ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

FLUORINATION OF POLYMERS VIA METAL-FREE AZIDE-ALKYNE CLICK REACTION

M.Sc. THESIS

Seren TURKUT

Department of Chemistry

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

METALSİZ AZİD-ALKİN KLİK TEPKİMESİ İLE POLİMERLERİN FLORLANMASI

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Seren TURKUT
509191217

Kimya Anabilim Dalı

Kimya Programı

Tez Danışmanı: Dr.Öğr.Üyesi Ufuk Saim GÜNAY

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Seren Turkut , a M.Sc. student of ITU Graduate School student ID 509191217, successfully defended the thesis entitled “FLUORINATION OF POLYMERS VIA METAL-FREE AZIDE-ALKYNE CLICK REACTION”, which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor : **Assist. Prof. Dr. Ufuk Saim GÜNAY**
İstanbul Technical University

Jury Members : **Prof. Dr. Hakan DURMAZ**
Istanbul Technical University

Assist. Prof. Dr. Pınar Sinem OMURTAG ÖZGEN
Marmara University

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To my family and my friends,

FOREWORD

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Seren TURKUT
Chemist

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ABBREVIATIONS

^{1}H NMR	: Hydrogen Nuclear Magnetic Resonance Spectroscopy
p-TSA	: p-Toluene sulfonic acid
PC	: Poly(carbonate)
PE	: Polyester
PSCMS	:Poly(styrene-*co*-4-chloromethylstyrene)
GPC	: Gel Permeation Chromatography
$CDCl_3$	: Deuterated chloroform
$CHCl_3$	: Chloroform
CuAAC	: Copper(I) catalyzed azide-alkyne cycloaddition
DBU	: 1,8-diazabicyclo[5.4.0]undec-7-ene
DCM	: Dichloromethane
DMAP	: 4-dimethylaminopyridine
FPT	: Freeze-Pump-Thaw
ROP	: Ring-opening polymerization
ATRP	: Atom Transfer Radical Polymerization
THF	: Tetrahydrofuran
TU	:1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea

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FLUORINATION OF POLYMERS VIA METAL-FREE AZIDE-ALKYNE CLICK REACTION

SUMMARY

Fluoropolymers are one of the best important materials from the family of fluorinated compounds. They are alluring macromolecules due to their specific properties. So, these specialty polymers exhibit aging, chemical, high thermal and weather resistance, excellent inertness, to hydrocarbons, to acids, to solvents low surface energy, low dielectric constants, low flammability, low refractive index, and moisture absorption. Hence, they can be related in High-Tech applications such as automotive, aeronautics, petrochemicals, optics, textile, microelectronics, chemical engineering, automotive, aerospace, and building industries. Among the fluorinated commercial polymers, poly(tetrafluoroethylene) (PTFE), poly (vinylidene fluoride) (PVDF), and poly(chlorotrifluoroethylene) (PCTFE) have become a prerogative and well-studied since the mid-1940s. However, despite their excellent properties, fluorinated polymers have some drawbacks such as contradiction with other hydrocarbon polymers, insolubility in common organic solvents, and hence chromatographic analysis problems. Trifluoromethyl (CF_3)-containing polymers are the special class of fluorinated polymers and have received great interest in recent years since they can overcome the above-mentioned problems associated with the fluorinated polymers while preserving unique properties of fluorine-containing polymers.

Polycarbonates (PC) are carbonate esters of alcohols or phenols but they cannot be synthesized by the condensation polymerization between diols and carbonic acid. Therefore, a derivative of carbonic acid, phosgene, is used. Sodium salts of diols are used to avoid evolution of gaseous HCl. As a result, sodium chloride is formed as a by-product which requires purification processes. As an alternative method, polycarbonates can be synthesized by the ring opening polymerization (ROP) of cyclic carbonates with five, six or more members.

Condensation polymerization is a form of polymerization where a small molecule is released each time two or more functional groups come together and react. Polyester is one example. Acyl chloride and hydroxyl groups react in a basic environment, forming an ester bond with the release of salt as a by-product.

1,3-dipolar cycloaddition reaction takes place between azide and alkyne groups. The cyclization reaction forms a triazole ring which is aromatic in character. Cycloaddition occurs in two ways. It is either at room temperature in the presence of Copper (I) salts which forms 1,4 triazole with regioselectivity or the thermal method where the reaction temperatures are well above the room temperature. The latter has no regioselectivity and produces both 1,4 and 1,5 triazole rings.

Polyurethanes are synthesized by the reaction of diisocyanates with diols where urethane linkages are formed without a release of a by-product. Since there are no by-products, it’s technically not a condensation polymerization, but the functional group rearranges.

In this study, modifications were done on synthetically and industrially important polymers with the use of metal-free azide-alkyne cyclocation reaction. PVC, polyepichlorohydrin (PECH), poly(styrene-co-4-chloromethylstyrene) polymer was azide functionalized by the nucleophilic substitution reaction with sodium azide prior to click reactions. Polyurethane, polyester and polycarbonate polymers were synthesized from azide functional monomers. Each azide-functional polymer was subjected to react with Ethyl 4,4,4-trifluoro-2-butynoate under thermal method conditions. The synthesized polymers were characterized by GPC, ^{19}F-NMR and ^{1}H-NMR.

METAL İÇERMEYEN AZİD-ALKİN TIKLAMA REAKSİYONU İLE POLİMERLERİN FLORLANMASI

ÖZET

Floropolimerler, florlu ürün ailesinin en önemli bileşiklerinden biridir. Spesifik özelliklerinden dolayı çekici makromoleküllerdir. Bu nedenle bu özel polimerler yüksek termal, kimyasal yaşlanma ve hava direnci, çözücülere,hidrokarbonlara, asitlere karşı mükemmel eylemsizlik, düşük yüzey enerjisi, düşük dielektrik sabitleri, düşük yanıcılık, düşük kırılma indisi ve nem emilimi sergiler. Bu özelliklerinden dolayı havacılık, mikroelektronik, optik, tekstil, petrokimya, otomotiv ve inşaat endüstrileri gibi Yüksek Teknoloji uygulamalarında yer alabilirler. Florlu ticari polimerler arasında, poli(tetrafloroetilen) (PTFE), poli(vinilidenflorür) (PVDF) ve poli(klorotrifloroetilen) (PCTFE) bir ayrıcalık haline geldi ve 1940'ların ortalarından beri iyi çalışıldı. Bununla birlikte, mükemmel özelliklerine rağmen, florlanmış polimerler, diğer hidrokarbon polimerleriyle uyumsuzluk, yaygın organik çözücüler içinde çözünmezlik ve dolayısıyla kromatografik analiz sorunları gibi bazı dezavantajlara sahiptir. Triflorometil (CF_3) içeren polimerler, florlu polimerlerin özel sınıfıdır ve flor içeren polimerlerin benzersiz özelliklerini korurken florlu polimerlerle ilişkili yukarıda belirtilen sorunların üstesinden gelebildikleri için son yıllarda büyük ilgi görmüştür.

Polikarbonatlar (PC) alkollerin veya fenollerin karbonat esterleridir. Polikarbonatların tekrarlayan ünitelerinde -OC(O)O- grupları bulunur. Karbonik asidin kararsız ve sıcakta bozunması sebebiyle polikarbonatlar karbonik asit ve diol bileşiğinin kondenzasyon polimerleşmesiyle elde edilemezler. Bu yüzden karbonik asidin türevlerinden biri olan fosgen kullanılır. Gaz olarak hidroklorik asit çıkmaması için ise diollerin sodyum tuzları reaksiyonda kullanılmaktadır. Bu da yan ürün olarak sodyum klorür tuzu oluşturmakta ve polimerin temizlenmesini gerektirmektedir. Alternatif bir yöntem olarak polikarbonatlar beş, altı veya daha yüksek sayıda üyeli siklik karbonatların halka açılma polimerizasyonu (ROP) yöntemi ile sentezlenebilmektedir.

Kondenzasyon polimerizasyonu iki veya daha fazla fonksiyonel grubun bir araya gelerek reaksiyon vermesi sonucu oluşan yeni yapıdan küçük bir molekülün ayrılması ile polimer sentezlenmesi olayıdır. Polyester sentezi bunlardan birisidir. Bazik ortamda teraftaloil klorür ile bir diolün reaksiyonu sonucu ester bağları meydana gelirken aynı zamanda açığa çıkan hidroklorik asidin baz ile oluşturduğu tuz ortamdan uzaklaşır.

1,3-dipolar siklokatılma reaksiyonu, 1 ve 3 konumlarından bağ yapan 3 üyeli yapılar ile bu tür yapılara bağlanan gruplar içeren moleküllerin reaksiyonu sonucu oluşan 5 üyeli yapıları anlatmaktadır. Azid-alkin arasında geçen 1,3-dipolar siklokatılma reaksiyonu triazol halkası oluşturur. Genel olarak Huisgen siklokatılma reaksiyonları olarak da bilinmektedirler. Dipolar yapıyla reaksiyona giren uçlar genelde alkin veya alken olmakla birlikte başka pi bağlarına sahip gruplarla da olabilmektedir. Bu uç alkin olduğunda oluşan yapı da aromatik karakterli olmaktadır. 1,3-dipolar siklokatılma iki şekilde meydana gelmektedir. Bunlardan ilki Bakır(I) tuzları varlığında oda sıcaklığında olmaktadır. Bakır(I) katalizli azid-alkin siklokatılmaları (CuAAC) 1,4 triazol halkalarını oluşturur ve regioizomer seçiciliği vardır. Diğer yöntem ise termal

yöntemdir ve oda sıcaklığından daha yüksek sıcaklıklarda meydana gelir. Bu yöntemin ise regioseçiciliği yoktur ve hem 1,4 hem de 1,5 triazol halkaları meydana getirmektedir. Klikte kullanılan alkin grubu içeren yapının simetrik olması ise oluşacak 1,4 ve 1,5 izomerin aynı yapıda olmasını sağlamaktadır.

Klik reaksiyonu küçük moleküller arasında yapılabildiği gibi, polimer üzerinde de yapılabilmektedir. Polimer üzerinde bulunan azid fonksiyonel gruplarıyla üçlü bağ içeren bileşikler arasında klik yapabileceği gibi, asetilen grupları içeren polimerlere de azidli bileşikler takılabilir. Bu reaksiyon bakırsız ortamda termal olarak yapıldığında toksik metaller içeren yapıların son üründe bulunmasının önüne geçilmektedir. Polimer üzerine belirli oranlarda tekrarlayacak şekilde klik ile bir bileşiğin bağlanması sonucu o polimere, üzerine bağlanan yapıya benzer özelliklerin bir kısmını geçmektedir.

Poliüretanlar da diizosiyanatlar ile diollerin reaksiyona girerek polimerleşmesiyle sentezlenmektedirler. İzosiyanat grubunun (-N=C=O), hidroksil (-OH) gruplarıyla reaksiyon verdiğinde üretan bağları oluşur. Ortama herhangi bir molekül çıkmadığından teknik olarak kondenzasyon polimerleşmesi denemez ancak fonksiyonel grup yeniden düzenlemeye uğrayarak üretan bağına dönüşür ve hidrojen alkolden koparak azot üzerine kayar.

Yapılan çalışmada endüstriyel ve sentetik öneme sahip polimerlerlerin, metalsiz azid-alkin siklokatılma reaksiyonuyla modifikasyonları ve karakterizasyonları yer almaktadır. PVC ve poliepiklorohidrin (PECH) hazır olarak alınmış, poli (stiren-co-4-klorometil stiren) polimerİ ise sentezlenerek elde edilmiştir. Bu üç polimer, önce sodyum azid ile nükleofilik yer değiştirme reaksiyonuyla azid uçlar takılarak fonksiyonlandırılmış, poliüretan, polyester ve polikarbonat yapıları ise azid fonksiyonlu monomerlerden sentezlenmiştir. Azid fonksiyonlu polimerler elde edildikten sonra ise Ethyl 4,4,4-trifluoro-2-butynoate ile termal yöntem kullanılarak klik yapılmıştır. Çalışmada kullanılan ve sentezlenen polimerler GPC, ^{1}H-NMR ve ^{19}F-NMR ile karakterize edilmiştir.

1. INTRODUCTION

In this thesis, polymers with fluorine pendant groups were synthesized with the strategy given in our research group's previous study [1]. A commercial compound, namely ethyl 4,4,4-trifluoro-2-butynoate, where a triple bond is bonded to a trifluoromethyl ($-CF_3$) group was reacted with various azide-functionalized synthetically and industrially important polymers, such as polyester (PE), polyurethane (PU), polycarbonate (PC), polystyrene (PS), polyvinyl chloride (PVC), and polyepichlorohydrin (PECH) in THF, through the metal-free azide-alkyne 1,3-dipolar cycloaddition reactions (Figure 1.1).

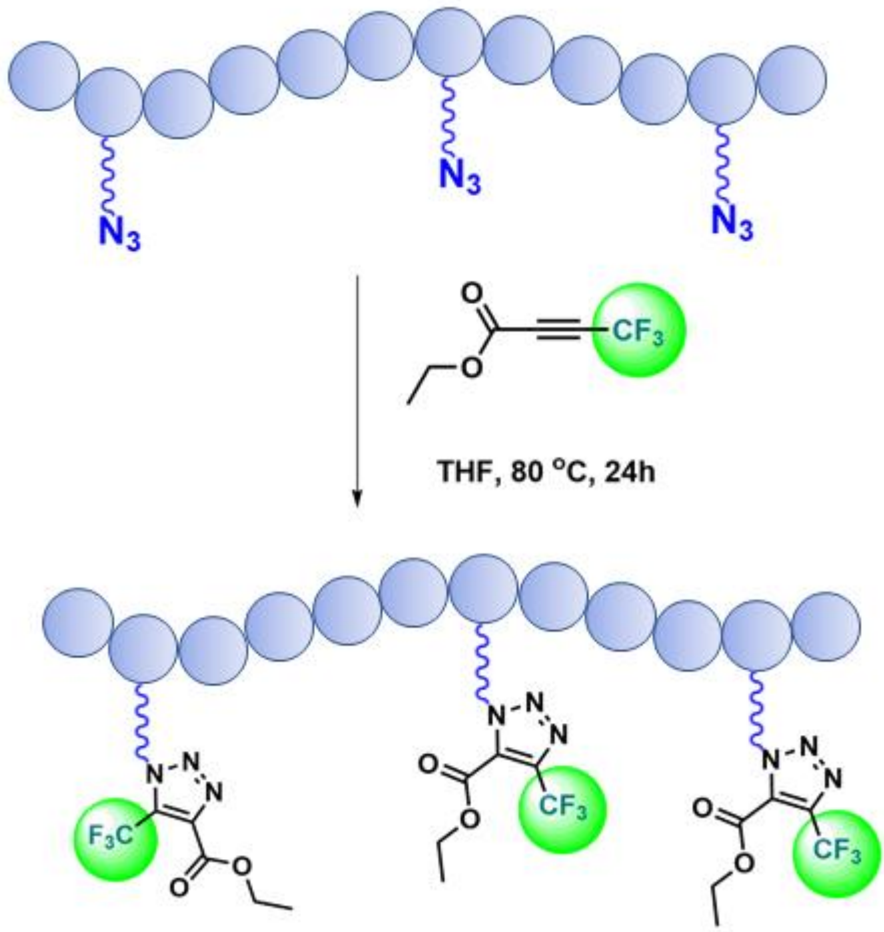

Figure 1.1 : General representation for the fluorination of synthetically and industrially important polymers.

2.THEORETICAL PART

2.1 Click Chemistry

It is famous that to combine two or more polymeric structures or adding a functional compound onto the preformed polymers through a chemical conversion on the side or at the chain-end of the polymers along with the efficient organic reactions is always essential to make ready functional materials based on polymers [2]. Polymer properties are mainly certain by the chemical composition, molecular weight and the functional groups that are connected to the polymer structure. Therefore, one can improve a polymer's properties by the control of those factors [3].

Click Chemistry is a term that was introduced by K. B. Sharpless in 2001 to define reactions that are high yielding, wide in scope, create only byproducts that can be removed without chromatography, are stereospecific, simple to perform, and can be conducted in easily removable or benign solvents [4]. The reaction between an azide and an alkyne group is an example for such a reaction which forms an aromatic triazole ring by carbon-nitrogen bond formation. This reaction was first studied by Huisgen [5] and nowadays, click reactions have been commanly used in polymer chemistry not only for the synthesis of polymeric structures, but also for the modification of the existing polymers [6].

