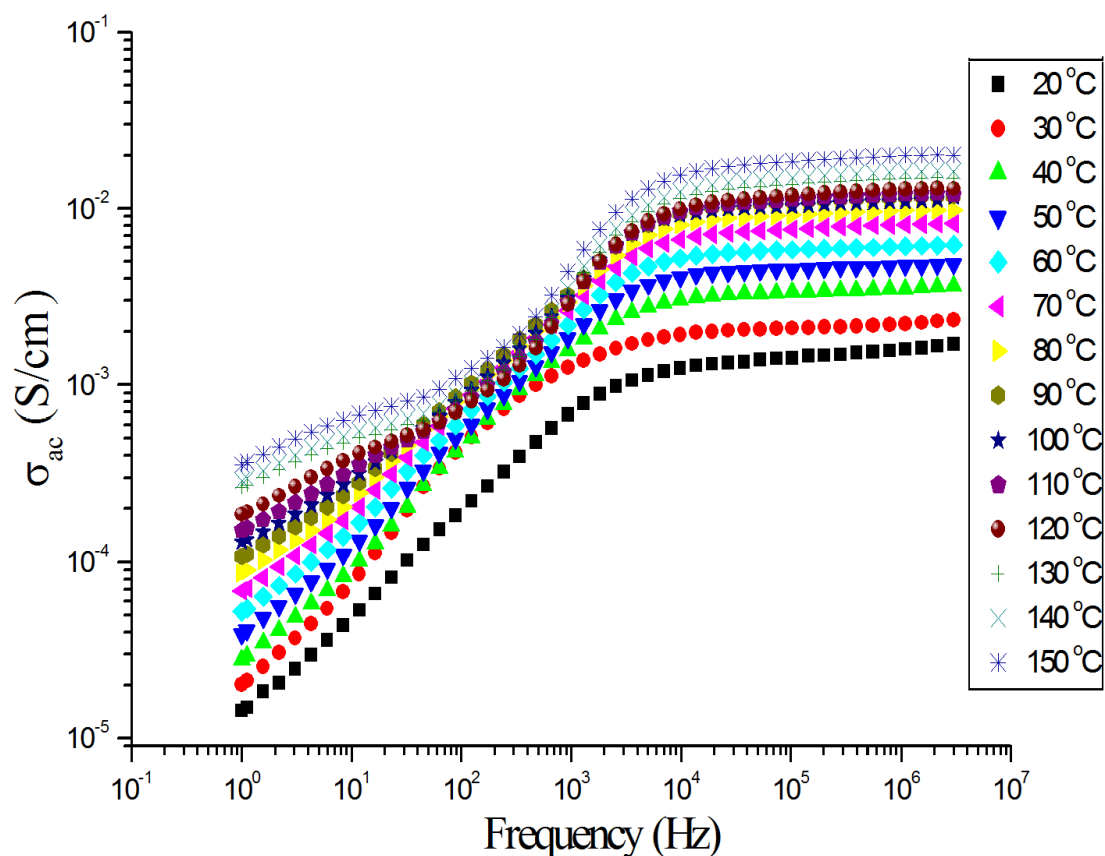


Figure 3.119 AC conductivity versus frequency of S3-2H₃PO₄ copolymer electrolyte membrane at several temperatures.

The DC conductivity (σ_{dc}) of the samples was derived from the plateaus of $\log \sigma_{ac}$ versus $\log$ frequency by linear fitting of the data and compared in Fig. 3. 120. It is clear that the DC conductivity strongly depends on the temperature and the doping ratio, x . The proton conductivity in this system was carried out over the -POH groups both by forming a B-O-P linkage and tetrazole groups. The proton could travel along the hydrogen bonds from one functional group to another. For all PA-doped samples, the conductivity isotherm can be fitted by Arrhenius equation. The activation energies of all PA-doped membranes are listed in Table 3.19 (Sinirlioglu et al., 2014f).

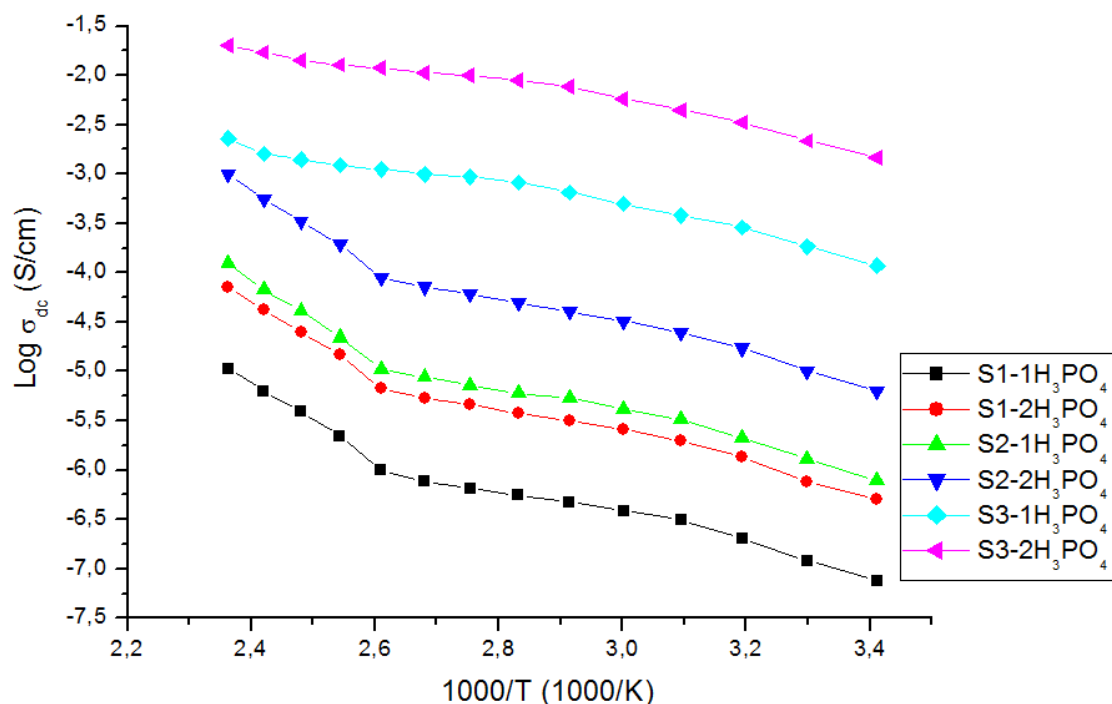


Figure 3.120 Variation of the DC proton conductivity of H₃PO₄ doped P(VBBA-co-MTet) copolymers as a function of reciprocal temperature.

In addition, boronic acid has a vacant p orbital and its acidic behavior is explained as Lewis acidity in which boronic acid ionizes water, takes one hydroxide and forms anionic tetrahedral structure. Furthermore, as illustrated the FT-IR spectrum, copolymer electrolytes as well as conductivity data, it can be concluded that a Grotthuss mechanism (structural diffusion) is the possible pathway which may convey proton transport over the -P-OH groups both by forming a B-O-P linkage and tetrazole groups (Hazarika and Jana, 2012; Cheng et al., 2011). Possible mechanism of proton transport in P(VBBA-co-MTet)-xH₃PO₄ (x=1.0 and 2.0), in which phosphoric acid is coordinated with boronic acid and tetrazole groups, is tentatively depicted in Fig. 3.121.

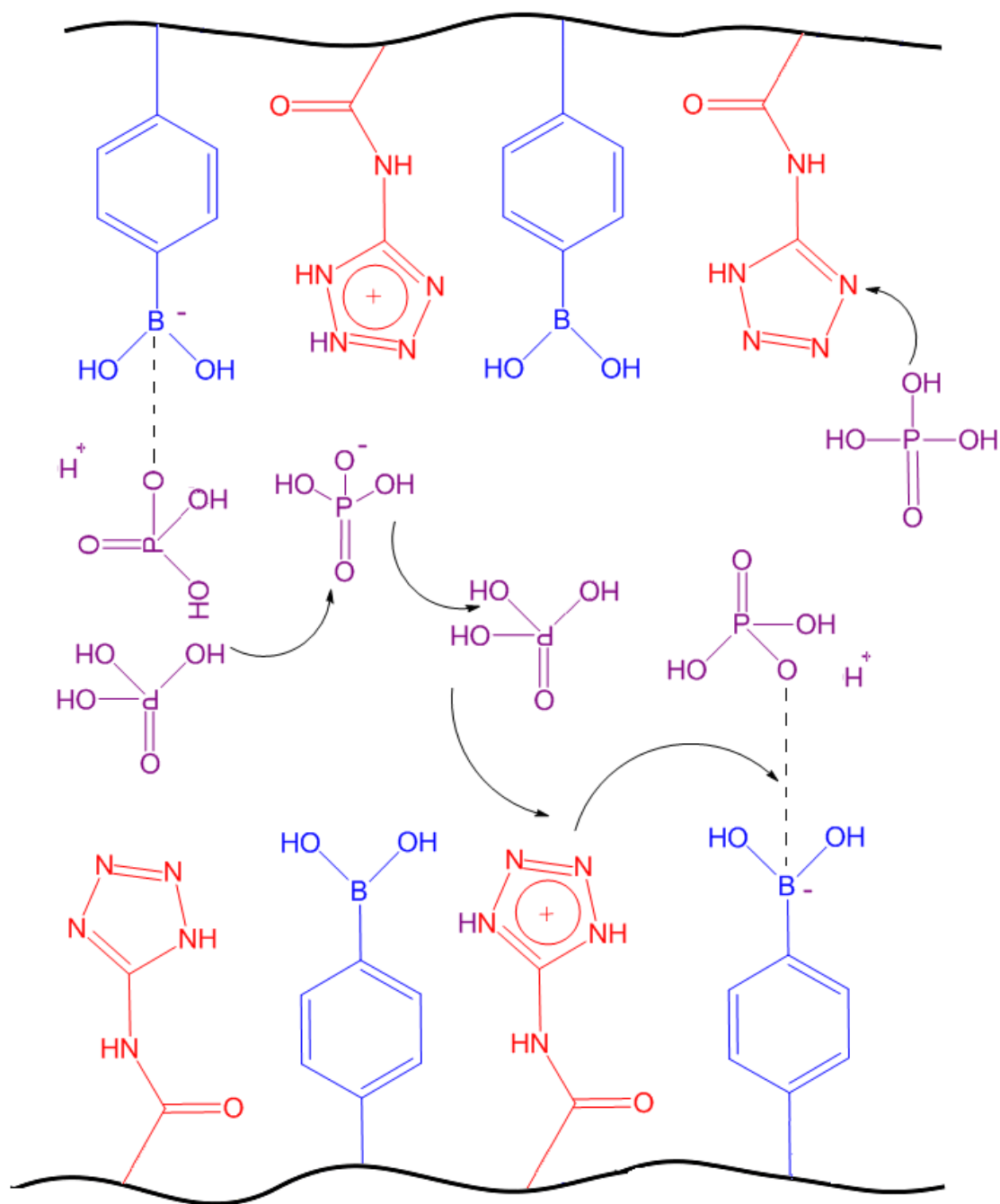


Figure 3.121 Possible mechanism of proton transport in P(VBBA-co-MTet)- $x\text{H}_3\text{PO}_4$ ($x=1.0$ and 2.0) copolymer electrolytes.

3.7.7 Cyclic Voltammetry

Cyclic voltammogram of P(VBBA-co-MTet)- $2\text{H}_3\text{PO}_4$ (S3- $2\text{H}_3\text{PO}_4$) was given in Fig. 3.122. The measurement was performed in a typical three electrode cell containing

0.1 mol dm⁻³ CH₃CN solution of tetrabutylammonium hexafluorophosphate (TBAPF6) using a platinum work electrode, a platinum auxiliary electrode, and an Ag/Ag⁺ reference electrode. The voltammogram shows that the copolymer comprises no peak within the anodic and cathodic sweep (-1.5 to 1.5V potential range). Thus, the electrochemical stability window is about 3V. These results imply that the copolymer had adequate electrochemical stability under fuel cell conditions (Sinirlioglu et al., 2014f).

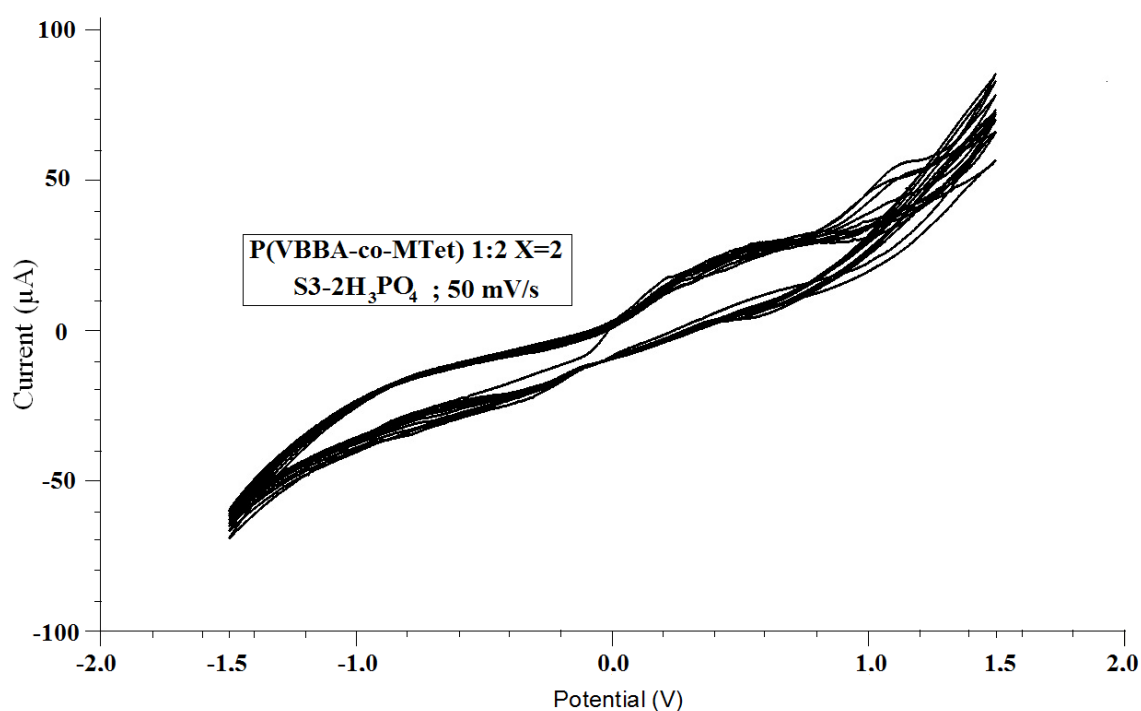


Figure 3.122 Cyclic voltammograms of P(VBBA-co-MTet) 1:2 x=2 (S3-2H₃PO₄) copolymer electrolyte membrane in 0.1 M TBATFB/acetonitrile. Curves were obtained with a scan rate of 50 mV/s.

3.8 SYNTHESIS OF ANHYDROUS PROTON EXCHANGE MEMBRANES VIA GRAFTING VINYLTRIAZOLE ONTO ALKALINE TREATED PVDF

Quite recently, to prepare proton exchange membranes that are composed of engineering plastics such as poly(vinylidene fluoride) (PVDF), polytetrafluoroethylene (PTFE), poly(tetrafluoroethylene-co-perfluoropropylvinylether) (PFA), poly(ethylene-

alt-tetrafluoroethylene) (ETFE) films. Among the above-mentioned fluoropolymers, PVDF, one of the most important engineering polymers, has attracted continuous interest due to low cost, high chemical resistance, enhanced thermal and mechanical properties. However, the application of PVDF is limited to some extent because native PVDF contains no reactive functional groups. As a result, it is necessary to modify PVDF to impart new functionalities.

Grafting offers an effective approach for incorporating functional groups into a material. However, studies on grafted films containing readily available azole functional monomers are very rare (Lepit et al., 2012). Therefore, it is remarkable that a graft copolymer consisting of 1-vinyl-1,2,4-triazole and a PVDF base matrix might be prepared via using the radical polymerization method after defluorination of PVDF powder by alkaline treatment to attain anhydrous PEMs (Sinirlioglu et al., 2014b).

In this study, high performance of poly(vinylidene fluoride) (PVDF) and proton conductivity of poly(1-vinyl-1,2,4-triazole) (PVTri) were combined in a graft copolymer, PVDF-*g*-PVTri, was first synthesized via radical copolymerization, which can be used modification of PVDF powder by alkaline treatment and the synthetic process is schematically shown in Fig. 3.123 (Sinirlioglu et al., 2014b). The composition of the PVDF based membranes was verified by energy dispersive X-ray spectrometry (EDS) and the results are summarized in Table 3.20. Azole content of the samples was calculated by using ^1H -NMR spectroscopy, and the results are summarized in Table 3.20. It is verified that vinyltriazole are about 21.30, 29.86 and 47.22 % accessible into PVDF-*g*-PVTri (C1-C3), respectively, when the weight ratio of PVTri was increased. The results evidenced that modification and grafting were successful. Finally, stoichiometric amounts of PVDF-*g*-PVTri films were admixed with TA in DMF and homogeneous solutions of PVDF-*g*-PVTri-(TA)_x (x= 1.0, 2.0 and 3.0) were produced, where x is the number of moles of TA per mole of triazole units. Anhydrous PEMs were obtained upon casting of the solutions in polished PTFE plates and drying (Sinirlioglu et al., 2014b) (Fig. 3.124).

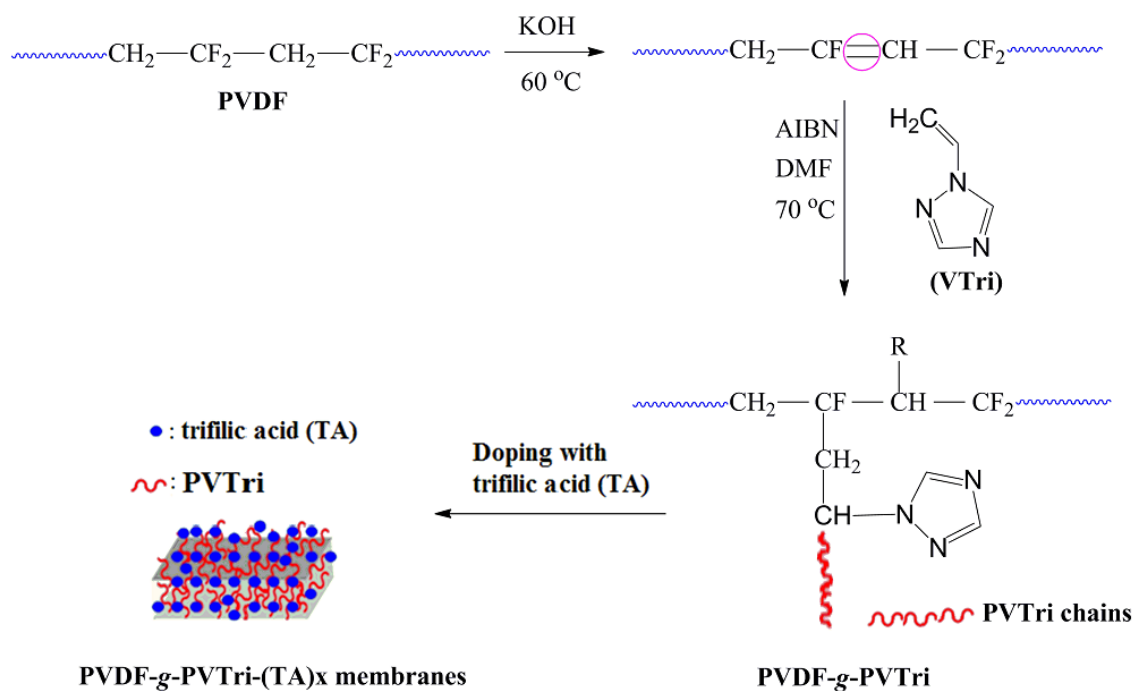


Figure 3.123 Schematic illustration for the copolymer synthesis and membrane formation.

Table 3.20 Chemical compositions of PVDF-*g*-PVTri (C1-C3) graft copolymers.

Sample	(weight ratio, g) PVDF : VTri	Grafting degree (%) ^a	Chemical elements (%) ^b		
			C	F	N
PVDF- <i>g</i> -PVTri, C1	4:1	21.30	39.61	54.50	5.91
PVDF- <i>g</i> -PVTri, C2	4:2	29.86	42.52	44.65	12.82
PVDF- <i>g</i> -PVTri, C3	4:4	47.22	49.96	31.05	18.99

a: calculated from ¹H-NMR on a % by mol basis, **b:** found from EDS results on a % by weight basis.



Figure 3.124 Free-standing film of PVDF-*g*-PVTri-TA₃ (C2-TA₃) membrane.

3.8.1 FTIR analysis

Infrared spectroscopy was used to provide information about the chemical structure of the pristine PVTri, PVDF, alkaline treatment PVDF, PVDF-*g*-PVTri (C1-C3), and triflic acid doped, PVDF-*g*-PVTri-(TA)_x ($x=1.0, 2.0$ and 3.0), graft copolymer membranes. The triazole rings of the pristine PVTri homopolymer give rise to several medium strong peaks in the $1430\text{--}1650\text{ cm}^{-1}$ range due to ring stretching (C-N, C=N) vibrations. The peak at 1270 cm^{-1} is due to the ring N-N stretching. The broad peak centered at 3430 cm^{-1} was assigned to O-H vibration of molecular water interacting with the pristine PVTri. The asymmetric and symmetric stretching vibrations of the CH₂ group in the PVDF base film were located, respectively, at 3024 cm^{-1} and 2982 cm^{-1} . The strong peak which appeared at 1404 cm^{-1} corresponds to -CH₂ stretching vibrations. Strong and wide peaks appearing between $1246\text{--}1070\text{ cm}^{-1}$ correspond to the C-F stretching and were characteristic peaks of the PVDF base film (Sinirlioglu et al., 2014b; Sasa et al., 2013; Golcuk et al., 2013; Tang et al., 2009). After PVDF powder

was treated by KOH, the absorption band in $1600\text{--}1740\text{ cm}^{-1}$ associated with C=O and C=C stretching peaks appear (Fig. 3.125c) due to defluorination (Tang et al., 2009; Liu et al., 2006; Ross et al., 2001; Ross et al., 2000). In comparison to the spectrum of pristine PVDF (Fig. 3.125b and Fig. 3.125c), PVDF-*g*-PVTri (Fig. 3.125 d) shows two additional peaks in the $1500\text{--}1660\text{ cm}^{-1}$ range due to ring stretching vibrations, which are assigned to C-N and C=N stretching vibrations from the VTri, respectively. This indicates the existence of PVTri side chains in the copolymer.

PVDF is a polymorphic, semi-crystalline polymer showing at least four different forms such as α , β , γ , δ and ε (Ram et al., 2014; Glaub et al., 2013; Mahadeva et al., 2013; Dong et al., 2013; Nah et al., 2013). A detailed examination of the characteristic absorption bands of virgin PVDF and alkaline treated PVDF yield the peaks at 487, 594, 664, 756, 863, 980 and 1398 cm^{-1} corresponding to α -phase. However, no peaks corresponding to β -phase are observed. Furthermore, the spectrum of virgin PVDF and alkaline treated PVDF does not show any characteristic absorption peaks at 812, 882, 1234 cm^{-1} corresponding to γ -phase (Sinirlioglu et al., 2014b).

After graft copolymerization of VTri onto alkaline treated PVDF, most of the peaks corresponding to α -phase have been diminished due to conversion of crystal phase from α -phase to β -phase as can be realized by the appearance of β -phase peaks at 835 and 1272 cm^{-1} (Ram et al., 2014) as depicted in Fig. 3.126. The results clearly demonstrate that VTri was successfully grafted. After doping of the graft copolymers, triflic acid gives several absorptions between 1000 cm^{-1} and 1250 cm^{-1} . The strong bands at 1208 and 1269 cm^{-1} are attributed to SO_2 , and a strong absorption peak at 1026 cm^{-1} most probably belongs to $-\text{SO}_3^-\text{[H}^+]$. The formation of a peak at around 3170 cm^{-1} shows the protonation of the triazole rings, in addition to the broad peaks around 3500 cm^{-1} (Sinirlioglu et al., 2014b). Similar absorption bands were also present in FTIR spectra as shown in Fig. 3.127 and Fig. 3.128, respectively.

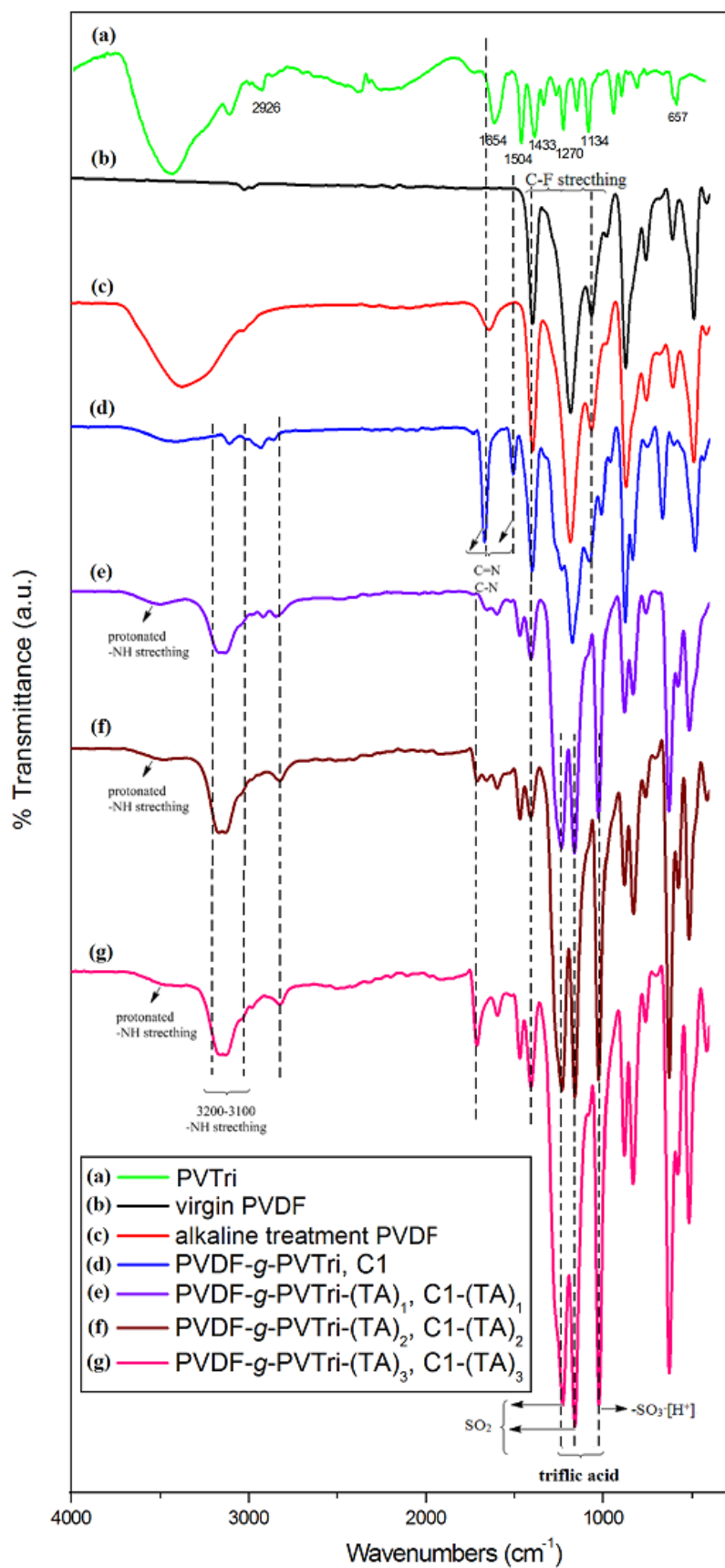


Figure 3.125 FTIR spectra of PVTri, PVDF, alkaline treatment PVDF, PVDF-*g*-PVTri (C1), and acid-doped PVDF-*g*-PVTri-(TA)_x (x=1.0, 2.0 and 3.0) graft copolymer membranes.

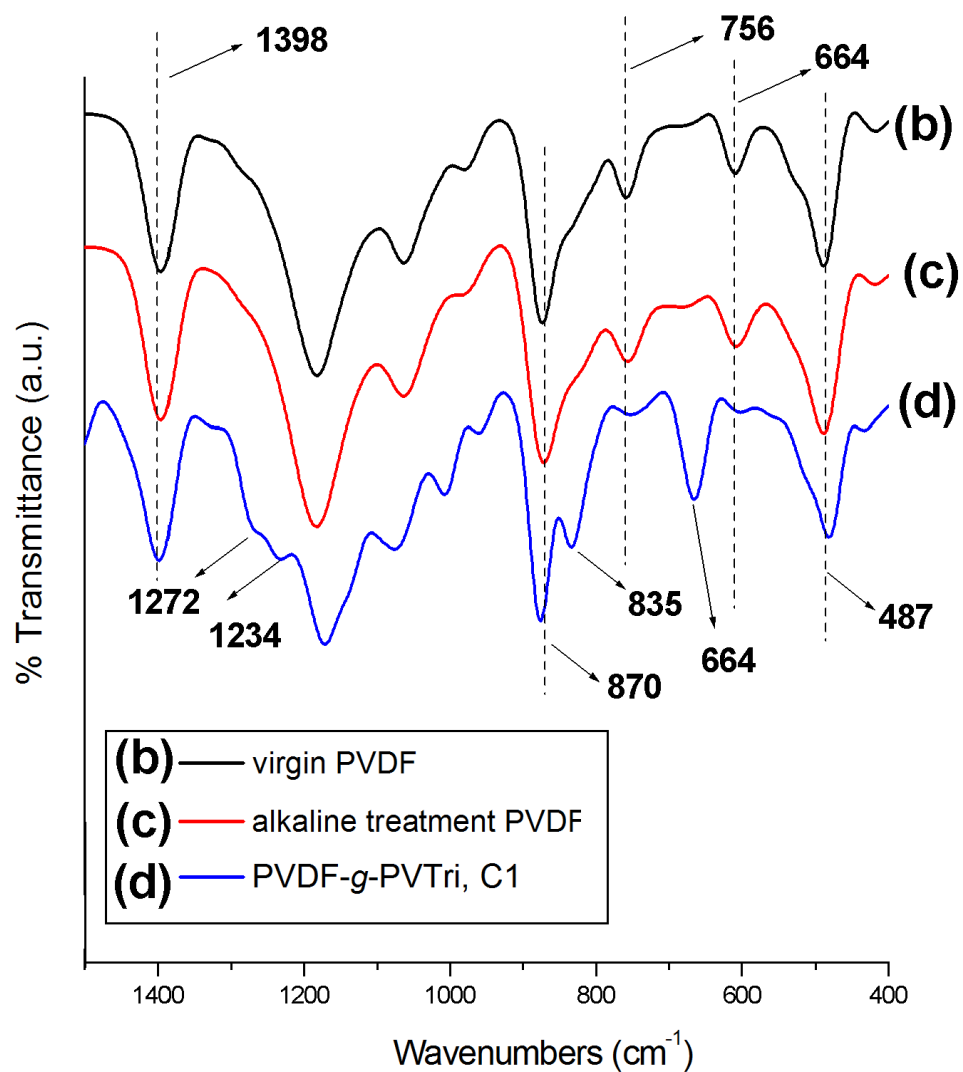


Figure 3.126 FTIR spectra of PVDF, alkaline treatment PVDF, PVDF-*g*-PVTri (C1): A detailed inspection within 1500-400 cm^{-1} .

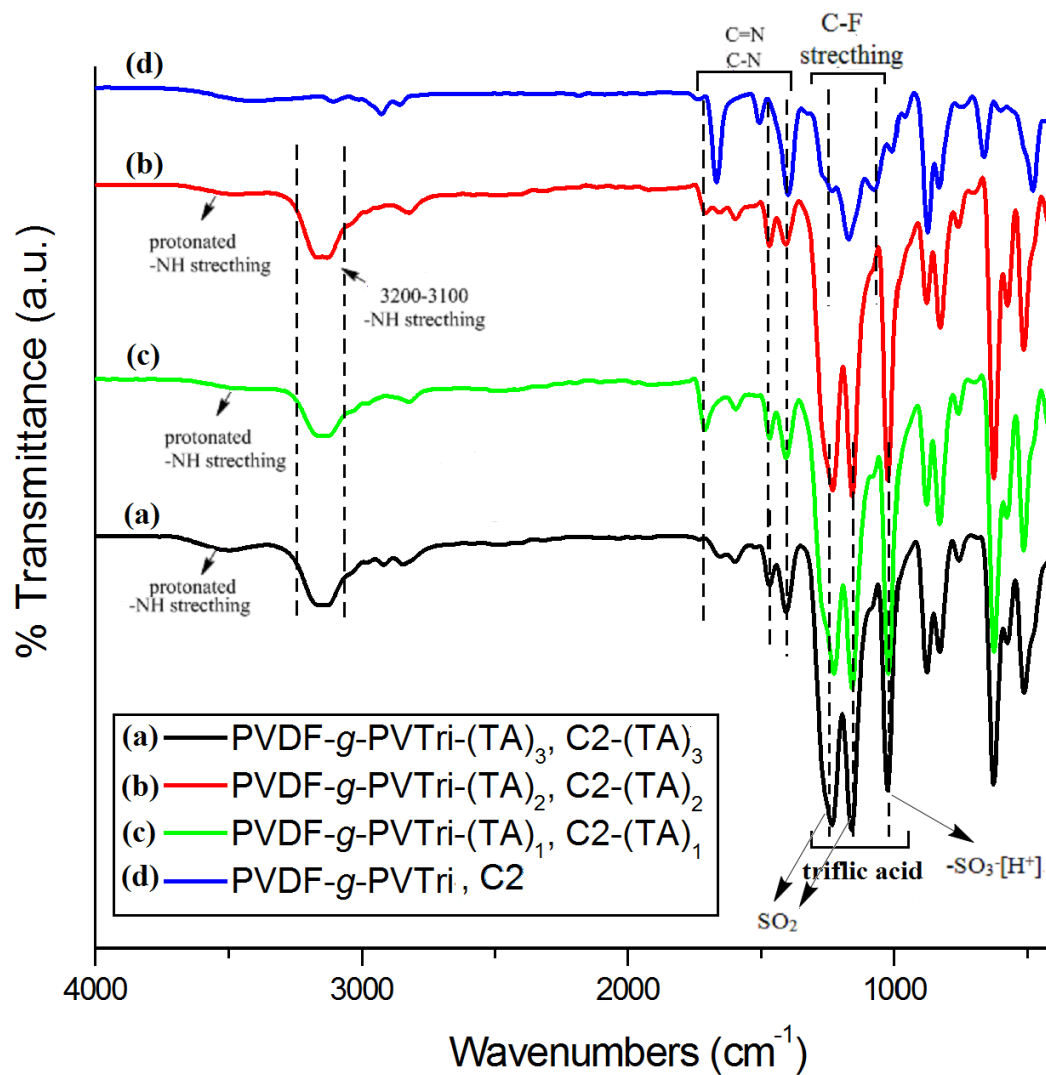


Figure 3.127 FTIR spectra of PVDF-*g*-PVTri (C2), and acid-doped PVDF-*g*-PVTri-(TA)_x (x=1.0, 2.0 and 3.0) graft copolymer membranes.

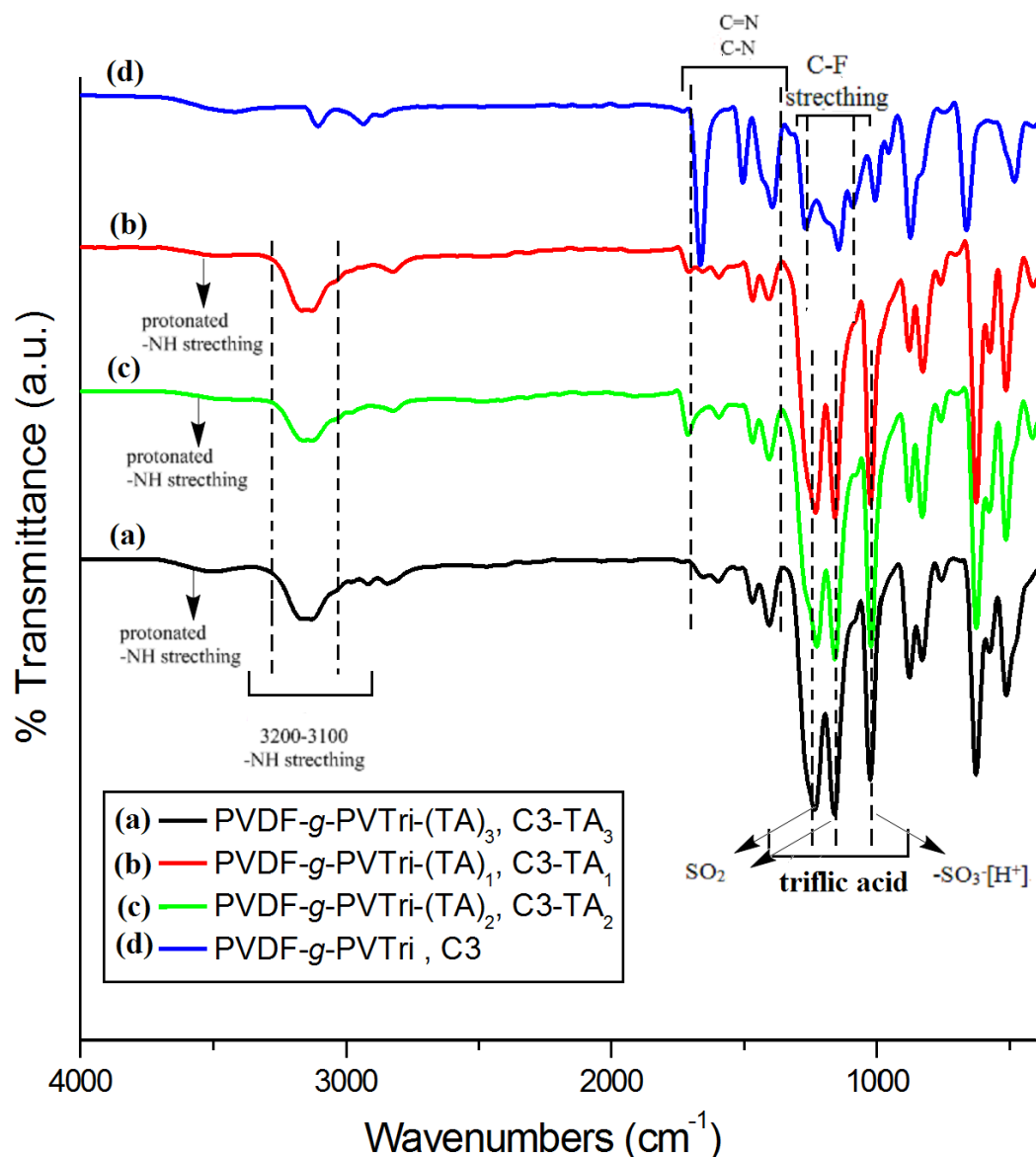


Figure 3.128 FTIR spectra of PVDF-*g*-PVTri (C3), and acid-doped PVDF-*g*-PVTri-(TA)_x (x=1.0, 2.0 and 3.0) graft copolymer membranes.

3.8.2 ¹H-NMR analysis

The successful graft copolymerization was confirmed using ¹H-NMR spectroscopy. The representative ¹H-NMR spectra of pristine PVDF and the synthesized PVDF-*g*-PVTri (C1, C2, C3) graft copolymers are shown in Fig.3.129. For all samples, the peaks of solvent (DMSO-*d*₆) and water (H₂O) appeared at 2.51 and 3.37 ppm, respectively (Sasa et al., 2013; Golcuk et al., 2013). The ¹H-NMR spectrum showed that there are two well-known peaks at the chemical shifts of about 2.90 (a) and 2.15 ppm

(d) due to the methylene groups in $-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-$ and $-\text{CF}_2-\text{CH}_2-\text{CH}_2-\text{CF}_2-$ sequences appearing in the normal tail-to-head and reversed tail-to-tail VDF additions (Arslantas et al., 2014; Sasa et al., 2013; Golcuk et al., 2013). Compared to the spectrum of PVDF, an obvious additional peak at around 8.47 and 7.25 ppm in the spectrum of all PVDF-*g*-PVTri graft copolymers was observed, which was ascribed to -CH proton of the triazole ring (b and c) in PVTri graft chains. The presence of these new peaks also indicates that PVTri has been successfully grafted onto PVDF main chains (Sinirlioglu et al., 2014b). The grafting degree (GD) of PVTri in the graft copolymer can also be calculated from the ^1H -NMR spectra by using the equation (3.2):

$$\text{Grafting Degree} = \frac{A(\text{b,c})}{A(\text{a,d})} \times 100 \quad (3.2)$$

where A(a,d) are the integral areas of the characteristic peak (a,d) of the PVDF main chain (used as reference peak) and -CH proton of the triazole ring (b,c) of PVTri, respectively.

The GD values of PVDF-*g*-PVTri graft copolymers calculated from ^1H -NMR spectra were summarized in Table 3.20. It was found that the grafting degree of PVDF-*g*-PVTri copolymer increases from 21.30 to 47.22 % with the increase of VTri concentration. A higher monomer concentration provided more chances for the free radicals on PVDF chains to contact with the PVDF chain and monomer, and thus a higher grafting degree was obtained. From the ^1H -NMR spectrum, the integration ratio of the protons confirmed that PVTri has been successfully grafted onto PVDF main chains as depicted in Fig.3.129 (Sinirlioglu et al., 2014b).

^{13}C -NMR spectra of PVDF and the synthesized PVDF-*g*-PVTri (C1-C3) graft copolymers are represented in Fig. 3.130. The peaks at around 20 and 45 ppm are assigned to the $-\text{CH}_2$ carbon of the PVDF main chains. The peaks in the range of 118 and 125 ppm belong to $-\text{CF}_2$ carbon of the PVDF main chains. The characteristic carbon peaks of the triazole ring are near 145 and 155 ppm and the signals corresponding to the carbon of the polymer backbone appear at 40 and 55 ppm (Sinirlioglu et al., 2014b).

