ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL

THE USE OF CHLORODIMETHYLSILANE-MEDIATED REDUCTIVE ETHERIFICATION REACTION IN MACROMOLECULAR ENGINEERING

Ph.D. THESIS

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ISTANBUL TEKNİK ÜNİVERSİTESİ ★ LİSANSÜSTÜ EĞİTİM ENSTİTÜSÜ

MAKROMOLEKÜLER MÜHENDİSLİKTE KLORODİMETİLSİLAN ARACILI İNDİRGEYİCİ ETERLEŞME REAKSİYONUNUN KULLANIMI

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To my late Dad,

FOREWORD

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I would like to specially thank to my late Dad, Serdar. His motivation and work ethics greatly inspired me to become the person I am today. I always feel his presence and love even when he is not here with us today. I hope and wish I make you proud now and then.

April 2023

Serter LÜLEBURGAZ
(Lecturer)

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ABBREVIATIONS

ADMET : Acylic Diene Methathesis
BA : Benzaldehyde
BD : 1,4-Butandiol
CDMS : Chlorodimethylsilane
^{13}C NMR : Carbon Nuclear Magnetic Resonance Spectroscopy
DCE : 1,2-Dichloroethane
DMAc : *N*,*N*-Dimethylacetamide
DMSO : *N*,*N*-Dimethylsulfoxide
DMF : *N*,*N*-Dimethylformamide
FT-IR : Fourier Transform Infrared Spectrophotometer
GPC : Gel Permeation Chromatography
HDT : 1,6-Hexanedithiol
^{1}H NMR : Hydrogen Nuclear Magnetic Resonance Spectroscopy
MeOH : Methanol
2-MeTHF : 2-Methyltetrahydrofuran
MHz : Mega Hertz
MSA : Methanesulfonic acid
NMP : *N*-Methylpyrrolidone
PEG : Poly(ethylene glycol)
PPM : Post-polymerization Modification
Ppm : Parts per million
PTA : Poly(thioacetal)
PTSA : *p*-Toluenesulfonic acid
RER : Reductive Etherification Reaction
ROS : Reactive Oxygen Species
TfOH : Trifluoromethanesulfonic acid
THF : Tetrahydrofuran
TPA : Teraphtalaldehyde

SYMBOLS

℃	**:** Degree Celcius
$\boldsymbol{M_n}$	**:** Number Average Molecular Weight
$\boldsymbol{M_w}$	**:** Mass Average Molecular Weight
Đ	**:** Polydispersity Index
t	**:** Time
δ	**:** Chemical Shift
cm^{-1}	**:** Wavenumber

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THE USE OF CHLORODIMETHYLSILANE-MEDIATED REDUCTIVE ETHERIFICATION REACTION IN MACROMOLECULAR ENGINEERING

SUMMARY

The reaction of a carbonyl compund (aldehydes or ketones) with a silane-based reducing agent along with a Brønsted or a Lewis acid yields symmetric or unsymmetrical ethers, and this reaction is called a reductive etherification reaction (RER) in organic chemistry. This strategy has been applied at the macromolecular level to some extent and has been out of scenery for about 20 years. Chlorodimethylsilane (CDMS) is a silane compound that act as both a Lewis acid and a reducing agent, and has been empolyed in RER in molecular level and showed promising results to obtain unsymmetrical ethers in the presence of an alcohol. Since it does not require additional addivites, CDMS-mediated RER can be considered as a new and straightforward method to synthesize ethers.

In this thesis, we present three different examples of the CDMS-mediated RER in macromolecular levels to revive RER in order to explore the scope of this reaction.

In the first study, we describe a straightforward post-polymerization modification (PPM) methodology from polyketone via CDMS-mediated RER. The polyketone platform was prepared via acyclic diene metathesis (ADMET) polymerization and reacted with a variety of alcohols in the presence of CDMS to create a wide range of polymers possessing pendant functional alkoxy structures under mild conditions. The effect of parameters such as solvent and the amount of reactants on RER were studied. We have also explored the effect of other silane compounds on RER, none of which provided as high efficiency as CDMS-mediated one. It has been found that the primary alcohols yielded corresponding alkoxy structures in high efficiencies, high isolated yields, and a wide range of functional group tolerance. It was also found that the formation of polyalcohol was inevitable, to some extent, during the RERs in addition to the alkoxy-functional polymers. All the polymers obtained were characterized in detail by various spectroscopic measurements and a mechanistic aspect was also presented to evaluate the product distributions. Since operationally simple chemical methods, with high yield and functional group tolerance, that can be easily adapted to macromolecular level are always desired in synthetic polymer chemistry, this study promises remarkable opportunities for synthesizing functional polymers and may pave a way for the development of a novel metal-free PPM method.

In the second study, CDMS-mediated reductive etherification reaction is introduced as a versatile strategy for polyether synthesis. Accordingly, terephthalaldehyde (TPA) and 1,4-butanediol were first reacted at room temperature in the presence of CDMS using nitromethane as the polymerization solvent to reveal the optimum conditions for the proposed system. Subsequently, a variety of diols ranging from linear to sterically congested diols were reacted with TPA (and its isomers) under the optimized conditions to create a polyether library. Meanwhile, in addition to polyether having the expected alternating units, the formation of polyether stem from the self-condensation of TPA was found to be inevitable in all cases. From the proposed strategy, polyethers

with a molecular weight up to 110.4 kDa and a high alternating unit up to 93% were obtained. The versatile and robust character of the presented strategy was supported by a model end-group study and the polymerization behavior was examined mechanistically. It is anticipated that the presented method might be a strong candidate for polyether synthesis with different backbones, given the unlimited sources of diols.

In the third study, we have focused on synthesising polythioacetals (PTAs) using CDMS as a catalyst. In one of our previous works, when CDMS was used to perform RER on a pendant aldehyde polymer platform along with thiols, thioacetal formation was observed. This result was not surprising since CDMS has both Lewis acid and reducing agent character, yet, strikingly unexpected. Inspired by this study, PTA synthesis using CDMS as a catalyst was proposed. Optimization of polymerization conditions was first carried out by comparing traditional acid sources with CDMS. The progress of polymerizations were kinetically monitored and CDMS was found to perform best. Various parameters such as equivalent of reactants, solvent, and time on polymerization were then examined. Finally, a library of PTA was created using a variety of aldehydes and dithiols from moderate to high molecular weights. A mechanistic approach for the polymerization was proposed and finally a model degradation study on a representative PTA was performed in the presence of hydrogen peroxide.

MAKROMOLEKÜLER MÜHENDİSLİKTE KLORODİMETİLSİLAN ARACILI İNDİRGEYİCİ ETERLEŞME REAKSİYONUNUN KULLANIMI

ÖZET

Periyodik tabloda karbon atomu ile aynı grupta bulunan silisyum, dünya üzerinde en çok bulunan elementlerden biridir. Silisyum bileşikleri arasında en çok karşımıza çıkan silan bileşikleri, silisyum-karbon ve silisyum-hidrojen bağlarını içeren bileşiklerdir. Bu bileşikler, içerdikleri silisyum-hidrojen bağı dolayısıyla birçok farklı tepkimede indirgeyici bir bileşik olarak davranırlar. Bu davranış, karbon-hidrojen analoğunda rastlanmayan bir davranıştır. Silisyum ve hidrojen atomlarının Pauling elektronegativite değeleri sırasıyla 1.90 ve 2.20 olarak hesaplanmıştır. Bu elektronegativite farkı, Si-H bağında hidrojen atomunun daha negatif polarlıkta olmasına sebep olur. Silan bileşiklerinin indirgeme özelliği, bu hidrojenin hidrür kaynağı olarak davranmasıyla açıklanabilir.

İndirgeyici eterleşme reaksiyonu (İER), silan bileşikleri aracılığıyla, bir Brønsted veya Lewis asit katalizörlüğünde, aldehit veya keton karbonillerinin simetrik ya da asimetrik eter bileşiklerine indirgenme reaksiyonudur. İER, bir alkol eşliğinde gerçekleştirildiğinde asimetrik eterler, sadece aldehit veya keton karbonili varlığında gerçekleştirildiğinde ise simetrik eterler elde edilir.

İER, ilk defa 1972 yılında başlayan çalışmalar serisi ile organik kimya literatürüne Doyle ve çalışma arkadaşları tarafından kazandırılmıştır. Burada indirgeyici silan bileşiği olarak trietil silan ve asit katalizör olarak sülfirik asit ve trifloro (ya da trikloro) asetik asit kullanılmıştır. Daha sonraki yıllarda, İER daha farklı silan bileşikleri kullanılarak ve daha fazla asit katalizör örneği ile genişletilmiştir.

Polimer kimyasında İER kullanımı, Yokozawa ve çalışma arkadaşları ile başlatılmış olup, farklı topografideki polieter yapılarının sentezlenmesi amacıyla bir dizi çalışmalar yapılmıştır. Alifatik ya da aromatik polieterlerin, birçok farklı ve yaygın kullanım alanları olmasına karşın, genelde kondenzasyon veya halka açılma polimerleşmesi (anyonik ya da katyonik) yöntemleri gibi zahmetli yöntemlerle sentezlenmesi gerekir. Bununla beraber, kullanılacak monomerler de polimerleşmeyi engelleyecek yönde olabileceğinden, polieter çeşitliliğinde kısıtlamalar olabilmektedir. Bu sebeple Yokozawa ve çalışma arkadaşları öncülüğünde önerilen İER kullanılarak polieter sentezi, polimer kimyagerlerinin elinde polieter sentezi adına önemli bir araç olabilecekken, yeterince ilgi görmemiş olup pek fazla çalışma yapılmamış bir yöntem olarak kalmıştır.

İndirgeyici silan bileşikleri arasından, Lee ve Morandi öncülüğünde klorodimetilsilan (CDMS) aracılığı ile gerçekletirilen İER'lerde, farklı eter yapıları iyi verimler ve iyi reaksiyon etkinlikleri ile elde edilmiştir. Eterler yapılırken farklı alkoller kullanılmış olup sterik engel oluşturabilecek hacimli alkollerde bile eter oluşumu gözlemlenmiştir. Aynı zamanda alkol dışında farklı nükleofiller (tiyol, karbamat gibi) kullanılarak CDMS aracılı İER ile eter dışında da farklı yapılar başarıyla sentezlenmiştir. Buradaki

belki de en önemli nokta, CDMS bileşiğinin hem bir indirgeyici bileşik hem de bir Lewis asidi olarak davranıp tepkimede ayrıca bir asit katalizöre gerek duyulmamasıydı.

Tüm bu çalışmalardan esinlenerek, bu tezde, İER kimyasını polimer kimyagerlerinin farklı amaçlar doğrultusunda kolaylıkla kullanılması umuduyla, CDMS aracılı İER kullanılarak 3 farklı çalışma derlenmiştir.

Bu çalışamların ilkinde, CDMS aracılı İER ile polimerleşme sonrası modifikasyon yapılması amacıyla, keton karbonili içeren bir polimer sentezlenmesi hedeflenmiştir. Bu polimerin sentezlenmesi, öncelikle 5-bromo-1-penten bileşiğinden Grignard reaktifi oluşturulduktan sonra, etil format bileşiği ile reaksiyonu sonucu oluşan sekonder alkolün, ketona yükseltgenmesi ile elde edilen monomerin, Grubbs 1.jenerasyon katalizörü varlığında asiklik dien metatez (ADMET) polimerleşmesi yöntemi ile gerçekleştirilmiştir. Daha sonra elde edilen bu polimerik platform üzerinde, alkoksi grupları elde edilmesi amacıyla CDMS aracılı İER gerçekleştirilmesi öngörülmüştür. Model alkol olarak etanol seçilerek en uygun reaktant oranları ve reaksiyon çözücüsü belirlenmiştir. Daha sonra, bu tepkime şartları altında birçok primer ve sekonder alkol kullanılarak farklı yapılarda polimerler sentezlenmiştir. İER sırasında keton karbonilinin, kaçınılmaz olarak sekonder alkole indirgendiği keşfedilmiştir. Hem alkoksit hem de alkol yapısı oluşumu için tepkime mekanizması önerilmiştir. Sentezlenen tüm polimerlerin yapısı ^{1}H NMR, ^{13}C NMR ve FT-IR spektroskopisi yöntemleri ile aydınlatılmıştır ve molekül ağırlığı jel geçirgenlik kromatografisi (GPC) yöntemi ile tayin edilmiştir.

İkinci çalışmada, CDMS aracılı İER kullanılarak adım polimerleşmesi yöntemi ile lineer polieter yapılarının sentezi hedeflenmiştir. Bu amaçla, öncelikle polimerleşme koşullarının belirlenmesi için teraftalaldehit ve 1,4-bütandiol model monomerler olarak seçilmiştir. Polimerleşme koşullarının belirlenmesi amacıyla birçok çalışma yapılmış olup en uygun reaktant oranlarının dialdehitin 1.1, diolün 1 ve CDMS'nin 6 eşlenik ve tepkime süresinin 1 saat olduğu gösterilmiştir. Farklı çözücülerin, polimerleşme üzerindeki etkisi de incelenmiştir. Daha sonra, farklı diol ve dialdehit yapıları kullanılarak çeşitli polieter yapıları başarıyla sentezlenmiştir. Polimerleşme için bir mekanizma önerilmiştir ve son olarak, polieter yapılarının uç gruplarının aydınlatılması amacıyla da bir çalışma yapılmıştır. Çalışma sırasındaki tüm aşamalarda ve sentezlenen tüm polimerlerin yapısının aydınlatılmasında ^{1}H NMR, ^{13}C NMR ve FT-IR spektroskopisi yöntemleri ve molekül ağırlıklarının belirlenmesinde ise GPC kullanılmıştır

Son olarak, yan bir çalışmada karşılaştığımız bir sonuçtan esinlenerek, CDMS'nin sadece Lewis asidi karakterinden yararlanarak yine adım polimerleşmesi yöntemi ile poli(tiyoasetal) sentezleri gerçekleştirilmiştir. Grubumuzca yapılan bir çalışmada, yan zincirinde aldehit içeren bir polimer üzerinde CDMS aracılı İER gerçekleştirildiğinde, nükleofil olarak tiyol kullanıldığı durumlarda önemli miktarda tiyoasetal yapısının da oluştuğu gözlemlenmiştir. Bu sonuçtan ilham alarak, CDMS aracılı poli(tiyoasetal) sentezi hedeflenmiştir. Polimerleşme koşulları benzaldehit ve 1,6-hekzanditiyol bileşikleri kullanılarak optimize edilmiştir. İlk etapta, literatürde bilinen ve poli(tiyoasetal) sentezinde kullanılan farklı Bronsted asitlerinin polimerleşmeye etkisi ile CDMS'nin etkisi karşılaştırılmıştır. Daha sonra, reaktant oranlarının polimerleşme üzerindeki etkisi incelenip, tepkime süresinin belirlenmesiyle birlikte, farklı çözücülerin polimerleşme üzerindeki etkileri çalışılmıştır. En uygun polimerleşme koşulları belirlendikten sonra, farklı aldehit ve ditiyol bileşikleri kullanılarak bir

poli(tiyoasetal) kütüphanesi yaratılmıştır. Daha sonra, CDMS aracılı poli(tiyoasetal) sentezi için mekanizma önerisi yapılmıştır. Son olarak, tiyoasetal bağı, H_2O_2 varlığında degrade edilmiştir ve kullanılan model polimerin tamamen parçalandığı gözlemlenmiştir. Çalışmanın aşamaları ^{1}H NMR, ^{13}C NMR ve FT-IR spektroskopisi yöntemleri ile izlenmiştir ve sentezlenen polimerlerin molekül ağırlıkları GPC ile tayin edilmiştir.

Bu tez kapsamında, CDMS aracılı İER ile farklı topografilere sahip polimerler sentezlenmiş ve etkin bir polimerleşme sonrası modifikasyon gerçekleştirilmiştir. Özellikle polieter gibi sentezi oldukça zahmetli ve çeşitliliği kısıtlı olan ticari öneme sahip polimerlerin sentezinde güçlü bir alternatif metot olarak kullanılabileceği öngörülmektedir. Bu sayede İER'nin polimer kimyasında tekrardan yer edineceği umulmaktadır. Tezin iki bölümünde gerçekleştirilen bu çalışmalar, üst düzey uluslararası dergilerde yayınlanmıştır. Gerçekleştirilen tüm bu çalışmalar için TÜBİTAK 1001 (119Z219) ve İTÜ BAP (TDK-2021-43456) projeleri ile destek alınmıştır.

1. INTRODUCTION

Organic chemistry seeks to create intricate structures through the merging of basic building blocks using eco-friendly methods that conserve energy and reduce carbon emissions. Polymer chemists have similarly taken cues from organic chemists, employing these efficient reactions to develop new, precisely defined polymers with diverse compositions and topologies. Polymer-polymer conjugation and post-polymerization modification (PPM) are some of the techniques adapted to achieve this.

The reductive etherification reaction (RER) is a convenient method for the production of ethers from aldehyde and ketone carbonyls. This process involves the use of organosilane-based reducing agents and can be performed with either Bronsted or Lewis acids which was first reported by Doyle and co-workers with a detailed series of works. After this pioneering work, many different acid catalysts and silane compounds were proposed to perform RER.

More recently, Lee and Morandi synthesized different unsymmetrical ethers, starting from aliphatic and aromatic ketones with primary and secondary alcohols, in the presence of chlorodimethlysilane (CDMS). Other than alcohols, they were also able to utilize this method to yield thioether, sulfonamide, and alkylated product of indole at the C-3 position. It should be noted here that since CDMS has both a reducing agent and a Lewis acid properties, it holds an additional advantage with respect to traditional silane reagents.

Yokozawa and co-workers were the first to to synthesize polyethers via RER at the macromolecular level. The group have performed series of elagant works to synthesize polyethers with different topologies, using triethylsilane (Et_3SiH) and trityl perchlorate ($TrClO_4$) as the reducing agent and an acid source, respectively. Since then, no studies of RER in synthetic polymer chemistry have been reported.

Therefore, in this thesis, the concept of RER has been revived and it has been shown that CDMS-mediated RER has been successfully used for polyether synthesis and PPM studies.

In this thesis, there are three different studies, two of which have already published in international polymer journals. The thesis is organized in such that each chapter has a specific topic and has its own introduction, experimental, results and discussion sections.

Chapter 2 represents the PPM of a polyketone via CDMS-mediated RER in order to yield pendant alkoxy functions on the polymer. After a series of experiments to reveal the optimum conditions for the PPM, 17 different alkoxy-pendant polymers were synthesized using the optimum conditions and then characterized in detail.

Chapter 3 represents a simple and universal synthetic pathway to synthesize polyethers via CDMS-mediated RER. Ideal conditions for the polymerizations were revealed with a series of optimization experiments and a polyether library was created using different diols and dialdehydes. The resulting polymer structures were analyzed by using various spectroscopic and chromatographic methods.

Chapter 4 represents poly(thioacetal) (PTA) synthesis cataylzed by CDMS. It is wort to mention here that in one of our previous studies, when RER was performed on a pendant aldehyde-containing polymer, the formation of a thioether was inevitable if thiols were used as the nucleophile instead of alcohols. In the light of this finding, a robust and straightforward PTA synthesis method was developed using CDMS as a catalyst. The results were compared with traditional acid catalysts and polymerization conditions were optimized by different studies. Lastly, a PTA library was produced and degradation study of a model PTA backbone was also shown.

Finally, concluding remarks are summarized in Chapter 5.

2. MODIFICATION OF POLYKETONE VIA CHLORODIMETHYLSILANE-MEDIATED REDUCTIVE ETHERIFICATION REACTION: A PRACTICAL WAY FOR ALKOXY FUNCTIONAL POLYMERS [1]

2.1 Introduction

Without a doubt, synthetic polymer chemistry always follows the developments in organic chemistry to effectively adapt new synthesis methods to the macromolecular level for both polymer-polymer conjugation reactions and post-polymerization modification (PPM) of polymers [1-3]. In this regard, since the last two decades several efficient organic reactions, often classified under the famous term "click" chemistry, [4, 5] are frequently utilized at the macromolecular level for the aforementioned purposes. Such reactions are mainly sorted as; copper-catalyzed azide-alkyne cycloaddition (CuAAC) reaction, Diels-Alder (DA)/retro-DA reaction, thiol-ene/-yne, Michael addition, oxime ligation, thio-bromo, amine/thiol-epoxy, multicomponent reactions, etc. [1-3, 6-20] Indeed, all these reactions have become a strong tool for synthetic polymer chemists to design and tailor the polymers on-demand and have found tremendous applications in the polymer literature. Thus, new organic synthesis methodologies offering efficiencies similar to the aforementioned reactions that can be adapted to the macromolecular level are always welcomed and desired in polymer science.

Organosilanes are useful compounds due to the inherent Si-H bond and are frequently utilized as reductants for the preparation of ethers from carbonyl compounds (e.g. aldehydes and ketones) [21-34]. The synthesis of both symmetrical and unsymmetrical ethers is possible depending on the reaction conditions, using organosilanes. For instance, the use of carbonyl compound alone without alcohol in the presence of an

[1] This chapter is based on the paper 'Luleburgaz, S., Hizal, G., Tunca, U. and Durmaz, H. (2021), Modification of Polyketone via Chlorodimethylsilane-Mediated Reductive Etherification Reaction: A Practical Way for Alkoxy-Functional Polymers. Macromolecules, 54 (11), 5106-5116. DOI: 10.1021/acs.macromol.1c00461'

organosilane affords symmetrical ether while unsymmetrical ether can be prepared using alcohol as the nucleophile. The process that leads to the synthesis of ethers from a carbonyl compound is called the reductive etherification reaction (RER) in organic chemistry [21-26]. Doyle and co-workers were the first to report Bronsted acid-catalyzed synthesis of unsymmetrical ethers from aldehydes and ketones using triethylsilane (Et_3SiH) as the reducing agent. It was presented that the use of excess acid and alcohol concerning the carbonyl compound and silane in the reactions delivered the desired unsymmetrical ethers in high yields [21]. The following studies have shown the preparation of symmetrical as well as unsymmetrical ethers via RER using various organosilane compounds together with a variety of Bronsted and Lewis acids [27-34]. In this regard, Roth and co-workers realized a systematic study to investigate the effect of aldehydes and ketones, as well as alcohols on RER. In their study, Et_3SiH was used as reductant and trifluoromethanesulfonic acid (TfOH) as a catalyst, and the reactions were performed at room temperature in nitromethane (CH_3NO_2). It was demonstrated that aldehydes provided both symmetrical and unsymmetrical ethers rapidly in high yields, while yields were found to be low in the case of ketones, particularly in the synthesis of unsymmetrical ethers. In the same study, it was also demonstrated that sulphur- and nitrogen-based nucleophiles could be pleasingly reacted with aldehydes and ketones under the same conditions, resulting in the formation of thioethers and amines [34]. Polymeric structures can also be prepared by RER [35-37]. For instance, isophtaldehyde was subjected to a self-polymerization reaction in CH_2Cl_2 in the presence of Et_3SiH using trityl perchlorate as a catalyst. The effect of temperature and other silane compounds on polymerization were studied, moderate molecular weight polymers were obtained in the range of low to moderate yields [35]. Moreover, in another study, various dialdehydes and bis(trimethylsilyl)ethers were reacted in the presence of bulky silanes, yielding polyethers in an alternating fashion [36].

From the above results, it is clear that RER is applicable in both small scale and polymer production, however, the requirement of an additive (e.g. catalyst) in addition to silane compounds to promote the reactions limits the practicability and operation simplicity of RER. In this regard, Lee and Morandi recently demonstrated that chlorodimethylsilane (CDMS), which has both reductive and Lewis acidic properties, can mediate RER between ketones and alcohols to obtain unsymmetrical ethers [38].

As it was shown, a variety of alcohols ranging from primary to sterically congested secondary alcohols could be easily coupled with various aliphatic or aromatic ketones in the presence of CDMS at room temperature in acetonitrile (CH_3CN), resulting in ethers with different functionalities in high yields. The authors also proved that CDMS-mediated RER employing ketones was also applicable for other heteroatom-based nucleophiles such as thiol and sulfonamide. Inspired by this study, we anticipated that CDMS-mediated RER could be a feasible PPM method to prepare alkoxy-functional polymers from polyketones, as the carbonyl group of a polyketone would be suitable for such a transformation. For this purpose, a polyketone was prepared via acyclic diene metathesis (ADMET) polymerization [39-41] and utilized as a polymer platform and reacted with a variety of functional alcohols using CDMS under mild conditions. RER optimization studies were meticulously carried out, thus a series of alkoxy-functional polymers were successfully obtained. The results indicate that RER is a highly promising PPM method in terms of creating functional polymers from polyketone. Interestingly, in addition to alkoxy-functional polymer formation, the polyalcohol formation was also prominent during RERs (Figure 2.1).

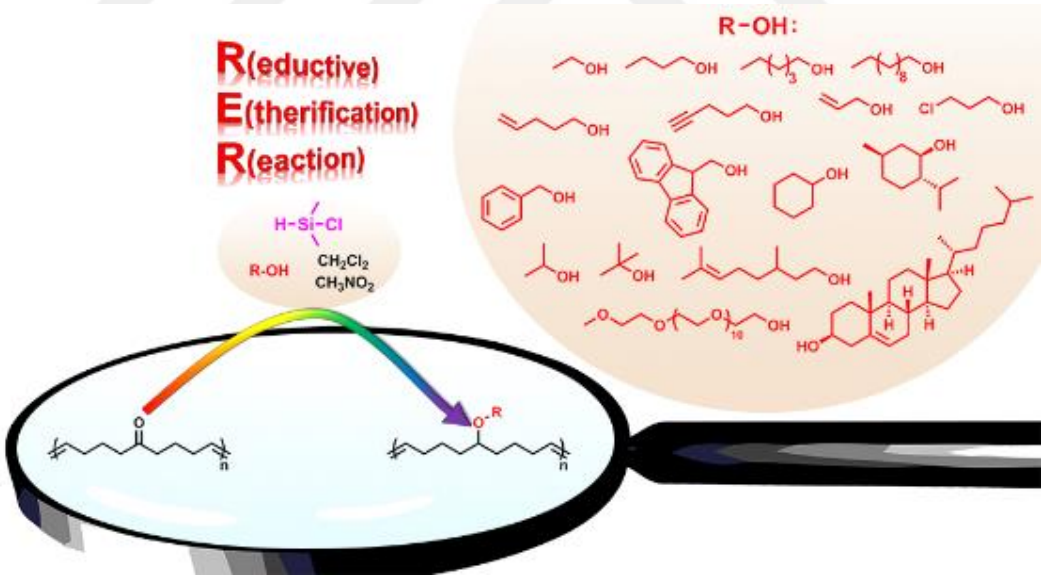


Figure 2.1 : Graphical abstract for chapter 1.

2.2 Results and Discussion

All the steps, from monomer to alkoxy-functional polymer synthesis, are depicted in Figure 2.2. First, **2** was synthesized in two steps via a previously described method, and ^{1}H NMR analysis confirms the structure [42]. Subsequently, **2** was polymerized

through ADMET polymerization using the first-generation Grubbs catalyst (G1). The structure of the resulting polyketone, P0, was evaluated by NMR and FT-IR analyses (Figures 1 and 2). ^{1}H NMR analysis shows that the methine protons of the internal *H*C=C*H* appeared at δ 5.40 ppm and the methylene protons next to the C=O group resonated at δ 2.38 ppm. Additionally, ^{13}C NMR analysis indicates that carbon of *C*=O resonated at δ 211.66 ppm. Furthermore, the FT-IR spectrum exhibited a strong C=O stretching vibration band at 1701 cm^{-1}, which was indicative of the polyketone.

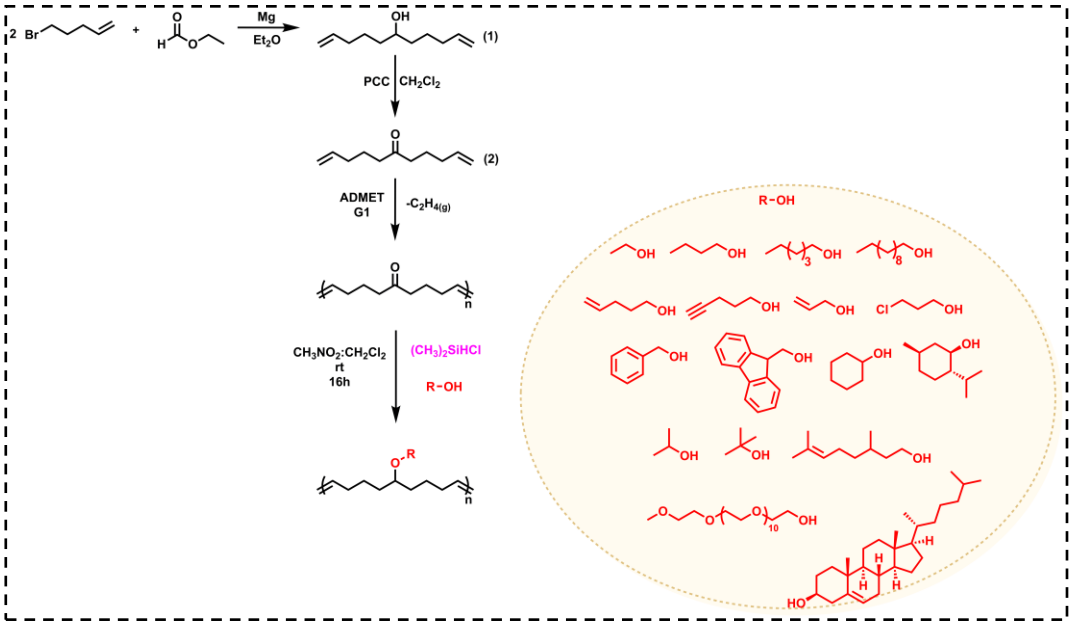


Figure 2.2 : Reaction steps in the synthesis of alkoxy-functional polymers via RER.

After the preparation of polyketone, the optimization of the reaction conditions; the effect of solvent and equivalent of alcohol and CDMS were studied, respectively. During optimizations, ethanol was chosen as the model alcohol to perform RERs. In all trials, P0 was reacted with 4 equivalents of ethanol and CDMS (per repeating unit of P0) in 2 mL (total) of solvent(s) for 16 h at room temperature. The efficiency of RER was calculated by ^{1}H NMR analysis comparing the integral area of the methine proton (-C*H*OCH$_2$CH$_3$) of ethoxy-functional polymer (P1) emerged at δ 3.21 ppm and the main chain olefin signals (C*H*=C*H*) at δ 5.40 ppm (Figure 1A). The RER efficiencies are given in Table 2.1. It can be seen that only 60% P1 formation was observed in CH$_3$CN though it was stated as suitable by Lee and Morandi (see run 1, Table 1) [38]. It should be noted here that P0 was not soluble in CH$_3$CN, hence the reaction was carried out in a heterogeneous medium. To dissolve P0 and thus to create a homogenous reaction medium, CH$_2$Cl$_2$ (1 mL) was used as a co-solvent with CH$_3$CN (1 mL) to perform RER, however, no significant change was found in the reaction

efficiency (run 2, Table 1). Next, CH_3NO_2, which is another strong candidate as a solvent for RER was examined [34]. When the reaction was carried out solely in CH_3NO_2, the efficiency of the formation of P1 was found to be 84%, yet P0 was also insoluble in CH_3NO_2, hence the reaction was performed in a heterogeneous medium (run 3, Table 1). This result clearly shows that CH_3NO_2 tremendously increases the efficiency of RER in the presence of CDMS when compared to CH_3CN. Also, when CH_2Cl_2 was used as a co-solvent in the presence of CH_3NO_2, the RER efficiency was found to be 90% (run 4, Table 1). Notably, when CH_2Cl_2 was used as the sole solvent, the RER efficiency was found to be 55% (run 5, Table 1). These results refer to the enhancing effect of CH_3NO_2 on RER. The effect of other co-solvents, such as $CHCl_3$, THF, and DMSO was also examined. Amongst, $CHCl_3$ provided the same high efficiency as that of CH_2Cl_2 in the formation of P1 (run 6, Table 1). On the other hand, the efficiency of the formation of P1 was decreased when THF was used as a co-solvent, (run 7, Table 1) and in the presence of DMSO, no reaction was observed (run 8, Table 1). More importantly, in each case, a polyalcohol formation was observed to some extent, which will be discussed below. Regarding our results, the mixture of CH_3NO_2/CH_2Cl_2 (1 mL/1 mL) was chosen as the ideal solvent system the results are given in Table 2.1.

Table 2.1 : Results of the solvent optimization study[a].

Run	Solvent	Co-Solvent[b]	Efficiency (%)[c/d]
1	CH_3CN[e]	-	60/5
2	CH_3CN	CH_2Cl_2	55/7
3	CH_3NO_2[e]	-	84/16
4	CH_3NO_2	CH_2Cl_2	90/10
5	CH_2Cl_2	-	55/5
6	CH_3NO_2	$CHCl_3$	90/10
7	CH_3NO_2	THF	76/17
8	CH_3NO_2	DMSO	No Reaction

[a]Reaction was carried out at room temperature under nitrogen for 16 h, P0/CDMS/ethanol was used at a mole ratio of 1/4/4 in 2 mL of solvent. [b]Same amounts (1 mL) of solvent and co-solvent were used. [c]Efficiency of the formation of P1 determined by ^{1}H NMR. [d]Efficiency of the formation of polyalcohol determined by ^{1}H NMR. [e]Reaction was carried out in a heterogeneous medium.

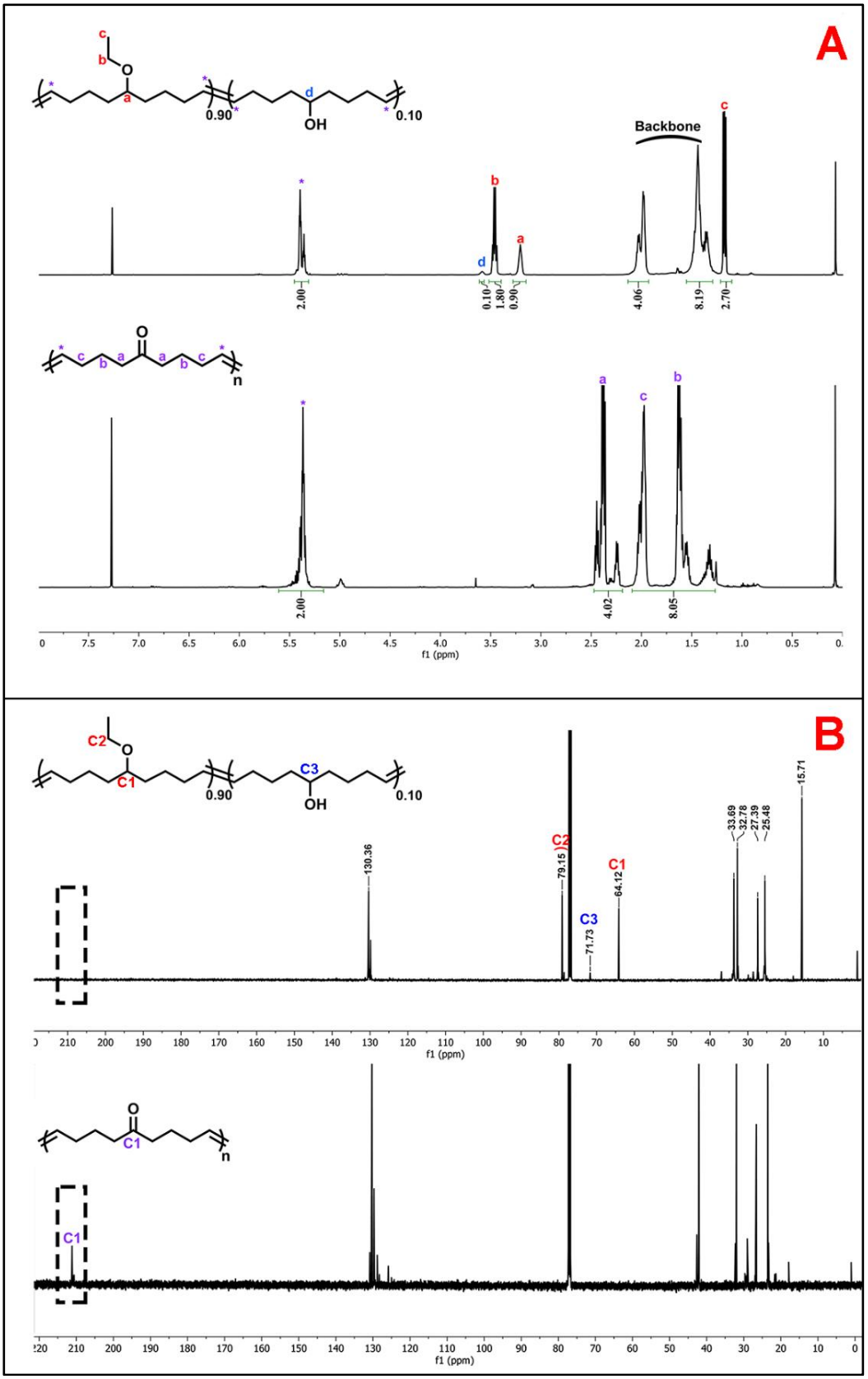


Figure 2.3 : Overlaid ^{1}H NMR spectra (A, 500 MHz), ^{13}C NMR spectra (B, 125 MHz) of P0 and P1.

Next, optimum equivalents of the alcohol and CDMS with respect to P0 (per repeating unit of the polyketone) were determined in the ideal solvent mixture (Table 2). Utilizing two equivalents of both ethanol and CDMS delivered P1 with 69% efficiency (run 2, Table 2). Two-fold increases in ethanol and CDMS, respectively, yielded P1 with 85 and 90% efficiencies, respectively (run 3 and 4, Table 2). The efficiency of the formation of P1 showed a little decline (80%) when the amount of ethanol was lowered to 1 equivalent while keeping CDMS at 4 equivalents (run 5, Table 2). No further improvement was found in the efficiency when the amount of CDMS was increased to 6 equivalents while keeping ethanol at 2 equivalents (run 6, Table 2). These results indicate that there is no difference when 4 or 2 equivalents of ethanol were used in the reactions along with 4 equivalents of CDMS to achieve the maximum efficiency. Thus, P0/alcohol/CDMS was used at a mole ratio of 1/2/4 and was considered as the standard reaction condition for the rest of the study along with the ideal solvent system.

Table 2.2 : Results of the equivalent optimization study[a].

Run	Ethanol (equiv.)[b]	CDMS (equiv.)[b]	Efficiency (%)[c/d]
1	4	4	90/10
2	2	2	69/15
3	4	2	85/15
4	2	4	90/10
5	1	4	80/20
6	2	6	90/10

[a]Reaction was carried out at room temperature in 2 mL of solvent mixture (CH_2Cl_2/CH_3NO_2, 1 mL/1 mL) under nitrogen for 16 h. [b]Per repeating unit of P0. [c]Efficiency of the formation of P1 determined by ^{1}H NMR. [d]Efficiency of the formation of polyalcohol determined by ^{1}H NMR.

As discussed previously, one of the main objectives of this study is to circumvent additional additives during RER. Despite this fact, we also explored the effect of different silane compounds together with Lewis or Bronsted acids in the functionalization of P0 via RER. Once more ethanol was chosen as the model alcohol and the reactions were carried out under the standard conditions. All the obtained results are collected in Table 3. A very low RER efficiency was achieved when Et_3SiH was used as the reductant and a Bronsted acid, TfOH, was used as the catalyst (run 1, Table 3), no reaction occurred when a Lewis acid used under the same conditions

(run 2, Table 3). Bulky silanes provided better RER efficiencies, particularly, when TfOH was used as a catalyst (run 3-6, Table 3). Amongst, $PhMe_2SiH$ showed a highly promising result, leading to P1 with 77% efficiency (run 5, Table 3). In contrast, a dramatic reduction in RER efficiency was found when $InCl_3$ was used as a catalyst together with a bulky silane. (run 7, Table 3). All these trials reveal the CDMS's effectiveness in functionalization studies, hence it was the best choice for RER.

Table 2.3 : Effect of silanes on the functionalization of P0 via RER[a].

Run	Silane	Acid Source (mol%)[b]	Efficiency (%)[c/d]
1	Et_3SiH	TfOH (10)	34
2	Et_3SiH	$InCl_3$ (10)	No Reaction
3	Ph_3SiH	TfOH (10)	64/12
4	Ph_2SiH_2	TfOH (10)	68
5	$PhMe_2SiH$	TfOH (10)	77/10
6	$PhMe_2SiH$	TfOH (20)	78/13
7	$PhMe_2SiH$	$InCl_3$ (10)	29/16

[a]Reaction was carried out at room temperature in CH_2Cl_2 (1 mL) and CH_3NO_2 (1 mL) mixture under nitrogen for 16 h, P0/ethanol/silane was used at a mole ratio of 1/2/4. [b]Per repeating unit of P0.[c]Efficiency of the formation of P1 determined by ^{1}H NMR. [d]Efficiency of the formation of polyalcohol determined by ^{1}H NMR.

After the optimization studies, a detailed characterization of P1 was carried out (Figures 1 and 2). In addition to the ^{1}H NMR analysis (discussed above), ^{13}C NMR, FT-IR, and GPC analyses were performed, respectively. When ^{13}C NMR spectra of P0 and P1 were compared, the complete disappearance of the carbonyl signal at δ 211.66 ppm was the clear evidence of the successful RER. Also, the signals at δ 79.15 and 64.12 ppm assignable to the etheric carbons (*C*HO*C*H_2CH_3) were easily detected from the ^{13}C NMR spectrum of P1 (Figure 1B). Moreover, FT-IR spectra of P0 and P1 exhibited the disappearance of C=O stretching at 1701 cm^{-1} and the appearance of stronger C-O ether stretching near 1100 cm^{-1} (Figure 2A). Meanwhile, a shift, as expected, was observed in the GPC toward the higher molecular weight region after RER, which is another proof for successful PPM (Figure 2B).