There are two types of azide-alkyne cycloaddition. One of them is copper-catalyzed azide-alkyne 1,3 dipolar cycloaddition (CuAAC) and the other one is thermal azide alkyne 1,3 dipolar cycloaddition (TAAC). The thermal reaction of terminal or internal alkynes with organic azides has been known for more than a century, the first 1,2,3-triazole being synthesized by A. Michael from phenyl azide and diethyl acetylenedicarboxylate in 1893. The reaction has been most thoroughly investigated by Huisgen and coworkers in 1950s–70s in the course of their studies of the larger family of 1,3-dipolar cycloaddition reactions. Although the reaction is highly exothermic (DH0 between 50 and 65 kcal mol^{-1}), its high activation barrier (approximately 25 kcal mol^{-1} for methyl azide and propyne) results in exceedingly low reaction rates for unactivated reactants even at elevated temperatures[7].

The thermal Huisgen 1,3-Dipolar Cycloaddition of alkynes to azides requires escalated temperatures and often produces mixtures of the two regioisomers when using asymmetric alkynes. Several efficient reactions, which are capable of producing a wide catalogue of functional synthetic molecules and organic materials have been grouped accordingly under the term click reactions. Characteristics of modular click reactions include a) high yields with by-products (if any) that are removable by non-chromatographic processes, b) regiospecificity and stereospecificity, c) insensitivity to oxygen or water, d) mild, solventless (or aqueous) reaction conditions, e) orthogonality with other common organic synthesis reactions, and f) amenability to a wide variety of readily available starting compounds [8].

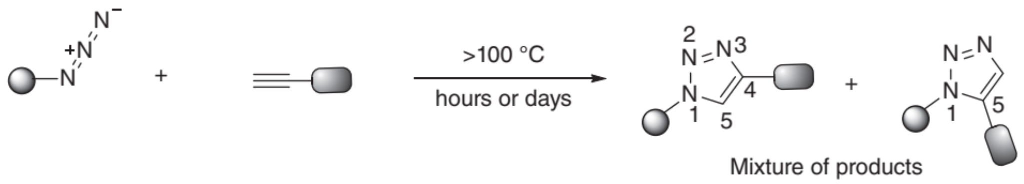

Figure 2.1 : Huisgen 1,4-1,5 dipolar cycloaddition.

The copper-catalyzed azide–alkyne 1,3-dipolar cycloaddition (CuAAC) is extensively used for the functionalization of well-defined polymeric materials. However, the necessity for copper, which is inherently toxic, limits the potential applications of these materials in the area of biology and biomedicine. The advancement of chemoselective, robust, and versatile transformations known as ‘‘click’’ reactions has allowed the modular build-up and functionalization of well-defined polymeric materials. The most frequently applied click reaction nowadays is the copper-catalyzed azide–alkyne 1,3-dipolar cycloaddition (CuAAC), which has been used forthe preparation of crosslinked networks and for the functionalization of both polymers in solution and polymeric coatings on surfaces. Click chemistry has furthermore played a major role in the development of polymer-based bioconjugates, which combine the versatility of standard synthetic polymers with advanced biological functions of proteins, polysaccharides, and DNA. Although potential applications of these polymer-based biohybrid systems are envisioned in the area of biology and biomedicine, the necessity to use the inherently toxic copper for the construction of these materials limitstheir possible use both in vitro and in vivo. Alternatively, several nontoxic copper-free click reactions have been developed within the field of chemical in recent years [9]. It is thus highly desirable to develop a click polymerization without transition-metal catalysts, i.e. metal-free click polymerization [10].

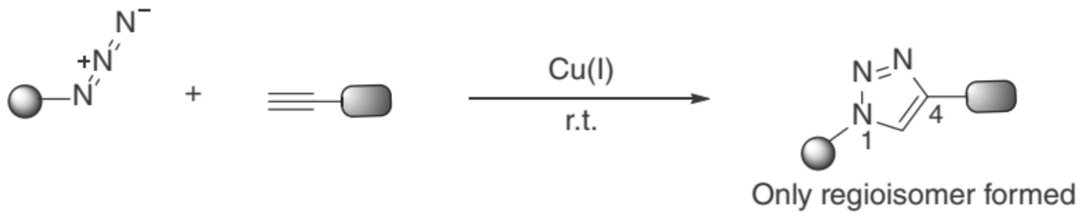

Figure 2.2 : Copper(I)-Catalyzed Azide-Alkyne Cycloaddition (CuAAC)

2.2. Nitroxide Mediated Radical Polymerization (NMP)

Nitroxide-mediated polymerization (NMP) is a controlled/living radical polymerization (CLRP) technique that provides the design of well-defined, functional and complex macromolecular structure [11]. The basic property of NMP are that it ensures polymers exhibiting very narrow mass deployment (Polydispersity index PDI o 1.5) and re-activable polymer chain ends permitting the re-initiation of the polymerization [12]. Of these procedures, those mediated by stable nitroxide free radicals, such as 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), are the most widely studied and a diversity of authors have shown that the polymerization of styrene based monomers can be controlled to levels beforehand just obtained using anionic or cationic procedures. Narrow polydispersity materials with controlled molecular weights, chain ends and chain structure can be readily prepared by heating the neat monomer with a nitroxide based initiator at 120-130 °C under an inert atmosphere [13]. Nitroxides are stable free radicals that can oxidize, reduce and react with other free radical species reversibly [3]. NMP has opened up tremendous possibilities for specialty polymers useful in a broad range of applications [14].

In this thesis, NMP technique was used in the preparation of the poly(styrene-co-4-chloromethylstyrene).

2.3 Ring Opening Polymerization (ROP)

Ring-opening polymerization has been used since the beginning of the 1900s to generate polymers. Ring-opening polymerization (ROP) is, together with chain (radical and ionic) polymerization and condensation polymerization, one of the three ways to the polymers that are so significant to life in the 21st century.Specially ROP has proved to be a helpful synthetic route to technologically interesting polymers with very specific, and controllable properties (e.g., refractive index), for preparing synthetic variants to naturally occurring polymers or to optimize biodegradable polymers for agricultural, medicinal and pharmaceutical applications[15]. In the past decades, increasing caution has been paid to biocompatible, biodegradable or bioresorbable polymers because of their potential uses in biomedical and environmental applications, such as drug-delivery systems and medical implants. As a type of surface erosion biodegradable materials, aliphatic polycarbonates are usually obtained ring-opening polymerization (ROP) of six-membered cyclic carbonate monomers and have acquired increasing interest for their potential use in biomedical and pharmaceutical applications due to their convenient nontoxicity, biocompatibility and biodegradability [7]. Organic catalysis in ring-opening polymerization (ROP) has become a robust alternate to more traditional metal-based catalysts. The field has improved to a spot at which there are not only great low cost and easy to use organocatalysts for day after day polymerizations, but the capability to precisely control the synthesis of advanced polymer architectures and ROP monomers that are immensely tough to polymerize with other catalysts now exists [16]. Ring-opening polymerization can proceed via radical, anionic, or cationic polymerization as described below.

2.3.1 Anionic Ring - Opening Polymerization

Ring - opening polymerizations using nucleophilic reagents as initiators can be categorized into ‘ anionic ROP ’ a general mechanism for which is shown in Figure 2.1. Nucleophilic reagents feasible to in starting most often contain organometals (alkyl lithium, alkyl magnesium bromide, alkyl aluminum, etc.), metal amides, phosphines, amines, alkoxides, alcohols and water. Monomers talented of ongoing anionic ROP possess polarized bonds such as carbonate, amide, ester, urethane and phosphate, which allow generation of the equaled to polycarbonate, polyester, polyurethane, polyamide, and polyphosphate, seriatimly.

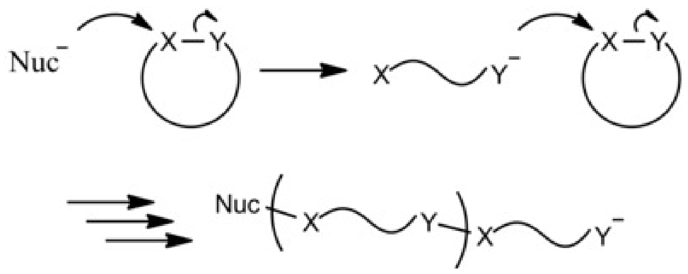

Figure 2.3 : The general mechanism for anionic ring-opening polymerization.

2.3.2 Cationic Ring - Opening Polymerization

On the contrary anionic ROP, ‘ cationic ROP ’ represents different class of polymerization where ‘ electrophilic ’ reagents are used as initiators. A common mechanism for cationic ROP is defined in Figure 2.2 , where the initiators with an electrophilic nature most frequently involve Brønsted acid, Lewis acid and alkyl esters of powerful organic acids such as sulfonic acid.

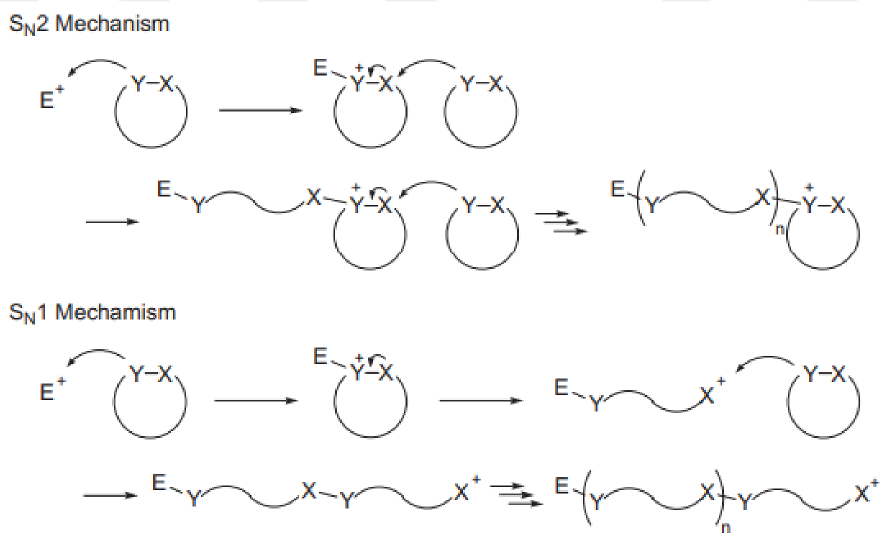

Figure 2.4 : The general mechanism for cationic ring-opening polymerization.

Similar to the monomers capable of anionic ROP, those able to undergo cationic ROP have polarized bonds represented by Y – X, where Y) has alone electron double so that it can act as Lewis base to react with electrophiles. X, which will become a cationic hub as a result of the ring - opening reaction, should be an atom in an electron – wealthy situation, such as an alkoxy - substituted carbon atom. In this path the ring - opening reaction of the monomer will be triggered by a nucleophilic assault of Y towards the electrophilic initiator (represented by E^+). The resulting cationic species, which have a cyclic structure, can be attacked by Y in another molecule of the monomer to undergo a ring - opening reaction (SN^2 mechanism); alternatingly, they can undergo a ring - opening reaction automatically to generate an acyclic cationic species that will be attacked by the monomer (SN^1 mechanism). The grade of preponderance of one of these two mechanisms over the other one depends on the stability of the X^+ cation. When X^+ is adequately stabilized by some factors such as electron donation by its vicinal atoms and functional groups, its lifetime will be increased such that the SN^1 mechanism will be predominant [17]. Ring-opening polymerization (ROP) has been applied initialy to the synthesis of aliphatic polyethers, such as poly(ethylene oxide)s. ROP has evident advantages in processing technologies, for example, reactive injection molding, over preformed high-molecular-weight polymers due to low melt viscosity of the cyclic oligomers(cyclomers) [18]. ROP is a chain-growth polymerisation where one end of the polymer chain carries a reactive centre for the extra of cyclic monomers. The resulting polymer will include end groups depending on the applied initiator and occurring termination reactions. The polymerisation reactions can be performed in collective or resolution [19]. Particularly ROP has proved to be a useful synthetic way to technologically interesting polymers with very specific, and manageable properties, for preparing synthetic versions to naturally occurring polymers or to optimize biodegradable polymers for agricultural, pharmaceutical and medicinal applications [15].

In this thesis, ROP was used to synthesize a functional polycarbonate polymer.

2.4 Condensation Polymerization

The condensation reaction is generally a type of reaction where two small molecules combine to form a larger molecule and smaller molecules such as H_2O. Polymers are synthesized mostly by chemical reactions - the polycondensation. Condensation polymers are those polymers that are formed from polyfunctional monomers, which are typically prepared by the reaction between two kinds of bifunctional symmetric monomers[20]. In condensation polymerization, molecules of monomer or lower molecular weight polymers chemically combine, producing longer chains that are much higher in molecular weight. The polymers usually formed by this mechanism have two functional groups, where functionality is defined as the average number of reacting groups per reacting molecule. The kinetics of polycondensation is usually affected by the formation of a lower molecular component generated during the polycondensation reaction . The molecular component will have a concentration and mass that negatively affects the reaction mechanism. The solution is to perform the reaction at a higher temperature and to maintain a deep vacuum, which will efficiently and effectively remove the by-products generated during the reaction, thereby favoring the production of higher molecular weight polymer[21]. Polycondensation is an important method of polymerization that yields not only engineering plastics such as polyamides, polyesters, and polyimides but also π-conjugated polymers. However, the molecular weight of these polymers is generally hard to control and their polydispersity index theoretically approaches 2 at high conversion, which is unlike the behavior of living polymerization. An uncontrolled molecular weight and broad molecular weight distribution do not stem naturally from the reaction type of condensation polymerization, that is, condensation steps with elimination of a small molecule species, but from a polymerization mechanism for step-growth polymerization. Even in artificial condensation polymerization of AB monomers, chain-growth mechanism can be involved if the reactivity of the polymer end group becomes higher than that of the monomer. In condensation polymerization of monomers with two functional groups at close position, the reactivity of one functional group of the monomer could be changed after reaction of the other functional group with the polymer end group [22].

A polyester and a polyurethane were synthesized by condensation polymerization in this thesis.

2.5 Fluorinated polymers

Fluorine-containing polymers are known to possess unique properties due to their low surface energy. The polymers are applied to a variety of surfaces and manufactured into thin films. The enhanced appearance of fluorinated portions on the surfaces of fluorinecontaining polymers is of importance in the potential applications as antithermal, water repellency, chemical proof, lubricant and electric insulation materials. Fluorinated polymers are highly solvophobic. For improving the solubility of fluorinated polymers in solvents, hybrid compounds with non-fluorinated moieties are synthesized. Then, amphiphilic copolymers are soluble and self-associated in solvents [23]. Fluorine-containing polymers have become more and more commercial, and their products have increased every year, in parallel to the huge demands of the communities. Among the fluorinated commercial polymers, poly(tetrafluoroethylene) (PTFE), poly(vinylidene fluoride) (PVDF), and poly(chlorotrifluoroethylene) (PCTFE) have become a privilege and well-studied since the mid-1940s. However, despite their excellent properties, fluorinated polymers have some drawbacks such as incompatibility with other hydrocarbon polymers, insolubility in common organic solvents, and hence chromatographic analysis problems. Trifluoromethyl (CF_3)-containing polymers are the special class of fluorinated polymers and have received great interest in recent years since they can overcome the above-mentioned problems associated with the fluorinated polymers while preserving unique properties of fluorine-containing polymers. Indeed, various methacrylate forms of CF_3-substituted monomers are readily available on the markets to achieve CF_3- substituted polymers, from which they can be polymerized by suitable polymerization methods [24].