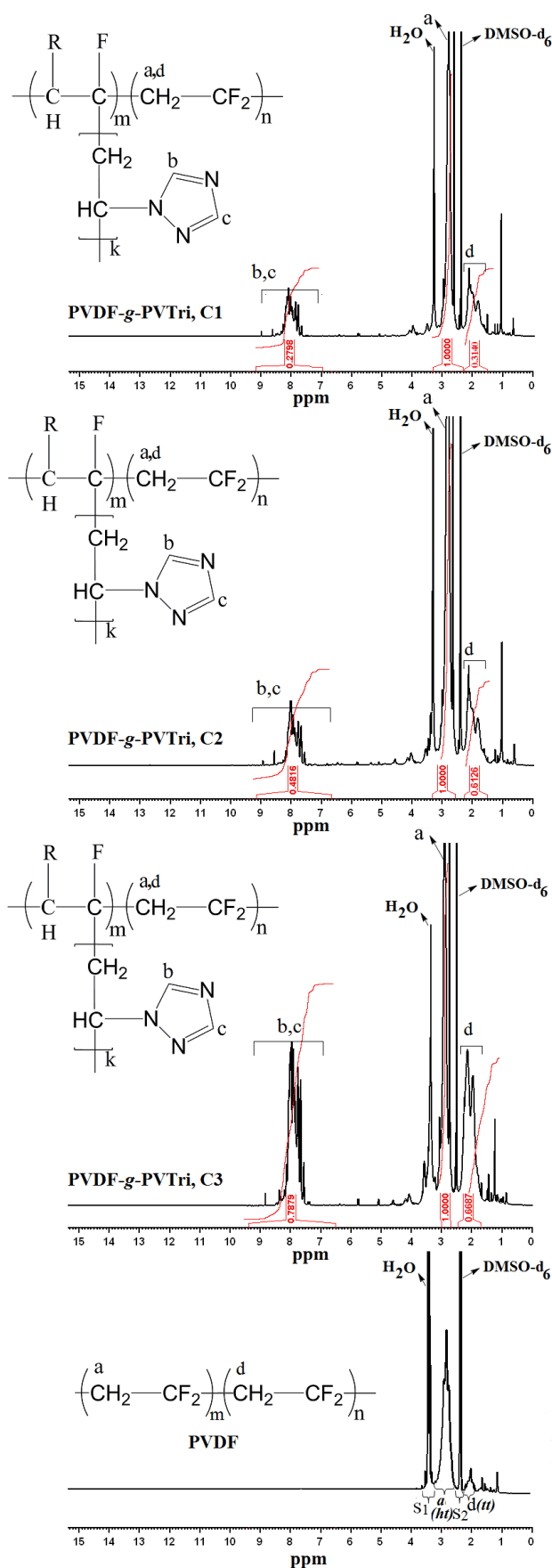


Figure 3.129 ^1H -NMR spectra (in the range of 0-16 ppm) of PVDF and, PVDF-*g*-PVTri copolymers with different weight ratios in the reaction system recorded in DMSO-d_6 .

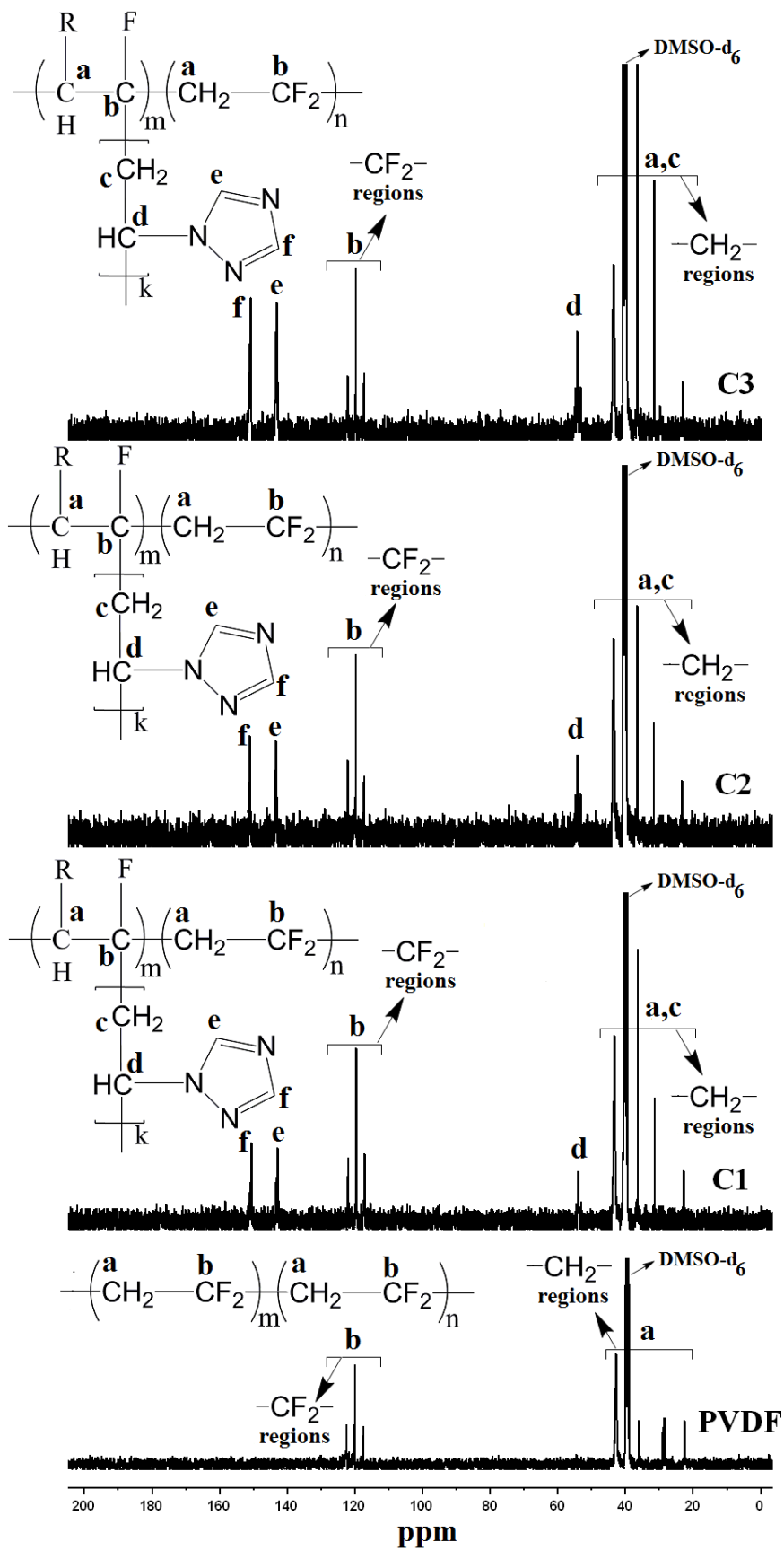


Figure 3.130 ^{13}C -NMR spectra of PVDF and, PVDF-*g*-PVTri copolymers with different weight ratios in the reaction system recorded in DMSO-d_6 .

3.8.3 Thermal Stability

Thermal stability is an important property of polymer electrolytes during application in PEMFCs. The thermal properties of all samples were investigated with TGA and DSC. Prior to the analysis, the samples were dried under vacuum at 80 °C for 24 h and stored in a glove box. The thermal stabilities of base pristine PVDF, PVDF-*g*-PVTri (C1), acid doped PVDF-*g*-PVTri-(TA)_x (x=1.0, 2.0 and 3.0) graft copolymer membranes were studied by TGA as shown in Fig. 3.131. PVDF showed excellent thermal stability up to 450 °C. PVTri homopolymer was reported to be thermal stability at least 350 °C (Celik et al., 2008c). After 350 °C, a remarkable weight loss in a single step originated from the thermal decomposition of triazole groups and the polymer backbone. The TGA curves of PVDF-*g*-PVTri (C1) graft copolymer membrane showed a satisfactory thermal stability up to 390 °C. 25 % of PVDF-*g*-PVTri (C1) graft copolymer membrane decomposes between 390 and 460 °C because of degradation of PVTri, after 470 °C, second weight loss region occurs because of degradation of PVDF (Sinirlioglu et al., 2014b). After doping the PVDF-*g*-PVTri polymer membrane with triflic acid, the thermal stability of the membranes decrease. All acid doped membranes, PVDF-*g*-PVTri-(TA)_x, (C1-TA_x), are thermally stable up approximately 310 °C. For all acid doped samples, there is a minor decomposition (10 % of the samples) at around 230 °C and major weight loss occurs between 350 and 410 °C which presumably derives from the decomposition of the polymer electrolyte main chain and PVDF backbone (Sinirlioglu et al., 2014b). PVDF-*g*-PVTri (C2) graft copolymer membrane exhibited a thermal stability up to 370 °C. 30 % of PVDF-*g*-PVTri (C2) graft copolymer membrane decomposes between 400 and 460 °C because of degradation of PVTri, after 470 °C, second weight loss region occurs because of degradation of PVDF. Upon doping of PVDF-*g*-PVTri (C2) graft copolymer with triflic acid, it exhibited a thermal stability up to 320 °C, after which it began to degrade (Fig. 3.132). PVDF-*g*-PVTri (C3) graft copolymer membrane was stable at least 340 °C. 40 % of PVDF-*g*-PVTri (C3) graft copolymer membrane breaks down between 380 and 420 °C because of degradation of PVTri, after 450 °C, second weight loss region occurs because of degradation of PVDF. Upon doping of PVDF-*g*-PVTri (C3) graft copolymer with triflic acid (TA), it exhibited a thermal stability up to 315 °C, after which it began to degrade (Fig. 3.133) (Sinirlioglu et al., 2014b).

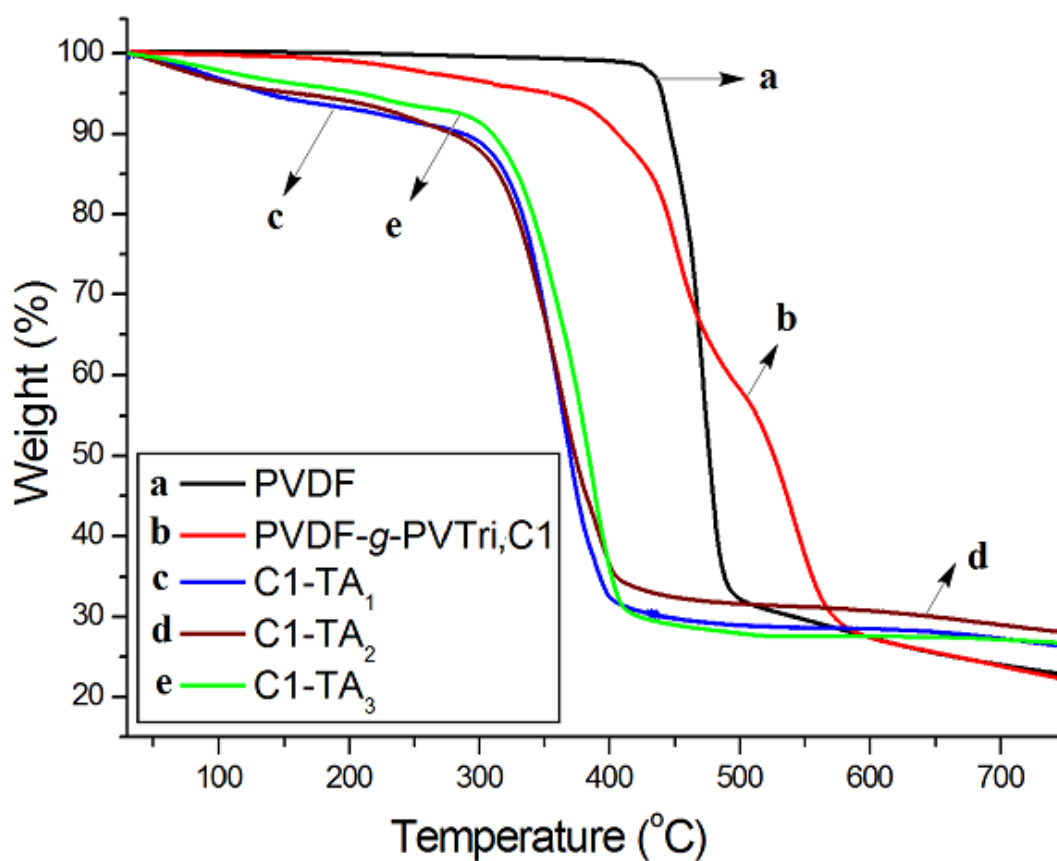


Figure 3.131 TG thermograms of PVDF powder, PVDF-*g*-PVTri (C1) and PVDF-*g*-PVTri-(TA)_x ($x=1.0, 2.0$ and 3.0) (C1-TA_x) membranes at a heating rate of 10 °C/min in inert atmosphere.

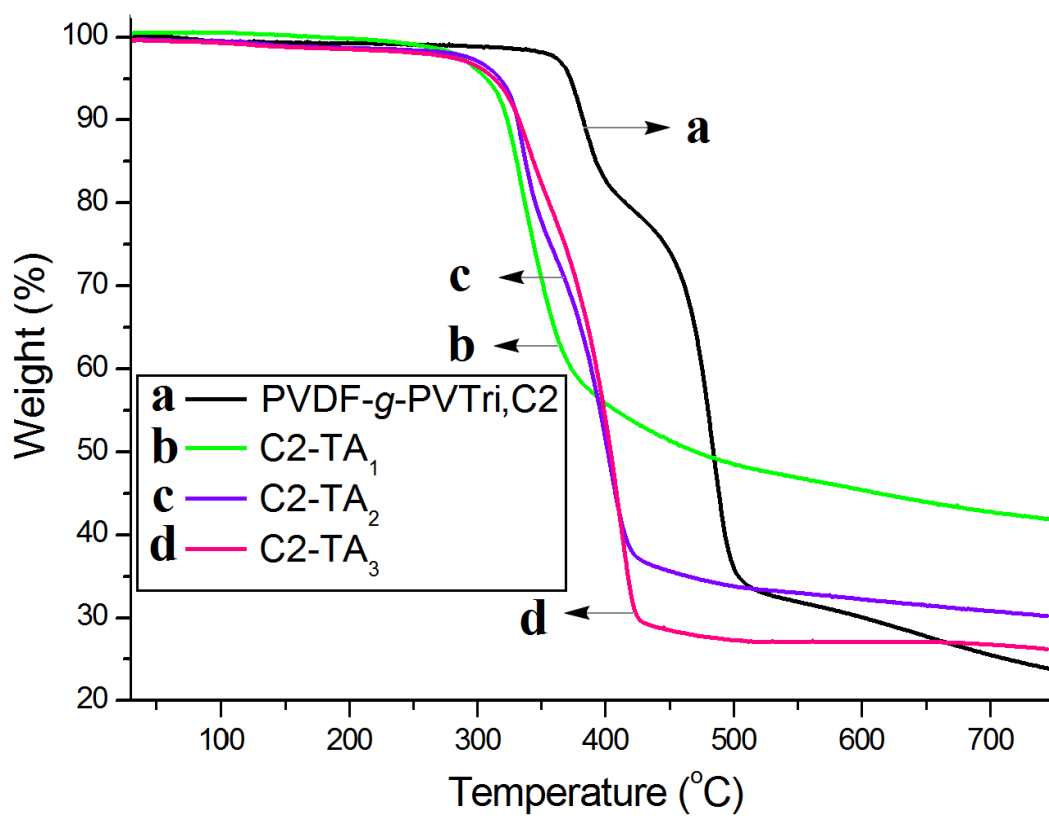


Figure 3.132 TG thermograms of PVDF-*g*-PVTri (C2) and PVDF-*g*-PVTri-(TA)_x (x=1.0, 2.0 and 3.0) (C2-TA_x) membranes at a heating rate of 10 °C/min in inert atmosphere.

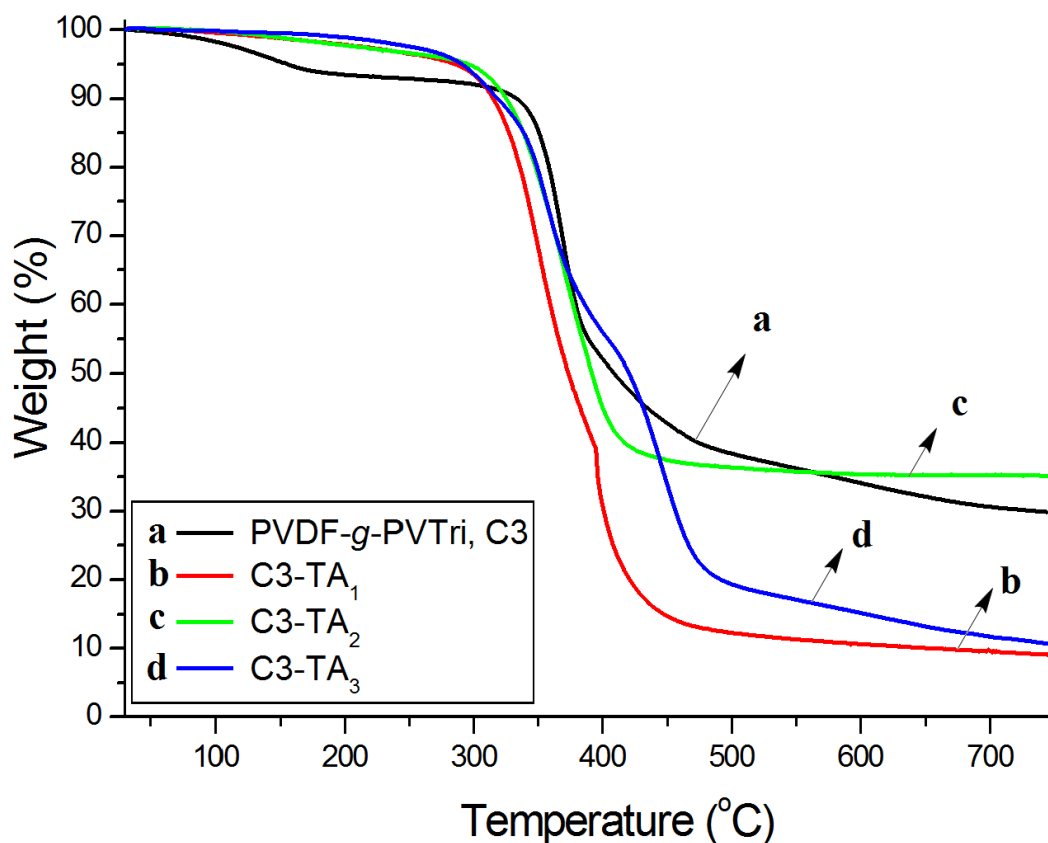


Figure 3.133 TG thermograms of PVDF-*g*-PVTri (C3) and PVDF-*g*-PVTri-(TA)_x (x=1.0, 2.0 and 3.0) (C3-TA_x) membranes at a heating rate of 10 °C/min in inert atmosphere.

The DSC measurements were carried out under inert atmosphere at a scan rate of 10 °C/min and the second heating curves were evaluated. Previously, the glass transition temperatures (T_g) of pure PVTri and PVDF were reported as 165 °C and -50 °C, respectively (Tang et al., 2011; Celik and Bozkurt, 2008c). The melting point (T_m) of PVDF powder was observed at 158.3 °C while the T_g could not be detected due to incapability of the device to operate below -30 °C (Sinirlioglu et al., 2014b). For the modified PVDF membranes, the T_m was observed due to the presence of ordered PVDF regions. For PVDF-*g*-PVTri (C1-C3) graft copolymers, a T_g might have been observed between 165 °C and -50 °C, however, no T_g could be detected. They only exhibited melting points (T_m) at approximately 157.2, 156.6 and 156.2 °C, respectively (Sinirlioglu et al., 2014b) (Fig. 3.134).

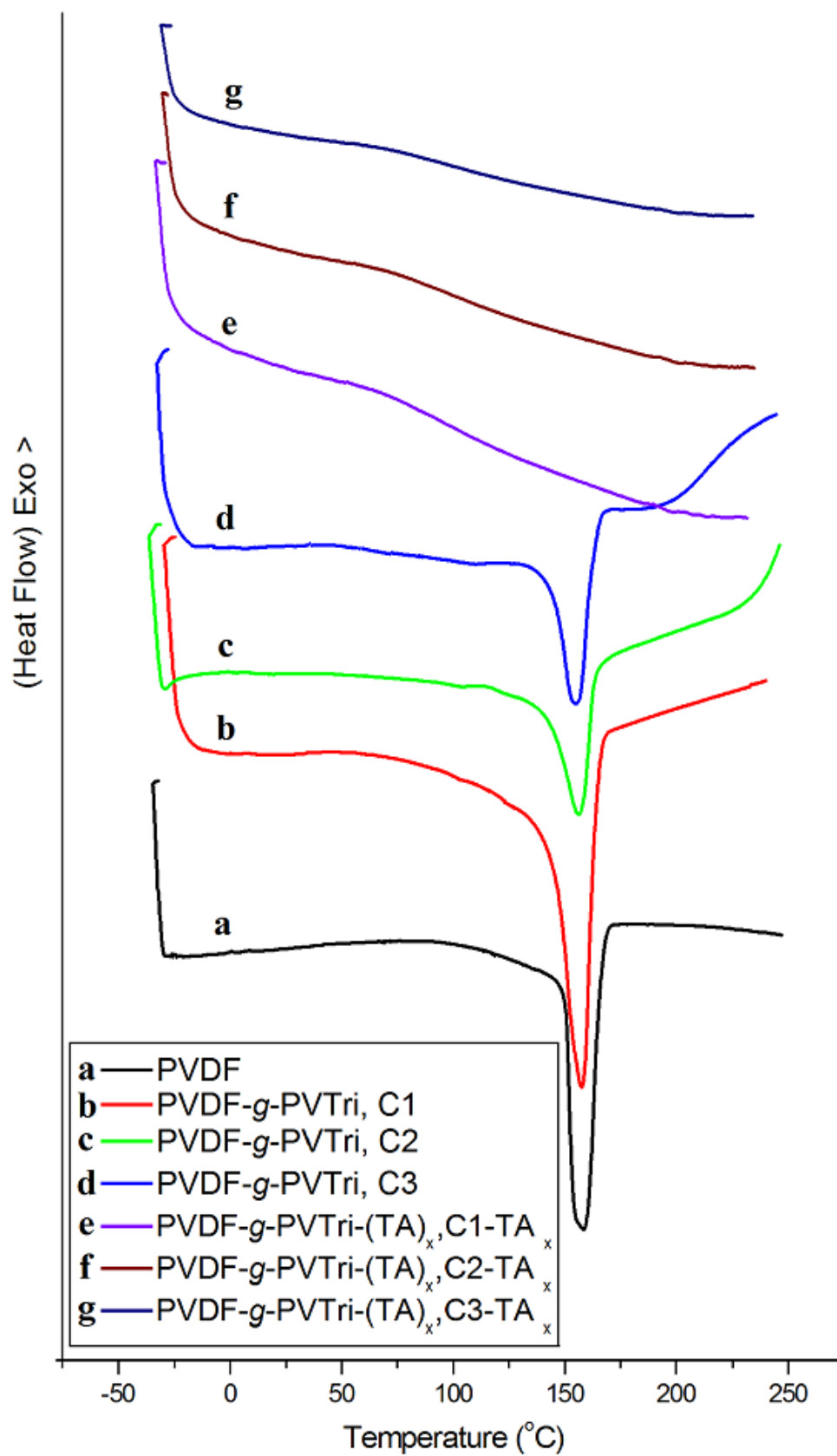


Figure 3.134 DSC thermograms of PVDF, PVDF-*g*-PVTri (C1, C2, C3) graft copolymers, all acid doped PVDF-*g*-PVTri-(TA)_x (x=1.0, 2.0 and 3.0) membranes recorded under N₂ atmosphere at a heating rate of 10 °C/min.

3.8.4 X-ray Diffraction (XRD)

The X-ray diffraction (XRD) measurement is a useful method to investigate the crystallinity of structure for PVDF and PVDF based membranes. Fig. 3.135 represents the XRD pattern of pure PVDF powder and PVDF-*g*-PVTri (C1-C3) graft copolymers. PVDF is a polymorphic, semi-crystalline polymer showing at least four different forms such as α , β , γ , δ and ϵ (Dong et al., 2013; Glaub et al., 2013). The peak obtained at around $2\theta = 18.7^\circ$, 20.0° , and 26.4° reflect α -crystal structure which can be indexed α (020), α (110) and α (021) for pure PVDF. The peaks at $2\theta = 34.8^\circ$ and 36.2° relate to the (200) plane of α -phase of PVDF and the peak at $2\theta = 39.2^\circ$ refers to the combined (201) and (111) reflections of the β -phase due to molecular defects caused by head-head and tail-tail sequences (Mahadeva et al., 2013; Arthanareeswari et al., 2013).

After grafting of PVTri on PVDF powder, the characteristic peaks at around $2\theta = 18.7^\circ$ and 26.4° of α -phase of PVDF disappeared completely for PVDF-*g*-PVTri (C1-C3) graft copolymers, respectively. This result revealed that the original crystalline structure of pure PVDF was seriously destroyed (Sinirlioglu et al., 2014b). The crystallinity of the graft copolymer membranes decreases when the PVTri content was increased into PVDF-*g*-PVTri. As can be seen, the peaks from XRD curves get decreased with the increasing of PVTri polymer which implies increase of amorphous nature of the obtained PVDF-*g*-PVTri (C1, C2 and C3) graft copolymers (Mahadeva et al., 2013; Arthanareeswari et al., 2013). For PVDF powder, the diffraction peaks are sharp owing to crystallite size which was calculated approximately 5.0 ± 2.0 nm according to Scherrer's equation (Sakai et al., 2010). After grafting of PVTri on alkaline treated PVDF, the crystallite size decreased with the increasing of PVTri polymer which implies increase of amorphous nature of the obtained PVDF-*g*-PVTri (C1-C3) graft copolymers (Sinirlioglu et al., 2014b). The XRD data showed that the crystallinity and crystallite size of pure PVDF reduced after grafting of PVTri. The results are summarized in Table 3.21.

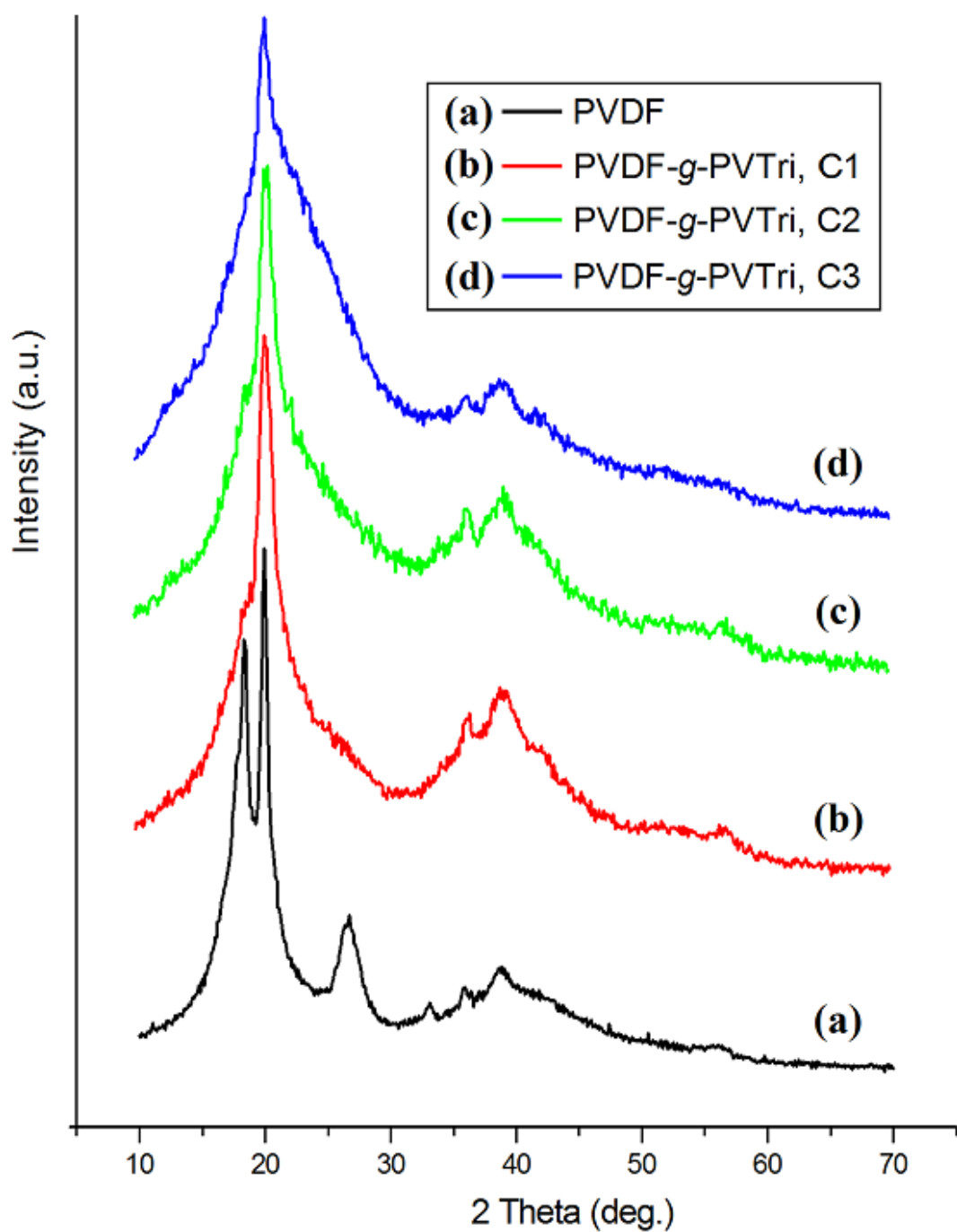


Figure 3.135 XRD patterns of (a) PVDF, (b) PVDF-*g*-PVTri (C1), (c) PVDF-*g*-PVTri (C2), (d) PVDF-*g*-PVTri (C3) graft copolymer membranes.

Table 3.21 The mean RMS roughness values with the standard deviations and the crystallite size of PVDF powder and PVDF-*g*-PVTri (C1-C3) copolymer membranes.

Samples	Roughness (nm) ^a	crystallite size (nm) ^b
PVDF (powder)	-----	5.0 ± 2.0
PVDF- <i>g</i> -PVTri, C1	139.04 ± 25.17	4.0 ± 2.0
PVDF- <i>g</i> -PVTri, C2	72.33 ± 10.91	3.0 ± 1.5
PVDF- <i>g</i> -PVTri, C3	25.89 ± 4.20	2.8 ± 1.4

a: calculated from AFM, **b:** calculated from XRD.

3.8.5 Morphology

The scanning electron microscopy (SEM) produces detailed photographs that provide important information about the surface structure. Surface morphologies of the virgin PVDF, PVDF-*g*-PVTri (C1-C3) graft copolymers and acid doped PVDF-*g*-PVTri-(TA)_x membranes were investigated by SEM. There is formation of a smooth surface of the pristine PVDF and a number of pores appear as depicted in Fig. 3.136. The morphology of films appears that the number of pores increases with the raising of the PVTri ratio, which leads to a decrease of porosity (Sinirlioglu et al., 2014b). These results agree with the phenomena of pure PVDF reported in previous work (Gregorio et al., 2008). It is presented that all of the samples exhibit uniform and porous structures. In addition, images (e,f,h,i) showed heterogeneity, which might be possibly due to salt formation between triflic acid-base (triazole groups) units while in image (b,d,g) at the nanometer scale, formation of a highly porous surface was observed (Sinirlioglu et al., 2014b; Dong et al., 2013; Lepit et al., 2012). These results confirmed that vinyl triazole (VTri) monomer is grafted onto the PVDF powder (b,d,g). In all samples, the images showed single phase formation. This result demonstrated that there was no agglomeration or phase separation at the nanometer level. The images of acid doped membranes (c, e and h) show some small cracks due to solvent evaporation in membrane preparation (Sinirlioglu et al., 2014b).

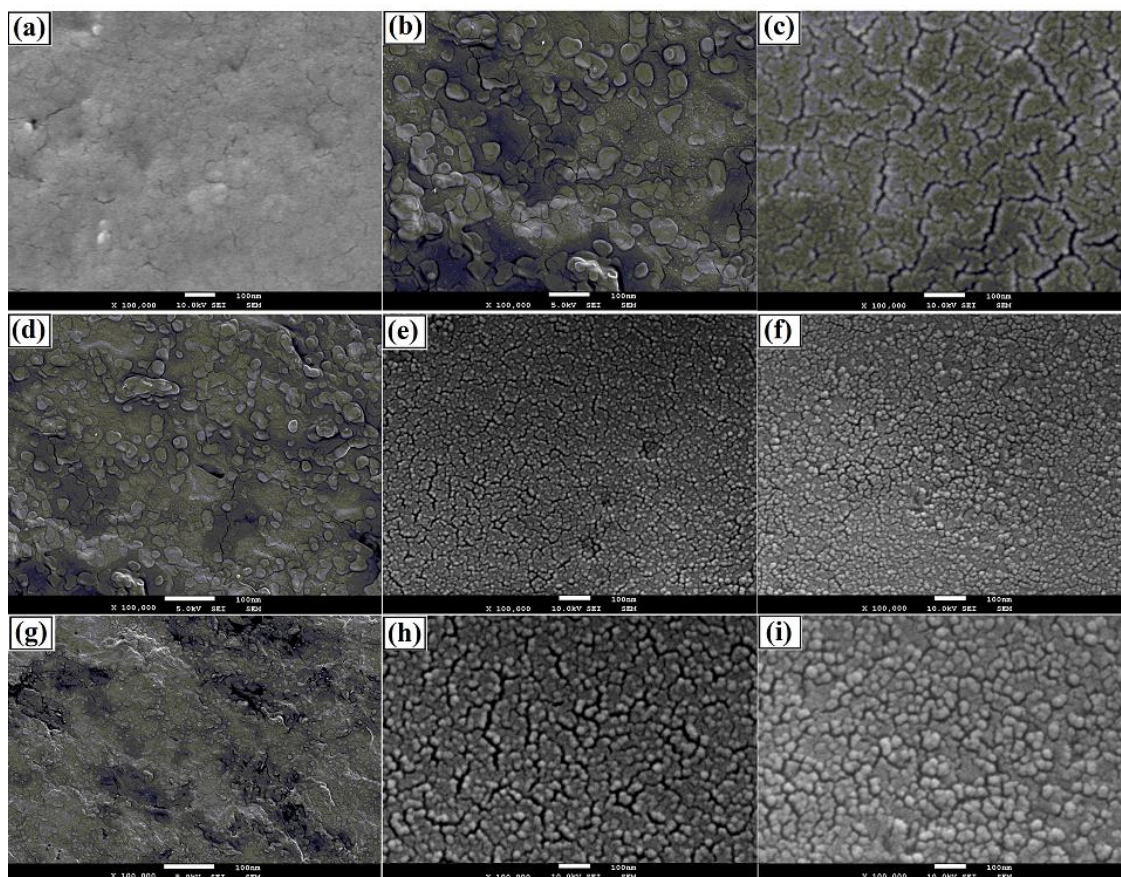


Figure 3.136 SEM images of the surface of (a) PVDF powder, (b) PVDF-*g*-PVTri (C1), (c) PVDF-*g*-PVTri-(TA)₃ (C1-TA₃), (d) PVDF-*g*-PVTri (C2), (e) PVDF-*g*-PVTri-(TA)₁ (C2-TA₁), (f) PVDF-*g*-PVTri-(TA)₃ (C2-TA₃), (g) PVDF-*g*-PVTri (C3), (h) PVDF-*g*-PVTri-(TA)₁ (C3-TA₁) and (i) PVDF-*g*-PVTri-(TA)₃ (C3-TA₃) graft copolymer membranes at 100 nm scale level by 100,000X magnification, respectively.

3.8.6 Atomic Force Microscopy (AFM)

AFM was used for the determination of phase morphology, heterogeneity or homogeneity of the membranes. In addition, the surface roughness of the membranes was determined using AFM. The selected AFM images of membranes are presented in Fig. 3.137. The mean values of surface roughness of PVDF-*g*-PVTri (C1, C2, C3) graft copolymer membranes and PVDF powder are listed in Table 3.21. 10×10 μm images were obtained at a resolution of 512 x 512 points within the range of 0.5-0.8 Hz scan rate and were subjected to first-order flattening. Surface roughness was calculated by using the Root Mean Square (RMS), that is, the standard deviation of the Z values within a given area, where Z_{ave} is the average, Z_i is the current Z value, and N is the number of points within the analyzed area (please see equation 2.4). It was noted that

the surface roughness depends on the curvature and size of the AFM tip and on the image processing. The RMS mean values and the standard deviations were obtained by analyzing at least 6 AFM images. The RMS roughness of the obtained graft copolymers (C1-C3) decreased from 139.04 nm to 25.89 nm when the PVTri amount was increased from 1 to 4 g (Table 3.21). Furthermore, for all the samples in Fig. 3.137, the images exhibit single phase formation and the membranes seem to be homogeneous at nanometer-scale level. This shows that the PVTri homopolymer was grafted and it uniformly dissipates onto PVDF. When the PVTri amount was increased from C1 to C3, formation of a highly smooth surface was observed at the nanometer scale. This results confirmed the SEM images (Figure 3.136 (b,d,g)) (Sinirlioglu et al., 2014b).

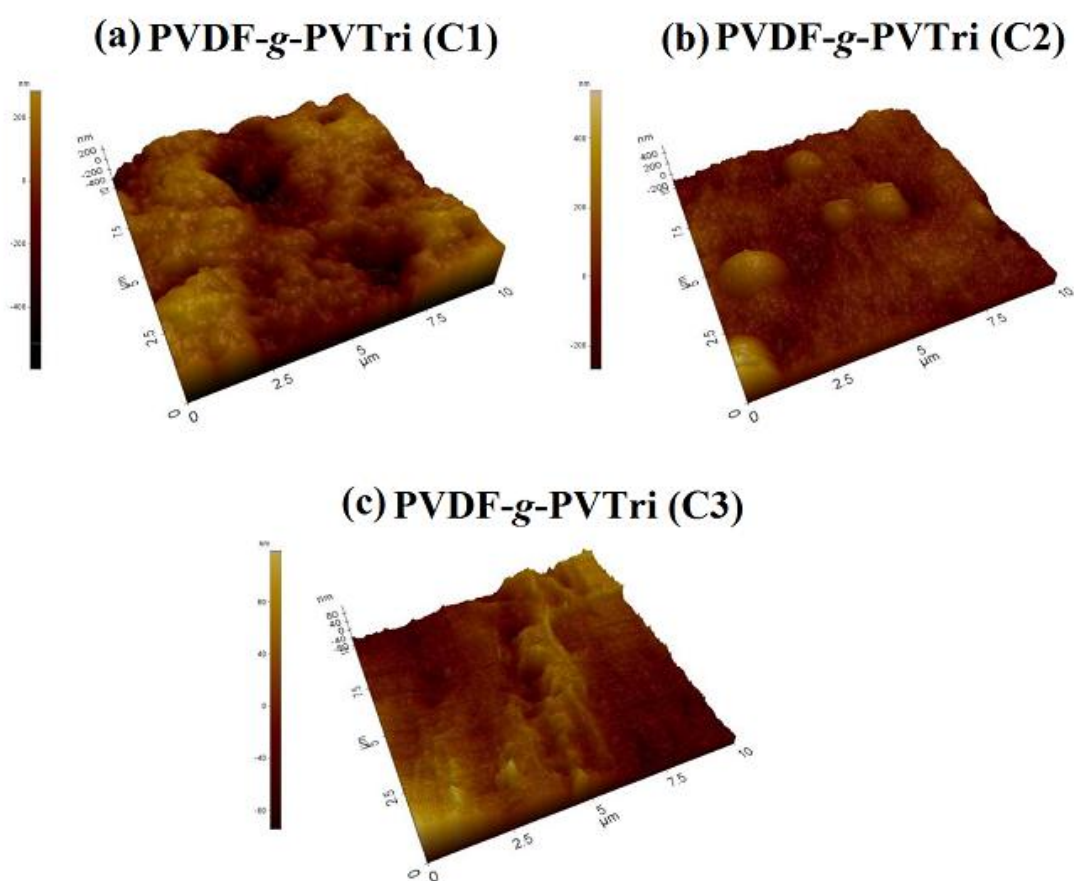


Figure 3.137 AFM pictures (3d) of (a) PVDF-*g*-PVTri (C1), (b) PVDF-*g*-PVTri (C2) and (c) PVDF-*g*-PVTri (C3) graft copolymer membranes.

3.8.7 Proton conductivity measurements

The proton conductivity of the membranes is the most essential properties to be studied for the potential application in fuel cell. The proton conductivities of all acid doped membranes were measured in the temperature range of 20 °C to 150 °C. The acid doped membranes was fixed between additional external parallel plate electrodes (between platinum blocking electrodes) to form a sandwich using the simple two-electrode method and impedance was measured by varying the temperature from 20 °C to 150 °C.

Fig. 3.138, Fig. 3.139, Fig. 3.140, Fig. 3.141, Fig. 3.142, Fig. 3.143, Fig. 3.144, and Fig. 3.145 show the AC conductivities of all PVDF-*g*-PVTri-(TA)_x membranes versus frequency at several temperatures. As expected the proton conductivity increases as temperature increases. At lower frequency regions, the conductivity increases with log frequency then leveled off which is due to electrode polarizations. The irregularities at the low frequency side correspond to polarization blocking the electrode-electrolyte interface and the conductivity increase at low temperature and high frequencies results from the regular dispersion in polymer electrolytes. Maximum proton conductivities of the obtained PEMs are listed in Table 3.22. It can be seen that as the amounts of triflic acid (TA) and VTri increase, the conductivity values increase as expected since both of them have a direct contribution in the conduction mechanism. In the anhydrous conditions, the highest maximum proton conductivity of PVDF-*g*-PVTri-(TA)₃ (C3-TA₃) was measured as 0.09 S/cm at 150 °C (Sinirlioglu et al., 2014b).