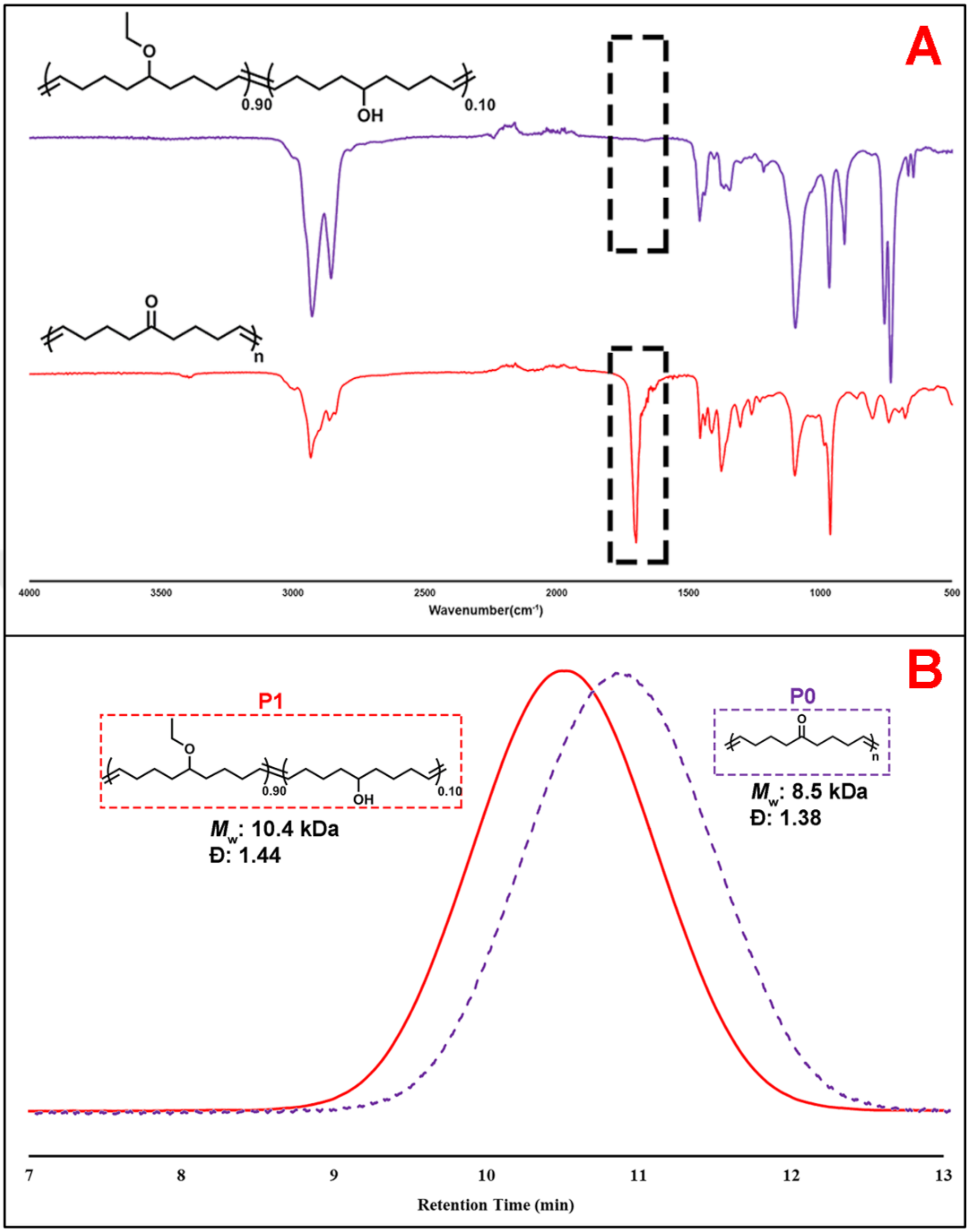


Figure 2.4 : Overlaid FT-IR spectra (A) and GPC traces (B) of P0 and P1.

More importantly, as stated above, although the excess amount of ethanol was used in RERs, the formation of polyalcohol was inevitable in all cases. We hypothesized, on the other hand, that we could take this process on our side and benefit from alcohol formation for further modifications. To this end, an esterification reaction was carried out between P1 and benzoyl chloride in the presence of Et_3N (Figure 3).

After purification, the obtained polymer was characterized by ^{1}H NMR analysis. It can be seen from the spectrum that methine proton (C*H*OH) at δ 3.59 ppm next to hydroxyl was completely removed and the new signal regarding this proton (C*H*OC=OPh) shifted to δ 5.16 ppm after the esterification reaction.

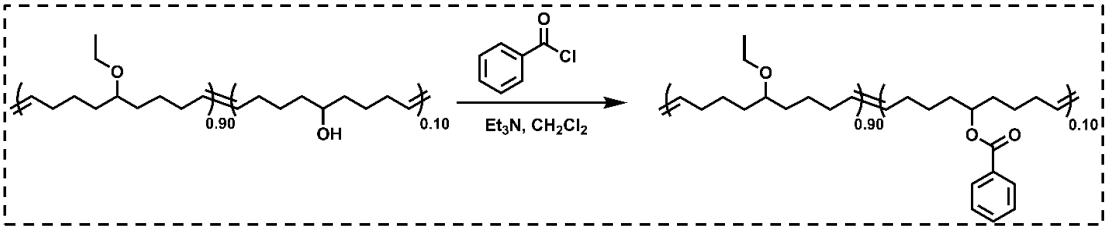


Figure 2.5 : Synthesis route for esterification reaction of P1 with benzoyl chloride.

In supporting, aromatic protons of the benzoyl ester were detected between δ 8.05-7.48 ppm, (Figure 4). This result proves the existence of –OH groups in the polymer and demonstrates its versatility for further functionalization.

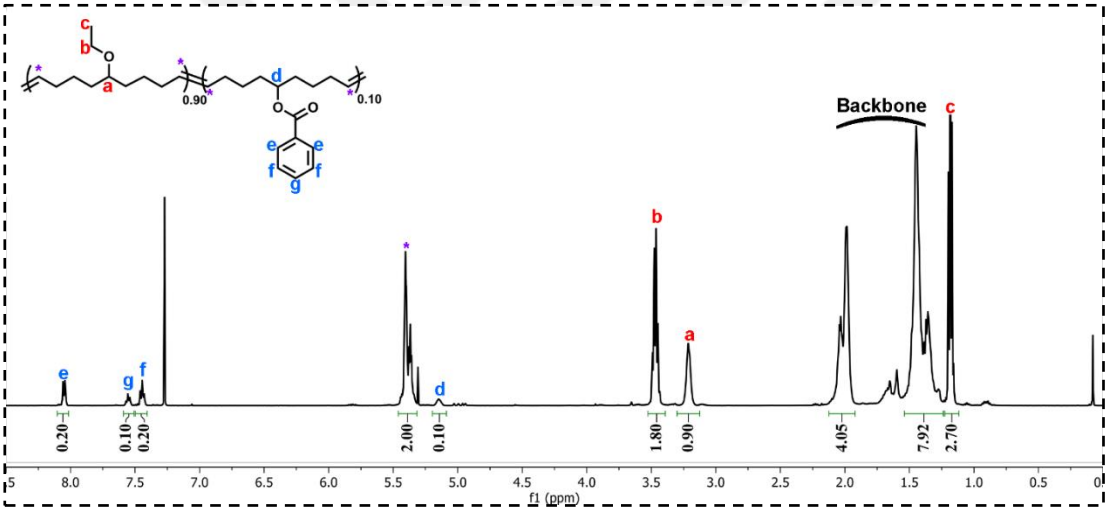


Figure 2.6 : ^{1}H NMR spectrum of P1 after esterification reaction with benzoyl chloride (500 MHz).

Having the standard conditions in hand, various alcohols were then used to explore the scope of this chemistry (Figure 5 and Table 4). Detailed information on the synthesis and characterizations of all polymers are given in the supporting information. Reaction efficiencies were calculated by ^{1}H NMR analysis comparing the integral area of methylene or methine protons of the formed alkoxy structures with the main chain olefin signals as described before. High RER efficiencies were found when primary alcohols having structural similarity to ethanol were used in the reactions (P2 and P3), a small decrease was observed in the efficiency as the chain length of the given substrate was increased (P4). A similar high-efficiency trend was also evident when

functional primary alcohols, such as benzyl, alkenyl, alkynyl, or halogenated alcohols were used in the reactions, indicating high functional group tolerance of the proposed chemistry (P5-11). Notably, in some examples, few ketone units remained unreacted (<10%) at the end of the reactions. As for the secondary alcohols, high RER efficiencies were found for isopropyl alcohol (P12) and cyclohexanol (P13), while a prominent decrease was observed for sterically congested alcohols (P14 and P15), which might be attributed to their low nucleophilicity. It should also be noted here that a significant amount of unreacted ketone units remained at the end of the reactions in the presence of these sterically hindered alcohols.

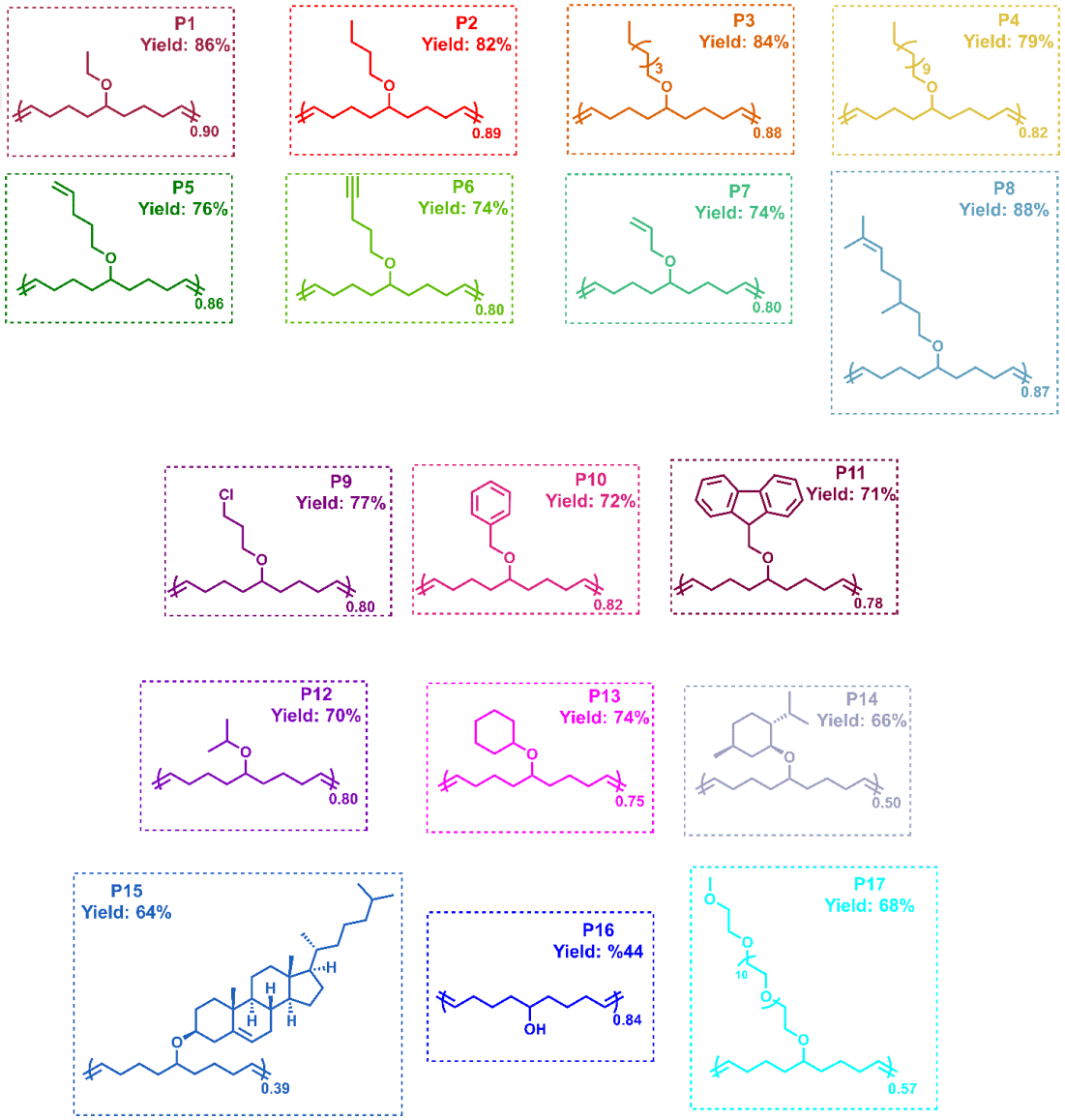


Figure 2.7 : Final structures of the resulting alkoxy-functional polymers. Yields were calculated after the second precipitation.

Besides, no alkoxy formation was observed when *tert*-butanol was used in the reaction, the sole product was the formation of polyalcohol in 84% efficiency (P16). This finding is expected since *tert*-butyl alcohol is a quite poor nucleophile. It is worth mentioning here that PEG_{550} monomethyl ether was also reacted with P0 yielding P17 near 57% RER efficiency, which is especially important since it mimics polymer-polymer conjugation.

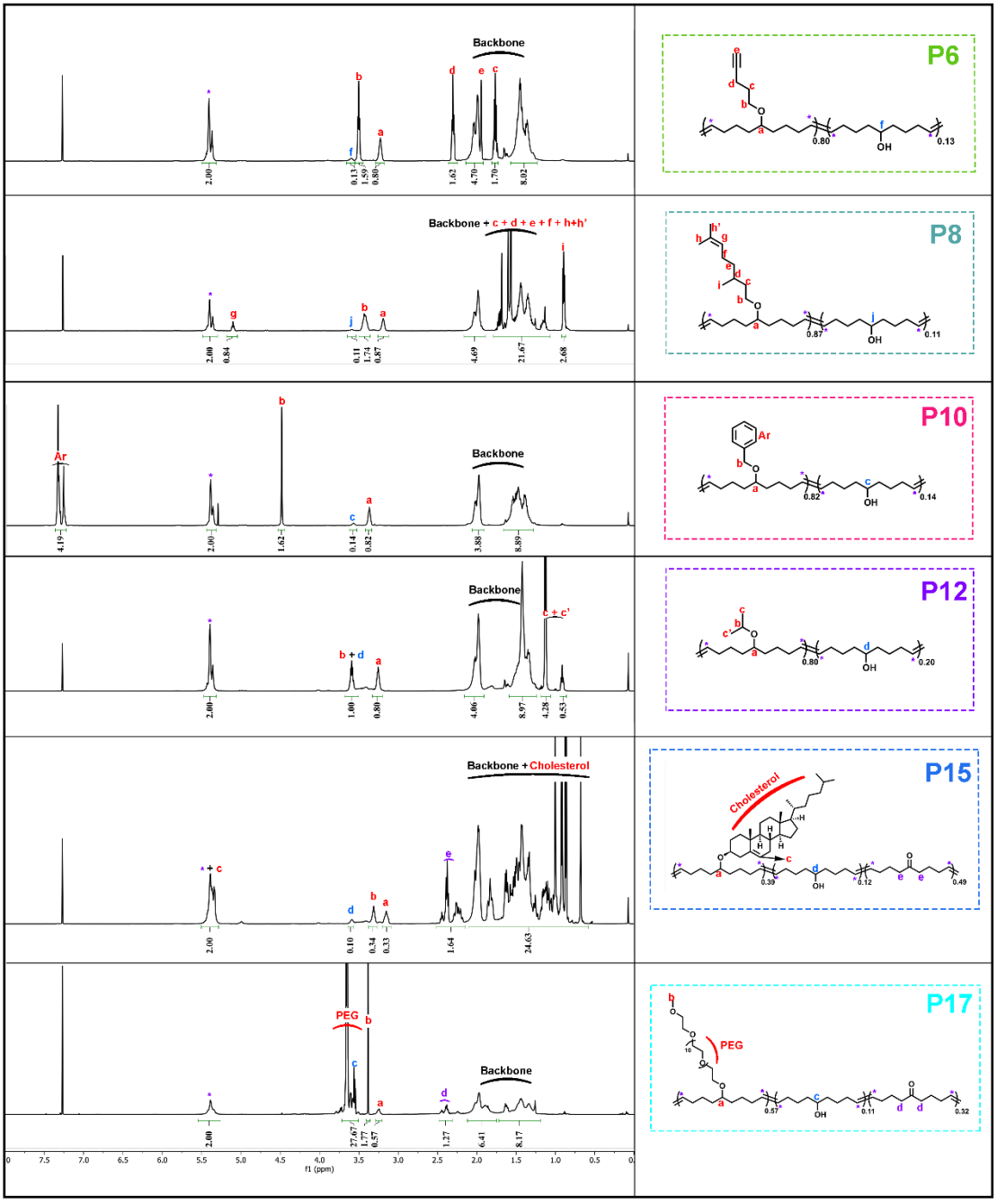


Figure 2.8 : From top to bottom; ^{1}H NMR spectra of P6, P8, P10, P12, P15, and P17 (500 MHz).

Figure 6 exhibits ^{1}H NMR spectra of representative polymers. Here, the characteristic signals of all alcohols employed facilitated to make a proper assessment of the efficiency of the reactions, after transformation to the corresponding alkoxy structures (Figure 6). Furthermore, the molecular weight of the resultant polymers increased after RERs as evidenced by the GPC measurements, M_w values were found in the range of 10.4-22.9 kDa (Table 4). Also, GPC traces of all modified polymers displayed a monomodal distribution, with no shoulders and tails, proving that the reactions smoothly proceeded. Moreover, FT-IR spectra of the resultant polymers exhibited, to a large extent, the disappearance of C=O stretching and the appearance of more prominent C-O ether stretching at around 1000-1200 cm^{-1}.

Table 2.4 : Results of RERs using different alcohols[a].

Polymer	Alcohol	Efficiency(%)[b/c]	M_w(kDa) [d]/$Đ$[d]
P0	-	-	8.5/1.38
P1	Ethanol	90/10	10.4/1.44
P2	1-Butanol	89/11	12.0/1.65
P3	1-Hexanol	88/12	13.6/1.48
P4	1-Dodecanol	82/18	16.1/1.74
P5	4-Pentene-1-ol	86/14	11.4/1.28
P6	4-Pentyne-1-o	80/13/7[e]	12.1/1.62
P7	Allyl alcohol	80/12/8[e]	11.3/1.60
P8	β-Citronellol	87/11/2[e]	13.4/1.43
P9	3-Chloro-1-propanol	80/20	12.7/1.66
P10	Benzyl alcohol	82/14/4[e]	14.5/1.61
P11	9-Fluorenemethanol	78/13/9[e]	17.4/1.79
P12	Isopropyl alcohol	80/20	11.2/1.54
P13	Cyclohexanol	75/10/15[e]	13.8/1.53
P14	Menthol	50/10/40[e]	14.3/1.49
P15	Cholesterol	39/12/49[e]	17.5/2.01
P16	*tert*-Butanol	84[c]/16[e]	22.9/2.04
P17	PEG_{550}	57/11/32[e]	17.7/1.80

[a]Reaction was carried out at room temperature in CH_2Cl_2 (1 mL) and CH_3NO_2 (1 mL) mixture under nitrogen for 16 h, P0/alcohol/silane was used at a mole ratio of 1/2/4. [b]Efficiency of the formation of alkoxy-functional polymers determined by ^{1}H NMR. [c]Efficiency of the formation of polyalcohol determined by ^{1}H NMR. [d]Determined by GPC calibrated based on linear PS standards in THF at 30°C. [e]Remaining polyketone unit.

In line with the product distributions obtained during RERs, it is possible to suggest a mechanism as depicted in Figure 7. Formation of the alkoxy-functional polymer starts first with silylation of polyketone in the presence of CDMS whilst chloride ion acting as the leaving group. Silylated polyketone then attacked by the alcohol, generating a hemiacetal structure. Following deprotonation-protonation steps, silanol leaves from the structure as a by-product. Meanwhile, a new CDMS molecule acts as the reducing agent, reduces the structure to give the corresponding alkoxy-functional polymer (Figure 7A). Since CDMS is in excess, silylated polyketone can directly be reduced to alcohol which causes the formation of the polyalcohol segments (Figure 7B).

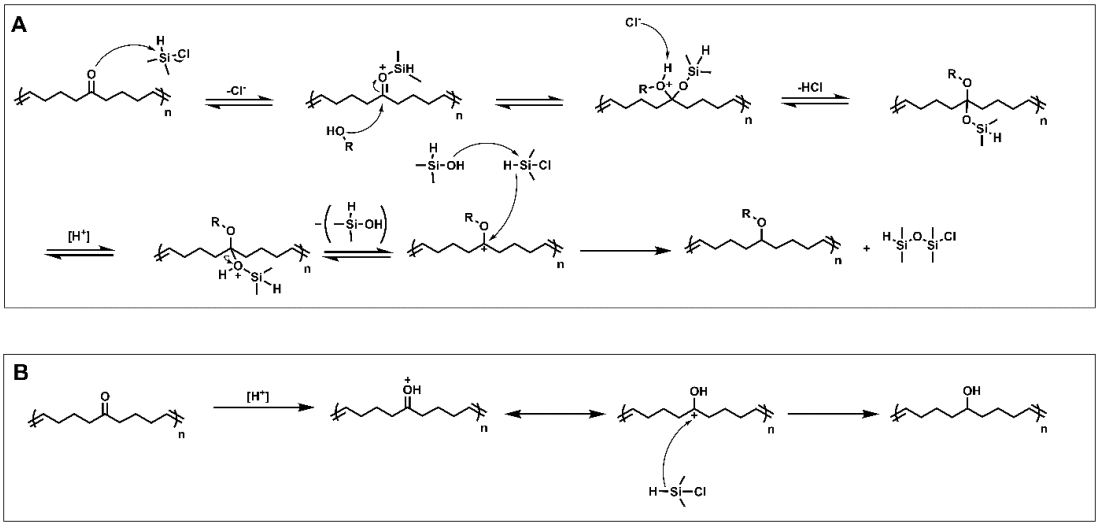


Figure 2.9 : Plausible mechanism for the formation of alkoxy-functional polymer (**A**) and polyalcohol (**B**) via RER.

2.3 Conclusions

We have demonstrated that RER can be a new PPM method for the synthesis of alkoxy-functional polymers with tunable functionality from polyketone under mild conditions. Optimization studies revealed that CH_3NO_2 is an essential solvent to promote RER, and CDMS, acting as both reductant and catalyst, was an efficient silane compound for such transformation reaction, enabling higher activity than other silane compounds. Broad alcohol substrates were examined under the standard conditions to demonstrate the scope of the proposed chemistry. Amongst, the primary alcohols furnished corresponding alkoxy structures with up to 90% efficiency, attributable to their good nucleophilicity, low or moderate RER efficiency was found for the secondary alcohols, and no reaction occurred in the case of a tert-alcohol. Alcohols containing aromatic, halogen, double or triple bonds were well tolerated under the

standard conditions. It was also inevitable that polyketone was directly reduced to polyalcohol during the reactions, but the presence of free –OH was considered as a second functional center for further modifications. The presented results show that a versatile PPM methodology was developed and promises a high reaction yield for alkoxy-functional polymer synthesis. The proposed methodology has also great potential for post-functionalization of polyketones and their transformation into high-performance materials.

2.4 Experimental Part

2.4.1 Materials

5-bromo-1-pentene (95%, ABCR), magnesium, (≥99.5%, turnings, Sigma-Aldrich), ethyl formate (97%, Sigma-Aldrich), pyridinum chlorochromate (PCC) (98%, Sigma-Aldrich), first-generation Grubbs catalyst (G1) (97%, Sigma-Aldrich), butyl vinyl ether (98%, Sigma-Aldrich), triethylsilane (Et_3SiH, 99%, ABCR), chlorodimethylsilane (CDMS, 99.5%, ABCR), dimethylphenylsilane ($PhMe_2SiH$, 98% ,Sigma-Aldrich), phenylsilane ($PhSiH_3$, 97%, Sigma-Aldrich), diphenylsilane (Ph_2SiH_2, 97%, Sigma-Aldrich), Indium (III) chloride ($InCl_3$, 98%, Sigma-Aldrich), trifluoromethanesulfonic acid (TfOH, 99% , Aldrich), ethanol (absolute, Sigma-Aldrich), 1-butanol (99.8% anhydrous, Sigma-Aldrich), 1-hexanol (99% anhydrous, Sigma-Aldrich), 1-dodecanol (98%, Sigma-Aldrich), 4-pentene-1-ol (99%, ACROS Organics™), 4-pentyn-1-ol (97%, Sigma-Aldrich), Allyl alcohol (99%, Sigma-Aldrich), benzyl alcohol (99.8%, Sigma-Aldrich) , β-citronellol (95%, Sigma-Aldrich), 9-fluorenylmethanol (98%, Fluka), 3-chloro-1-propanol (98%, Aldrich), PEG_{550}-monomethyl ether (average M_n= 550, Sigma-Aldrich), isopropyl alcohol (99.7%, Sigma-Aldrich), cyclohexanol (98%, Merck), (-)-Menthol (99%, Sigma-Aldrich), cholesterol (95%, ABCR), *tert*-butanol (99.5% anhydrous, Sigma-Aldrich), triethylamine (99.5%, Sigma-Aldrich), benzoyl chloride (98%, TCI) were used as received. Tetrahydrofuran (THF HPLC Grade, 99%, Aldrich), nitromethane (CH_3NO_2, 96%, Merck), dimethyl sulfoxide (DMSO, 99.9%, Aldrich), acetonitrile (CH_3CN, 99.8%, Aldrich), toluene (99.8%, Aldrich), chloroform ($CHCl_3$, 99%, Aldrich), dichloromethane (CH_2Cl_2, 99.8%, Aldrich), were anhydrous of high-performance liquid chromatography quality and used without further purification. Methanol and diethyl ether were of reagent grade and used as received.

2.4.2 Instrumentation

^{1}H (500 MHz) and ^{13}C (125 MHz) spectra were recorded using an Agilent VNMRS 500 instrument in $CDCl_3$. Fourier transform infrared (FT-IR) spectra were recorded on a Cary 630 FT-IR (Agilent Technologies) instrument over the range 4000–500 cm^{-1} and Perkin-Elmer Spectrum One FT-IR (ATR sampling accessory) over the range 4000–650 cm^{-1}. Gel permeation chromatography (GPC) measurements were carried out with Viscotek TDA 302 with an Agilent pump (series 1200), mainly using refractive index detector, loaded with TOSOH TSKgel columns (HM-M and SuperH3000, both 6 mm internal diameter, 150 mm length, packed with 3 µm particles). The effective molecular weight ranges of the columns were 10^2- 4×10^8 and 10^2- 6×10^4 g/mol, respectively. THF was used as eluent at a flow rate of 0.5 mL/min at 30 °C, and 2,6-di-*tert*-butyl-4-methylphenol (BHT) was used as an internal standard. The weight-average molecular weights (M_w) and dispersities ($Đ$) of the polymers were calculated based on linear polystyrene (PS) standards (Polymer Laboratories).

2.4.3 Synthetic procedures and characterization

2.4.3.1 Synthesis of Undeca-1,10-dien-6-one (2)

Undeca-1,10-dien-6-one (2) was synthesized according to the literature procedure [42].

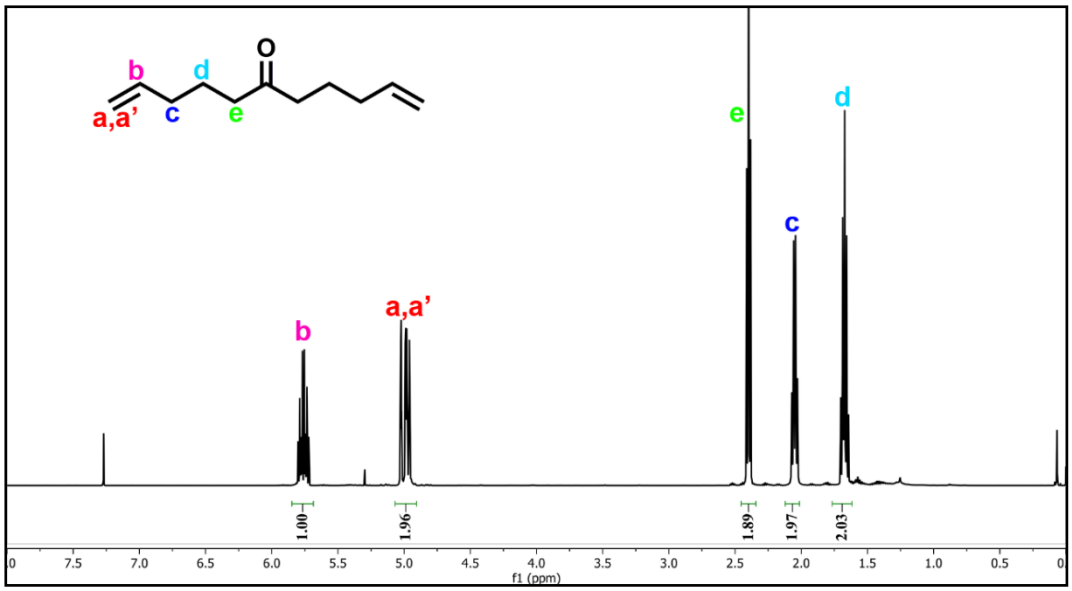


Figure 2.10 : ^{1}H NMR spectrum of **2** (500 MHz).

2.4.3.2 Synthesis of Polyketone via ADMET Polymerization (P0)

Polyketone (P0) was synthesized according to the literature procedures with slight changes [43, 44]. First-generation Grubbs catalyst (G1, 47.8 mg, 5.81 µmol) was weighed into a 25 mL Schlenk flask, dissolved in 1 mL of CH_2Cl_2, and immediately submerged to liquid nitrogen. Then 2 g of **2** was added to Schlenk flask whilst in liquid nitrogen. The reaction mixture was allowed to warm to room temperature under argon atmosphere. When very slow to moderate bubbling was observed, the reaction temperature was increased to 65 ^oC and exposed to intermittent vacuum to remove ethylene and remaining solvent. As the polymerization proceeds, the reaction mixture was observed to solidify. The reaction was kept stirring overnight at this temperature. The reaction was cooled to room temperature then butyl vinyl ether (0.5 mL) and CH_2Cl_2 (5 mL) were added under nitrogen atmosphere to terminate the reaction and the solution was allowed to stir for an additional 30 min. Finally, the solution was precipitated into cold methanol (200 mL), and the dissolution-precipitation procedure (CH_2Cl_2-cold methanol) was repeated two times to give P0 as an off-white solid in nearly quantitative yield.

^1H NMR ($CDCl_3$, δ) 5.40 (m, 2H, backbone-C*H*=C*H*), 2.38 (m, 4H, backbone-CH_2C=O), 1.92-1.62 (m, 8H, backbone-CH_2). ^{13}C NMR ($CDCl_3$, δ) 211.66, 130.26, 42.10, 31.96, 26.60, 23.54.

2.4.3.3 General Procedure for RER

Briefly, 50 mg of polyketone (P0) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. Alcohol (2 equiv. per repeating unit of P0) and CDMS (4 equiv. per repeating unit of P0) were then added to the reaction medium, respectively, and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield the final products.

2.4.3.4 Synthesis of P1 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer

solution. Ethanol (0.72 mmol, 42.3 µL) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively, and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to give P1 as a brown sticky solid. (Yield= 52 mg, 86%). ^{1}H NMR ($CDCl_3$, δ) 5.40 (m, 2H, C*H*=C*H*), 3.59 (s, 1H, C*H*OH), 3.47 (m, 2H, CHOC*H*$_2$CH$_3$), 3.21 (s, 1H, C*H*OCH$_2$CH$_3$), 2.00 (m, 4H, main backbone), 1.52-1.38 (m, 8H, main backbone), 1.18 (m, 3H, CHOCH$_2$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ) 130.36, 79.15, 71.73, 64.12, 33.69, 32.78, 27.39, 25.48, 15.71.

2.4.3.5 Esterification Reaction of P1 with Benzoyl Chloride

P1 (run 1, Table 4) 52 mg (0.037 mmol) was dissolved in 3 mL of CH_2Cl_2 and cooled to 0 ^{o}C in an ice bath, then Et_3N (5 equiv. per polyalcohol unit, 0.185 mmol, 26.0 µL) was added to this solution. Benzoyl chloride (3 equiv. per polyalcohol unit, 0.111 mmol, 13.0 µL) was dissolved in 3 mL of CH_2Cl_2 and added dropwise to this solution. The reaction mixture was stirred at 0 ^{o}C for 30 min, warmed to room temperature, and stirred overnight. The reaction mixture was then directly precipitated into 15 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield the final product as a brown sticky solid in quantitative yield. ^{1}H NMR ($CDCl_3$, δ) 8.05-8.02 (m, 2H, Ar*H*), 7.54 (m, 1H, Ar*H*), 7.48 (m, 2H, Ar*H*), 5.40 (m, 2H, C*H*=C*H*), 5.16 (s, 1H, C*H*OC=O), 3.47 (m, 2H, CHOC*H*$_2$CH$_3$), 3.21 (s, 1H, C*H*OCH$_2$CH$_3$), 2.05-1.97 (m, 4H, main backbone), 1.52-1.38 (m, 8H, main backbone), 1.18 (m, 3H, CHOCH$_2$C*H*$_3$).

2.4.3.6 Synthesis of P2 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. 1-Butanol (0.72 mmol, 66.3 µL) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P2 as a brown sticky solid. (Yield= 58 mg, 82%). ^{1}H NMR ($CDCl_3$,

δ) 5.40 (m, 2H, C*H*=C*H*), 3.59 (s, 1H, C*H*OH), 3.47 (m, 2H, CHOCH_2CH$_2$CH$_2$CH$_3$), 3.21 (s, 1H, C*H*OCH$_2$CH$_2$CH$_2$CH$_3$), 1.99 (m, 4H, main backbone), 1.62-1.28 (m, 12H, main backbone and CHOCH$_2$CH_2CH_2CH$_3$), 0.93 (m, 3H, CHOCH$_2$CH$_2$CH$_2$CH_3). ^{13}C NMR (CDCl$_3$, δ) 130.35, 129.87, 79.22, 78.71, 71.73, 68.64, 33.62, 32.37, 27.39, 25.45, 19.46, 13.95.

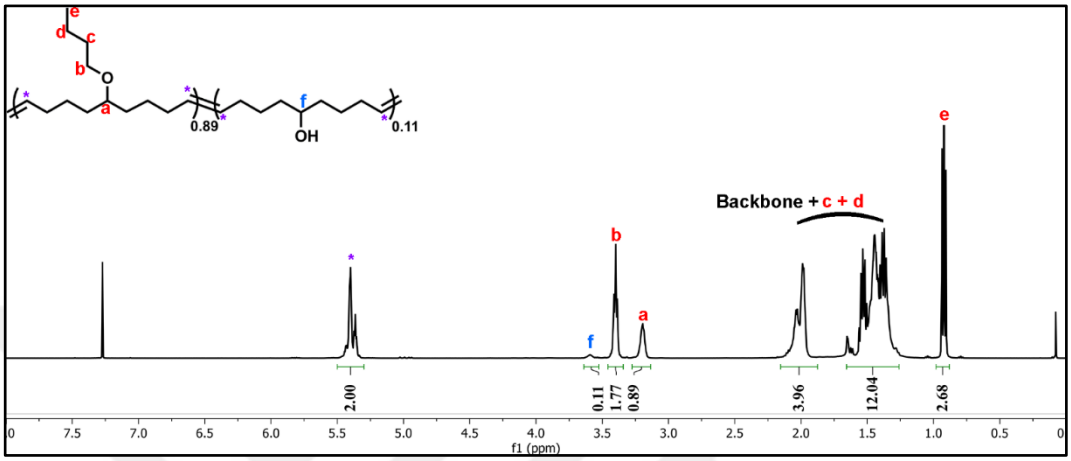


Figure 2.11 : ^{1}H NMR spectrum of P2 (500 MHz).

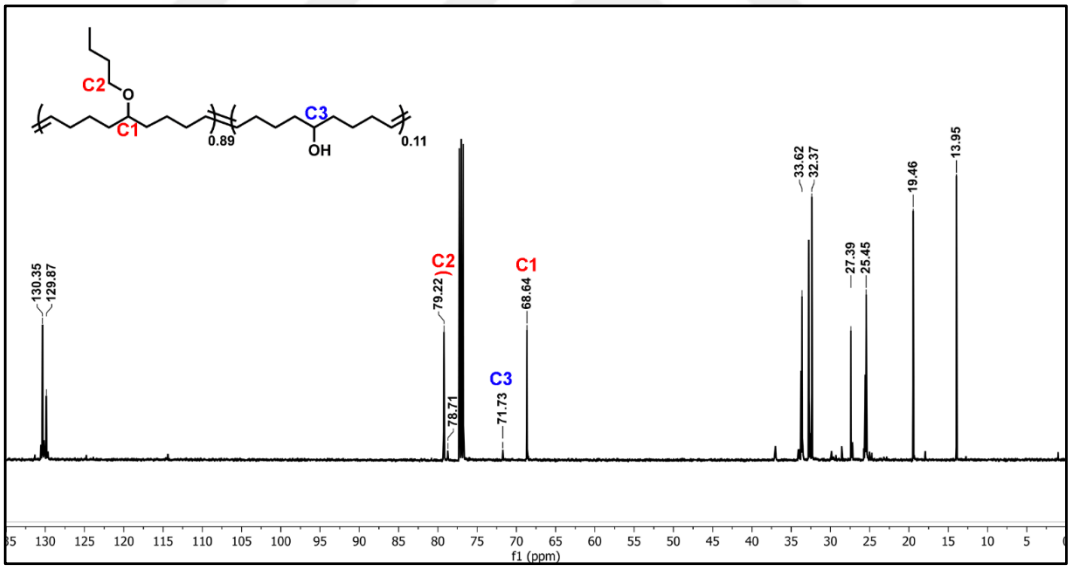


Figure 2.12 : ^{13}C NMR spectrum of P2 (125 MHz).

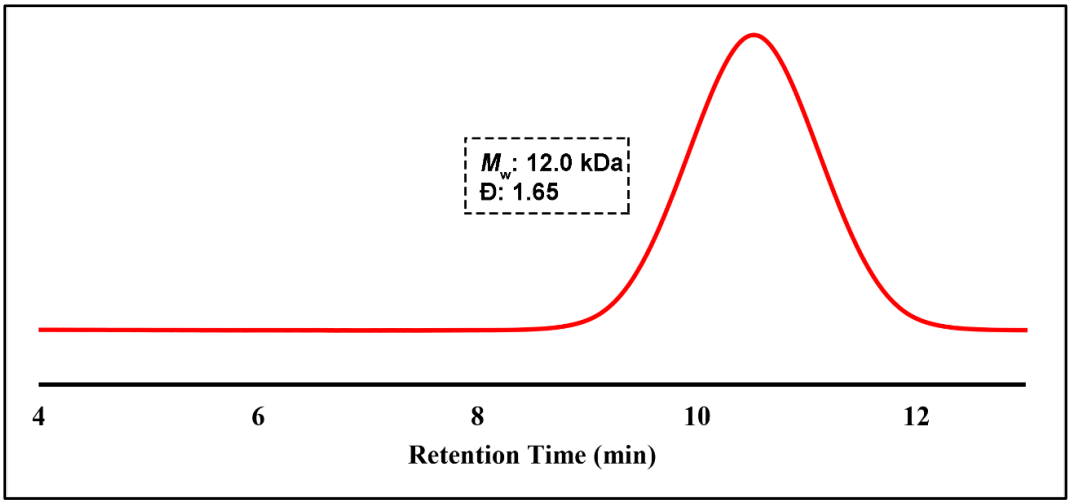


Figure 2.13 : GPC trace of P2.

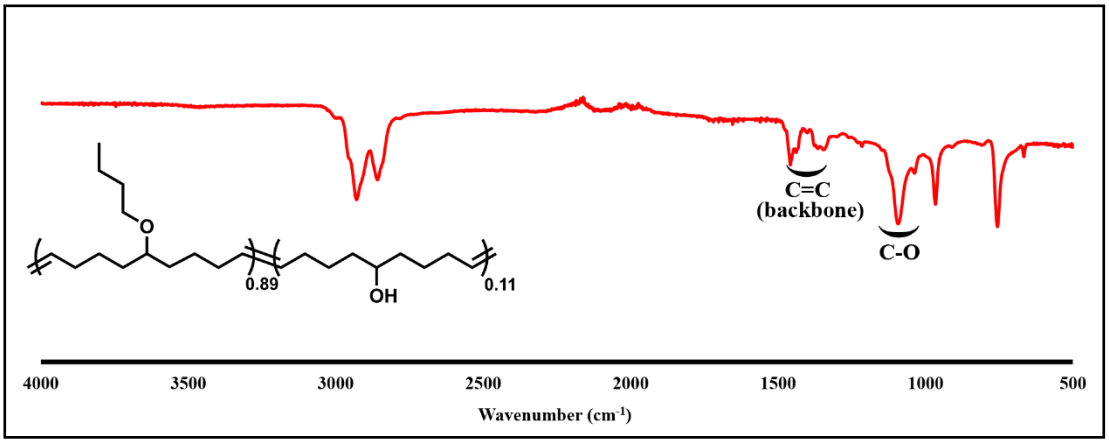


Figure 2.14 : FT-IR spectrum of P2.

2.4.3.7 Synthesis of P3 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. 1-Hexanol (0.72 mmol, 90.0 µL) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P3 as a light brown sticky solid. (Yield= 68 mg, 84%). ^{1}H NMR ($CDCl_3$, δ) 5.40 (m, 2H, C*H*=C*H*), 3.59 (s, 1H, C*H*OH), 3.48 (m, 2H, CHOC*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 3.21 (s, 1H, C*H*OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.99 (m, 4H, main backbone), 1.67-1.28 (m, 16H, main backbone and

$CHOCH_2CH_2CH_2CH_2CH_2CH_3$), 0.94 (m, 3H, $CHOCH_2$ $CH_2CH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, δ) 130.35, 128.30, 78.82, 71.75, 70.76, 33.40, 32.75, 27.39, 25.35.

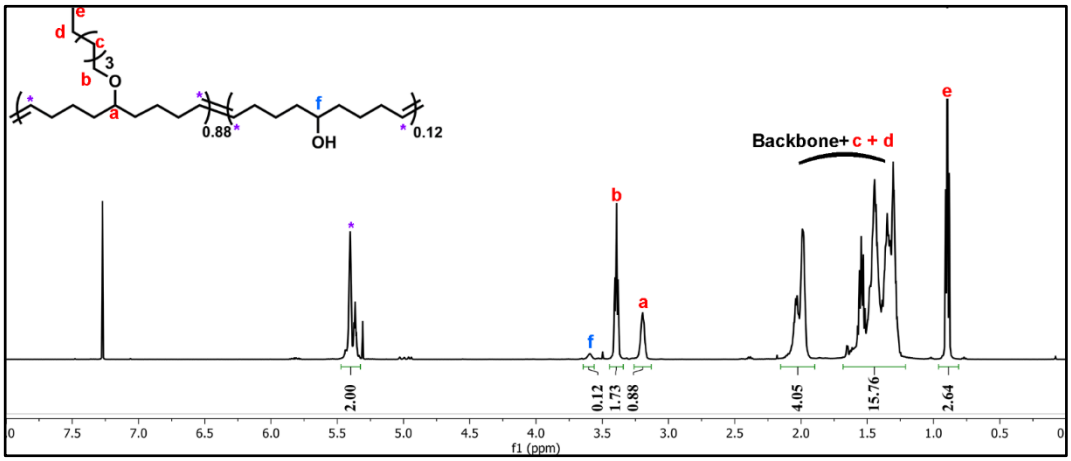


Figure 2.15 : ^{1}H NMR spectrum of P3 (500 MHz).