3.EXPERIMENTAL

3.1 Materials

Ethyl 4,4,4-trifluoro-2-butynoate (97%, Sigma-Aldrich), triethylamine (99%, Sigma-Aldrich), polyepichlorohydrin (PECH, M_w ~ 700 kDa, Sigma-Aldrich), poly(vinyl chloride) (PVC, M_n ~ 35 kDa, Sigma-Aldrich), sodium azide (99%, Sigma-Aldrich), 2,2-bis(hydroxymethyl)propionic acid (98%, Sigma-Aldrich), phenylacetylene (98%, Aldrich), CuBr (98%, Aldrich), N,N,N′,N″,N″-pentamethyldiethylenetriamine (PMDETA, 98%, Sigma-Aldrich), 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, 99%, Fluka), N,N′-Dicyclohexylcarbodiimide (DCC, 99%, Sigma-Aldrich), N,N-Dimethylpyridin-4-amine (DMAP, 99%, Sigma-Aldrich), p-Toluenesulfonic acid monohydrate (p-TsOH, %98.5, Sigma-Aldrich), terephthaloyl chloride (99%, Sigma-Aldrich), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, 98%, Sigma-Aldrich), dibutyltin dilaurate (95%, Sigma-Aldrich), benzyl alcohol (99%, Sigma-Aldrich), ethyl chloroformate (97%, Sigma-Aldrich) and hexamethylene diisocyanate (HMDI, 99%, Aldrich) were used as received. Styrene (99%, Sigma-Aldrich) and 4-vinylbenzyl chloride (90%, Sigma-Aldrich) were purified by passing through a basic alumina column before use. All other solvents were purchased from Sigma-Aldrich and used as recieved.

3.2 Instrumentation

^{1}H (500 MHz) and ^{13}C (125 MHz) spectra were obtained on an Agilent VNMRS 500 instrument. ^{19}F (376 MHz) NMR spectra were measured using the Bruker 400 instrument. Gel permeation chromatography (GPC) measurements were carried out with an Agilent instrument (Model 1100) with a pump, refractive index and UV detectors and four Waters Styragel columns (HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 µm particles). The effective molecular weight ranges of columns were 2000–4,000,000, 50–100,000, 500–30,000, and 500–20,000 g/mol, respectively. THF was used as eluent at a flow rate of 0.3 mL/min at 30 C and toluene was used as an internal standard. The number average molecular weights (M_n) and dispersities ($Đ$) of the polymers were calculated based on linear polystyrene (PS) standards (Polymer Laboratories).

3.2 Synthetic Procedures

Azidoethanol (**1**) [25], 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (**2**) [25], 2-azidoethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (**3**) [25], 2-azidoethyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (**4**) [25], 2-azidoethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (**5**) [1], azide-functionalized polyester (**PE-N$_3$**) [1], azide-functionalized polyurethane (**PU-N$_3$**) [1], azide-functionalized polycarbonate (**PC-N$_3$**) [1], poly(styrene-*co*-4-chloromethylstyrene) (**PSCMS**) [26], azide-functionalized polystyrene (**PS-N$_3$**) [1], azide-functionalized PVC (**PVC-N$_3$**) [27], and azide-functionalized polyepichlorohydrin (**PECH-N$_3$**) [28] were synthesized according to the previously published procedures.

3.3.1 Synthesis of azidoethanol (1)

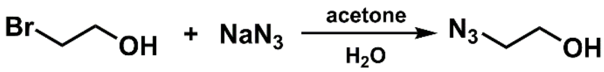

Figure 3.1 : Synthesis of azidoethanol (1).

Sodium azide (4.13g, 93.7mmol) in 15 mL of water and 2-bromoethanol (5 g, 62.45mmol) in 60 mL of acetone mixture were stirred overnight under reflux at 60 °C. After the specified time, the reaction mixture was evaporated to remove acetone. The remaining water phase was extracted with DCM and the organic layer was isolated and dried with sodium sulfate. The solvent was evaporated to yield the product as yellow oil (3.69 g, 77%).

^{1}H NMR ($CDCl_3$, δ): 3.79 (q, 2H, NCH_2CH_2), 3.46 (t, 2H, NCH_2).

3.3.2 Synthesis of 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (2)

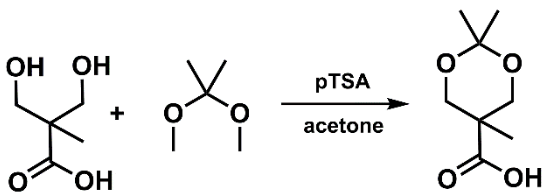

Figure 3.2 : Synthesis of 2,2,5-trimethyl-1,3-dioxane-5-carboxylic acid (2).

2,2-bis(hydroxymethyl) propionic acid (16 g, 119.2 mmol), p-toluenesulfonic acid (0.9 g, 4.64mmol) and 2,2-dimethoxypropane (22.4 mL, 178.8 mmol) were dissolved in 80 mL of dry acetone and the mixture was stirred for 2h. After the specified time, the reaction was neutralized by the addition of 12 mL of ammonium hydroxide (25%) and absolute ethanol mixture (1/1, v/v). By-products were filtered off and the liquid phase was diluted with DCM and washed with water. The organic phase was dried with sodium sulfate and the solvent removed under vacuum to give white solid crystals (16.67 g, 80%).

^{1}H NMR ($CDCl_3$, δ): 4.18 (d, 2H, $CC\mathit{H}_2O$), 3.69 (d, 2H, $CC\mathit{H}_2O$), 1.42 (d, 6H, $OCC\mathit{H}_3$), 1.22 (s, 3H, $CH_2CC\mathit{H}3$).

3.3.3 Synthesis of 2-azidoethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (3)

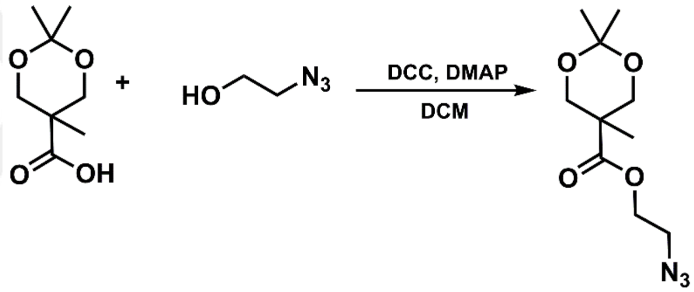

Figure 3.3 : 2-azidoethyl 2,2,5-trimethyl-1,3-dioxane-5-carboxylate (3).

A solution of azidoethanol (1) (2.84 g, 32.65 mmol), compound (2) (6.25 g, 35.95 mmol) and DMAP (1.98 g, 16.25 mmol) in 50 mL of DCM was stirred for 10 min. DCC (7.43 g, 36 mmol) in 25 mL of DCM was then added to the reaction mixture and stirred overnight at room temperature. The by-products was filtered off and the solvent was evaporated. The crude product was purified by column chromatography (1:10 EtOAc–hexane) to yield the product as a white solid (4.68 g, 59%) .

^{1}H NMR ($CDCl_3$, δ): 4.33 (t, 2H, $NCH_2C\mathit{H}_2$), 4.21 (d, 2H, $OC\mathit{H}_2CCO$), 3.68 (d, 2H, $OC\mathit{H}_2CCO$), 3.49 (t, 2H, $NC\mathit{H}_2$), 1.44 (s, 3H, $OCC\mathit{H}_3$), 1.39 (s, 3H, $OCC\mathit{H}_3$), 1.21 (s, 3H, $COCC\mathit{H}_3$).

3.3.4 Synthesis of 2-azidoethyl 3-hydroxy-2-(hydroxymethyl)-2 methylpropanoate (4) (azide functional diol monomer)

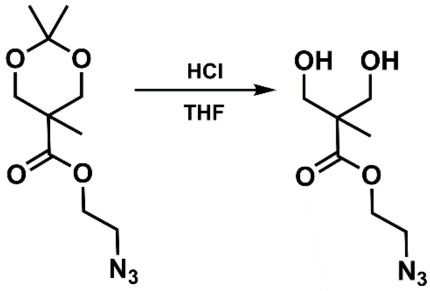

Figure 3.4 : Synthesis of 2-azidoethyl 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoate (4).

Compound (3) (4.68 g, 19.26 mmol) was dissolved in a mixture of 50 mL of 1M HCl and 50 mL of THF. The reaction mixture was stirred for 2h at room temperature. After 2h, THF was removed under reduced pressure and the water phase was extracted by DCM. Organic phase was dried over sodium sulfate and concentrated to give yellow liquid (3.5 g, 90%).

^{1}H NMR ($CDCl_3$, δ): 4.34 (t, 2H, OCH_2CH_2N$_3$), 3.91 (d, 2H, CCH_2OH), 3.75 (d, 2H, CCH_2OH), 3.52 (t, 2H, OCH$_2$CH_2N$_3$), 2.96 (br, 2H, OH), 1.11 (s, 3H, CCH_3).

3.3.5 Synthesis of 2-azidoethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (5) (azide functional carbonate monomer)

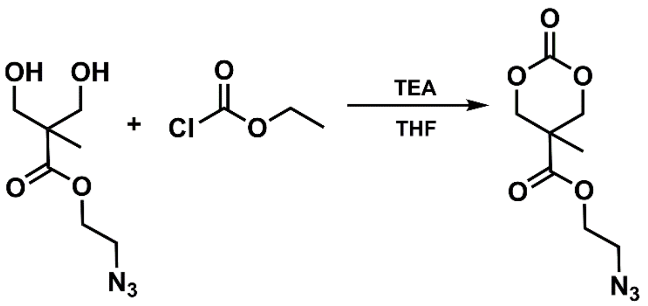

Figure 3.5 : Synthesis of 2-azidoethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (5).

Compound 4 (2.5g, 12.8mmol) was added into a 125 mL round bottom flask and dissolved in 50 mL of THF. The flask was placed in an ice bath and cooled to 0°C, and first, a solution of ethyl chloroformate ($C_3H_5ClO_2$) (3.4mL, 35.86mmol) in 12.5 mL of THF and later, a solution of triethylamine ($C_6H_{15}N$) (7.42mL, 53.78mmol) in 12.5 mL of THF was added dropwise. The solution was stirred for 2h at 0°C and then at ambient temperature for overnight. The ammonium salt was filtered off and the solvent was evaporated under reduced pressure to give a yellow product that was further purified by crystallization in diethylether to give viscous oil (1.65 g, 59%).

[1]H NMR ($CDCl_3$, δ): 4.71 (d, 2H, CCH_2O), 4.38 (t, 2H, $OCH_2CH_2N_3$), 4.22 (d, 2H, CCH_2O), 3.54 (t, 2H, $OCH_2CH_2N_3$), 1.37 (s, 3H, CCH_3).

3.3.6 Synthesis of azide-functionalized polyester (PE-N_3)

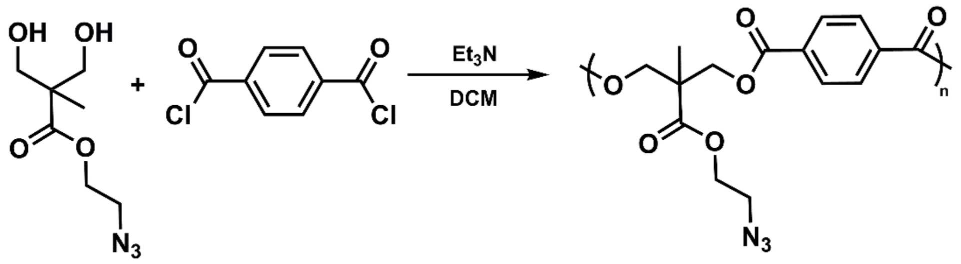

Figure 3.6 : Synthesis of azide-functionalized polyester (PE-N_3).

Compound 4 (500 mg, 2.46 mmol) and triethylamine (1.025 mL, 7.38 mmol) were dissolved in 5 mL of CH_2Cl_2 in a round bottom flask and placed in an ice bath. To this mixture, terephthaloyl chloride (499.5 mg, 2.46 mmol) was slowly added while stirring. One hour later, formed orange solution was precipitated in excess methanol. The precipitate was dissolved in chloroform and precipitated into excess methanol for further purification. The obtained product was dried in a vacuum oven at 40 ^oC for 24 h to give yellow solid polymer (0.45 g, 55%), (M_w: 5150 g/mol, M_n: 3600 g/mol, $Đ$: 1.43).

[1]H NMR ($CDCl_3$, δ): 8.07 (m, 4H, Ar-*H*), 4.63 (m, 4H, OCH_2CCH_2O), 4.35 (t, 2H, $C{=}OOCH_2CH_2N_3$), 3.49 (t, 2H, CH_2N_3), 1.49 (s, 3H, CCH_3).

3.3.7 Fluorination of PE-N_3 (Synthesis of PE-F)

PE-N_3 (100 mg, 0.3 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of THF. Then, ethyl 4,4,4-trifluoro-2-butynoate (100 mg, 86.2 μL, 0.6 mmol) was added. The mixture was degassed via two freeze-pump-thaw (FPT) cycles, placed into an oil bath thermostated at 80 ^oC, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in $CHCl_3$ and precipitated into cold hexane one more time and the solvent was decanted. The polymer was finally dried in a vacuum oven for 24 h (120 mg, 80%), (M_w: 5250 g/mol, M_n: 3900 g/mol, $Đ$: 1.35).

[1]H NMR ($CDCl_3$, δ): 8.03 (m, 4H, Ar-*H*), 5.07-4.87 (m, 2H, OCH_2CH_2N), 4.67 (s, 2H, OCH_2CH_2N), 4.53 (m, 4H, OCH_2CCH_2O), 4.44 (m, 2H, $C{=}OOCH_2CH_3$), 1.40 (m, 6H, $C{=}OOCH_2CH_3$ & CCH_3).

3.3.8 Synthesis of azide-functionalized polyurethane (PU-N_3)

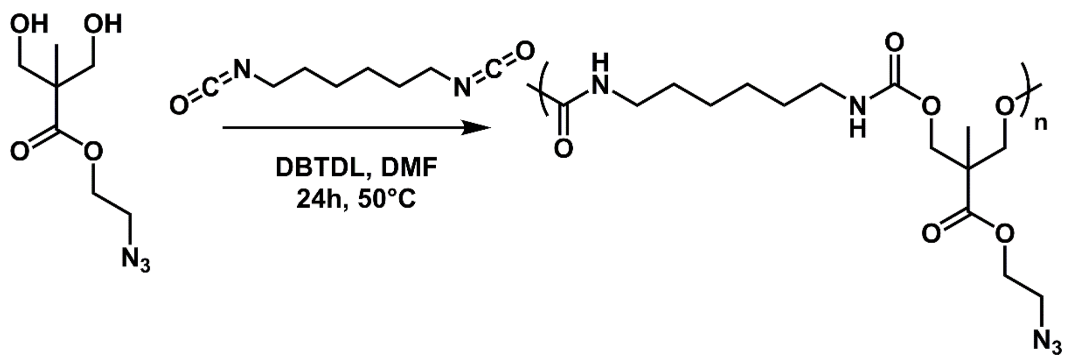

Figure 3.7 : Synthesis of azide-functionalized polyurethane (PU-N_3).

HMDI (217.29 mg, 1.29 mmol) was placed in a dried Schlenk tube with a magnetic stir bar and dissolved in 2 mL of DMF. Compound 4 (262.5 mg, 1.29 mmol) and a few blob of dibutyltin dilaurate was also added and the flask was capped. After degassing via three FPT cycles, the tube was placed in an oil bath thermostated at 50 °C, and stirred for 24 h. After the specified time, the solution was precipitated into MeOH. The crude polymer was dissolved in $CHCl_3$ and precipitated into MeOH one more time. The purified polymer was finally dried in a vacuum oven for 24 h to give transparent viscous polymer (0.36 g, 75%), (M_w: 8040 g/mol, M_n: 5430 g/mol, $Đ$: 1.48).

[1]H NMR ($CDCl_3$, δ): 5.00 (br, 2H, N*H*), 4.29-4.21 (m, 6H, $CH_2CH_2N_3$ & OCH_2CCH_2O), 3.49 (m, 2H, $CH_2CH_2N_3$), 3.15 (m, 4H, $C{=}ONHCH_2$), 1.49 (s, 4H, $NHCH_2CH_2CH_2$), 1.32-1.25 (m, 7H, CCH_3 & $NHCH_2CH_2CH_2CH_2$).

3.3.9 Fluorination of PU-N_3 (Synthesis of PU-F)

PU-N_3 (100 mg, 0.27 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of THF. Then, ethyl 4,4,4-trifluoro-2-butynoate (90 mg, 77.6 µL, 0.54 mmol) was added. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 °C, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in $CHCl_3$ and precipitated into cold hexane one more time and the solvent was decanted. The polymer was finally dried in a vacuum oven for 24 h (140 mg, 97%), (M_w: 11870 g/mol, M_n: 8200 g/mol, $Đ$: 1.45).