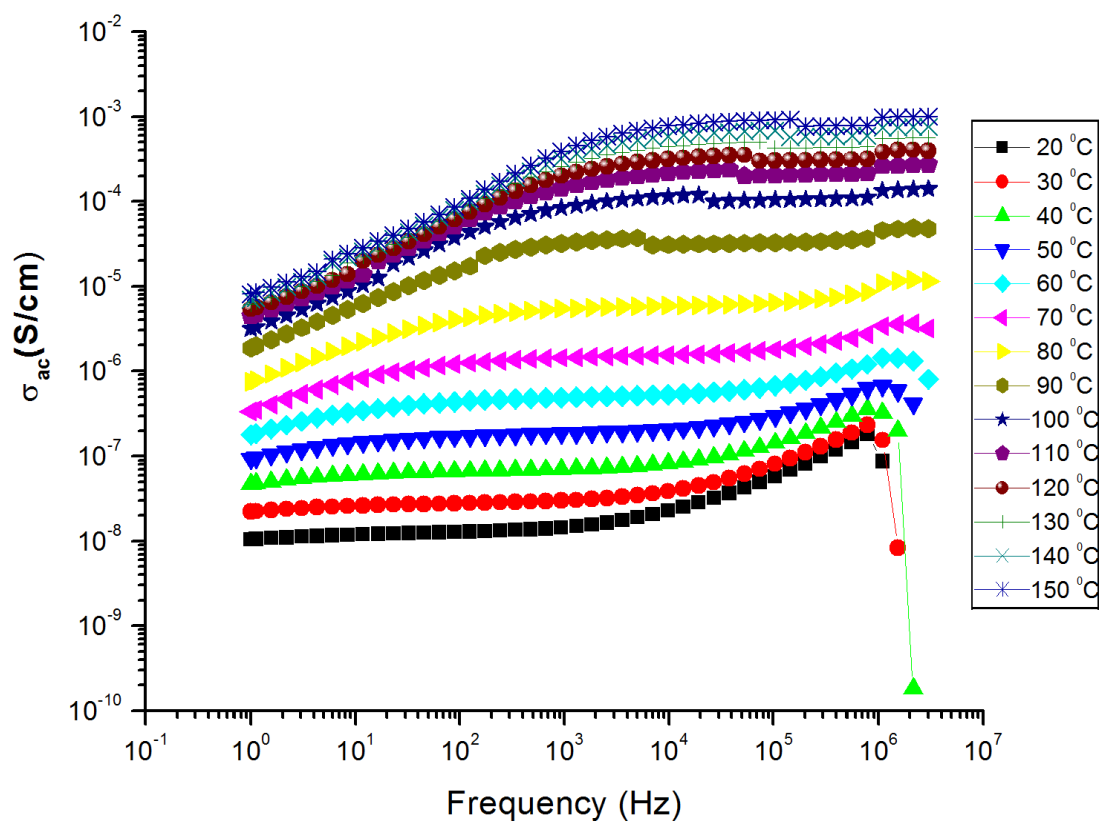


Figure 3.138 AC conductivity versus frequency of (C1-TA₁) copolymer membrane at several temperatures.

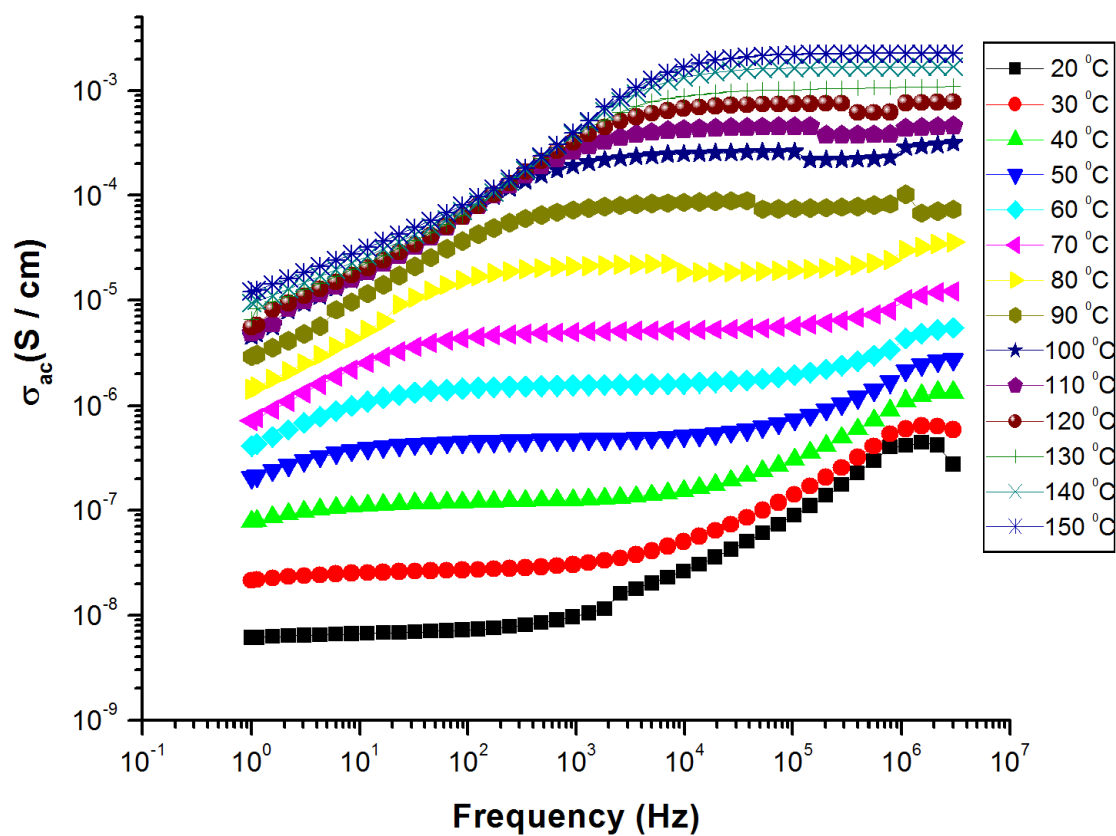


Figure 3.139 AC conductivity versus frequency of (C1-TA₂) copolymer membrane at several temperatures.

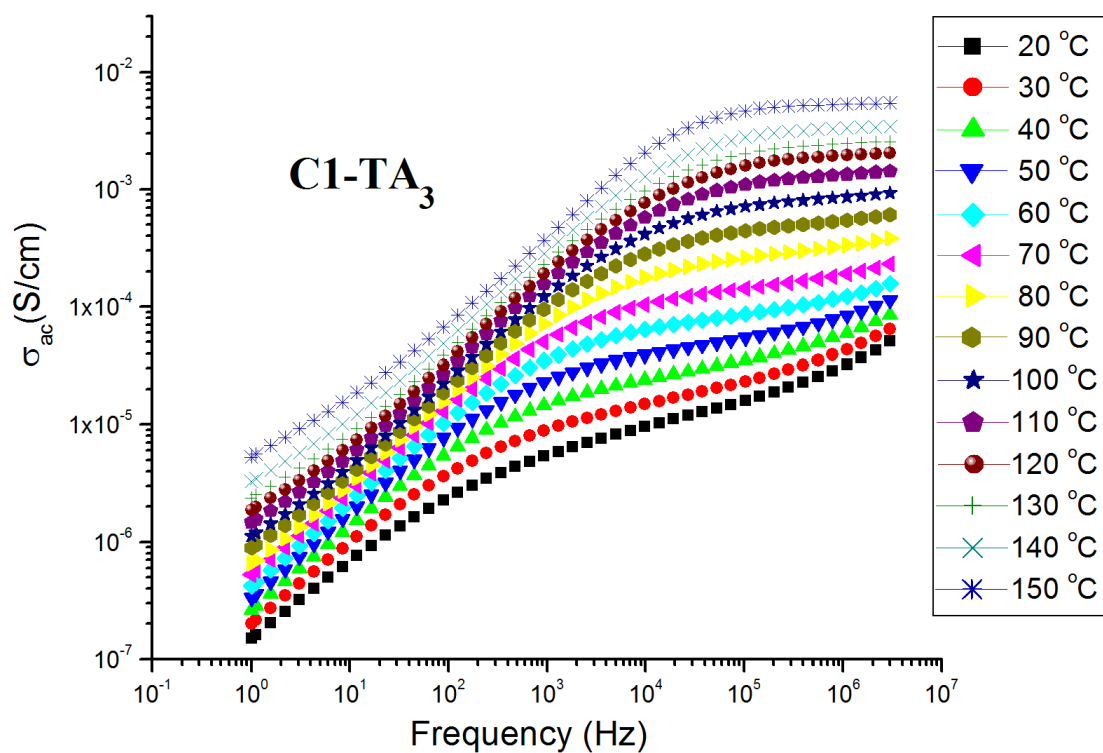


Figure 3.140 AC conductivity versus frequency of (C1-TA₃) copolymer membrane at several temperatures.

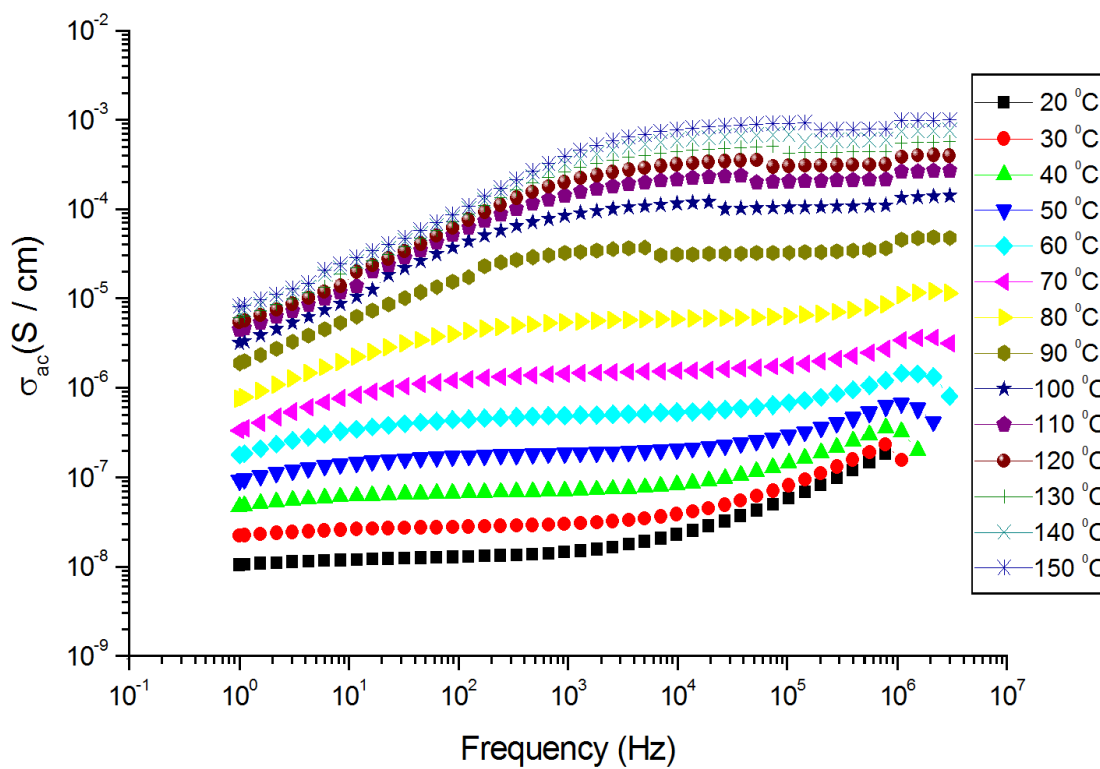


Figure 3.141 AC conductivity versus frequency of (C2-TA₁) copolymer membrane at several temperatures.

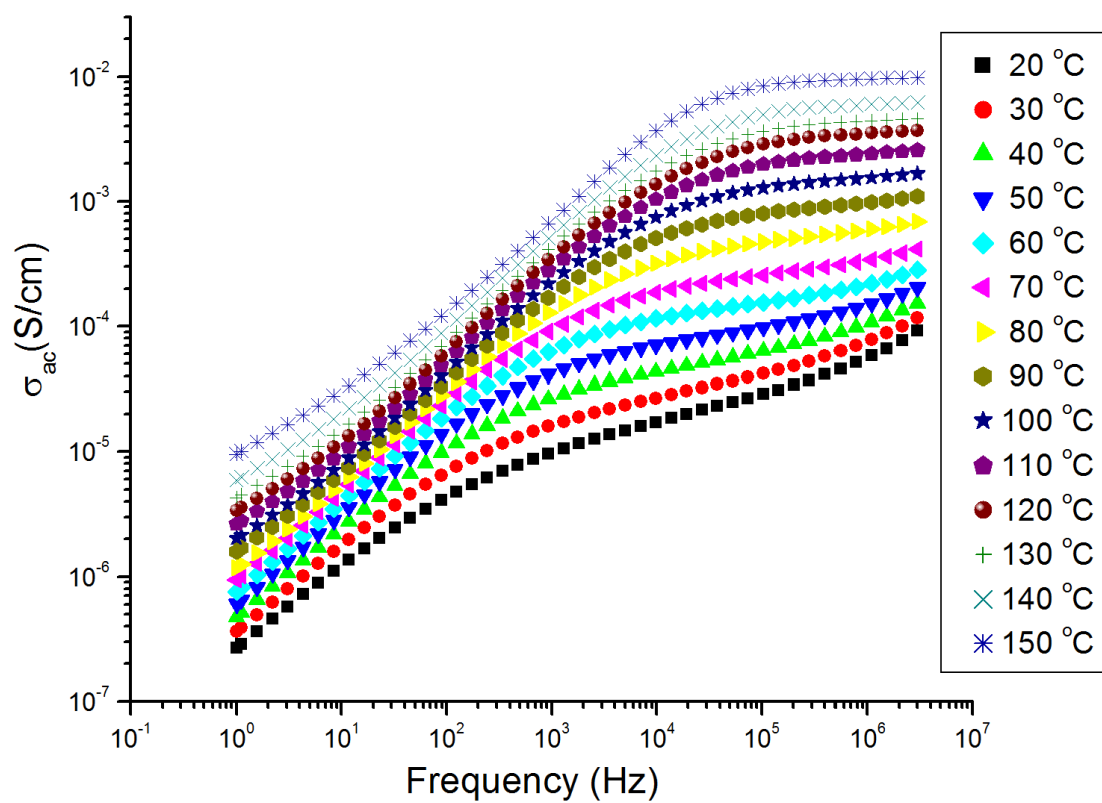


Figure 3.142 AC conductivity versus frequency of (C2-TA₂) copolymer membrane at several temperatures.

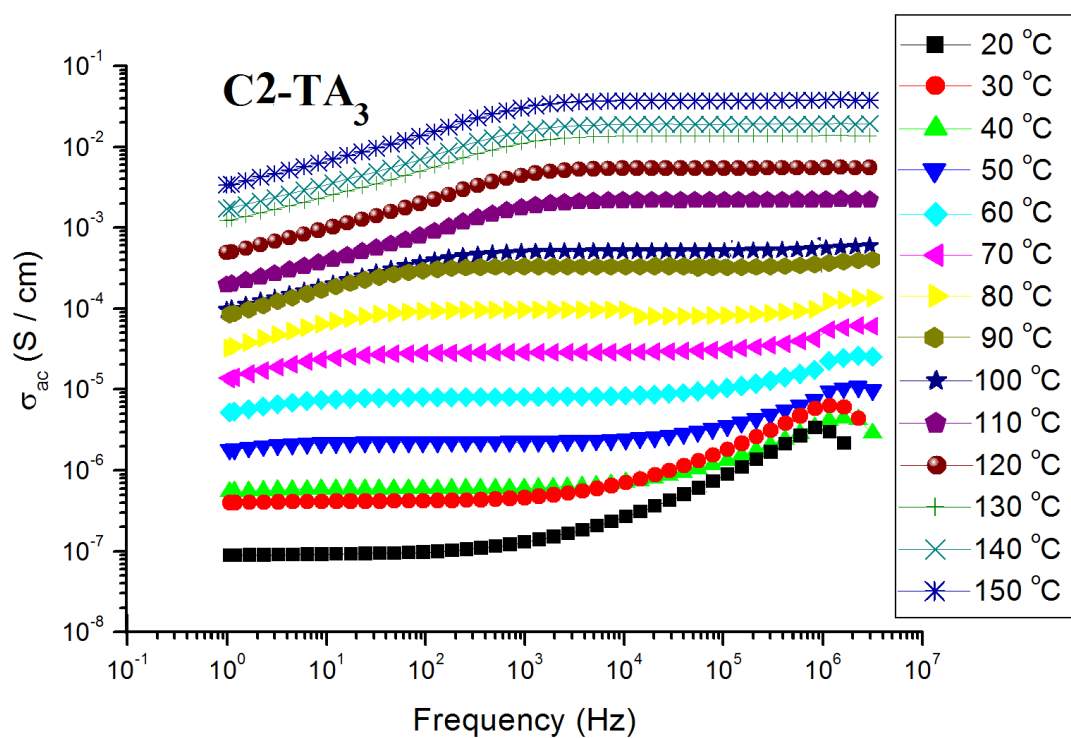


Figure 3.143 AC conductivity versus frequency of (C2-TA₃) copolymer membrane at several temperatures.

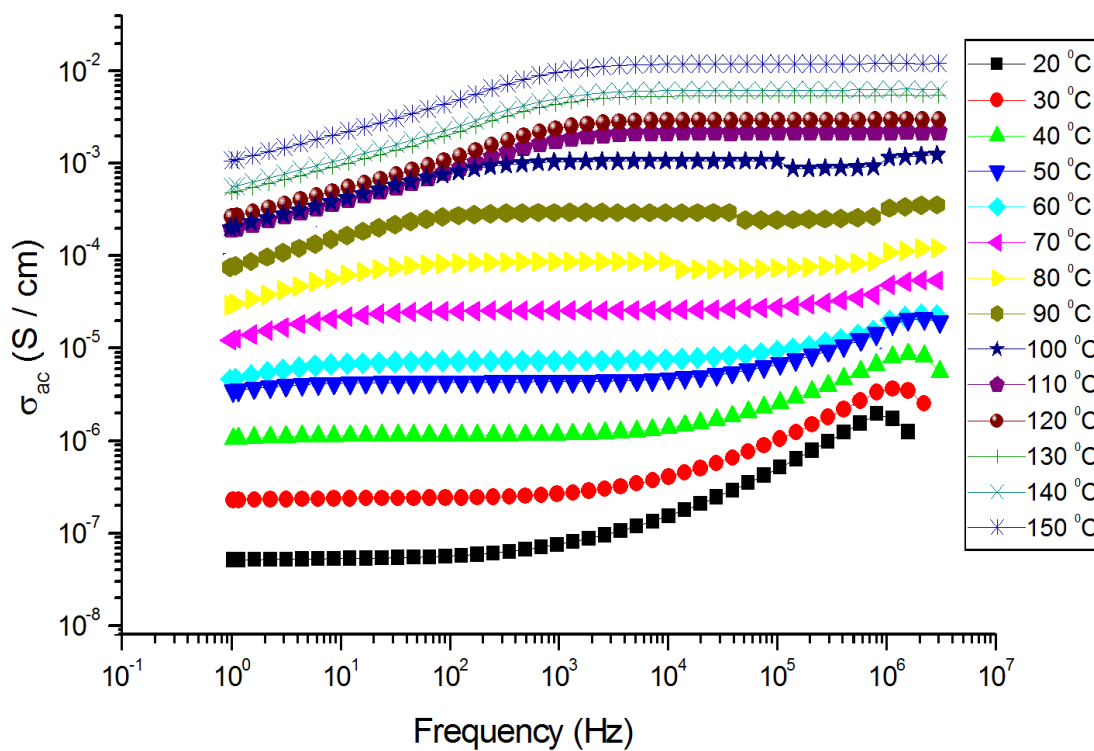


Figure 3.144 AC conductivity versus frequency of (C3-TA₁) membrane at several temperatures.

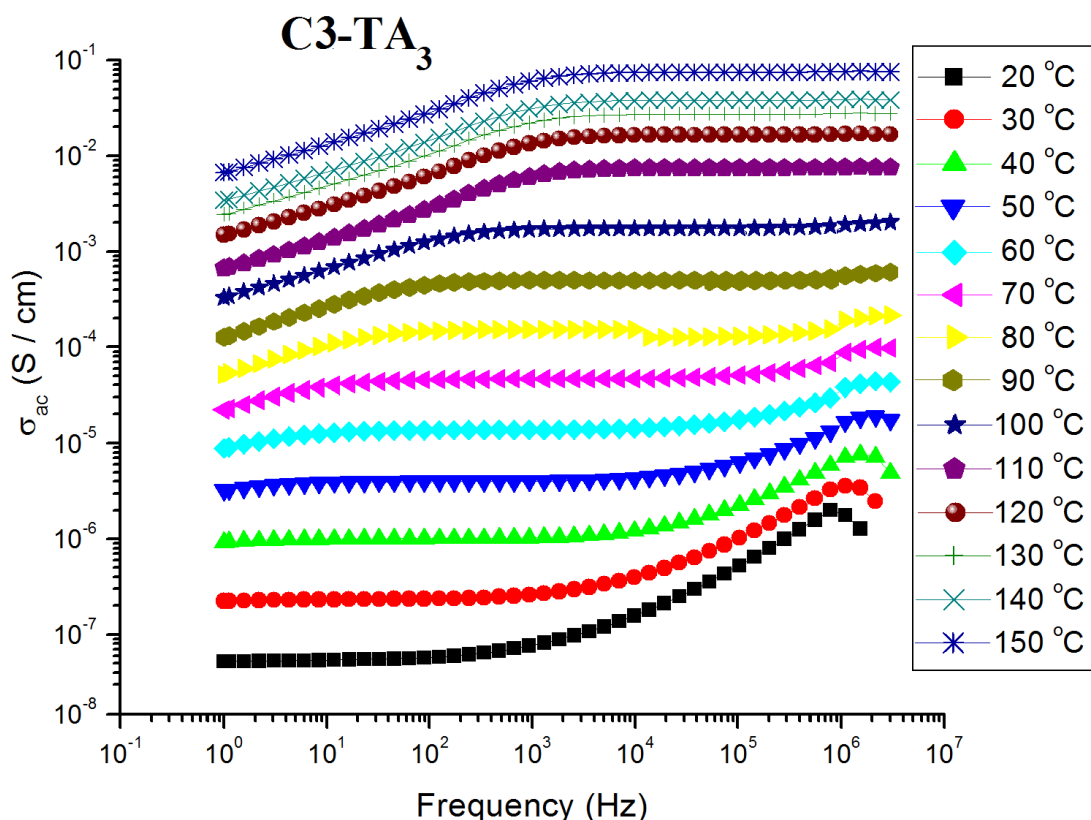


Figure 3.145 AC conductivity versus frequency of (C3-TA₃) membrane at several temperatures.

The DC conductivity (σ_{dc}) of the samples was derived from the plateaus of $\log \sigma_{ac}$ versus $\log F$ by linear fitting of the data. The DC conductivities of the samples were compared in Fig. 3.146. The conductivity isotherm illustrates that the DC conductivity depends on the temperature and doping ratio of TA. The DC curves are closer to linear type curves which can be explained with Arrhenius equation. Arrhenius behavior is generally observed in the matrices where during the measurement temperature range no T_g was observed and there is no change in linearity of DC curve. Herein, it can be said that the segmental motions have little contribution to the conductivity. In that grafted matrix the proton conductivity is carried out between triazole and triflic acid units. Since the triazole attachment and doping were performed in solution medium, we expect that a matrix with hydrophobic PVDF backbone and a channel with triazole units might have formed, in which triazole units interact with triflic acid molecules. Here, the acid ratio is not very high and we do not expect a Vehicular type proton conductivity but a Grotthous mechanism is proposed in that matrix (Fig. 3.147). Moreover, PVDF

provided a high thermally and mechanically stable matrix and good film formability (Sinirlioglu et al., 2014b).

Table 3.22 Doping ratio with TA and maximum proton conductivity values of PVDF and PVDF based membranes.

Sample Name	Doping ratio with TA	Max. Proton Conductivity (S/cm) at 150 °C
PVDF	-----	-----
PVTri	-----	1.13×10^{-7}
PVDF- <i>g</i> -PVTri, C1	-----	-----
PVDF- <i>g</i> -PVTri, C2	-----	-----
PVDF- <i>g</i> -PVTri, C3	-----	-----
PVDF- <i>g</i> -PVTri-(TA) ₁ (C1-TA ₁)	1:1	9×10^{-4}
PVDF- <i>g</i> -PVTri-(TA) ₂ (C1-TA ₂)	1:2	0.002
PVDF- <i>g</i> -PVTri-(TA) ₃ (C1-TA ₃)	1:3	0.005
PVDF- <i>g</i> -PVTri-(TA) ₁ (C2-TA ₁)	1:1	0.001
PVDF- <i>g</i> -PVTri-(TA) ₂ (C2-TA ₂)	1:2	0.011
PVDF- <i>g</i> -PVTri-(TA) ₃ (C2-TA ₃)	1:3	0.041
PVDF- <i>g</i> -PVTri-(TA) ₁ (C3-TA ₁)	1:1	0.012
PVDF- <i>g</i> -PVTri-(TA) ₂ (C3-TA ₂)	1:2	0.042
PVDF- <i>g</i> -PVTri-(TA) ₃ (C3-TA ₃)	1:3	0.09

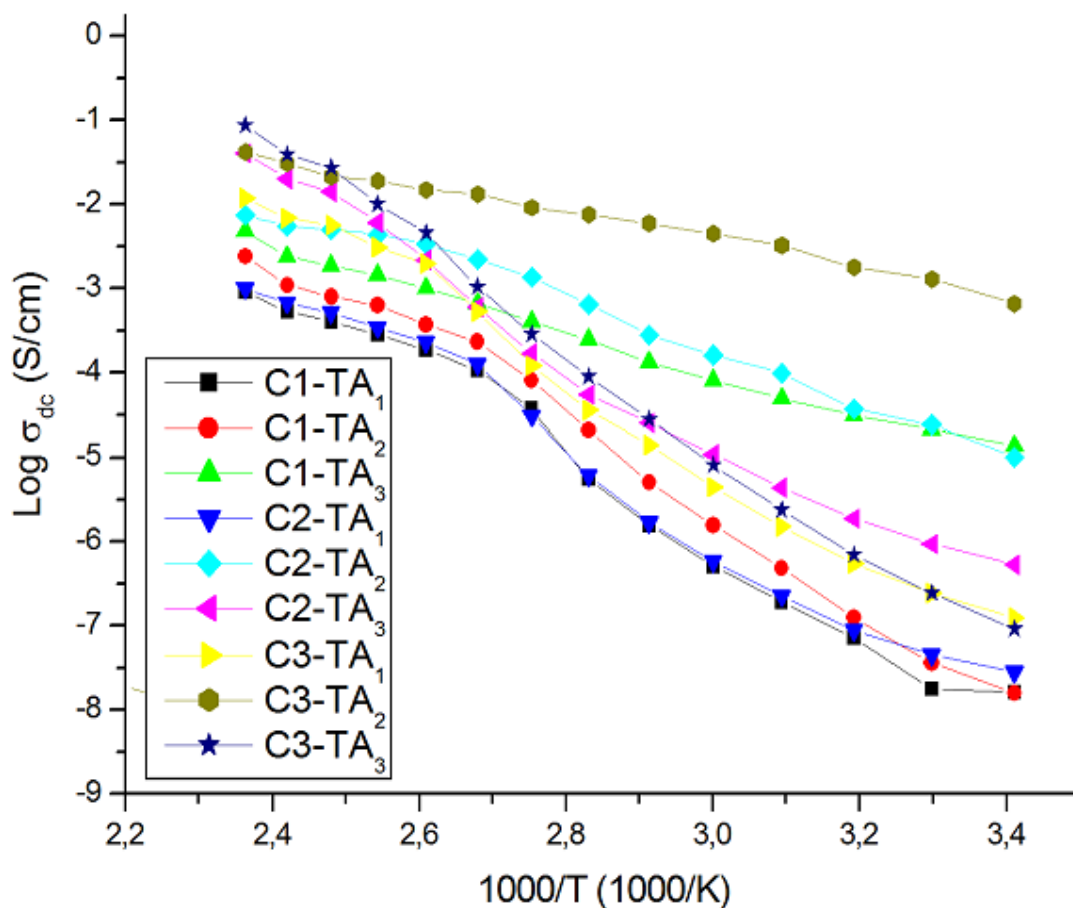


Figure 3.146 Variation of the DC proton conductivity of PVDF-*g*-PVTri-(TA)*x* (*x*=1.0, 2.0 and 3.0) membranes as a function of reciprocal temperature.

Recently, many researchers have tried to employ very different methods such as UV-light (Golcuk et al., 2013; Sasa et al., 2013), irradiation (Lepit et al., 2012; Liu et al., 2011; Fei et al., 2010) or ATRP methods (Sui et al., 2012; Meng et al., 2011; Liu et al., 2010; Roh et al., 2010; Kim et al., 2008) and alkaline treatment (Liu et al., 2013; Tang et al., 2009) to prepare polymer electrolyte membranes that consist of PVDF since it is cheaper than Nafion while similar in chemical nature to Nafion. The proton conductivity in these studies are based on the humidity content and consequently these membranes were not suitable for high temperature applications.

So far, very few studies of PVDF and azole based anhydrous PEM designs were reported (Arslantas et al., 2014; Sezgin et al., 2014, Golcuk et al., 2013; Sasa et al., 2013; Lepit et al., 2012). In these studies, a novel UV induced polymerization method

was employed in the grafting of styrene and 4-(chloromethyl)styrene onto partially fluorinated poly(vinylidene difluoride) (PVDF). Golcuk et al. reported the preparation of triazole doped poly(styrenesulfonic acid) grafted PVDF, PVDF-*g*-PSSA(Tri)₂, with a maximum proton conductivity of 5×10^{-5} S/cm at 150 °C and anhydrous conditions (Golcuk et al., 2013). In another work reported by Sasa et al., a maximum proton conductivity of 0.02 S/cm at 150 °C was found for triflic acid doped triazole-functional poly(chloromethyl styrene) grafted PVDF, PVDF-*g*-PCMS-Tri-1TA (Sasa et al., 2013). Sezgin et al. studied the synthesis of a graft copolymer consisting of 1-vinyl-1,2,4-triazole (VTri) and a PVDF base matrix under UV light in one step to achieve, PVDF-*g*-PVTri-(TA)_x, anhydrous PEMs. Arslantas et al. reported the preparation of triflic acid doped aminotetrazole-functional PVDF-*g*-PGMA-ATet anhydrous membranes, with a maximum proton conductivity of 0.011 S/cm at 150 °C and anhydrous conditions. Besides, Lepit et al. reported a maximum proton conductivity of 1×10^{-3} S/cm at 100 °C for 1-vinylimidazole and PVDF based PEMs prepared via radiation-induced grafting (Lepit et al., 2012). In the present study, the highest maximum proton conductivity of PVDF-*g*-PVTri-(TA)₃ (C3-TA₃) was measured as 0.09 S/cm at 150 °C, a superior conductivity value as compared to the afore-mentioned ones (Sinirlioglu et al., 2014b).

The pristine heterocyclic polymers generally show a low conductivity due to a weak dissociation of the heterocyclic species, most of the azole based anhydrous PEM reports use small strong acids to enhance the proton conductivity (Tang et al., 2009). The proton conductivity of PVTri homopolymer at 150 °C was measured as 1.13×10^{-7} S/cm. In our study, the proton conductivities of all acid doped membranes at 150 °C is higher when compared to neat PVTri homopolymer and undoped PVDF-*g*-PVTri graft copolymers. There are several reasons for the superior conductivity of all acid doped graft copolymers: (i) because of the large electronegativity of fluorine present in acid doped membranes (PVDF-*g*-PVTri-(TA)_x (x=1.0, 2.0 and 3.0)), the fluorine moiety activates nearby H⁺ of the N-H bond of the triazole rings. This makes an additional contribution for the proton transport in the membranes, resulting higher proton conductivity of the obtained membranes; (ii) because of the presence of excess triazole rings, the graft copolymer membranes are holding more triflic acid, which increases the conductivity; and (iii) because of the porous morphology. Therefore, the conductivity values for all acid doped graft copolymers have high proton conductivity (Sinirlioglu et al., 2014b).

Furthermore, as seen in SEM images, the obtained graft copolymer membranes (PVDF-*g*-PVTri; C1, C2, C3) have a porous morphology (Fig. 3.136 b,d,g). Because of the presence of pores, the graft membranes can hold more triflic acid. This increases the proton conductivity, since conductivity is directly proportional to the amount of triflic acid in the membrane. Also, the porous nature of the membranes facilitate better proton conduction, resulting in high proton conductivity due to strong interaction between -SO₃H groups of triflic acid and the triazole units of PVTri. This continuous pathway may convey proton transport over the sulfonic acid groups and triazole groups. The proton could travel along the hydrogen bonds from one functional group to another (Hazarika and Jana, 2012). A comparison of morphology (Fig. 3.136 b,d,g) and conductivity (Fig. 3.146) data brings an important correlation between the morphology and conductivity of the membrane. The porous nature increases as we increase the PVTri and triflic acid contents (C3-(TA)_x graft copolymers); the conductivity also increases. Therefore, the morphology of the membrane influences the conductivity (Sinirlioglu et al., 2014b; Hazarika and Jana, 2012). Possible mechanism of proton transport in PVDF-*g*-PVTri-(TA)_x, in which triflic acid is coordinated with triazole groups is tentatively illustrated in Fig. 3.147.

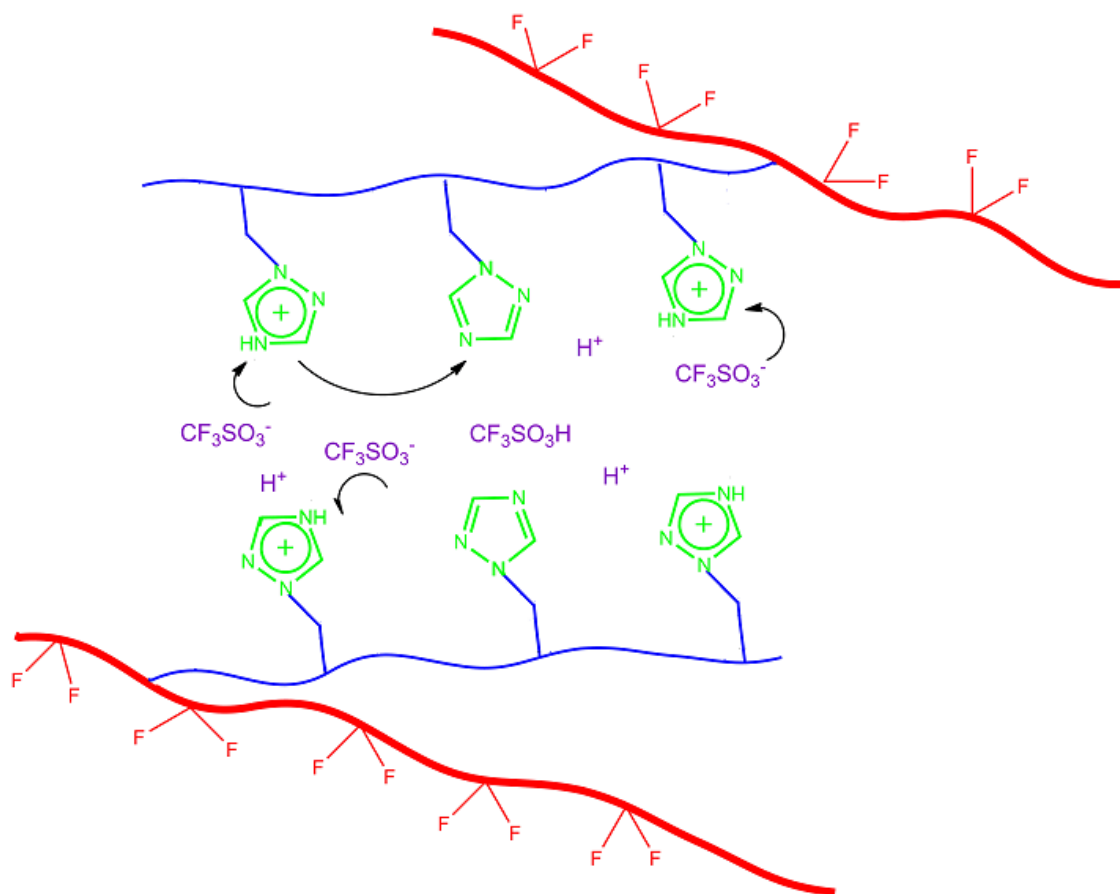


Figure 3.147 Possible mechanism of proton transport in PVDF-*g*-PVTri-(TA)_x (*x*=1.0, 2.0 and 3.0) membranes.

3.8.8 Cyclic Voltammetry

Cyclic voltammogram of PVDF-*g*-PVTri-(TA)₃ (C3-TA₃) was given in Fig. 3.148. The measurement was performed in a typical three electrode cell containing 0.1 mol dm⁻³ CH₃CN solution of tetrabutylammonium hexafluorophosphate (TBAPF₆) using a platinum work electrode, a platinum auxiliary electrode, and an Ag/Ag⁺ reference electrode. The voltammogram shows that the graft copolymer membrane (C3-TA₃) comprises no peak within in the anodic and cathodic sweep (-2.0 to 2.0 V potential range). Thus the electrochemical stability window is about 4V. These results implied that the (C3-TA₃) membrane had adequate electrochemical stability under fuel cell conditions (Sinirlioglu et al., 2014b).

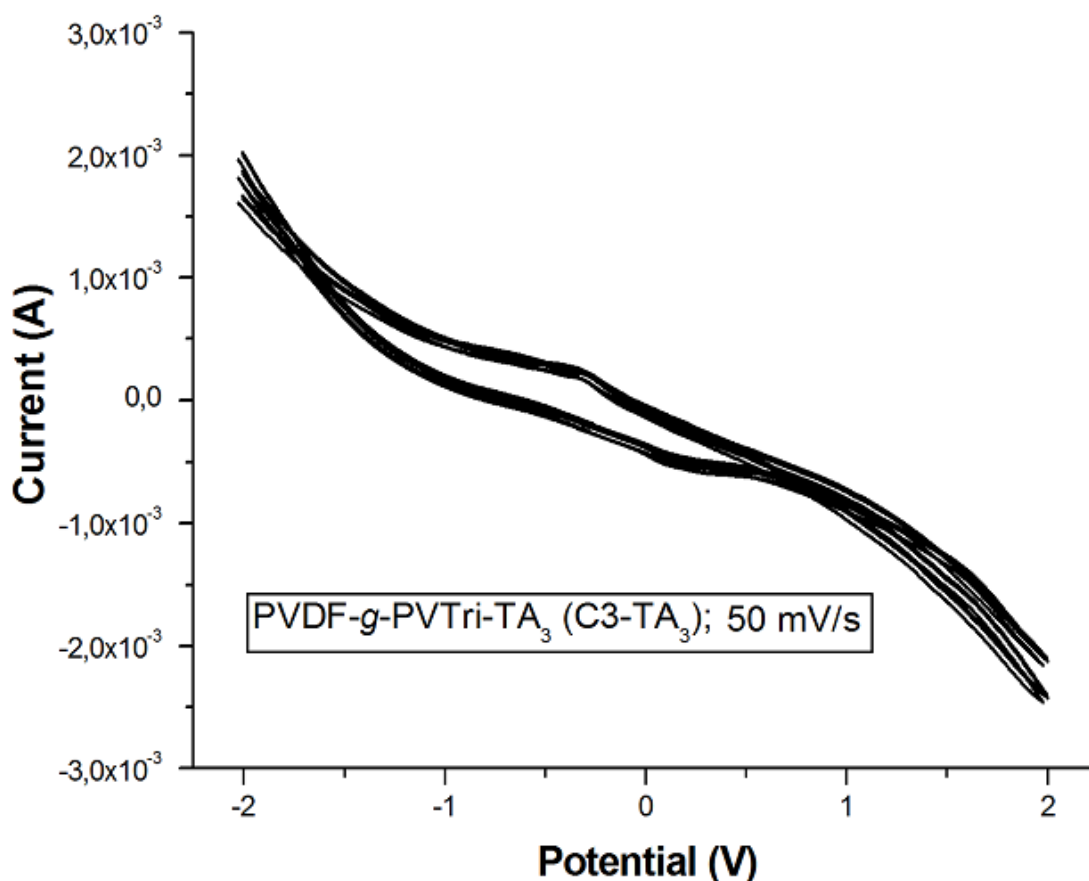


Figure 3.148 Cyclic voltammograms of PVDF-*g*-PVTri-(TA)₃ (C3-TA₃) in 0.1 M TBATFB/acetonitrile. Curves were obtained with a scan rate of 50 mV/s.

3.9 SYNTHESIS OF PERFLUORINATED PROTON EXCHANGE MEMBRANES BY CHEMICALLY COMBINING POLY(VINYL PHOSPHONIC ACID) WITH PVDF BY MEANS OF POLY(GLYCIDYL METHACRYLATE) GRAFTS

Recently, the development of proton exchange membranes (PEMs) has attracted significant interest among researchers since they play a critical role in the efficient operation of fuel cells by exchanging protons between anode and cathode (Arslantas et al., 2014; Dutta et al., 2014; Pu et al., 2014). The requirements for PEMs to be successfully employed in PEMFC include high proton conductivity, good mechanical properties, enhanced chemical stability, and low permeability. Keeping these considerations in mind, research efforts have been directed toward developing alternative membranes which are robust as Nafion and show high proton conductivities.

PVDF based PEMs among others have shown some promising results as PVDF offers many favorable features such as durability, thermal stability and chemical resistance for efficient and prolonged operation of the fuel cell. In their blends, the high hydrophobicity of PVDF might present some problems such as incompatibility with hydrophilic components and phase separation leading to disturbance in the proton transport mechanism (Singha et al., 2014; Dutta et al., 2014; Hua Wang et al., 2014). Therefore, homogeneous or surface grafting methods were more preferred to adopt hydrophilic nature to the PVDF membranes and maintain increased proton conductivity. In this respect, we have decided to explore the potential of PVPA functionality in PVDF based PEMs which has similar structure to Nafion. For this purpose, extremely hydrophobic and chemically resistant poly(vinylidene fluoride) (PVDF) grafted with glycidyl methacrylate (GMA) can represent a new substrate material with high mechanical properties with the potential for the preparation of polymer electrolyte membranes for fuel cell applications. Moreover, considerable improvements on proton conductivity at elevated temperatures could have been achieved by incorporating phosphonic acid groups within the chemical structure of PVDF-*g*-PGMA membranes since the PVPA provides a hydrophilicity and imparting a high proton attracting and transporting ability in PEM (Sinirlioglu et al., 2015b).

In this contribution, PVDF-*g*-PGMA was synthesized via free radical-initiated graft copolymerization of glycidyl methacrylate (GMA) from alkaline-treated PVDF backbone, followed by reaction of the oxirane rings in the GMA side chains with poly(vinyl phosphonic acid) (PVPA), eventually fabricating various PVDF-*g*-PGMA-*g*-PVPA(*x*) membranes as depicted in Fig. 3.149. Free-standing films were obtained (Fig. 3.150). The composition of PVDF-*g*-PGMA was determined by EDS analysis and the results are summarized in Table 3.23, which were well supported by C, F, and O content calculated in conjunction with grafting degree obtained from $^1\text{H-NMR}$ (Sinirlioglu et al., 2015b).