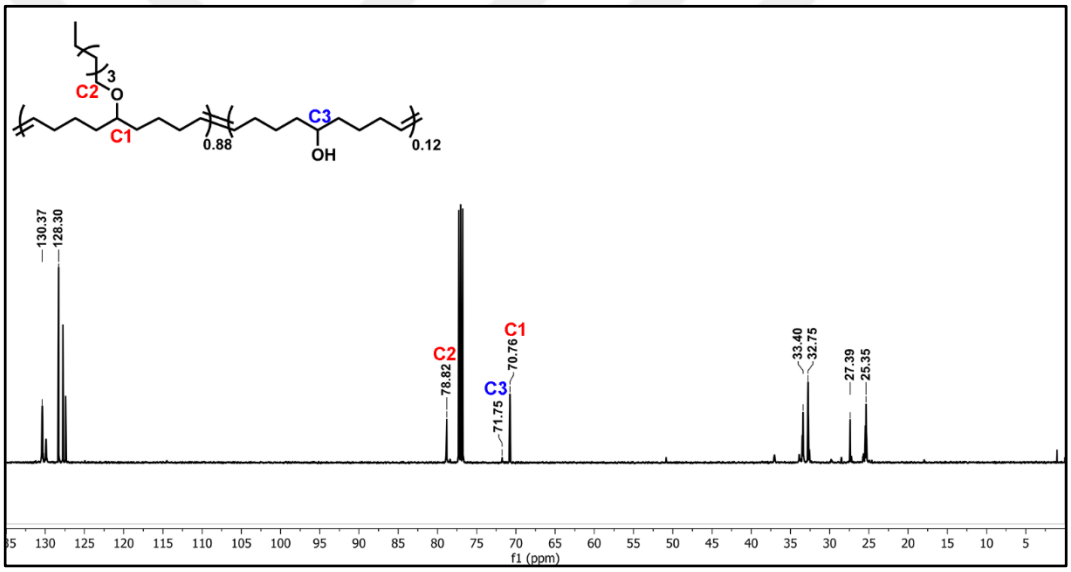


Figure 2.16 : ^{13}C NMR spectrum of P3 (125 MHz).

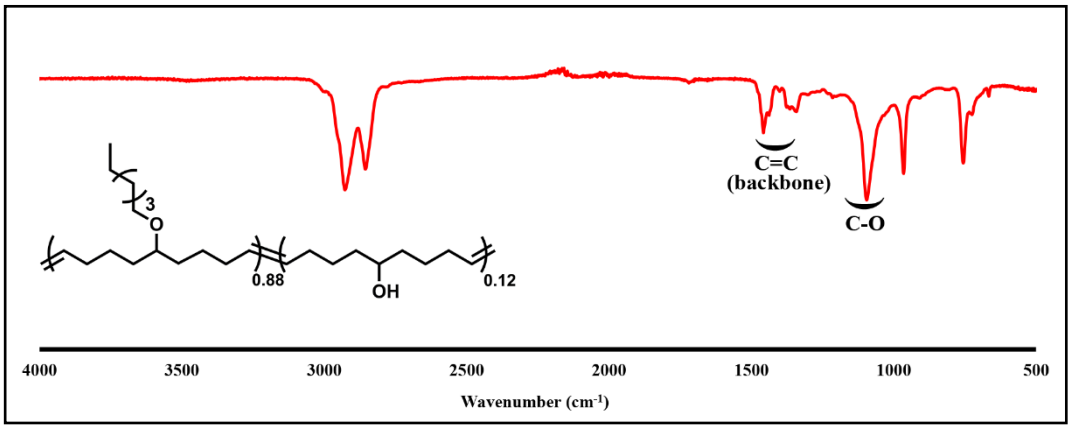


Figure 2.17 : FT-IR spectrum of P3.

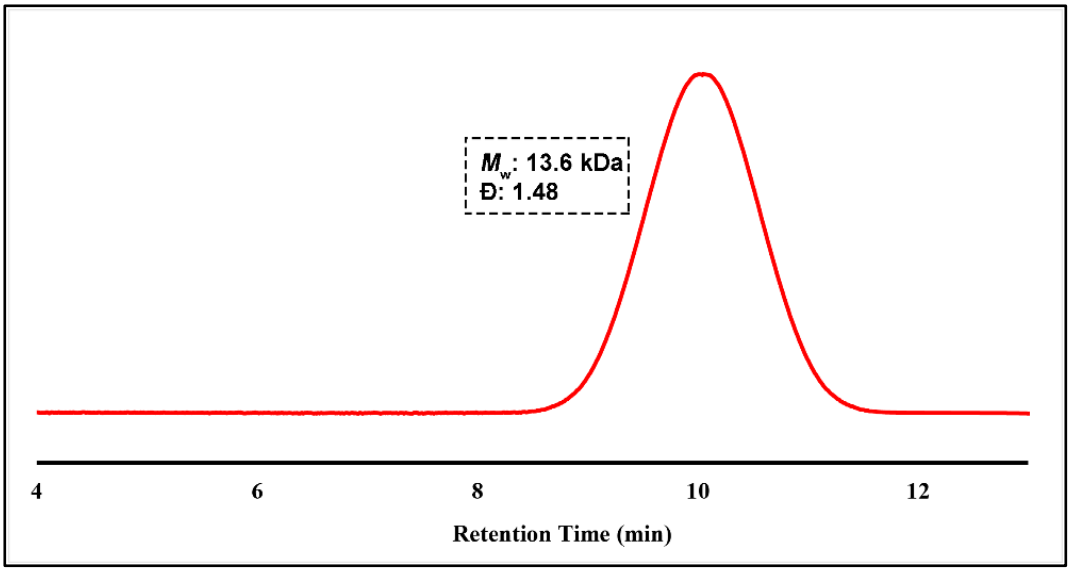


Figure 2.18 : GPC trace of P3.

2.4.3.8 Synthesis of P4 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. 1-Dodecanol (0.72 mmol, 162.5 µL) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P4 as an off-white waxy solid. (Yield= 88 mg, 79%). ^{1}H NMR ($CDCl_3$, δ) 5.40 (m, 2H, C*H*=C*H*), 3.60 (s, 1H, C*H*OH), 3.39 (m, 2H, CHOC*H*$_2$(CH_2)$_9$$CH_3$), 3.19 (s, 1H, C*H*O$CH_2$($CH_2$)$_9$$CH_3$), 1.99 (m, 4H, main backbone), 1.64-1.26 (m, 26H, main backbone, CHOCH_2(C*H*$_2$)$_9$$CH_3$), 0.89 (m, 3H, CHO$CH_2$($CH_2$)$_9$C*H*$_3$). ^{13}C NMR ($CDCl_3$, δ) 130.35, 79.24, 78.75, 71.74, 69.01, 31.93, 29.66, 22.69, 14.12.

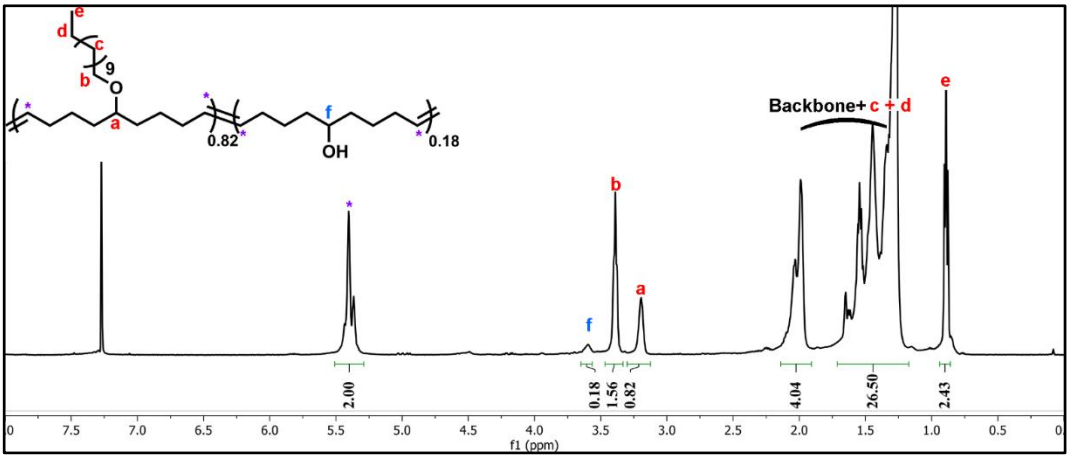


Figure 2.19 : ^{1}H NMR spectrum of P4 (500 MHz).

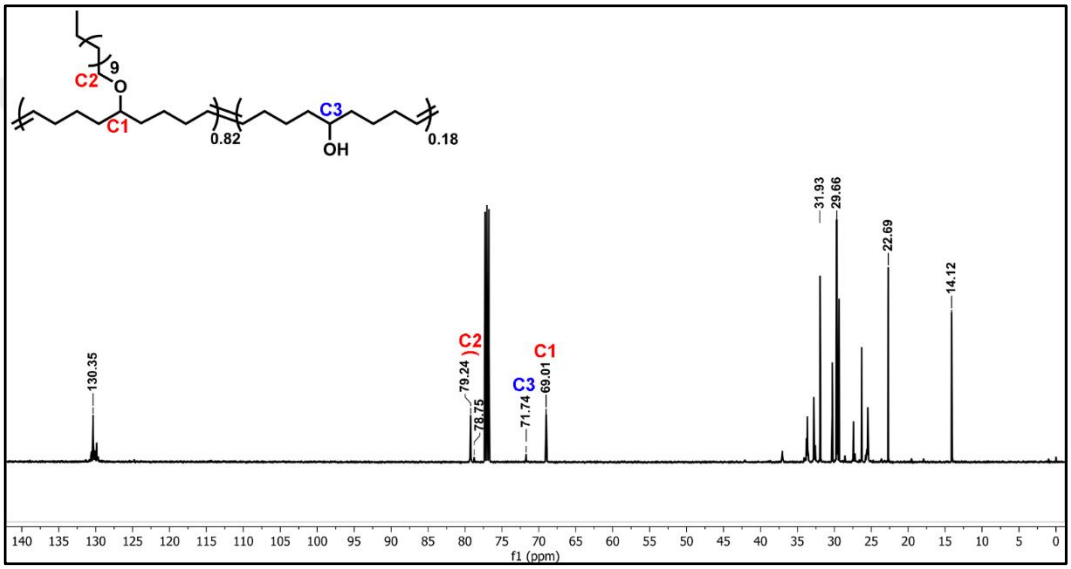


Figure 2.20 : ^{13}C NMR spectrum of P4 (125 MHz).

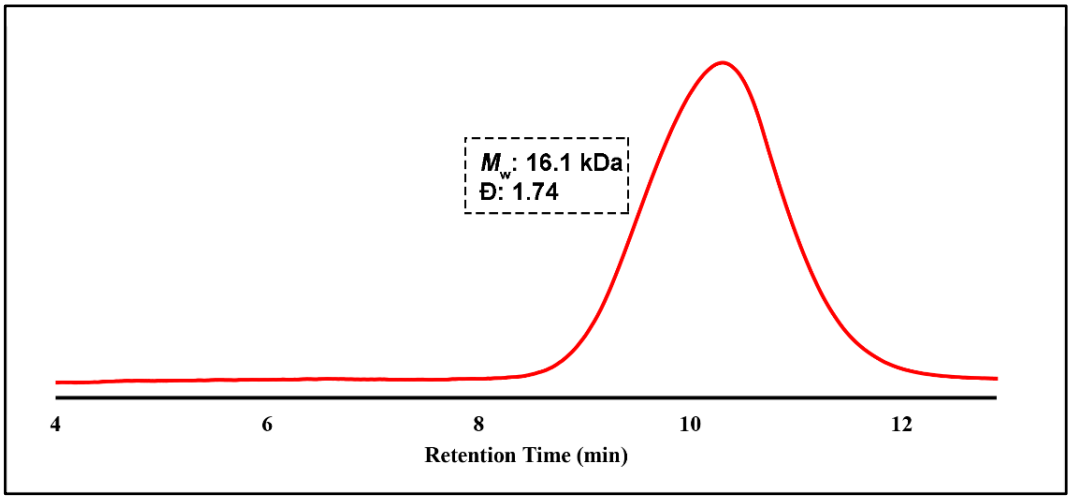


Figure 2.21 : GPC trace of P4.

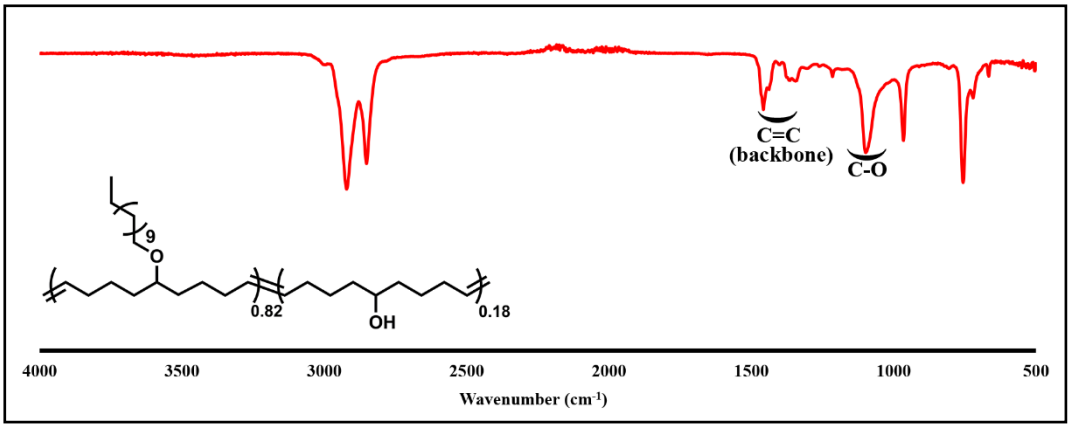


Figure 2.22 : FT-IR spectrum of P4.

2.4.3.9 Synthesis of P5 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. 4-pentene-1-ol (0.72 mmol, 74.9 µL) and CDMS (1.44 mmol, 161.0 µL) were then added to the medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P5 as a yellow sticky solid. (Yield= 52 mg, 76%). ^{1}H NMR ($CDCl_3$, δ) 5.83 (m, 1H $CHOCH_2CH_2CH_2C\mathit{H}=CH_2$), 5.40 (m, 2H, $C\mathit{H}=C\mathit{H}$), 5.05-4.97 (m, 2H, $CHOCH_2CH_2CH_2CH=C\mathit{H}_2$), 3.59 (s, 1H, $C\mathit{H}OH$), 3.41 (m, 2H, $CHOC\mathit{H}_2CH_2CH_2CH=CH_2$), 3.21 (s, 1H, $C\mathit{H}OCH_2CH_2CH_2CH=CH_2$), 2.14 (m, 2H, $CHOCH_2CH_2C\mathit{H}_2CH=CH_2$) 2.00 (m, 4H, main backbone), 1.65 (m, 2H, $CHOCH_2C\mathit{H}_2CH_2CH=CH_2$) 1.45-1.36 (m, 8H, main backbone).^{13}C NMR ($CDCl_3$, δ) 138.48, 130.35, 114.62, 79.30, 78.81, 71.75, 68.14, 33.60, 32.77, 30.45, 29.42, 27.39, 25.45.

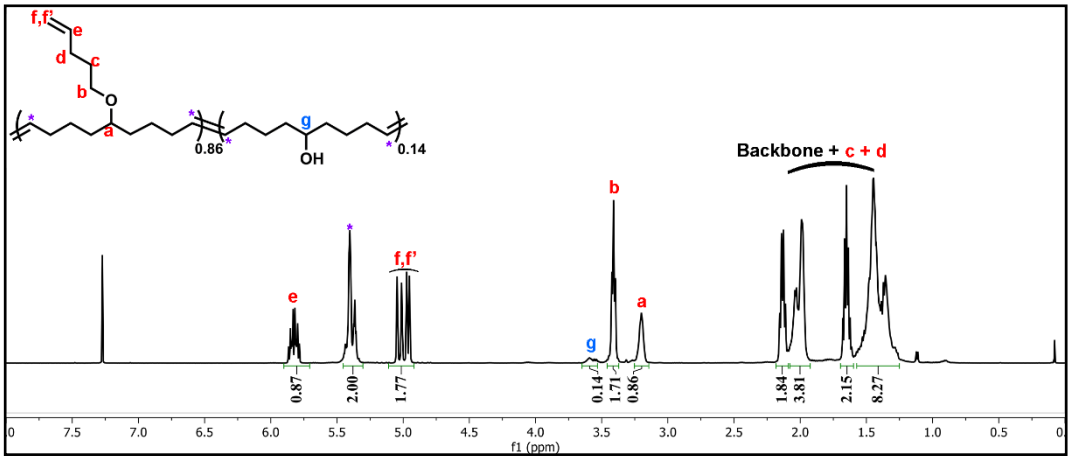


Figure 2.23 : ^{1}H NMR spectrum of P5 (500 MHz).

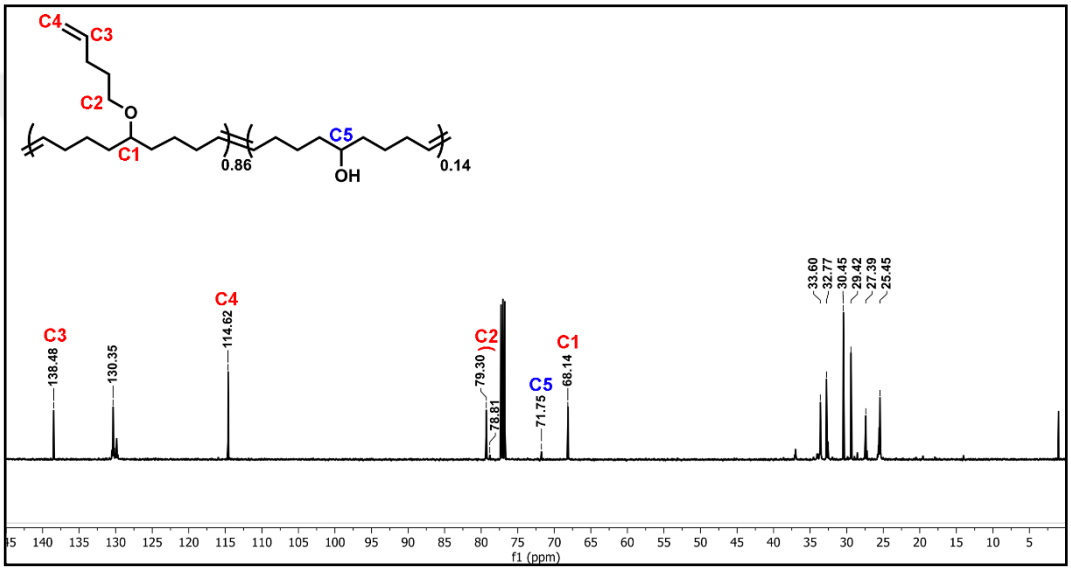


Figure 2.24 : ^{13}C NMR spectrum of P5 (125 MHz).

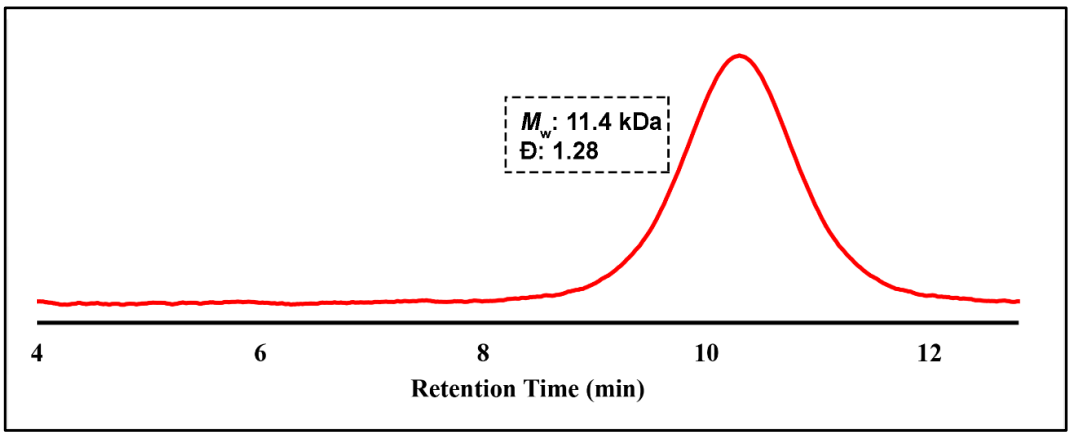


Figure 2.25 : GPC trace of P5.

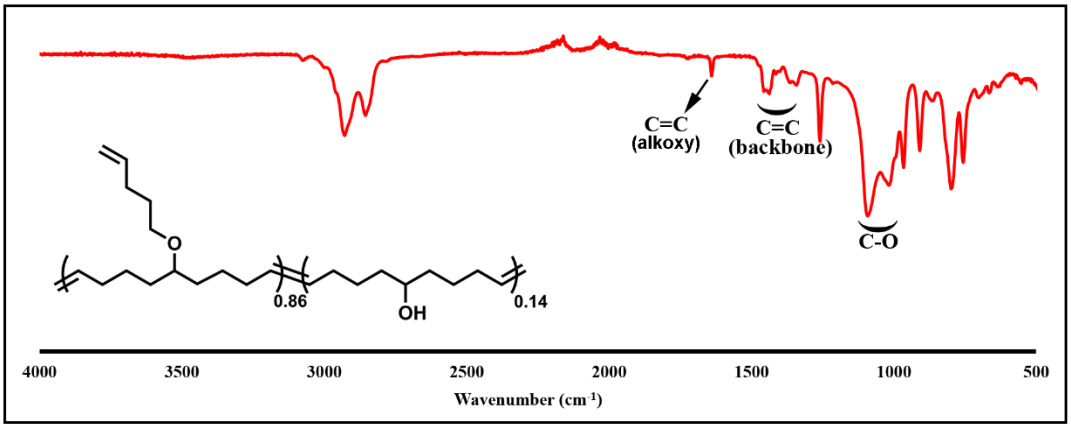


Figure 2.26 : FT-IR spectrum of P5.

2.4.3.10 Synthesis of P6 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. 4-pentyne-1-ol (0.72 mmol, 67.4 µL) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P6 as a yellow sticky solid. (Yield= 55 mg, 74%). ^{1}H NMR ($CDCl_3$, δ) 5.40 (m, 2H, C*H*=C*H*), 3.59 (s, 1H, C*H*OH), 3.48 (m, 2H, CHOC*H*$_2$CH$_2$CH$_2$C≡CH), 3.21 (s, 1H, C*H*OCH$_2$CH$_2$CH$_2$C≡CH), 2.30 (m, 2H, CHOCH$_2$CH$_2$C*H*$_2$C≡CH) 1.99 (m, 4H, main backbone), 1.94 (s, 1H, CHOCH$_2$CH$_2$CH$_2$C≡C*H*), 1.76 (m, 2H, CHOC*H*$_2$CH$_2$CH$_2$C≡CH), 1.52-1.38 (m, 8H, main backbone).^{13}C NMR ($CDCl_3$, δ) 130.35, 84.16, 79.41, 71.76, 68.38, 66.95, 32.76, 29.10, 15.35.

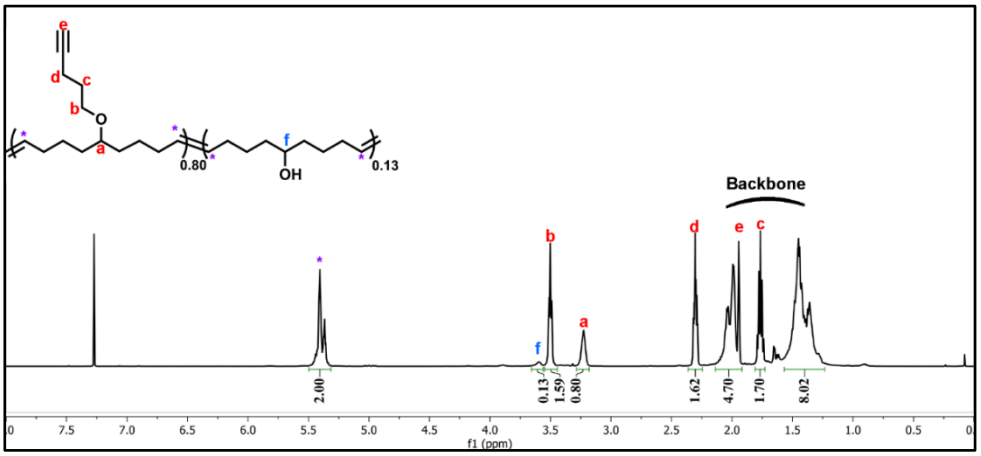


Figure 2.27 : ^{1}H NMR spectrum of P6 (500 MHz).

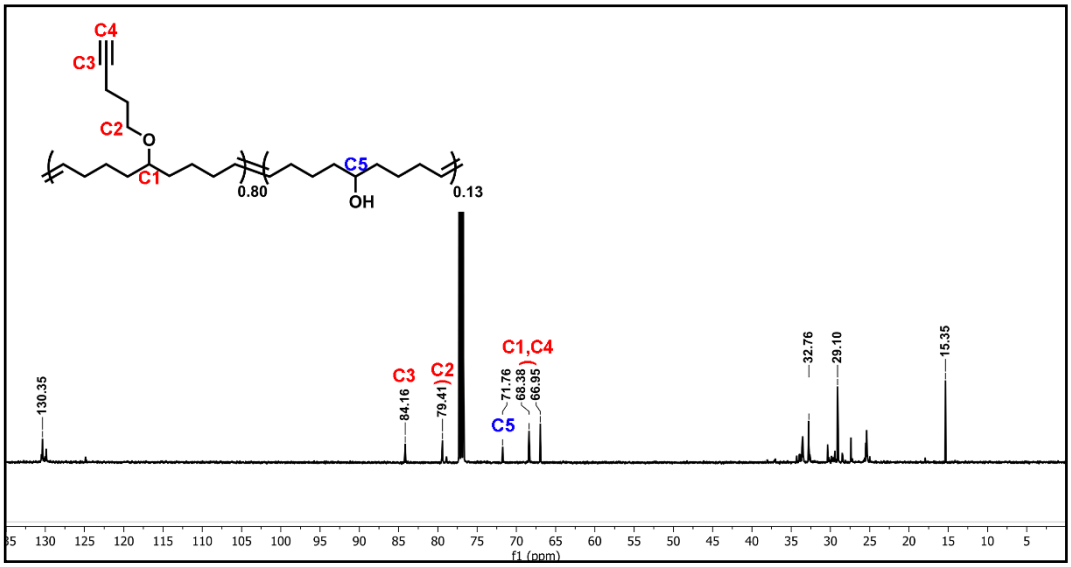


Figure 2.28 : ^{13}C NMR spectrum of P6 (125 MHz).

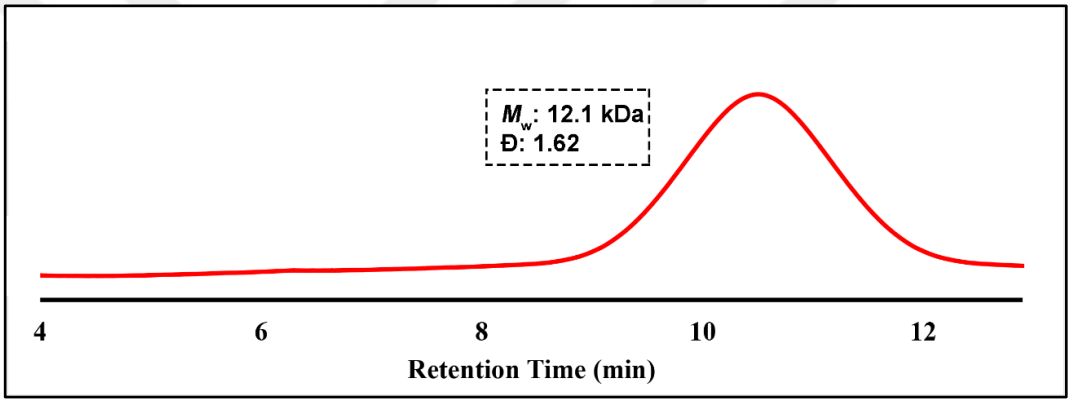


Figure 2.29 : GPC trace of P6.

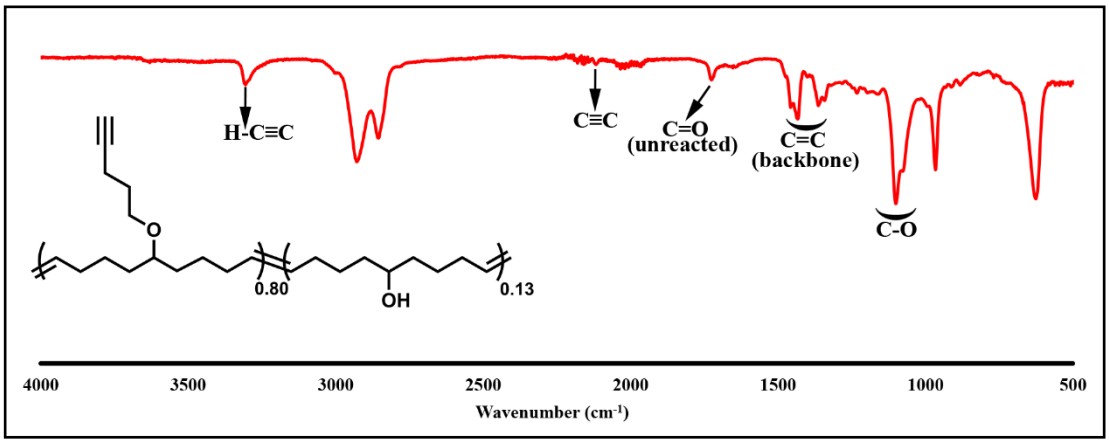


Figure 2.30 : FT-IR spectrum of P6.

2.4.3.11 Synthesis of P7 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. Allyl alcohol (0.72 mmol, 49.3 µL) and CDMS (1.44 mmol, 161.0 µL) were

then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P7 as a brown sticky solid. (Yield= 48 mg, 74%). ^{1}H NMR ($CDCl_3$, δ) 5.93 (m, 1H $CHOCH_2CH$=CH_2), 5.40 (m, 2H, C*H*=C*H*), 5.28, 5.15 (d, 2H, $CHOCH_2CH$=CH_2), 3.96 (s, 2H, $CHOCH_2CH$=CH_2), 3.59 (s, 1H, C*H*OH), 3.21 (s, 1H, C*H*OCH_2CH=CH_2), 1.99 (m, 4H, backbone), 1.52-1.38 (m, 8H, backbone).^{13}C NMR ($CDCl_3$, δ) 135.65, 130.35, 116.35, 78.84, 78.41, 71.73, 69.88, 33.47, 32.75, 27.38, 25.50.

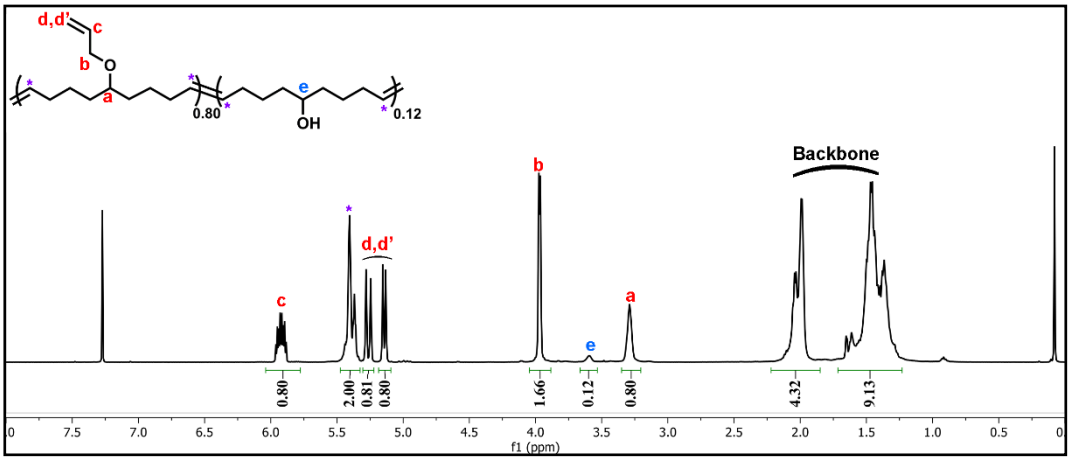


Figure 2.31 : ^{1}H NMR spectrum of P7 (500 MHz).

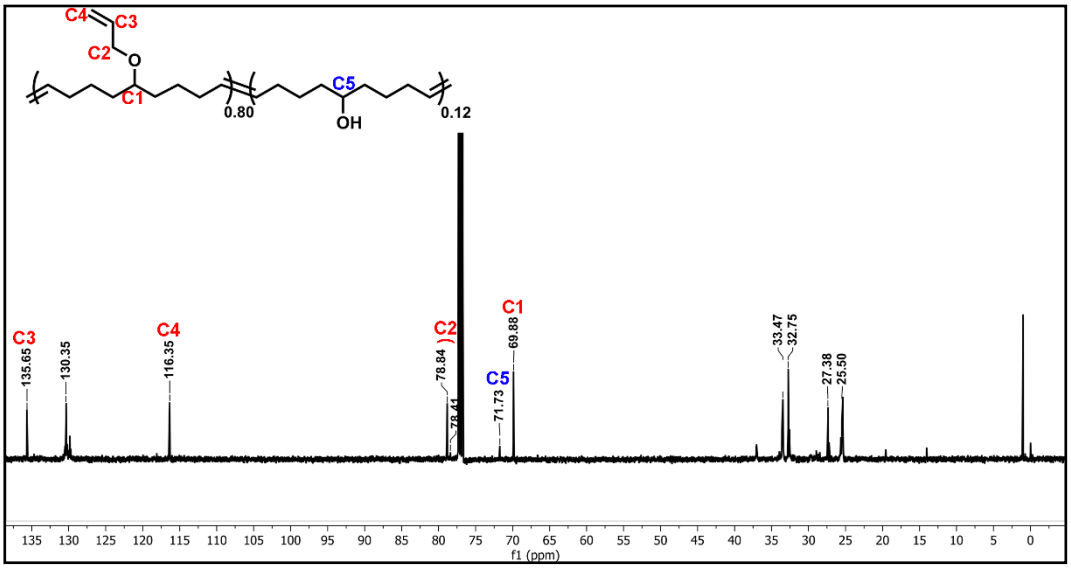


Figure 2.32 : ^{13}C NMR spectrum of P7 (125 MHz).

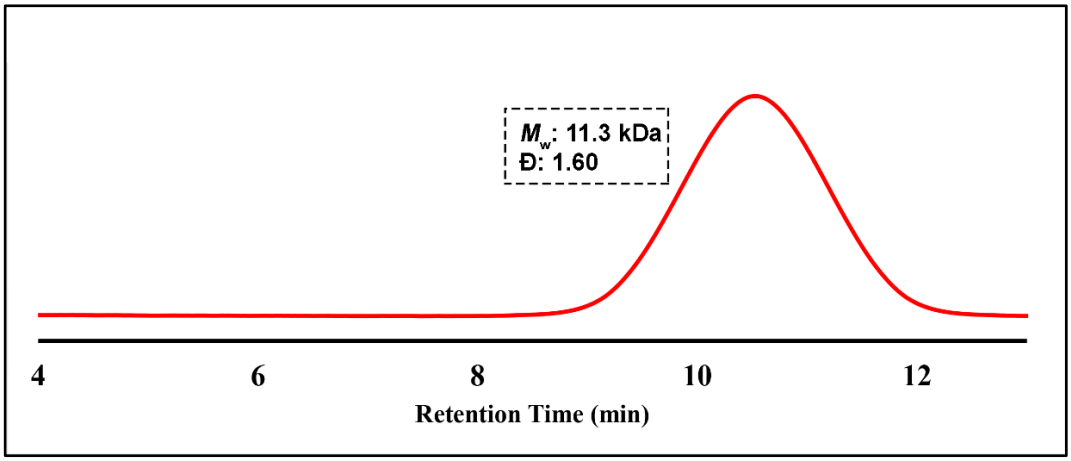


Figure 2.33 : GPC trace of P7.

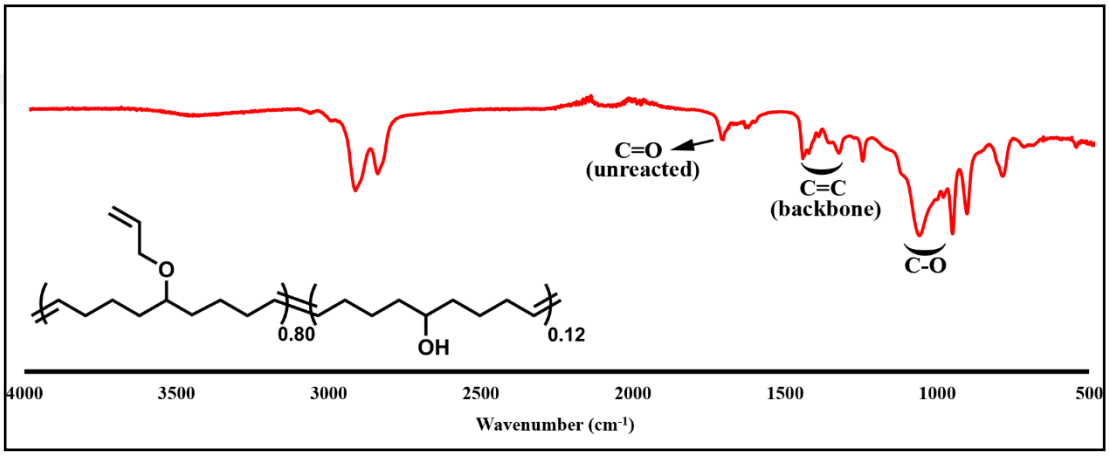


Figure 2.34 : FT-IR spectrum of P7.

2.4.3.12 Synthesis of P8 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. β-citronellol (0.72 mmol, 132.1 µL) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P8 as a yellow sticky solid. (Yield= 88 mg, 88%). ^{1}H NMR ($CDCl_3$, δ) 5.40 (m, 2H, C*H*=C*H*), 5.10 (m, 1H, CH_3CH_3C=C*H*), 3.59 (s, 1H, C*H*OH), 3.47 (m, 2H, CHOC*H*$_2$), 3.21 (s, 1H, C*H*OCH_2), 1.99 (m, 4H, main backbone), 1.69-1.14 (m, 21H, main backbone and β-citronellyl), 0.90 (m, 3H, CH_2CHCH_3). ^{13}C NMR ($CDCl_3$, δ) 130.35, 124.90, 79.33, 78.82, 71.19, 67.06, 46.32, 37.30, 32.45, 29.69, 25.49, 22.49, 19.57, 17.64.

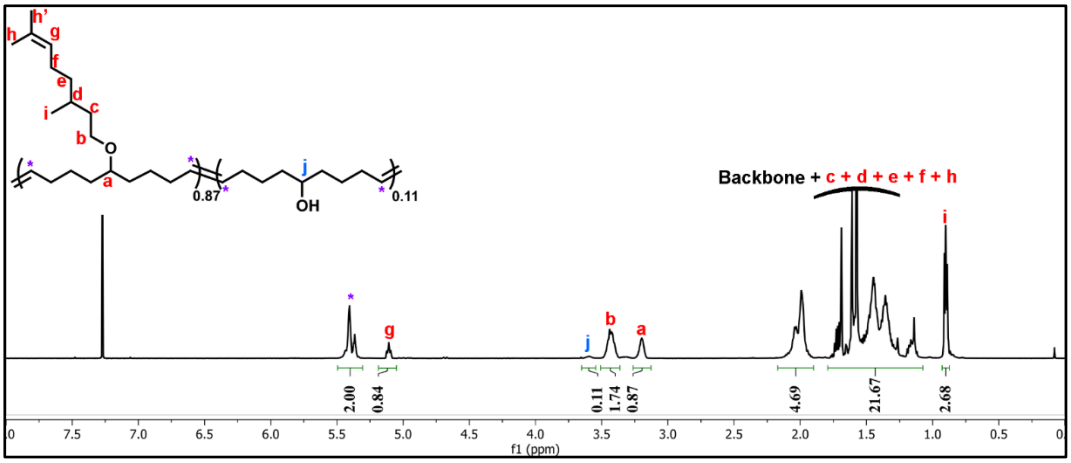


Figure 2.35 : ^{1}H NMR spectrum of P8 (500 MHz).

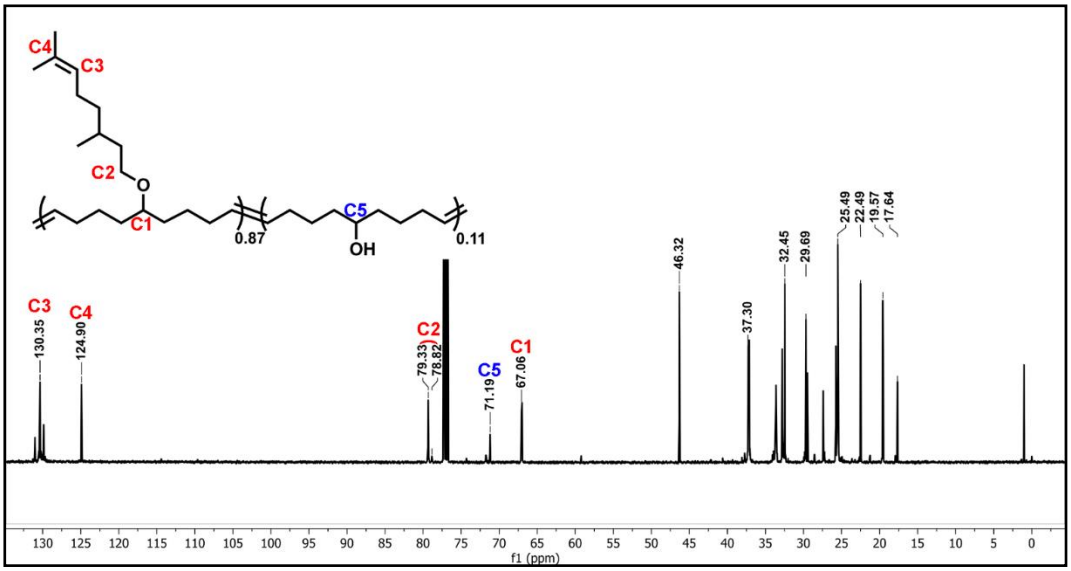


Figure 2.36 : ^{13}C NMR spectrum of P8 (125 MHz).