^{1}H NMR ($CDCl_3$, δ): 5.24 (br, 2H, N*H*), 5.04-4.87 (m, 2H, OCH_2CH_2N), 4.60 (s, 2H, OCH_2CH_2N), 4.46 (m, 2H, $C{=}OOCH_2CH_3$), 4.11-4.05 (m, 4H, OCH_2CCH_2O), 1.49-1.12 (m, 14H, $NHCH_2CH_2CH_2CH_2CH_2$, CCH_3 & $C{=}OOCH_2CH_3$).

3.3.10 Synthesis of azide-functionalized polycarbonate (PC-N_3)

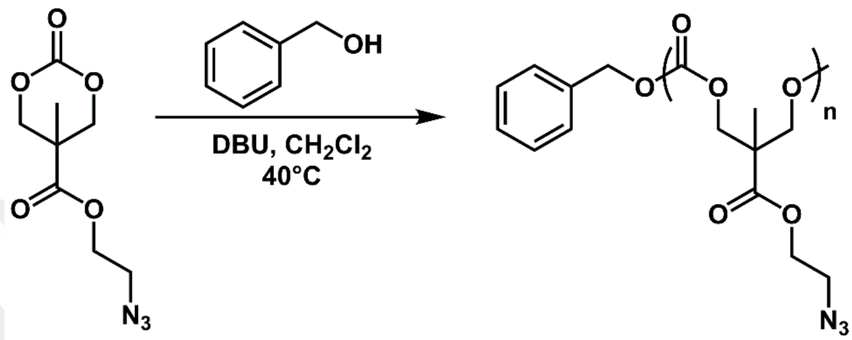

Figure 3.8 : Synthesis of azide-functionalized polycarbonate (PC-N_3).

2-azidoethyl 5-methyl-2-oxo-1,3-dioxane-5-carboxylate (5) (0.56 g, 2.44 mmol) was added to a 25 mL Schlenk tube with a magnetic stir bar and dissolved in 5 mL of dichloromethane. Benzyl alcohol (5.8 µL, 0.0485 mmol), DBU (7.25 µL 0.0485mmol) and 1-(3,5-bis(trifluoromethyl)phenyl)-3-cyclohexylthiourea (TU:cocatalyst) (17.95 mg, 0.0485 mmol) were also added then the flask was capped. After degassing via three FPT cycles, the tube was placed in an oil bath thermostated at 40 °C, and stirred for 14 h. After the specified time, the solution was concentrated by evaporation and precipitated into MeOH. The dissolution-precipitation procedure (CH_2Cl_2-MeOH) was repeated two times. The purified polymer was finally dried in a vacuum oven for 24 h to give transparent viscous polymer (170 mg, 31%), (M_w: 5770 g/mol, M_n: 3900 g/mol, $Đ$: 1.48).

^{1}H NMR ($CDCl_3$, δ): 7.38 (m, Ar*H*), 4.32 (m, 6H, OCH_2CCH_2O & $OCH_2CH_2N_3$), 3.49 (m, 2H, CH_2N_3), 1.31 (m, 3H, CCH_3).

3.3.11 Fluorination of PC-N_3 (Synthesis of PC-F)

PC-N_3 (105 mg, 0.45 mmol) was placed in a dried 25mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of THF. Then, ethyl 4,4,4-trifluoro-2-butynoate (150 mg, 129.3 µL, 0.9 mmol) was added. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 °C, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in $CHCl_3$ and precipitated into cold hexane one more time and the solvent was decanted. The polymer was finally dried in a vacuum oven for 24 h (120 mg, 66%), (M_w: 8050 g/mol, M_n: 5600 g/mol, $Đ$: 1.44).

^{1}H NMR ($CDCl_3$, δ): 7.38 (m, Ar*H*), 5.04-4.88 (m, 2H, OCH_2CH_2N), 4.60 (s, 2H, OCH_2CH_2N), 4.45 (m, 2H, $C{=}OOCH_2CH_3$), 4.20 (s, 4H, OCH_2CCH_2O), 1.41 (m, 3H, $C{=}OOCH_2CH_3$), 1.19 (m, 3H, CCH_3).

3.3.12 Synthesis of poly(styrene-*co*-4-chloromethylstyrene) (PSCMS)

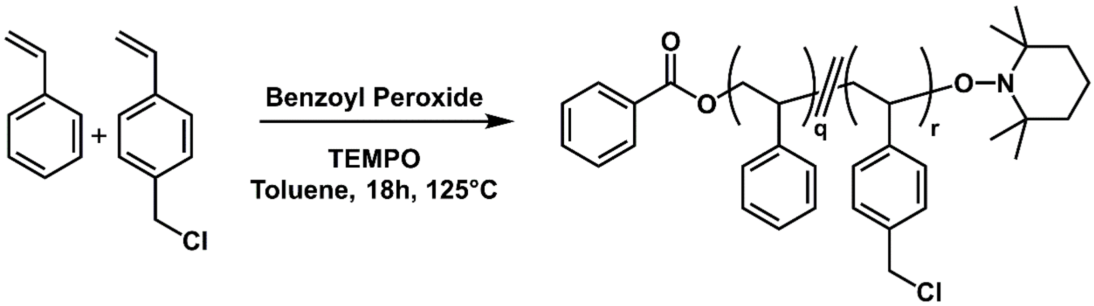

Figure 3.9 : Synthesis of poly(styrene-*co*-4-chloromethylstyrene) (PSCMS).

To a 25 mL schlenk tube, styrene (1.75 mL, 15 mmol), chloromethyl styrene (0.71 mL, 5 mmol), TEMPO (0.025 g, 0.10 mmol), 1 mL of toluene and benzoyl peroxide (24.23 mg, 0.1 mmol) were added in that order. After 2 FTP cycles, the schlenk tube was placed in an oil bath at 125°C for 18h. After the specidied time, THF was added to the viscous orange solution and precipitated in excess methanol. The dissolution-precipitation procedure ($CHCl_3$-methanol) was repeated two times. Finally, the polymer was filtered and placed in a vacuum oven for 24h. Chloromethyl styrene to styrene ratio was calculated to be 2:5 by mole based on the ^{1}H-NMR spectrum of the polymer (0.93 g, 39%), (M_w: 11460 g/mol, M_n: 9910 g/mol, $Đ$: 1.16).

^{1}H NMR ($CDCl_3$, δ): 7.22-6.23 (m, Ar*H*), 4.53 (s, $ArCH_2Cl$), 2.02-1.26 (m, 3H, CH_2CH).

3.3.13 Synthesis of azide-functionalized polystyrene (PS-N_3)

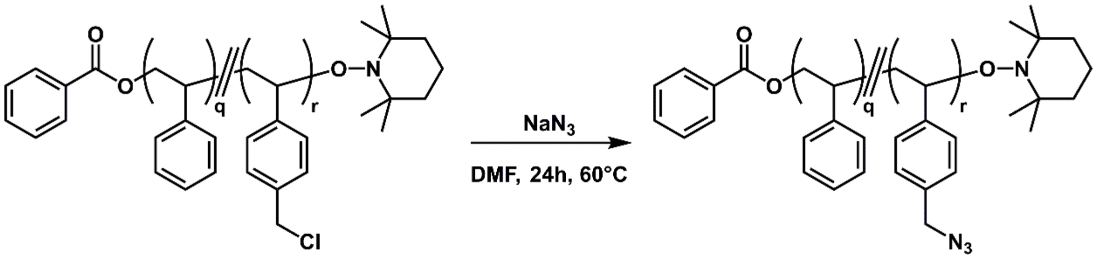

Figure 3.10 : Synthesis of azide-functionalized polystyrene (PS-N_3).

PSCMS (0.93 g, 2.43 mmol) was dissolved in 7.5 mL of DMF and sodium azide (2.92 g, 45 mmol) was added into the round bottom flask, placed into an oil bath thermostated at 60 °C, and stirred for 24 h. After the specified time, the product was filtered and precipitated into excess MeOH. The crude polymer was dissolved in $CHCl_3$ and precipitated into MeOH one more time and filtered. The purified polymer was finally dried in a vacuum oven for 24 h (Yield: 0.7 g, 75%), (M_w: 11240 g/mol, M_n: 9360 g/mol, $Đ$: 1.20).

^{1}H NMR ($CDCl_3$, δ): 7.06-6.57 (m, 17H, Ar*H*), 4.24 (br, 2H, ArCH_2N_3), 1.80-1.42 (m, 12H, ArC*H*CH_2).

3.3.14 Fluorination of PS-N_3 (Synthesis of PS-F)

PS-N_3 (100 mg, 0.24 mmol) was placed in a dried 25mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of THF. Then, ethyl 4,4,4-trifluoro-2-butynoate (79 mg, 68.1 µL, 0.48 mmol) was added. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 °C, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in $CHCl_3$ and precipitated into cold hexane one more time and the solvent was decanted. The polymer was finally dried in a vacuum oven for 24 h (130 mg, 93%), (M_w: 16470 g/mol, M_n: 14100 g/mol, $Đ$: 1.17).

^{1}H NMR ($CDCl_3$, δ): 7.02-6.45 (br, 17H, Ar*H*), 5.82-5.64 (br, 2H, ArCH_2N), 4.48-4.38 (m, 2H, C=OOCH_2CH_3), 1.80-1.34 (m, 15H, ArC*H*CH_2 & C=OOCH_2CH_3).

3.3.15 Synthesis of azide-functionalized PVC (PVC-N_3)

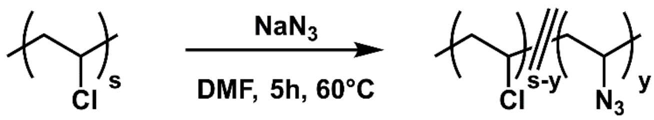

Figure 3.11 : Synthesis of azide-functionalized PVC (PVC-N_3).

PVC (1 g, 16 mmol) was dissolved in 12,5 mL of DMF and sodium azide (NaN_3) (2.05 g, 32 mmol) was added into the round bottom flask. The flask was placed in an oil bath at 60 ^oC with a magnetic stirrer for 5h. Then, the solution was filtered and precipitated into 100 mL of methanol. The dissolution-precipitation procedure (THF-methanol) was repeated two times. The filtered polymer was dried in vacuum oven for 24h (0.91g, 85%), (M_w: 55830 g/mol, M_n: 31830 g/mol, *Đ*: 1.75).

^1H NMR ($CDCl_3$, δ): 4.61-3.45 (m, 2H, C*H*Cl & C*H*N_3) 2.09-1.28 (m, 4H, ClCHCH_2 & NCHCH_2).

3.3.16 Model reaction of PVC-N_3 with phenylacetylene [1]

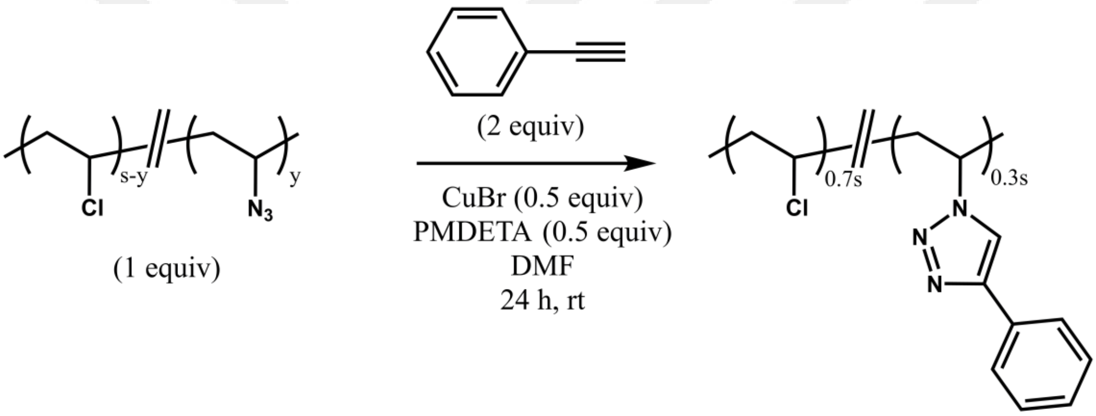

Figure 3.12 : Model reaction of PVC-N_3 with phenylacetylene.

PVC-N_3 (0.1 g, 1.60 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of DMF. Phenylacetylene (327 mg, 3.20 mmol), PMDETA (0.167 mL, 0.80 mmol) and CuBr (120 mg, 0.80 mmol) were also added respectively. After degassing via three FPT cycles, the solution was left to stir at room temperature for 24 h. Afterwards, the solution was diluted with THF and passed through a short column of neutral alumina for the removal of copper salts. Excess solvent was evaporated under vacuum and the remaining solution was precipitated into MeOH. The dissolution-precipitation procedure (THF-MeOH) was repeated two times. According to ^1H NMR analysis, the azidation efficiency was calculated to be 30% (65 mg, 45%).

^1H NMR (DMSO-d6, δ): 8.77-8.11 (m, 3H, CC*H*N), 7.82-7.32 (m, 15H, Ar*H*), 5.16-3.57 (m, 10H, ClC*H* & N_3C*H*), 2.91-1.83 (br, 20H, ClCHCH_2 & N_3CHC*H*2).

3.3.17 Fluorination of PVC-N_3 (Synthesis of PVC-F)

PVC-N_3 (100 mg, 0.76 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of THF. Then, ethyl 4,4,4-trifluoro-2-butynoate (252.5 mg, 217.7 µL, 1.52 mmol) was added. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 ^{o}C, and stirred for 24 h. After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in $CHCl_3$ and precipitated into cold hexane one more time and the solvent was decanted. The polymer was finally dried in a vacuum oven for 24 h (200 mg, 88%), (M_w: 86500 g/mol, M_n: 43800 g/mol, $Đ$: 1.98).

^{1}H NMR ($CDCl_3$, δ): 5.92-5.52 (m, 3H, C*H*N), 4.61-3.50 (m, 13H, C*H*Cl & C=OOC$H_2$$CH_3$), 3.00-1.65 (m, 20H, ClCHCH_2 & NCHCH_2), 1.42 (br, 9H, C=OOCH_2CH_3).

3.3.18 Synthesis of azide-functionalized PECH (PECH-N_3)

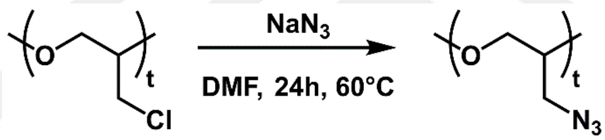

Figure 3.13 : Synthesis of azide-functionalized PECH (PECH-N_3).

Polyepichlorohydrin (average M_w ~700,000 by GPC) was converted into poly(glycidyl azide) (PGA). PECH (1 g, 10.81 mmol) was dissolved in 7.5 mL of DMF and sodium azide (1.40 g, 21.62 mmol) was added to the solution, which then stirred at 60°C for 24 h. After 24 h, the solution was filtered and precipitated into methanol. The precipitate was then dissolved in THF and precipitated into methanol to give a transparent viscous liquid and it was further dried in vacuum at 40 °C for 24 h (1 g, 94%), (M_w: 221180 g/mol, M_n: 148130 g/mol, $Đ$: 1.49).

^{1}H NMR ($CDCl_3$, δ): 3.66 (m, 3H, CH_2CHO & CH_2C*H*O), 3.41 (m, 2H, C$H_2$$N_3$).

3.3.19 Fluorination of PECH-N_3 (Synthesis of PECH-F)

PECH-N_3 (100 mg, 1.01 mmol) was placed in a dried 25 mL Schlenk tube with a magnetic stir bar and dissolved in 1 mL of THF. Then, ethyl 4,4,4-trifluoro-2-butynoate (335.5 mg, 289.2 µL, 2.02 mmol) was added. The mixture was degassed via two FPT cycles, placed into an oil bath thermostated at 80 ^{o}C, and stirred for 24 h.