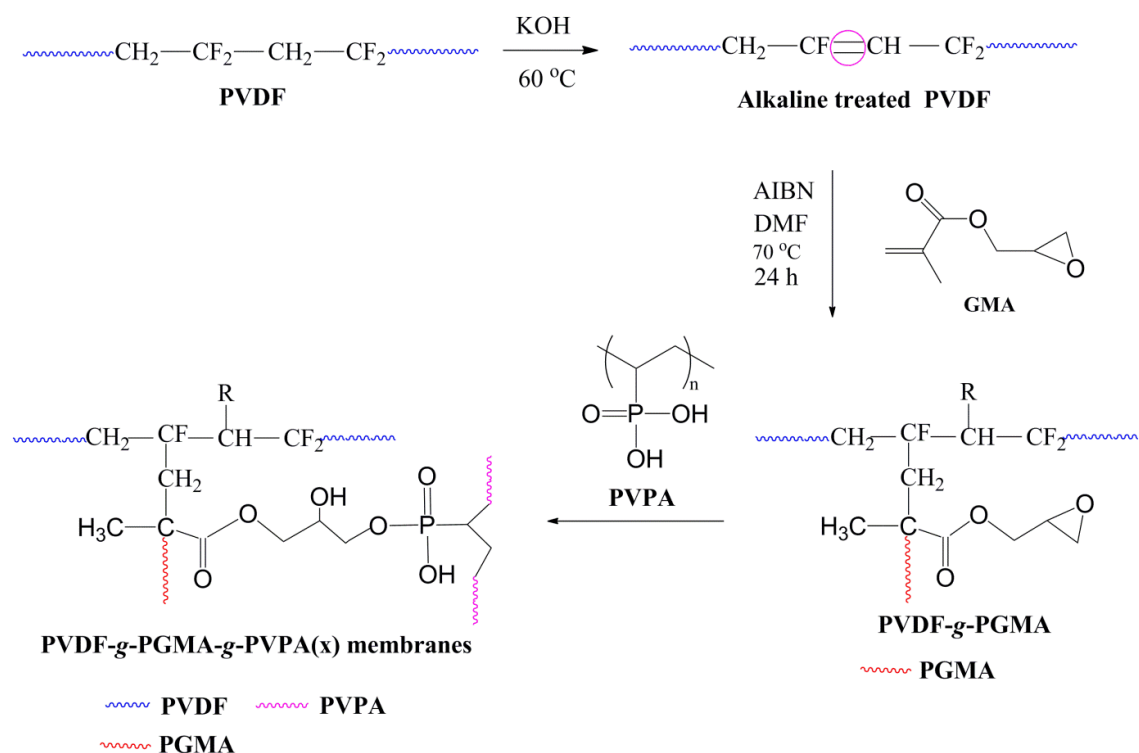


Figure 3.149 Schematic illustration for the PVDF-*g*-PGMA copolymer synthesis and PVDF-*g*-PGMA-*g*-PVPA(x) membrane formation.

Table 3.23 Chemical compositions of PVDF-*g*-PGMA graft copolymers.

	Sample	GD (%) ^a	GD (%) ^b	Chemical elements (%) ^c		
				C	F	O
Calculated	PVDF- <i>g</i> -PGMA	-----	-----	46.01	33.51	15.02
Found	PVDF- <i>g</i> -PGMA	36.30	80.62	49.62	32.91	15.19

a: calculated from ¹H-NMR on a % by mol basis, **b:** calculated from ¹H-NMR on a % by weight basis, **c:** found from EDS results on a % by weight basis. (GD: grafting degree)

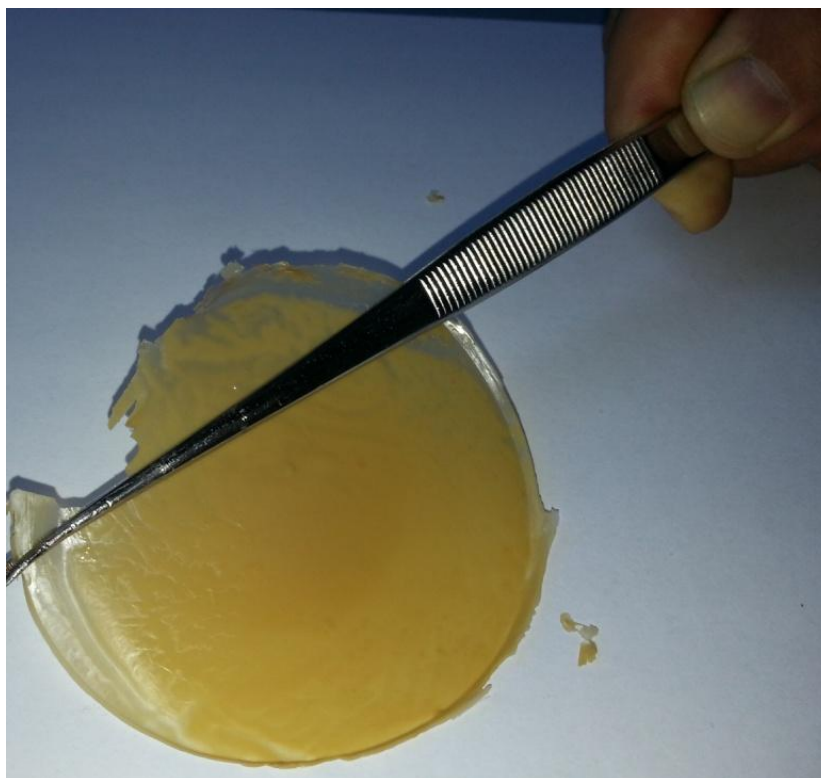


Figure 3.150 Free-standing film of PVDF-*g*-PGMA-*g*-PVPA(20) graft copolymer membrane.

The critical concern associated with grafting via alkaline treatment of PVDF is whether the alkaline treatment actually produces double bonds and that the GMA units polymerize through these bonds forming PVDF-*g*-PGMA. Previously, Ross et. al. reported a detailed study on surface modification of PVDF by alkaline treatment. They investigated the possibility of both defluorination and oxygenation and proposed a degradation mechanism. They were able to prove the formation of conjugated double bond structures by using ToF-SIMS (time-of-flight secondary ion mass spectroscopy), XPS (X-ray photoelectron spectroscopy), Raman spectroscopy, and FT-IR. In the present work, we have determined considerable spectroscopic evidence for double bond formation on PVDF upon treatment. These will be discussed below. Furthermore, it can well be expected that the “Grafting Through” strategy works under these conditions, that is, the double bonds situated on PVDF backbone contributes to propagation. The reason is that spectroscopic evidence attributed to PGMA to be discussed below can not originate from homopolymer formation since it is expected that all the possibly formed

homopolymer must have been removed upon thorough washing with excess chloroform for 24 h (Sinirlioglu et al., 2015b).

3.9.1 FTIR analysis

To provide evidences for grafting PGMA and PVPA, FTIR analysis was performed on the membrane in comparison with PGMA, PVDF and alkaline treated PVDF homopolymers, and PVDF-*g*-PGMA films as shown in the FTIR spectra are represented in Fig. 3.151. In PGMA, the carbonyl group gives a strong peak at 1725 cm^{-1} and the strong peaks at 1140 cm^{-1} and 1260 cm^{-1} are attributed to C-O stretching of the ester group. The absorption peak at 906 cm^{-1} belongs to epoxy (oxirane) rings (Fig. 3.151a). The spectrum of PVDF film exhibited a number of strong bands in the range of 1000-1370 cm^{-1} representing CF_2 groups, in addition to, a small band between at 3024 cm^{-1} and 2982 cm^{-1} representing stretching vibrations of $-\text{CH}_2$ groups. Degradation of PVDF was performed by alkaline treatment (defluorination due to alkaline treatment leading to the introduction of hydroxyl and carbonyl groups). FTIR spectra of alkaline treated PVDF show that the broad absorption peaks between 3600-3000 cm^{-1} might be due to H-bonded $-\text{OH}$ groups while those between 1740 cm^{-1} and 1600 cm^{-1} can be associated with the stretching vibrations of $\text{C}=\text{O}$ and $\text{C}=\text{C}$ groups in different molecular frames (Sinirlioglu et al., 2015b). Differing from that of the alkaline treated PVDF homopolymer, the grafted films, PVDF-*g*-PGMA, showed additional characteristic bands in the at 1735 cm^{-1} , attributable to the ester stretching mode of the grafted GMA segments. The bands at 2800-3000 cm^{-1} were assigned for C-H of the grafted GMA. Furthermore, PVDF-*g*-PGMA shows the absorption at 903 cm^{-1} which is assigned to stretching vibration of the epoxy group (Sinirlioglu et al., 2015b). The strong peaks at 1257 cm^{-1} and 1143 cm^{-1} are attributed to C-O stretching of the ester group. Furthermore, disappearance of the relatively broad peak at 1649 cm^{-1} corresponding to carbon-carbon double bond indicates that PGMA has been grafted through PVDF upon rupture of $\text{C}=\text{C}$ double bond during polymerization (Sinirlioglu et al., 2015b) (Fig. 3.151d).

Fig. 3.152 shows the FTIR spectra of PVPA homopolymer, PVDF-*g*-PGMA, and PVDF-*g*-PGMA-*g*-PVPA(x) membranes, respectively. PVPA has strong bands at 990 and 910 cm^{-1} that belong to asymmetric stretching vibrations of the P-OH group and at 1150 cm^{-1} that corresponds to $\text{P}=\text{O}$ stretching. The $\text{C}=\text{C}$ band of the vinyl phosphonic

acid was evident at 1635 cm^{-1} . Peaks associated with -CH stretchings ($=\text{CH}$, $=\text{CH}_2$) were observed in the vinyl phosphonic acid between 2800 and 3000 cm^{-1} (Sinirlioglu et al., 2015b). In the PVPA grafted PVDF-*g*-PGMA membranes, at higher VPA ratio (Fig. 3.152e), the P-O-H vibration at 930 cm^{-1} becomes stronger, indicating the existence of excess acidic protons. The intensity of these peaks increased in parallel with the concentration of PVPA into the grafted membranes. These peaks are overlapped with the corresponding peaks of PVDF units of grafted-matrix and became broader (Fig. 3.152(c-e)). Furthermore, the band broadening between 3500 cm^{-1} and 2000 cm^{-1} is due to the hydrogen bonding network between epoxy groups of PGMA and phosphonic acid units of PVPA which is necessary for proton conduction. These signs evidenced that PVPA was immobilized onto PVDF-*g*-PGMA (Sinirlioglu et al., 2015b).

As mentioned in the FTIR analysis above, the disappearance of the relatively broad peak at 1649 cm^{-1} corresponding to carbon-carbon double bond indicates that PGMA has been grafted through PVDF upon rupture of $\text{C}=\text{C}$ double bond during polymerization. This is also supported by ^1H -NMR as the peak between 6.0-6.5 ppm diminished to a great extent. Based on the integral ratios after grafting, the double bonds in PVDF were involved in propagation with an efficiency of 94 % (Sinirlioglu et al., 2015b).

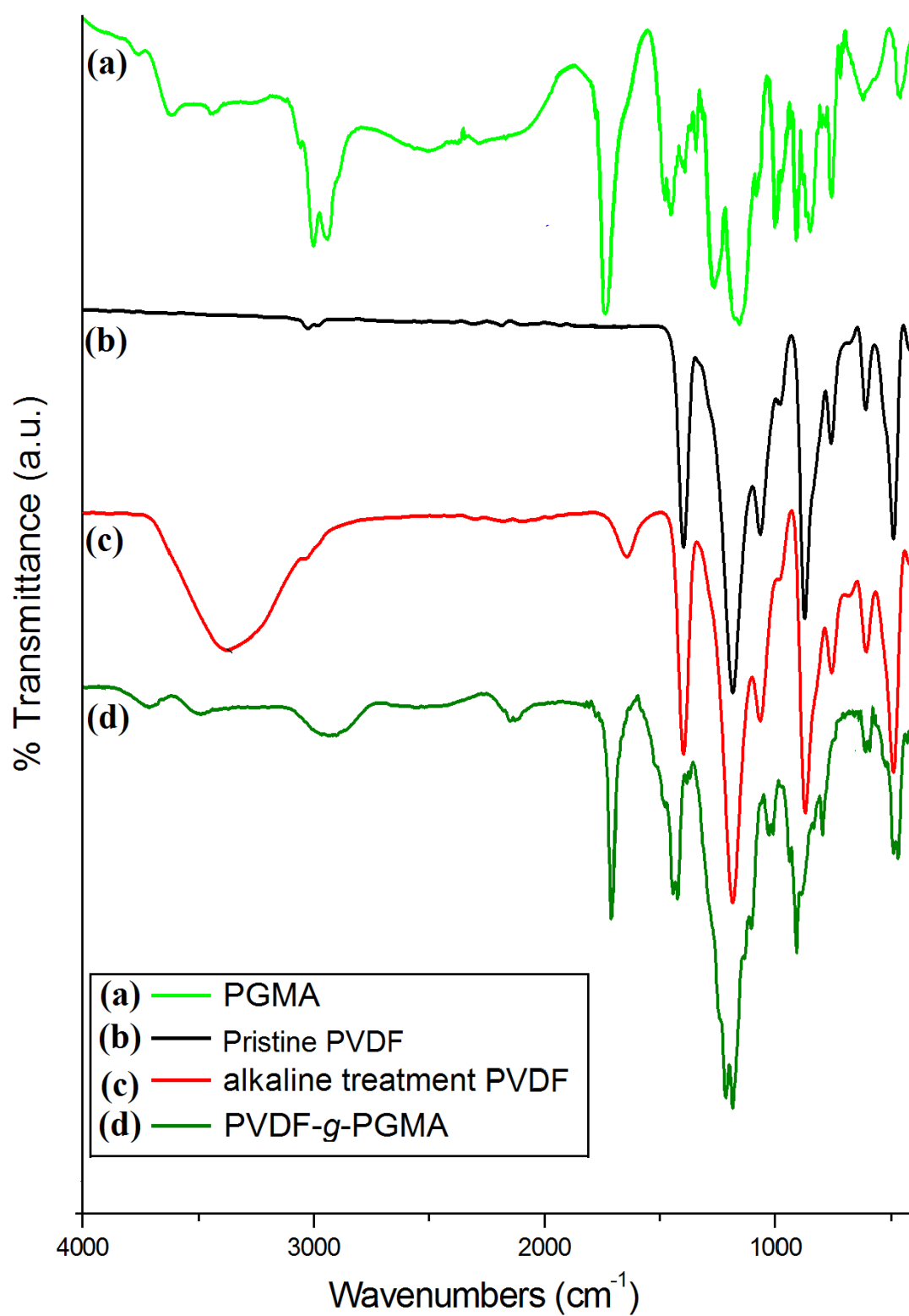


Figure 3.151 FTIR spectra of (a) PGMA, (b) pristine PVDF, (c) alkaline treatment PVDF and (d) PVDF-*g*-PGMA.

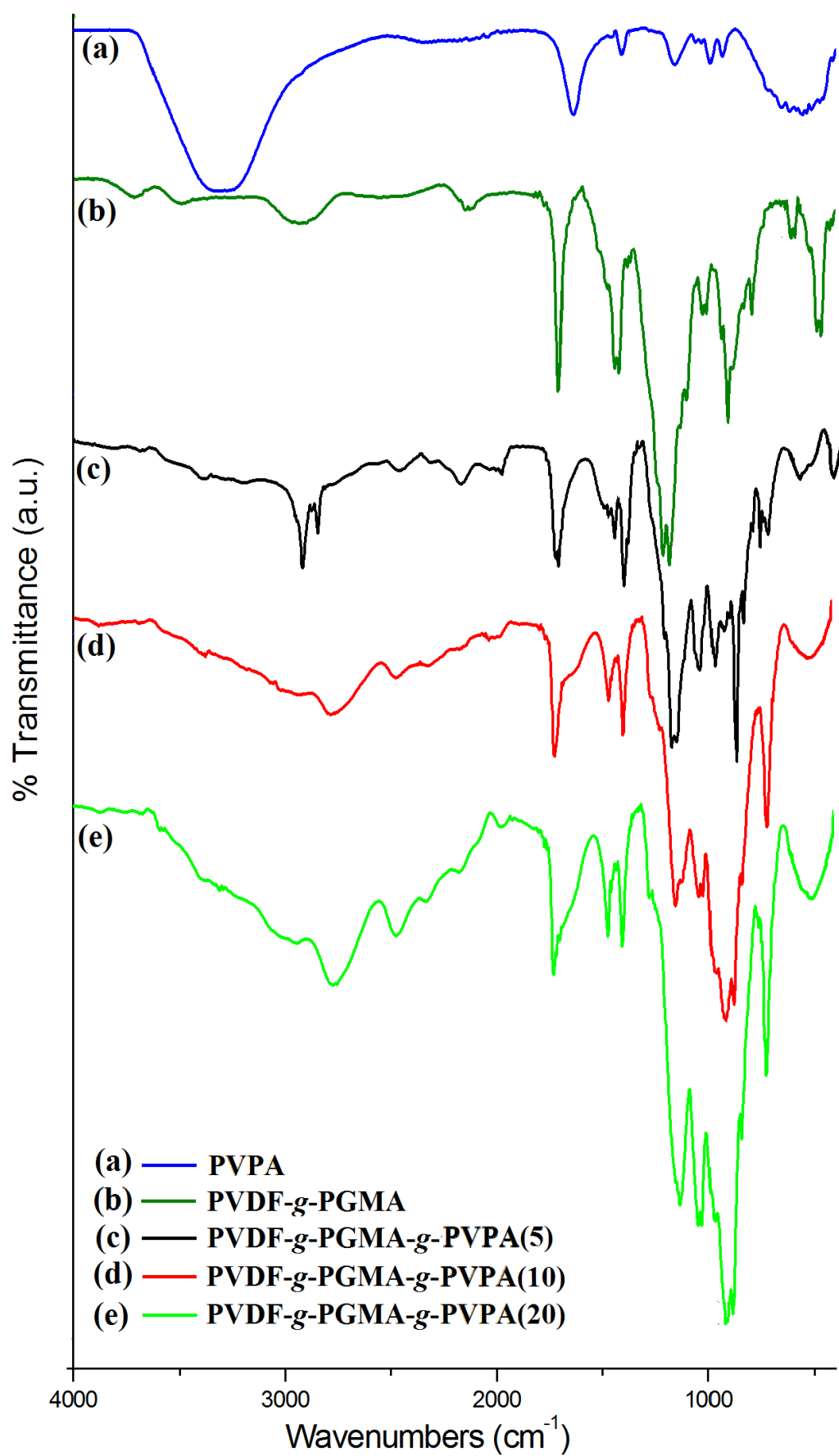


Figure 3.152 FTIR spectra of (a) PVPA, (b) PVDF-*g*-PGMA, (c) PVDF-*g*-PGMA-*g*-PVPA(5), (d) PVDF-*g*-PGMA-*g*-PVPA(10), and (e) PVDF-*g*-PGMA-*g*-PVPA(20).

3.9.2 ^1H -NMR studies

The successful graft copolymerization was confirmed using ^1H -NMR and ^{19}F -NMR spectroscopy. Fig. 3.153 shows ^1H -NMR spectra of alkaline treated PVDF and PVDF-*g*-PGMA. For all samples, the peaks of solvent (DMSO) and water appeared at 2.51 and 3.37 ppm, respectively. The ^1H -NMR spectrum exhibited the characteristic multiplets centered at 2.91 and 2.28 ppm originating from the methylene groups in $-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-$ and $-\text{CF}_2-\text{CH}_2-\text{CH}_2-\text{CF}_2-$ sequences appearing in the normal head-to-tail (ht) and reversed tail-to-tail (tt) VDF additions (Sinirlioglu et al., 2015b). The new multiple peaks at 6.0-6.5 ppm in alkaline treated PVDF correspond to the protons on the double bonds ($-\text{CH}_2-\text{CF}=\text{CH}-\text{CF}_2-$) after the elimination of HF from PVDF. These peaks evidenced the formation of the double bonds ($-\text{CH}_2-\text{CF}=\text{CH}-\text{CF}_2-$) in the alkaline treated PVDF. The amount of double bonds formed in PVDF after alkaline treatment was calculated on the basis of integral ratios from ^1H -NMR spectra and was determined as 3% by mole (Sinirlioglu et al., 2015b). The methylene groups of PGMA backbone exhibited signals at 1.89 and 1.82 ppm (b). The signals observed at 0.98 and 0.81 ppm (c) are due to the protons in the $-\text{CH}_3$ groups of PGMA. The spectrum also indicated two signals at 4.35 and 3.75 ppm (d), attributable to $-\text{COOCH}_2-$ group of PGMA. The peaks at 3.25 ppm (e), 2.8 and 2.66 ppm (f) are due to the protons of the oxirane ring (Sinirlioglu et al., 2015b).

The successfully introduced double bond in the PVDF could also be confirmed by ^{19}F -NMR. The spectra of PVDF, alkaline treated PVDF, and PVDF-*g*-PGMA graft copolymer are shown in Fig. 3.154. The structure of PVDF is dominated by the presence of VDF-VDF head-to-tail (ht) ($-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-$) sequences appearing between -92 and -96 ppm, and VDF-VDF tail-to-tail (tt) ($-\text{CF}_2-\text{CH}_2-\text{CH}_2-\text{CF}_2-$) structure appearing between -114 and -117 ppm. Compared with PVDF, the new signals emerging at around -107 ppm in alkalined treated PVDF could be assigned to the F atoms in the double bond ($-\text{CH}_2-\text{CF}=\text{CH}-\text{CF}_2-$) units. The same peaks at around -107 ppm were also detectable in the spectrum of PVDF-*g*-PGMA, supporting that grafting has successfully occurred. It is also noteworthy that signals attributed to PGMA can not originate from homopolymer formation since it is expected that all the possibly formed homopolymer must have been removed upon thorough washing with excess chloroform for 24 h as previously mentioned (Sinirlioglu et al., 2015b). The integration

ratio of the protons in the ^1H -NMR yielded a degree of grafting of 80.62 % using the equation (3.5):

$$\text{Degree of Grafting (GD) (\%)} = \frac{\text{Mw}(\text{glycidyl methacrylate}) \times A(d+d)}{\text{Mw}(\text{PVDF}) \times A(a)} \times 100 \quad (3.5)$$

where Mw(PVDF) is molecular weight of repeating unit of PVDF, A(a) are the integral areas of the characteristic peak (a) of the PVDF main chain (used as reference peak) and $-\text{CH}_2$ protons of the glycidyl methacrylate (d) of PGMA, respectively.

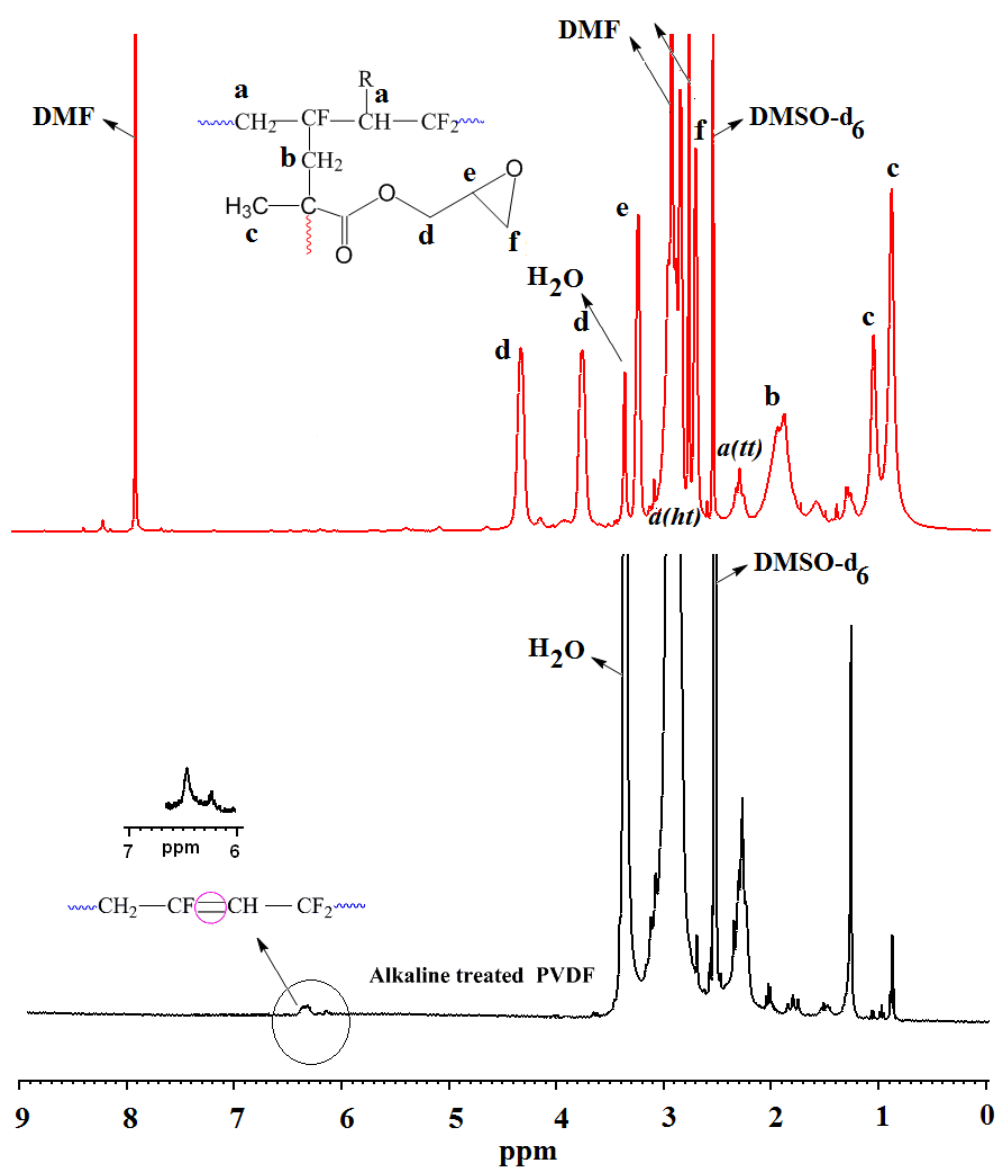


Figure 3.153 ^1H -NMR spectra of alkaline treated PVDF and PVDF-g-PGMA graft copolymer recorded in DMSO-d_6 .

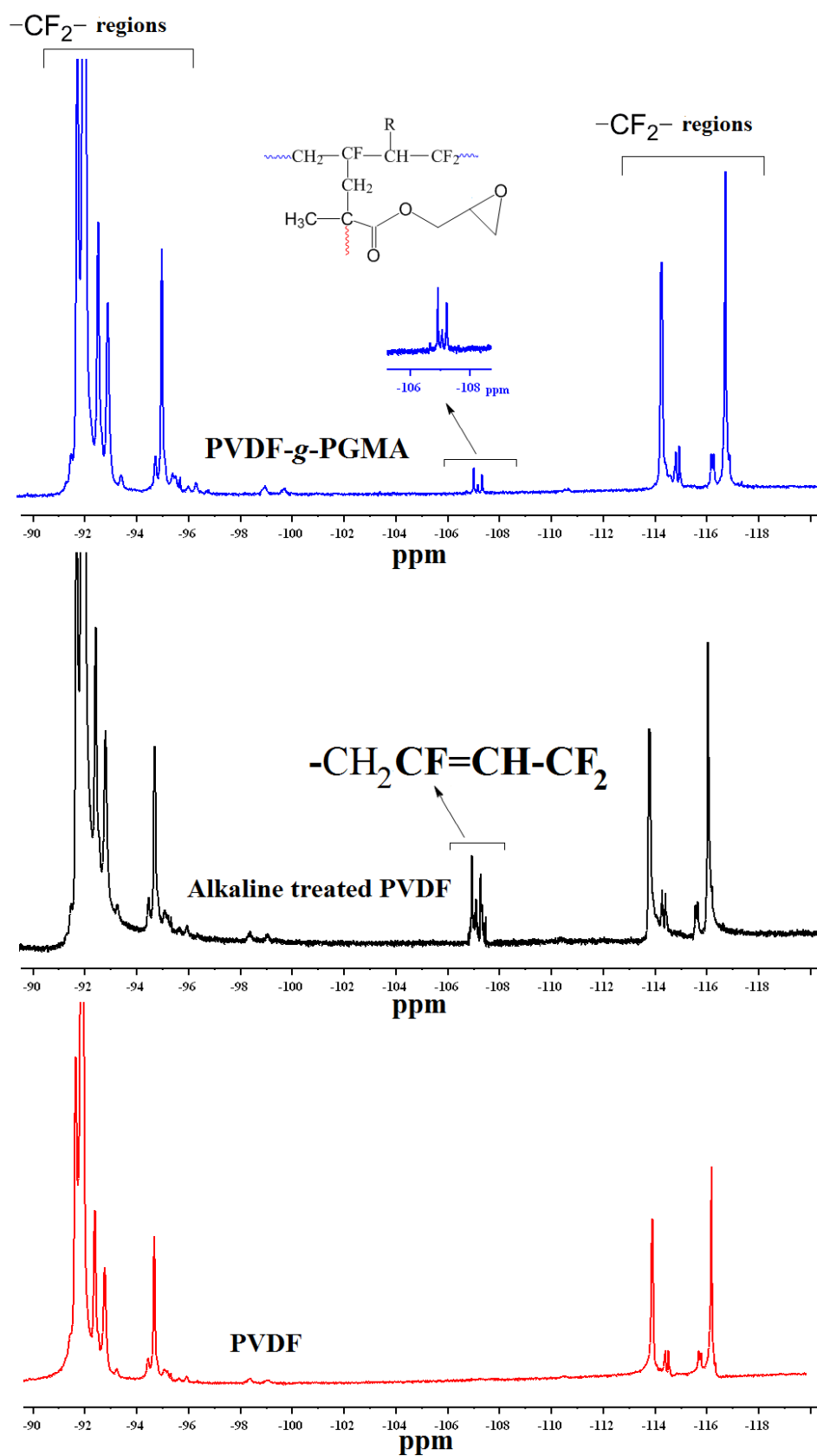


Figure 3.154 ^{19}F -NMR spectra of PVDF, alkaline treated PVDF, and PVDF-*g*-PGMA graft copolymer recorded in DMSO-d_6 .

3.9.3 Thermal Analysis

The DSC measurements were carried out under inert atmosphere at a scan rate of 10 °C/min and the second heating curves were evaluated. DSC thermograms of the original PVDF, PVDF-*g*-PGMA, PVDF-*g*-PGMA-*g*-PVPA(x) membranes are given in Fig. 3.155. Previously, pure PVPA was reported to have a T_g of -23 °C (Aslan and Bozkurt, 2009). The T_g of the PGMA homopolymer and original PVDF were studied as 74 °C (Celik and Bozkurt, 2008a), and -50 °C (Sasa et al., 2013), respectively. PVDF-*g*-PGMA displayed a glass transition at approximately 106.8 °C. The melting point (T_m) was observed at approximately 157.2 °C due to the presence of ordered PVDF regions. For PVDF-*g*-PGMA-*g*-PVPA membranes, a T_g might have been observed between 106.8°C and -23°C, however, no T_g could be detected. They only demonstrated melting points at approximately 156.5 °C, 156.1 °C and 155.6 °C, respectively, as given in Fig. 3.155. The lessening in the melting point could be considerably decrease of the crystalline region of PVDF-*g*-PGMA with the amorphous PVPA grafts (Sinirlioglu et al., 2015b). The thermal stability of the membranes was analyzed with TGA in comparison with the PVDF, PVDF-*g*-PGMA, and PVDF-*g*-PGMA-*g*-PVPA membranes and the obtained TGA curves are represented in Fig. 3.156. PGMA was reported to be thermally stable up to 200 °C. PVPA homopolymer is thermally stable until 200 °C. PVDF showed a single-step degradation pattern with transition at about 460 °C due to the decomposition of molecular chains of PVDF film, whereas the PGMA grafted PVDF film showed a two-step degradation pattern at 275 and 460 °C due to the decomposition of PGMA grafts and the PVDF matrix, respectively. The TGA curves of PVDF-*g*-PGMA-*g*-PVPA(x) membranes showed a satisfactory thermal stability up to 210 °C. The initial weight loss at around 100 °C (~1 %) can be attributed to the loss of loosely bound water (or moisture) that was possibly absorbed during storage. There was a small weight loss (~5 %) between 140 °C-180 °C due to condensation of phosphonic acid units of PVPA-side chains. After 275 °C, a remarkable weight loss in a single step originated from thermal decomposition of PGMA while PVPA started to decompose at around 420 °C. Finally, the final weight loss region occurs at 490 °C due to decomposition of PVDF backbone. Clearly, the dried materials are thermally stable up to at least 210 °C, after which, they decompose. As a result, the obtained membranes can be used for testing in high temperature PEMFCs operation up to 200 °C (Sinirlioglu et al., 2015b).

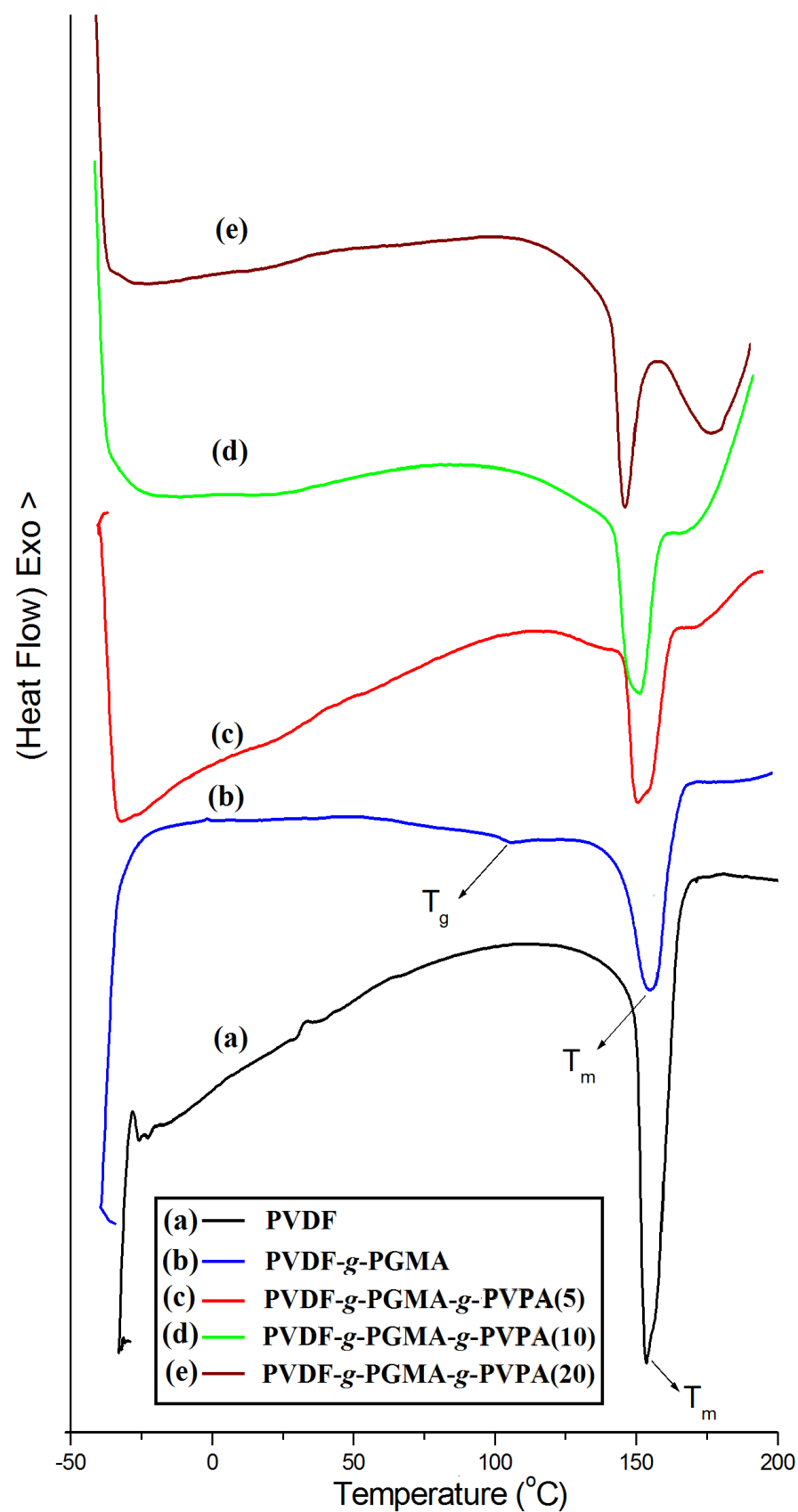


Figure 3.155 DSC thermograms of (a) original PVDF, (b) PVDF-*g*-PGMA, (c) PVDF-*g*-PGMA-*g*-PVPA(5), (d) PVDF-*g*-PGMA-*g*-PVPA(10), (e) PVDF-*g*-PGMA-*g*-PVPA(20) membranes recorded under N₂ atmosphere at a heating rate of 10 °C/min.

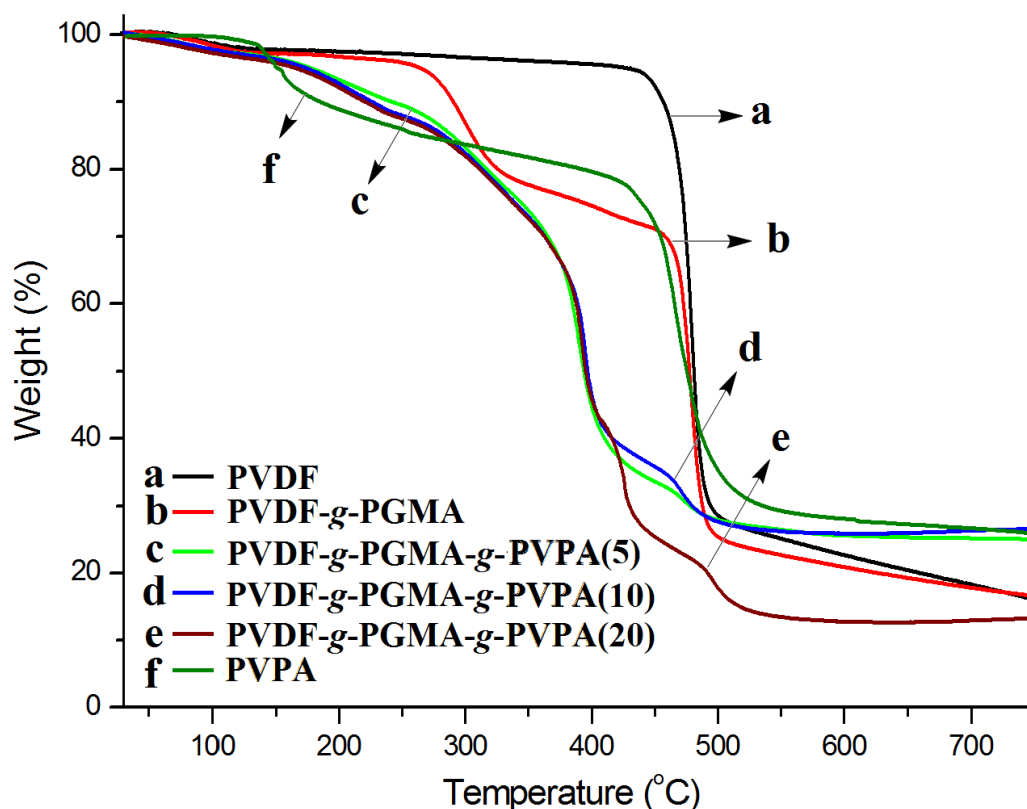


Figure 3.156 TG thermograms of (a) original PVDF, (b) PVDF-*g*-PGMA, (c) PVDF-*g*-PGMA-*g*-PVPA(5), (d) PVDF-*g*-PGMA-*g*-PVPA(10), (e) PVDF-*g*-PGMA-*g*-PVPA(20) membranes, and (f) PVPA homopolymer at a heating rate of 10°C/min in inert atmosphere.

3.9.4 Water Uptake

The water uptake is closely related to the efficiency of the fuel cells and basic properties of the membranes such as proton conductivity, mechanical property and stability. It plays an essential role in the membrane behavior which affects a large extent the proton conductivity depends the amount of water absorbed and even the proton conducting mechanism is influenced by it. Thus, the suitable water uptake is necessary. The water uptake of the membranes were measured at room temperature under immersion in deionized water (Sinirlioglu et al., 2015b).

Water uptakes of the PVDF-*g*-PGMA-*g*-PVPA(*x*) membranes are represented in Fig. 3.157. Generally, the water uptake increases with increasing hydrophilicity of the polymers. As can be seen from Fig. 3.157, water uptake increased with increasing of

PVPA content because of swelling and hydrophilic properties of PVPA in the graft copolymer membranes. As anticipated, the water uptake values decreased monotonously with increasing hydrophobic block size of the membranes. For instance, PVDF-*g*-PGMA-*g*-PVPA(5) membrane consisting the longest hydrophobic block showed relatively lower water uptakes of 28 wt %. PVDF-*g*-PGMA-*g*-PVPA(20) membrane has the highest water uptake value (225 %). Clearly, the results demonstrated that the increasing of PVPA content in PVDF-*g*-PGMA-*g*-PVPA(*x*) enhanced the water uptake, and brought about better hydrophilicity (Sinirlioglu et al., 2015b).

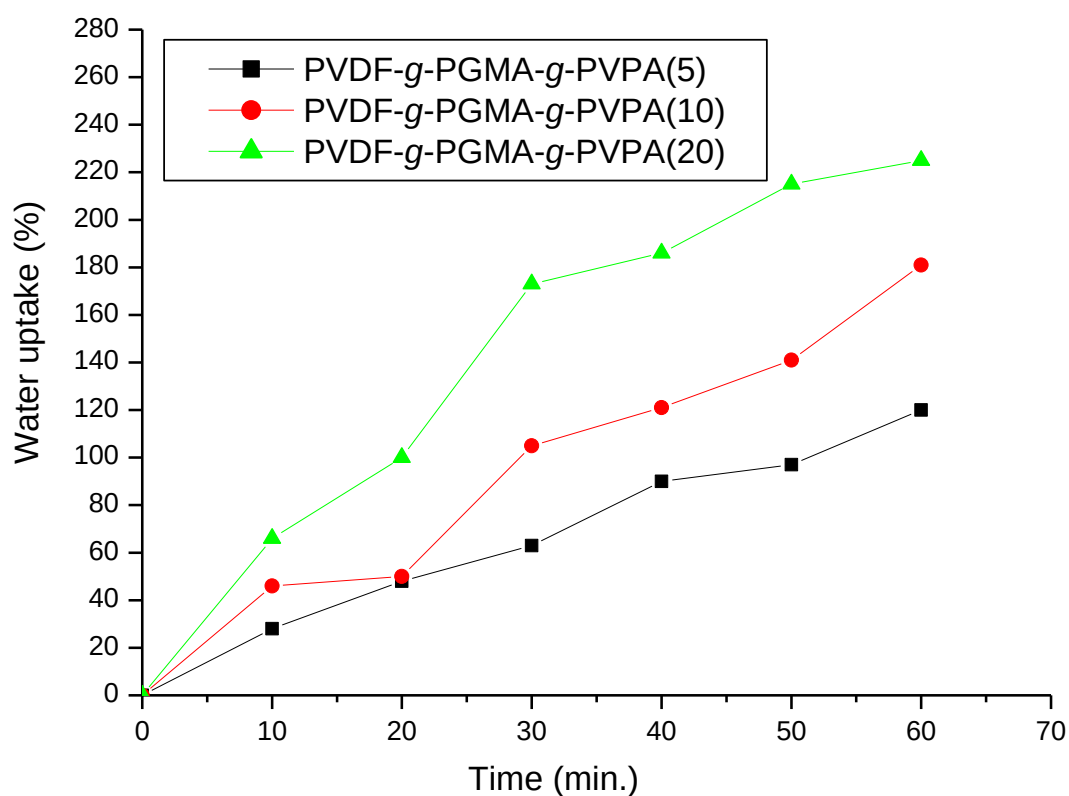


Figure 3.157 Water uptakes of PVDF-*g*-PGMA-*g*-PVPA(*x*) (*x*=5, 10, 20 wt %) at the time of 10-60 min in deionized water at 25 °C.