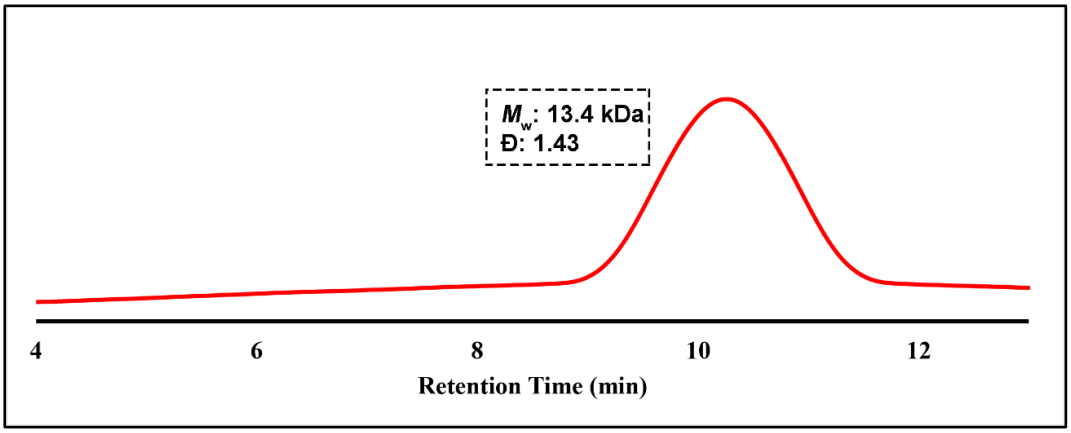


Figure 2.37 : GPC trace of P8.

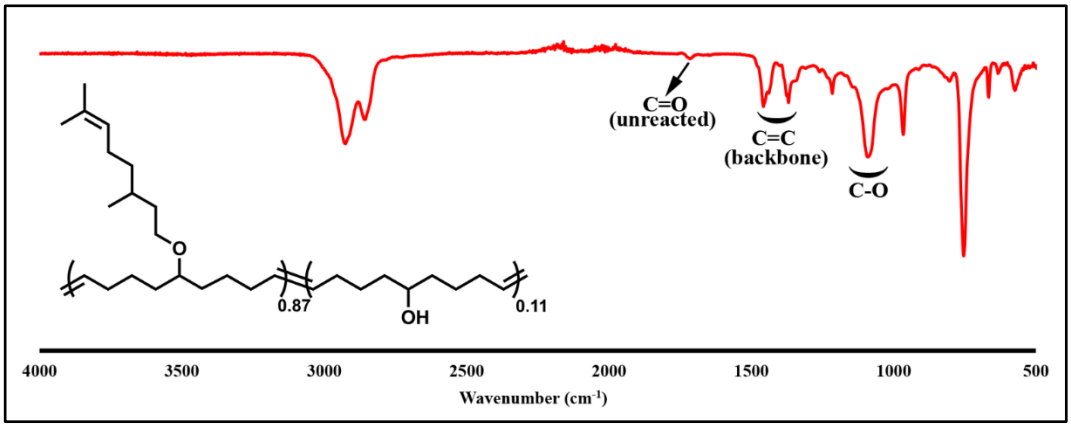


Figure 2.38 : FT-IR spectrum of P8.

2.4.3.13 Synthesis of P9 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. 3-chloro-1-propanol (0.72 mmol, 66.0 µL) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P9 as a yellow sticky solid. (Yield= 60 mg, 77%). ^{1}H NMR ($CDCl_3$, δ) 5.40 (m, 2H, C*H*=C*H*), 3.66 (t, 2H, CHOC*H*$_2$CH$_2$CH$_2$Cl) 3.54 (s, 3H, C*H*OH and CHOCH$_2$CH$_2$C*H*$_2$Cl), 3.24 (s, 1H, C*H*OCH$_2$CH$_2$CH$_2$Cl), 1.99 (m, 6H, main backbone and CHOCH$_2$C*H*$_2$CH$_2$Cl), 1.44-1.36 (m, 8H, main backbone). ^{13}C NMR ($CDCl_3$, δ) 130.35, 79.51, 78.97, 71.74, 64.91, 42.18, 33.21, 27.36, 25.34.

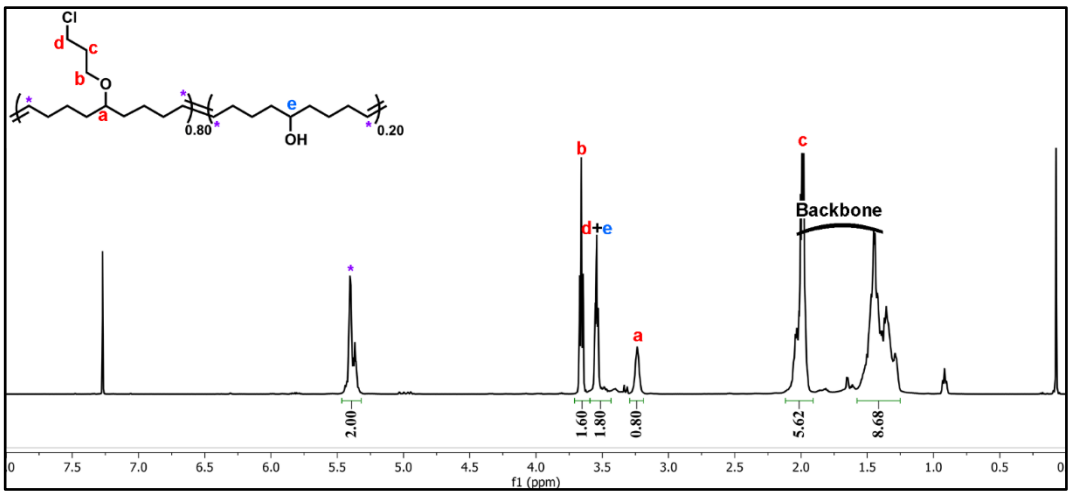


Figure 2.39 : ^{1}H NMR spectrum of P9 (500 MHz).

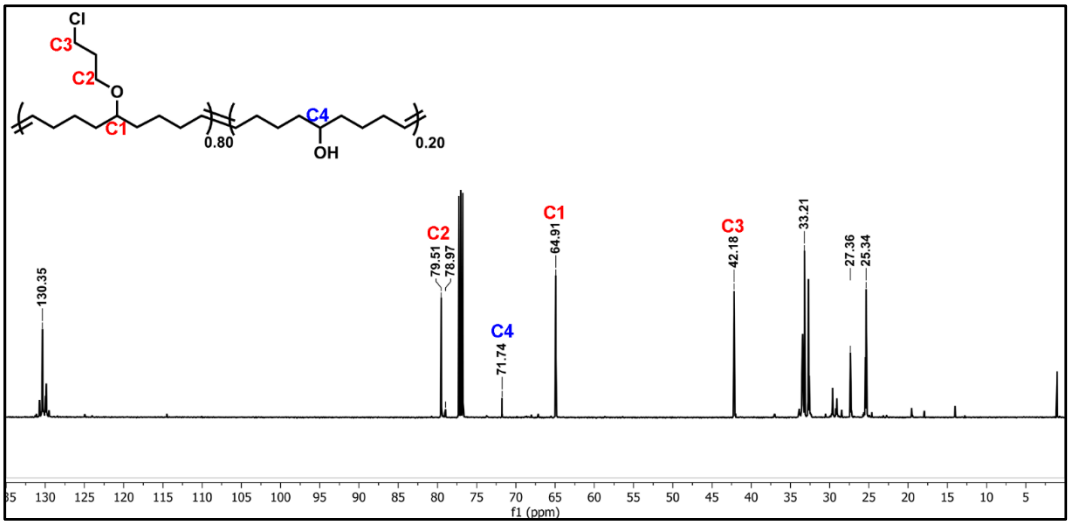


Figure 2.40 : ^{13}C NMR spectrum of P9 (125 MHz).

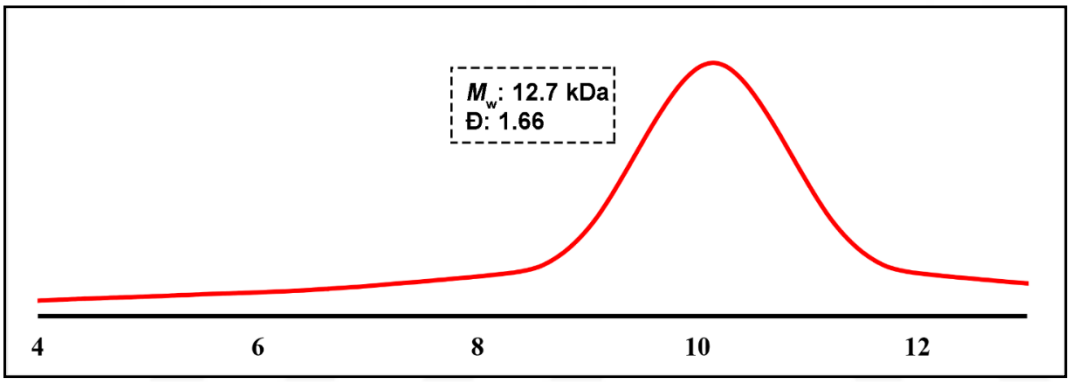


Figure 2.41 : GPC trace of P9.

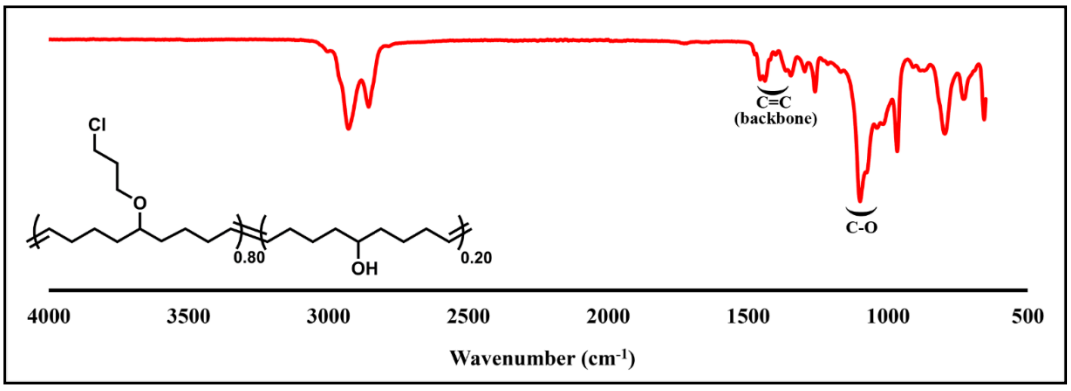


Figure 2.42 : FT-IR spectrum of P9.

2.4.3.14 Synthesis of P10 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. Benzyl alcohol (0.72 mmol, 75.3 µL) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then

diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P10 as a light brown sticky solid. (Yield= 60 mg, 72%). ^{1}H NMR ($CDCl_3$, δ) 7.34-7.23 (m, 5H $CHOCH_2C_6H_5$), 5.40 (m, 2H, C*H*=C*H*), 4.50 (s, 2H, $CHOCH_2C_6H_5$), 3.58 (s, 1H, C*H*OH), 3.38 (s, 1H, $CHOCH_2C_6H_5$), 1.99 (m, 4H, main backbone), 1.55-1.40 (m, 8H, main backbone).^{13}C NMR ($CDCl_3$, δ) 138.94, 135.65, 130.35, 79.24, 78.72, 71.75, 69.00, 33.45, 32.11, 29.69, 25.49, 22.49, 12.63.

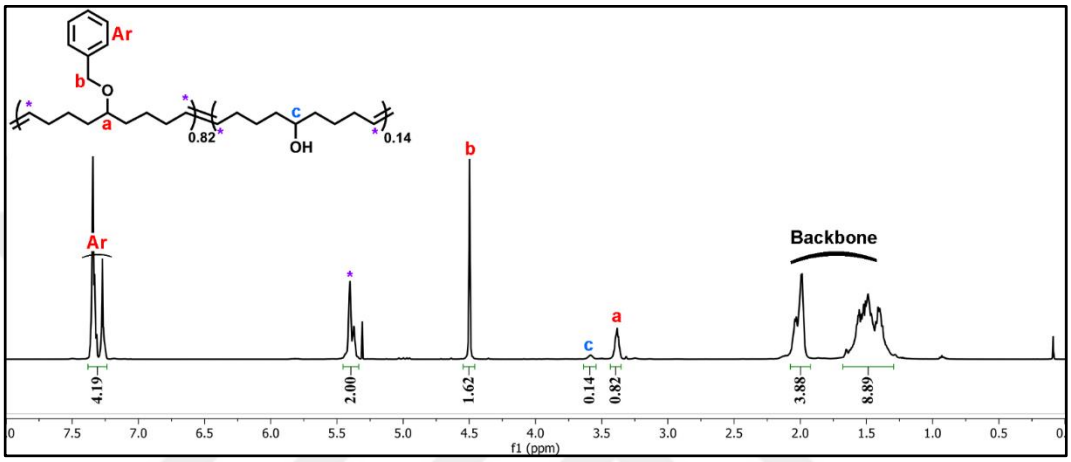


Figure 2.43 : ^{1}H NMR spectrum of P10 (500 MHz).

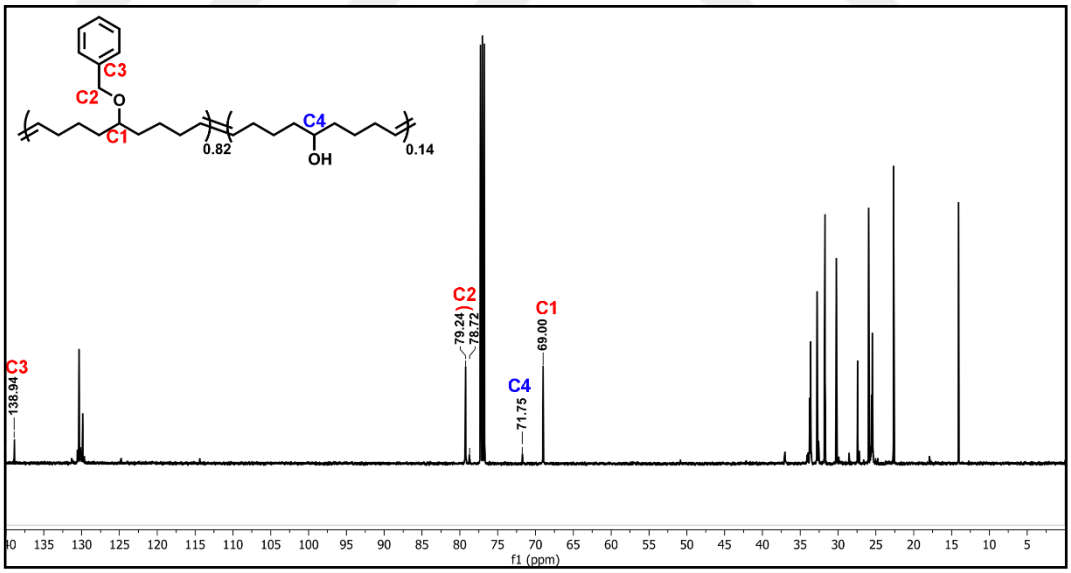


Figure 2.44 : ^{13}C NMR spectrum of P10 (125 MHz).

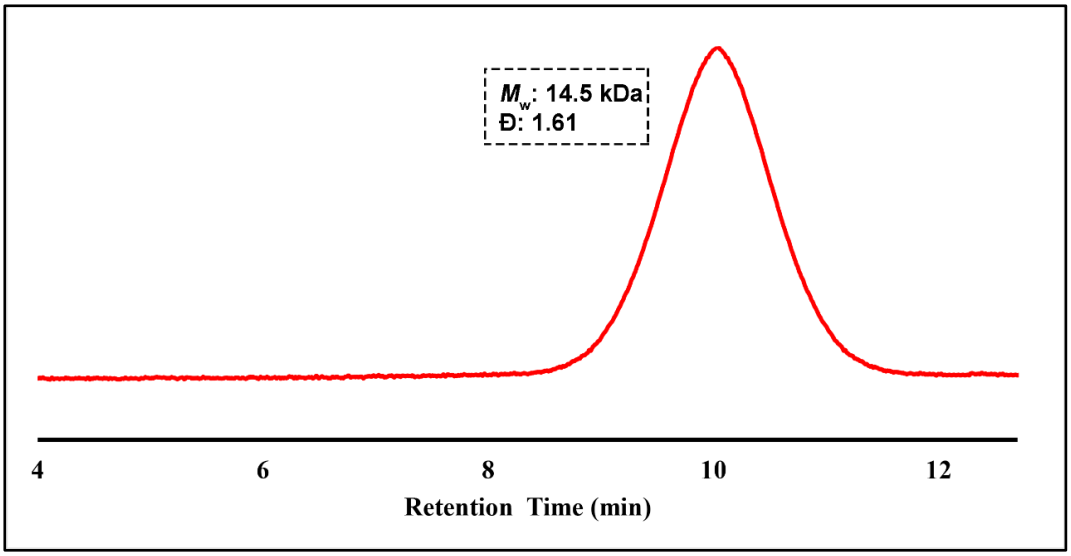


Figure 2.45 : GPC trace of P10.

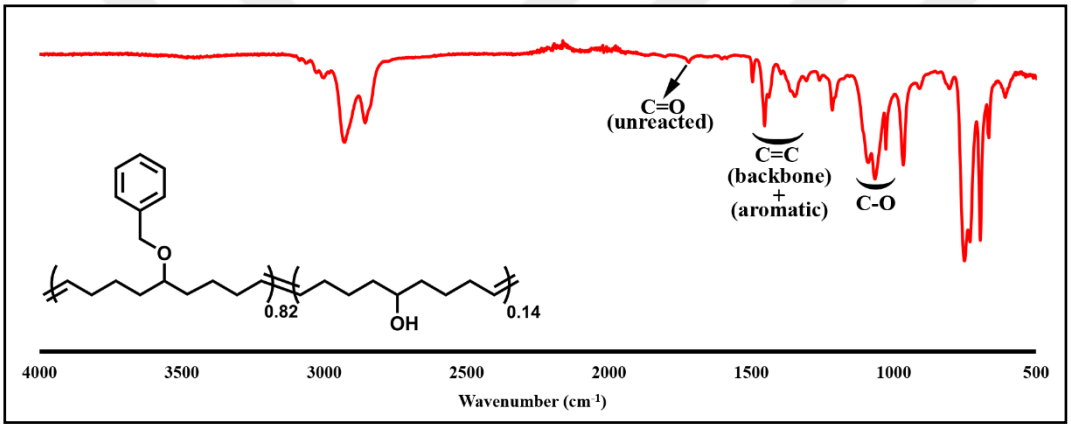


Figure 2.46 : FT-IR spectrum of P10.

2.4.3.15 Synthesis of P11 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. 9-fluorenemethanol (0.72 mmol, 142 mg) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield the final P11 as a yellow sticky solid. (Yield= 74 mg, 71%). ^{1}H NMR ($CDCl_3$, δ) 7.77-7.68, 7.35-7.31 (d, d- 8H, $CHOCH_2CH(C_6H_4)_2$), 5.41 (m, 2H, C*H*=C*H*), 4.15 (s, 2H, $CHOCH_2CH(C_6H_4)_2$), 3.70, (s, 2H, $CHOCH_2CH(C_6H_4)_2$) 3.59 (s, 1H, C*H*OH), 2.00 (m, 4H, main backbone), 1.66-1.31 (m, 8H, main

backbone).[13]C NMR ($CDCl_3$, δ) 145.27, 141.22, 130.37, 127.31, 126.80, 125.42, 119.77, 79.86, 79.41, 71.64, 65.21, 48.59, 32.78, 29.69, 27.44, 25.35.

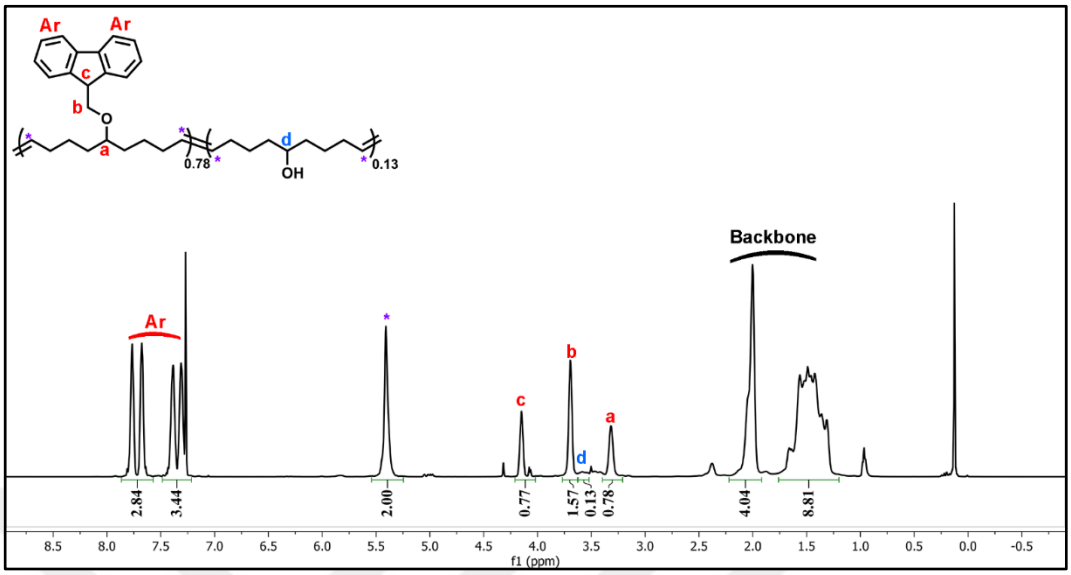


Figure 2.47 : [1]H NMR spectrum of P11 (500 MHz).

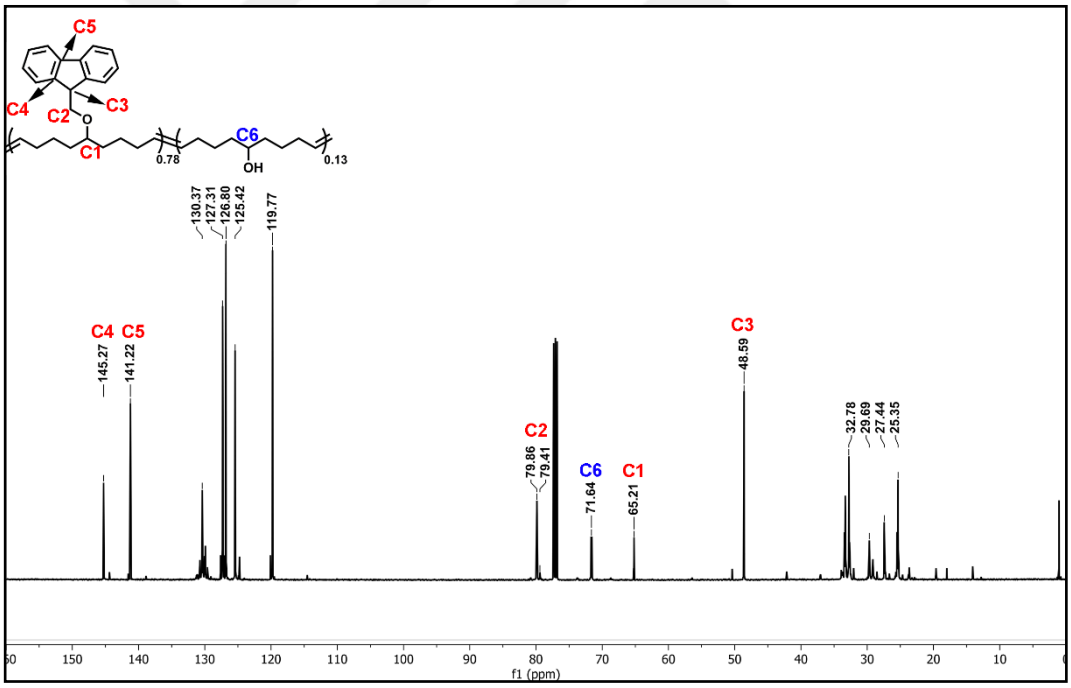


Figure 2.48 : [13]C NMR spectrum of P11 (125 MHz).

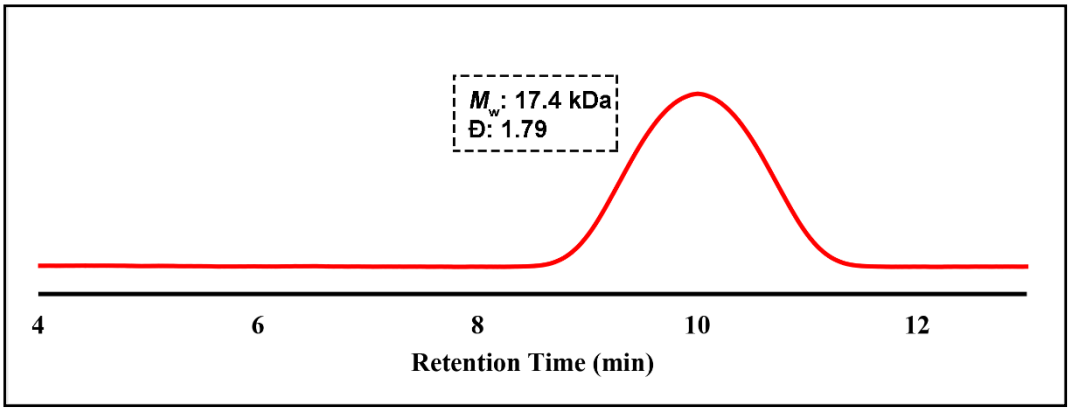


Figure 2.49 : GPC trace of P11.

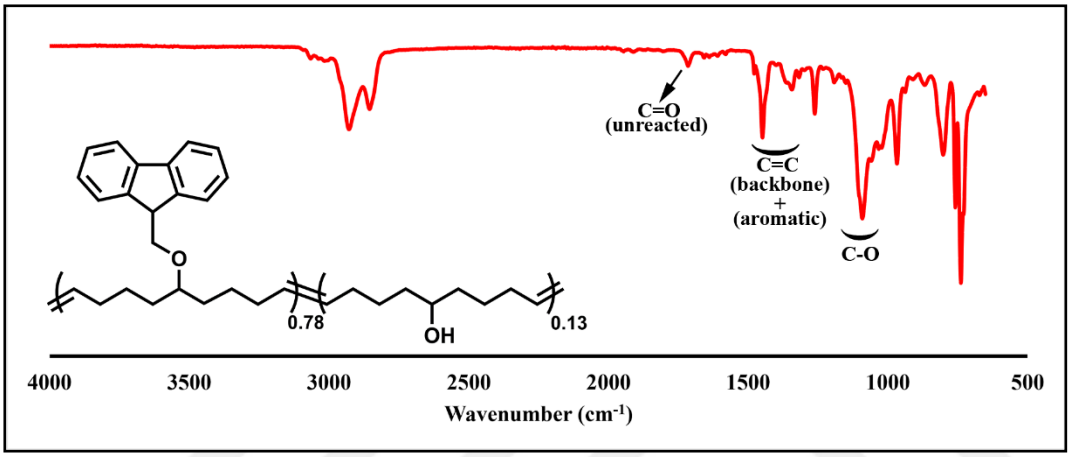


Figure 2.50 : FT-IR spectrum of P11.

2.4.3.16 Synthesis of P12 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. Isopropyl alcohol (0.72 mmol, 55.5 µL) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield final P12 as a transparent sticky solid. (Yield= 46 mg, 70%). ^{1}H NMR ($CDCl_3$, δ) 5.40 (m, 2H, C*H*=C*H*), 3.59 (s, 2H, C*H*OH and CHOC*H*$(CH_3)_2$), 3.25 (s, 1H, C*H*OCH$(CH_3)_2$), 1.98 (m, 4H, main backbone), 1.42-1.38 (m, 8H, main backbone), 1.12. (m, 6H, CHOCH(C*H*$_3)_2$). ^{13}C NMR ($CDCl_3$, δ) 130.35, 76.70, 71.72, 69.39, 34.36, 32.81, 27.45, 25.56, 22.91.

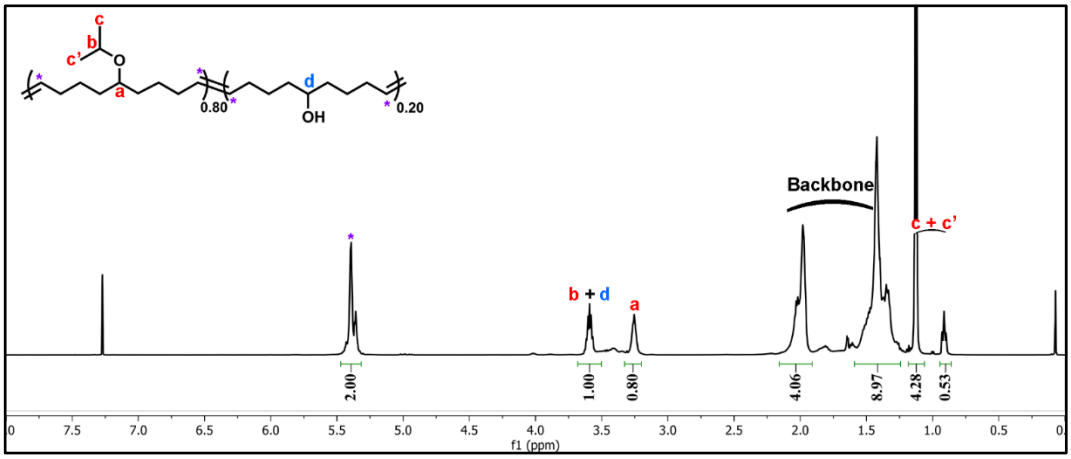


Figure 2.51 : ^{1}H NMR spectrum of P12 (500 MHz).

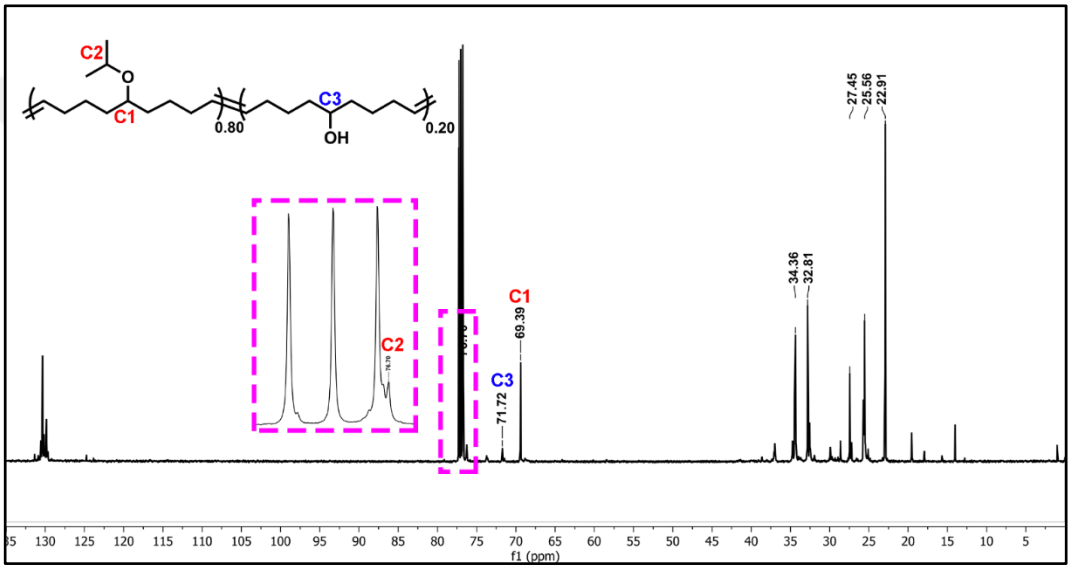


Figure 2.52 : ^{13}C NMR spectrum of P12 (125 MHz).

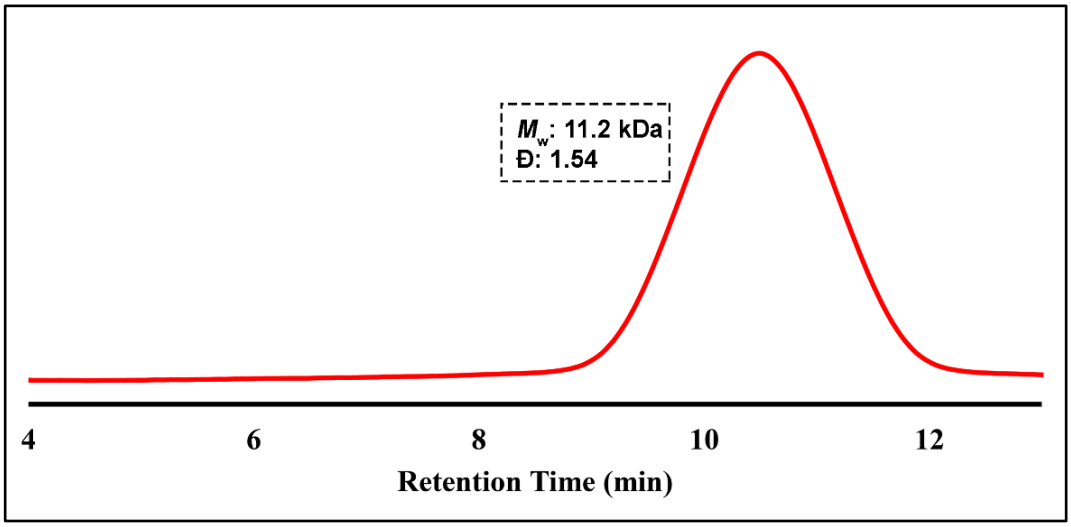


Figure 2.53 : GPC trace of P12.

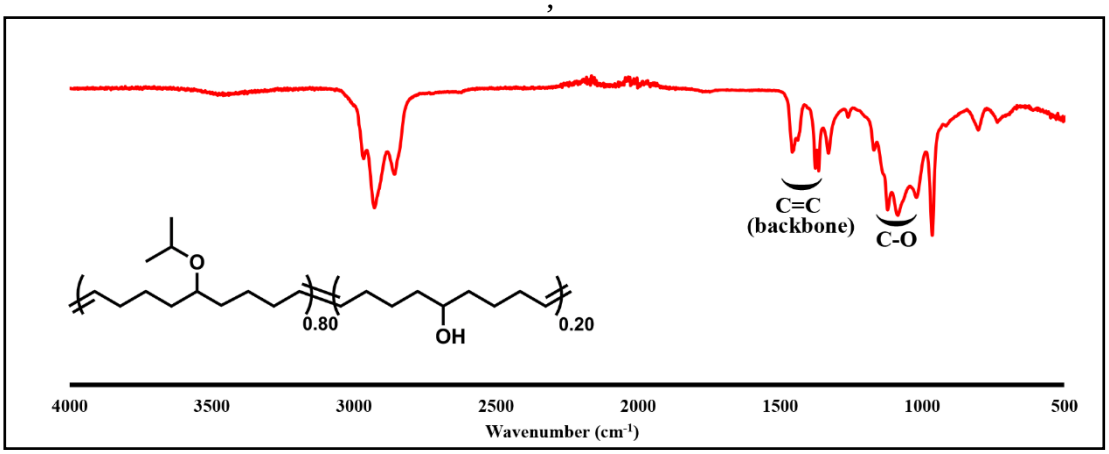


Figure 2.54 : FT-IR spectrum of P12.

2.4.3.17 Synthesis of P13 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. Cyclohexanol (0.72 mmol, 280 mg) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P13 as a transparent sticky solid. (Yield= 60 mg, 74%). ^{1}H NMR ($CDCl_3$, δ) 5.40 (m, 2H, C*H*=C*H*), 3.61 (s, 1H, C*H*OH), 3.32 (s, 1H, CHOC*H*-cyclohexyl), 3.31 (s, 1H, C*H*OCH-cyclohexyl), 2.38 (m, 4H, $CH_2C{=}OCH_2$), 1.98-1.38 (m, 22H, main backbone and cyclohexyl). ^{13}C NMR ($CDCl_3$, δ) 130.36, 76.49, 75.80, 72.12, 34.48, 33.28, 29.64, 27.48, 25.84, 24.58.

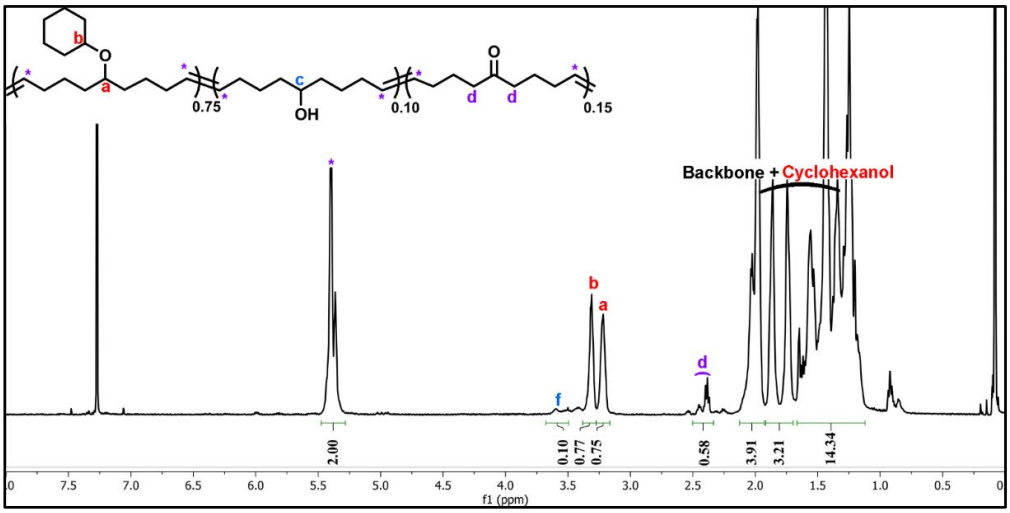


Figure 2.55 : ^{1}H NMR spectrum of P13 (500 MHz).

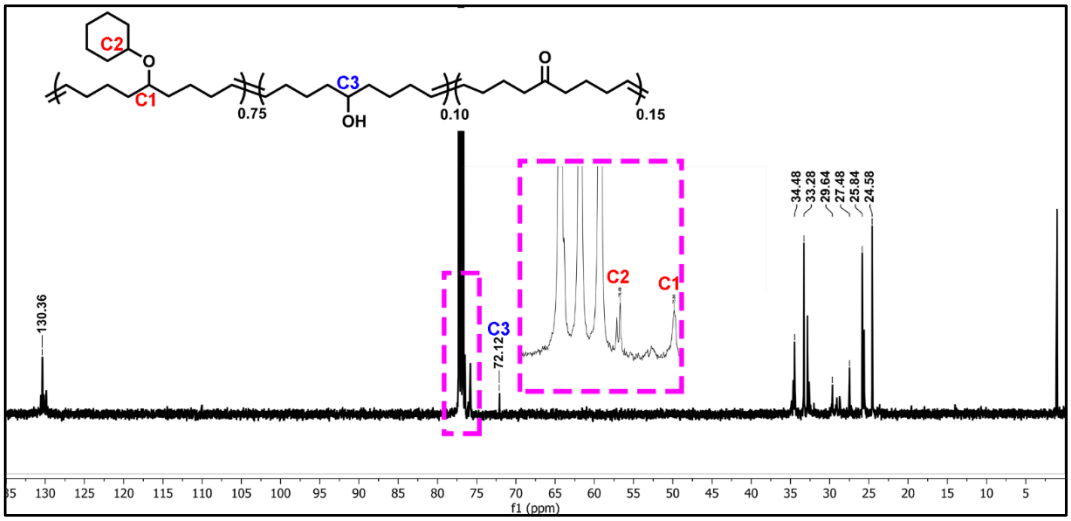


Figure 2.56 : ^{13}C NMR spectrum of P13 (125 MHz).

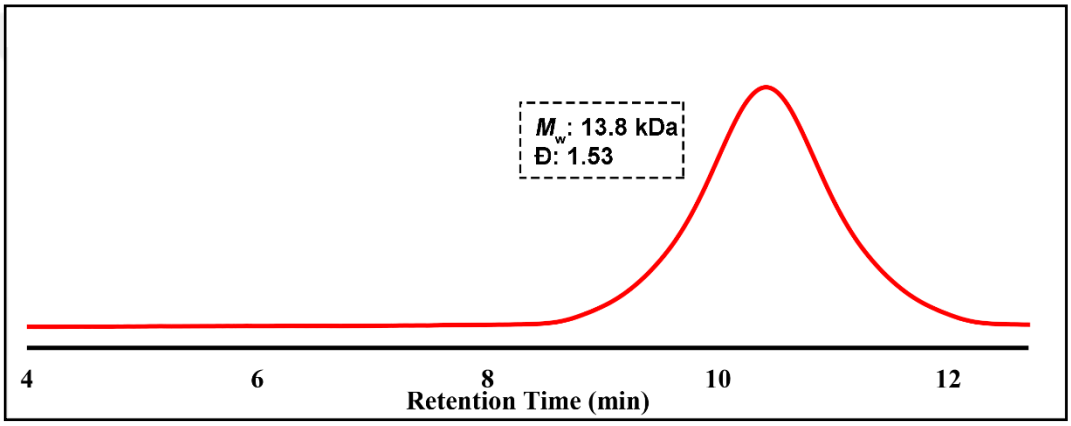


Figure 2.57 : GPC trace of P13.

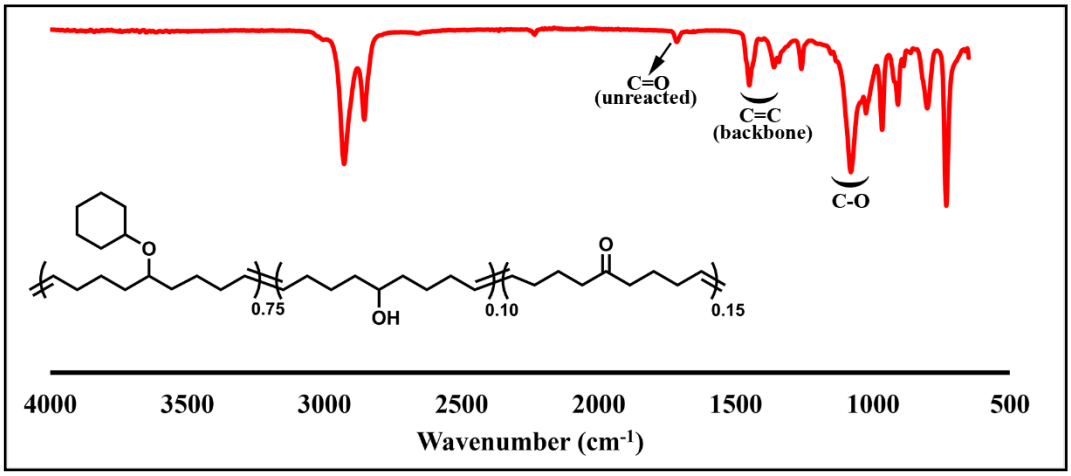


Figure 2.58 : FT-IR spectrum of P13.

2.4.3.18 Synthesis of P14 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer

solution. (-)-Menthol (0.72 mmol, 112 mg) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P14 as a white sticky solid. (Yield= 66 mg, 66%). ^{1}H NMR ($CDCl_3$, δ) 5.40 (m, 2H, C*H*=C*H*), 3.60 (s, 1H, C*H*OH), 3.32 (s, 1H, CHOC*H*-menthyl), 3.31 (s, 1H, C*H*OCH-menthyl), 2.38 (m, 4H, CH_2C=OCH_2), 1.99 (m, 4H, main backbone) 1.63-0.76 (m, 24H, main backbone and menthyl). ^{13}C NMR ($CDCl_3$, δ) 211.11, 130.34, 76.50, 76.19, 71.75, 48.68, 41.80, 34.56, 31.66, 24.74, 22.47, 21.43, 16.04.