After the specified time, the reaction mixture was cooled to room temperature and precipitated into cold hexane. The crude polymer was dissolved in $CHCl_3$ and precipitated into cold hexane one more time and the solvent was decanted. The polymer was finally dried in a vacuum oven for 24 h to (240 mg, 89%), (M_w: 327300 g/mol, M_n: 166500 g/mol, $Đ$: 1.97).

^{1}H NMR ($CDCl_3$, δ): 4.75-4.58 (m, 2H, CH_2N), 4.40 (s, 4H, OCH_2CCH_2O), 3.92-3.41 (m, 3H, CH_2CHO & CH_2CHO), 1.37 (m, 3H, C=OOCH_2CH_3).

4. RESULTS AND DISCUSSION

4.1 Azide-functionalized polymers

Azide functional monomers, compounds 4 and 5, were synthesized as described in the experimental section. The ^{1}H NMR spectra of the obtained monomers are shown in Figure 4.1.

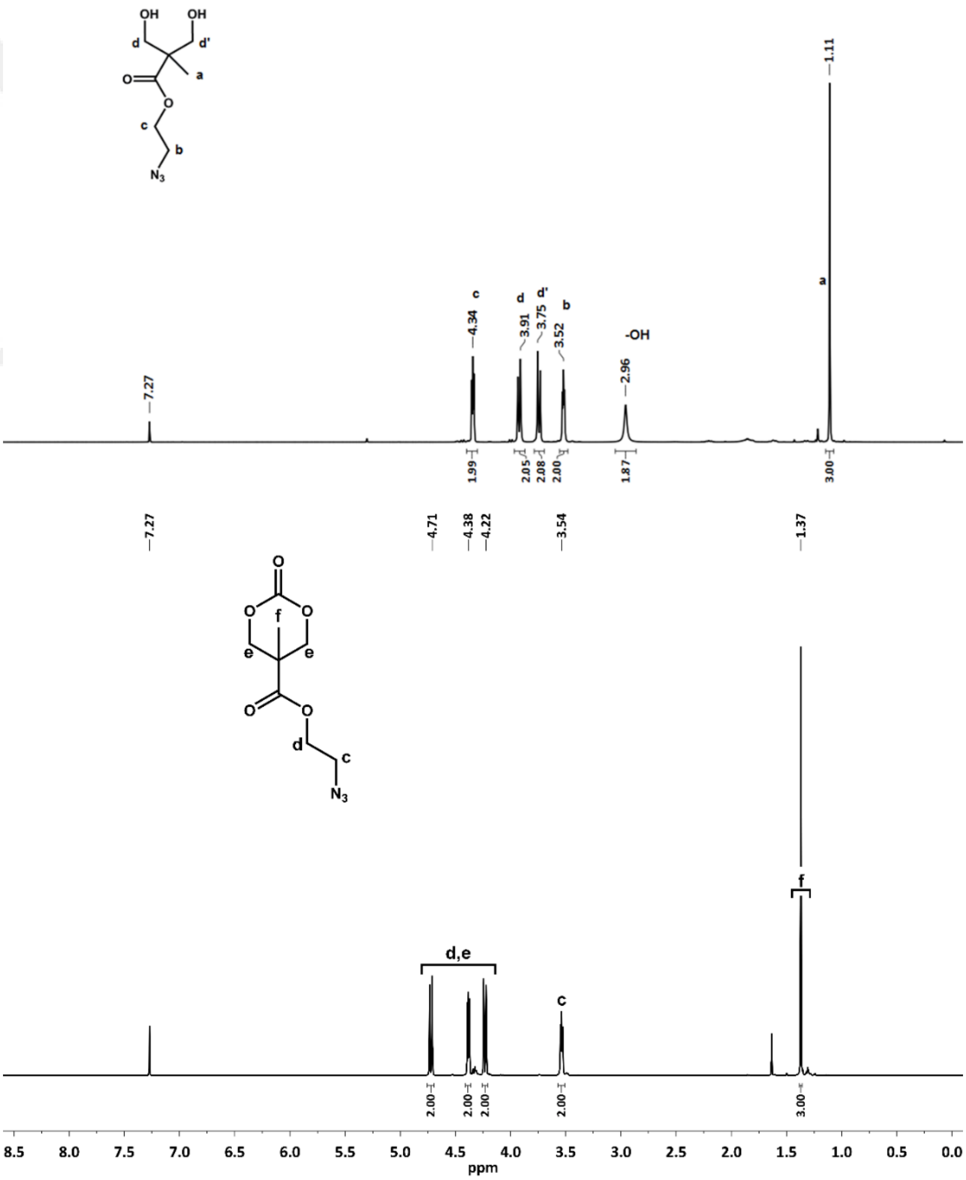

Figure 4.1 : ^{1}H-NMR spectra of 4 and 5 in $CDCl_3$.

The structures of azide-functionalized polymers employed in this thesis and synthesis routes of these polymers are depicted in Figure 4.2.

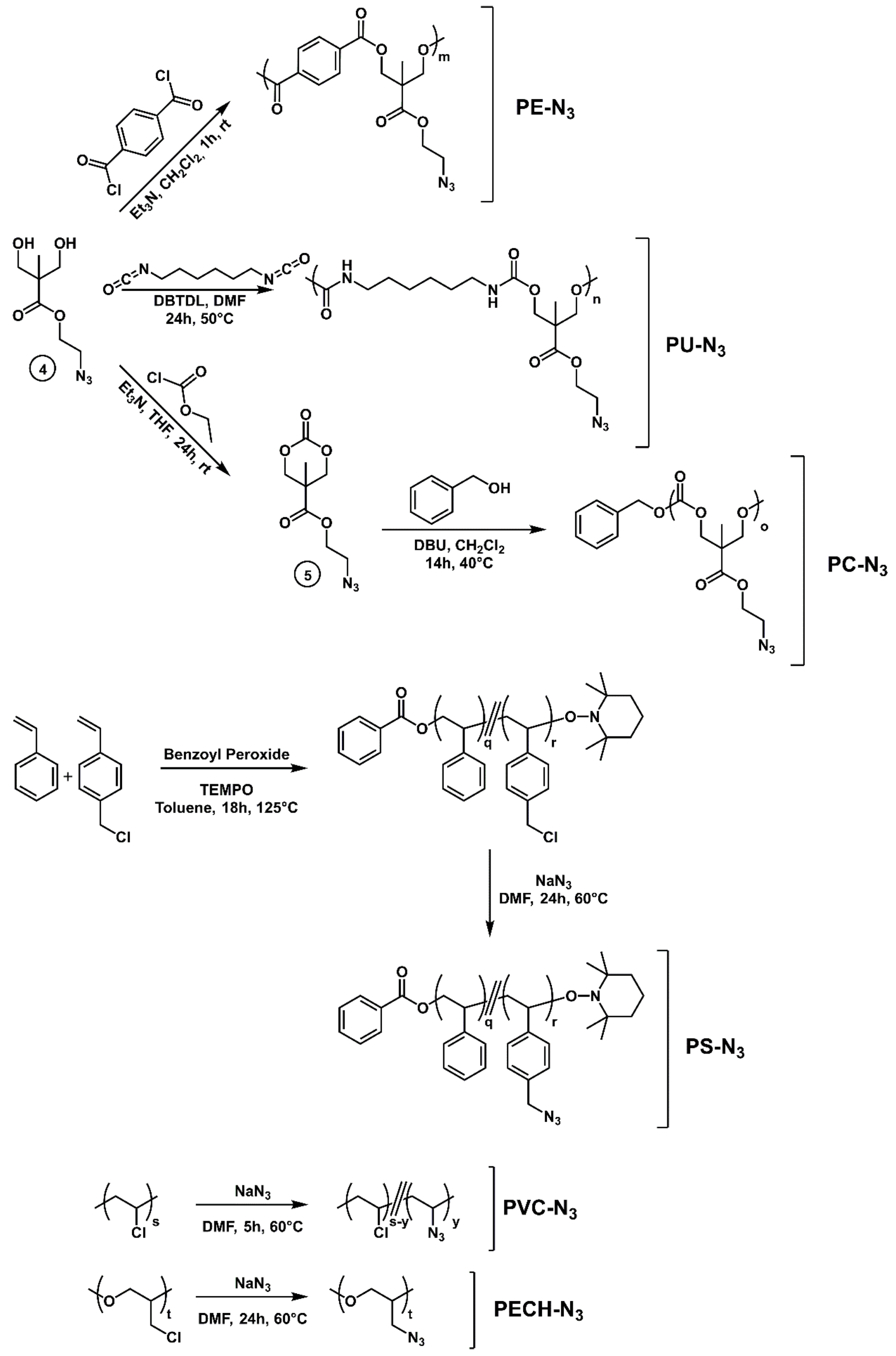

Figure 4.2 : Synthesis routes for azide-functionalized polymers.

Azide functional diol compound (**4**) was used as a monomer for the synthesis of azide-functionalized polyester (**PE-N_3**) and azide-functionalized polyurethane (**PU-N_3**). Azide functional carbonate compound (**5**) was used as a monomer for the synthesis of azide-functionalized polycarbonate (**PC-N_3**).

On the other hand, azide-functionalized polystyrene (**PS-N_3**), azide-functionalized PVC (**PVC-N_3**), and azide-functionalized polyepichlorohydrin (**PECH-N_3**) were obtained by substitution reaction of Cl group by azide group in each polymer.

4.2 Fluorination of PE-N_3 (PE-F)

Fluorinated PE (PE-F) was obtained with the metal-free azide-alkyne click reaction between azide group of PE-N_3 and electron-deficient alkyne group of ethyl 4,4,4-trifluoro-2-butynoate.

^{1}H-NMR spectra of PE-N_3 and PE-F are given in Figure 4.3. After the click reaction the methylene protons next to azide group has shifted from 3.49 ppm to 5.05-4.87 ppm which is due to the aromatic nature of the triazole ring.

In addition to this, ^{1}H NMR spectrum of PE-F shows two new distinctive peaks, arising from the C=OOCH_2CH_3 protons of ethyl 4,4,4-trifluoro-2-butynoate which added to the structure. The normalized integration values show additional 3 protons at 1.40 ppm and 2 protons at 4.44 ppm which is consistent with the final structure.

The efficiency of the click reaction was calculated from ^{1}H NMR spectrum with the comparison of methylene protons next to triazole unit appeared at 5.05-4.87 ppm and the methylene protons of C=OOC$H_2$$CH_3$ at 4.44 ppm, and found to be 100%.

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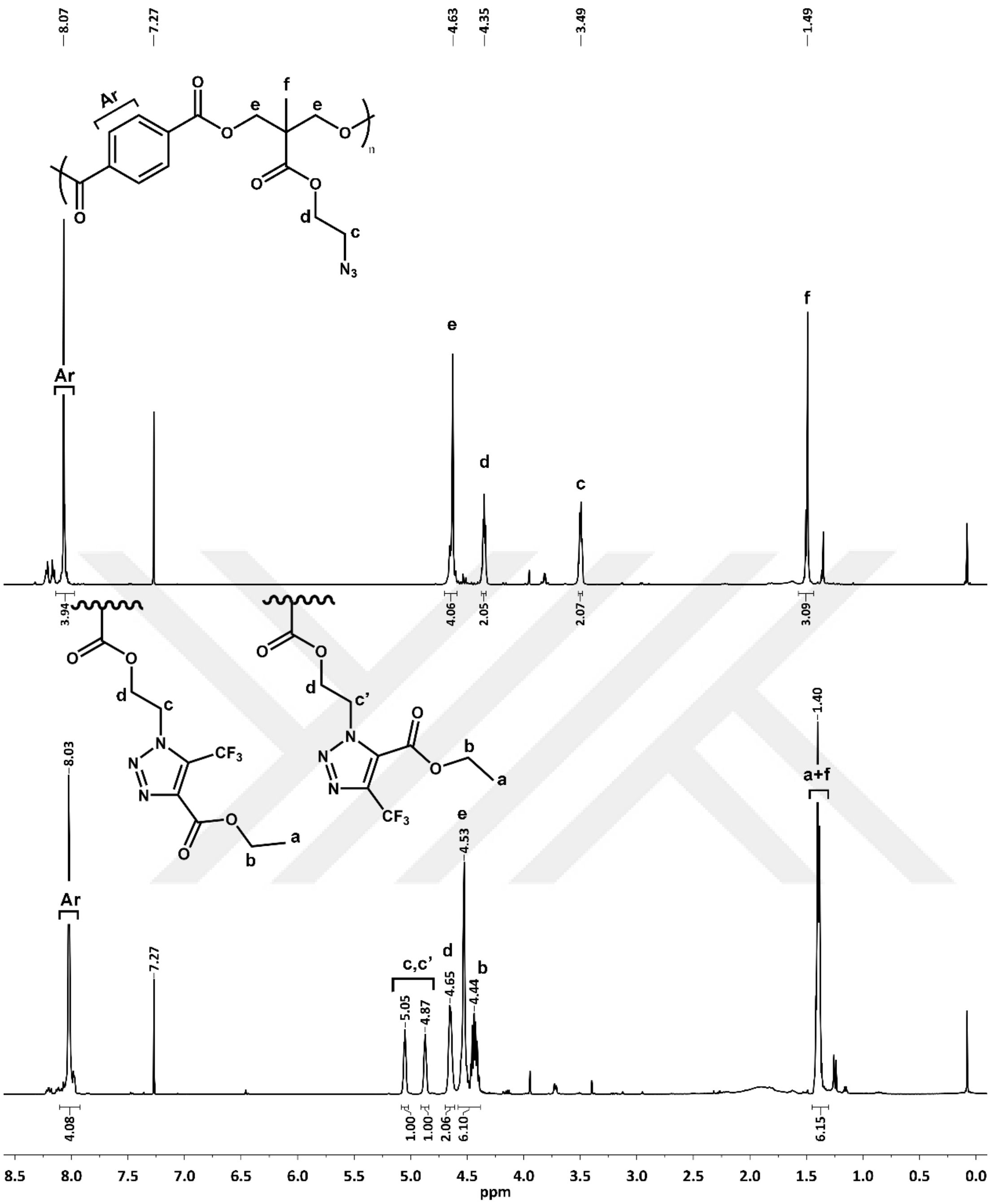

Figure 4.3 : [1]H-NMR spectra of PE-N_3 (up) and PE-F (down) in $CDCl_3$.

As an asymmetric alkyne was used, the triazole pendant units in the final structure have two regioisomers, which resulted in two different peaks in ^{19}F NMR spectrum of PE-F (Figure 4.4).

Both modified and unmodified polymers were characterized with GPC (Figure 4.5).

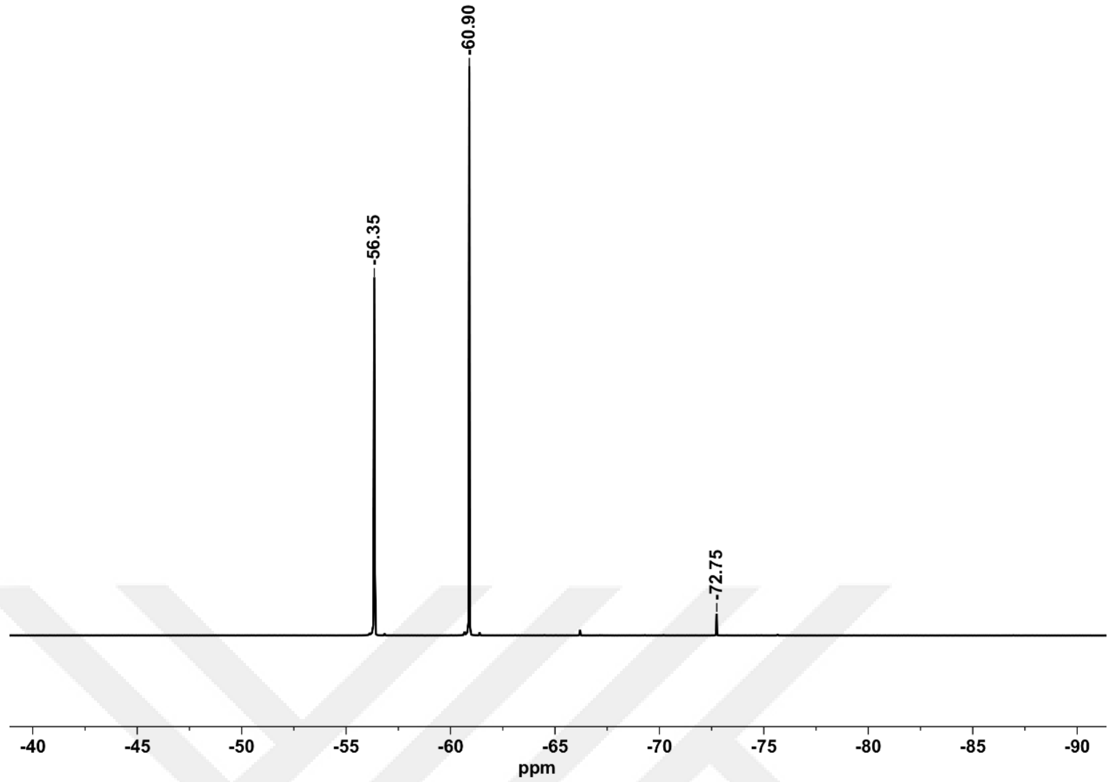

Figure 4.4 : ^{19}F NMR spectrum of PE-F in $CDCl_3$.