3.9.5 Methanol Permeability

The methanol permeability of PEMs is an important property in direct methanol fuel cells. But, it is a possible problem in the application of the membranes in fuel cells. The membranes with low methanol diffusion coefficient are required because methanol diffuses from the anode side to the cathode side leads to lower cell voltage and decreases fuel efficiency due to polarization losses. In this work, methanol permeability of the composite membranes was measured by simple homemade diaphragm diffusion cell similar to the study of the previous work (Gasa et al. 2007). The cell was filled with 2 mL methanol and the mass flow was recorded as a function of time (Fig. 3.158).

The permeability is directly proportional to the molar flux. The molar flux of the PVDF-*g*-PGMA-*g*-PVPA(*x*) graft copolymer membranes are depicted in Fig. 3.158. The values are $3.12 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, $2.78 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ and $2.28 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ for PVDF-*g*-PGMA-*g*-PVPA(5), PVDF-*g*-PGMA-*g*-PVPA(10), and PVDF-*g*-PGMA-*g*-PVPA(20) membranes, respectively. Previously, the methanol permeability of Nafion 112 in the same conditions we measured and determined as $1.89 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ (Sen et al., 2008). As seen in Fig.3.158, the methanol permeability of the graft copolymer membranes are very close to Nafion 112 (Sinirlioglu et al., 2015b). This means that the PVDF-*g*-PGMA-*g*-PVPA(*x*) membranes might be prospective to be used as a candidate of Nafion in PEMFCs.

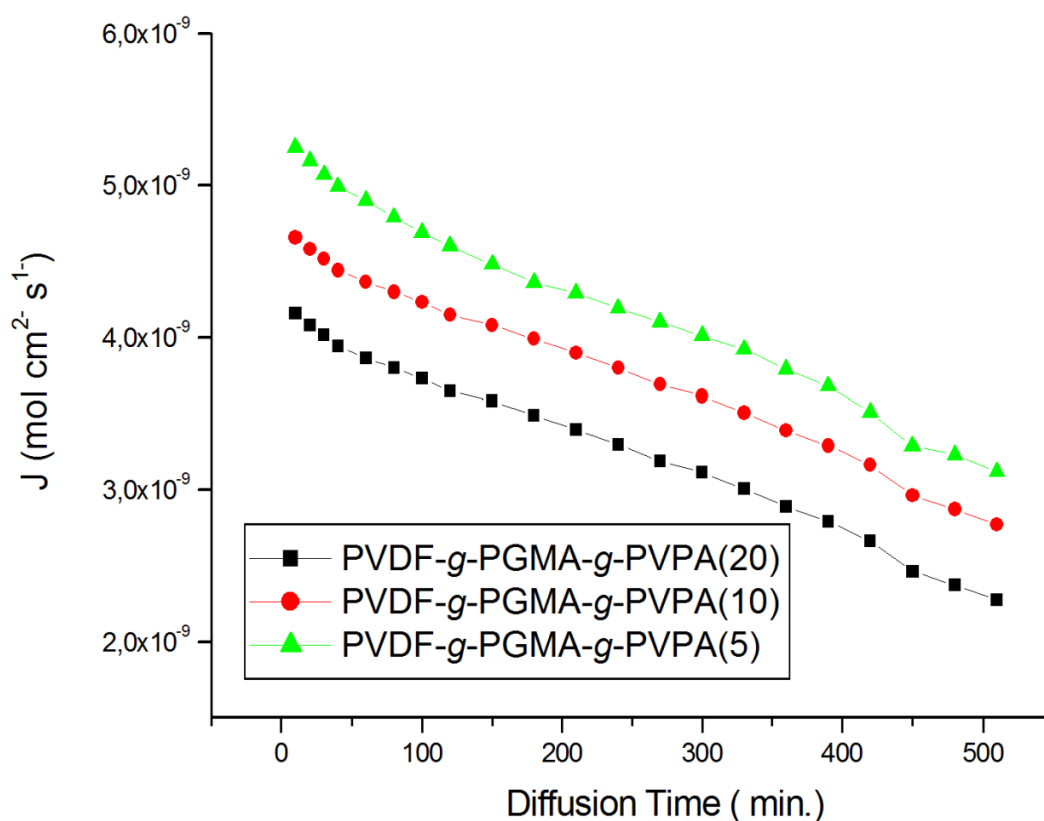


Figure 3.158 Methanol permeability of PVDF-*g*-PGMA-*g*-PVPA(*x*) membranes.

3.9.6 X-ray Diffraction (XRD)

The XRD measurement is a constructive method to examine the crystallinity of the membranes. X-ray diffractometry measurements were carried out to investigate the structural changes induced by the introduction of PGMA grafts to the PVDF films and subsequent followed grafting of the obtained PVDF-*g*-PGMA membranes with PVPA homopolymer. Fig. 3.159 represents the XRD pattern of original PVDF, PVDF-*g*-PGMA, and PVDF-*g*-PGMA-*g*-PVPA graft copolymer membranes. PVDF is a polymorphic, semi-crystalline polymer showing at least four different forms such as α , β , γ , δ and ϵ . The peak obtained at around $2\theta = 18.7^\circ$, 20.0° , and 26.4° reflect α -crystal structure which can be indexed α (020), α (110) and α (021) for pure PVDF. The peaks at $2\theta = 34.8^\circ$ and 36.2° relate to the (200) plane of α -phase of PVDF and the peak at $2\theta = 39.2^\circ$ refers to the combined (201) and (111) reflections of the β -phase due to

molecular defects caused by head-head and tail-tail sequences (Sinirlioglu et al., 2015b).

After grafting of PGMA onto alkaline treated PVDF, the crystallinity of PVDF-*g*-PGMA graft copolymer (Fig. 3.159b) did not undergo any changes. The position of peaks is almost similar to those observed in alkaline treated PVDF. There was no additional phase detected in the PVDF matrix due to chemical modifications which means PGMA chains were grafted only on the surface of PVDF (Sinirlioglu et al., 2015b; Giang Bach et al., 2013). For PVDF-*g*-PGMA-*g*-PVPA(5) membrane, the characteristic peak at around $2\theta = 26.4^\circ$ which can be indexed α (021) almost disappeared immediately. In addition, the peak at around $2\theta = 18.7^\circ$ which can be indexed α (020) almost cleared instantly. The peaks at $2\theta = 26.4^\circ$, 34.8° and 36.2° relate to the (021) and (200) planes of α -phase of PVDF and the peak at $2\theta = 39.2^\circ$ refers to the combined (201) and (111) reflections of the β -phase due to molecular defects caused by head-head and tail-tail sequences were keenly destructed as can be seen in Fig. 3.159d and Fig. 3.159e. These results showed that the original crystalline structure of pure PVDF and PVDF-*g*-PGMA graft copolymer was seriously destroyed (Sinirlioglu et al., 2015b). When the PVPA content was increased, the crystallinity of the PVPA-grafted membranes diminished. As can be seen from XRD curves, amorphous nature of the obtained PVPA-grafted copolymer membranes increased. This behavior was depicted as the elimination of hydrogen bonding network between epoxy rings of PVDF-*g*-PGMA graft copolymer and phosphonic acid units of PVPA at higher acid compositions. Because of the crystallite size that determined nearly 5.0 ± 2.0 nm by using Scherrer's equation (Sakai et al., 2010), the diffraction peaks for PVDF powder appear to be sharp.

After grafting of PGMA onto alkaline treated PVDF, the crystallite size reduced while increasing of PVPA. This denotes the increasing of amorphous nature of the obtained PVDF-*g*-PGMA-*g*-PVPA(x) membranes. The observation of the XRD data revealed that the crystallinity and crystallite size of pure PVDF and PVDF-*g*-PGMA lessened after grafting of PVPA. The results are summarized in Table 3.24 (Sinirlioglu et al., 2015b).

Table 3.24 The mean RMS roughness values with the standard deviations and the crystallite size of PVDF powder, PVDF-*g*-PGMA and PVDF-*g*-PGMA-*g*-PVPA(x) membranes.

Samples	Roughness (nm) ^a	crystallite size (nm) ^b
PVDF	50.24 $\pm$ 8.16	5.0 $\pm$ 2.0
PVDF- <i>g</i> -PGMA	193.12 $\pm$ 27.75	4.5 $\pm$ 0.6
PVDF- <i>g</i> -PGMA- <i>g</i> -PVPA(5)	100.05 $\pm$ 13.88	3.2 $\pm$ 0.4
PVDF- <i>g</i> -PGMA- <i>g</i> -PVPA(10)	64.33 $\pm$ 8.88	2.8 $\pm$ 0.3
PVDF- <i>g</i> -PGMA- <i>g</i> -PVPA(20)	26.78 $\pm$ 5.06	1.8 $\pm$ 0.5

a: calculated from AFM, **b:** calculated from XRD.

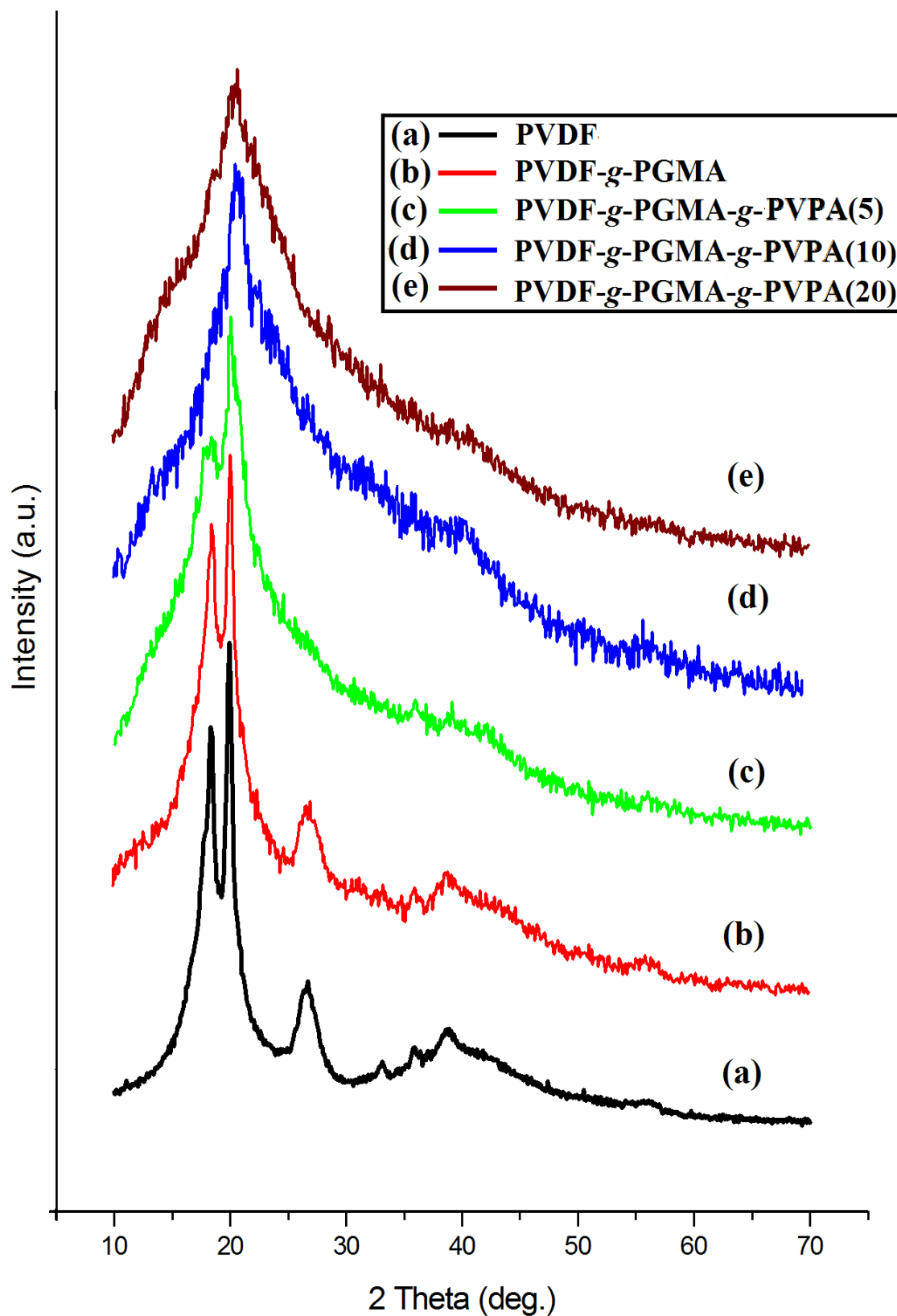


Figure 3.159 XRD patterns of (a) PVDF, (b) PVDF-*g*-PGMA, (c) PVDF-*g*-PGMA-*g*-PVPA(5), (d) PVDF-*g*-PGMA-*g*-PVPA(10), (e) PVDF-*g*-PGMA-*g*-PVPA(20) graft copolymer membranes.

3.9.7 Atomic Force Microscopy (AFM)

AFM was used for the determination of phase morphology, heterogeneity, or homogeneity of the membranes. Moreover, the surface roughness of the membranes was determined. The changes in surface topography of the alkaline-treated PVDF after each modification (grafting) steps were measured up by AFM. Fig. 3.160 displays the representative AFM height images of the alkaline treated-PVDF and functionalized PVDF membrane surfaces with scanned areas of $10\mu\text{m} \times 10\mu\text{m}$ which were obtained at a resolution of 512×512 points within the range of 0.5-0.8 Hz scan rate and were subjected to first-order flattening. The RMS mean values and the standard deviations were obtained by analyzing at least 6 AFM images. The mean values of surface roughness of alkaline treated-PVDF and functionalized PVDF membranes are listed in Table 3.24.

The alkaline-treated PVDF is relatively uniform and smooth with the root-mean-square (RMS) surface roughness values of about 50.24 nm (Fig. 3.160b). Upon grafting of PGMA, the surface roughness of PVDF-*g*-PGMA membrane reveals an obvious increase about 193.12 nm. This result was consistent with the previous findings that the grafting of the PGMA can lead to a significant increase in surface roughness value, as well as surface morphology (Sinirlioglu et al., 2015b; He et al., 2014; Singh et al., 2005). After modification of PVDF-*g*-PGMA membrane with PVPA, by increasing the PVPA ratio, it was noticed a considerable diminishing of the surface roughness from 100.05 nm to 26.73 nm. The immobilization of PVPA can contract the PGMA domains on the PVDF surface, thus resulting in a further decrease in the surface roughness. Furthermore, the images exhibit single phase formation and the membranes seem homogeneous at nanometer-scale level except of image (b). As a consequence, the surface topography measured by AFM is an alternative way to ascertain successful modification of PVDF (Sinirlioglu et al., 2015b).

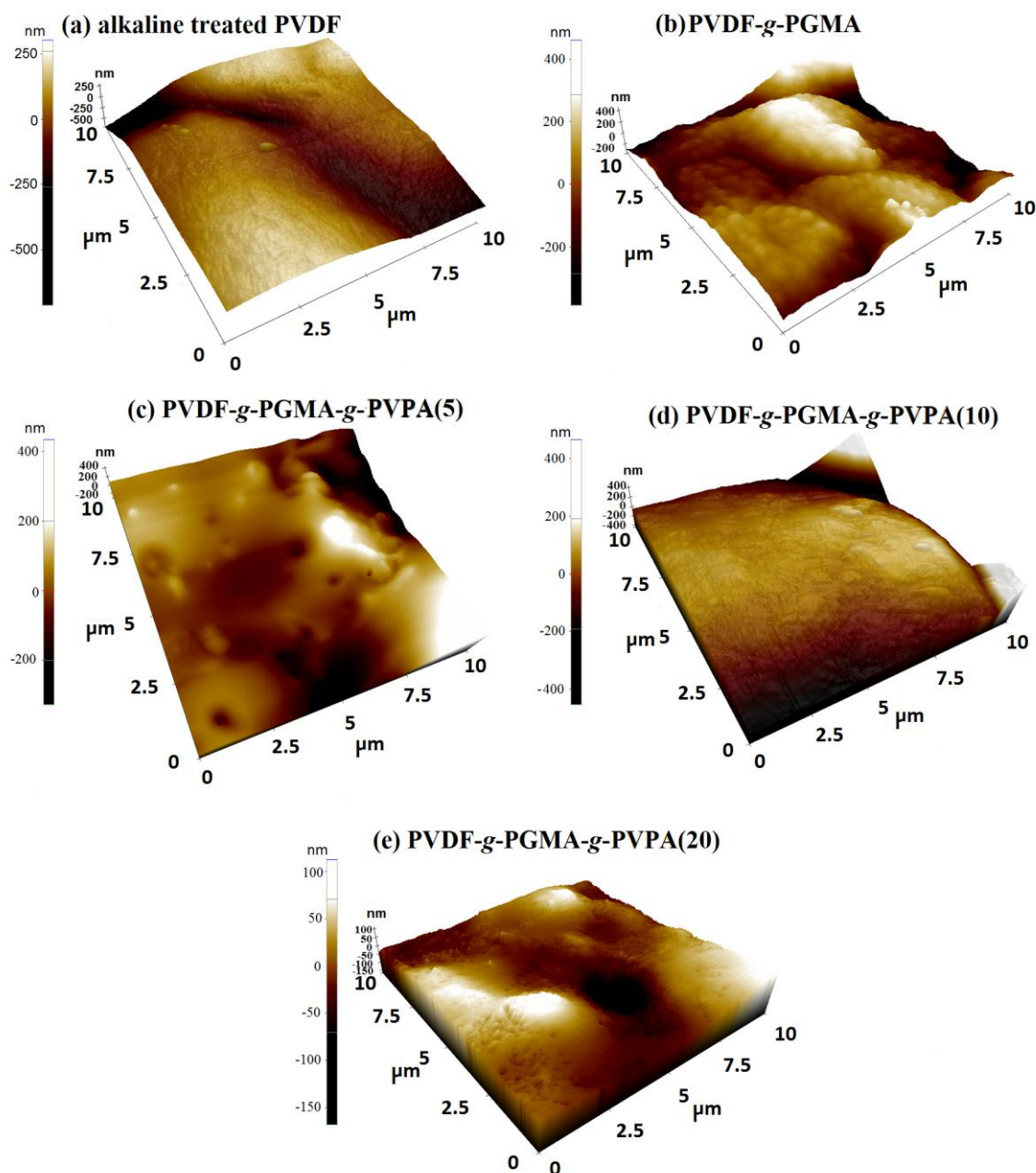


Figure 3.160 Surface topography determined by representative AFM images of the (a) alkaline-treated PVDF, (b) PVDF-*g*-PGMA, (c) PVDF-*g*-PGMA-*g*-PVPA(5), (d) PVDF-*g*-PGMA-*g*-PVPA(10), and (e) PVDF-*g*-PGMA-*g*-PVPA(20). The root-mean-squared (RMS) surface roughness of the different PVDF based membranes was obtained over a scan size of 10 μm x 10 μm.

3.9.8 Morphology

Surface morphologies of the membranes were systematically analyzed using SEM and the images of alkaline-treated PVDF, PVDF-*g*-PGMA, and PVDF-*g*-PGMA-*g*-PVPA(*x*) graft copolymer membranes are represented in Fig. 3.161. There is formation

of a smooth surface of the alkaline-treated PVDF powder and a number of pores appear as depicted in Fig. 3.161(A) (He et al., 2014; Abu-Saied et al., 2013; Dong et al., 2013; Lepit et al., 2012). Upon grafting of PGMA onto the alkaline treated PVDF, the surface morphology of PVDF films becomes rougher than that of the alkaline treated PVDF surface. It has a much more uniform pore size distribution and a higher degree of porosity, induced by the PGMA graft chains, than those of the alkaline-treated PVDF. It is presented that the image (B) exhibits uniform and porous structure. It is clear from the image (B) that no phase separation has been observed upon grafting step. It is also clear that no cracks were observed which indicates homogeneity of the grafting process. These results confirmed that GMA monomer is grafted onto the PVDF (Sinirlioglu et al., 2015b).

After modification of PVDF-*g*-PGMA graft copolymer with PVPA, we observed that all samples (Fig. 3.161(C-E)) were homogeneously dissipated with increasing the PVPA content and the images showed single phase formation due to strong interaction between phosphonic acid groups of PVPA and epoxy units of PVDF-*g*-PGMA. In all samples (Fig. 3.161(C-E)), the images showed single phase formation. This result demonstrated that there was no agglomeration or phase separation at the nanometer level. As a result, these results are well consistent with those from the observation of AFM images (Sinirlioglu et al., 2015b).

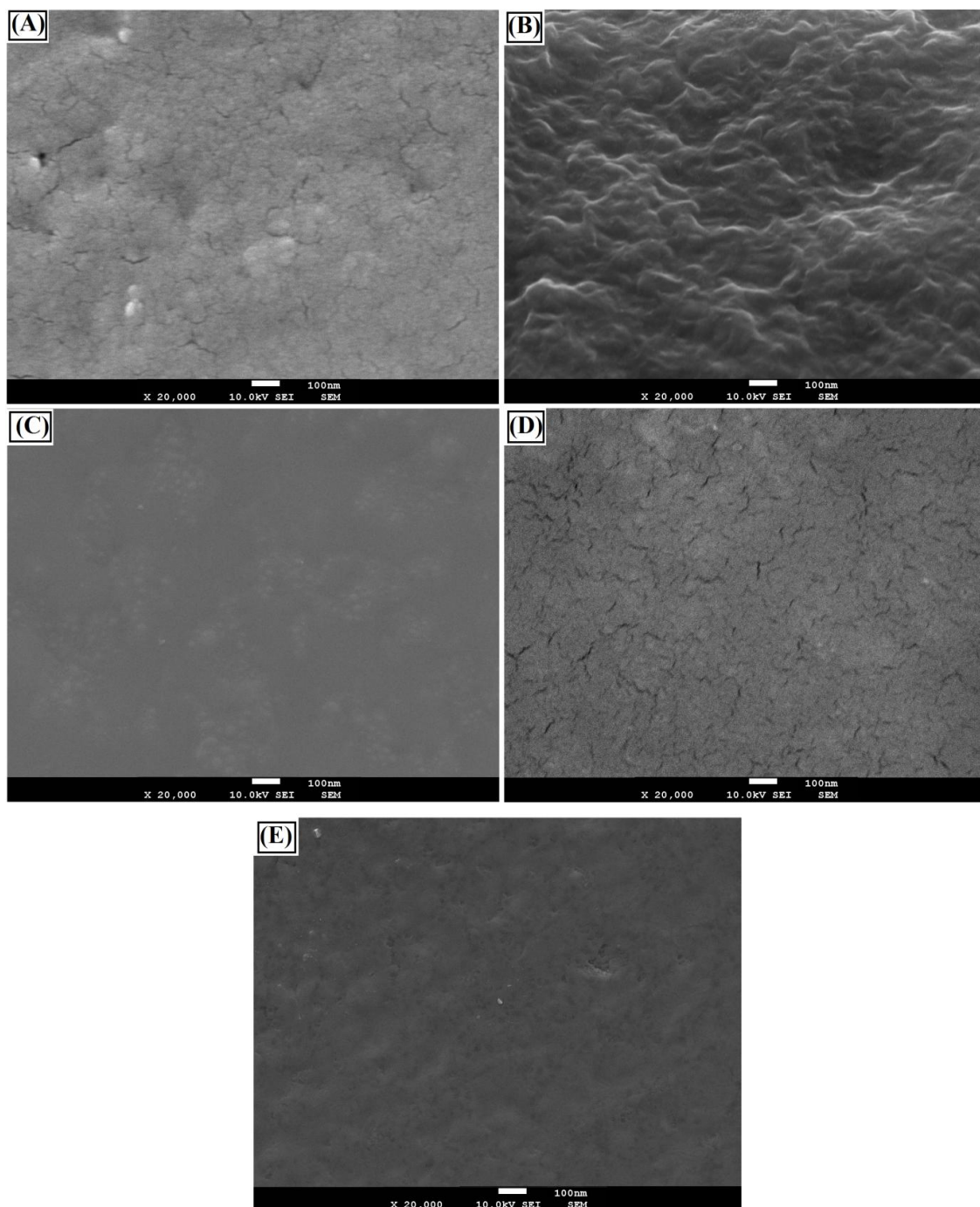


Figure 3.161 SEM images of the surface of (A) alkaline-treated PVDF powder, (B) PGMA-grafted PVDF (PVDF-*g*-PGMA), (C) PVDF-*g*-PGMA-*g*-PVPA(5), (D) PVDF-*g*-PGMA-*g*-PVPA(10), and (E) PVDF-*g*-PGMA-*g*-PVPA(20) graft copolymer membranes at 100 nm scale level by 20,000X magnification, respectively.

3.9.9 Proton conductivity measurements

The proton conductivity of PEM is the crucial factor to be investigated for the potential application in high temperature proton exchange membrane fuel cells (HT-

PEMFCs). The design and development of high performance PEMs with high proton conductivity in anhydrous conditions have been fascinated. The proton conductivities of the PVPA homopolymer, PVDF-*g*-PGMA graft copolymer membrane, and PVDF-*g*-PGMA-*g*-PVPA(*x*) (*x*=5.0, 10.0, and 20.0) membranes were measured between 20 °C to 150 °C. All membranes were fixed between additional external parallel plate electrodes (between platinum blocking electrodes) to make a sandwich using the simple two-electrode method and impedance was measured by varying the temperature from 20 °C to 150 °C (Sinirlioglu et al., 2015b).

The proton conductivity plots of PVPA homopolymer, PVDF-*g*-PGMA graft copolymer, and PVDF-*g*-PGMA-*g*-PVPA(*x*) membranes under anhydrous conditions are shown in Fig. 3.162, Fig. 3.163, Fig. 3.164, Fig. 3.165, and Fig. 3.166, respectively, as a function of temperature. At lower frequency regions, the conductivity increases with log frequency then leveled off which is due to electrode polarizations. The irregularities at the low frequency side correspond to polarization blocking the electrode-electrolyte interface and the conductivity increases at low temperature and high frequencies results from the regular dispersion in polymer electrolytes. Membrane with higher PVPA content exhibit the highest proton conductivity due to the higher concentration of protons arising from the acidic groups of PVPA. Furthermore, the proton conductivity rises with temperature due to the higher proton mobility, as expected. Maximum proton conductivities of the obtained PEMs are listed in Table 3.25. In the anhydrous conditions, the highest proton conductivity of PVDF-*g*-PGMA-*g*-PVPA(20) was found as 0.0023 S/cm at 150 °C (Sinirlioglu et al., 2015b).

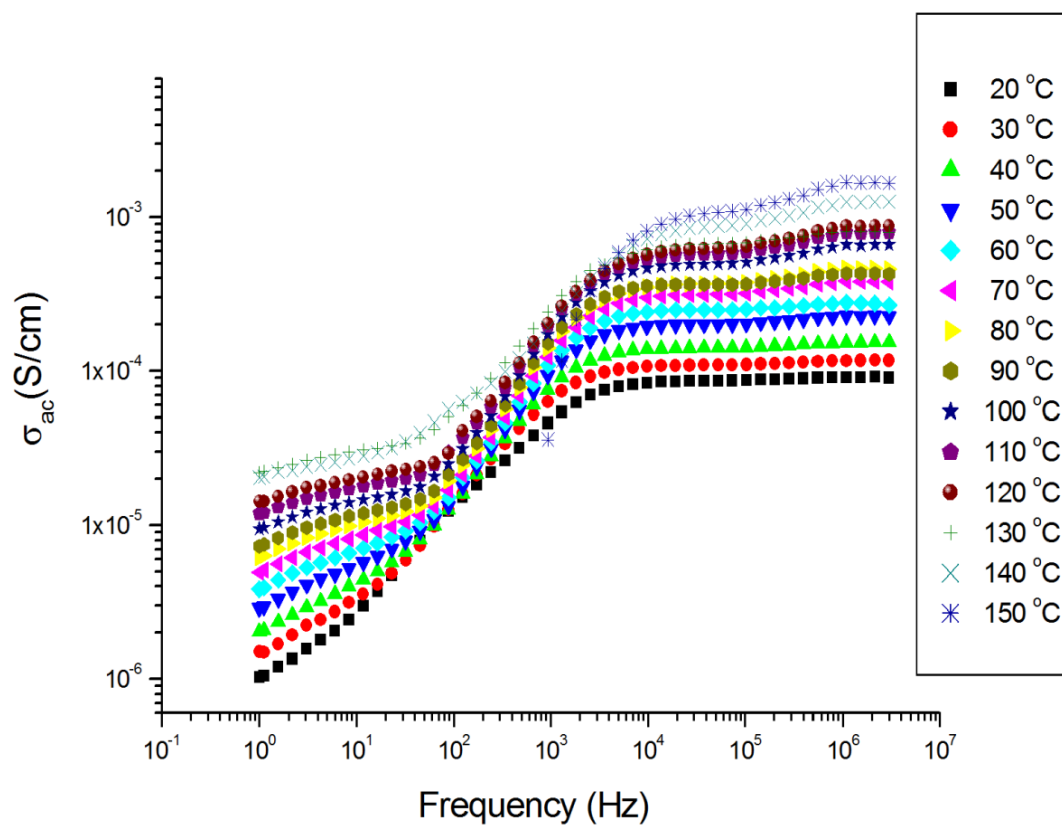


Figure 3.162 AC conductivity versus frequency of PVPA homopolymer at several temperatures.

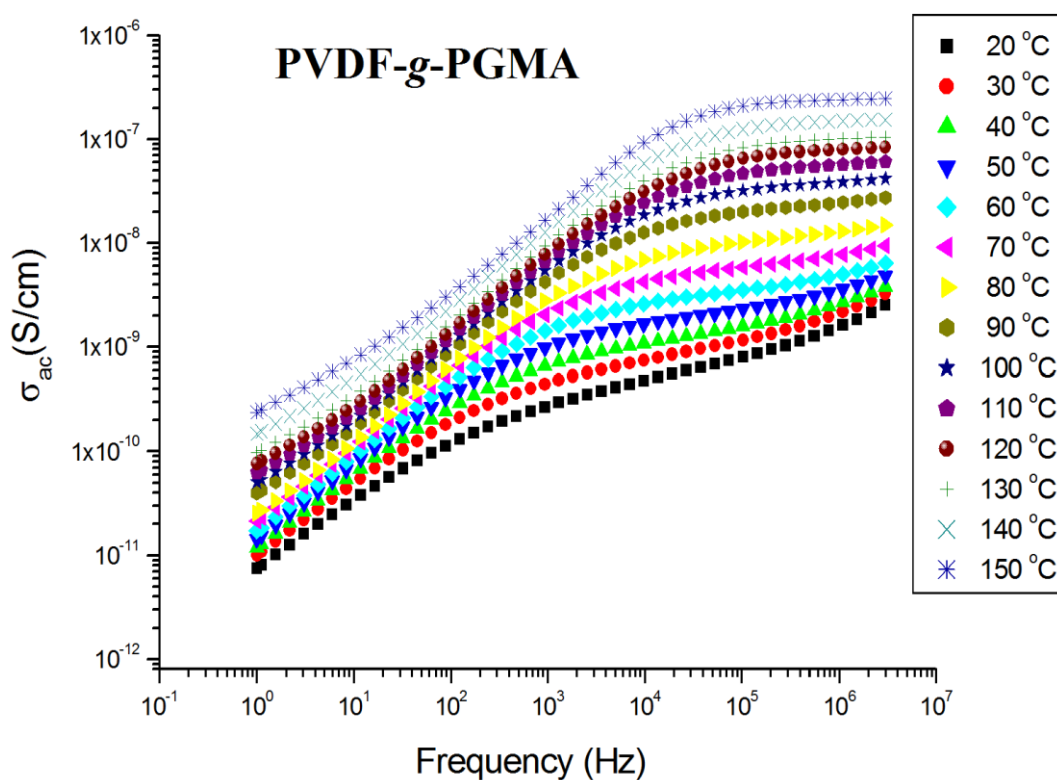


Figure 3.163 AC conductivity versus frequency of PVDF-*g*-PGMA graft copolymer at several temperatures.

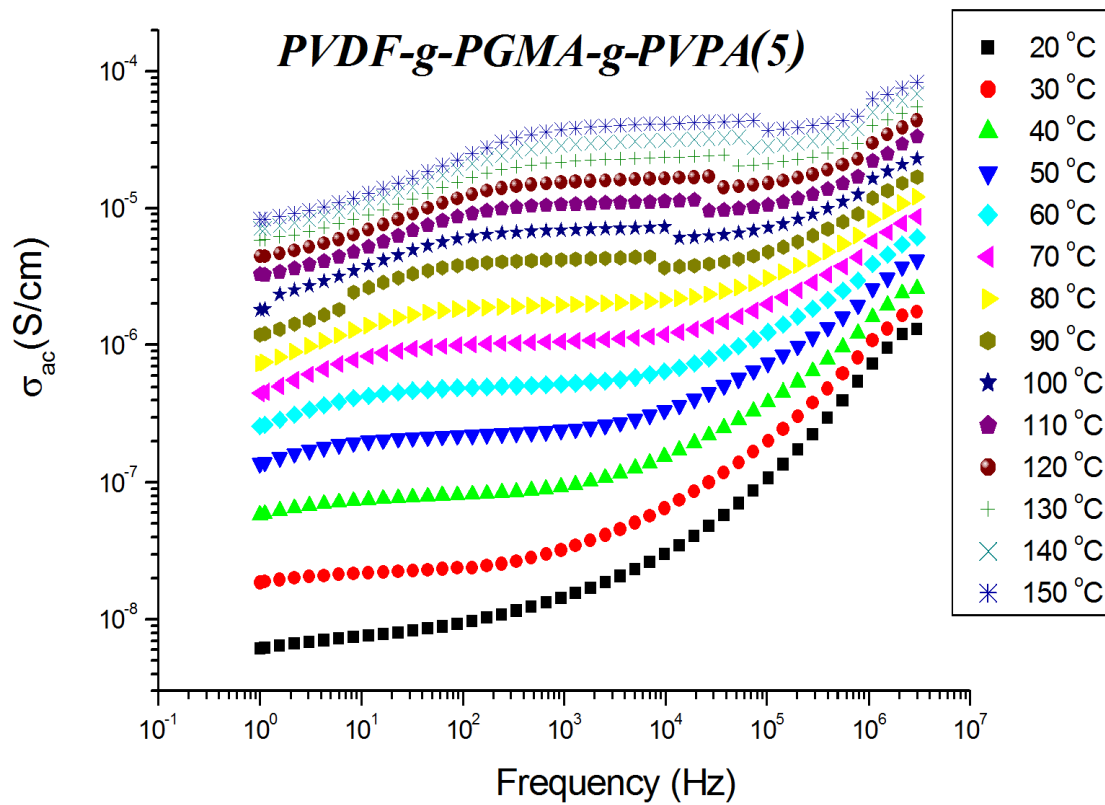


Figure 3.164 AC conductivity versus frequency of PVDF-*g*-PGMA-*g*-PVPA(5) at several temperatures.

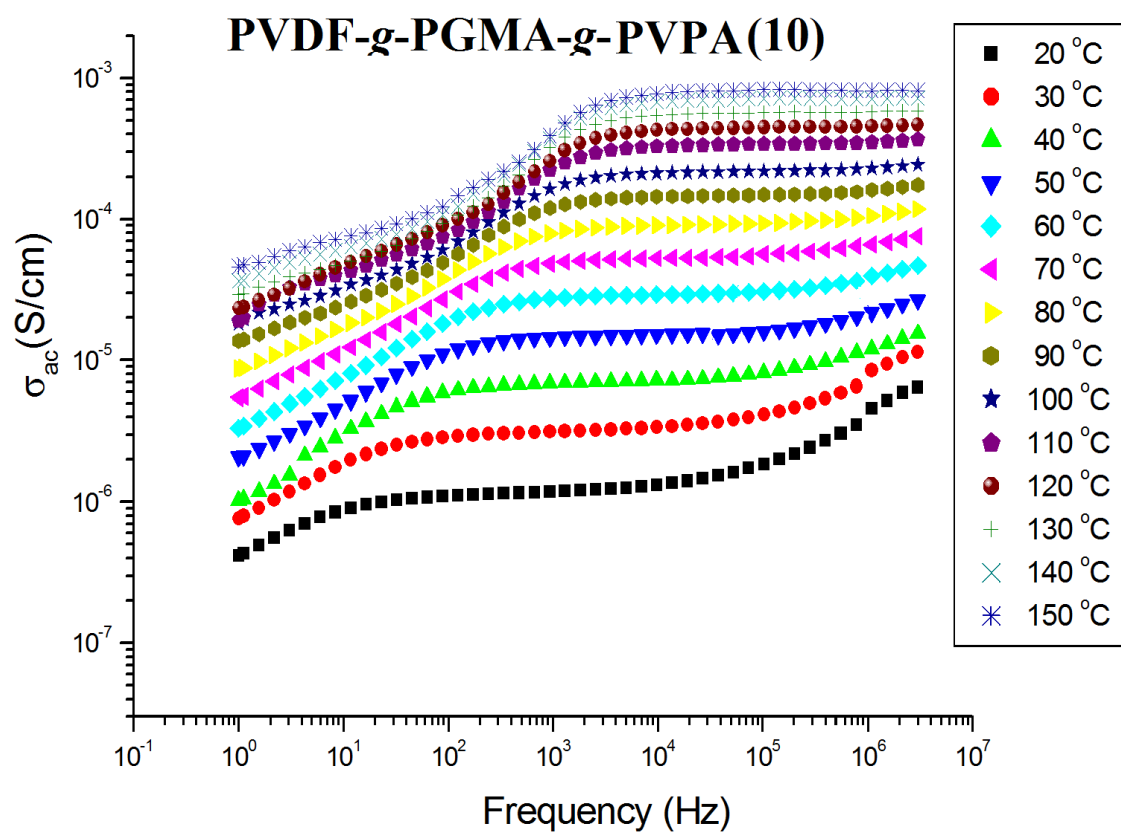


Figure 3.165 AC conductivity versus frequency of PVDF-*g*-PGMA-*g*-PVPA(10) at several temperatures.

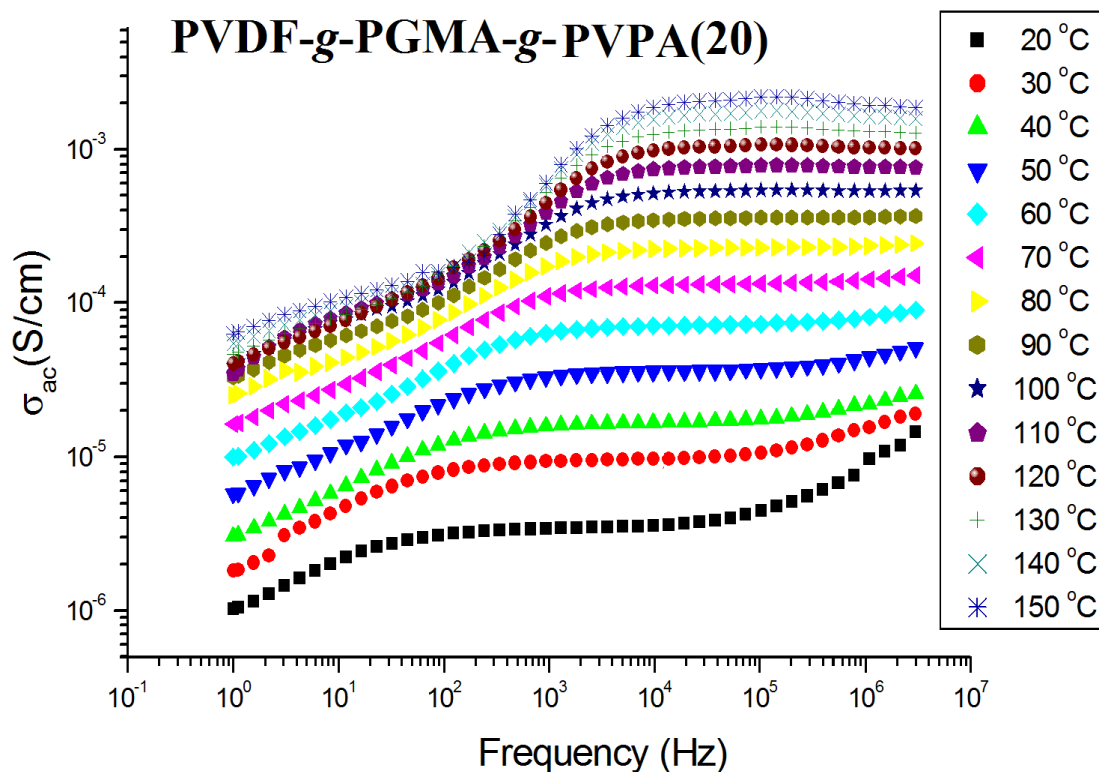


Figure 3.166 AC conductivity versus frequency of PVDF-*g*-PGMA-*g*-PVPA(20) at several temperatures.

The temperature dependence of the proton conductivities (DC conductivities) of the PVDF-*g*-PGMA graft copolymer, PVDF-*g*-PGMA-*g*-PVPA(*x*) membranes, PVPA homopolymer and commercial Nafion 117 were compared Fig. 3.167 and listed in Table 3.25. It can be seen that the proton conductivity display a linear dependence on the temperature and PVPA content. Generally, the DC curve can be explained with Arrhenius or Vogel-Tamman-Fulcher (VTF) behavior depending on the type of the curve where during the measurement temperature range no T_g was observed and there is no change in linearity of DC curve (Fig. 3.167). Herein, the curves are close to linearity. Therefore, we can say that the PVPA homopolymer, PVDF-*g*-PGMA and PVDF-*g*-PGMA-*g*-PVPA(*x*) membranes show Arrhenius behavior in the measurement range (Sinirlioglu et al., 2015b).