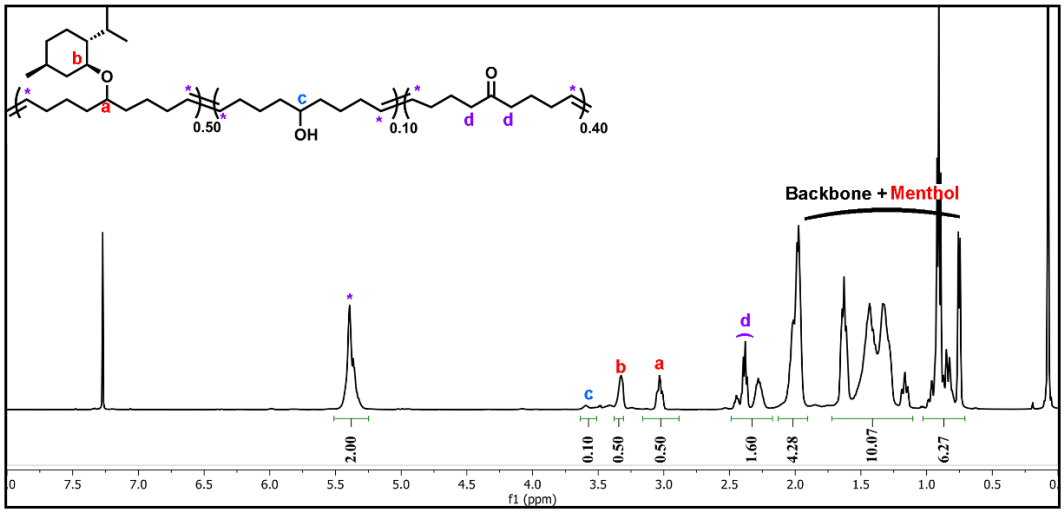


Figure 2.59 : ^{1}H NMR spectrum of P14 (500 MHz).

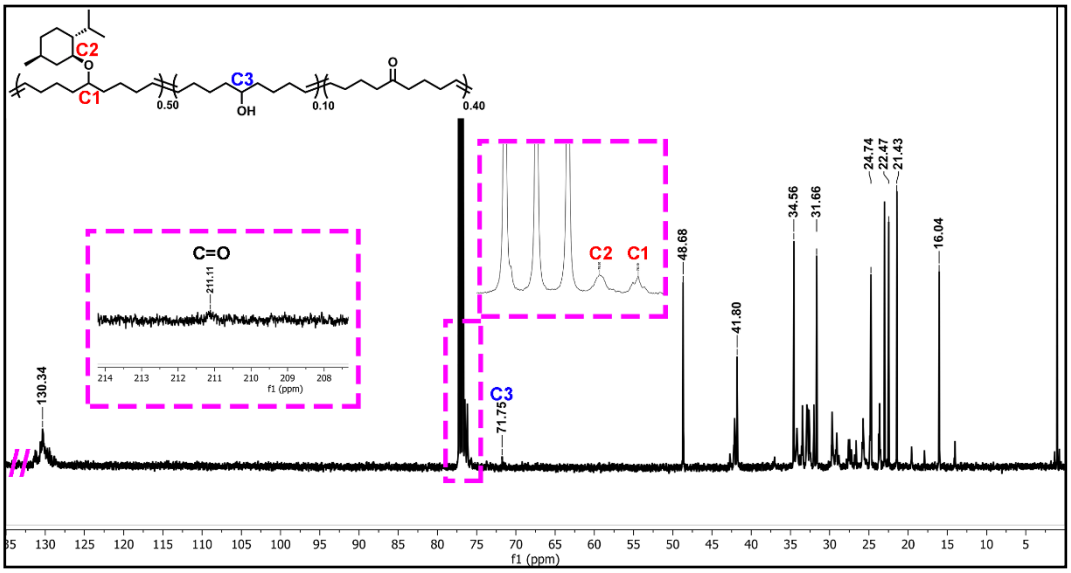


Figure 2.60 : ^{13}C NMR spectrum of P14 (125 MHz).

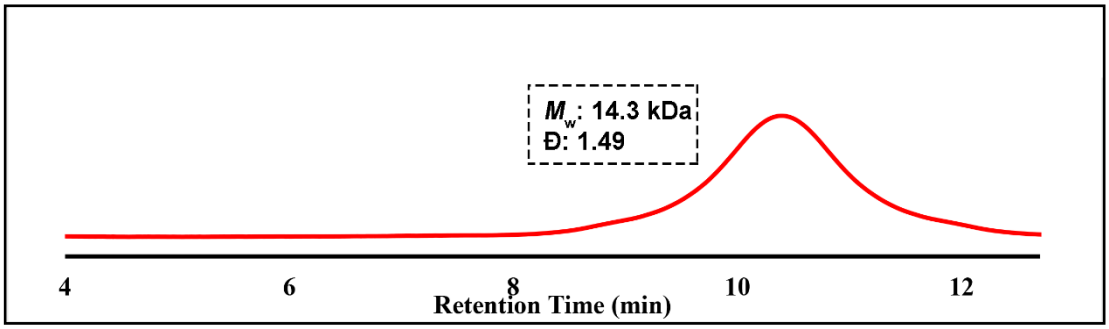


Figure 2.61 : GPC trace P14.

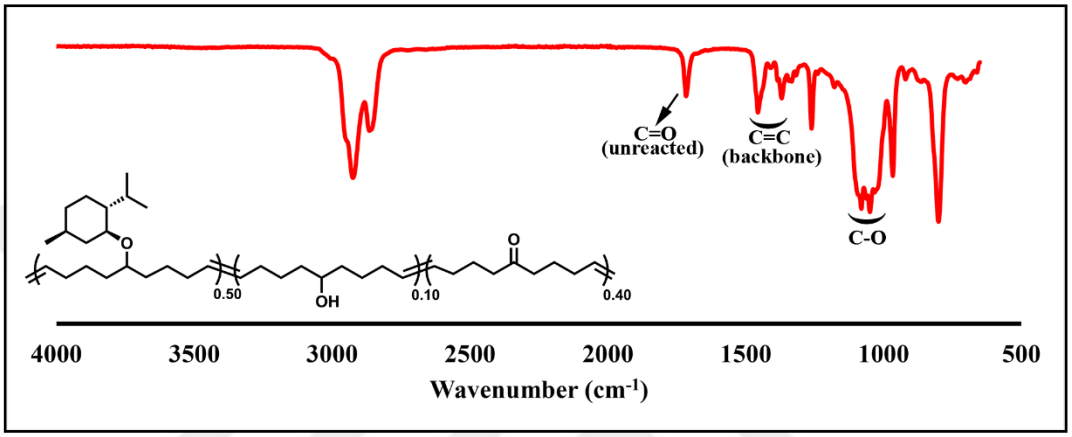


Figure 2.62 : FT-IR spectrum of P14.

2.4.3.19 Synthesis of P15 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. Cholesterol (0.72 mmol, 280 mg) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P15 as an off-white sticky solid. (Yield= 118 mg, 64%). ^{1}H NMR ($CDCl_3$, δ) 5.40 (m, 2H, C*H*=C*H*, C=C*H*-cholesteryl), 3.60 (s, 1H, C*H*OH), 3.31 (m, 1H, CHOC*H*-cholesteryl), 3.13 (s, 1H, C*H*OCH-cholesteryl), 2.38 (m, 4H, $CH_2C{=}OCH_2$), 1.98-0.68 (m, main backbone and cholesteryl). ^{13}C NMR ($CDCl_3$, δ) 210.99, 141.41, 130.35, 121.27, 77.41, 76.93, 71.69, 56.81, 50.27, 42.33, 39.52, 28.01, 22.82, 18.73, 11.87.

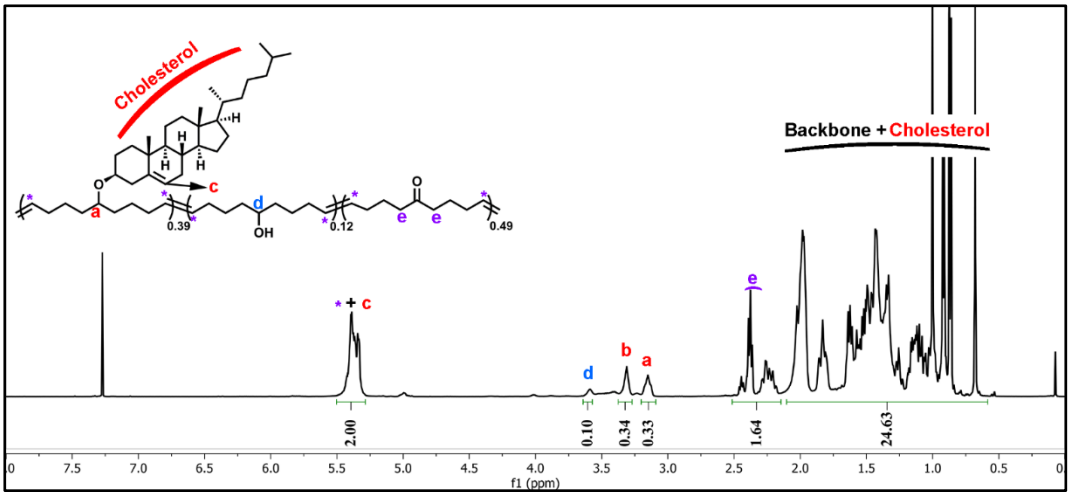


Figure 2.63 : ^{1}H NMR spectrum of P15 (500 MHz).

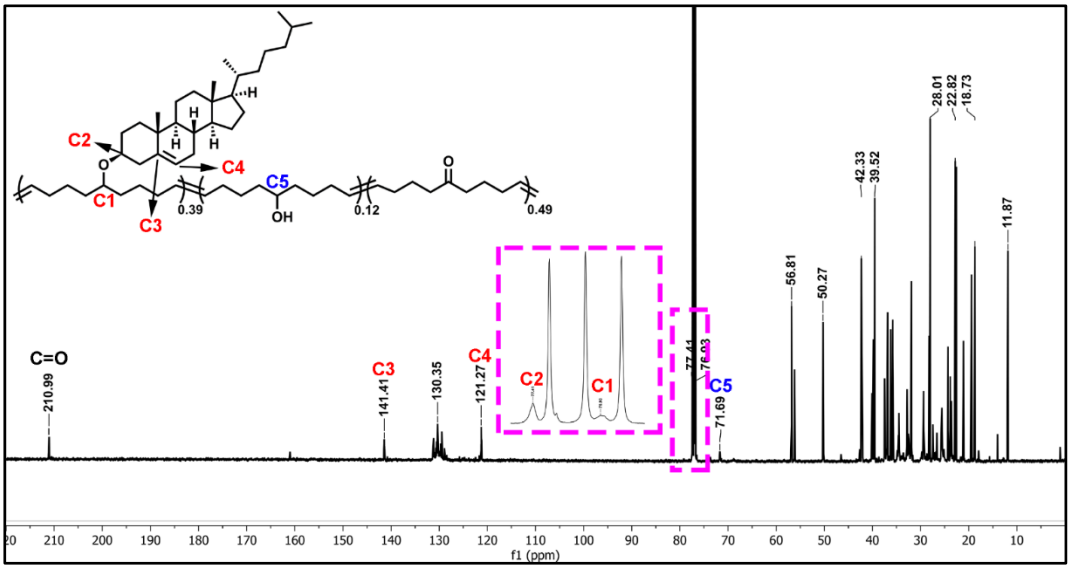


Figure 2.64 : ^{13}C NMR spectrum of P15 (125 MHz).

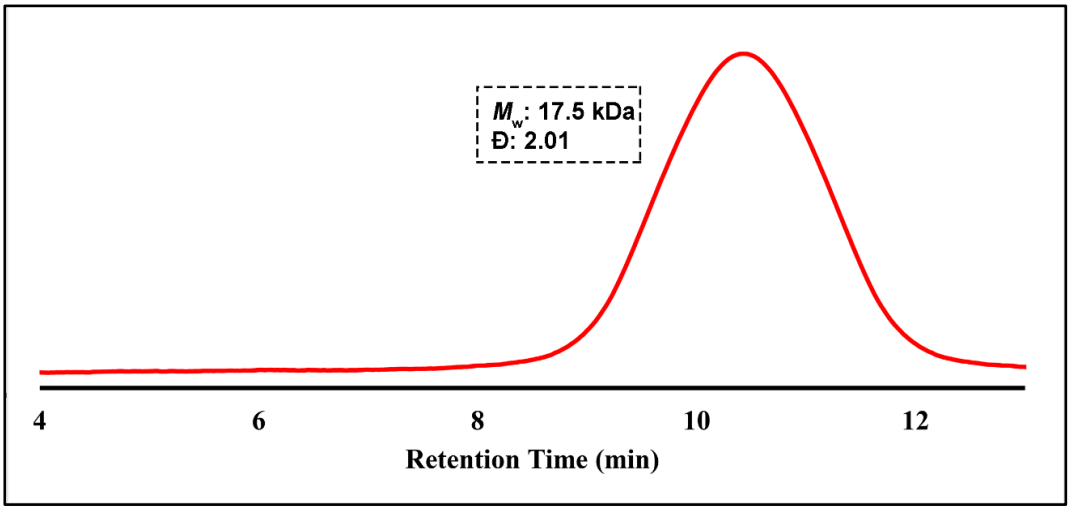


Figure 2.65 : GPC trace of P15.

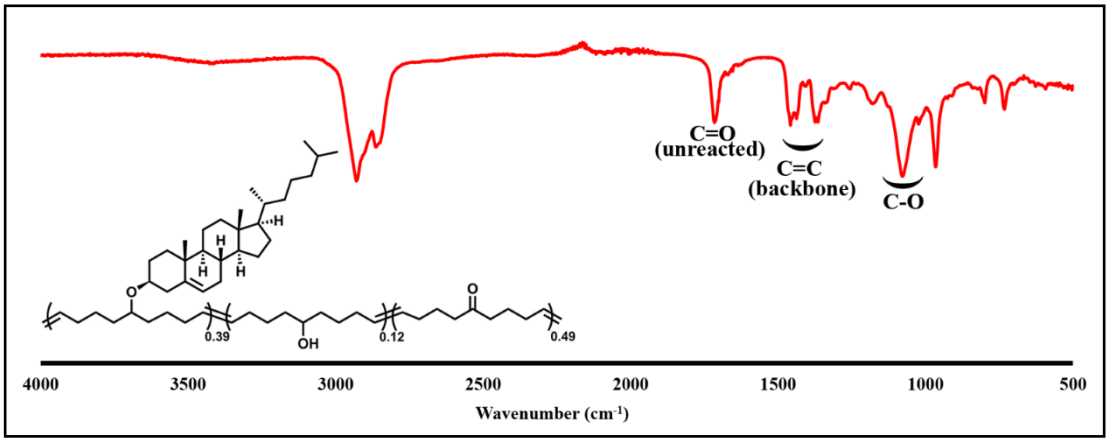


Figure 2.66 : FT-IR spectrum of P15.

2.4.3.20 Synthesis of P16 via RER

50 mg polyketone (P0, 0.36 mmol) was placed to a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. *tert*-Butanol (0.72 mmol, 69.3 µL) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with 2 mL of CH_2Cl_2 and precipitated into 30 mL of methanol and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-methanol) was repeated two times to yield P16 as a transparent sticky solid. (Yield= 31 mg, 44%). ^{1}H NMR ($CDCl_3$, δ) 5.40 (m, 2H, C*H*=C*H*), 3.60 (s, 1H, C*H*OH), 1.99 (m, 4H, main backbone), 1.72-1.26 (m, 8H, main backbone). ^{13}C NMR ($CDCl_3$, δ) 208.20, 130.41, 71.65, 36.85, 32.51, 27.18, 25.55.

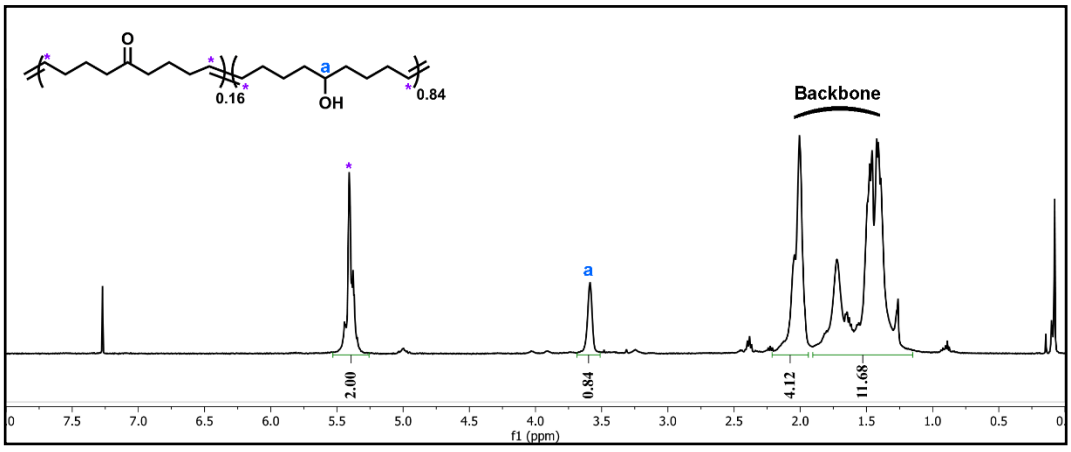


Figure 2.67 : ^{1}H NMR spectrum of P16 (500 MHz).

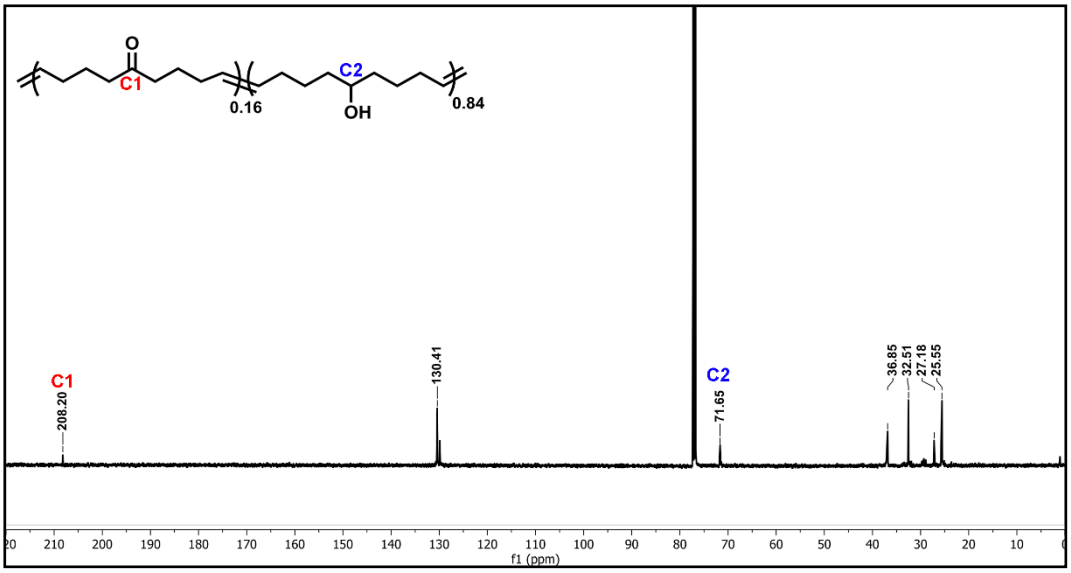


Figure 2.68 : ^{13}C NMR spectrum of P16 (125 MHz).

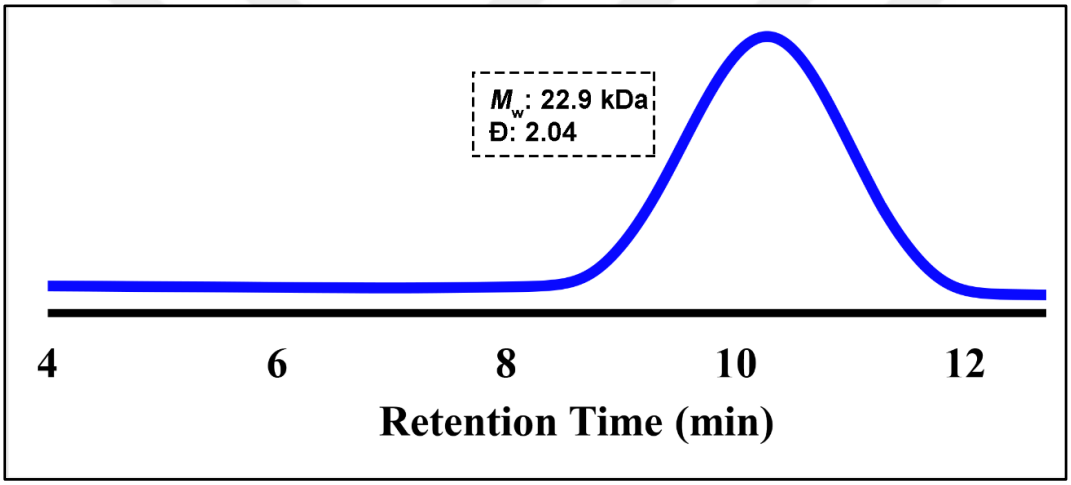


Figure 2.69 : GPC trace of P16.

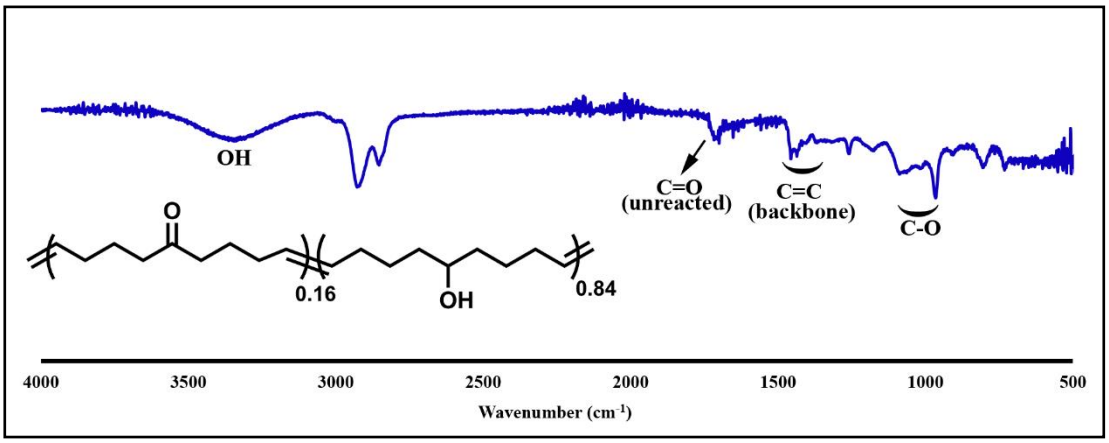


Figure 2.70 : FT-IR spectrum of P16.

2.4.3.21 Synthesis of P17 via RER

P0 (50 mg, 0.36 mmol) was placed in a 10 mL round-bottom flask and dissolved in 1 mL of CH_2Cl_2 at room temperature, then 1 mL of CH_3NO_2 was added to this polymer solution. Monomethoxy PEG_{550} (0.72 mmol, 398 mg) and CDMS (1.44 mmol, 161.0 µL) were then added to the reaction medium, respectively and the reaction mixture was stirred at room temperature under nitrogen for 16 h. The reaction mixture was then diluted with CH_2Cl_2 and extracted with water. The organic layer was thoroughly washed with water, organic phases dried over anhydrous Na_2SO_4 and the solvent was concentrated under reduced pressure. Finally, P17 was precipitated into 30 mL of diethyl ether and the solvent was decanted. The dissolution-precipitation procedure (CH_2Cl_2-diethyl ether) was repeated two times to yield P17 as an off-white sticky solid. (Yield= 166 mg, 68%). ^{1}H NMR ($CDCl_3$, δ) 5.39 (m, 2H, C*H*=C*H*), 3.65 (m, 29H, CH_2 of PEG and C*H*OH), 3.38 (s, 3H, PEG-OC*H*$_3$), 3.24 (b, 1H, C*H*O-PEG), 2.38 (m, 4H, $CH_2C{=}OCH_2$), 1.99 (m, 4H, main backbone), 1.52-1.38 (m, 8H, main backbone). ^{13}C NMR ($CDCl_3$, δ) 211.02, 130.26, 79.87, 72.74, 71.84, 70.23, 68.78, 61.50, 58.94, 33.51, 32.65, 27.32, 25.42.

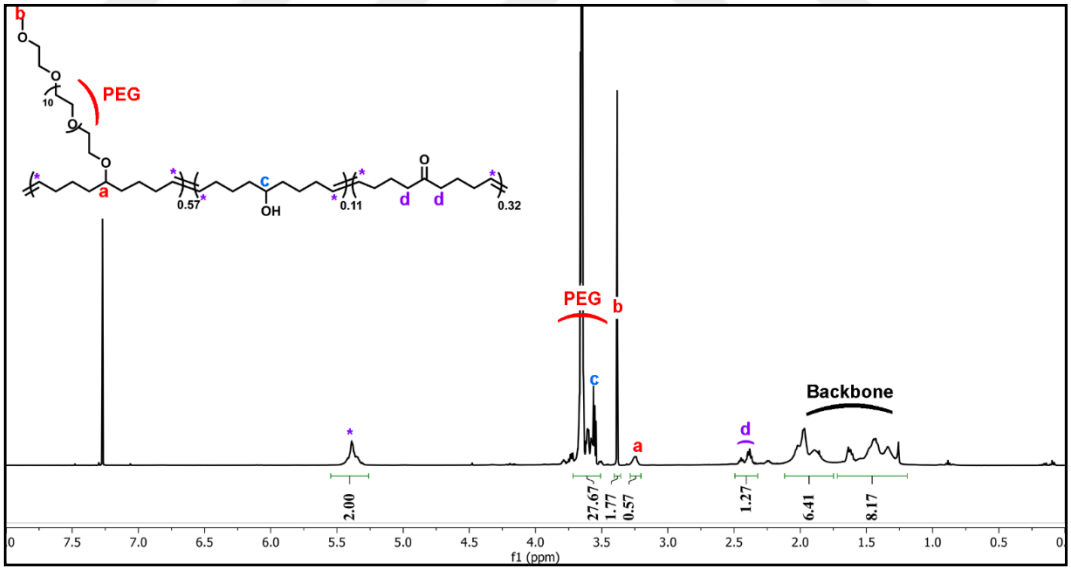


Figure 2.71 : ^{1}H NMR spectrum of P17 (500 MHz).

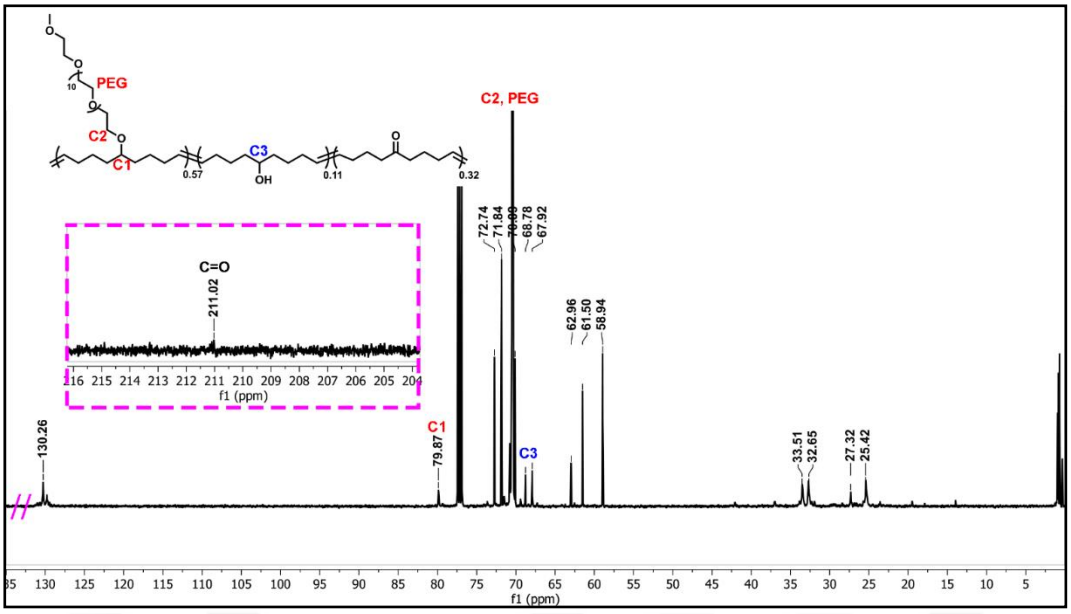


Figure 2.72 : ^{13}C NMR spectrum of P17 (125 MHz).

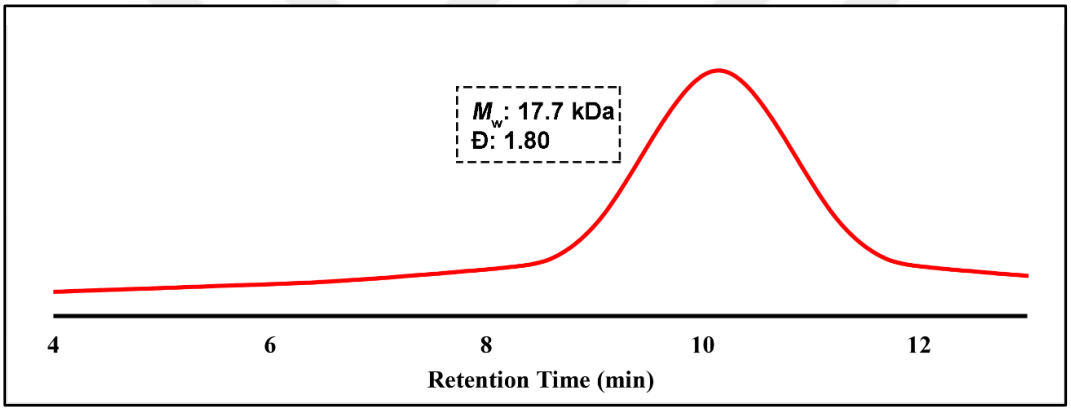


Figure 2.73 : GPC trace of P17.

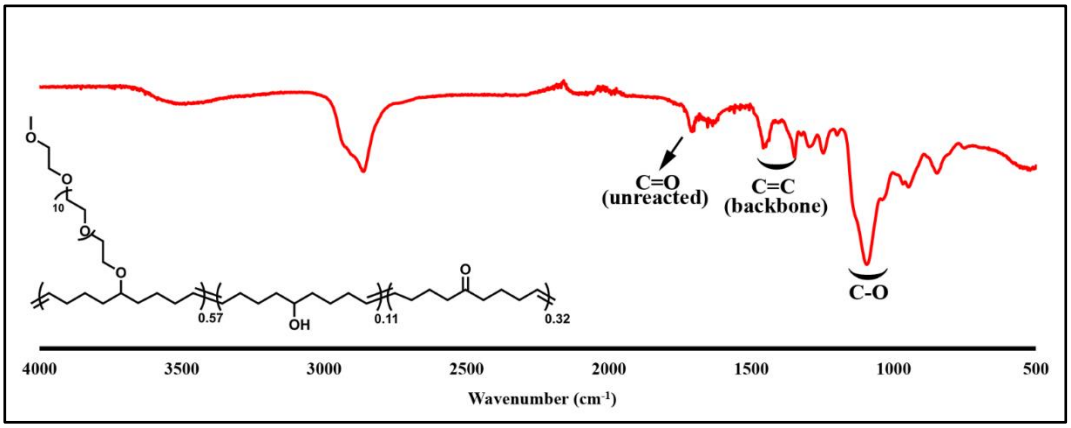


Figure 2.74 : FT-IR spectrum of P17.

3. CHLORODIMETHYLSILANE-MEDIATED REDUCTIVE ETHERIFICATION REACTION : A ROBUST METHOD FOR POLYETHER SYNTHESIS[2]

3.1 Introduction

Polyethers are special classes of polymer chemistry and are extensively used on both scientific and industrial scales. The characteristic property of polyethers is due to the C-O-C bond located in the main and/or in the side chain, which provides polymers with high flexibility and facile processability below the degradation temperature [45-58]. Thus, it is not surprising that they have been used in a wide range of applications ranging from biomedical fields to material science [59-65]. Polyethers are mostly synthesized by ionic (i.e. anionic and cationic) polymerization methods. Hence, in addition to the limited range of applicable monomers, harsh reaction conditions are required in polymerization processes to maintain the reactivity of the ionic species produced to allow the polymerizations to proceed smoothly [45-52]. Besides, since various functional groups such as alkene, alkyne, acrylate, maleimide, etc. are generally incompatible with the ionic polymerization methods, it is necessary to protect the monomers carrying these groups before the polymerization, or these functional groups should be added to the polymer after the polymerization. Given this information, it is clear that facile routes to produce polyethers are desired in terms of synthetic polymer chemistry.

The reductive etherification reaction (RER) is a convenient method to produce both symmetrical and unsymmetrical ethers through a coupling reaction between aldehydes and ketones with alcohols in the presence of organosilane compounds, which are used as the reducing agent, together with a variety of Bronsted and Lewis acid catalysts. The first studies on ether synthesis via RER were reported by Doyle and co-workers in the early 1970s [21, 23, 24]. Various symmetrical and unsymmetrical ethers were

[2] This chapter is based on the paper 'Luleburgaz, S., Hizal, G., Tunca, U. and Durmaz, H. (2022), Chlorodimethylsilane-Mediated Reductive Etherification Reaction: A Robust Method for Polyether Synthesis. Macromolecules 55 (5), 1533-1543. DOI: 10.1021/acs.macromol.2c00051'

synthesized in good yields in these studies, whereby harsh acidic conditions were required. Following these seminal studies, many improvements have been made by various groups to synthesize ethers via RER under milder conditions while maintaining high product yields [27, 31-34, 66-70]. The RER chemistry was first applied at the macromolecular level thanks to successive studies by Yokozawa and coworkers starting in the mid of 1990s. In the group's first study, isophtaldehyde was underwent a self-condensation polymerization reaction in CH_2Cl_2 using triethylsilane (Et_3SiH) as the reducing agent and trityl perchlorate as the catalyst. The polymerization reactions were able to conduct at 0 ℃ or below to prevent side reactions such as cross-linking, and low to moderate molecular weight polymers were obtained in 24 h in moderate yields [35]. As an extension of their previous work, the group synthesized polyethers that proceeded in an alternating fashion using dialdehydes and bis(trimethylsilyl)ethers under the same conditions described in their first study. The authors pointed out that bulky silanes were essential reducing agents to maintain alternating progress, as aliphatic silanes promoted self-condensation polymerization of dialdehydes [71]. Also, the group explored the three-component polycondensation reaction of dialdehydes, bis(trimethylsilyl)ethers, and various silyl nucleophiles to produce polyethers having varying pendant groups, such as allyl [36], cyano [72], and propargyl [73]. In each attempt, the precursor monomer ratios in the resulting polymers were found to be very close to the feeding ratios, which indicated the formation of polyethers that proceeded in an alternating fashion. It is worth to mention here that two things were clear in all these polymerizations: 1) The obtained molecular weights were low or moderate. 2) The alcohols used in polymerizations were in protected form, i.e. alkoxysilane. Our group's interest in RER has started with an elegant work reported by Lee and Morandi [38]. The authors revealed that chlorodimethylsilane (CDMS), a halogenated silane compound with both reducing and Lewis acid properties, could mediate RER between ketones and alcohols to afford unsymmetrical ethers. This dual property of CDMS, on the other hand, provides a clear advantage in reactions when compared to other organosilanes in terms of operational simplicity and applicability. More recently, our group employed CDMS-mediated RER at the macromolecular level for the first time. In this study, a polyketone platform was synthesized by acyclic diene metathesis (ADMET) polymerization and reacted with a series of structurally different alcohols via CDMS-mediated RER, resulting in the formation of polymers with various pendant alkoxy structures. It was found the

primary alcohols delivered the corresponding alkoxy pendant polymers in high RER efficiency (up to 90 %), a similar high- efficiency trend was also observed in the case of secondary alcohols (up to 80 %), and no reaction was observed when a *tert*-alcohol was used. It should be noted here that the formation of free hydroxyl functional polymers was inevitable during RERs due to the direct reduction of the ketone carbonyl to the secondary alcohol in the presence of excess amounts of CDMS in the reactions. We hypothesized that CDMS-mediated RER may also be a suitable and viable method for the preparation of linear polyethers, enabling the direct use of unprotected alcohols in polymerizations. To further demonstrate the versatility of RER chemistry, in the current study, a wide range of diols were reacted with terephthalaldehyde (TPA) (and its isomers) in the presence of CDMS through a step-growth polymerization technique, yielding polyethers with different chemical backbones (Figure 3.1).

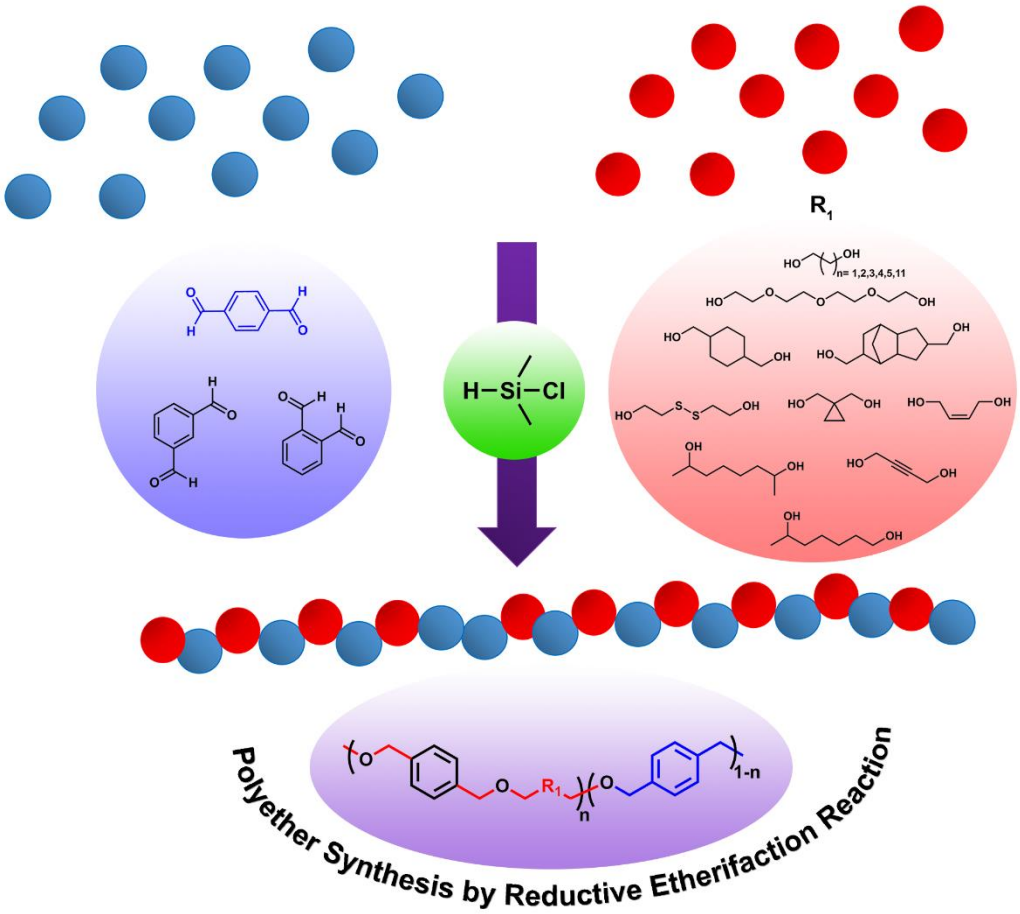


Figure 3.1 : Graphical abstract for chapter 2.

3.2 Results and discussion

Optimization of the reaction conditions for polyether (P1) synthesis via RER was carried out in multiple aspects (Figure 3.2). During these studies, TPA and BD were chosen as model monomers and the reactions proceeded 24 h at room temperature.

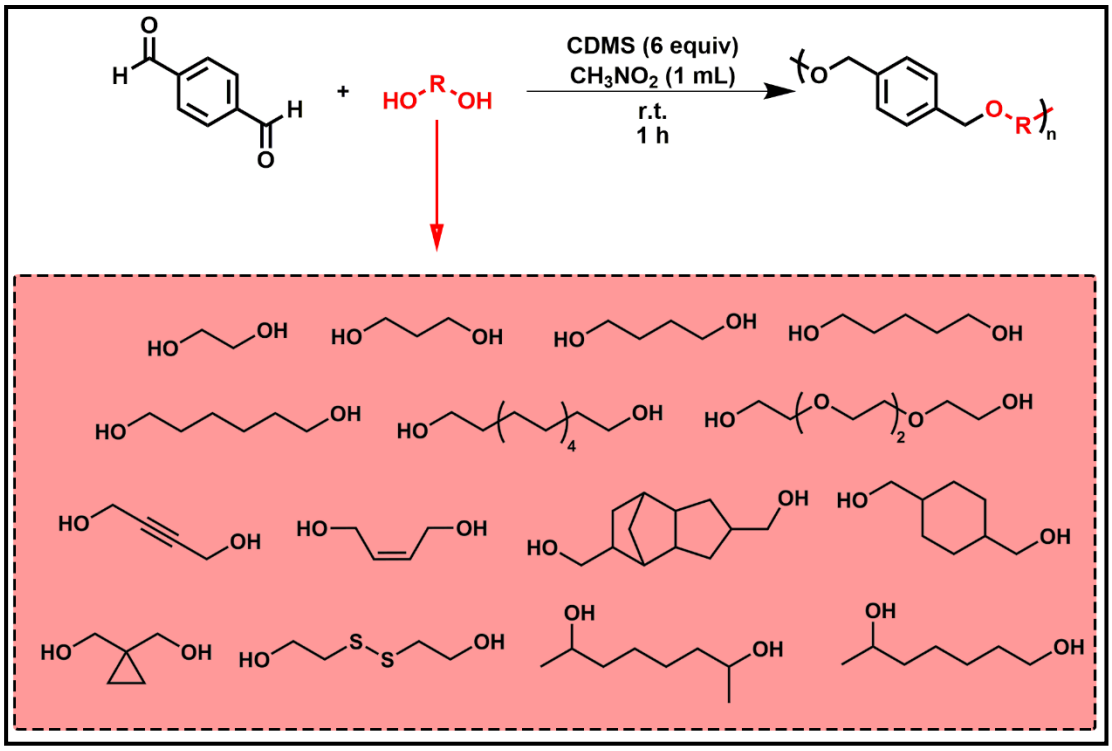


Figure 3.2 : Synthetic route for the synthesis of polyethers via CDMS-mediated RER.