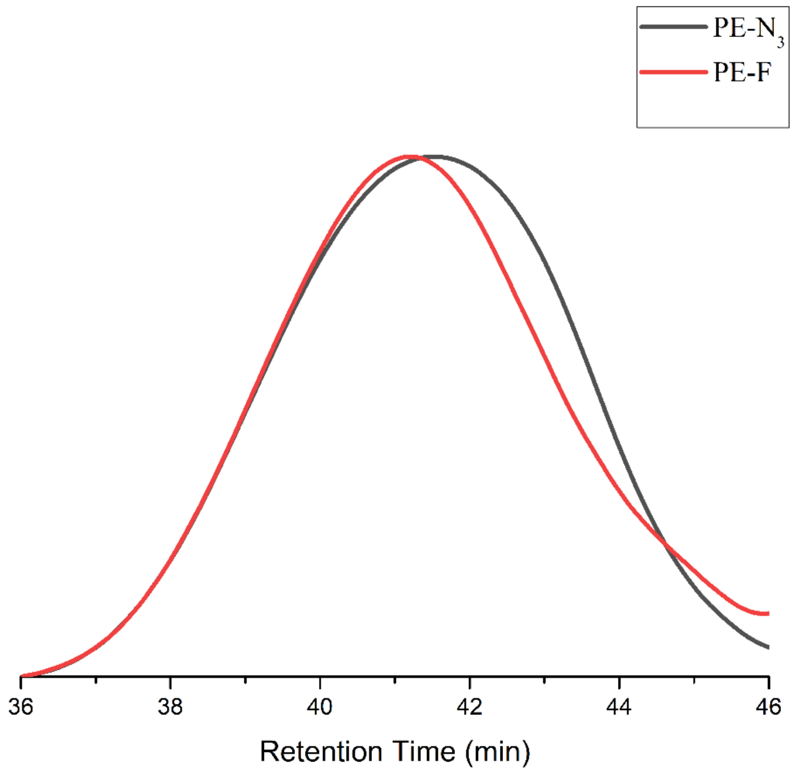

Figure 4.5 : Overlaid GPC traces of **PE-N3** (black) and **PE-F** (red) in THF.

4.3 Fluorination of PU-N_3 (PU-F)

Fluorinated PU (PU-F) was obtained with the metal-free azide-alkyne click reaction between azide group of PU-N_3 and electron-deficient alkyne group of ethyl 4,4,4-trifluoro-2-butynoate.

[1]H-NMR spectra of PU-N_3 and PU-F are given in Figure 4.6. After the click reaction the methylene protons next to azide group has shifted from 3.49 ppm to 5.04-4.87 ppm which is due to the aromatic nature of the triazole ring.

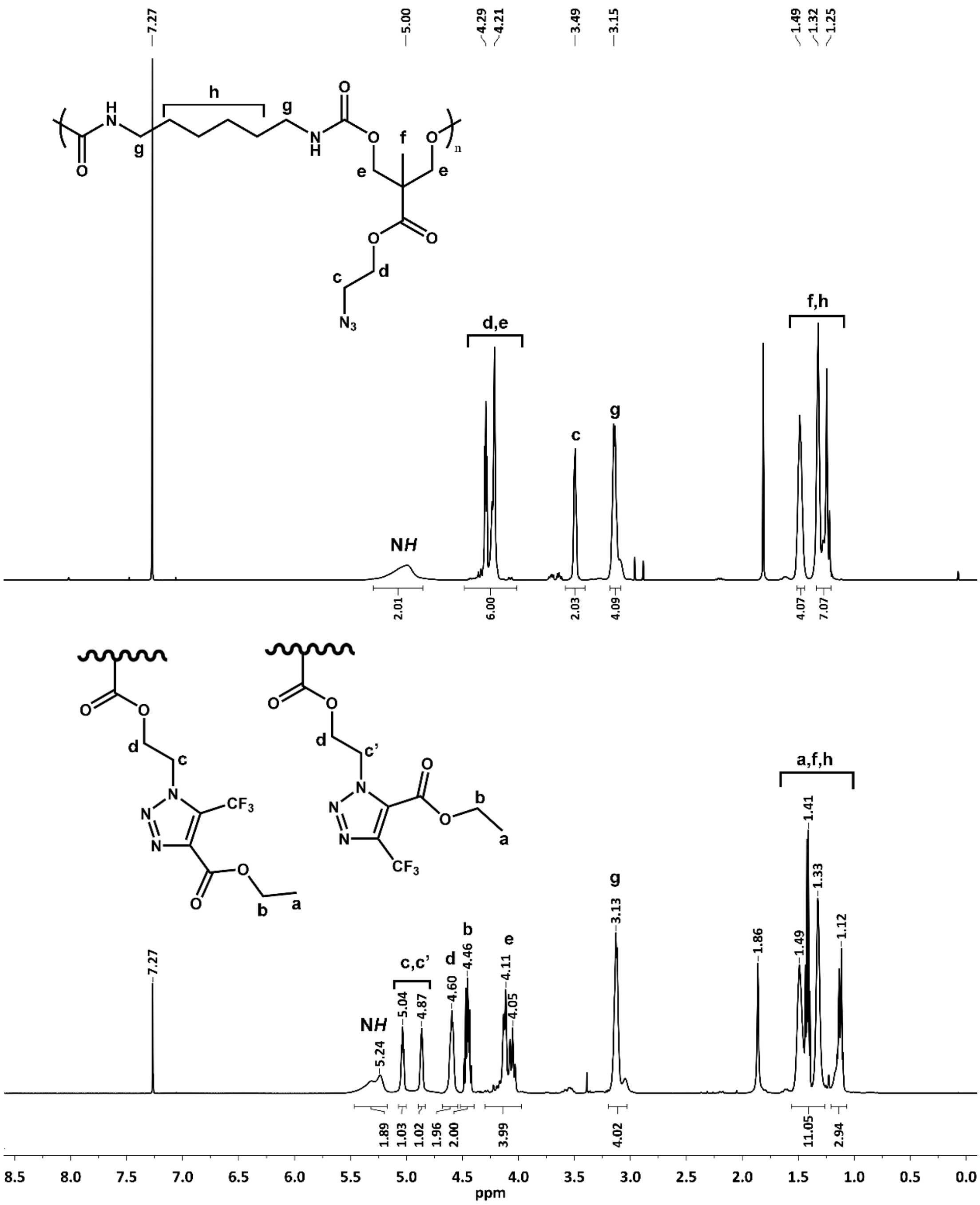

Figure 4.6 : [1]H-NMR spectra of PU-N_3 (up) and PU-F (down) in $CDCl_3$.

In addition to this, ^{1}H NMR spectrum of PU-F shows two new distinctive peaks, arising from the $C{=}OOC\mathit{H_2}C\mathit{H_3}$ protons of ethyl 4,4,4-trifluoro-2-butynoate which added to the structure. The normalized integration values show additional 3 protons at 1.41 ppm and 2 protons at 4.46 ppm which is consistent with the final structure.

The efficiency of the click reaction was calculated from ^{1}H NMR spectrum with the comparison of methylene protons next to triazole unit appeared at 5.04-4.87 ppm and the methylene protons of $C{=}OOC\mathit{H_2}CH_3$ at 4.46 ppm, and found to be 100%.

As an asymmetric alkyne was used, the triazole pendant units in the final structure have two regioisomers, which resulted in two different peaks in ^{19}F NMR spectrum of PU-F (Figure 4.7).

Both modified and unmodified polymers were characterized with GPC (Figure 4.8).

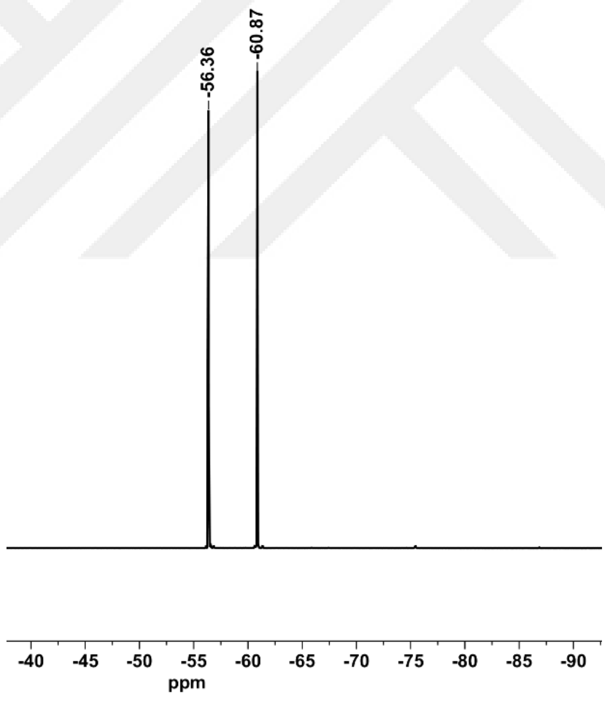

Figure 4.7 : ^{19}F NMR spectrum of PU-F in $CDCl_3$.

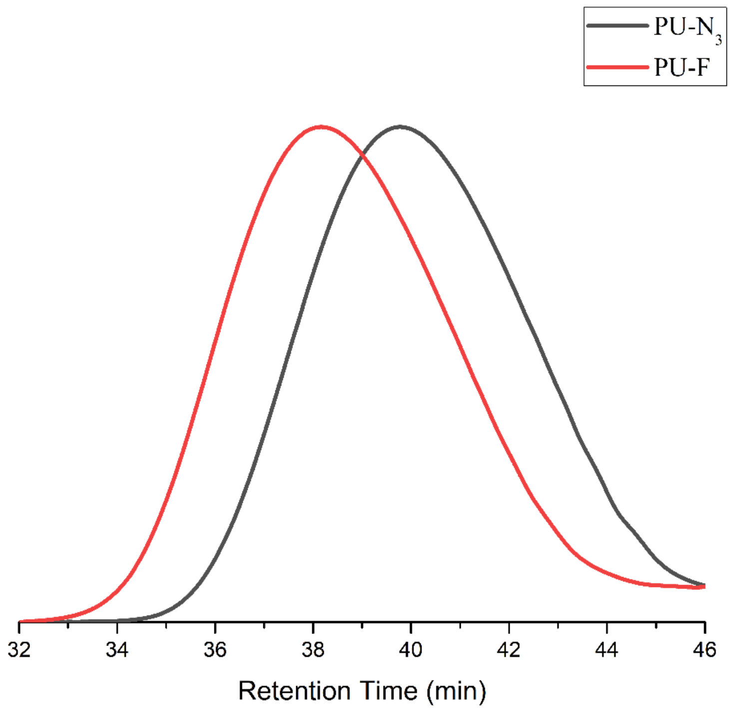

Figure 4.8 : Overlaid GPC traces of **PU-N$_3$** (black) and **PU-F** (red) in THF.

4.4 Fluorination of PC-N$_3$ (PC-F)

Fluorinated PC (PC-F) was obtained with the metal-free azide-alkyne click reaction between azide group of PC-N$_3$ and electron-deficient alkyne group of ethyl 4,4,4-trifluoro-2-butynoate.

^{1}H-NMR spectra of PC-N$_3$ and PC-F are given in Figure 4.9. After the click reaction the methylene protons next to azide group has shifted from 3.49 ppm to 5.04-4.88 ppm which is due to the aromatic nature of the triazole ring.

In addition to this, ^{1}H NMR spectrum of PC-F shows two new distinctive peaks, arising from the C=OOCH_2CH_3 protons of ethyl 4,4,4-trifluoro-2-butynoate which added to the structure. The normalized integration values show additional 3 protons at 1.41 ppm and 2 protons at 4.45 ppm which is consistent with the final structure.

The efficiency of the click reaction was calculated from ^{1}H NMR spectrum with the comparison of methylene protons next to triazole unit appeared at 5.04-4.88 ppm and the methylene protons of C=OOCH_2CH$_3$ at 4.45 ppm, and found to be 100%.

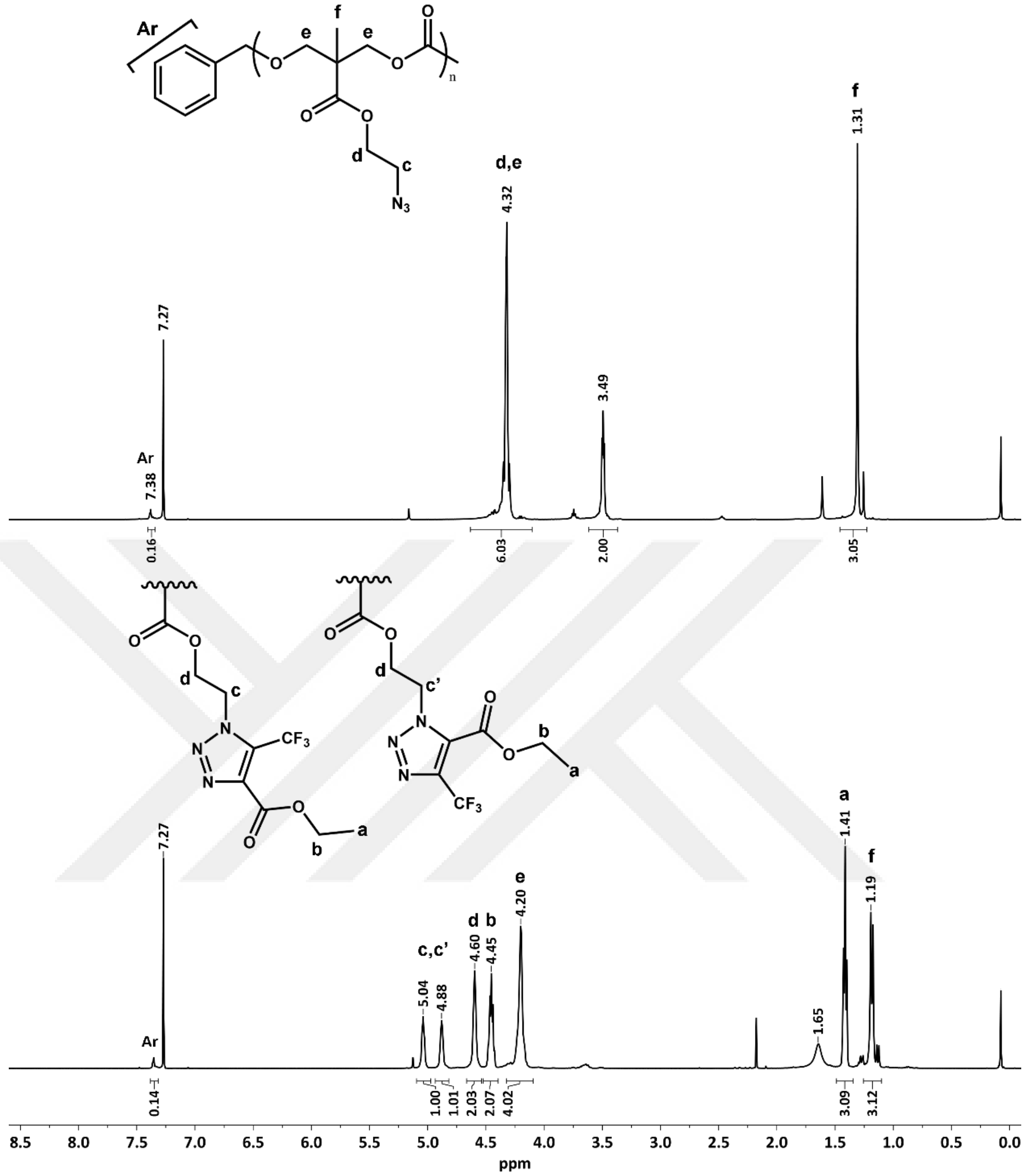

Figure 4.9 : ^{1}H-NMR spectra of PC-N_3 (up) and PC-F (down) in $CDCl_3$.