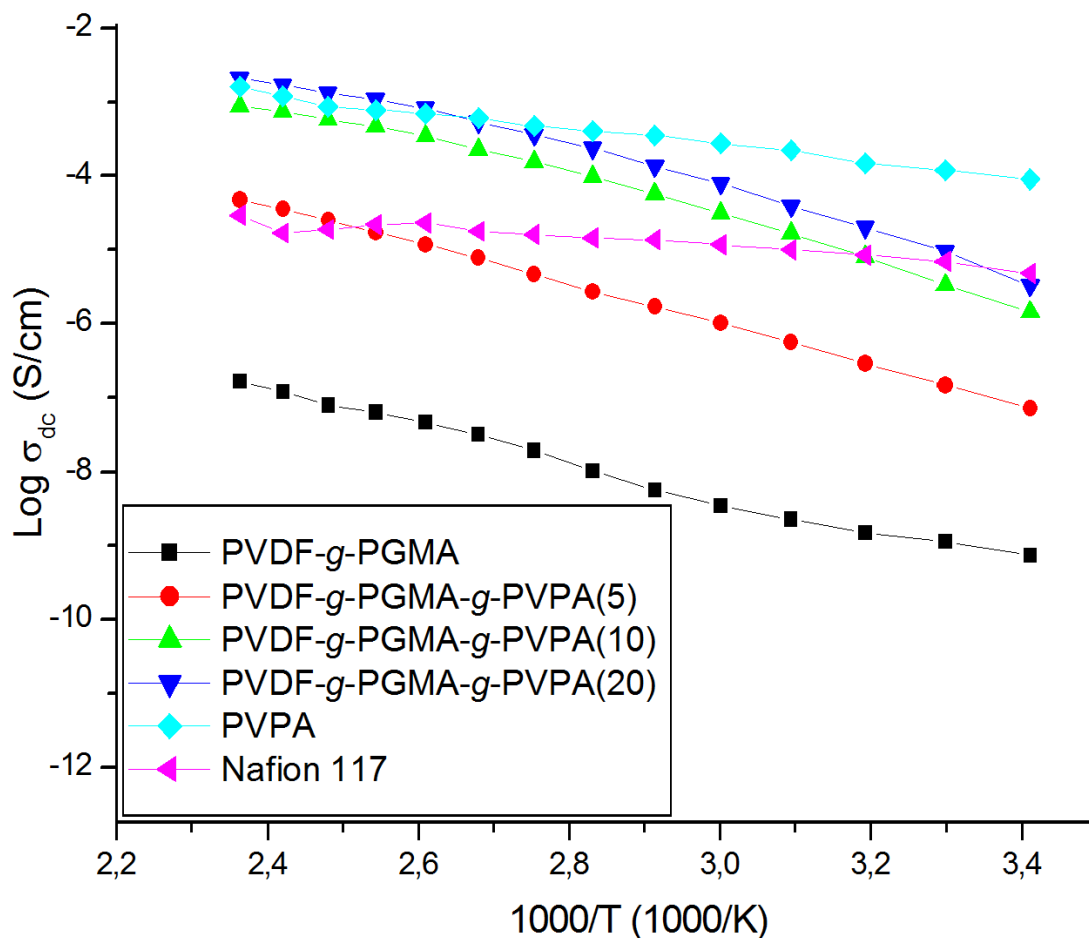


Figure 3.167 Variation of the DC proton conductivity of Nafion 117, PVPA homopolymer, PVDF-*g*-PGMA membrane, and PVDF-*g*-PGMA-*g*-PVPA(*x*) membranes as a function of reciprocal temperature.

PVDF has a similar backbone with Nafion and it provided a high thermally and mechanically stable matrix and good film formability. PVPA is an acidic polymer. It has high proton conductivity (10^{-3} S/cm) and good film forming property, which are important characteristics of a polymer electrolyte membrane. Although pure PVPA has several advantages, its water solubility makes it an improper material for PEMFC applications. Previously, Sen et al. reported the preparation of PVPA blended Nafion, Nafion-P(VPA)₃, with a maximum proton conductivity of 1.1×10^{-5} S/cm at 130 °C and anhydrous conditions (Sen et al., 2013). In another work reported by Aslan et al., a maximum proton conductivity of 5×10^{-5} S/cm at 150 °C was found for PVPA-grafted poly(glycidyl methacrylate), P(GMA)-*g*-P(VPA)₁₀ (Aslan and Bozkurt, 2009). In the present study, the highest maximum proton conductivity of PVDF-*g*-PGMA-*g*-

PVPA(20) was measured as 0.0023 S/cm at 150 °C, a superior conductivity value as compared to the afore-mentioned ones. As expected, we obtained free standing films (see Fig. 3.149).

Table 3.25 Water uptake, methanol permeability, and maximum proton conductivity values of the obtained PVDF based membranes.

Sample	Methanol Permeability (mol cm ⁻² s ⁻¹)	Relative humidity (%)	Max. Proton Conductivity (S/cm)
PVDF	-----	-----	-----
PVDF- <i>g</i> -PGMA	-----	-----	2.39x10 ⁻⁷ S/cm at 150 °C
PVDF- <i>g</i> -PGMA- <i>g</i> -PVPA(5)	-----	50	0.024 S/cm at 100 °C
PVDF- <i>g</i> -PGMA- <i>g</i> -PVPA(5)	3.12x10 ⁻⁹	-----	6.44x10 ⁻⁵ S/cm at 150 °C
PVDF- <i>g</i> -PGMA- <i>g</i> -PVPA(10)	-----	50	0.031 S/cm at 100 °C
PVDF- <i>g</i> -PGMA- <i>g</i> -PVPA(10)	2.78x10 ⁻⁹	-----	8.51x10 ⁻⁴ S/cm at 150 °C
PVDF- <i>g</i> -PGMA- <i>g</i> -PVPA(20)	-----	50	0.034 S/cm at 100 °C
PVDF- <i>g</i> -PGMA- <i>g</i> -PVPA(20)	2.28x10 ⁻⁹	-----	0.0023 S/cm at 150 °C
PVPA	-----	-----	1.51x10 ⁻³ S/cm at 150 °C
Nafion 117	1.89x10 ⁻⁹	-----	2.95x10 ⁻⁵ S/cm at 150 °C

In our study, PVPA provides a hydrophilic channel in PVDF-*g*-PGMA-*g*-PVPA(x) membranes similar to Nafion. Herein, the proton conductivity of the membranes is improved with PVPA content and maximum conductivity was observed for PVDF-*g*-PGMA-*g*-PVPA(20) membrane. These results showed that in PVDF-*g*-PGMA-*g*-PVPA(x) systems, the PVPA composition is highly effective on the proton conductivity of the membranes. PVPA interacts with PGMA units of PVDF-*g*-PGMA backbone and the major part of proton transport might be provided over the phosphonic acid phase (Sinirlioglu et al., 2015b).

Furthermore, the importance of membrane's quality on proton conductivity is further underscored from the comparison between SEM images and the measured proton conductivities. It is evident from Fig. 3.161 that the morphologies of the membranes seem to be smoothness. The smoothness of the membranes, which indicating formation of continuous conducting channels essential for enhancement of proton conductivity, increases with the increment of PVPA content in the PVDF-*g*-PGMA-*g*-PVPA(*x*) systems. PVDF-*g*-PGMA-*g*-PVPA(20) showed the smoothest surface and the highest proton conductivity (Nadzrinahamin et al., 2012).

The proton conductivity was investigated also in humidified condition and illustrated in Fig. 3.168. The proton conductivity values generally depend on both temperature and water at humidified conditions. Previously, the temperature dependence of proton conductivity of Nafion 117 at various humidity levels was studied (Takimoto et al., 2009; Casciola et al., 2006). When the membrane was fully (RH=100 %) humidified, the proton conductivity of Nafion 117 membrane was ranged from 0.11 S/cm at room temperature to 0.20 S/cm at elevated temperatures. Previously, the proton conductivity of Nafion117 at 50 % relative humidity was measured as 0.03 S/cm at 40 °C (Takimoto et al., 2009). In our study, similar to anhydrous systems at high temperature, maximum proton conductivity was measured for the sample with *x*=20. In the relative humidity (RH= 50 %), the highest maximum proton conductivity of PVDF-*g*-PGMA-*g*-PVPA(20) membrane was found as 0.023 S/cm at 80 °C and 0.034 S/cm at 100 °C, a good proton conductive PEM material which has similar structure of Nafion (Sinirlioglu et al., 2015b).

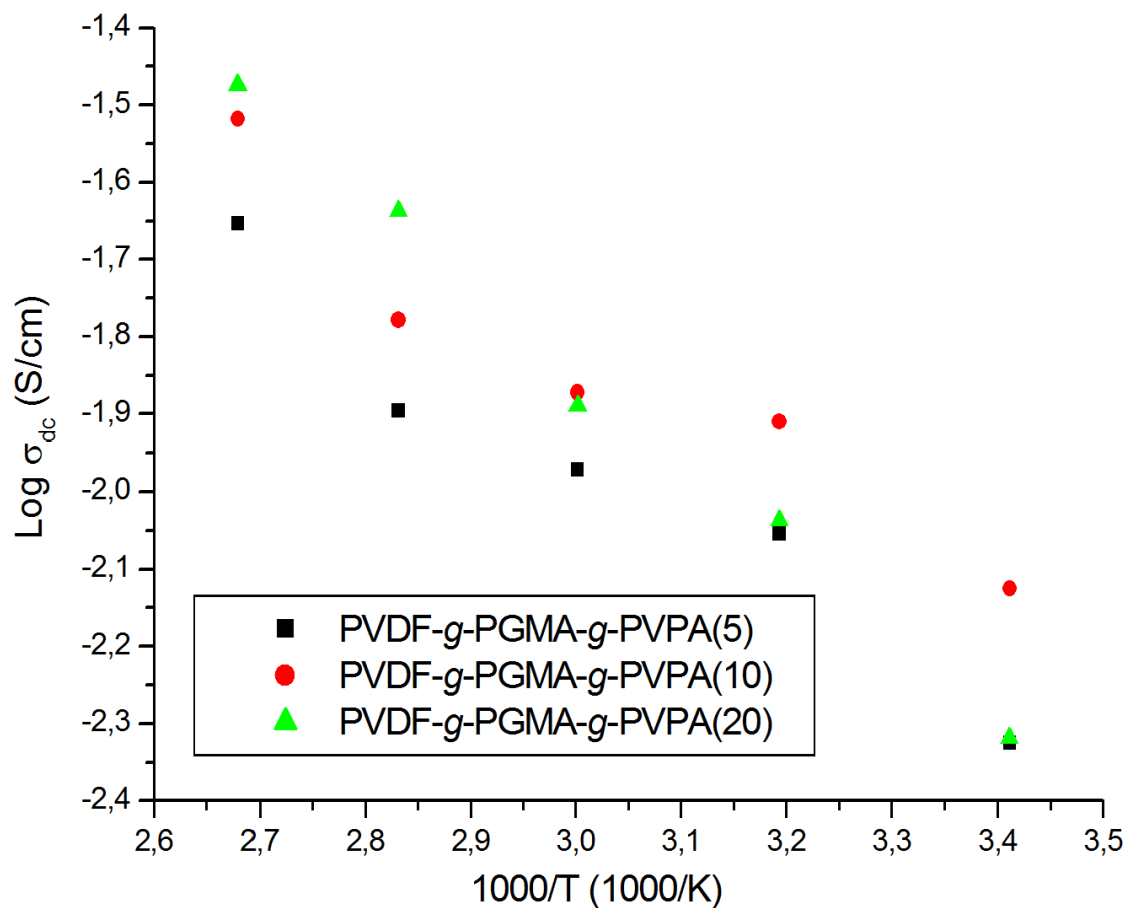


Figure 3.168 The effect of PVPA content on DC proton conductivities of 50 % humidified PVDF-*g*-PGMA-*g*-PVPA(*x*) membranes (RH=50 %) as a function of reciprocal temperature.

3.9.10 Cyclic Voltammetry

Cyclic voltammogram of PVDF-*g*-PGMA-*g*-PVPA(20) was given in Fig. 3. 169. The measurement was performed in a typical three electrode cell containing 0.1 mol dm⁻³ CH₃CN solution of tetrabutylammonium chloride (TBACl) using a platinum work electrode, a platinum auxiliary electrode, and an Ag/Ag⁺ reference electrode. The voltammogram shows that the graft copolymer membrane comprises no peak within in the anodic and cathodic sweep (-1.5 to 1.5 V potential range). Thus the electrochemical stability window is about 3V. These results implied that the PVDF-*g*-PGMA-*g*-PVPA(20) membrane had adequate electrochemical stability under fuel cell conditions (Sinirlioglu et al., 2015b).

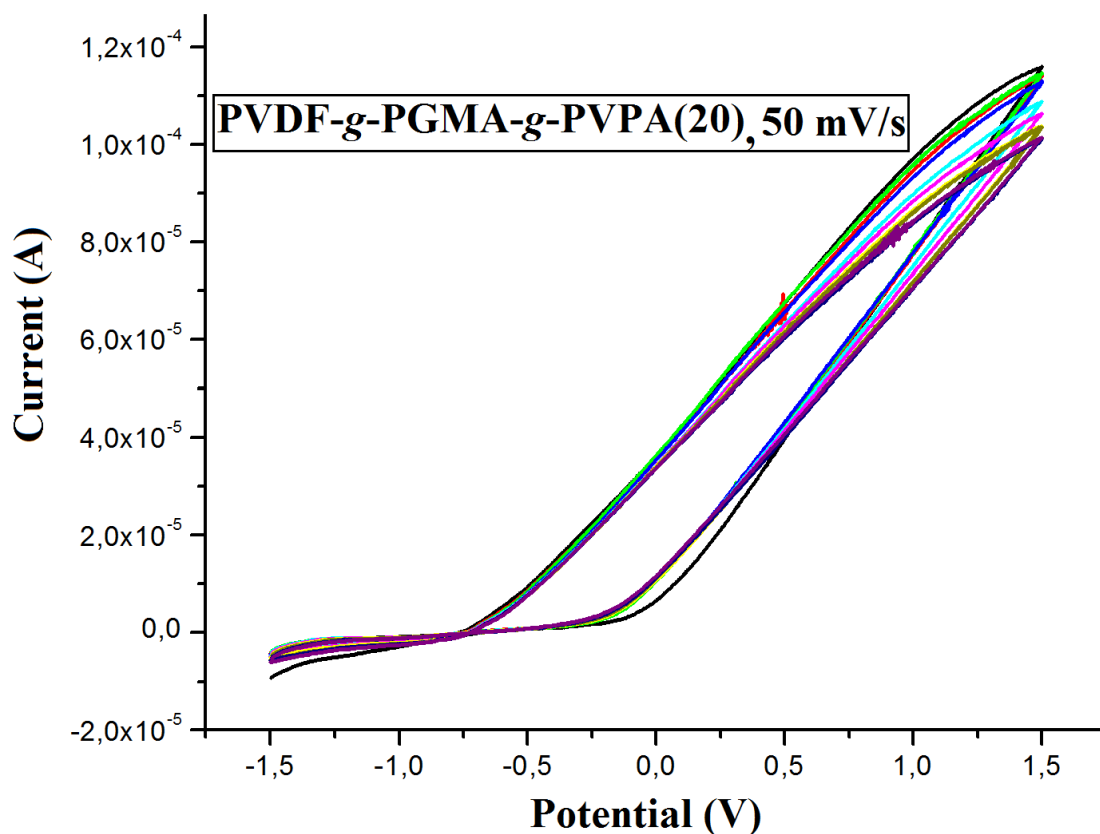


Figure 3.169 Cyclic voltammograms of PVDF-*g*-PGMA-*g*-PVPA(20) in 0.1 M TBACl / acetonitrile. Curves were obtained with a scan rate of 50 mV/s.

3.10 SYNTHESIS OF PVDF BASED ANHYDROUS PROTON EXCHANGE MEMBRANES PREPARED VIA A FACILE “GRAFTING THROUGH” STRATEGY

Poly(vinylidene fluoride) (PVDF) has a number of advantages such as low cost, high chemical resistance, and enhanced thermal and mechanical properties, making it a powerful candidate to be employed as a PEM material. Thus far, modified PVDF films have been prepared using grafting methods and their potential in several applications has been explored. Homogeneous or surface grafting methods were more preferred to adopt hydrophilic nature to the PVDF membranes and maintain increased proton conductivity (Sinirlioglu et al., 2015c).

Previously, we have reported the first time fabrication of anhydrous PEMs by the use of alkaline treated PVDF powder and *N*-heterocyclic monomer in a “grafting through” strategy (Sinirlioglu et al., 2014b). The method seemed interesting for

designing further PVDF based membranes for fuel cells, since it offered an easy and versatile fabrication of PVDF based PEMs with relatively high grafting efficiencies and high proton conductivities.

Quite recently, we have employed a direct surface-initiated AGET-ATRP method in the surface grafting of glycidyl methacrylate (GMA) onto PVDF. Upon functionalizing PVDF-*g*-PGMA with 5-aminotetrazole and subsequent doping with triflic acid (TA), anhydrous PEMs were obtained with a maximum proton conductivity of 0.011 S/ cm at 150 °C. However, this method was not successful in achieving high degrees of grafting, which would limit its use in the production of diverse membranes (Arslantas et al., 2014).

In the present study, our goal is to adopt the versatile and facile alkaline treatment method in the grafting of GMA onto PVDF and, thus, obtain 5-aminotetrazole functional PVDF-*g*-PGMA-ATet PEMs having improved degrees of grafting and higher maximum proton conductivities (Sinirlioglu et al., 2015c). In this contribution, PVDF-*g*-PGMA graft copolymers were produced via free radical copolymerization of GMA and alkaline treated PVDF, in which, the latter served as a macromonomer in the “Grafting through” strategy. Particularly, alkaline treatment method worked well yielding high degrees of grafting (please see Table 3.26). PVDF-*g*-PGMA (C3) with the highest degree of grafting of 80.62 % by weight was selected and functionalized with 5-aminotetrazole by the ring opening of epoxide group. Upon doping with triflic acid (TA) at different mole ratios with respect to aminotetrazole units, various PVDF-*g*-PGMA-ATet-(TA)_x membranes were fabricated. The synthetic process is schematically given in Fig. 3.170 while anhydrous membranes can be seen in Fig. 3.171 (a) and (b) (Sinirlioglu et al., 2015c). According to reaction scheme, it may be expected that crosslinking could take place due to the presence of amino and azole functionalities located on the same molecule, reacting with epoxy groups. However, since PVDF-*g*-PGMA-ATet was completely soluble in DMF, crosslinking does not occur (Sinirlioglu et al., 2015c).

Main issue to be confirmed about grafting via alkaline treatment of PVDF is that double bonds are actually generated on PVDF by alkaline treatment and that modified PVDF is involved as a macromonomer in the copolymerization with GMA to yield PVDF-*g*-PGMA. Previously, Ross et. al. reported a comprehensive study on alkaline

treatment of PVDF (Ross et al., 2000; Ross et al., 2001). On the basis of a degradation mechanism they proposed, they explored the possibility of both defluorination and oxygenation by using ToF-SIMS (time-of-flight secondary ion mass spectroscopy), XPS (X-ray photoelectron spectroscopy), Raman spectroscopy, and FTIR. In the present contribution, we have also found out significant spectroscopic evidence for the formation of conjugated double bonds on PVDF upon alkaline treatment as will be discussed below. Moreover, it is quite likely that the double bonds positioned on PVDF backbone contribute to propagation in a “Grafting Through” approach. It is noteworthy that existence of PGMA as will be spectroscopically discussed below can not arise from homopolymer formation since it can well be expected that all the possibly formed homopolymer must have been removed upon careful washing with excess chloroform for 24 h (Sinirlioglu et al., 2015c).

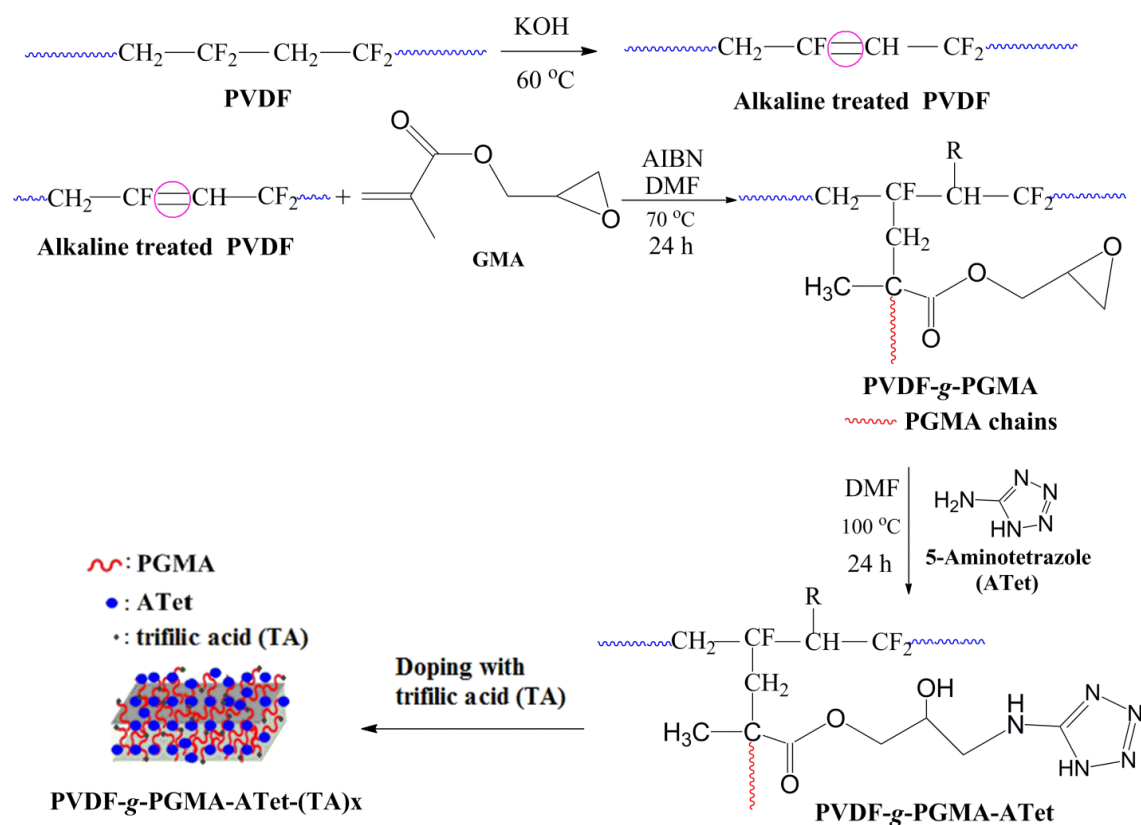


Figure 3.170 Schematic illustration for the graft copolymer synthesis and membrane formation.

**(a)****(b)**

Figure 3.171 Free standing membranes of **(a)** PVDF-*g*-PGMA (C3), and **(b)** PVDF-*g*-PGMA-ATet (C3-ATet).

3.10.1 FTIR analysis

Fig. 3.172 shows the FTIR spectra of PGMA, PGMA-ATet, PVDF, alkaline treated PVDF, PVDF-*g*-PGMA, and PVDF-*g*-PGMA-ATet membranes. In PGMA, the carbonyl group gives a strong peak at 1725 cm^{-1} and the strong peaks at 1140 cm^{-1} and 1260 cm^{-1} are attributed to C-O stretching of the ester group. The absorption peak at 906 cm^{-1} belongs to epoxy (oxirane) rings. PGMA-ATet exhibited a medium absorption at 1648 cm^{-1} and 1555 cm^{-1} due to amine bond and tetrazole ring vibrations, respectively. The epoxy absorption peak at 906 cm^{-1} is assigned to stretching vibration of the epoxy group which disappeared upon tetrazole functionalization. The asymmetric and symmetric stretching vibrations of the $-\text{CH}_2$ groups in the PVDF base film were located, respectively, at 3024 cm^{-1} and 2982 cm^{-1} . The FTIR spectra of PVDF show a strong peak at 1404 cm^{-1} , corresponding to $-\text{CH}_2$ bending. Strong and wide peaks appearing between $1246\text{--}1070\text{ cm}^{-1}$ correspond to the C-F stretching and were characteristic peaks of the PVDF. Degradation of PVDF was performed by alkaline treatment (defluorination due to alkaline treatment leading to the introduction of hydroxyl and carbonyl groups). FTIR spectra of alkaline treated PVDF show that the broad absorption peak at 3387 cm^{-1} might be due to H-bonded $-\text{OH}$ groups while those between 1730 cm^{-1} and 1630 cm^{-1} can be associated with the stretching vibrations of C=O and C=C groups in different molecular frames. In comparison to the spectrum of alkaline treated PVDF, PVDF-*g*-PGMA shows an additional peak at 1735 cm^{-1} due to the ester stretching mode of the grafted GMA segments. The strong peaks at 1257 cm^{-1} and 1143 cm^{-1} are attributed to C-O stretching of the ester group. Furthermore, the absorption peak at 903 cm^{-1} is assigned to stretching vibration of the epoxy group. Furthermore, disappearance of the relatively broad peak at 1649 cm^{-1} corresponding to carbon-carbon double bond indicates that PGMA has been grafted through PVDF upon rupture of C=C double bond during polymerization. After modification of PVDF-*g*-PGMA with ATet, PVDF-*g*-PGMA-ATet exhibited a medium absorption at 1648 cm^{-1} and 1550 cm^{-1} due to amine bond and tetrazole ring vibrations, respectively. The epoxy absorption peak at 906 cm^{-1} disappeared on tetrazole functionalization. These signs evidenced that ATet was immobilized onto PVDF-*g*-PGMA (Sinirlioglu et al., 2015c).

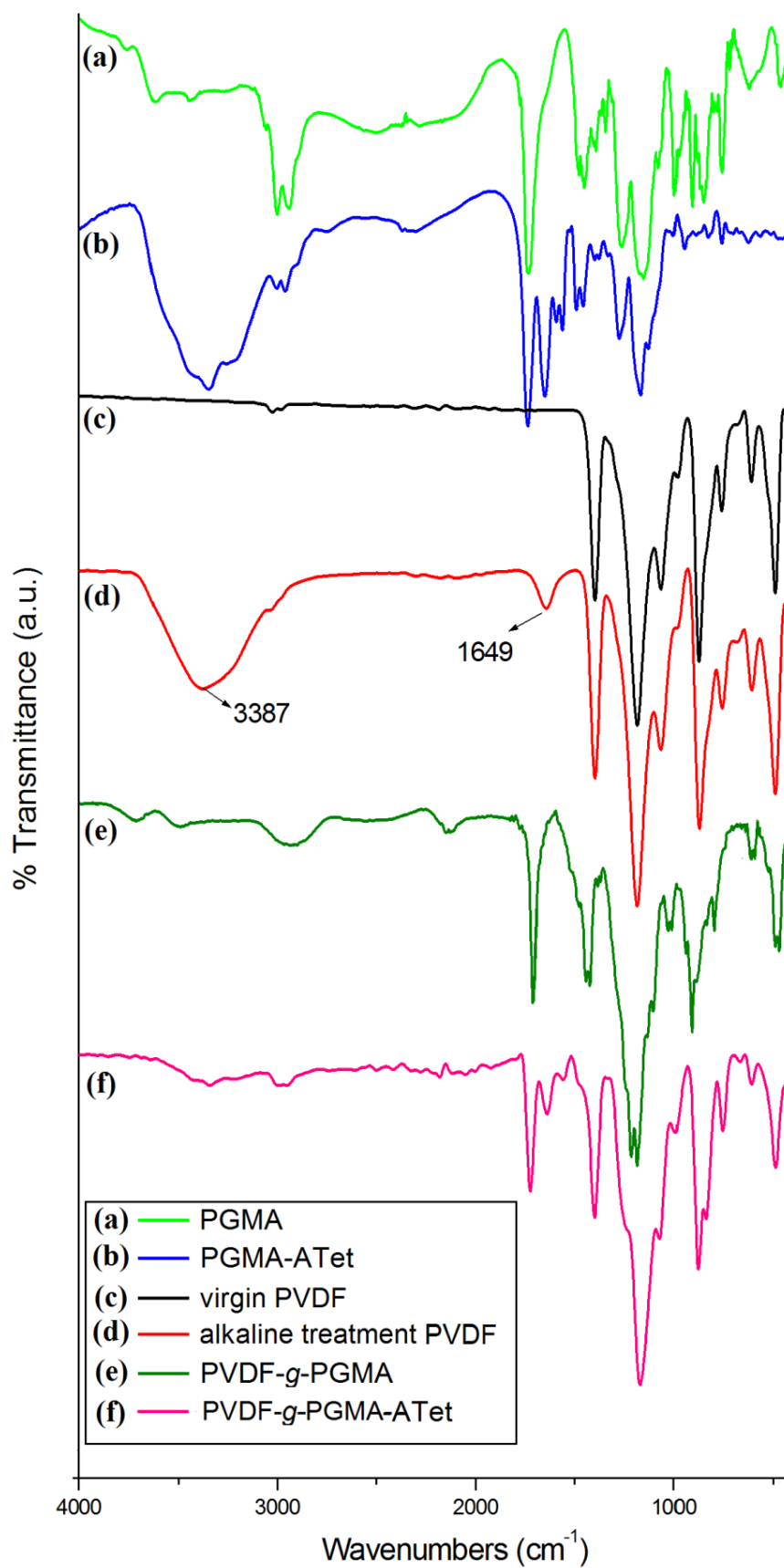


Figure 3.172 FTIR spectra of (a) PGMA, (b) PGMA-ATet, (c) PVDF, (d) alkaline treated PVDF, (e) PVDF-*g*-PGMA (C3), and (f) PVDF-*g*-PGMA-ATet (C3-ATet) membranes.

Fig. 3.173 shows the FTIR spectra of PVDF-*g*-PGMA-ATet (C3-ATet) membrane, and acid-doped PVDF-*g*-PGMA-ATet membranes, respectively (see page 275). After doping PVDF-*g*-PGMA-ATet membranes with TA, the intensity of the peak at 1553 cm^{-1} decreases which may show the protonation of the tetrazole ring. Furthermore, the carbonyl stretching band at 1721 cm^{-1} decreases and broadens due to protonation of the C=O bond. TA gives several absorptions between 1030 cm^{-1} and 1232 cm^{-1} . The strong bands at 1160 and 1232 cm^{-1} are attributed to SO_2 , and a strong absorption peak at 1026 cm^{-1} most probably belongs to $-\text{SO}_3^-\text{[H}^+]$. The formation of a peak at around 3180 cm^{-1} shows the protonation of the tetrazole rings, in addition to the broad peaks around 3510 cm^{-1} (Sinirlioglu et al., 2015c).

3.10.2 NMR analysis

The successful graft copolymerization was verified using ^1H -NMR and ^{19}F -NMR spectroscopy. As shown in the assignment of original PVDF and alkaline treated PVDF containing double bonds in ^1H -NMR spectra in Fig. 3.174, the two multiple peaks appearing at 2.91 and 2.28 ppm in the original PVDF and alkaline treated PVDF are related to the methylene protons on VDF units in the typical head-to-tail (ht) ($-\text{CH}_2-\text{CF}_2-\text{CH}_2-\text{CF}_2-$) and reversed tail-to-tail (tt) ($-\text{CF}_2-\text{CH}_2-\text{CH}_2-\text{CF}_2-$) connections, respectively (Sinirlioglu et al., 2015c). Differing from that of original PVDF, the new multiple peaks at 6.0-6.5 ppm in alkaline treated PVDF correspond to the protons on the double bonds ($-\text{CH}_2-\text{CF}=\text{CH}-\text{CF}_2-$) after the elimination of HF from PVDF. These peaks evidenced the formation of the double bonds ($-\text{CH}_2-\text{CF}=\text{CH}-\text{CF}_2-$). All the information strongly suggests that the elimination reaction and the formation of internal unsaturation occur in the alkaline treated PVDF. The amount of double bonds formed in PVDF after alkaline treatment was calculated on the basis of integral ratios from ^1H -NMR spectra and was determined as 3% by mole (Sinirlioglu et al., 2015c).

Fig. 3.175 shows the ^1H -NMR spectra of PVDF-*g*-PGMA (C3) and PVDF-*g*-PGMA-ATet (C3-ATet) membranes. The spectrum exhibited two peaks at 2.90 and 2.26 ppm, assigned to the head-to-tail (ht) and tail-to-tail (tt) bonding arrangements of vinylidene fluoride units, respectively (Sasa et al., 2013). The signals at 1.89 and 1.82 ppm (b) originates from the methylene groups of PGMA backbone. The signals observed at 0.98 and 0.82 ppm (c) are due to the protons in the methyl groups of PGMA. The spectrum also indicated two signals at 4.35 and 3.75 ppm (d), attributable

to $-\text{COOCH}_2-$ group of PGMA. The peaks at 3.25 ppm (e), 2.8 and 2.66 ppm (f) are due to the protons of the oxirane ring. After modification of PVDF-*g*-PGMA (C3) copolymer with ATet, the appearance of the peaks belonging to $-\text{NH}$ proton of the tetrazole ring between 6.80-6.40 ppm (h) and $-\text{CH}_2-\text{NH}$ proton of aliphatic chain between 6.00-5.50 ppm (g) are a typical indication for the successful evidence of modification reaction of PVDF-*g*-PGMA graft copolymer as depicted in Fig. 3.175. For all samples, the peaks of solvent (DMSO) and water appeared at 2.51 and 3.37 ppm, respectively. In addition, the signals at 2.75, 2.89 and 7.99 ppm belong to the DMF (Sinirlioglu et al., 2015c).

As mentioned in the FTIR analysis above, the disappearance of the relatively broad peak at 1649 cm^{-1} corresponding to carbon-carbon double bond indicates that PGMA has been grafted through PVDF upon rupture of $\text{C}=\text{C}$ double bond during polymerization. This is also supported by ^1H -NMR as the peak between 6.0-6.5 ppm diminished to a great extent. Based on the integral ratios after grafting, the double bonds in PVDF were involved in propagation with an efficiency of 94 % (Sinirlioglu et al., 2015c).

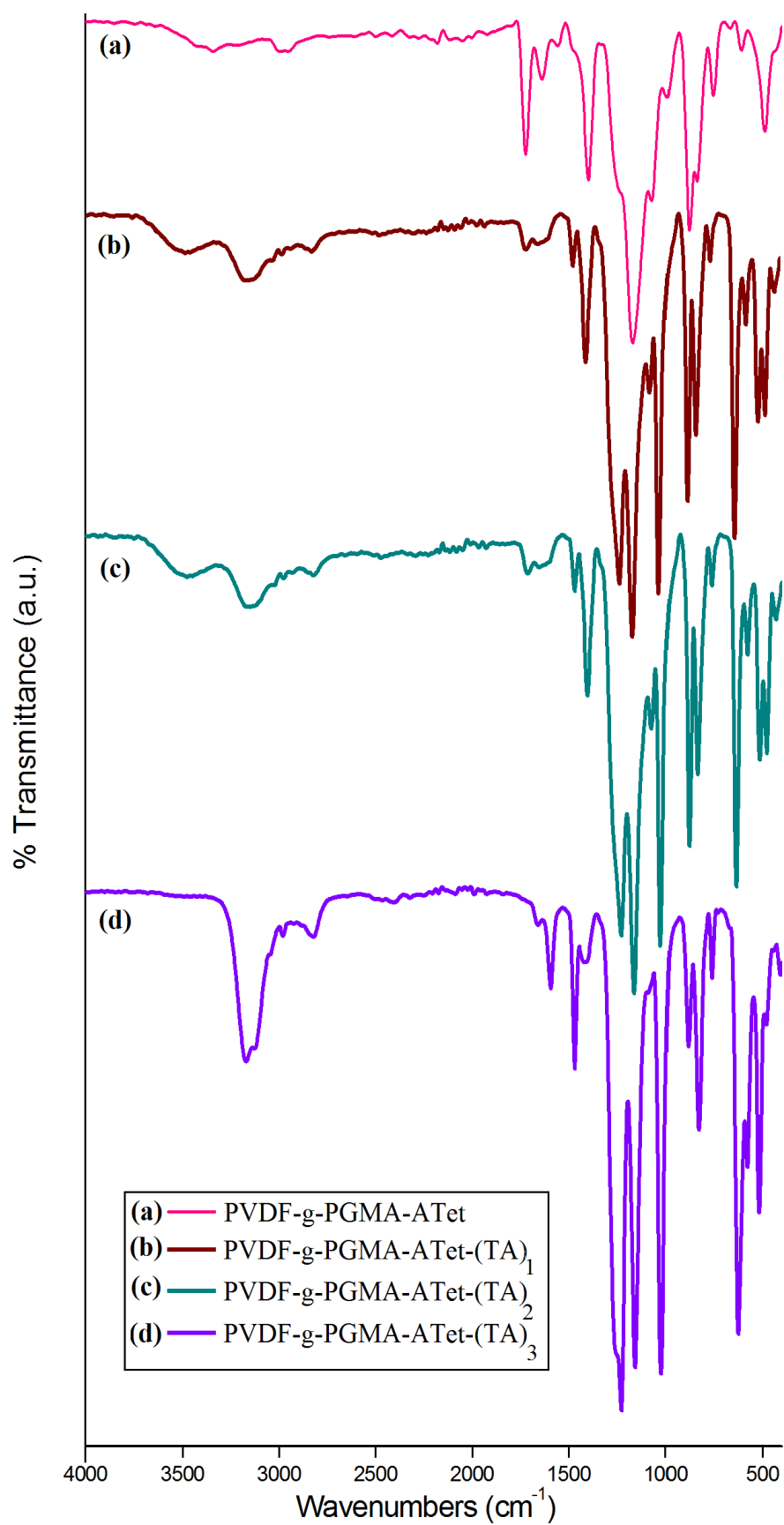


Figure 3.173 FTIR spectra of (a) PVDF-*g*-PGMA-ATet (C3-ATet), (b) C3-ATet-(TA)₁, (c) C3-ATet-(TA)₂, and (d) C3-ATet-(TA)₃ membranes.

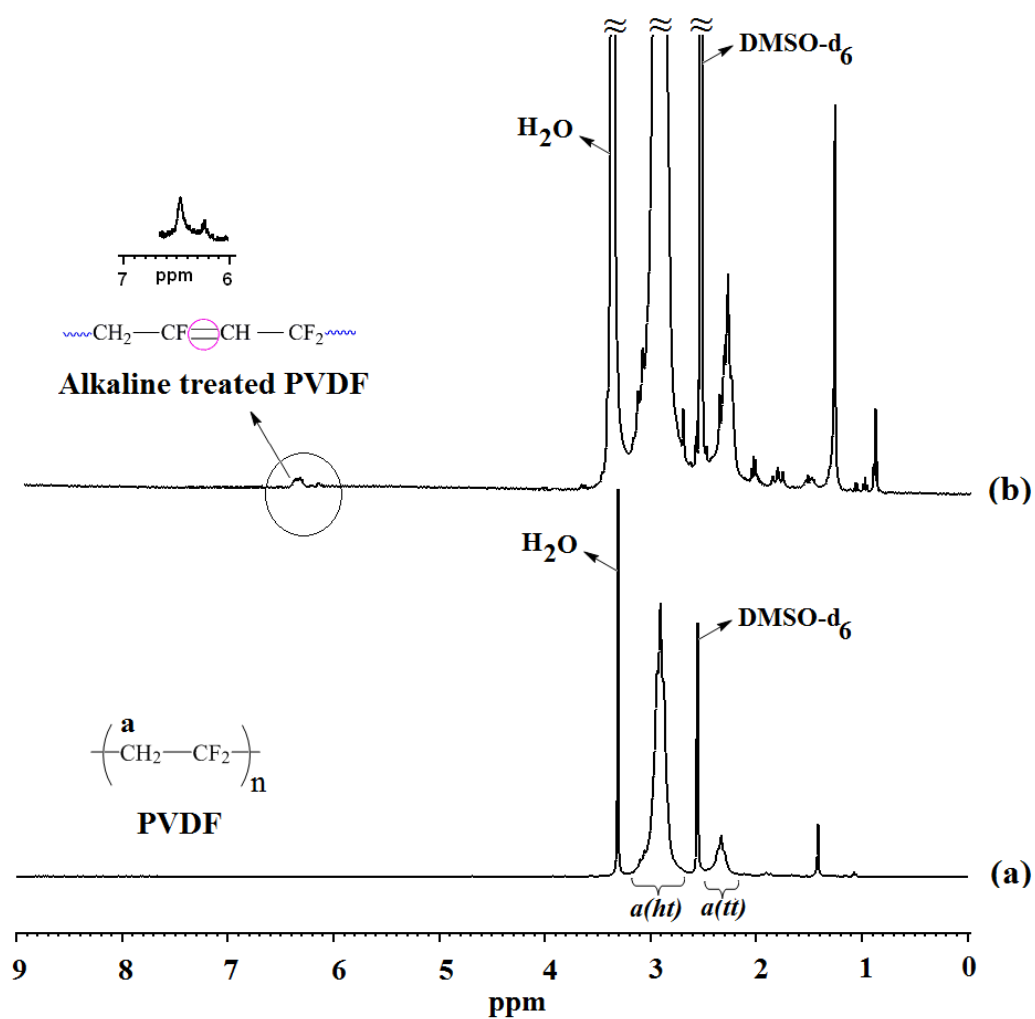


Figure 3.174 ^1H -NMR spectra of (a) PVDF, and (b) alkaline treated PVDF recorded in DMSO-d_6 .

Figure 3.175 ^1H -NMR spectra of PVDF-*g*-PGMA (C3) graft copolymer membrane, and PVDF-*g*-PGMA-ATet (C3-ATet) graft copolymer membrane recorded in DMSO- d_6 .

The composition of PVDF-*g*-PGMA copolymers (C1-C3) was verified by EDS analysis and the results are summarized in Table 3.26, which were well supported by C, F, and O content calculated in conjunction with grafting degree (GD) obtained from ^1H -NMR. The integration ratio of the protons in the ^1H -NMR yielded, respectively, a degree of grafting of 28.61 %, 41.47 %, 80.62 % using the following equation:

$$\text{Degree of Grafting (GD) (\%)} = \frac{\text{Mw}(\text{glycidyl methacrylate}) \times A(d+d)}{\text{Mw}(\text{PVDF}) \times A(a)} \times 100$$

where Mw(PVDF) is molecular weight of repeating unit of PVDF, A(a) are the integral areas of the characteristic peak (a) of the PVDF main chain (used as reference peak) and -CH₂ protons of the glycidyl methacrylate (d) of PGMA, respectively (Sinirlioglu et al., 2015c).

Aminotetrazole content of the PVDF-*g*-PGMA-ATet (C3-ATet) membrane, which was calculated on the basis of nitrogen analysis, was determined as 97 % by weight (Table 3.27). The results confirmed that the grafting and modification were successful. Furthermore, azole content of the PVDF-*g*-PGMA-ATet (C3-ATet) membrane, which was also calculated on the basis of integral ratios from ^1H -NMR spectra, was found as 94.85 % by weight. Thus, ^1H -NMR spectra supported the EDS results (Sinirlioglu et al., 2015c).