Firstly, the equivalent optimization study for TPA, BD, and CDMS was studied and the results are summarized in Table 3.1. We previously reported that CH_3NO_2 was the essential solvent for CDMS-mediated RER, and excess amounts of CDMS were required for high RER efficiency. Hence, in the first attempt equimolar amounts of TPA and BD were reacted in 1 mL of CH_3NO_2 using 4 equiv of CDMS. The molecular weight of the resulting polyether (P1) was found to be 16.6 kDa (run 1, Table 1). When CDMS amount was decreased to 3 equiv, the molecular weight was found to be 10.0 kDa (run 2, Table 1). Increasing CDMS to 6 equiv resulted in an increase in the molecular weight to 25.4 kDa (run 3, Table 1), but no significant change was found in the molecular weight (M_w = 26.7 kDa, run 4, Table 1) with a further increase of CDMS (7.5 equiv). From the results obtained, the optimum molar equivalent of CDMS was considered to be 6 with respect to the monomers. Additionally, a slight decrease in the molecular weight (M_w = 22.0 kDa) was observed when the amount of CH_3NO_2 was

doubled (run 5, Table 1) and no significant change in the molecular weight (M_w = 25.6 kDa) was observed when its amount was reduced by half (run 6, Table 1). It should be noted here that in all the above-mentioned studies when CH_3NO_2 was added to the mixture, an exothermic reaction occurred and the reaction medium became a slurry within a few minutes and remained the same during the progress of the polymerization.

Table 3.1 : The effect of organosilanes on polymerization[a]

Run	TPA (equiv)	BD (equiv)	CDMS (equiv)	M_w (kDa)[g]	$Đ$[g]
1	1	1	4	16.6	1.52
2	1	1	3	10.0	1.54
3	1	1	6	25.4	1.56
4	1	1	7.5	26.7	1.71
5[b]	1	1	6	22.0	1.57
6[c]	1	1	6	25.6	1.54
7	1.1	1	6	77.5	1.56
8	1.2	1	6	42.0	1.77
9[d]	1.1	1	6	3.7	1.42
10[e]	1.1	1	6	36.0	1.48
11[f]	1.1	1	6	6.3	1.33
12	1	1.1	6	9.6	1.59

[a]All reactions were carried out using 1 mL of CH_3NO_2 for 24 h at room temperature unless otherwise stated. [b]2 mL of CH_3NO_2 was used. [c]0.5 mL of CH_3NO_2 was used. [d]Reaction was performed at 0 °C [e]Reaction was carried out using an additional 1 mL of DCM. [f]Reaction was performed in bulk. [g]Determined by GPC calibrated based on linear PS standards in THF at 30 °C.

As highlighted in the introduction part, the formation of alcohol segment due to reduction of the carbonyl to alcohol was inevitable during the functionalization of polyketone via CDMS-mediated RERs. Given this information, we hypothesized that if such a reduction occurs, this may lead to a loss at the aldehyde end, which in turn may trigger the self-condensation polymerization of TPA. Thus, when the ^{1}H NMR spectrum (Figure S1) of P1 (run 3, Table 1) was investigated, two different benzylic proton signals were found in the resulting polymer; the one that resonated at 4.49 ppm as a result of the alternating structure, and the signal at 4.54 ppm was due to the self-condensation of TPA. The integral ratios of these signals were found to be 1:0.1, which means that the percentage of ether segment that proceeded in alternating fashion is

around 91%, while the ether segment that proceeded with self-condensation is around 9% in P1. It is evident that the formation of self-condensing segment arises a problem due to the equivalent imbalance between TPA and BD, though relatively high molecular weights were obtained. As such, a new reaction was conducted between TPA and BD in which TPA equiv was increased to 1.1 (run 7, Table 1).

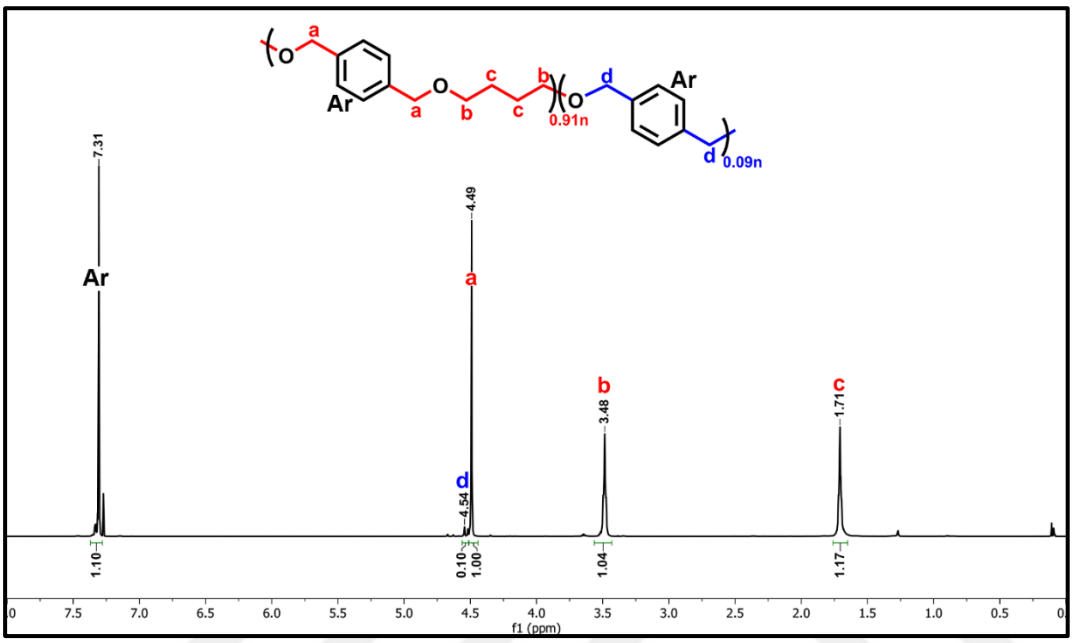
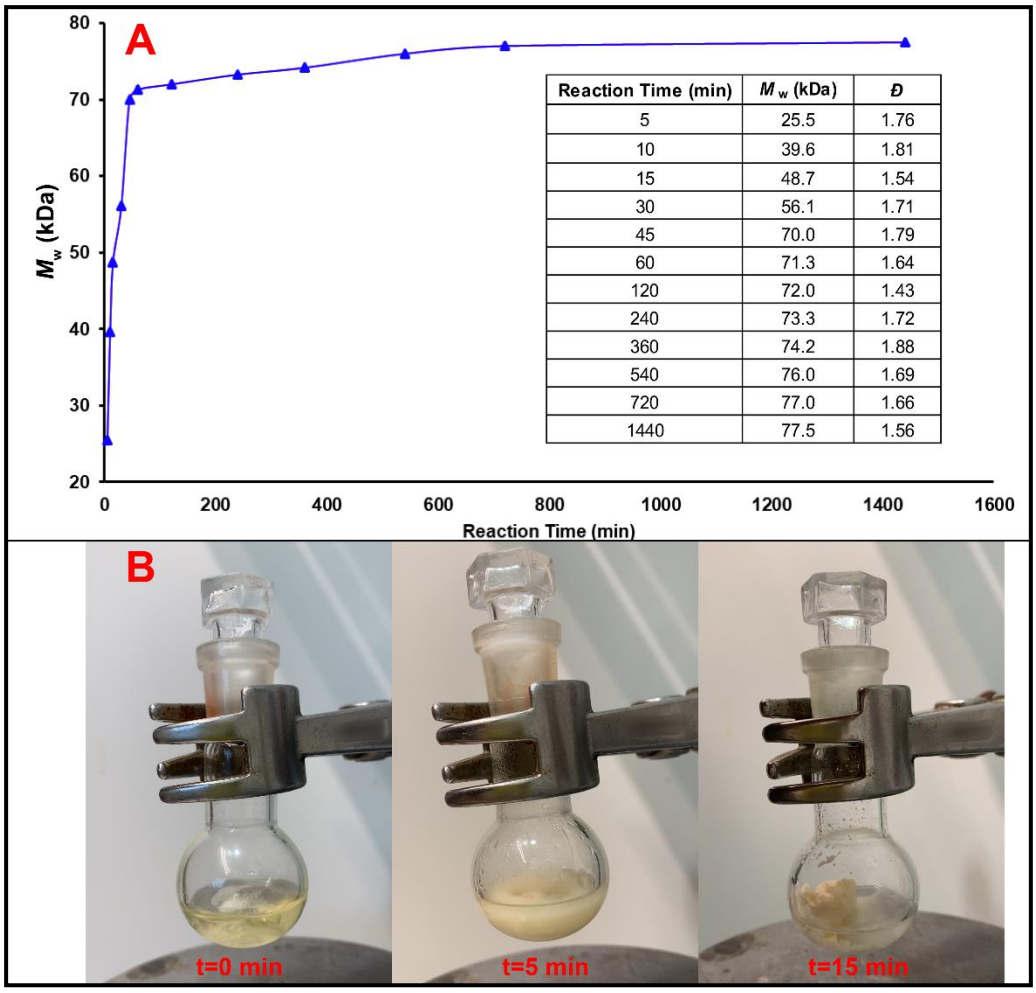


Figure 3.3 : ^{1}H NMR spectrum of P1 (run 3, Table 1) using TPA/BD/CDMS at a mole ratio of 1/1/6 in $CDCl_3$ (500 MHz).

We are delighted to say that a 10% increment in TPA resulted in a tremendous increase in the molecular weight of P1 (M_w = 77.5 kDa). Notably, the polymerization occurred even more exothermic than the aforementioned studies using 1 equiv of TPA. Importantly, a rapid transformation from turbid polymerization medium to the formation of a gum-like polymer was observed within 15 minutes in the reaction medium (Figure 1B). Interestingly, the polymerization process was found not to be adversely affected by this situation (see below for kinetic study). It is worth mentioning here that the percentages of alternating and self-condensing segments (90% and 10%, respectively) were found to be close to the equimolar case by increasing TPA equiv to 1.1, as judged by ^{1}H NMR analysis (Figure 2A), indicating that increasing TPA did not change the percentage of self-condensing segments in the resulting polymer. The results obtained clearly demonstrate that the real stoichiometric balance was achieved when the TPA equivalent was increased to 1.1. Yet, when TPA equiv was increased to 1.2, the molecular weight was found to decrease (M_w = 42.0 kDa), which can be

attributed to a new stoichiometric imbalance between the two monomers (run 8, Table 1). In summary, the ideal equivalents for TPA/BD/CDMS were found to be 1.1/1/6 in 1 mL of CH_3NO_2 and these conditions were used in the next studies. Importantly, when the reaction was performed at 0 °C, a polymer with very low molecular weight (M_w = 3.7 kDa) was obtained, indicating that the reactivity of CDMS is minimized at lower temperatures (run 9, Table 1). Additionally, a relatively high molecular weight polymer (M_w = 36.0 kDa) was obtained when DCM, known as a suitable co-solvent in the RER [34], was used together with CH_3NO_2 (run 10, Table 1). Meanwhile, unlike the studies mentioned above, the reaction medium was initially homogeneous then turned turbid after a few hours, and remained the same until the end of polymerization. Moreover, a low molecular weight (M_w = 6.3 kDa) was obtained from polymerization reaction when no solvent was used (run 11, Table 1), indicating the crucial role of CH_3NO_2 in the proposed polymerization system. Next, the progress of polymerization was monitored by taking samples from the reaction medium at regular intervals to determine the optimum duration for polymerization using the optimized conditions described above, and the results showing molecular weight evolution by time are collected in Figure 1A. It can be seen that the molecular weight increment started early in polymerization and a molecular weight of 25.5 kDa was obtained in 5 min. As emphasized previously, a gum-like polymer was achieved within 15 minutes and the molecular weight of this polymer was found to be 48.7 kDa. The increasing trend in molecular weight in the gummy form continued up to 1 h (M_w = 71.3 kDa), no distinct change was observed up to 24 h (M_w = 77.5 kDa) thereafter. Consequently, the polymerization duration for the proposed strategy was set to 1 h for all the other studies, together with the aforementioned optimized conditions. As highlighted before, RER can take place with many other silane compounds together with Lewis or Bronsted acids. To explore the silane effect on polymerization, different silane compounds and acid sources were examined under the optimized conditions: TPA/BD/organosilane: 1.1/1/6 and 0.1 equiv of an acid catalyst in the presence of 1 mL of CH_3NO_2. Amongst, when Et_3SiH was used together with TfOH, a polyether was obtained with a molecular weight of 37.0 kDa (run 1, Table 2). When the ^1H NMR spectrum of the resulting polymer (Figure S2) was analyzed, the percentages of alternating and self-condensing units were found to be 71% and 29%, respectively.



Reaction Time (min)	M_w (kDa)	Đ
5	25.5	1.76
10	39.6	1.81
15	48.7	1.54
30	56.1	1.71
45	70.0	1.79
60	71.3	1.64
120	72.0	1.43
240	73.3	1.72
360	74.2	1.88
540	76.0	1.69
720	77.0	1.66
1440	77.5	1.56

Figure 3.4 : The molecular weight growth of P1 (run 7, Table 1) vs time via CDMS-mediated RER (**A**). The visual appearance of polymerization medium in different time intervals (**B**).

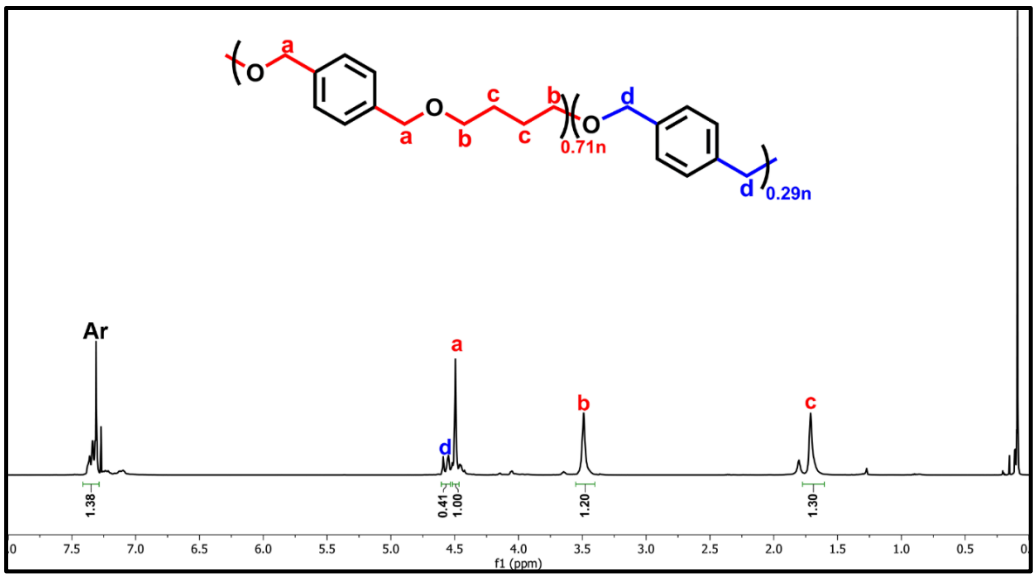


Figure 3.5 : ^{1}H NMR spectrum of P1 (run 1, Table 2) in $CDCl_3$ using TPA/BD/Et_3SiH/TfOH at a mole ratio of 1.1/1/6/0.1 (500 MHz).

Meanwhile, similar to CDMS-mediated RERs, an exothermic reaction occurred and the reaction medium became a slurry during the polymerization. In addition, when Lewis acids were used as a catalyst together with Et_3SiH, no polymer formation was observed (runs 2 and 3, Table 2). When $PhSiH_3$ was used with any acid source, gel formation was observed during the reactions (runs 4-6, Table 2). The reason for gelation might be attributed to acid-catalyzed electrophilic aromatic substitution reactions, leading to cross-linking during the polymerizations [71]. Notably, no polymer product was achieved with any acid sources in the presence of bulky silanes (runs 7-12, Table 2). The reason why a polymeric product could not be obtained is likely due to the amount of silane compounds (6 equiv) used in the reactions, which directly reduce the carbonyl groups of TPA to alcohol before reacting with BD, inhibiting the polymerizations.

Except for the promising result obtained from Et_3SiH/TfOH case, it is evident from the above results that using excess amounts of other silane compounds under the optimized conditions determined in this study is not suitable for producing polyethers; hence, CDMS-mediated RER is still a robust, convenient, and better choice to produce polyether.

Table 3.2 : The effect of organosilanes on polymerization[a]

Run	Organosilane	Catalyst (10%)	M_w (kDa)/$Đ^b$
1	Et_3SiH	TfOH	37.0/1.88
2	Et_3SiH	$BiCl_3$	No Polymerization
3	Et_3SiH	$FeCl_3$	No Polymerization
4	$PhSiH_3$	TfOH	Gelation
5	$PhSiH_3$	$BiCl_3$	Gelation
6	$PhSiH_3$	$FeCl_3$	Gelation
7	Ph_2SiH_2	TfOH	No Polymerization
8	Ph_2SiH_2	$BiCl_3$	No Polymerization
9	Ph_2SiH_2	$FeCl_3$	No Polymerization
10	$Ph(CH_3)_2SiH$	TfOH	No Polymerization
11	$Ph(CH_3)_2SiH$	$BiCl_3$	No Polymerization
12	$Ph(CH_3)_2SiH$	$FeCl_3$	No Polymerization

[a]All reactions were carried out using TPA/BD/organosilane at a mole ratio of 1.1/1/6 in 1 mL of CH_3NO_2 for 1 h at room temperature. [b]Determined by GPC calibrated based on linear PS standards in THF at 30 °C.

Before examining the scope of reactants, P1 was characterized in detail by various spectroscopic measurements. To this end, when ^{1}H NMR was further analyzed, it can be seen that the aromatic protons of P1 are detected at 7.31 ppm and the methylene protons regarding BD at 3.49 and 1.72 ppm (Figure 2A). From the ^{13}C NMR spectrum of P1, it was found the benzylic carbon signals of alternating and self-condensing polyether segments were assigned at 72.64 and 71.82 ppm, respectively. Also, aromatic carbons of P1 were detected at 137.91 and 127.67 ppm, together with the methylene carbons which resonated at 70.12 and 26.53 ppm (Figure 2B). Lastly, the GPC chromatogram of P1 showed a monomodal distribution curve with a polydispersity index of 1.64, which is an indication of smooth polymerization via RER (Figure S3).

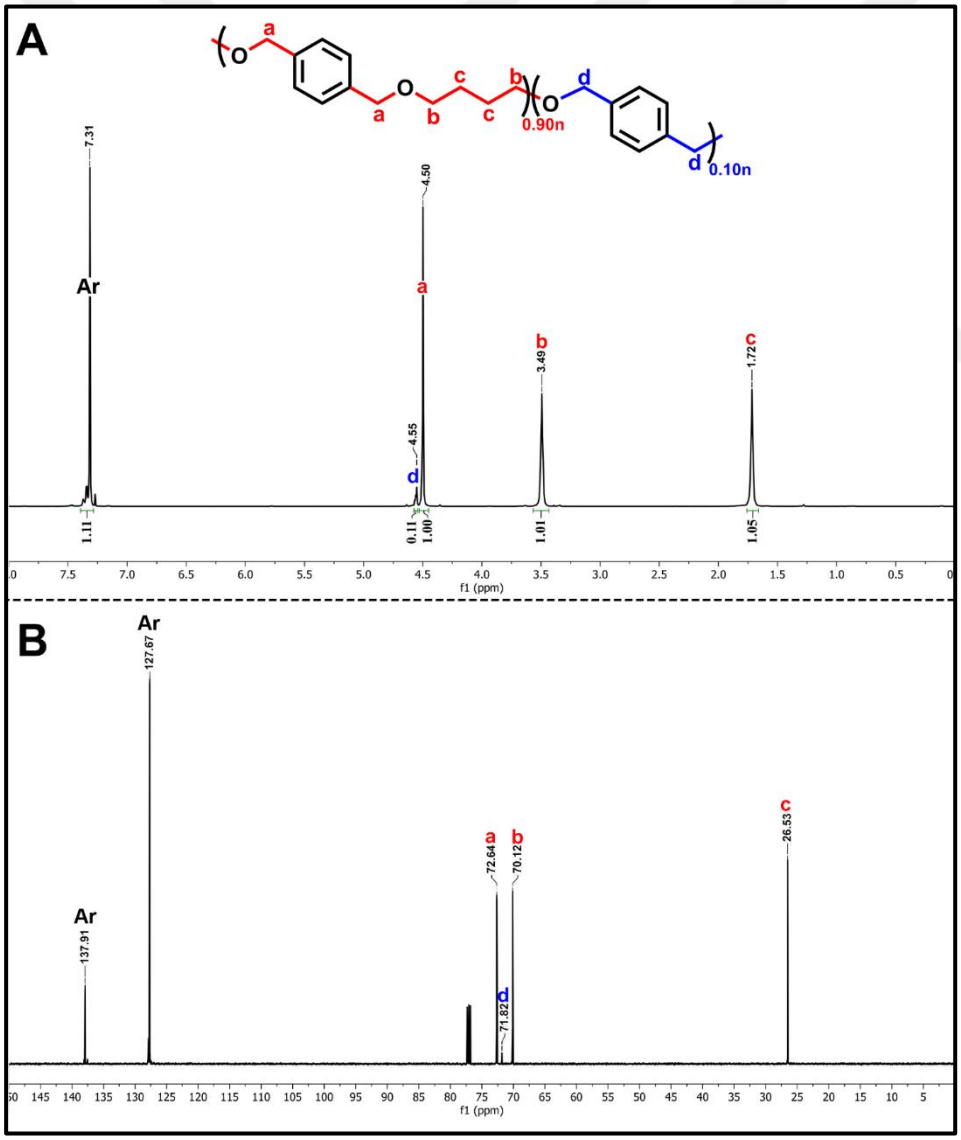


Figure 3.6 : ^{1}H NMR spectrum (A, $CDCl_3$, 500 MHz) and ^{13}C NMR spectrum (B, $CDCl_3$, 125 MHz) of P1 (run 7, Table 1).

A variety of alcohols and aldehydes were then reacted to generate a library of polyethers via CDMS-mediated RER using the optimized conditions and the results achieved are collected in Table 3. The final structures of the obtained polymers and the ^{1}H NMR spectra of representative polymers confirming the chemical structure of precursor monomers that are used in polymerizations can be seen in Figures 3 and 4. Similar to P1, high molecular weight polyethers with high alternating units (>90%) were obtained when linear aliphatic diols involving long alkyl chains such as 1,5-pentanediol (P2, M_w=110.4 kDa), 1,6-hexanediol (P3, M_w=41.5 kDa), and 1,12-dodecandiol (P4, M_w=40.2 kDa) were used in reactions. In contrast, short alkyl chain diols yielded polyethers with low molecular weights; ethylene glycol (P5, M_w = 9.8 kDa) and 1,3-propanediol (P6, M_w = 14.0 kDa) and relatively high alternating units, 73% and 75%, respectively. The distinct low reactivity of short alkyl chain diols toward polyether synthesis might be ascribed to side reactions such as the formation of 5- and 6-membered acetals between the aldehyde carbonyl and the diols, resulting in a stoichiometric imbalance between the two monomers. The results obtained from tetraethylene glycol and bis(2-hydroxyethyl)disulfide were promising. Both diols afforded corresponding polyethers, P7 and P8, in high molecular weights and high alternating units: 28.9 kDa and 34.3 kDa and 90% and 82%, respectively. A low molecular weight polyether (P9, M_w = 14.5 kDa) together with relatively high alternating units (74%) was achieved when *cis*-2-butene-1,4-diol was used in the reaction. The lowest molecular weight (M_w = 3.3 kDa) and the lowest alternating units (60%) in this study were obtained in the case of 2-butyne-1,4-diol (P10). These results might be attributed to the low nucleophilicity of unsaturated diols and/or the possible interaction of unsaturated bonds (particularly the triple bonds) with CDMS during the progress of polymerizations. Moreover, 1,4-cyclohexanedimethanol (P11) resulted in a molecular weight of 15.7 kDa with high alternating units (89%), in which the relatively low molecular weight can be ascribed to the conformational limitation of the cyclohexyl ring. Notably, a moderate molecular weight (M_w = 18.9 kDa) with relatively high alternating units (75%) was found when 1,1-(bishydroxymethyl)cyclopropane (P12) was used in the polymerization, though a reduction in reactivity i.e. nucleophilicity was expected due to cyclopropane ring. Sterically congested diol, 4,8-bis(hydroxymethyl)tricyclo[5.2.1.0^{2,6}]decane, afforded corresponding polyether (P13) with a high molecular weight (M_w =35.1 kDa) and high alternating units (88%). This result was particularly striking since lower

nucleophilicity was expected from this compound due to its rigid ring system. Diols comprising secondary alcohols were then examined. Accordingly, when, 2,5-hexanediol (P14) was used, polymerization proceeded smoothly and resulted in a molecular weight of 24.3 kDa with 88% alternating units. Also, 1,5-hexanediol (P15) having both primary and secondary alcohol functionalities, resulted in even higher alternating units up to 93% with a moderate molecular weight of 19.5 kDa. Aldehyde scope was also examined using constitutional isomers of TPA, and BD was used as the model diol. To this end, when isophthalaldehyde was used, the molecular weight of the obtained polymer (P16) was found to be 56.6 kDa with 91% alternating units. Phthalaldehyde (P17), on the other hand, showed a drastic decrease in molecular weight (24.5 kDa) and resulted in 93% alternating units. The difference in molecular weight between P16 and P17 might be attributed to the steric hindrance of the growing polymer chains in the *m*- and *o*- positions. Meanwhile, an insoluble polymer was obtained in the presence of 4,4'-biphenyldicarboxyaldehyde (P18).

It is noteworthy that, similar to P1, a sticky gum was observed in the reaction medium during the synthesis of P2, while the reaction medium remained slurry or turbid in all other polymers except these two polymers.

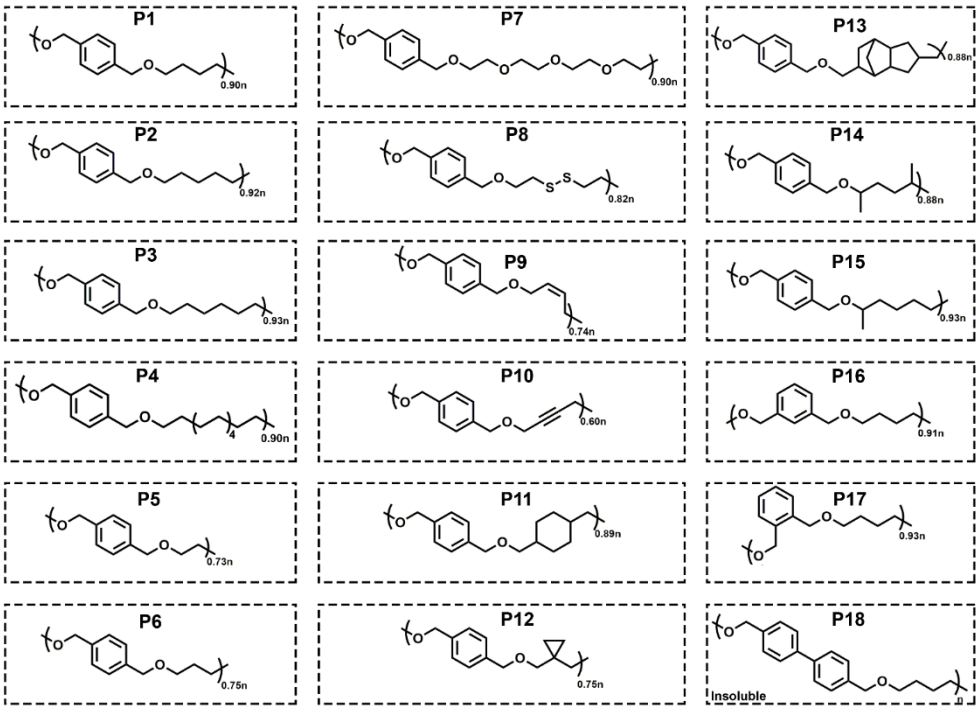


Figure 3.7 : The final structures of the resulting polymers. For clarity, only alternating units were presented.

Table 3.3 : Reactant scope and the obtained results in CDMS-mediated RER[a]

Polymer	Aldehyde	Alcohol	M_w (kDa)[b]	$Đ$[b]	Ratio(%)[c,d]
P1	TPA	1,4-Butanediol	71.3	1.64	90/10
P2	TPA	1,5-Pentanediol	110.4	1.54	92/8
P3	TPA	1,6-Hexanediol	41.5	1.53	93/7
P4	TPA	1,12-Dodecanediol	40.2	1.61	90/10
P5	TPA	Ethylene Glycol	9.8	1.51	73/27
P6	TPA	1,3-Propandiol	14.0	1.54	75/25
P7	TPA	Tetraethylene Glycol	28.9	1.61	90/10
P8	TPA	Bis(2-hydroxyethyl)disulfide	34.3	1.61	82/18
P9	TPA	Cis-2-buten-1,4-diol	14.5	1.58	74/26
P10	TPA	2-Butyne-1,4-diol	3.3	1.19	60/40
P11	TPA	1,4-Cyclohexanedimethanol	15.7	1.42	89/11
P12	TPA	1,1-Bis(hydroxymethyl)cyclopropane	18.9	1.53	75/25
P13	TPA	4,8-Bis(hydroxylmethyl)tricyclo[5.2.1.$0^{2,6}$]decane	35.1	1.65	88/12
P14	TPA	2,5-Hexanediol	24.3	1.51	88/12
P15	TPA	1,5-Hexanediol	19.5	1.45	93/7
P16	Isophthalaldehyde	1,4-Butanediol	56.6	1.56	91/9
P17	Phthalaldehyde	1,4-Butanediol	24.5	1.47	93/7
P18	4,4’-biphenyldicarboxyaldehyde	1,4-Butanediol	-	-	-

[a]All reactions were carried out using Aldehyde/Alcohol/CDMS at a mole ratio of 1.1/1/6 in 1 mL of CH_3NO_2 for 1 h at room temperature. [b]Determined by GPC calibrated based on linear PS standards in THF at 30 °C. [c]Percentage of alternating units calculated by ^{1}H NMR. [d]Percentage of self-condensing units calculated by ^{1}H NMR.

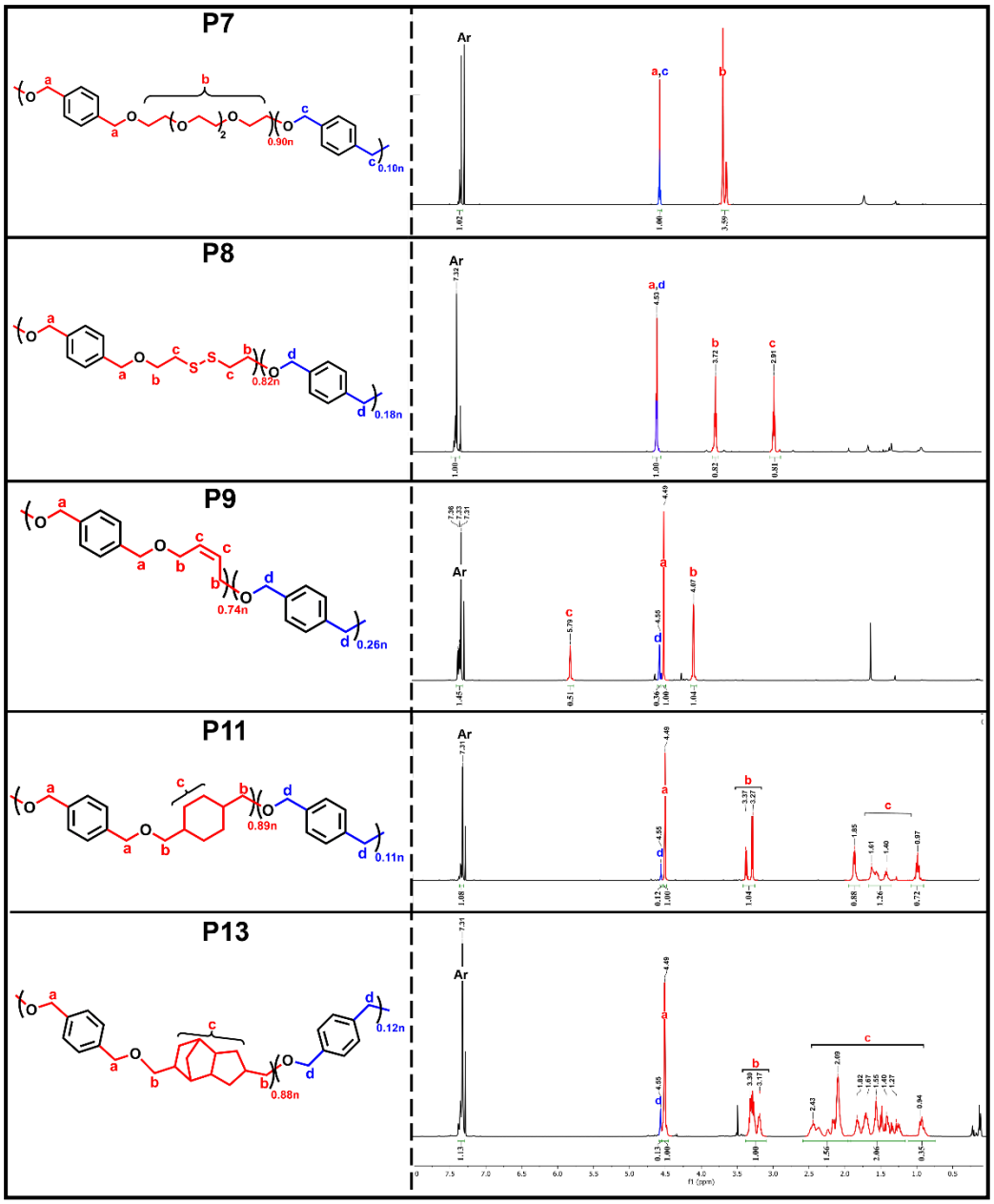


Figure 3.8 : ^{1}H NMR spectra of representative polymers in $CDCl_3$ (500 MHz).

The CDMS-mediated RER described in this study was then examined in terms of mechanistic aspect. Figure 5 exhibits the formation of both alternating and self-condensing units. The formation of alternating units starts with the silylation of TPA in the presence of CDMS, whereby chlorine ion acts as the leaving group to yield silylated TPA (**I**). Then, **I** is attacked by the alcohol, creating an acetal-type intermediate **II**, protonation of this intermediate generates **III**, followed by silanol leaves from the structure to form **IV**. Lastly, a hydride of a new CDMS molecule reduces **IV** to give **V**. Then, the alternating unit is formed by the condensation reaction between **I** and **V**. (Figure 5A). Yet, excess of CDMS causes silylated TPA (**VI**) to

reduce to benzenedimethanol (**VII**). Thus, the self-condensing unit is formed by the condensation reaction between **VII** and **I** (Figure 5B).

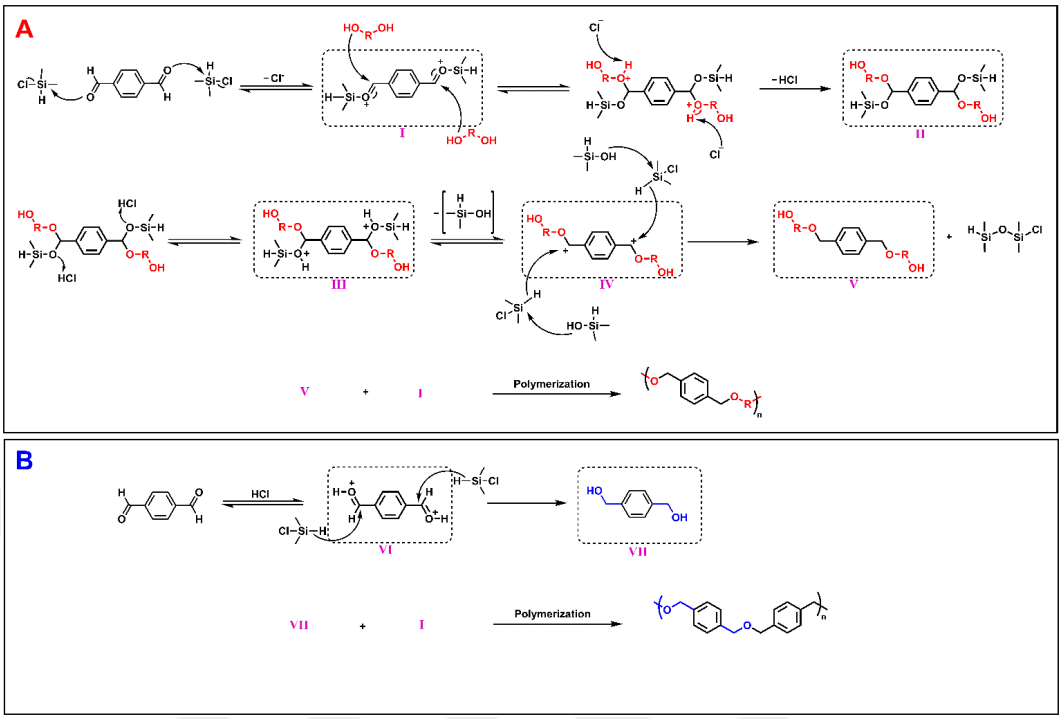


Figure 3.9 : Proposed mechanism for CDMS-mediated RER for polyether synthesis. A: The formation of the alternating unit; B: The formation of the self-condensing unit.

To show the versatility of the proposed system, an end-group modification of the resulting polyethers was performed by choosing a polyether that was prepared by using a slightly excess of BD to ensure both ends were capped with hydroxyl groups. To this end, an esterification reaction was performed between P1 (run 12, Table 1) with acryloyl chloride in the presence of Et_3N in DCM at room temperature for 24 h (Figure 6). The purified polymer was characterized by ^1H NMR. The terminal methylene protons next to -OH at 3.65 ppm completely disappeared and the new protons associated with these protons shifted downfield and appeared at 4.19 ppm, together with the characteristic double bond signals of the acrylate group that appeared at 6.38, 6.13, and 5.81 ppm, indicating the successful esterification reaction (Figure S4).

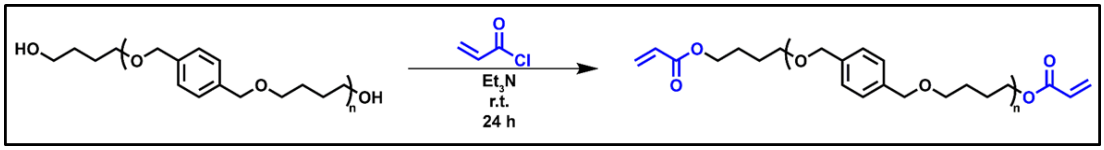


Figure 3.10 : End-group modification of P1 (run 12, Table 1) with acryloyl chloride.

3.3 Conclusions

We have successfully employed CDMS-mediated RER for the synthesis of polyethers. Optimization studies that took place between TPA and BD revealed that slightly excess of TPA (1.1 equiv) together with 6 equiv of CDMS are crucial to reach high molecular weight polymers. The proposed method proceeded under mild conditions and high molecular weight polyethers with high alternating units were achieved at short durations (1 h); molecular weights were varied between 3.3 and 110.4 kDa and the alternating units between 73 and 93% were obtained. The chemical structure of the obtained polyethers can be tuned by the selection of diols, resulting in the formation of a huge polyether library. More importantly, unlike the previously described RERs for synthesizing polyethers that require the protection of alcohols prior to polymerizations, the presented CDMS-mediated RER can benefit from the direct use of alcohols, circumventing an additional step. Also, when the optimized conditions were extended to other silane compounds, a polyether with a promising molecular weight and high alternating units was only obtained when using Et_3SiH as the reducing agent and TfOH as the catalyst; gelation or no polymer formation was observed in all the other silane compounds under the optimized conditions. The versatility of the obtained polyether structure was explored by an end-group functionalization study, and it was found that such polyether structure has a great potential to undergo a post-polymerization modification reaction.

It is believed that the proposed CDMS-mediated RER provides promising results in terms of synthesizing polyethers in a practical way, thereby circumventing the harsh reaction conditions required in classical polyether synthesis. We believe the CDMS-mediated RER described in this study will take considerable attention from the polymer chemistry literature and will become a strong tool in the hands of polymer scientists to develop new polyether-based structures.

3.4 Experimental Part

3.4.1 Materials

Terephthalaldehyde (TPA, 98%, Sigma-Aldrich), 1,4-butanediol (BD, 99%, Sigma-Aldrich), chlorodimethylsilane (CDMS, 98%, Aldrich), 1,5-pentanediol (>97%, Sigma-Aldrich), 1,6-hexanediol (99%, Sigma-Aldrich), 1,4-cyclohexanedimethanol (99%, Sigma-Aldrich), 4,8-bis(hydroxymethyl)tricyclo[5.2.1.$0^{2,6}$]decane (96%, Sigma-Aldrich), 1,1-bis(hydroxymethyl)cyclopropane (96%, TCI), ethylene glycol (99.8%, Sigma-Aldrich), 1,3-propanediol (98%, Sigma-Aldrich), tetraethylene glycol (99%, Sigma-Aldrich), cis-2-butene-1,4-diol (97%, Sigma-Aldrich), 2-butyne-1,4-diol (99%, Sigma-Aldrich), bis(2-hydroxyethyl)sulfide (98.0%, TCI), 2,5-hexanediol (99%, Sigma-Aldrich), 1,5-hexanediol (99%, Sigma-Aldrich), isophthalaldehyde (97%, Sigma-Aldrich), phthalaldehyde (97%, Sigma-Aldrich), 4,4'-biphenyldicarboxyaldehyde (97%, Thermo Scientific), triethylsilane (Et_3SiH, 99%, ABCR), dimethylphenylsilane ($PhMe_2SiH$, 98%, Sigma-Aldrich), phenylsilane ($PhSiH_3$, 97%, Sigma-Aldrich), diphenylsilane (Ph_2SiH_2, 97%, Sigma-Aldrich), iron(III) chloride ($FeCl_3$, 98%, Sigma-Aldrich), bismuth(III) chloride ($BiCl_3$, 98%, Sigma-Aldrich), trifluoromethanesulfonic acid (TfOH, 99%, Sigma-Aldrich), triethylamine (99.5%, Sigma-Aldrich), and acryloyl chloride (98%, TCI) were used as received. Nitromethane (CH_3NO_2, 96%, Merck), dichloromethane (DCM, 99.8%, Sigma-Aldrich), chloroform ($CHCl_3$, ≥99%, Sigma-Aldrich) were anhydrous of high-performance liquid chromatography quality and used without further purification. Methanol (CH_3OH) and diethyl ether were of reagent grade and used as received.

3.4.2 Instrumentation

^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded using an Agilent VNMRS 500 instrument in $CDCl_3$. Gel permeation chromatography (GPC) measurements were carried out with Agilent Instrument (series 1100), using refractive index detector, loaded with 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 the columns are 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 2,6-di-*tert*-butyl-4-methylphenol (BHT) was used as an internal standard.