As an asymmetric alkyne was used, the triazole pendant units in the final structure have two regioisomers, which resulted in two different peaks in ^{19}F NMR spectrum of PC-F (Figure 4.10).

Both modified and unmodified polymers were characterized with GPC (Figure 4.11).

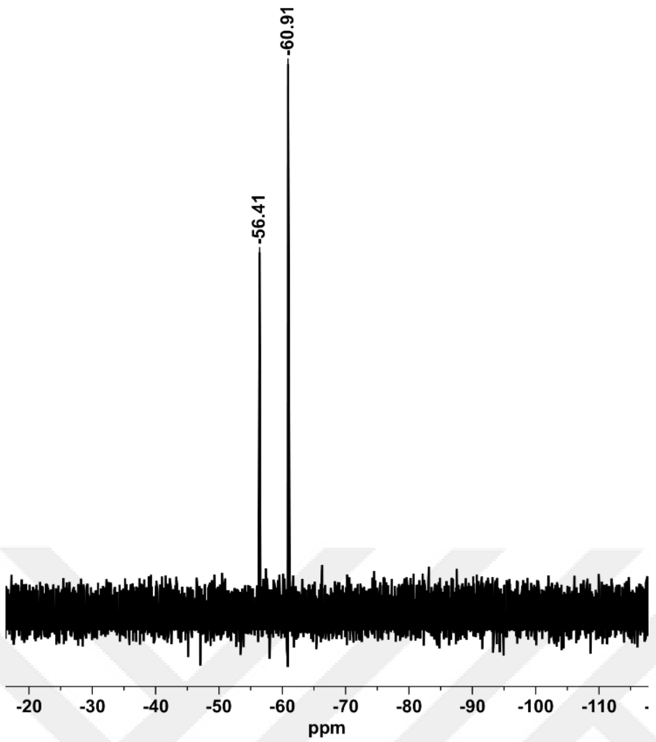

Figure 4.10 : ^{19}F NMR spectrum of PC-F in $CDCl_3$.

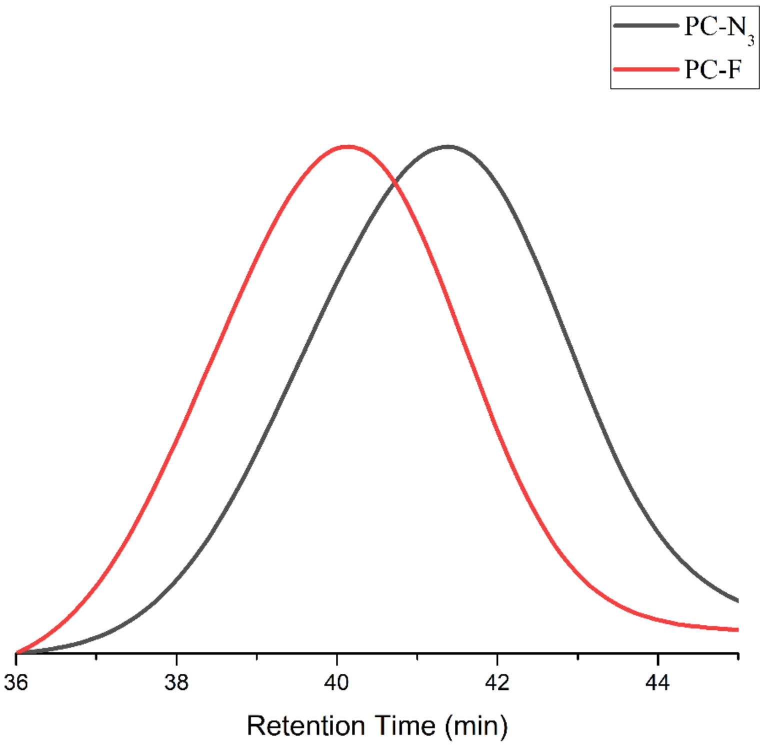

Figure 4.11 : Overlaid GPC traces of **PC-N3** (black) and **PC-F** (red) in THF.

4.5 Fluorination of $PS-N_3$ (PS-F)

Fluorinated PS (PS-F) was obtained with the metal-free azide-alkyne click reaction between azide group of $PS-N_3$ and electron-deficient alkyne group of ethyl 4,4,4-trifluoro-2-butynoate.

^{1}H-NMR spectra of $PS-N_3$ and PS-F are given in Figure 4.12. After the click reaction the methylene protons next to azide group has shifted from 4.24 ppm to 5.82-5.64 ppm which is due to the aromatic nature of the triazole ring.

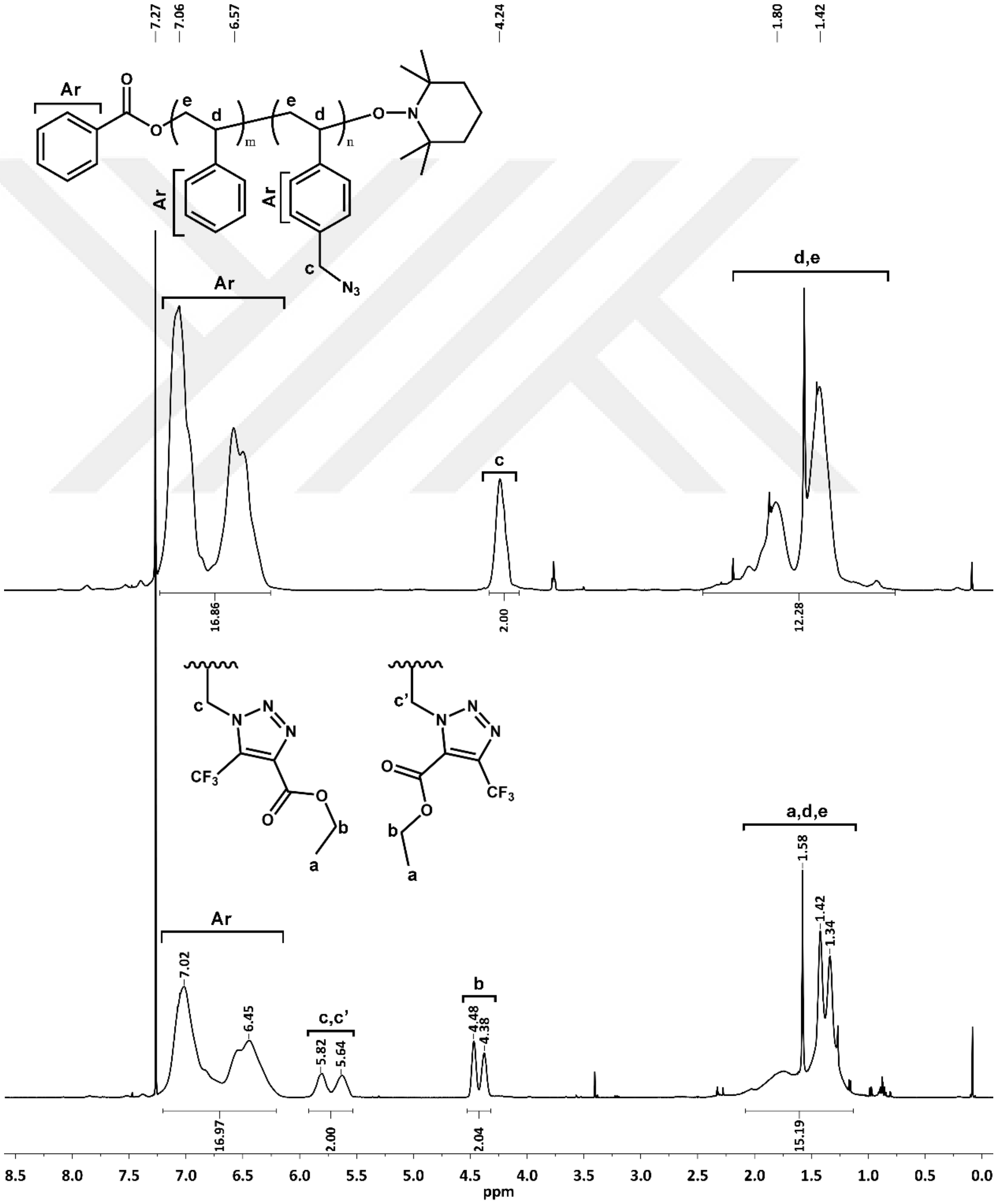

Figure 4.12 : ^{1}H-NMR spectra of $PS-N_3$ (up) and PS-F (down) in $CDCl_3$.

In addition to this, ^{1}H NMR spectrum of PC-F shows two new distinctive peaks, arising from the $C{=}OOC\mathit{H}_2C\mathit{H}_3$ protons of ethyl 4,4,4-trifluoro-2-butynoate which added to the structure. The normalized integration values show additional 3 protons at aliphatic region and 2 protons at 4.48-4.38 ppm which is consistent with the final structure.

The efficiency of the click reaction was calculated from ^{1}H NMR spectrum with the comparison of methylene protons next to triazole unit appeared at 5.82-5.64 ppm and the methylene protons of $C{=}OOC\mathit{H}_2CH_3$ at 4.48-4.38 ppm, and found to be 100%.

As an asymmetric alkyne was used, the triazole pendant units in the final structure have two regioisomers, which resulted in two different peaks in ^{19}F NMR spectrum of PS-F (Figure 4.13).

Both modified and unmodified polymers were characterized with GPC (Figure 4.14).

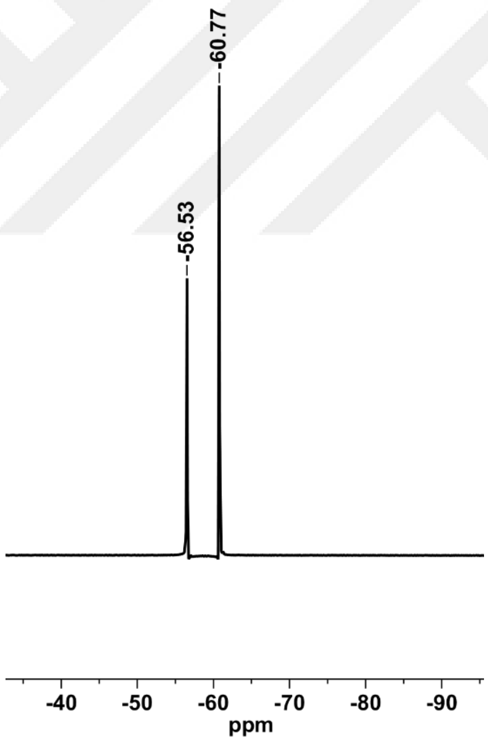

Figure 4.13 : ^{19}F NMR spectrum of PS-F in $CDCl_3$.

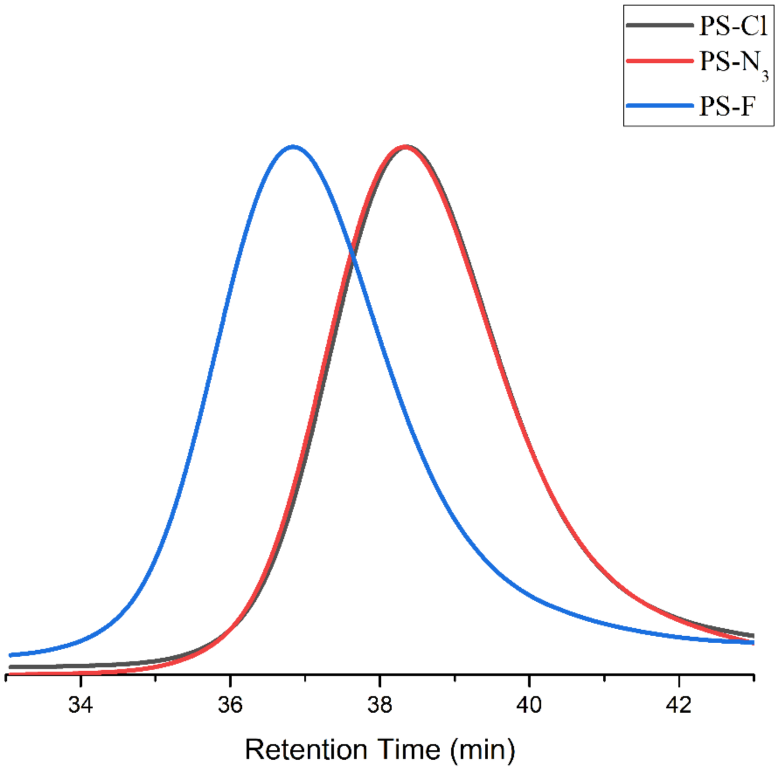

Figure 4.14 : Overlaid GPC traces of **PS-Cl** (black), **PS-N_3** (red) and **PS-F** (blue) in THF.

4.6 Fluorination of PVC-N_3 (PVC-F)

Fluorinated PVC (PVC-F) was obtained with the metal-free azide-alkyne click reaction between azide group of PVC-N_3 and electron-deficient alkyne group of ethyl 4,4,4-trifluoro-2-butynoate.

^{1}H-NMR spectra of PVC-N_3 and PVC-F are given in Figure 4.15. After the click reaction the methyne protons next to azide group has shifted to 5.92-5.52 ppm which is due to the aromatic nature of the triazole ring.

In addition to this, ^{1}H NMR spectrum of PVC-F shows two new distinctive peaks, arising from the $C{=}OOC\mathit{H}_2C\mathit{H}_3$ protons of ethyl 4,4,4-trifluoro-2-butynoate which added to the structure. The normalized integration values show additional 3 protons at 1.42 ppm and 2 protons at 4.47 ppm which is consistent with the final structure.

The efficiency of the click reaction was calculated from ^{1}H NMR spectrum with the comparison of methyne protons next to triazole unit appeared at .92-5.52 ppm and the methyl protons of $C{=}OOCH_2C\mathit{H}_3$ at 1.42 ppm, and found to be 100%.