The successfully introduced double bond in the PVDF could also be confirmed by ^{19}F -NMR. The spectra of PVDF, alkaline treated PVDF, and PVDF-*g*-PGMA graft copolymer membrane are compared in Fig. 3.176. The structure of PVDF is dominated by the presence of VDF-VDF head-to-tail (ht) (-CH₂-CF₂-CH₂-CF₂-CH₂-CF₂-) sequences appearing between -92 and -96 ppm, and VDF-VDF tail-to-tail (tt) (-CF₂-CH₂-CH₂-CF₂-) structure appearing between -114 and -117 ppm. Compared with PVDF, the new signals emerging at around -107 ppm in alkalined treated PVDF could be assigned to the F atoms in the double bond (-CH₂-CF=CH-CF₂-) units. The same peaks at around -107 ppm were also detectable in the spectrum of PVDF-*g*-PGMA, supporting that grafting has successfully occurred (Sinirlioglu et al., 2015c).

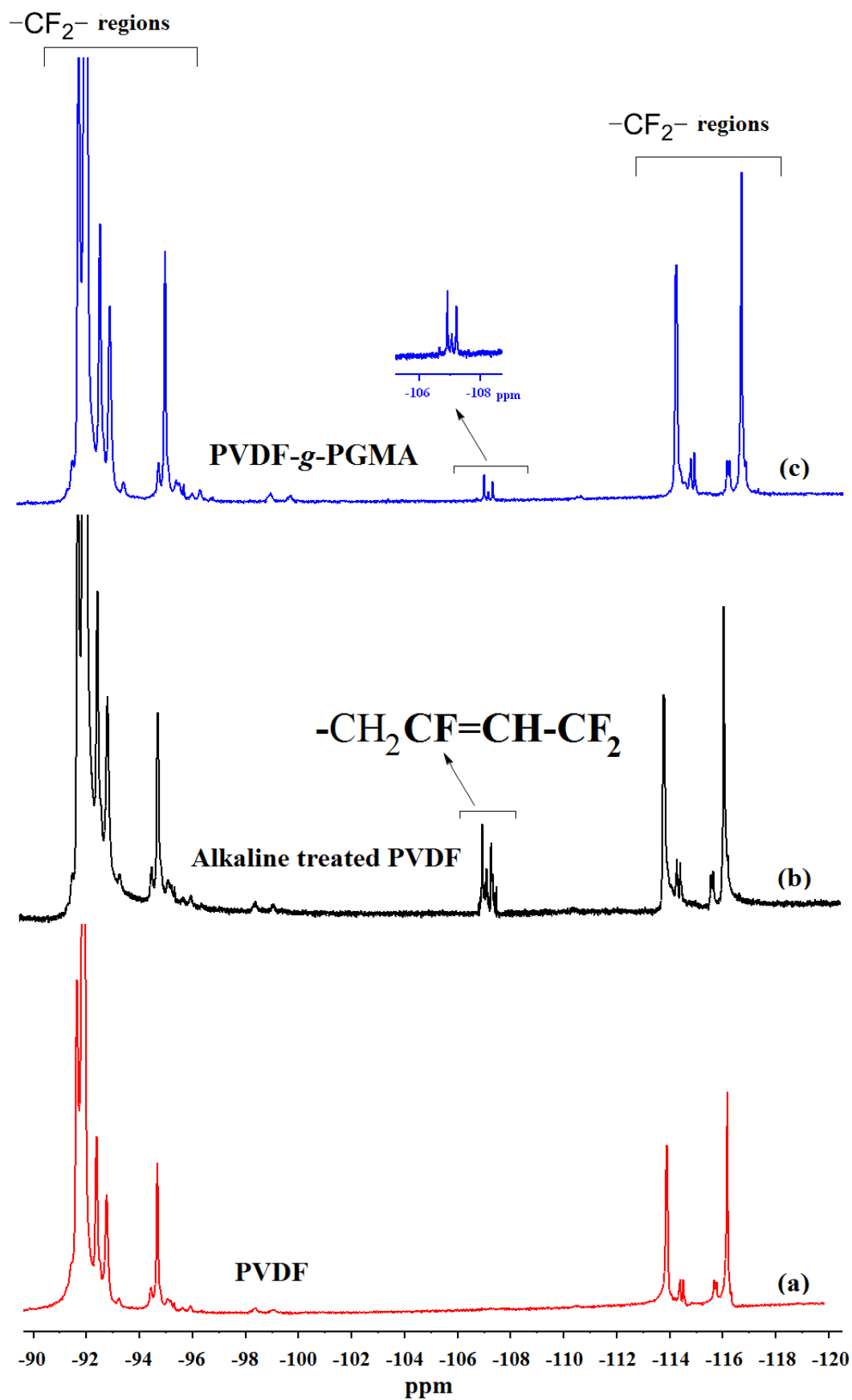


Figure 3.176 ^{19}F -NMR spectra of (a) PVDF, (b) alkaline treated PVDF, and (c) PVDF-*g*-PGMA graft copolymer recorded in DMSO-d_6 .

Table 3.26 Chemical compositions of PVDF-*g*-PGMA (C1-C3) copolymer membranes.

Sample	(weight ratio, g) treated PVDF : GMA	GD (%) ^a	GD (%) ^b	Chemical elements (%) ^c			
				C	F	O	
C1	5:1	12.63	28.61	42.92	46.90	7.52	Theoretical
				42.84	48.31	8.85	Found
C2	5:3	18.69	41.47	43.79	40.77	13.96	Theoretical
				44.74	40.99	14.28	Found
C3	5:5	36.30	80.62	46.01	33.51	15.02	Theoretical
				49.62	32.91	15.19	Found

a: found from ¹H-NMR on a % by mol basis, **b:** found from ¹H-NMR on a % by weight basis, **c:** found from EDS results on a % by weight basis. (GD: Grafting degree)

Table 3.27 Tetrazole content of PVDF-*g*-PGMA-ATet (C3-ATet) calculated by EDS

Sample	C (%)	F (%)	O (%)	N (%)	Azole (%)*	
C3-ATet	40.40	10.09	17.65	30.71	100	Theoretical
	41.25	9.35	18.17	29.74	97	Found

* found from EDS results on a % by weight basis.

3.10.3 Thermal analysis

The thermal properties of all polymers were examined with TGA and DSC. Firstly, the samples were dried under vacuum at 100 °C for 48 h and stored in a glove box. The DSC measurements were studied under inert atmosphere at a scan rate of 10 °C/min and the second heating curves were evaluated. Previously, the glass transition temperatures of the PGMA and PVDF were reported as 74 °C and -50 °C, respectively. The melting point (T_m) of PVDF powder was observed at 158.3 °C. The glass transition temperature of T_g of the PVDF-*g*-PGMA (C3) was found as 107 °C and the melting point (T_m) was measured at approximately 155 °C as depicted in Fig. 3.177, which was

due to the presence of ordered PVDF regions. For PVDF-*g*-PGMA-ATet, there is a glass transition at 88 °C, and T_m was observed at approximately 152 °C. The DSC curve of acid doped membranes, PVDF-*g*-PGMA-ATet-(TA)_x, exhibited no T_g , which may be due to ionic interaction of acid-base units. They only have melting points (T_m) at approximately 148, 123, and 118 °C, respectively (Fig. 3.177) (Sinirlioglu et al., 2015c).

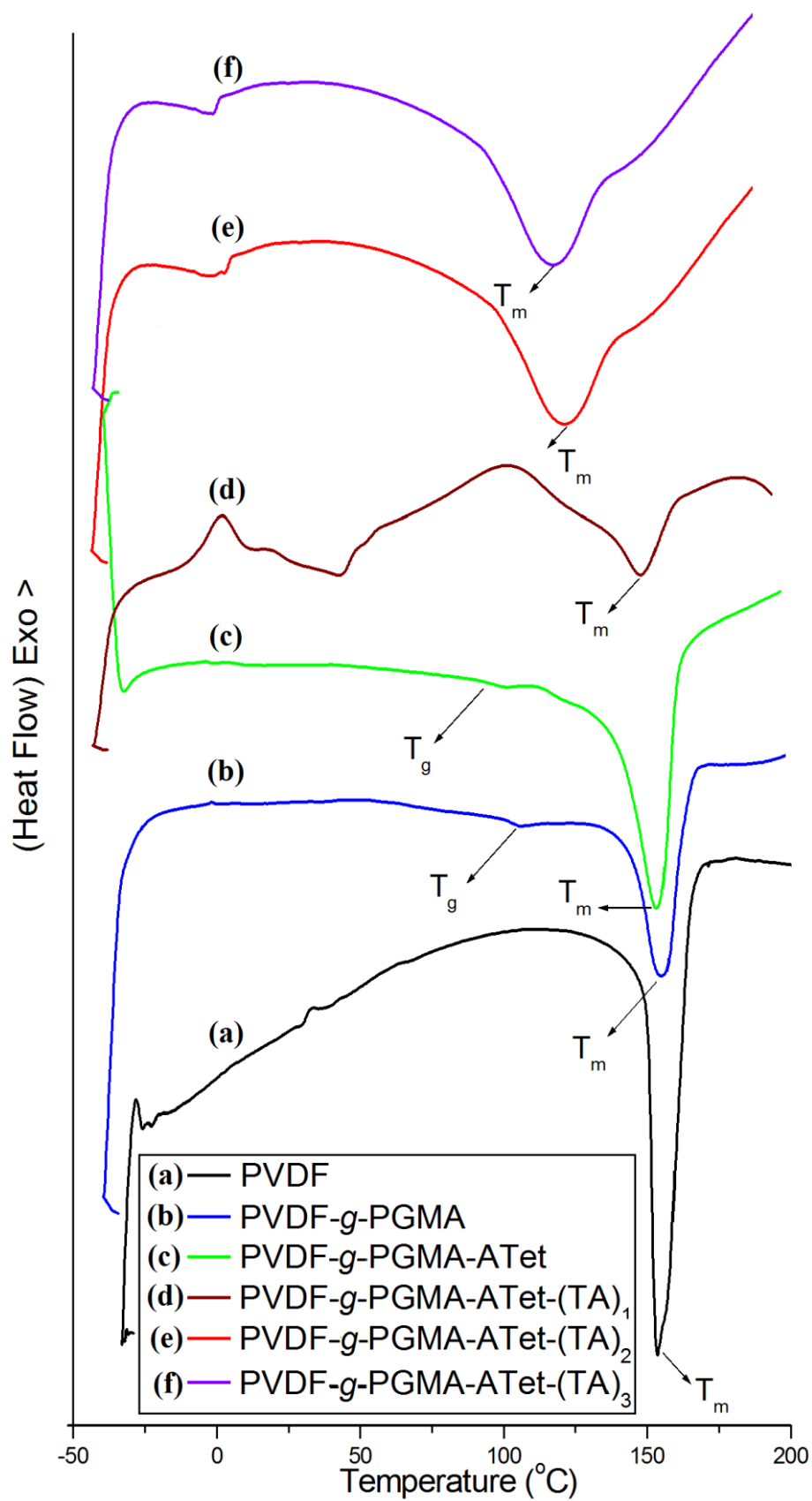


Figure 3.177 DSC thermograms of (a) PVDF, (b) PVDF-*g*-PGMA (C3), (c) C3-ATet, (d) C3-ATet-(TA)₁, (e) C3-ATet-(TA)₂, and (f) C3-ATet-(TA)₃ recorded under N₂ atmosphere at a heating rate of 10 °C/min.

The thermal stabilities of the membranes were evaluated using TGA and their results are presented in Fig. 3.178. PVDF decomposed in a single step which was thermally stable up to 460 °C, whereas PVDF-*g*-PGMA membrane showed a two-step degradation pattern at 275 and 460 °C due to the decomposition of PGMA grafts and the PVDF matrix, respectively. 20 % of PVDF-*g*-PGMA polymer decomposes at around 340 °C because of degradation of PGMA polymer side chain, after 460 °C, second weight loss region occurs because of degradation of PVDF. The TGA curves of PVDF-*g*-PGMA-ATet (C3-ATet) membranes showed a satisfactory thermal stability up to 210 °C. Upon doping of the PVDF-*g*-PGMA-ATet with TA, the thermal stability of the membranes increased for all samples. PVDF-*g*-PGMA-ATet-(TA)_x membranes were thermally stable up to 350 °C (x= 1.0), 320 °C (x= 2.0) and 250 °C (x=3.0).

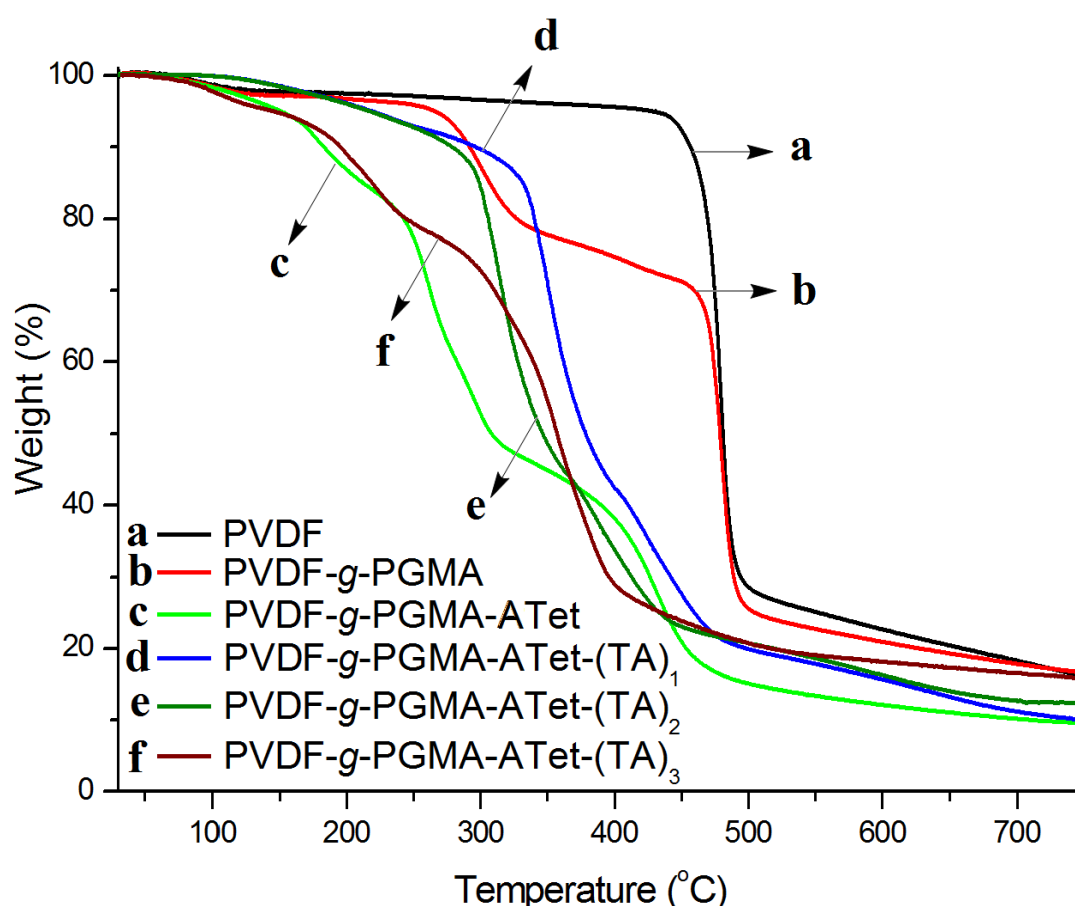
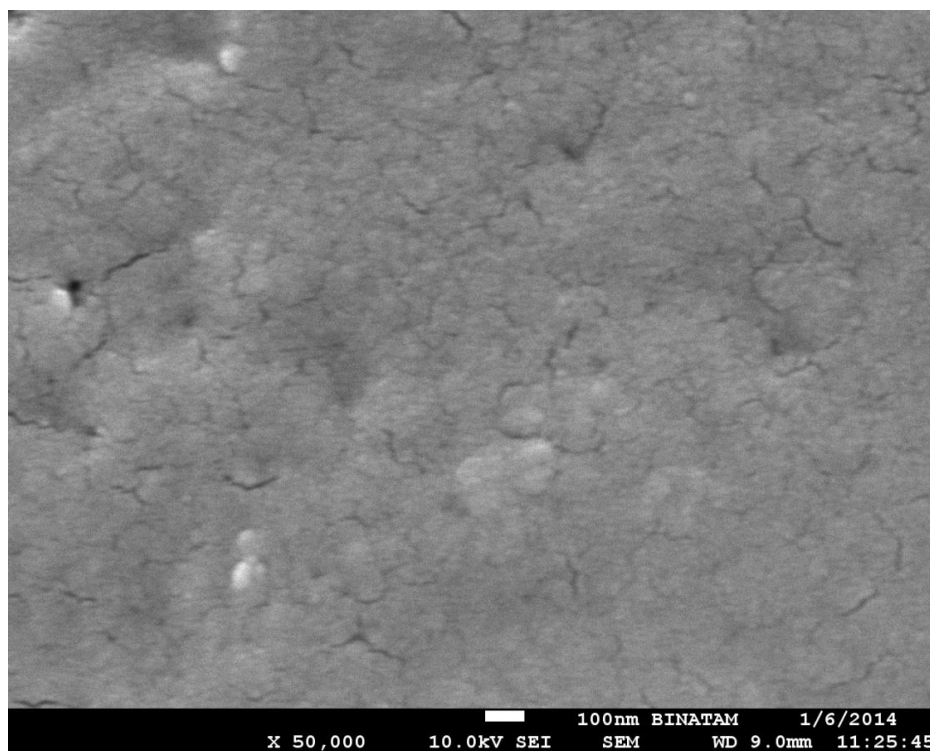


Figure 3.178 TG thermograms of (a) PVDF, (b) PVDF-*g*-PGMA, (c) PVDF-*g*-PGMA-ATet, (d) PVDF-*g*-PGMA-ATet-(TA)₁, (e) PVDF-*g*-PGMA-ATet-(TA)₂, and (f) PVDF-*g*-PGMA-ATet-(TA)₃ membranes at a heating rate of 10 °C/min in inert atmosphere.

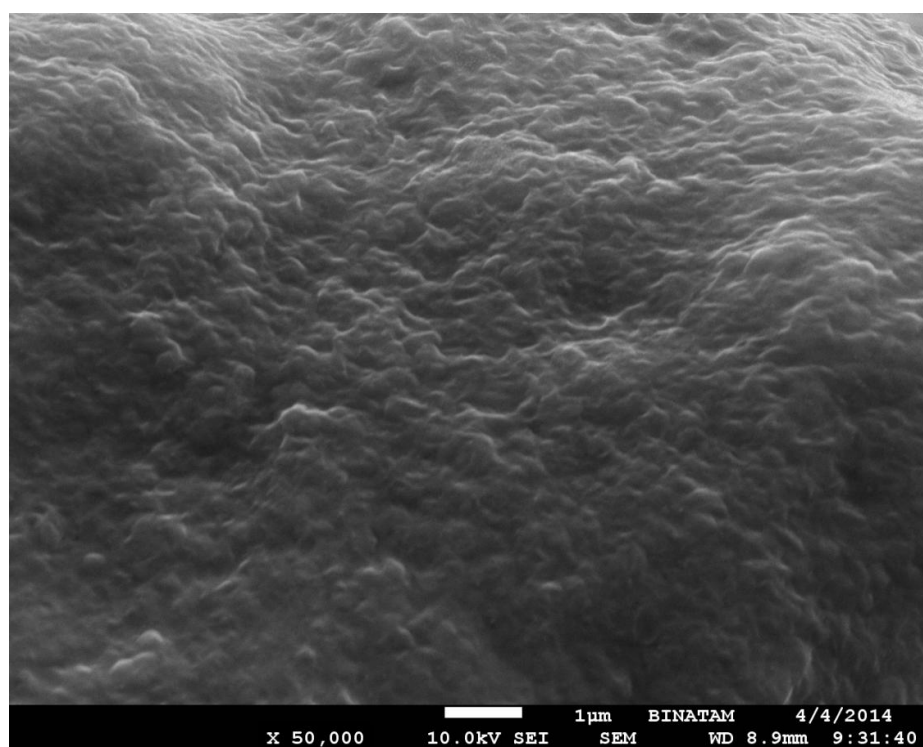
3.10.4 Morphology

Surface morphologies of the membranes were systematically analyzed using scanning electron microscopy (SEM) and the images of alkaline-treated PVDF, PVDF-*g*-PGMA (C3), PVDF-*g*-PGMA-ATet (C3-ATet), and PVDF-*g*-PGMA-ATet-(TA)₃ (C3-ATet-(TA)₃) membranes are compared in Fig. 3.178. There is formation of a smooth surface of the alkaline-treated PVDF powder and a number of pores appear as depicted in Fig. 3.178 (a). Upon grafting of PGMA onto the alkaline treated PVDF, the surface morphology of PVDF films becomes rougher than that of the alkaline treated PVDF surface. Appearance of hills on the surface of PVDF-*g*-PGMA (C3) membrane might signify the presence of PGMA graft chains. These results confirmed that GMA monomer is grafted onto the PVDF (Sinirlioglu et al., 2015c).

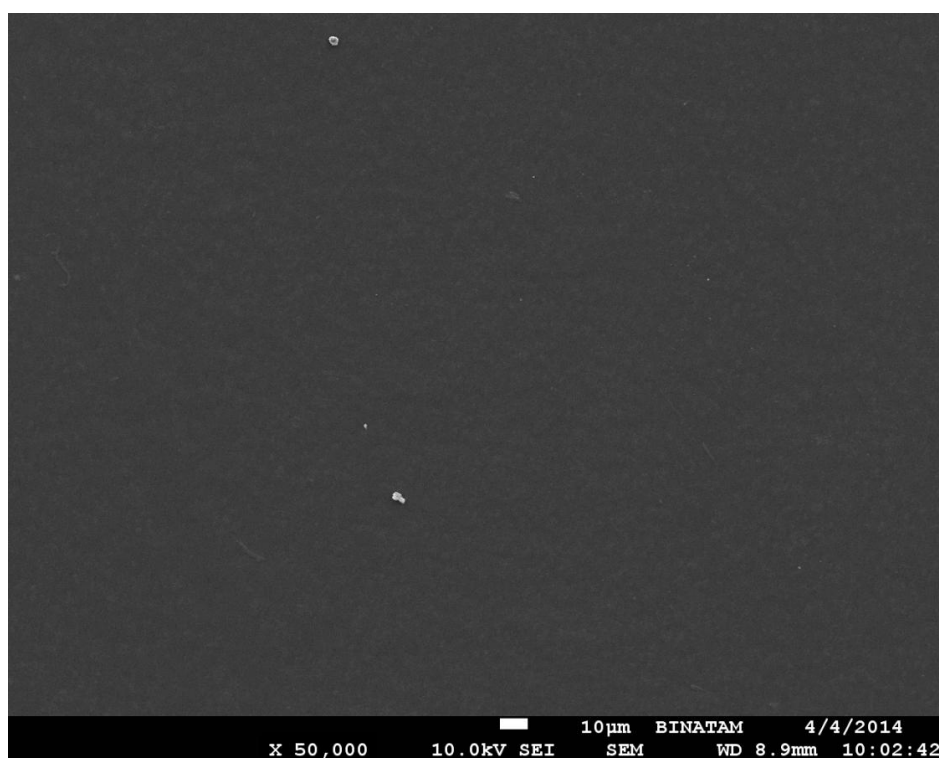
Upon modifying of PVDF-*g*-PGMA with aminotetrazole, followed by doping with triflic acid, we observed that all images showed single phase formation due to strong interaction between acidic groups of triflic acid and azole groups of PVDF-*g*-PGMA-ATet. This results showed that there was no agglomeration or phase separation at the nanometer and micrometer levels (Sinirlioglu et al., 2015c).



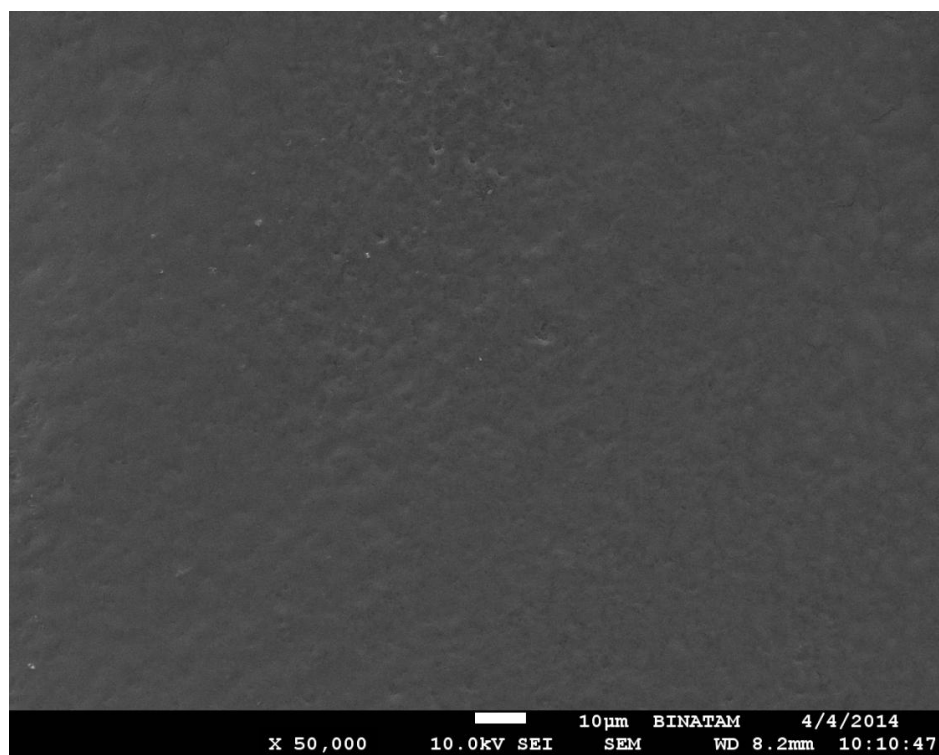
(a)



(b)



(c)



(d)

Figure 3.179 SEM images of the surface of (a) alkaline-treated PVDF, (b) PVDF-*g*-PGMA (C3), (c) C3-ATet, and (d) C3-ATet-(TA)₃ membranes, respectively.

3.10.5 X-ray Diffraction (XRD)

The crystalline structure of the membranes was evaluated from the XRD patterns, as shown in Fig. 3.180. Pure ATet is a crystalline compound which has four peaks at 18.04° , 22.75° , 28.03° , and 57.74° , respectively. PVDF is a polymorphic, semi-crystalline polymer which are primarily four kinds of crystal structures such as α , β , γ , δ , wherein α type and β type are the main crystal structures of PVDF. The strong peaks at around $2\theta = 20.0^\circ$ which corresponds to (110) reflection of the α phase and (200 / 110) reflections of the β -phase, and distinctive peaks at the 2θ values of 18.7° , and 26.4° , which correspond to (020) and (021) reflections of the α phase, respectively, indicate the coexistence of the α and β -phases. In addition, the peaks at $2\theta = 34.8^\circ$ and 36.2° relate to the (200) plane of α -phase of PVDF and the peak at $2\theta = 39.2^\circ$ refers to the combined (201) and (111) reflections of the β -phase due to molecular defects caused by head-head and tail-tail sequences (Sinirlioglu et al., 2015c).

After grafting of PGMA onto alkaline treated PVDF, the crystallinity of PVDF-*g*-PGMA graft copolymer (Fig. 3.180 (c)) did not undergo any changes. The position of peaks is almost similar to those observed in alkaline treated PVDF. There was no additional phase detected in the PVDF matrix due to chemical modifications which means PGMA chains were grafted only on the surface of PVDF (Sinirlioglu et al., 2015c). As seen in Fig. 3.180, upon modifying of PVDF-*g*-PGMA (C3) graft copolymer with ATet, the peaks in the XRD pattern of the PVDF-*g*-PGMA-ATet (C3-ATet) was observed due to the crystalline nature of ATet which has at 18.27° (020), 22.86° for (021) plane, 28.33° for (021) plane, and 58.87° . The other observed peaks in Fig. 3.180 (d) belong to the PVDF-*g*-PGMA (C3) graft copolymer membrane (Sinirlioglu et al., 2015c).

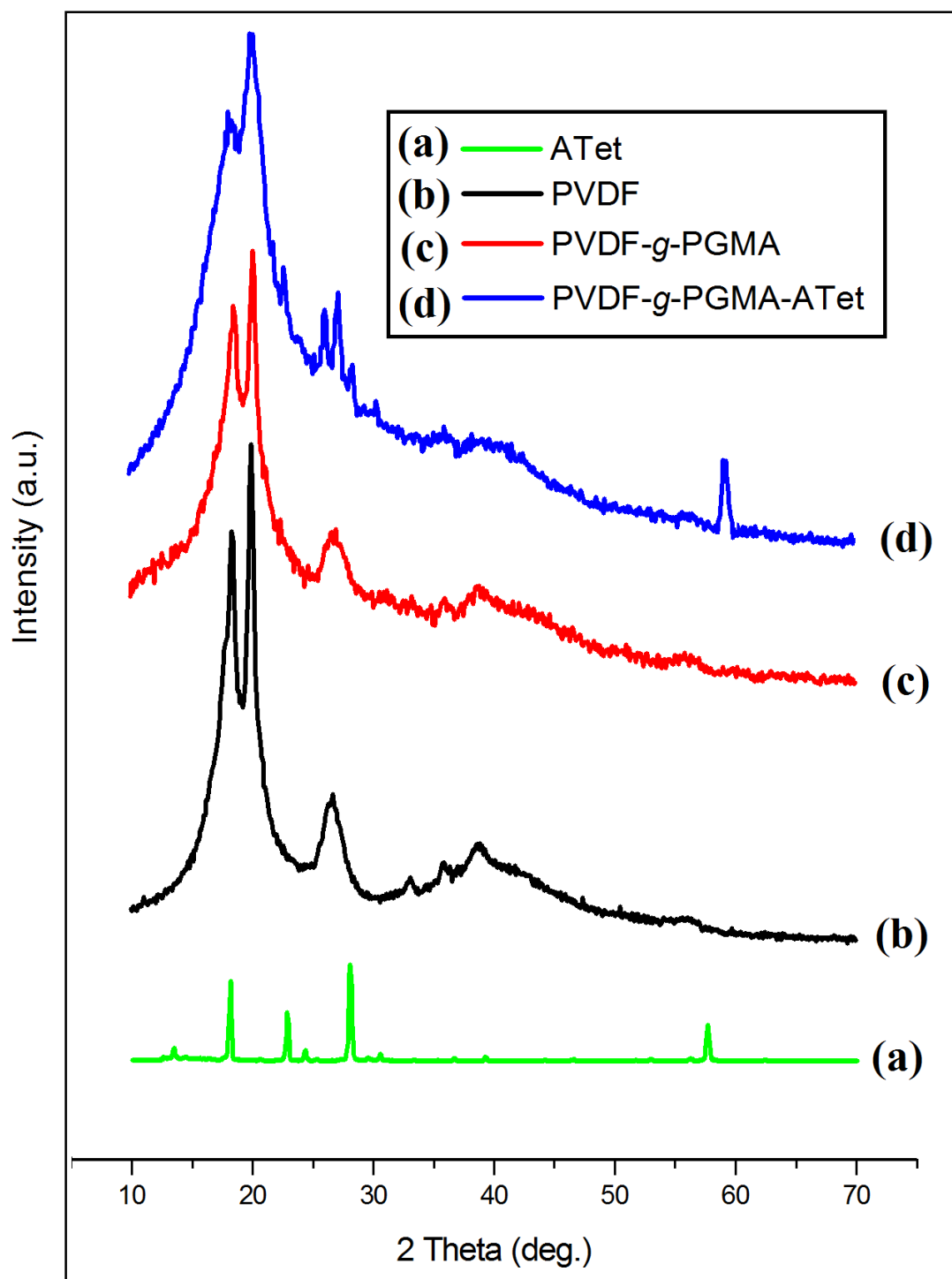


Figure 3.180 XRD patterns of (a) pure ATet, (b) PVDF, (c) PVDF-*g*-PGMA (C3), and (d) PVDF-*g*-PGMA-ATet (C3-ATet) membranes.

3.10.6 Proton conductivity measurements

The performance of a fuel cell is usually based on the proton conductivity of the PEM material. In this study, the samples were cut into thin slices and the proton conductivities of all membranes were measured using the simple two-electrode method, in which, the samples were sandwiched between additional external parallel plate electrodes (between platinum blocking electrodes). Fig. 3.181 shows the AC conductivity of PVDF-*g*-PGMA-ATet-(TA)₃ membrane versus frequency at several temperatures ranging between 20 °C and 150 °C. At lower frequency regions, the conductivity increases with log frequency then leveled off which is due to electrode polarizations. At lower frequencies, an increase in conductivity up to certain level is due to electrode polarization. An increase in conductivity at higher frequencies is due to dispersions in polymers. The thickness and maximum proton conductivities of the PEMs are listed in Table 3.28. In the absence of humidity, the highest proton conductivity of PVDF-*g*-PGMA-ATet-(TA)₃ was measured as 0.04 S/cm at 150 °C.

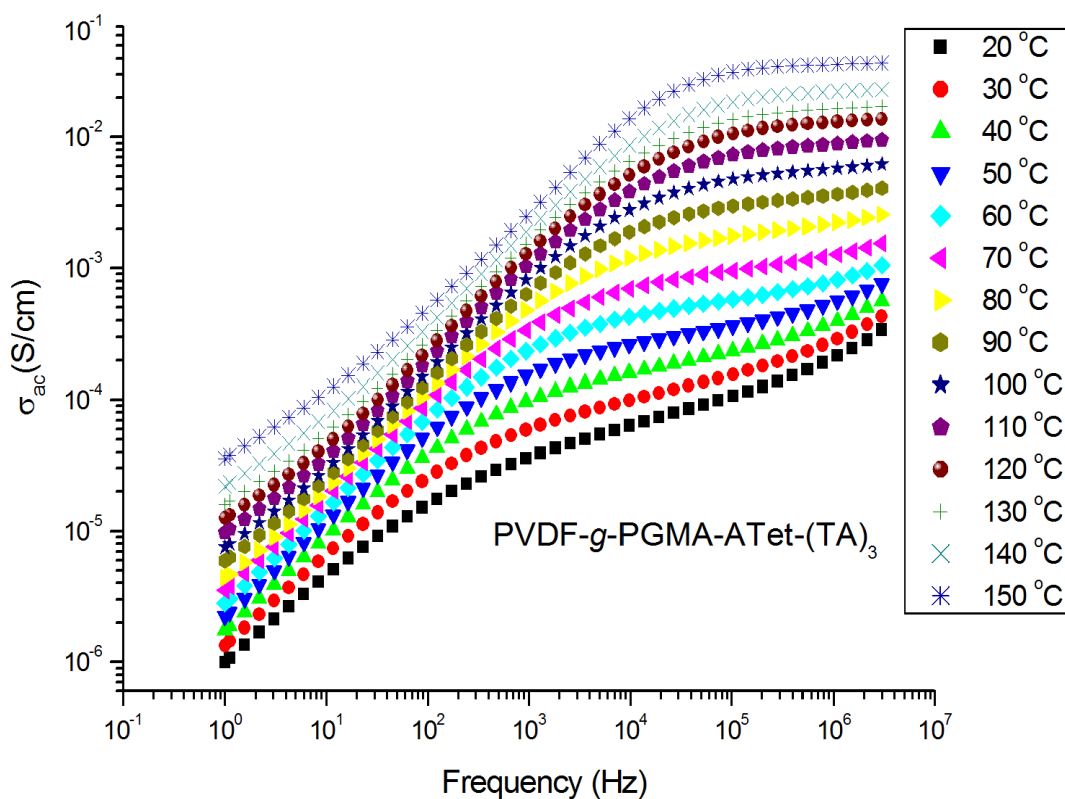


Figure 3.181 AC conductivity versus frequency of PVDF-*g*-PGMA-ATet-(TA)₃ (C3-ATet-(TA)₃) at several temperatures.

The DC proton conductivity with respect to temperature was derived from the plateaus of $\log \sigma_{ac}$ versus $\log F$ by linear fitting of the data and given in Fig. 3.182. The obtained DC curves can be explained with Arrhenius behavior based on the facts that no T_g was observed in the measurement temperature range and DC curves do not deviate from linearity (Fig. 3.182).

Table 3.28 Thickness, maximum proton conductivity, water uptake, and methanol permeability of the membranes and Nafion 117.

Sample	Membrane Thickness (μm)	Max. Proton Conductivity at 150 °C (S/cm)	Water uptake (%)	Methanol Permeability ($\text{mol cm}^{-2} \text{s}^{-1}$)
PVDF- <i>g</i> -PGMA (C3)	142	2.39×10^{-7}	-----	No methanol crossover
PVDF- <i>g</i> -PGMA-ATet (C3-ATet)	96	4.83×10^{-6}	-----	No methanol crossover
(C3-ATet-(TA) ₁)	94	4.70×10^{-4}	88	5.83×10^{-9}
(C3-ATet-(TA) ₂)	92	0.009	68	4.11×10^{-9}
(C3-ATet-(TA) ₃)	96	0.04	56	3.33×10^{-9}
Nafion 117	93	2.95×10^{-5}	-----	1.89×10^{-9}

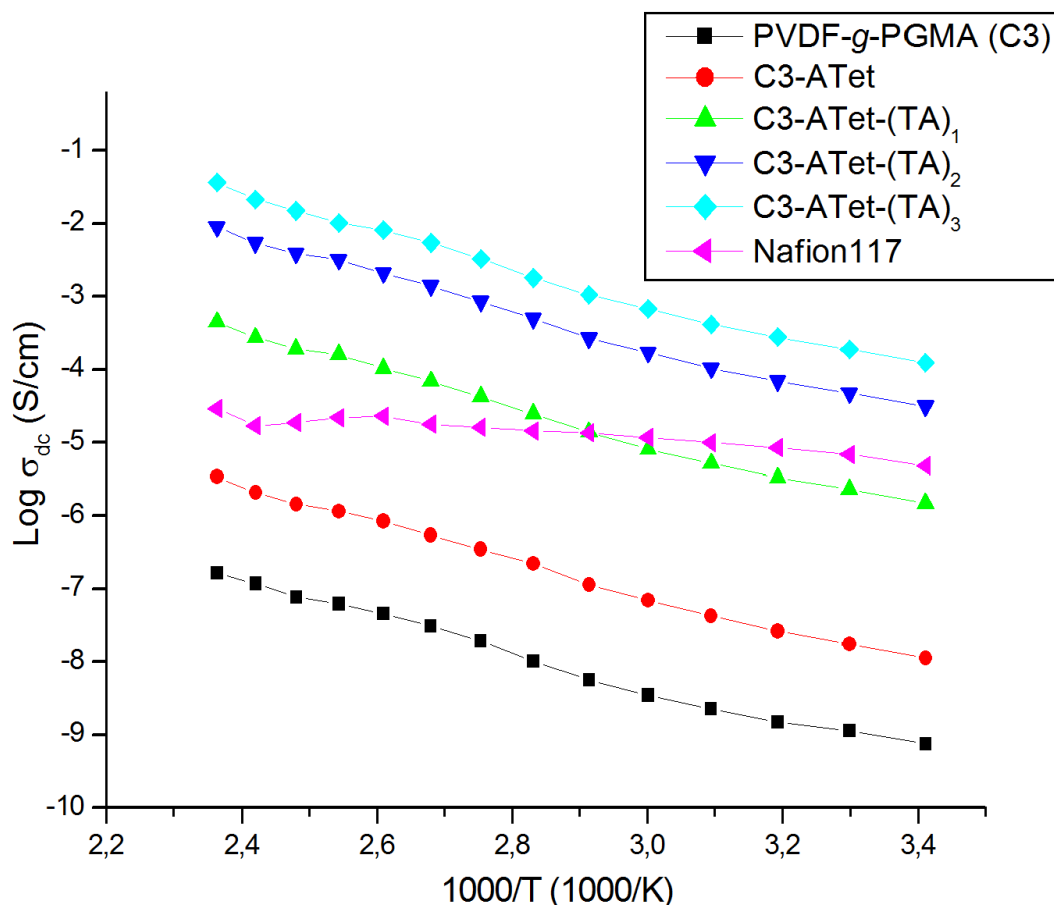


Figure 3.182 Variation of the DC proton conductivity of Nafion 117, PVDF-*g*-PGMA (C3), PVDF-*g*-PGMA-ATet (C3-ATet), PVDF-*g*-PGMA-ATet-(TA)_x (C3-ATet-(TA)_x) membranes as a function of reciprocal temperature.

Proton conductivity is a crucial PEM property concerning its application in PEMFCs. Quite recently, PVDF based polymer electrolyte membranes (PEMs) among others have shown some promising results as PVDF offers many favorable features such as durability, thermal stability and chemical resistance for efficient and prolonged operation of the fuel cell (Sinirlioglu et al., 2015c).

Very few studies of PVDF and azole based anhydrous PEM designs were reported. In these studies, a novel UV induced polymerization method was carried out in the grafting of styrene and 4-(chloromethyl)styrene onto partially fluorinated poly(vinylidene difluoride) (PVDF). Golcuk et al. reported the preparation of triazole doped poly(styrene sulfonic acid) grafted PVDF, PVDF-*g*-PSSA(Tri)₂, with a maximum proton conductivity of 5×10^{-5} S/cm at 150 °C and anhydrous conditions (Golcuk et al., 2013). In another work reported by Sasa et al. a maximum proton conductivity of 0.02

S/cm at 150 °C was found for triflic acid doped triazole-functional poly(chloromethyl styrene) grafted PVDF, PVDF-*g*-PCMS-Tri-1TA. Sezgin et al. studied the synthesis of triflic acid doped poly(vinyltriazole) grafted PVDF under UV light in a one step to achieve, PVDF-*g*-PVTri-(TA)_x, with a degree of grafting of 21% and with a maximum proton conductivity of 6×10^{-3} S/cm at 150 °C in the absence of humidity (Sezgin et al., 2014). Besides, Lepit et al. reported a maximum proton conductivity of 1×10^{-3} S/cm at 100 °C for 1-vinylimidazole and PVDF based PEMs prepared via radiation-induced grafting (Lepit et al., 2012). In another work declared by our group via using alkaline treatment method, a maximum proton conductivity of 0.09 S/cm at 150 °C was found for triflic acid doped vinyltriazole grafted PVDF, PVDF-*g*-PVTri-(TA)₃ (Sinirlioglu et al., 2014b). In that study, the method seemed interesting for designing further PVDF based membranes for fuel cells, since it offered an easy and versatile fabrication of PVDF based PEMs with relatively high grafting efficiencies and high proton conductivities (Sinirlioglu et al., 2015c). In another work reported by our group, the proton conductivity of triflic acid doped aminotetrazole-functional PVDF-*g*-PGMA-ATet anhydrous membranes via using AGET-ATRP method was found as 0.011 S/cm at 150 °C in the absence of humidity. However, this method was not successful in achieving high degrees of grafting, which would limit its use in the production of diverse membranes (Arslantas et al., 2014).