The weight-average molecular weight (M_w) and dispersity ($Đ$) of the polymers were calculated based on narrow linear polystyrene (PS) standards (Polymer Laboratories) ranging between 2300− 3 050 000 g/mol.

3.4.3 Synthetic procedures and characterization

3.4.3.1 General Procedure for the Synthesis of Polyether (Synthesis of P1)

TPA (0.443 g, 0.33 mmol) and BD (0.27 g, 0.30 mmol) were added into a 10 mL round bottom flask at room temperature. Then, with continuous stirring, CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were added, respectively, to this solution. Upon addition of CH_3NO_2 to the mixture, a highly exothermic reaction occurred, the reaction mixture became turbid within the first few minutes, became a slurry after 5 minutes, and a sticky gum was observed in the reaction medium within 15 min (see the images in Figure 1B). The reaction was allowed to stir at room temperature for 1 h in gummy form. Afterwards, 5 mL of $CHCl_3$ was added to the reaction mixture to dissolve the gum-like product and the viscous solution was precipitated into 50 mL of CH_3OH. The dissolution-precipitation procedure ($CHCl_3$-CH_3OH) was repeated two times. Finally, the obtained polymer, P1, was dissolved in 5 mL of $CHCl_3$ and transferred to a glass vial and the solvent was evaporated to yield a white solid. (Yield = 553 mg, 96%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (4H, Ar*H*), 4.55 (4H, ArC*H*$_2$O), 4.50 (4H, ArC*H*$_2$O), 3.49 (4H, OC*H*$_2$CH$_2$CH$_2$C*H*$_2$O), 1.72 (4H, OCH$_2$C*H*$_2$C*H*$_2$CH$_2$O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.91 (Ar*C*), 127.67 (Ar*C*), 72.64 (Ar*C*H$_2$O), 71.82 (Ar*C*H$_2$O), 70.12 (O*C*H$_2$CH$_2$CH$_2$*C*H$_2$O), 26.53 (OCH$_2$*C*H$_2$*C*H$_2$CH$_2$O) ppm.

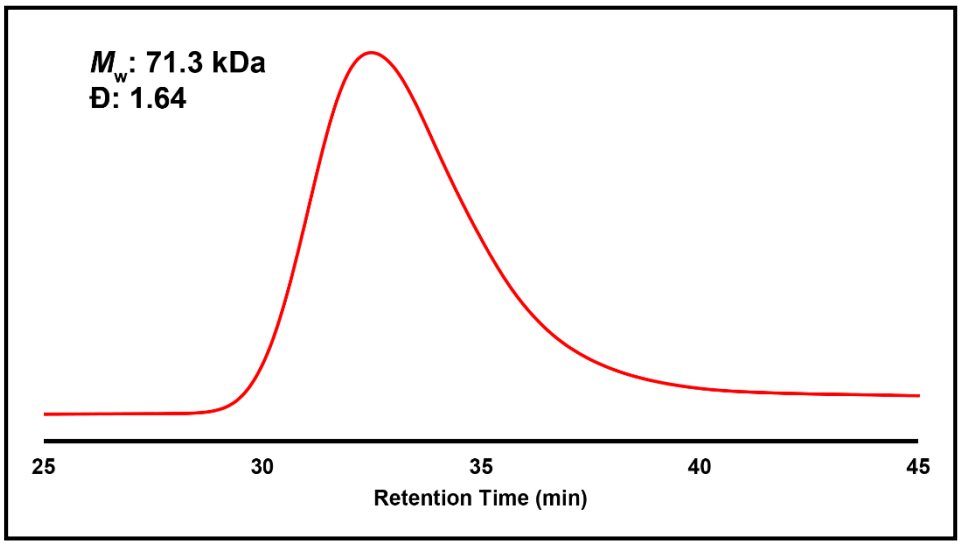


Figure 3.11 : GPC chromatogram of P1.

3.4.3.2 Synthesis of P2

General procedure was followed. TPA (0.443 g, 0.33 mmol), 1,5-pentanediol (0.312 g, 0.30 mmol), CDMS (2 mL, 1.8 mmol) and 1 mL of CH_3NO_2 were used. A sticky gum was observed during the course of the reaction. P2 was obtained as a white sticky solid. (Yield = 599 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (4H, Ar*H*), 4.54 (4H, ArC*H*$_2$O), 4.49 (4H, ArC*H*$_2$O), 3.46 (4H, OC*H*$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$O), 1.63 (4H, OCH$_2$C*H*$_2$CH$_2$C*H*$_2$CH$_2$O), 1.45 (2H, OCH$_2$CH$_2$C*H*$_2$CH$_2$CH$_2$O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.91 (Ar*C*), 127.68 (Ar*C*), 72.67 (Ar*C*H$_2$O), 71.81 (Ar*C*H$_2$O), 70.30 (O*C*H$_2$CH$_2$CH$_2$CH$_2$*C*H$_2$O), 29.59 (OCH$_2$*C*H$_2$CH$_2$*C*H$_2$CH$_2$O), 22.85 (OCH$_2$CH$_2$*C*H$_2$CH$_2$CH$_2$O) ppm.

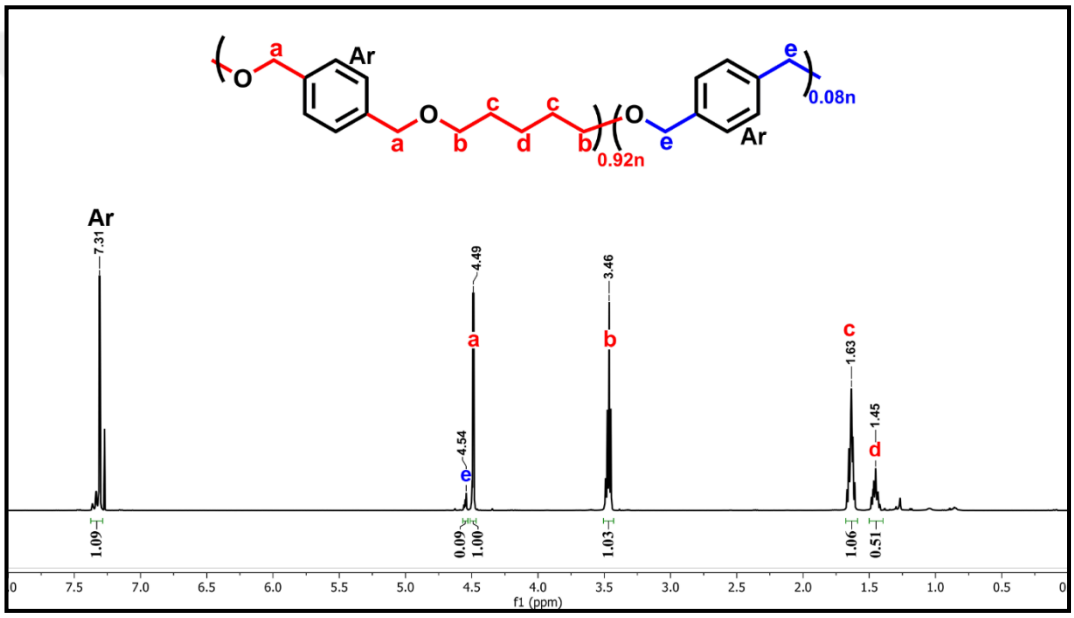


Figure 3.12 : ^{1}H NMR spectrum of P2 in $CDCl_3$ (500 MHz).

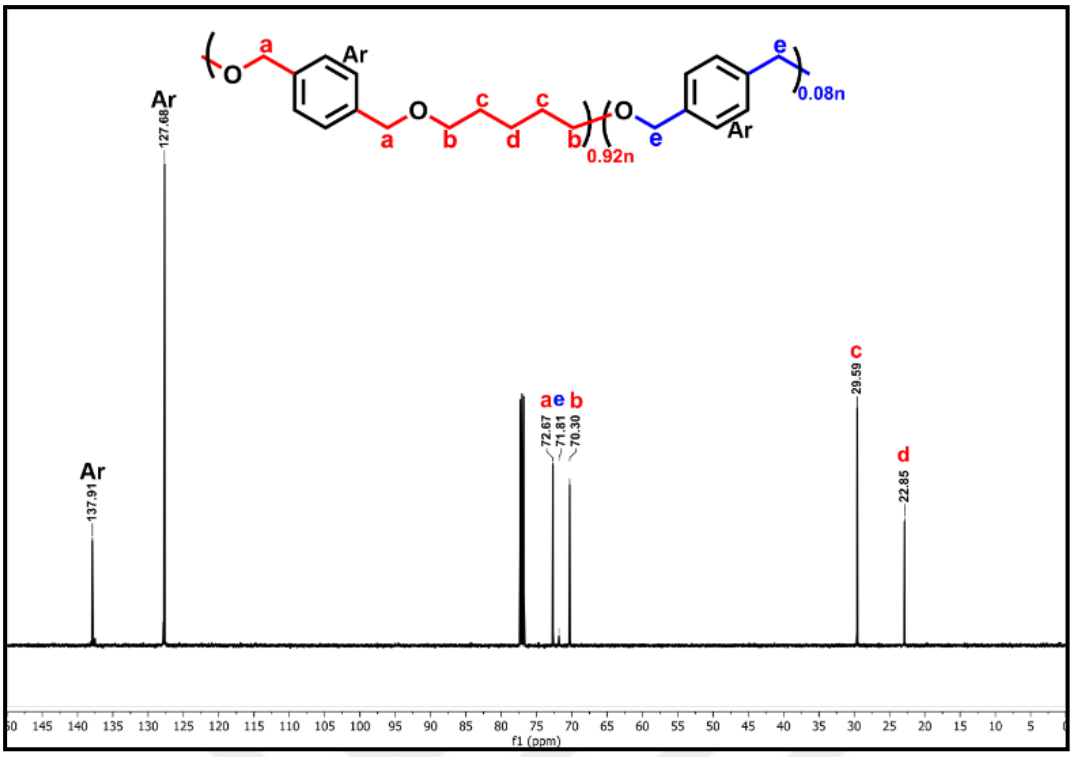


Figure 3.13 : ^{13}C NMR spectrum of P2 in $CDCl_3$ (125 MHz).

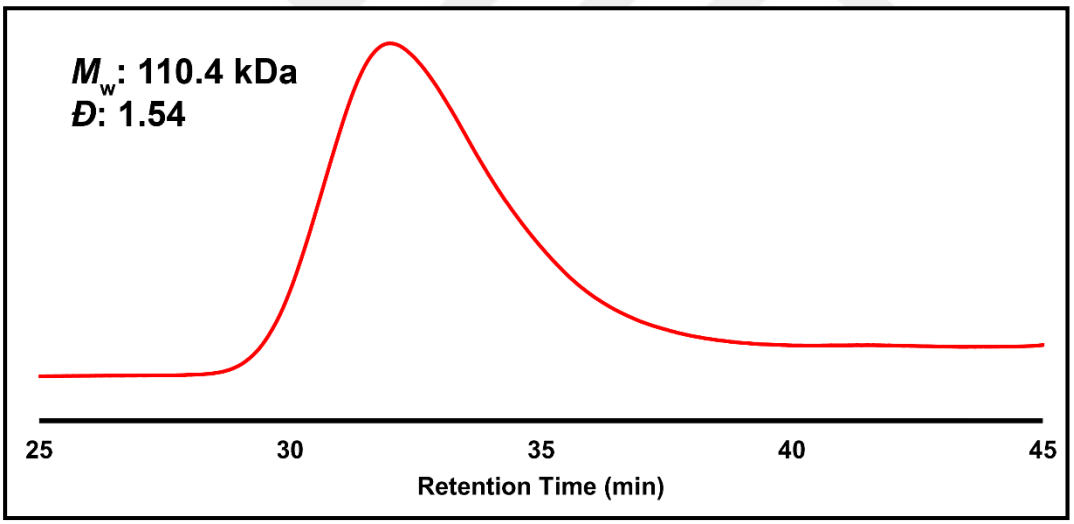


Figure 3.14 : GPC chromatogram of P2.

3.4.3.3 Synthesis of P3

General procedure was followed. TPA (0.443 g, 0.33 mmol), 1,6-hexanediol (0.354 g, 0.30 mmol), CDMS (2 mL, 1.8 mmol) and 1 mL of CH_3NO_2 were used. The reaction medium was slurry during the course of the reaction. P3 was obtained as a white waxy solid. (Yield = 634 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (4H, Ar*H*), 4.50 (4H, ArC*H*$_2$O), 4.49 (4H, ArC*H*$_2$O), 3.46 (4H, OC*H*$_2$CH$_2$CH$_2$CH$_2$CH$_2$C*H*$_2$O), 1.62 (4H, OCH$_2$C*H*$_2$CH$_2$CH$_2$C*H*$_2$CH$_2$O), 1.39 (2H, OCH$_2$CH$_2$C*H*$_2$C*H*$_2$CH$_2$CH$_2$O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.93 (Ar*C*), 127.68 (Ar*C*), 72.65 (Ar*C*H$_2$O), 71.82

(ArCH_2O), 70.37 (O$CH_2CH_2CH_2CH_2CH_2$O), 29.73 (O$CH_2CH_2CH_2CH_2CH_2$O), 26.09 (O$CH_2CH_2CH_2CH_2CH_2$O) ppm.

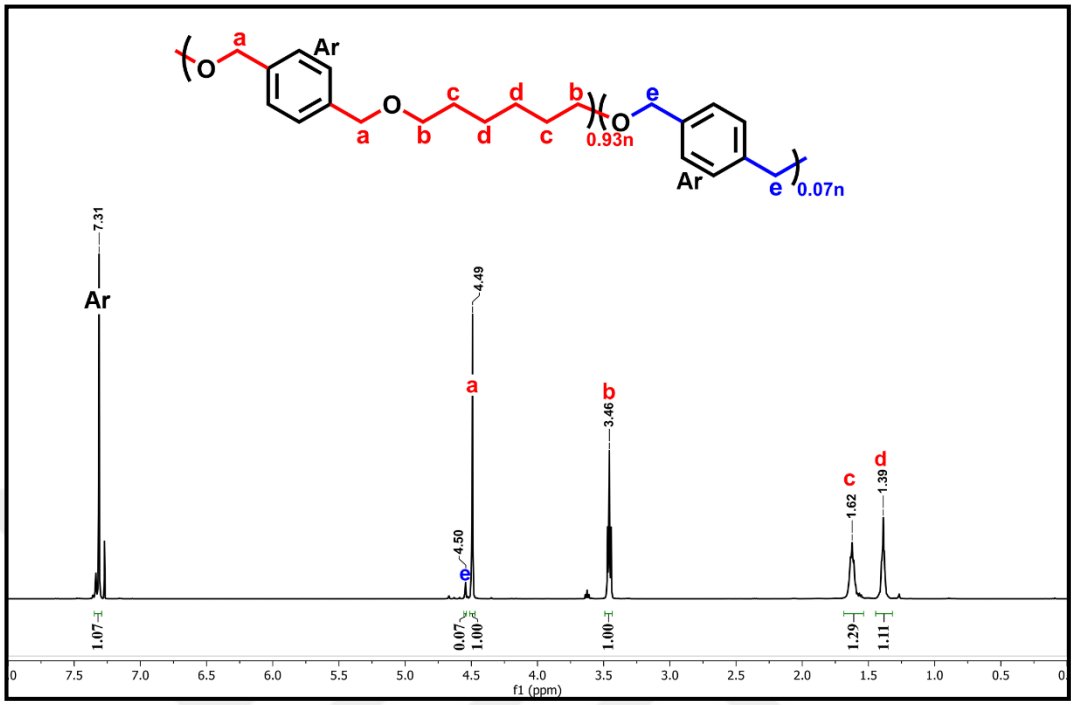


Figure 3.15 : ^{1}H NMR spectrum of P3 in $CDCl_3$ (500 MHz).

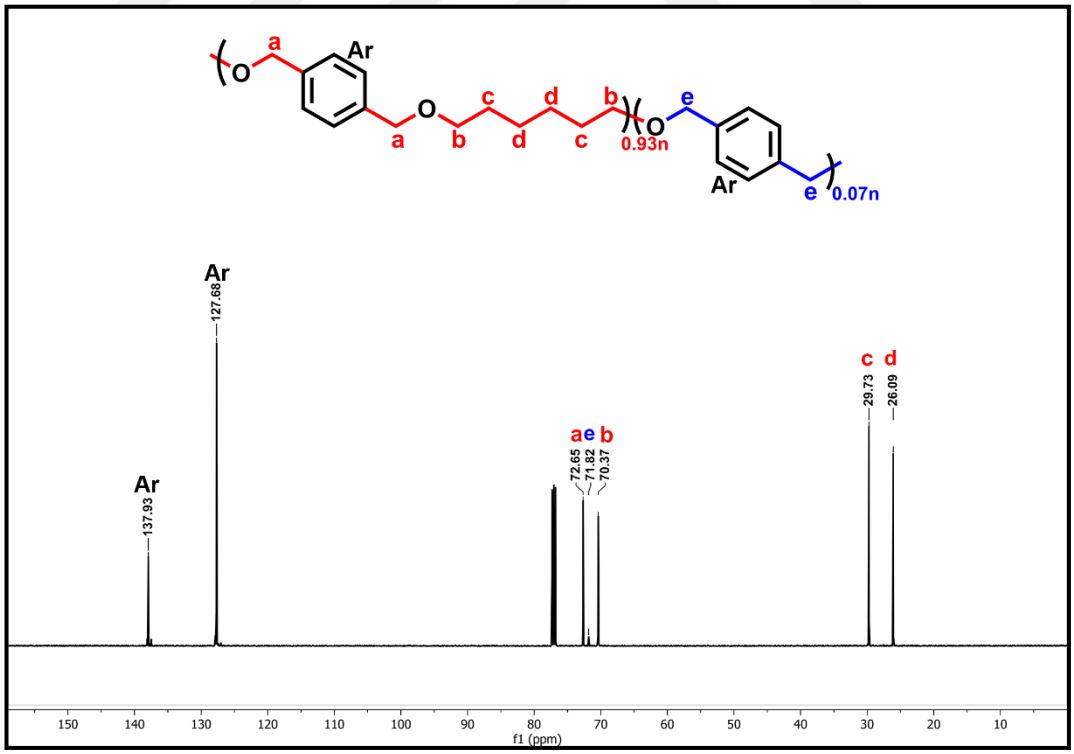


Figure 3.16 : ^{13}C NMR spectrum of P3 in $CDCl_3$ (125 MHz).

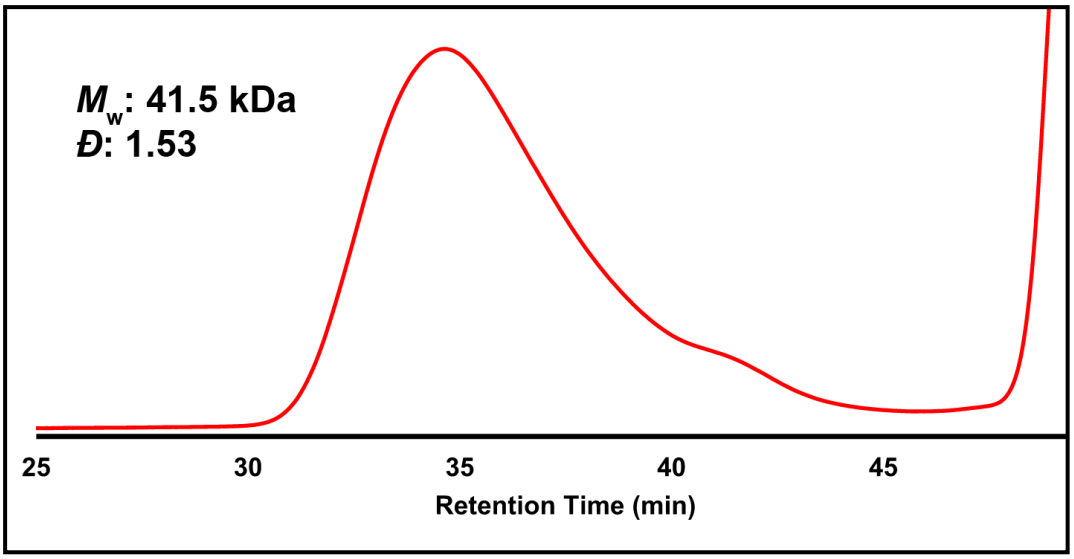


Figure 3.17 : GPC chromatogram of P3.

3.4.3.4 Synthesis of P4

General procedure was followed. TPA (0.443 g, 0.33 mmol), 1,12-dodecanediol (0.607 g, 0.30 mmol), CDMS (2 mL, 1.8 mmol) and 1 mL of CH_3NO_2 were used. The reaction mixture was slurry during the course of the reaction. P4 was obtained as a white waxy solid. (Yield = 759 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.32 (4H, Ar*H*), 4.54 (4H, ArC*H*$_2$O), 4.49 (4H, ArC*H*$_2$O), 3.45 (4H, OC*H*$_2$CH$_2$(CH$_2$CH$_2$)$_4$CH$_2$C*H*$_2$O), 1.61-1.27 (20H, OCH$_2$C*H*$_2$(C*H*$_2$C*H*$_2$)$_4$C*H*$_2$CH$_2$O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.97 (Ar*C*), 127.59 (Ar*C*), 76.16 (Ar*C*H$_2$O), 73.71 (Ar*C*H$_2$O), 72.81 (Ar*C*H$_2$O), 71.84 (O*C*H$_2$CH$_2$(CH$_2$CH$_2$)$_4$CH$_2$*C*H$_2$O), 38.31 (OCH$_2$*C*H$_2$(CH$_2$CH$_2$)$_4$*C*H$_2$CH$_2$O), 29.49/25.85 (OCH$_2$*C*H$_2$(*C*H$_2$*C*H$_2$)$_4$*C*H$_2$CH$_2$O) ppm.

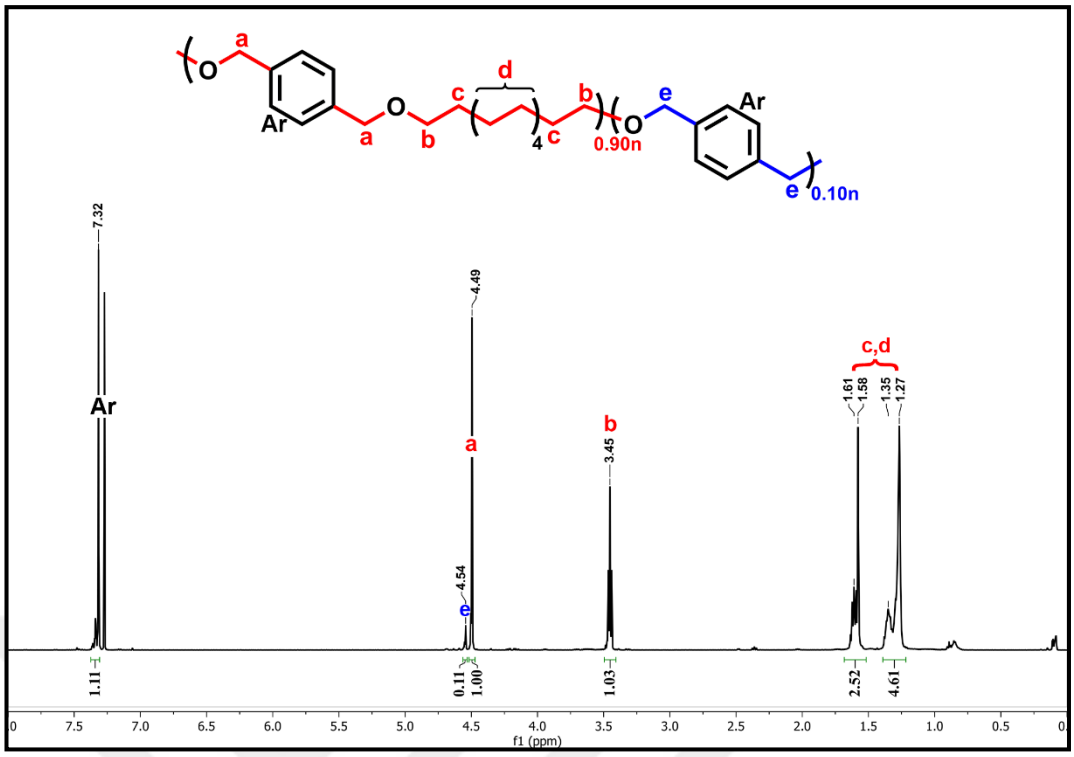


Figure 3.18 : ^{1}H NMR spectrum of P4 in $CDCl_3$ (500 MHz).

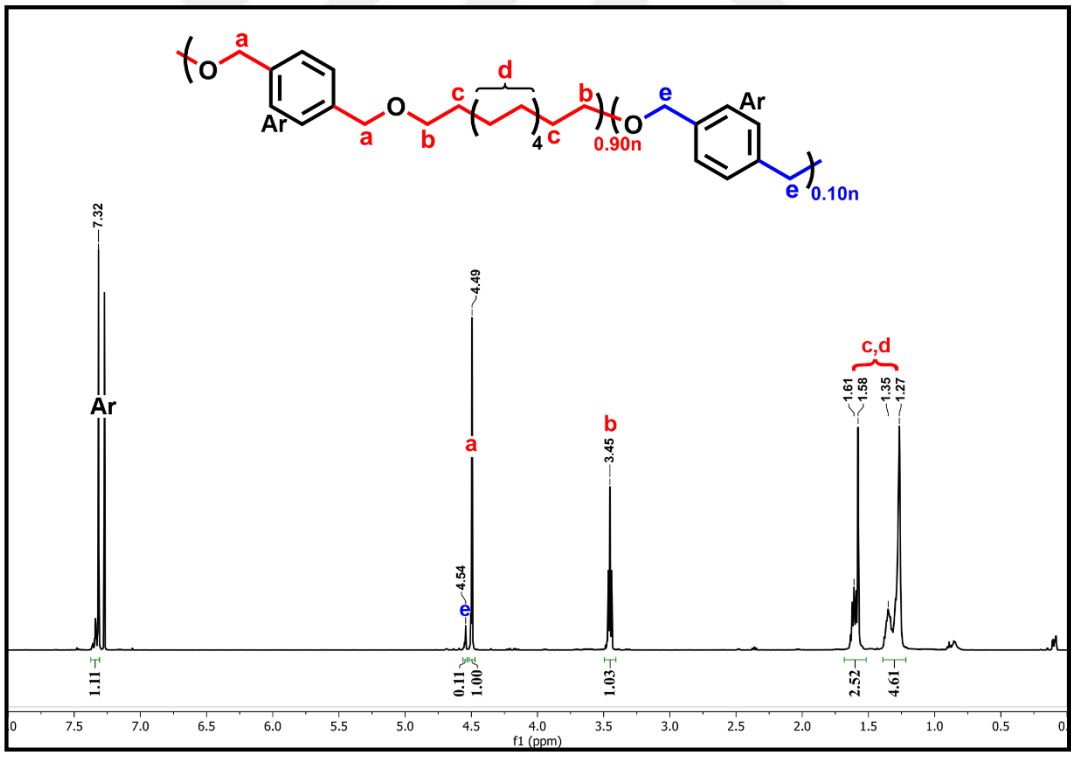


Figure 3.19 : ^{13}C NMR spectrum of P4 in $CDCl_3$ (125 MHz).

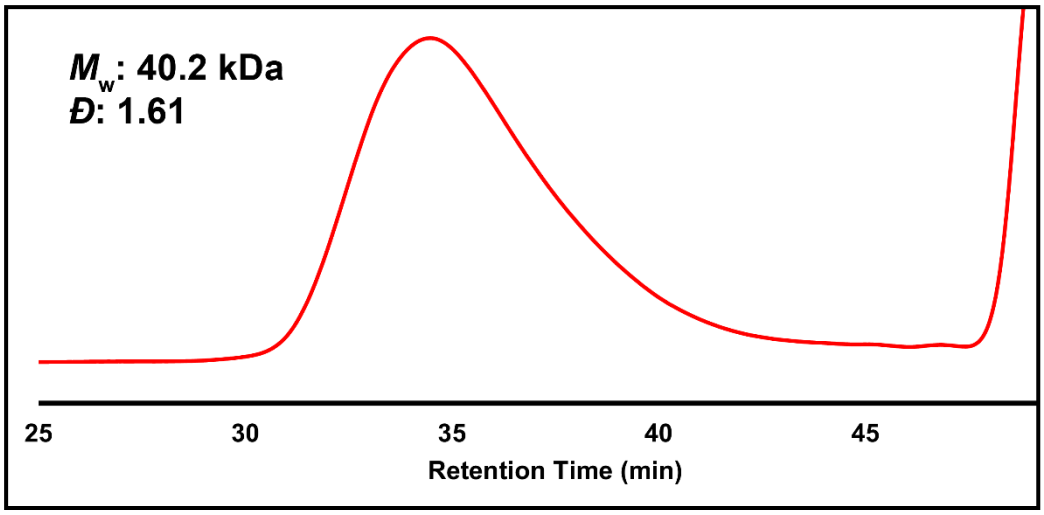


Figure 3.20 : GPC chromatogram of P4.

3.4.3.5 Synthesis of P5

General procedure was followed. TPA (0.443 g, 0.33 mmol), ethylene glycol (0.186 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction mixture was observed to be turbid during the course of the reaction. P5 was obtained as a transparent sticky solid. (Yield = 351 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34-7.33 (4H, Ar*H*), 4.57 (4H, ArC*H*$_2$O), 4.54 (4H, ArC*H*$_2$O), 3.65 (4H, OC*H*$_2$C*H*$_2$O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.65 (Ar*C*), 127.83 (Ar*C*), 73.05 (Ar*C*H$_2$O), 71.84 (Ar*C*H$_2$O), 69.48 (OCH$_2$*C*H$_2$O) ppm.

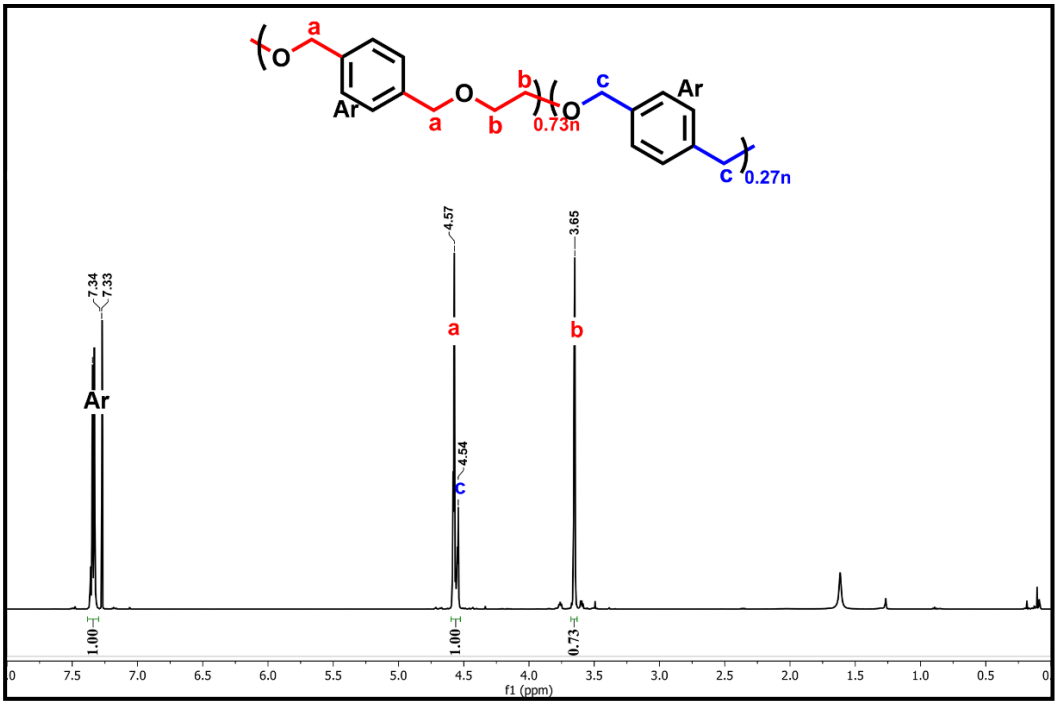


Figure 3.21 : ^{1}H NMR spectrum of P5 in $CDCl_3$ (500 MHz).

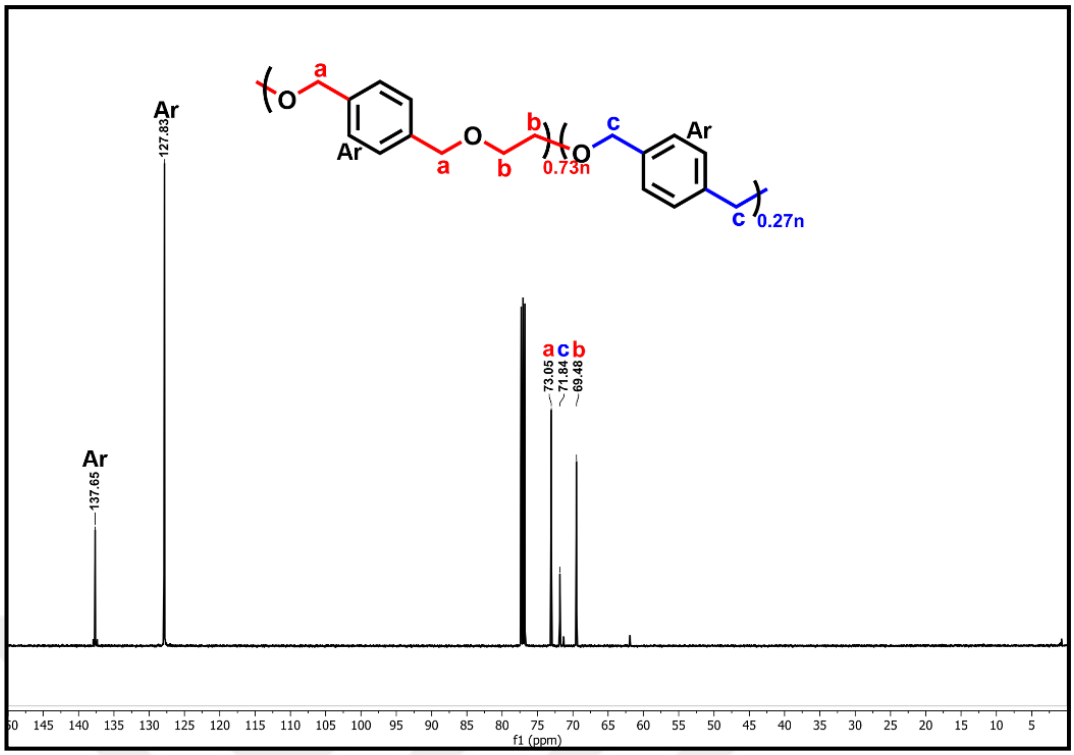


Figure 3.22 : ^{13}C NMR spectrum of P5 in $CDCl_3$ (125 MHz).

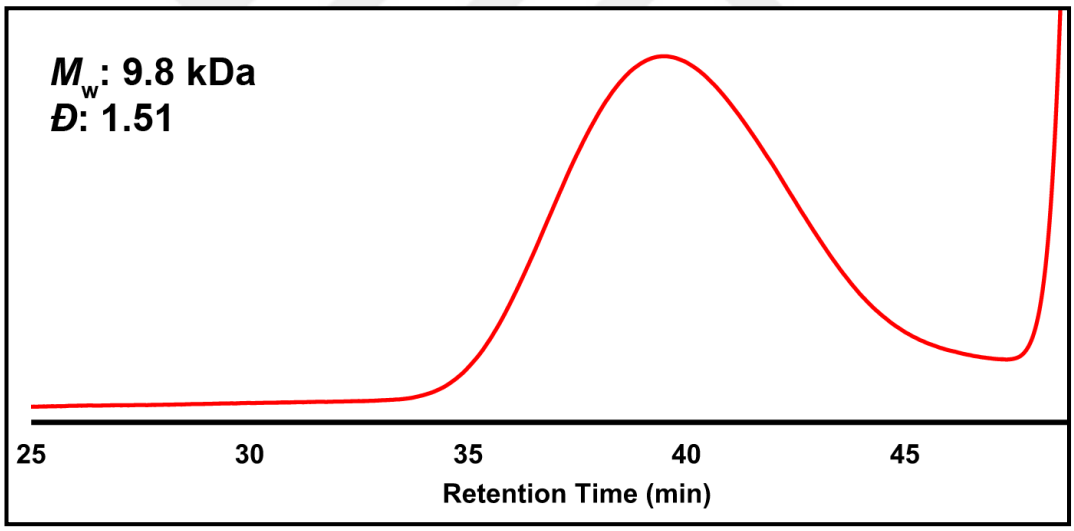


Figure 3.23 : GPC chromatogram of P5.

3.4.3.6 Synthesis of P6

General procedure was followed. TPA (0.443 g, 0.33 mmol), 1,3-propanediol (0.228 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction mixture was observed to be turbid during the course of the reaction. P6 was obtained as a transparent sticky solid. (Yield = 403 mg, 81%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.34-7.30 (4H, Ar*H*), 4.54 (4H, ArCH_2O), 4.49 (4H, ArCH_2O), 3.58 (4H, OCH_2CH$_2$CH_2O), 1.93 (2H, OCH$_2$CH_2CH$_2$O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ =

137.86/137.58 (Ar*C*), 127.70 (Ar*C*), 72.76 (Ar*C*H$_2$O), 71.81 (Ar*C*H$_2$O), 67.35 (OCH_2CH_2*C*H$_2$O), 30.19 (OCH$_2$*C*H$_2$CH$_2$O) ppm.

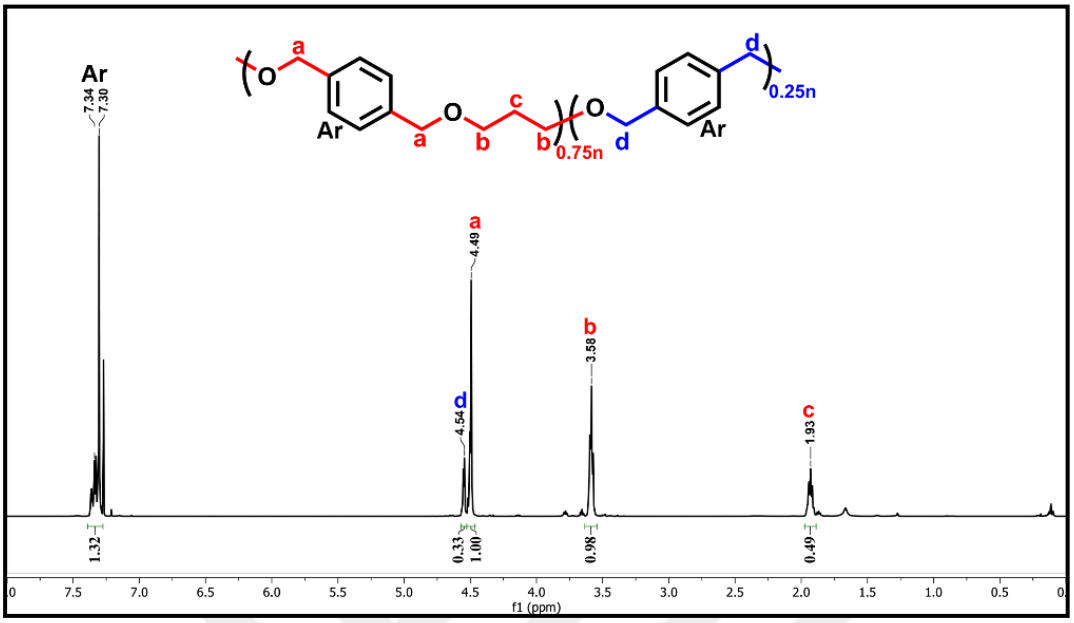


Figure 3.24 : ^{1}H NMR spectrum of P6 in $CDCl_3$ (500 MHz).

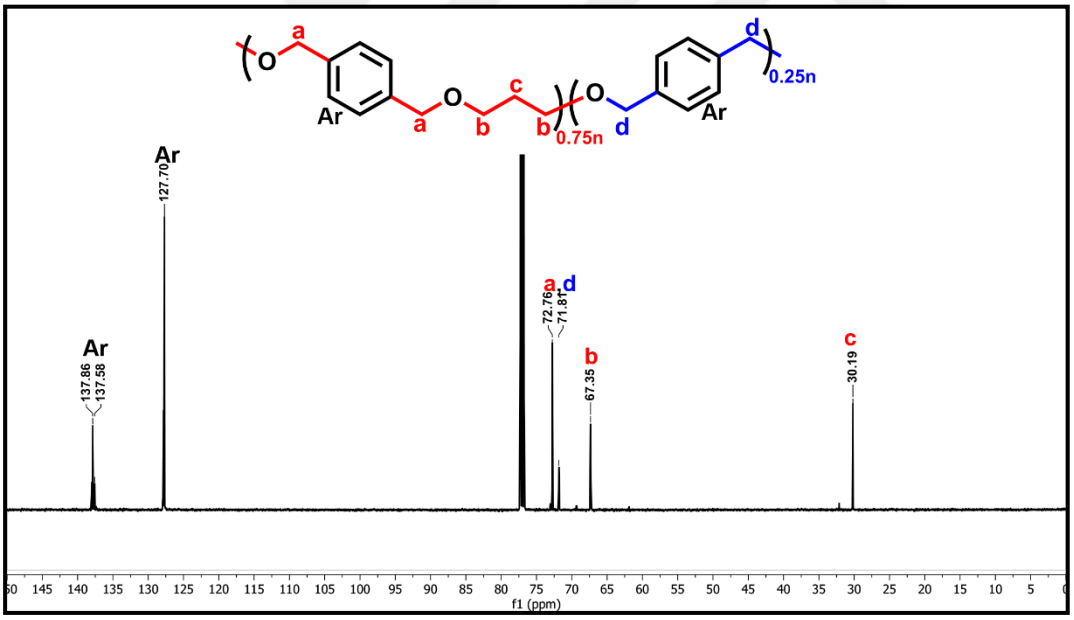


Figure 3.25 : ^{13}C NMR spectrum of P6 in $CDCl_3$ (125 MHz).