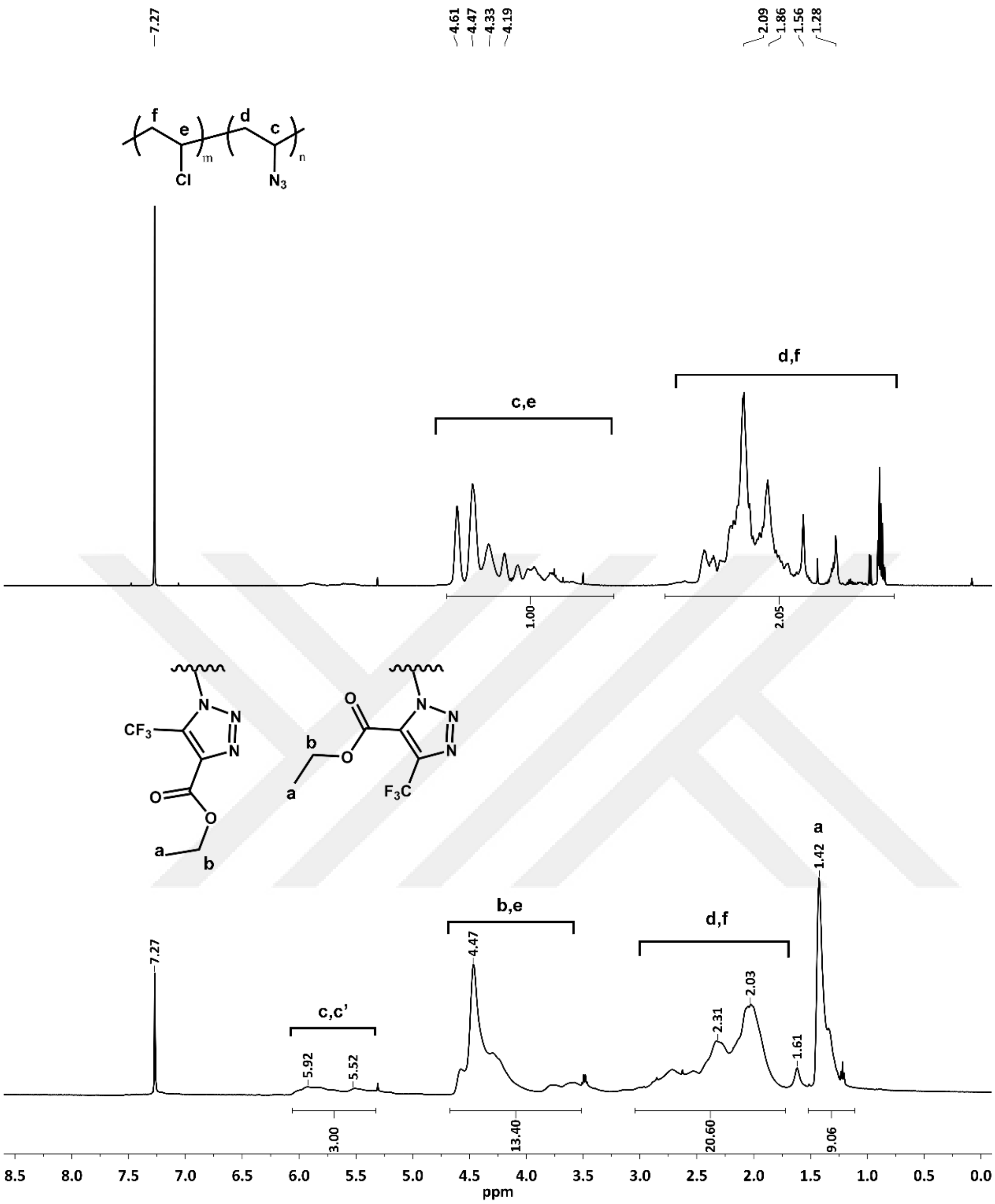

Figure 4.15 : ^{1}H-NMR spectra of PVC-N_3 (up) and PVC-F (down) in $CDCl_3$.

As an asymmetric alkyne was used, the triazole pendant units in the final structure have two regioisomers, which resulted in two different peaks in ^{19}F NMR spectrum of PVC-F (Figure 4.16).

Both modified and unmodified polymers were characterized with GPC (Figure 4.17).

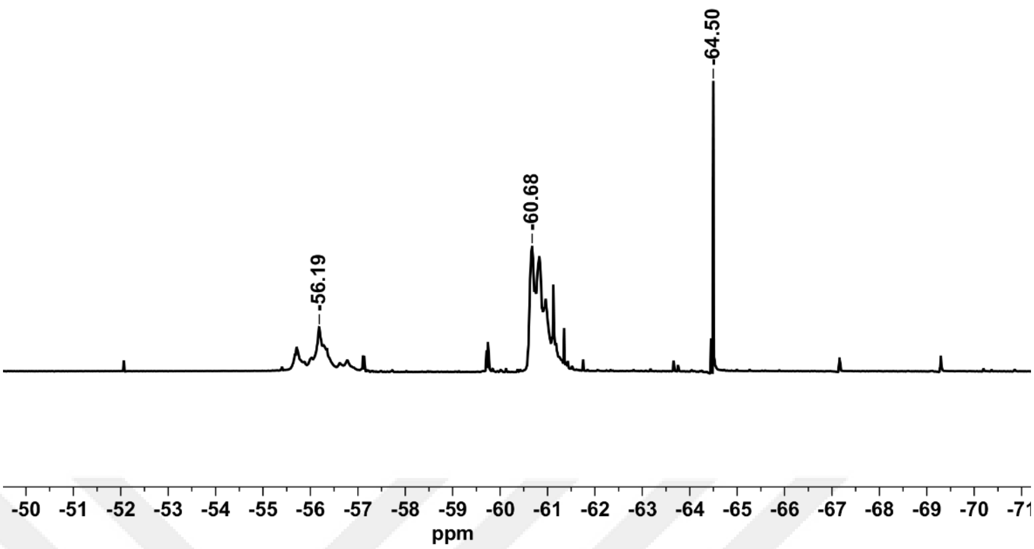

Figure 4.16 : ^{19}F NMR spectrum of PVC-F in $CDCl_3$.

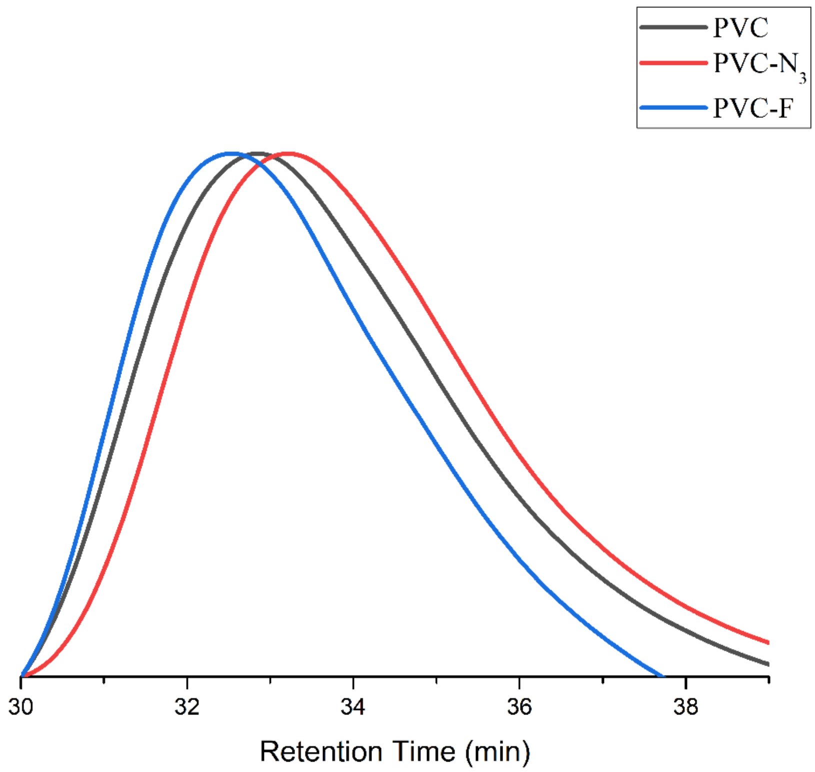

Figure 4.17 : Overlaid GPC traces of **PVC** (black), **PVC-N_3** (red) and **PVC-F** (blue) in THF.

4.7 Fluorination of PECH-N_3 (PECH-F)

Fluorinated PECH (PECH-F) was obtained with the metal-free azide-alkyne click reaction between azide group of PECH-N_3 and electron-deficient alkyne group of ethyl 4,4,4-trifluoro-2-butynoate.

^{1}H-NMR spectra of PECH-N_3 and PECH-F are given in Figure 4.18. After the click reaction the methylene protons next to azide group has shifted to from 3.41 ppm to 4.75-4.58 ppm which is due to the aromatic nature of the triazole ring.

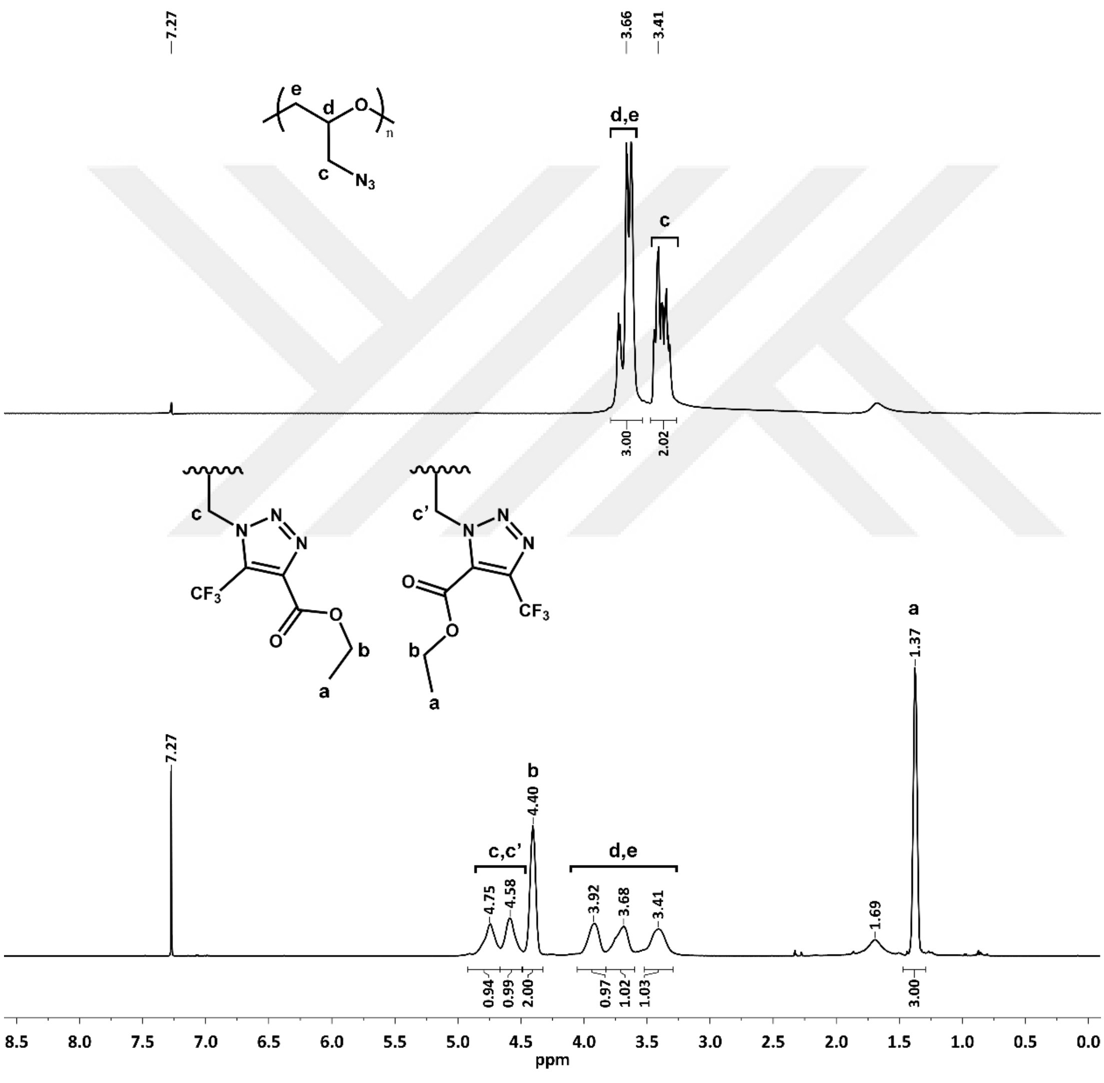

Figure 4.18 : ^{1}H-NMR spectra of PECH-N_3 (up) and PECH-F (down) in $CDCl_3$

In addition to this, ^{1}H NMR spectrum of PECH-F shows two new distinctive peaks, arising from the C=OOCH_2CH_3 protons of ethyl 4,4,4-trifluoro-2-butynoate which added to the structure. The normalized integration values show additional 3 protons at 1.37 ppm and 2 protons at 4.40 ppm which is consistent with the final structure.

The efficiency of the click reaction was calculated from ^1H NMR spectrum with the comparison of methylene protons next to triazole unit appeared at 4.75-4.58 ppm and the methylene protons of $C{=}OOCH_2CH_3$ at 4.40 ppm, and found to be 100%.

As an asymmetric alkyne was used, the triazole pendant units in the final structure have two regioisomers, which resulted in two different peaks in ^{19}F NMR spectrum of PECH-F (Figure 4.19).

Both modified and unmodified polymers were characterized with GPC (Figure 4.20).

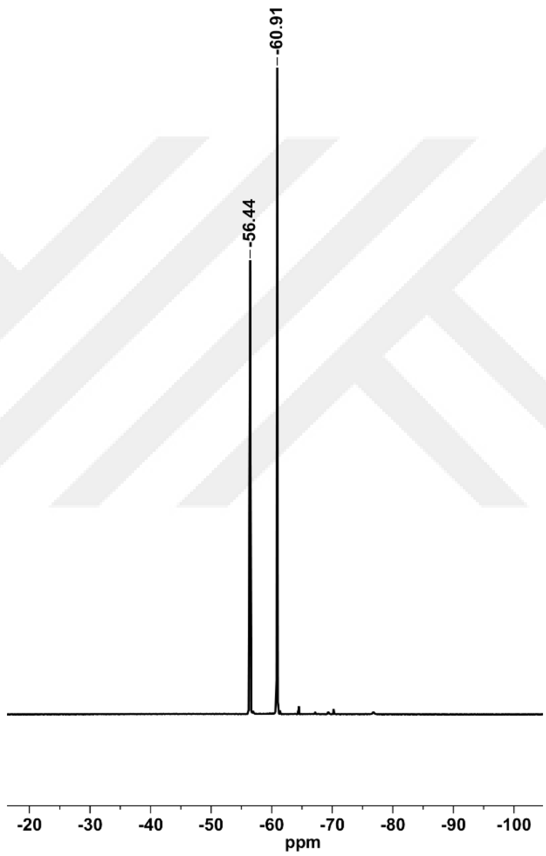

Figure 4.19 : ^{19}F NMR spectrum of PECH-F in $CDCl_3$.

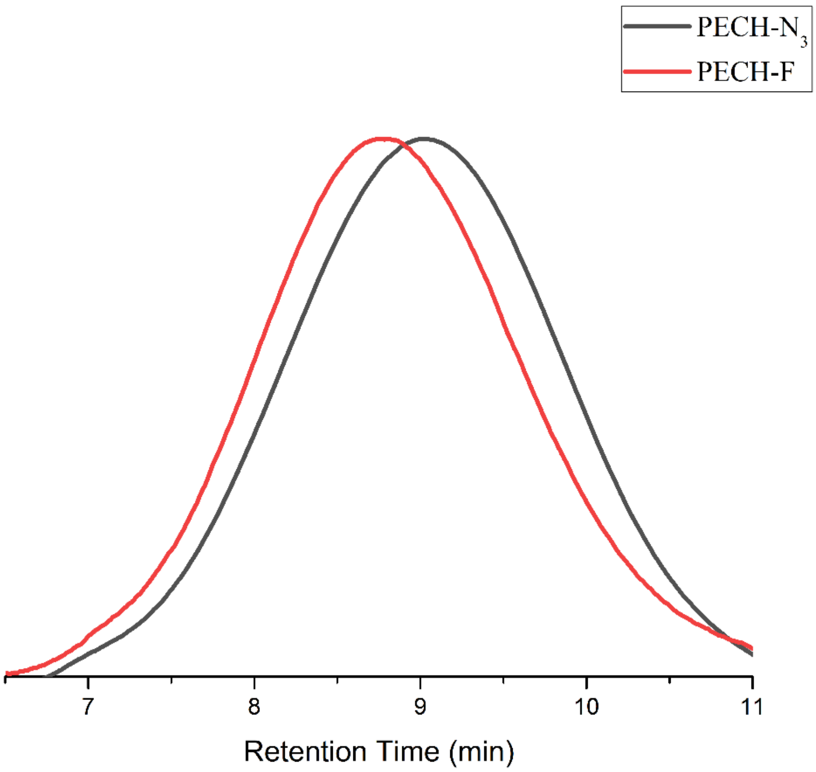

Figure 4.20 : Overlaid GPC traces of **PECH-N_3** (black) and **PECH-F** (red) in THF.

5. CONCLUSION

In this thesis, ethyl 4,4,4-trifluoro-2-butynoate having electron-deficient in character was successfully reacted with various azide-functionalized polymers through the metal-free azide-alkyne 1,3-dipolar cycloaddition reactions with quantitative efficiency. Detailed spectroscopic measurements were performed to reveal the structures of newly formed polymers.

With this synthetic strategy polymers with azide pendant groups were converted to fluorine containing polymers.

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CURRICULUM VITAE

Name Surname : Seren TURKUT

EDUCATION

- **B.Sc. :** 2018, Istanbul University, The Faculty of Engineering Faculty, Chemistry Department
- **M.Sc. :** 2021, Istanbul Technical University, Faculty of Arts and Letters, Department of Chemistry