Normally, there are two different transport mechanisms that contribute to the proton conductivity in acid-doped polymer electrolytes. The first is the structural diffusion (Grotthuss mechanism) in which the conductivity is mainly controlled by proton transport through the tetrazole ring. The second is the vehicle mechanism where the protons travel through the material on a neutral or charged “vehicle” (Sinirlioglu et al., 2015c). The Grotthuss mechanism is expected to be predominant in this study due to the presence of azole-functional side groups. Herein, the protons of triflic acid transferred to the heterocycles are conducted via breaking and forming process of hydrogen bonds between the neighboring tetrazole units. Meanwhile, the triflate anions stay close to the protonated azole rings to provide charge neutrality (Fig. 3.183) (Sinirlioglu et al., 2015c). Possible mechanism of proton transport in acid doped membranes is tentatively shown in Fig. 3.183.

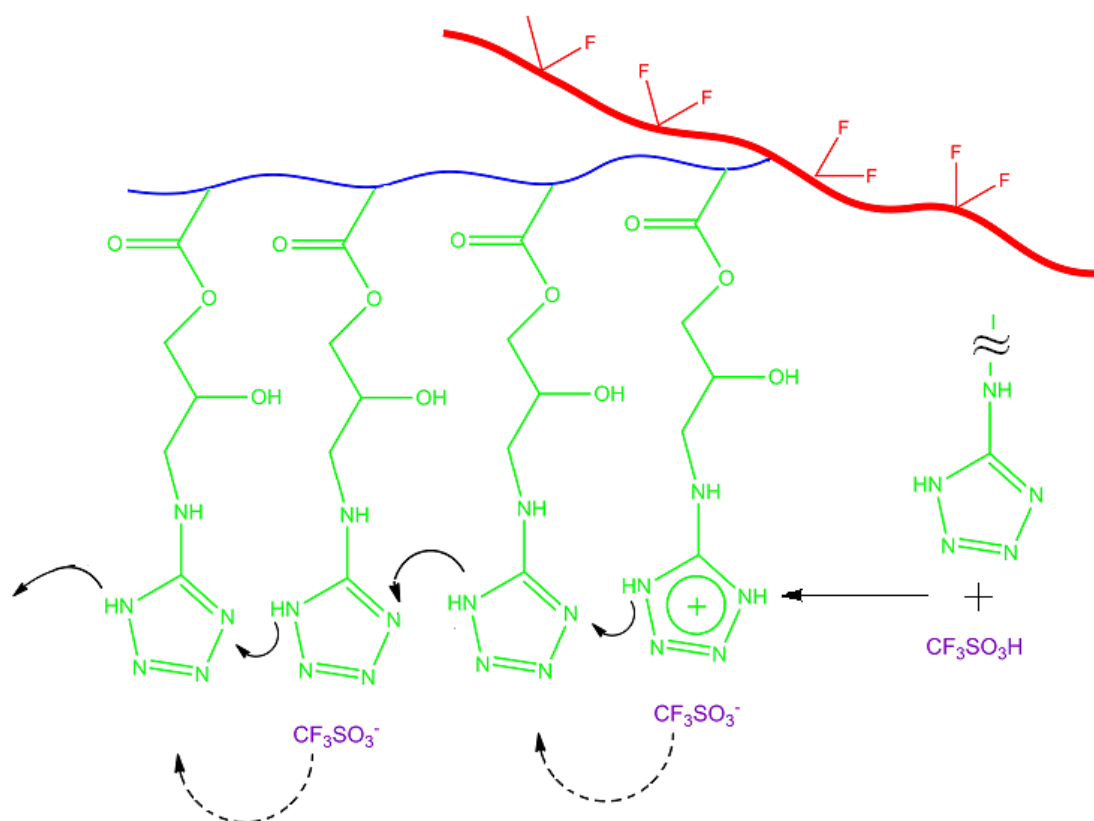


Figure 3.183 Possible mechanism of proton transport in acid doped membranes.

3.10.7 Cyclic Voltammetry

Cyclic voltammogram of PVDF-*g*-PGMA-ATet-(TA)₃ (C3-ATet-(TA)₃) membrane was presented in Fig. 3.184. The measurement was performed in a typical three electrode cell containing 0.1 mol/dm³ CH₃CN solution of tetrabutylammonium chloride (TBACl) using a platinum work electrode, a platinum auxiliary electrode, and an Ag/Ag⁺ reference electrode. The voltammogram shows that the C3-ATet-(TA)₃ membrane comprises no peak within in the anodic and cathodic sweep (-1.5 to 1.5 V potential range). Thus, the electrochemical stability window is about 3 V. These results implied that the C3-ATet-(TA)₃ membrane had adequate electrochemical stability under fuel cell conditions (Sinirlioglu et al., 2015c).

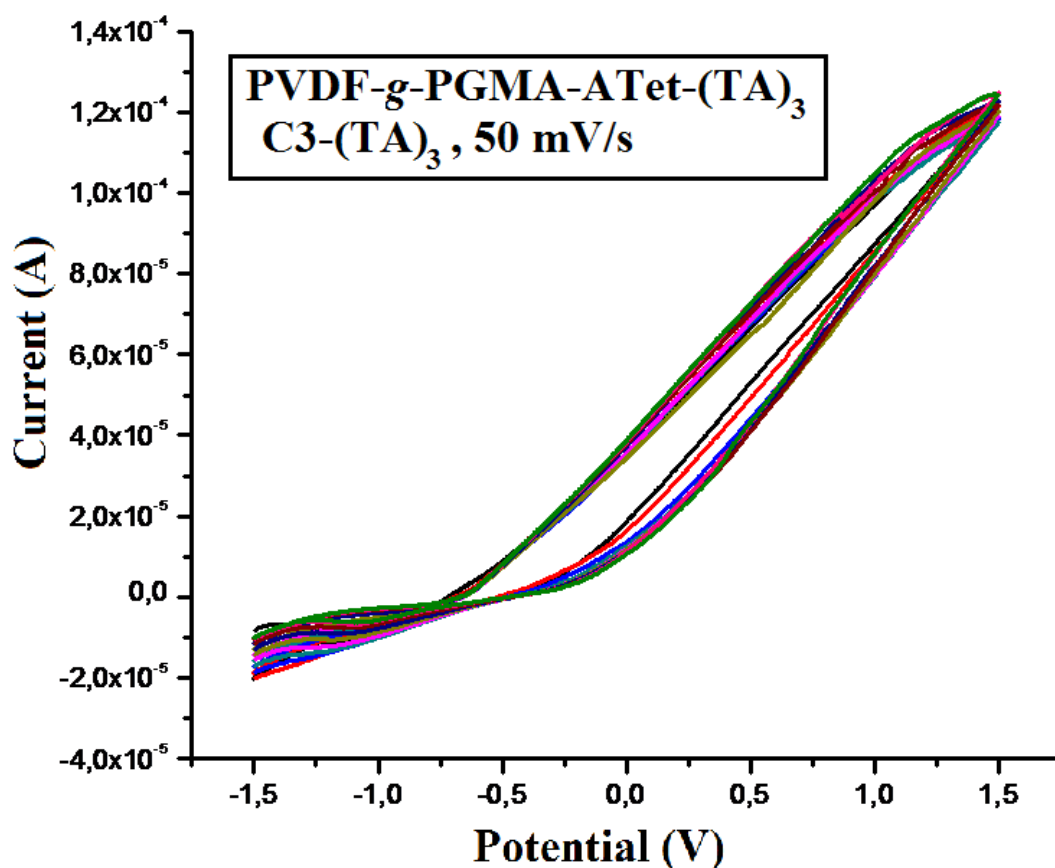


Figure 3.184 Cyclic voltammograms of C3-ATet-(TA)₃ in 0.1 M TBACl / acetonitrile. Curves were obtained with a scan rate of 50 mV/s.

3.10.8 Water Uptake Measurements

The water uptake is closely related to the efficiency of the fuel cells and basic properties of the membranes such as proton conductivity, mechanical property and stability. The water uptakes of the PVDF-*g*-PGMA-ATet-(TA)_x membranes were measured at room temperature under immersion in deionized water and they were compared in Fig. 3.185. Water uptake measurement was carried out by the weight difference between the fully hydrated membranes and dried membranes. The membranes were vacuum-dried at 120 °C before testing. As seen in the Fig. 3.185, water uptake of the membranes decreased with the triflic acid content, and acid doped membranes reached saturation after 20 min. The decrease in the swelling ratio might be due to strong ionic interaction of the dopant content with the azole functional polymers. The highest water uptake values are listed in Table 3.28.

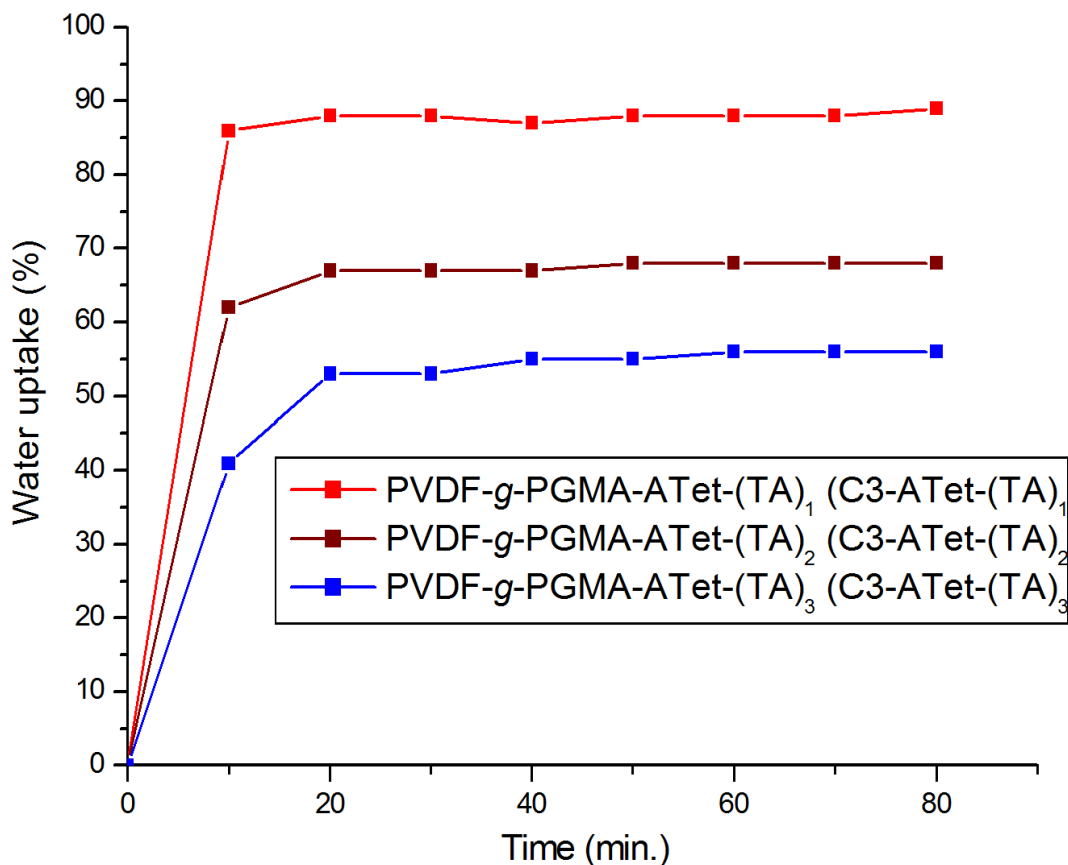


Figure 3.185 Water uptakes of PVDF-*g*-PGMA-ATet-(TA)_x membranes at the time of 10-80 min in deionized water at 25 °C.

3.10.9 Methanol Permeability Measurements

Finally, methanol permeability of the membranes was measured according to the literature (Gasa et al., 2007). The cell was filled with 2 mL methanol and the mass flow was recorded as a function of time and the results are listed in Table 3.28. Molar methanol flux (J) through PVDF-*g*-PGMA-ATet-(TA)_x membranes was calculated using eq. (2.2) Methanol permeability of the membranes may be calculated using molar flux (J) shown in eq. (2.3) (please see characterizations part).

As seen in the equations, the methanol permeability is directly proportional to the molar flux. We observed that there was no methanol crossover through the PVDF-*g*-PGMA, and PVDF-*g*-PGMA-ATet membranes. It was believed that this is attributed to the hydrophobic nature of PVDF which restricts methanol solubility in the PVDF rich

membranes (Sinirlioglu et al., 2015c). The molar flux of the membranes were compared in Fig. 3.186. The values are $5.83 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, $4.11 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ and $3.33 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, respectively, for PVDF-*g*-PGMA-ATet-(TA)_x (x=1.0, 2.0, and 3.0) membranes. Previously, the methanol permeability of Nafion 112 in the same conditions was determined as $1.89 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ (Sen et al., 2008). As seen in Fig. 3.186, the methanol permeability of the membranes are very close to Nafion 112. These membranes might be potentially useful to serve as PEMs in PEMFC.

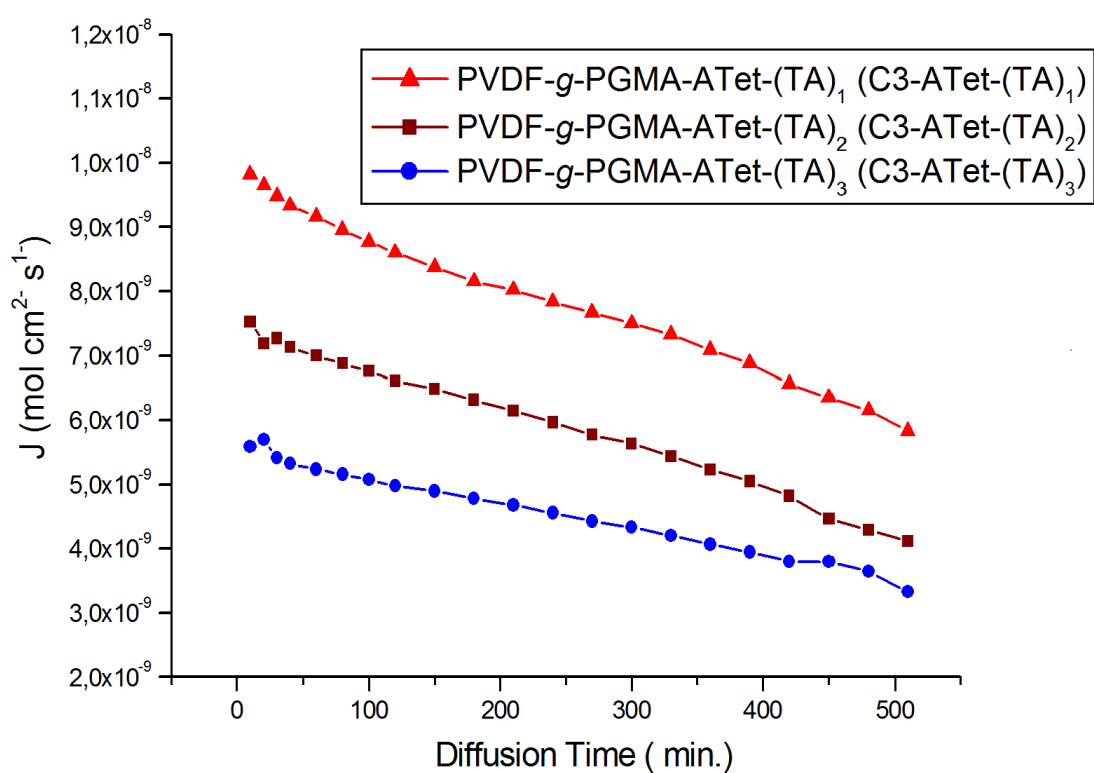


Figure 3.186 Methanol permeability of PVDF-*g*-PGMA-ATet-(TA)_x membranes.

CHAPTER 4

CONCLUSIONS

In the scope of this dissertation, ten different experiments were performed. In the first part of this thesis, we have investigated methacrylate/methacrylamide based novel proton-conducting polymers consisting of poly(methacryloylchloride) (PMAC) and 5-aminotetrazole, 3-aminotriazole, 1*H*-1,2,4-triazole, respectively. The pristine polymer was prepared by free radical polymerization of methacryloylchloride and then, it was chemically modified with 5-aminotetrazole, 3-aminotriazole, 1*H*-1,2,4-triazole, respectively. Elemental analysis result showed that PMAC was modified by 5-aminotetrazole, 3-aminotriazole and 1*H*-1,2,4-triazole with 41 %, 48 % and 38 %, respectively. The structure was confirmed by FTIR and ¹³C-NMR spectroscopies. The functional polymers were doped with triflic acid (TA) at several stoichiometric ratios. TGA analysis showed that the samples are thermally stable up to approximately 200 °C. DSC results illustrated the homogeneity of the materials as well as plasticizing effect of the dopant. The proton conductivity of these materials increased with dopant concentration and temperature. At 150 °C and anhydrous conditions, PMA-ATet-(TA)₄, PMA-Tri-(TA)₄ and PMA-ATri-(TA)₄ showed maximum proton conductivities of 0.01 S/cm, 0.02 S/cm and 8.7x10⁻⁴ S/cm, respectively.

In the second part of this thesis, 5-(methacrylamido)tetrazole monomer, prepared by the reaction of methacryloyl chloride with 5-aminotetrazole, was polymerized via conventional free radical mechanism to achieve poly(5-(methacrylamido)tetrazole) (PMTet) homopolymer. Novel composite membranes, SPSU-PM Tet(x), were successfully produced by incorporating sulfonated polysulfone (SPSU) into poly(5-(methacrylamido)tetrazole). The sulfonation of polysulfone was performed with trimethylsilyl chlorosulfonate and high degree of sulfonation (140 %) was obtained.

^1H -NMR and FTIR confirmed the sulfonation of PSU and the ionic interaction between sulfonic acid and PMTet units. TGA showed that the polymer electrolyte membranes are thermally stable up to approximately 190 °C. Methanol permeability experiments demonstrated that the composite membranes have similar methanol permeability values with Nafion 112. SEM analysis indicated the homogeneity of the membranes. This result was also supported by the appearance of a single T_g in the DSC curves of the blends. It is clear that the DC conductivity strongly depends on the temperature and SPSU ratio. The maximum proton conductivity of anhydrous SPSU-PMTet0.5 at 150 °C was determined as 2.2×10^{-6} S/cm while in humidified conditions a value of 6×10^{-3} S/cm at 20 °C was found for SPSU-PMTet2. In that study, tetrazole has high contribution to the proton conduction and the sample with the highest tetrazole content (SPSU-PMTet2) has considerable conductivity in the humidified condition and low methanol permeability. This shows that it may be used as a membrane in the fuel cell applications.

In the third part of this thesis, we have investigated novel proton-conducting copolymers based on MTet and vinyl triazole (VTri). The copolymers, P(VTri-co-MTet), were synthesized by conventional free-radical copolymerization of the corresponding monomers, by changing the molar feed ratios of the monomers, using azobisisobutyronitrile (AIBN) as an initiator. The molecular weight of copolymers and mol ratio of monomers were calculated by ^1H -NMR. TGA demonstrated that the materials were thermally stable up to at least 220 °C. DSC results illustrated both the homogeneity of the materials by the appearance of a single T_g and the plasticizing effect of the dopant. SEM analysis provided further evidence for the homogeneity of the membranes. CV study illustrated that electrochemical stability domain for S3-2H₃PO₄ extended over 3.0 V. In the anhydrous state, S1-2H₃PO₄, S2-2H₃PO₄ and S3-2H₃PO₄ copolymers showed maximum proton conductivities of 0.012 S/cm, 0.014 S/cm and 0.016 S/cm, respectively, at 150 °C.

In the fourth part of this thesis, novel proton-conducting copolymers based on 5-(methacrylamido)tetrazole (MTet) and vinyl phosphonic acid (VPA) were investigated. The P(MTet-co-VPA) membranes were synthesized by free-radical copolymerization of the corresponding monomers, by altering the molar feed ratios of the monomers, using α,α' -azodiisobutyramidine dihydrochloride (AIBADC) as an initiator. The copolymers

were characterized with FTIR, NMR, EDS and elemental analysis (EA). The compositions of copolymers were determined via EDS and elemental analysis, respectively. TGA results demonstrated that the materials were thermally stable up approximately 185 °C. TGA showed that the materials become more stable against phosphonic acid anhydride formation, but condensation could not be completely prevented, as shown by ^{31}P NMR. The presence of a glass transition in the copolymers illustrated that the presence of ionic interactions does not prevent cooperative relaxations of the copolymers. DSC results illustrated the homogeneity of the materials by the appearance of a single Tg. SEM analysis provided further evidence for the homogeneity of the membranes. CV study illustrated that electrochemical stability domain for poly(MTet-co-VPA) (S2) extended over 3.0 V and these copolymers have adequate electrochemical stability to use in fuel cells. In the anhydrous state, the copolymer electrolytes, poly(MTet-co-VPA) (S1, S2, S3) showed maximum proton conductivities of 0.01 S/cm, 0.004 S/cm and 8×10^{-4} S/cm, at 150 °C, respectively.

In the fifth part of this thesis, MTet monomer, produced by the reaction of methacryloyl chloride with 5-aminotetrazole, was polymerized via conventional free radical mechanism to attain PMTet homopolymer. Novel composite membranes, PMTetP(VPA)_x (x=0.5, 1.0, 2.0, and 4.0), were successfully produced by incorporating PVPA into PMTet. The FTIR data confirms that protonation occurs through transfer of protons from phosphonic acid units to heterocyclic rings. TGA results verified that the materials were thermally stable up approximately 210 °C. DSC results illustrated the homogeneity of the materials by the appearance of a single Tg. In the anhydrous state, the maximum proton conductivity of PMTetP(VPA)₄ composite membrane at 150 °C was found as 0.06 S/cm. It is clear that the DC conductivity strongly depends on the temperature and PVPA ratio. PMTetP(VPA)₄ showed the highest proton conductivity due to excess PVPA ratio. However, PMTetP(VPA)₂ with a lower conductivity (0.005 S/cm) is expected to be a better candidate material since it forms a good membrane. Thus, CV study conducted for PMTetP(VPA)₂ showed that electrochemical stability domain extended over 3.0 V and this composite membrane has adequate electrochemical stability to be used in fuel cells. These results show that PMTetP(VPA)₂ membrane may be a suitable candidate for high-temperature PEMFC applications.

In the sixth part of this thesis, new proton-conducting copolymers based on MTet and 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) were carried out. The P(MTet-co-AMPS) copolymer electrolyte membranes with high proton conductivity and low methanol permeability (S1) have been successfully prepared by conventional free-radical copolymerization of the corresponding monomers, by varying the molar feed ratios of the monomers, using AIBN as an initiator. The copolymers were characterized with FTIR and $^1\text{H-NMR}$ spectroscopies. The composition of copolymers was determined via elemental analysis. TGA results revealed that the all copolymers were thermally stable up approximately 275 °C which have more thermal stability than corresponding PMTet and PAMPS. DSC results illustrated the homogeneity of the materials by the appearance of a single Tg. Methanol permeability experiments demonstrated that the methanol permeability of copolymers increased with the rise of AMPS content and the methanol permeabilities of P(MTet-co-AMPS) (S1, S2 and S3) copolymers were determined as $1.60 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, $2.71 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$ and $3.32 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, respectively, which were comparable with that of Nafion 112 ($1.89 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$) under the same testing conditions. CV study showed that electrochemical stability domain for P(MTet-co-AMPS) (S2) extended over 3.0 V and has adequate electrochemical stability to use in fuel cells. It is clear that the DC conductivity strongly depends on the temperature and AMPS ratio (S1-S3). In the anhydrous state, the maximum proton conductivities of anhydrous copolymer electrolyte membranes, P(MTet-co-AMPS) (S1, S2 and S3) copolymers at 150 °C was found as $7.09 \times 10^{-5} \text{ S/cm}$, $8.88 \times 10^{-4} \text{ S/cm}$, and 0.009 S/cm , respectively. Especially, S2 and S3 copolymers showed higher proton conductivities when compared to the PMTet and PAMPS homopolymers. These results indicated that the P(MTet-co-AMPS) (S1-S3) copolymer electrolyte membranes were remarkably promising to be used as proton exchange membranes in PEMFCs.

In the seventh part of this thesis, we have investigated new proton-conducting copolymer electrolytes based on 5-(methacrylamido) tetrazole (MTet) and vinyl benzene boronic acid (VBBA). The insoluble P(VBBA-co-MTet) copolymer membranes with high proton conductivity have been successfully synthesized by conventional free-radical copolymerization of the corresponding monomers, by altering the molar feed ratios of the monomers. The copolymers were characterized with FTIR and $^1\text{H-NMR}$. The composition of copolymers was determined via elemental analysis.

TGA results confirmed that the materials were thermally stable up at least 170 °C. SEM analysis provided further evidence for the homogeneity of the membranes. CV study demonstrated that electrochemical stability domain for P(VBBA-*co*-MTet)-2H₃PO₄ (S3-2H₃PO₄) extended over 3.0 V and has adequate electrochemical stability to use in fuel cells. The proton conductivity of acid doped copolymers was studied by dielectric-impedance spectroscopy. The proton conductivity increased with the content of MTet units in the polymer chain and also with the dopant ratio, “x”. In the anhydrous state, the maximum proton conductivity of anhydrous copolymer electrolyte membrane, S3-2H₃PO₄, at 150 °C was found as 0.021 S/cm. This value was higher than those of previously reported acid doped P(VBBA-*co*-VIm) and P(VBBA-*co*-VTri) copolymers. Formation of highly conductive, flexible and insoluble free standing films indicates that the matrix were remarkably promising to be used in proton exchange membrane fuel cells (PEMFC). Therefore, this work would make a contribution to the study of boronic acid containing anhydrous polymer electrolyte membranes.

In the eighth part of this thesis, a novel graft copolymer consisting of a poly(vinylidene fluoride) (PVDF) backbone and poly(vinyltriazole) side chains, PVDF-*g*-PVTri, was synthesized using the radical polymerization method after modification of PVDF powder by alkaline treatment, followed by doping with triflic acid to achieve PVDF-*g*-PVTri-(TA)_x (x=1.0, 2.0 and 3.0) membranes, where x is the number of moles of TA per mole of VTri. The FTIR and ¹H-NMR results showed the successful tethering of the PVTri polymer chains onto PVDF via radical polymerization. ¹H-NMR results showed grafting efficiencies of 21.30 %, 29.86 % and 47.22 % for PVDF-*g*-PVTri (C1, C2, C3), respectively. Furthermore, the success of grafting was evidenced using EDS. Thermal properties were examined by TGA and DSC. The obtained graft copolymers (C1- C3) and all acid doped copolymer membranes show good thermal stabilities which decreases as the PVTri ratio in the membranes increases. TGA showed that the PVDF-*g*-PVTri (C1) and PVDF-*g*-PVTri-(TA)_x (C1-TA_x) membranes were thermally stable up 390 °C and 310 °C, respectively. The XRD analysis reveals the increase in amorphous nature of the polymer electrolytes with the increasing amount of PVTri. The morphology of the membranes governs the conduction behavior of the graft copolymer membranes. The proton conductivities of the membranes were investigated for PVDF-*g*-PVTri-(TA)_x. We found that the porous morphology of the graft copolymer membranes caused the loading of a larger amount of triflic acid and, consequently,

showed high proton conductivity. The maximum proton conductivity was measured for PVDF-*g*-PVTri-(TA)₃ (C3-TA₃) with a degree of grafting of 47.22 % as 0.09 S/cm at 150 °C in anhydrous condition. This study is the first to report on the fabrication of anhydrous PEMs by the use of alkaline treated PVDF powder and *N*-heterocyclic monomers in a “grafting through” strategy and can be interesting for designing further membranes for fuel cells, since the method offers an easy and versatile fabrication of PEMs with relatively high grafting efficiencies and high proton conductivities. Therefore, this thermo-mechanically stable and highly conducting graft copolymer membrane may be a suitable candidate to be employed in high temperature fuel cells.

In the ninth part of this thesis, we have fabricated novel proton exchange membranes (PEMs) consisting of a PVDF membrane with poly(vinyl phosphonic acid) functional-poly(glycidyl methacrylate) side chains, (PVDF-*g*-PGMA-*g*-PVPA(x)), for application in PEMFCs. Herein, alkaline treated PVDF was used as a macromolecule in conjunction with GMA in the graft copolymerization using a simple “grafting through” approach. Novel PEMs were synthesized via free radical-initiated graft copolymerization of glycidyl methacrylate (GMA) from alkaline-treated PVDF backbone, followed by reaction of the oxirane rings in the GMA side chains with poly(vinyl phosphonic acid), eventually fabricating various PVDF-*g*-PGMA-*g*-PVPA(x) membranes. The FTIR and ¹H-NMR results confirmed the successful tethering of the PGMA polymer chains onto PVDF. ¹H-NMR results showed grafting efficiency of 80.62 % for PVDF-*g*-PGMA graft copolymers. Furthermore, the success of grafting was evidenced using EDS. Thermal properties of the membranes were examined by TGA and DSC. TGA showed that the PVDF-*g*-PGMA and PVDF-*g*-PGMA-*g*-PVPA(x) membranes were thermally stable up to 275 °C and 210 °C, respectively. Methanol permeability experiments exhibited that the PVDF-*g*-PGMA-*g*-PVPA(x) graft copolymer membranes have similar methanol permeability values with Nafion 112. The XRD analysis revealed the crystallinity of the membranes. After grafting of PGMA onto alkaline treated PVDF, the crystallinity of PVDF-*g*-PGMA did not undergo any changes. After modification of PVDF-*g*-PGMA membrane with PVPA, the XRD results showed that the amorphous nature of the obtained membranes increases with the increasing amount of PVPA. The morphology of the membranes regulates the conduction behavior of the obtained graft copolymer membranes. The proton conductivities of the membranes were measured by using impedance analyzer.

The maximum proton conductivity was found for PVDF-*g*-PGMA-*g*-PVPA(20) with a degree of grafting of 80.62 % as 0.0023 S/cm at 150 °C in anhydrous condition. The proton conductivity of the same material was measured as 0.034 S/cm at 100 °C with relative humidity (RH= 50 %). In that study, PVPA has high contribution to the proton conduction and the sample with the highest PVPA content, PVDF-*g*-PGMA-*g*-PVPA(20), has considerable conductivity in the humidified condition and low methanol permeability. This study presents the fabrication of novel PEMs similar structure to Nafion by the use of alkaline treated PVDF and GMA in a “grafting through” strategy which can be interesting for designing further membranes for fuel cells, since the method offers an easy and versatile fabrication of PEMs with relatively high grafting efficiencies and high proton conductivities both anhydrous and humidified (RH=50 %) conditions. Furthermore, the obtained membranes may a suitable candidate to be employed in fuel cells and they can be commercialized since their structures seem to Nafion. Moreover, the humidified graft copolymer membranes represented conductivity which is comparable to Nafion at the same humidification level.

In the last part of this thesis, PVDF-*g*-PGMA-ATet-(TA)_x anhydrous proton exchange membranes were fabricated based on a “grafting through” strategy, in which an alkaline-treated PVDF was employed as a macromonomer in conjunction with GMA. Success of grafting was evidenced by FTIR, ¹H-NMR, and ¹⁹F-NMR. Functionalization with aminotetrazole was confirmed by using EDS, and ¹H-NMR. ¹H-NMR results showed grafting efficiencies of 28.61 %, 41.47 %, 80.62 % for PVDF-*g*-PGMA (C1-C3) copolymers, respectively. TGA results showed that the PVDF-*g*-PGMA, PVDF-*g*-PGMA-ATet, and PVDF-*g*-PGMA-ATet-(TA)₃ membranes were thermally stable up to 275 °C, 230 °C and 250 °C, respectively. The water uptake of the membranes decreased with the triflic acid content, and acid doped membranes reached saturation after 20 min. The decrease in the swelling ratio might be due to strong ionic interaction of the dopant content with the azole functional polymers. Methanol permeability experiments exhibited that the obtained graft copolymer membranes have similar methanol permeability values with Nafion 112. The XRD analysis was carried out to observe the crystallinity of the obtained membranes. The maximum proton conductivity was measured for PVDF-*g*-PGMA-ATet-(TA)₃ as 0.04 S/cm at 150 °C in the absence of humidity. This result is higher than the previously reported 0.011 S/cm at 150 °C (Arslantas et al., 2014), which demonstrates that the present method is more

effective than AGET-ATRP in the production of PEMs with better conductivities. The “grafting through” approach outlined in this thesis can be useful in producing various PEMs to be used in fuel cells, since the method offers a facile synthesis, high grafting efficiencies, and high proton conductivities.

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APPENDIX A

DECLARATION STATEMENT FOR THE ORIGINALITY OF THE THESIS, FURTHER STUDIES AND PUBLICATIONS FROM THESIS WORK

A.1 DECLARATION STATEMENT FOR THE ORIGINALITY OF THE THESIS

I hereby declare that this thesis comprises my original work. No material in this thesis has been previously published and written by another person, except where due reference is made in the text of the thesis. I further declare that this thesis contains no material which has been submitted for a degree or diploma or other qualifications at any other university.

Signature:

Date: January 14, 2016

A.2 FURTHER STUDIES

Further studies related to this thesis work can be done in the following areas:

- (a) Employing anhydrous membranes with optimal PEM characteristics in fuel cells and testing their cell performances.
- (b) Improvement of mechanical properties in the PVDF graft copolymer anhydrous PEMs for prolonged use in fuel cell applications.

A.3 PUBLICATIONS FROM THESIS WORK

Academic Journals

- Sinirlioglu, D., Muftuoglu, A.E., “ Investigation of proton conductivity of PVDF based anhydrous proton exchange membranes (PEMs) obtained via a facile “Grafting Through” strategy”, *Journal of Polymer Research*, Vol. 22, No:12, Article number: 232, pp.1-16, 2015.
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- Sinirlioglu, D., Muftuoglu, A.E., Bozkurt, A., “5-(Methacrylamido)tetrazole and Vinyl triazole Based Copolymers as Novel Anhydrous Proton Conducting Membranes”, *Journal of Polymer Research*, Vol. 20, No.9, Article number: 242, pp. 1-10, 2013.

Conference Proceedings

- Sinirlioglu, D., Muftuoglu, A.E., Bozkurt, A., ““Alkalinasyon” Yöntemi Kullanılarak Poli(vinilidin florür) (PVDF) Esaslı Yeni Proton İletken Kopolimer Membranların Hazırlanması ve Karakterizasyonu”, 5. Fiziksel Kimya Kongresi, Konya-Türkiye, Abstract no: S39, Mayıs 2015.
- Sinirlioglu, D., Muftuoglu, A.E., Bozkurt, A., “5-(Methacrylamido)tetrazole and Vinyl triazole Based Copolymers as Novel Anhydrous Proton Conducting Membranes”, *IUPAC 2013-International Union of Pure and Applied Chemistry-44th World Chemistry Congress*, Istanbul-Turkey, Abstract no: 1171, August 2013.

Posters

- Sinirlioglu D., Celik S.U., Muftuoglu A.E., Bozkurt A., “Novel Membranes Based on Poly(5-(methacrylamido)tetrazole) and Sulfonated Polysulfone for Proton Exchange Membrane Fuel Cells”, *IUPAC 2013-International Union of Pure and Applied Chemistry - 44th World Chemistry Congress*”, Istanbul-Turkey, August 2013.

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EDUCATION

Ph.D., Department of Chemistry, Fatih University, Istanbul, Turkey, January 2016.

Dissertation: “The Production of Azole Functional Novel Proton Conductive Membranes For Polymer Electrolyte Membrane Fuel Cell (PEMFC) Applications”

M.S., Department of Chemistry, Fatih University, Istanbul, Turkey, July 2010.

Thesis: “Synthesis and Characterization of Inorganic-Organic Nanocomposite Polymeric Materials via Controlled Polymerization Methods and Click Reactions”

B.S., Department of Chemistry, Erciyes University, Kayseri, Turkey, February 2008.

PROFESSIONAL EXPERIENCE

- Research Assistant, Department of Chemistry, Fatih University, Istanbul, Turkey, (2008 - present).
- Teaching Assistant, Department of Chemistry, Fatih University, Istanbul, Turkey, (2008 - present).

AWARDS AND HONORS

- Received full university scholarship for graduate studies in Chemistry at Fatih University, (2008-2010)
- Received full university scholarship for graduate studies in Chemistry at Fatih University, (2010-2015)

PUBLICATIONS

Academic Journals

- Sinirlioglu, D., Muftuoglu, A.E., Bozkurt, A., “ Investigation of perfluorinated proton exchange membranes prepared via a facile strategy of chemically combining poly(vinyl phosphonic acid) with PVDF by means of poly(glycidyl methacrylate) grafts”, *Journal of Polymer Research*, Vol. 22, No:8, Article number: 154, pp.1-17, 2015.

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Posters

- Akel, M., Sinirlioglu, D., Celik, S.U., Bozkurt, A., Ata, A., “Nano Hexagonal Boron Nitride-Nafion Composite Membranes for Proton Exchange Membrane Fuel Cells”, *International Nanoscience & Nanotechnology For Next Generation (NanoNG2014)*, Elazığ-Turkey, August 2014.
- Tutgun M.S., Sinirlioglu D, Celik S.U., Bozkurt A., “Investigation of Proton Conductivity of Nanocomposite Membranes Based on Poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPS) and Nitrilotri(methyl triphosphonic acid) (NMPA)/Hexagonal Boron Nitride (h-BN) for Proton Exchange Membrane Fuel Cells”, *International Nanoscience & Nanotechnology For Next Generation (NanoNG2014)*, Elazığ-Turkey, August 2014.
- Sinirlioglu D., Celik S.U., Muftuoglu A.E., Bozkurt A., “Novel Membranes Based on Poly(5-(methacrylamido)tetrazole) and Sulfonated Polysulfone for Proton Exchange Membrane Fuel Cells”, *IUPAC 2013-International Union of Pure and Applied Chemistry - 44th World Chemistry Congress*, Istanbul-Turkey, August 2013.
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- Golcuk, S., Sinirlioglu, D., Muftuoglu, A.E., Celik, S.U., Bozkurt, A., Ozpinar, C., “Synthesis and Characterization of Proton Conducting Membranes via Photoinduced Grafting”, “*APME 2011-IUPAC 9th International Conference on Advanced Polymers via Macromolecular Engineering*”, Cappadocia-Turkey, 2011.
- Eren F., Sinirlioglu D., Muftuoglu A.E., “Synthesis And Characterization of Amphiphilic Polymers via Controlled Radical Polymerization Routes And ‘Click’ Reactions”, “*APME 2011-IUPAC 9th International Conference on Advanced Polymers via Macromolecular Engineering*”, Cappadocia-Turkey, 2011.

RESEARCH PROJECTS

- Rekombinant Lakkaz Enzimi Üretimi ve Biyoteknolojik Ürün Geliştirme, Bilim, Sanayi ve Teknoloji Bakanlığı (0534.TGSD.2015), Haziran 2015-Haziran 2016, Araştırmacı, *Miktarı: 98500 TL*
- Azol Fonksiyonel Gruplar İçeren PVDF Bazlı Proton Geçirgen Membranların (PEMs) Üretilmesi ve Karakterizasyonları (2015-07-01-KAP01), Yıldız Teknik Üniversitesi (YTU), Kapsamlı Araştırma Projesi (KAP), Üniversite Araştırma Proje Fonu, April 2015-April 2017, Araştırmacı, Amount: 24.988,30 TL.
- Azol Fonksiyonel Gruplar İçeren Metakrilamit Bazlı Yeni Homopolimer ve Kopolimer Proton Geçirgen Membranların (PEMs) Üretilmesi ve Karakterizasyonları (2014-07-01-KAP02), Yıldız Teknik Üniversitesi (YTU), Kapsamlı Araştırma Projesi (KAP), Üniversite Araştırma Proje Fonu, May 2014-May 2016, Araştırmacı, Amount: 24.988,91 TL.
- Polimer-Bor Nitrür (BN) Kompozit Membranlar Hazırlanarak Termal, Elektriksel ve Mekanik Özelliklerinin Araştırılması, TUBITAK112M488, TUBITAK, Dec 2012-Dec 2014, Araştırmacı (Bursiyer), Amount: 213000 TL
- Azol Fonksiyonel Gruplar İçeren Metakrilat Bazlı Homopolimer ve Kopolimer Membranların Üretilmesi ve Karakterizasyonları, Fatih Üniversitesi Üniversite Araştırma Proje Fonu, Apr 2013-Apr 2014, Araştırmacı, *Miktarı: 12000 TL.*
- Atom Transfer Radikal Polimerizasyonu (ATRP) Yöntemi ile PVDF Bazlı Proton İletken Aşı Kopolimer Membranların Hazırlanması ve Karakterizasyonu, Fatih Üniversitesi Üniversite Araştırma Proje Fonu, Apr 2013-Apr 2014, Araştırmacı, *Miktarı: 10000 TL.*
- Fotobaşlatılmış Yüzey Aşılama Yöntemiyle PVDF Esaslı Polimer Elektrolit Membranların Hazırlanması, Fatih Üniversitesi Üniversite Araştırma Proje Fonu, Apr 2012-Apr 2013, Araştırmacı, *Miktarı: 8000 TL.*
- Azol Fonksiyonel Gruplar İçeren Akrilik Polimer Membranların Üretilmesi ve Karakterizasyonları, Fatih Üniversitesi Üniversite Araştırma Proje Fonu, Apr 2012-Apr 2013, Araştırmacı, *Miktarı: 17000 TL.*
- Foto Aşılama Yöntemiyle Proton İletken Membranların Sentezi ve Karakterizasyonu, Fatih Üniversitesi Üniversite Araştırma Proje Fonu, Nov 2010-Feb 2012, Araştırmacı, *Miktarı: 9000 TL*
- Kontrollü Polimerizasyon Yöntemleri ve Klik Tepkimeleriyle Amfifilik Polimerlerin Sentezi ve Karakterizasyonu, Fatih Üniversitesi Üniversite Araştırma Proje Fonu, Jun 2010-Jul 2011, Araştırmacı, *Miktarı: 8757 TL.*
- Synthesis and Characterization of Inorganic-Organic Nanocomposite Polymeric Materials via New Synthetic Routes, Fatih Üniversitesi Üniversite Araştırma Proje Fonu, Jun 2009-Jun 2010, Araştırmacı, *Miktarı: 10.000 TL.*