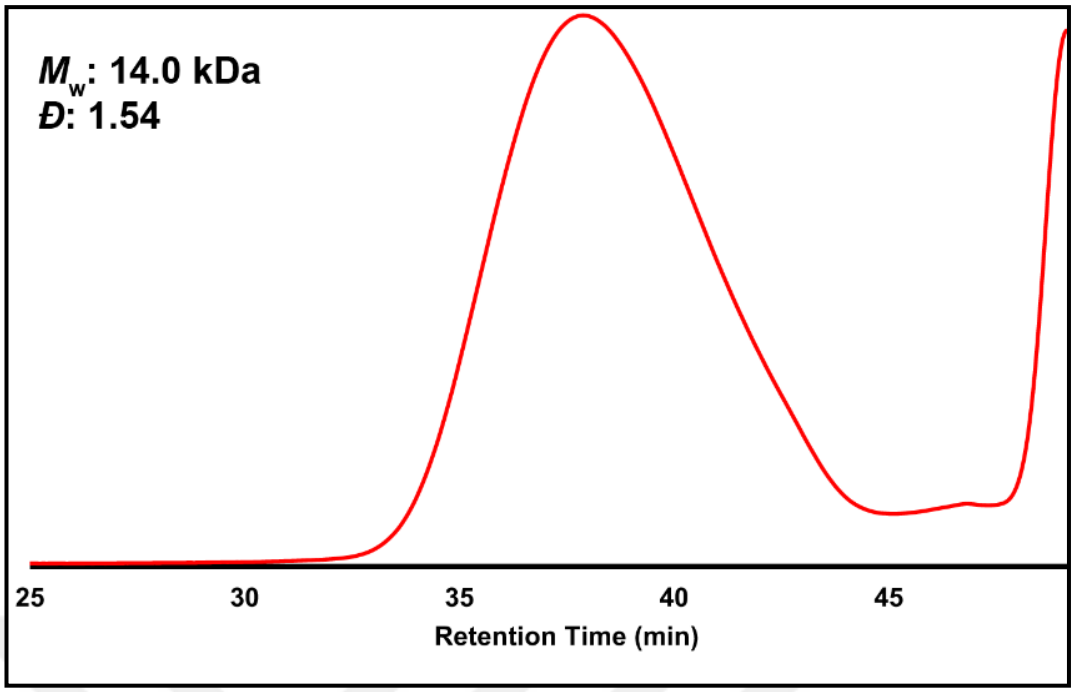


Figure 3.26 : GPC chromatogram of P6.

3.4.3.7 Synthesis of P7

General procedure was followed. TPA (0.443 g, 0.33 mmol), tetraethylene glycol (0.583 g, 0.30 mmol), CDMS (2 mL, 1.8 mmol) and 1 mL of CH_3NO_2 were used. The reaction mixture was observed to be turbid during the course of the reaction. P7 was obtained as a transparent sticky solid. (Yield = 790 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34-7.30 (4H, Ar*H*), 4.55 (8H, ArC*H*$_2$O), 3.67-3.62 (16H, OC*H*$_2$C*H*$_2$(OC*H*$_2$C*H*$_2$)$_2$OC*H*$_2$C*H*$_2$O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.65 (Ar*C*), 127.81 (Ar*C*), 73.00 (Ar*C*H$_2$O), 71.83 (Ar*C*H$_2$O), 70.63/69.39 (O*C*H$_2$*C*H$_2$(O*C*H$_2$*C*H$_2$)$_2$O*C*H$_2$*C*H$_2$O) ppm.

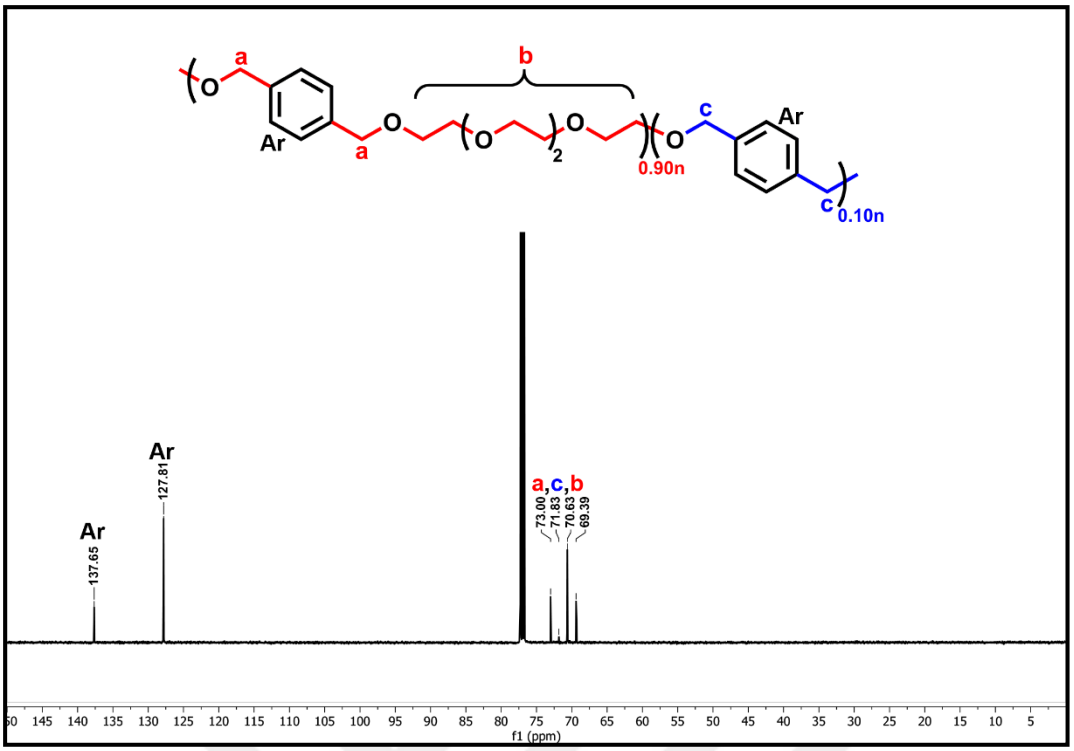


Figure 3.27 : ^{13}C NMR spectrum of P7 in $CDCl_3$ (125 MHz).

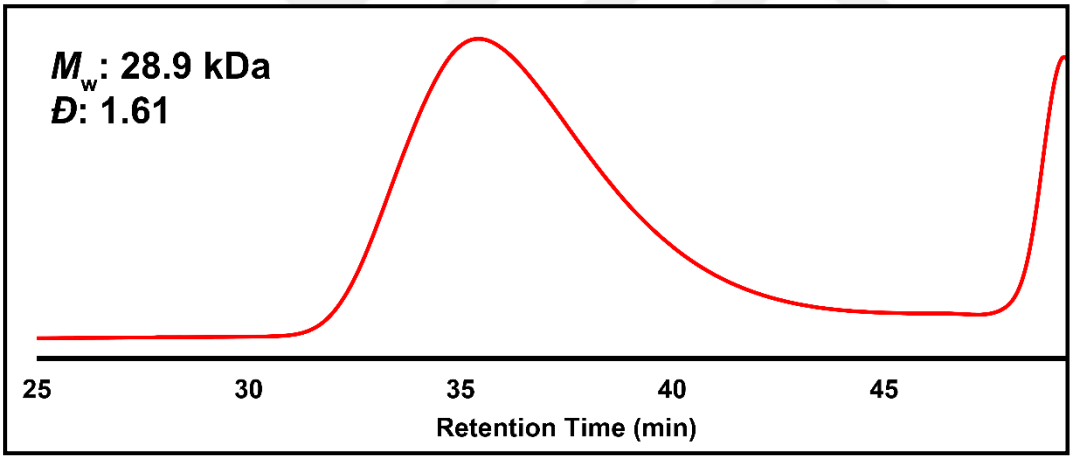


Figure 3.28 : GPC chromatogram of P7.

3.4.3.8 Synthesis of P8

General procedure was followed. TPA (0.443 g, 0.33 mmol), bis(2-hydroxyethyl)disulfide (0.463 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction medium was observed to be slurry during the course of the reaction. P8 was obtained as a transparent sticky solid. (Yield = 645 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.34-7.30 (4H, Ar*H*), 4.53 (8H, ArC*H*$_2$O), 3.72 (4H, OC*H*$_2$CH$_2$SSCH$_2$C*H*$_2$O), 2.91 (4H, OCH$_2$C*H*$_2$SSC*H*$_2$CH$_2$O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.52 (Ar*C*), 127.87 (Ar*C*), 72.84 (ArCH$_2$O), 71.83 (ArCH$_2$O), 68.45 (O*C*H$_2$CH$_2$SSCH$_2$*C*H$_2$O), 38.72 (OCH$_2$*C*H$_2$SS*C*H$_2$CH$_2$O) ppm.

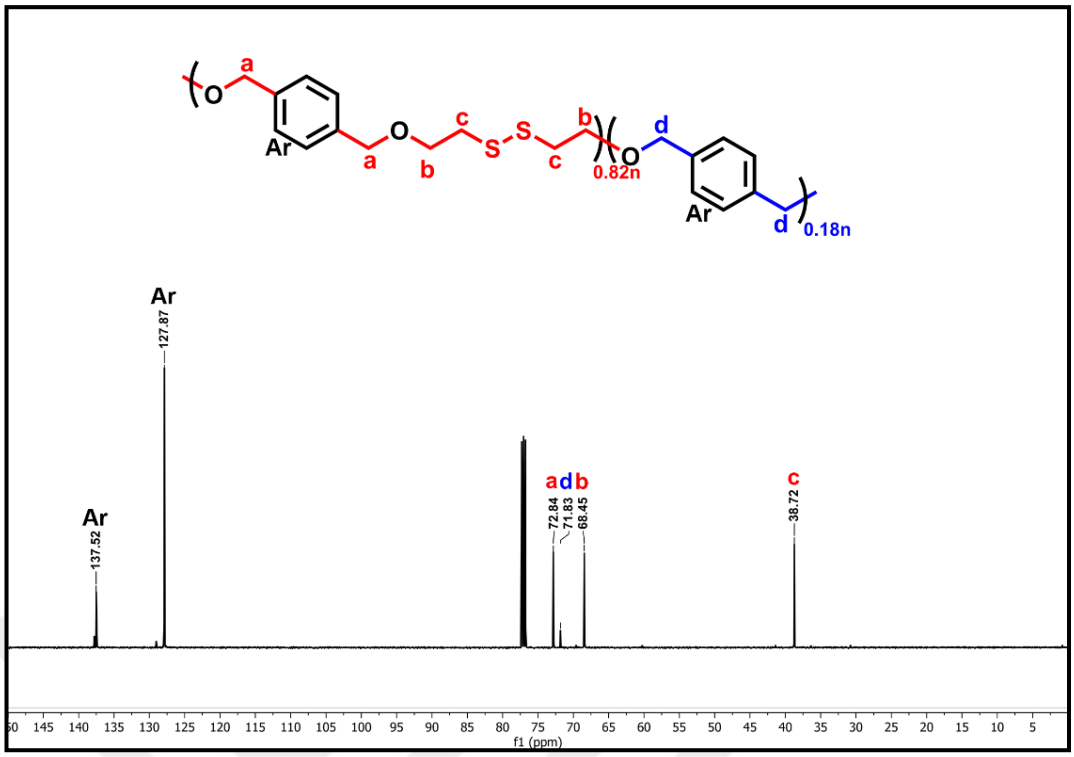


Figure 3.29 : ^{13}C NMR spectrum of P8 in $CDCl_3$ (125 MHz).

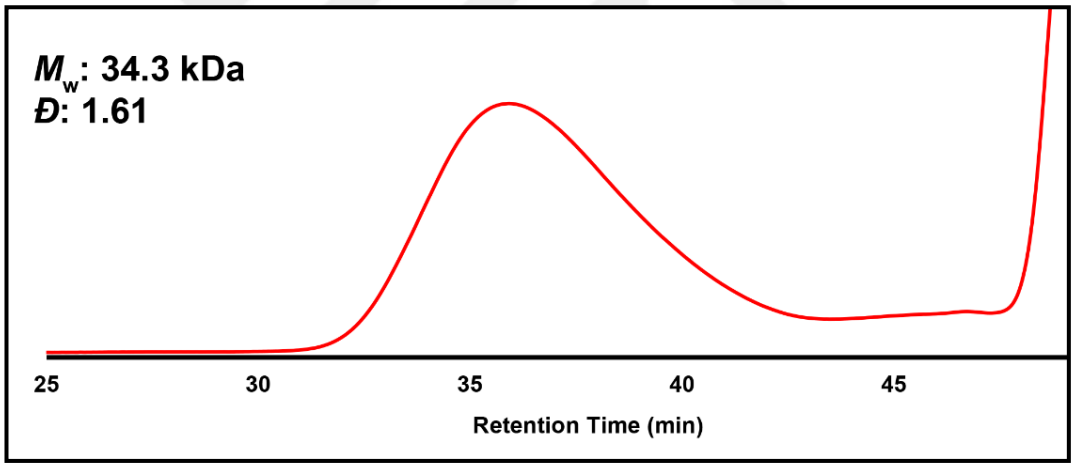


Figure 3.30 : GPC chromatogram of P8.

3.4.3.9 Synthesis of P9

General procedure was followed. TPA (0.443 g, 0.33 mmol), cis-2-butene-1,4-diol (0.264 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction medium was observed to be slurry during the course of the reaction. P9 was obtained as a pale yellow transparent sticky solid. (Yield = 439 mg, 77%). ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36-7.31 (4H, Ar*H*), 5.79 (2H, OCH_2CH=C*H*CH_2O), 4.55 (4H, $ArCH_2O$), 4.49 (4H, $ArCH_2O$), 4.07 (4H, OCH_2CH=$CHCH_2O$) ppm. ^{13}C

NMR (125 MHz, $CDCl_3$): δ = 137.52 (Ar*C*), 129.49 ($OCH_2CH{=}CHCH_2O$), 127.88 (Ar*C*), 72.04 ($ArCH_2O$), 71.83 ($ArCH_2O$), 65.85 ($OCH_2CH{=}CHCH_2O$) ppm.

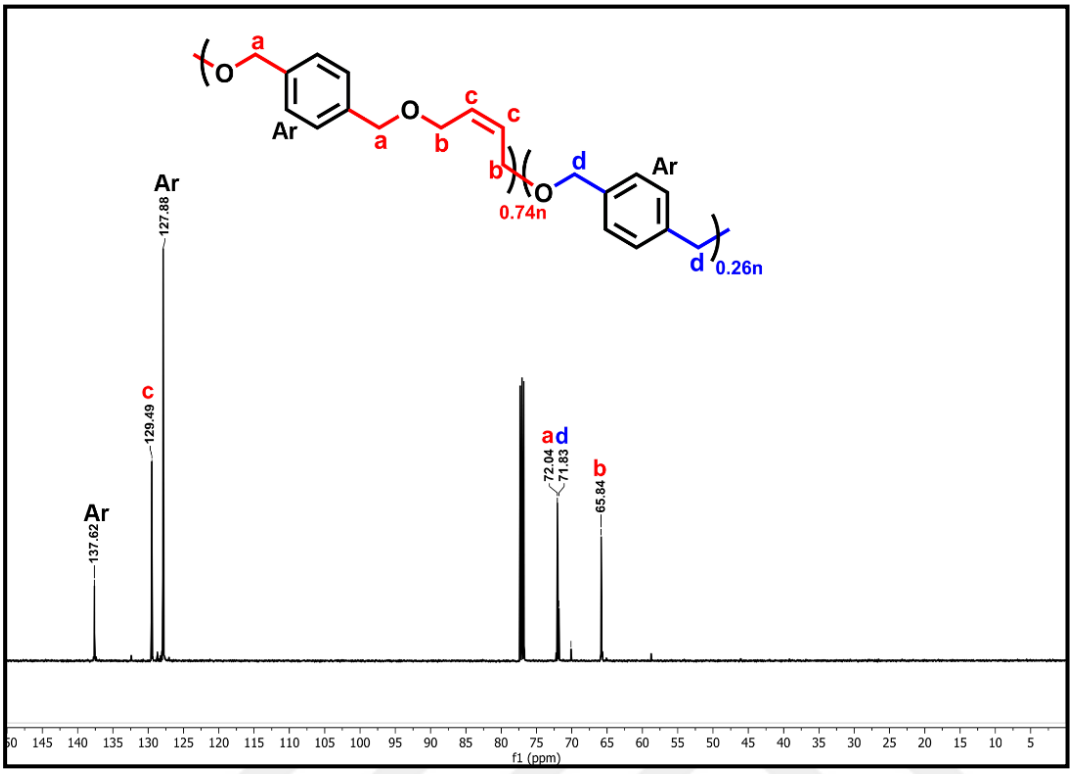


Figure 3.31 : ^{13}C NMR spectrum of P9 in $CDCl_3$ (125 MHz).

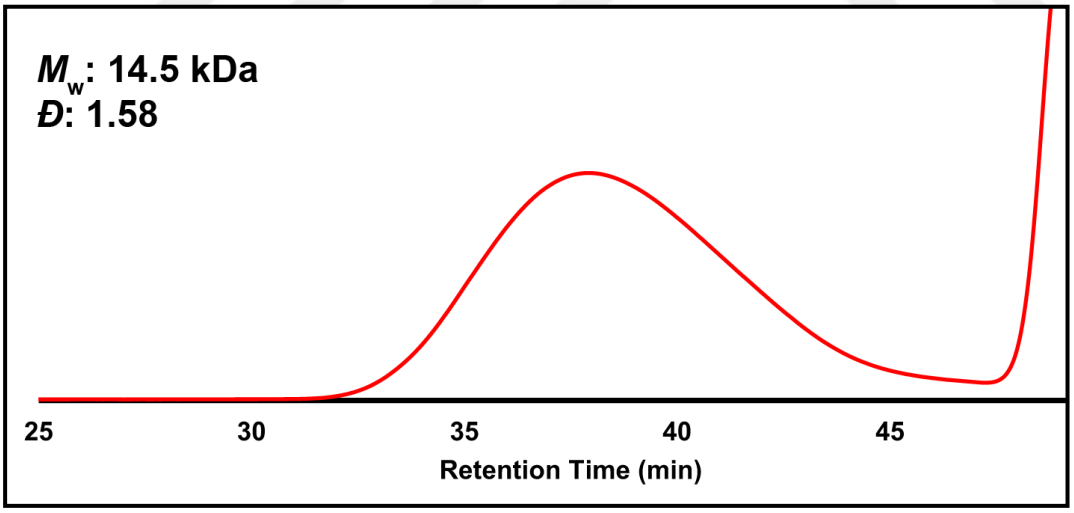


Figure 3.32 : GPC chromatogram of P9.

3.4.3.10 Synthesis of P10

General procedure was followed. TPA (0.443 g, 0.33 mmol), 2-butyne-1,4-diol (0.264 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction medium was observed to be turbid during the course of the reaction. P10 was obtained as an orange transparent sticky solid. (Yield = 406 mg, 72%). ^1H NMR (500

MHz, $CDCl_3$): δ = 7.36 (4H, Ar*H*), 4.61 (4H, ArCH_2O), 4.55 (4H, ArCH_2O), 4.24 (4H, OCH_2C≡CCH_2O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.08 (Ar*C*), 128.21 (Ar*C*), 127,93 (Ar*C*), 82.51 (OCH$_2$*C*≡*C*CH$_2$O), 71.84 (Ar*C*H$_2$O), 71.35 (Ar*C*H$_2$O), 57.41 (O*C*H$_2$C≡C*C*H$_2$O) ppm.

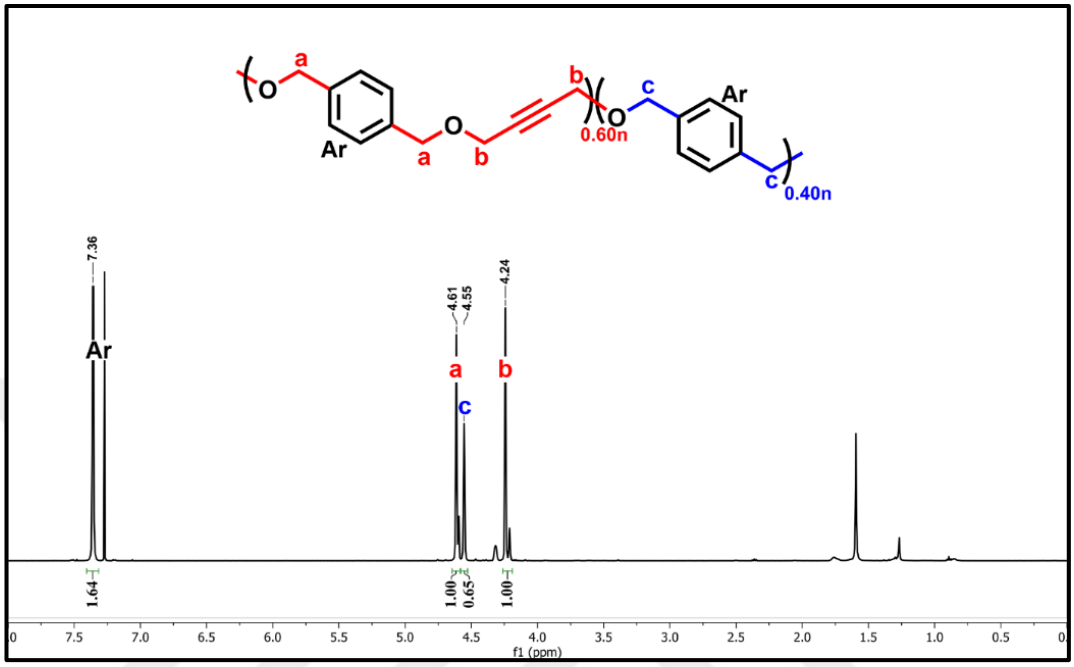


Figure 3.33 : ^{1}H NMR spectrum of P10 in $CDCl_3$ (500 MHz).

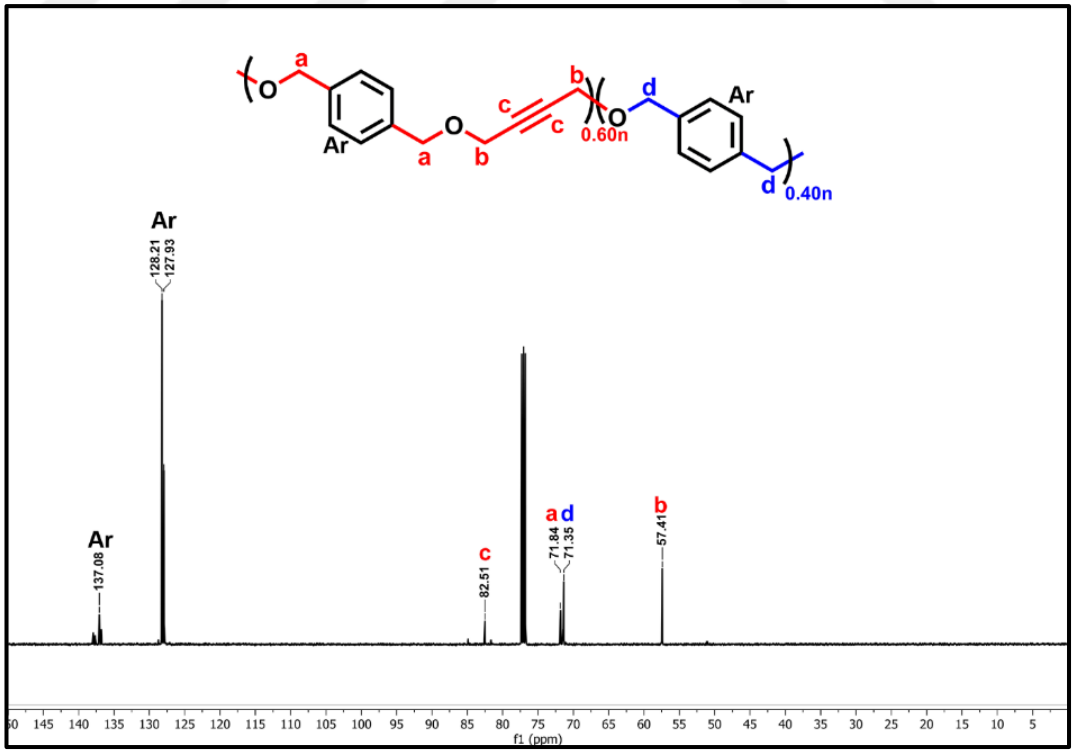


Figure 3.34 : ^{13}C NMR spectrum of P10 in $CDCl_3$ (125 MHz).

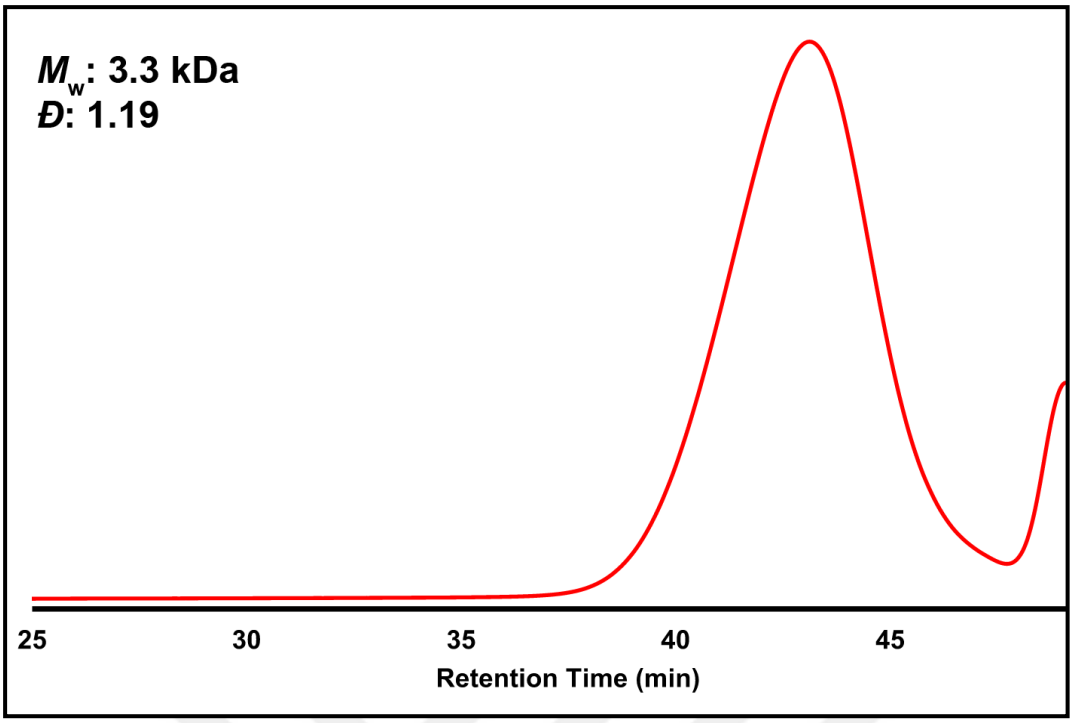


Figure 3.35 : GPC chromatogram of P10

3.4.3.11 Synthesis of P11

General procedure was followed. TPA (0.443 g, 0.33 mmol), 1,4-cyclohexanedimethanol (0.424 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction was observed to be slurry during the course of the reaction. P11 was obtained as a white solid. (Yield = 627 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (4H, Ar*H*), 4.55 (4H, ArC*H*$_2$O), 4.49 (4H, ArC*H*$_2$O), 3.37 (4H, OC*H*$_2$-cyclohexyl), 1.85, 1.61, 1.40, 0.97 (10H, aliphatic protons of cyclohexane) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.95 (Ar*C*), 127.68 (Ar*C*), 72.65 (Ar*C*H$_2$O), 71.82 (Ar*C*H$_2$O), 70.50 (O*C*H$_2$-cyclohexyl), 29.62/26.21 (aliphatic carbons of cyclohexane) ppm.

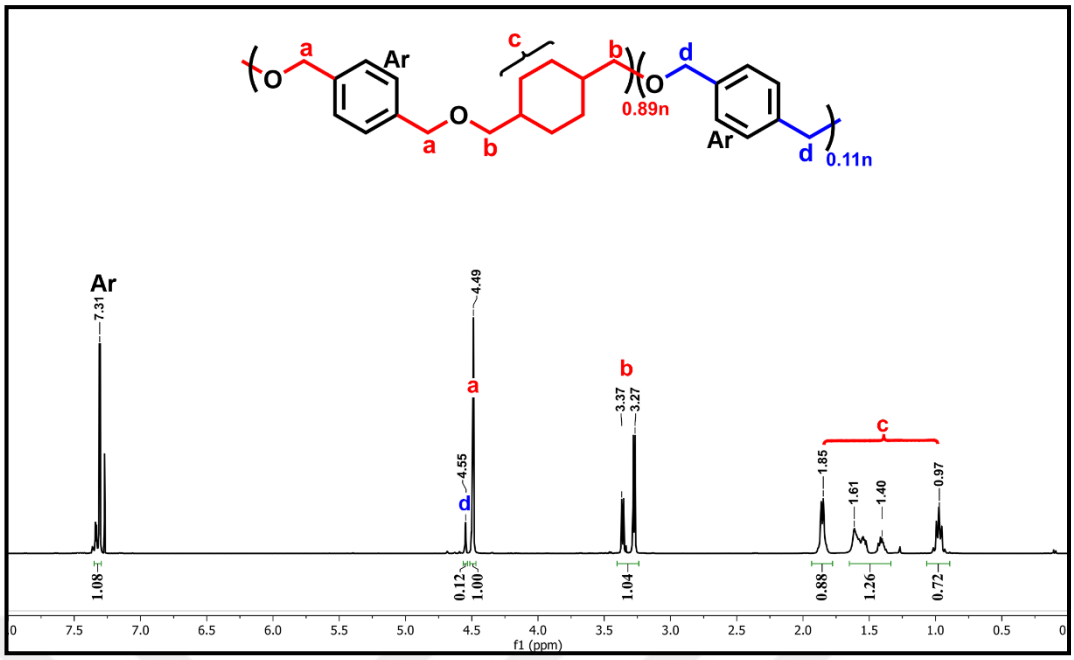


Figure 3.36 : ^{1}H NMR spectrum of P11 in $CDCl_3$ (500 MHz).

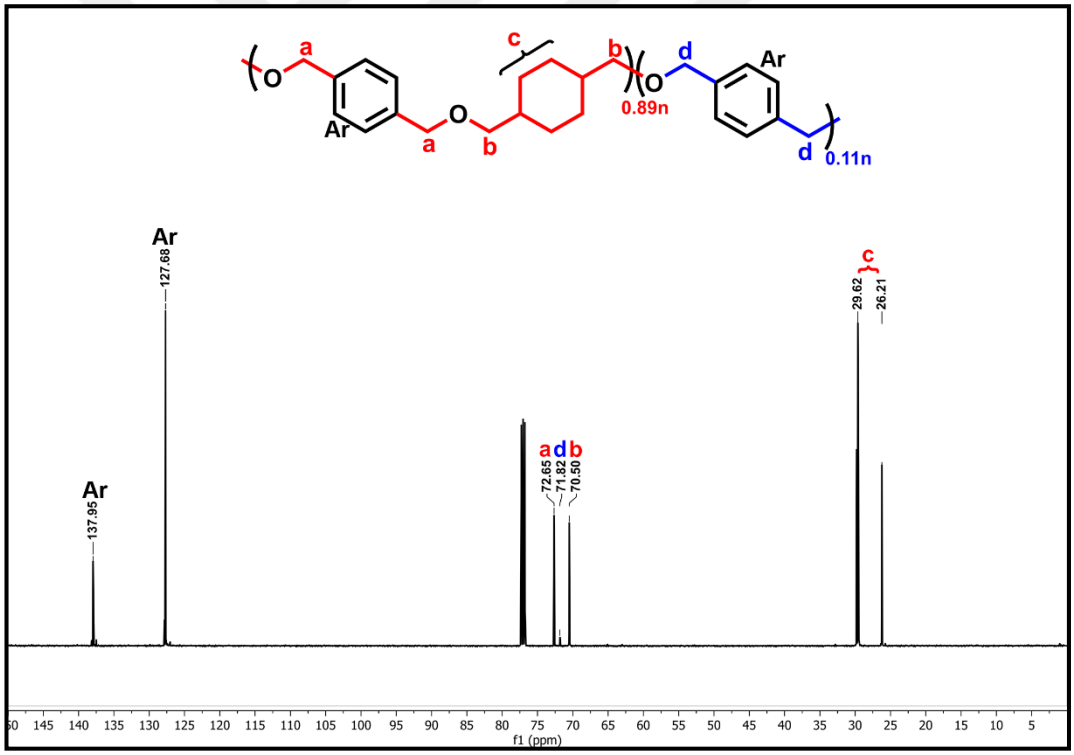


Figure 3.37 : ^{13}C NMR spectrum of P11 in $CDCl_3$ (125 MHz).

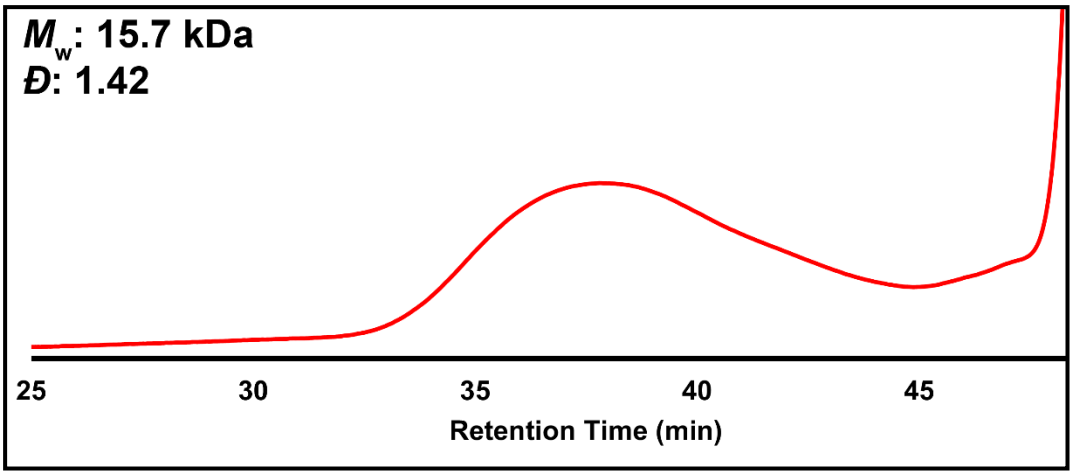


Figure 3.38 : GPC chromatogram of P11.

3.4.3.12 Synthesis of P12

General procedure was followed. TPA (0.443 g, 0.33 mmol), 1,1-bis(hydroxymethyl)cyclopropane (0.306 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction medium was observed to be slurry during the course of the reaction. P12 was obtained as a white sticky solid. (Yield = 514 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29 (4H, Ar*H*), 4.55 (4H, ArCH_2O), 4.51 (4H, ArCH_2O), 3.42 (4H, OCH_2-cyc), 0.49 (4H, CH_2 of cyclopropane). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.91 (Ar*C*), 127.65 (Ar*C*), 72.64 (Ar*C*H$_2$O), 72.66 (Ar*C*H$_2$O), 71.86 (O*C*H$_2$-cyc), 20.77/8.62 (aliphatic carbons of cyclopropane) ppm.

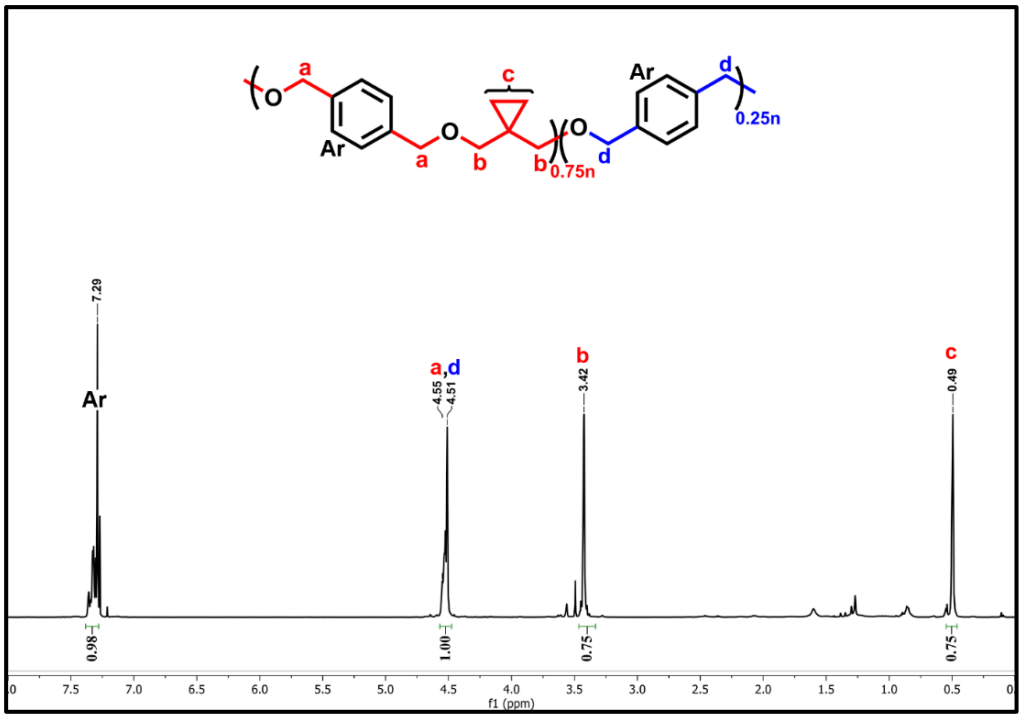


Figure 3.39 : ^{1}H NMR spectrum of P12 in $CDCl_3$ (500 MHz).

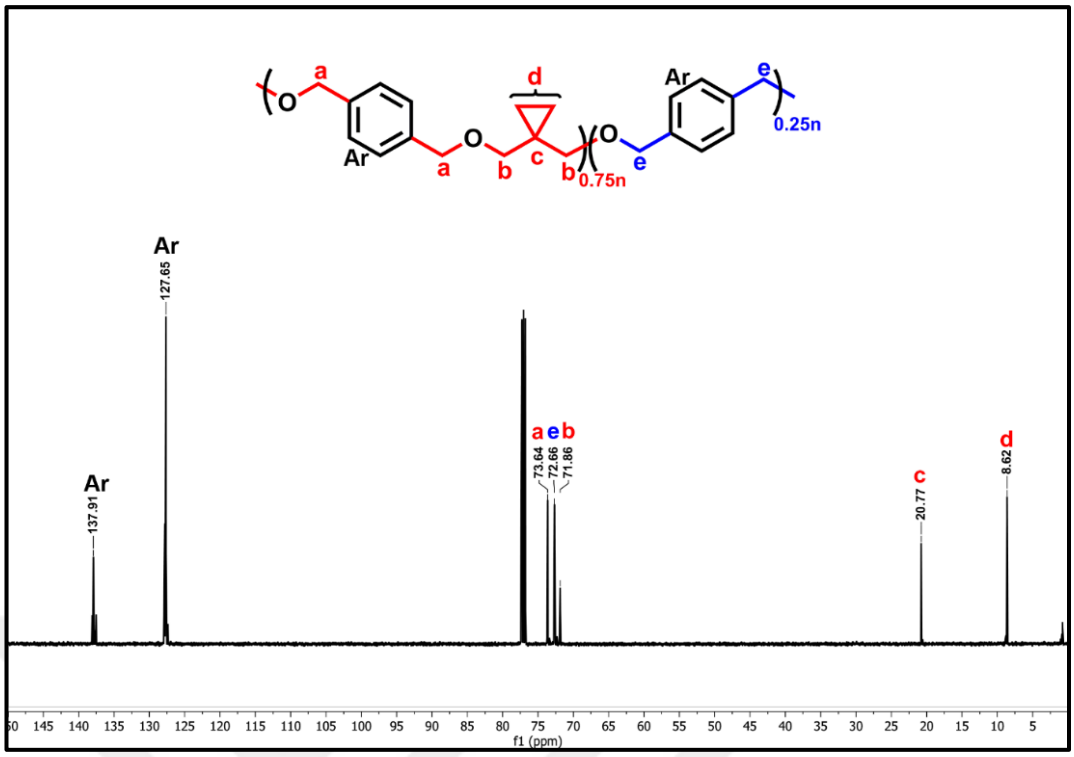


Figure 3.40 : ^{13}C NMR spectrum of P12 in $CDCl_3$ (125 MHz).

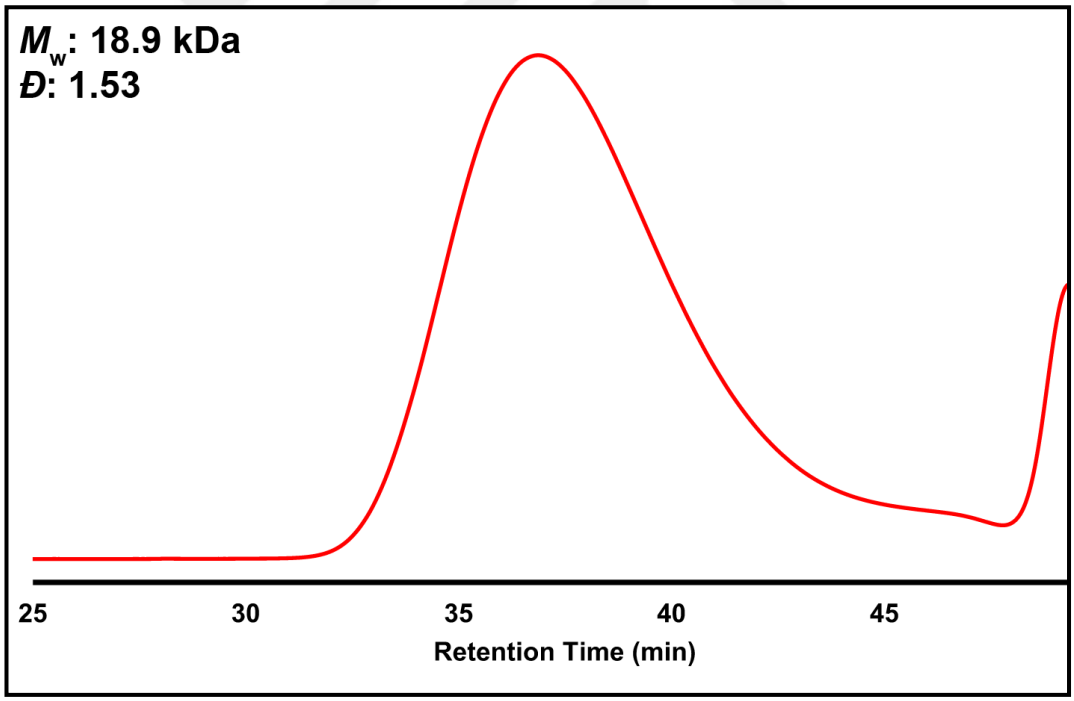


Figure 3.41 : GPC chromatogram of P12.

3.4.3.13 Synthesis of P13

General procedure was followed. TPA (0.443 g, 0.33 mmol), 4,8-bis(hydroxymethyl)tricyclo[5.2.1.$0^{2,6}$]decane (TDMol, 0.589 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction medium was

observed to be slurry during the course of the reaction. P13 was obtained as a white waxy solid. (Yield = 813 mg, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (4H, Ar*H*), 4.55 (4H, ArC*H*$_2$O), 4.49 (4H, ArC*H*$_2$O), 3.30-3.17 (4H, OC*H*$_2$-TDMol), 2.43-0.94 (14H, aliphatic protons of TDMol) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.99 (Ar*C*), 127.61 (Ar*C*), 74.73 (Ar*C*H$_2$O), 72.66 (Ar*C*H$_2$O), 71.86 (O*C*H$_2$-TDMol), 49.12/45.11/40.53/34.29/31.28/28.64/24.71 (aliphatic carbons of TDMol) ppm.

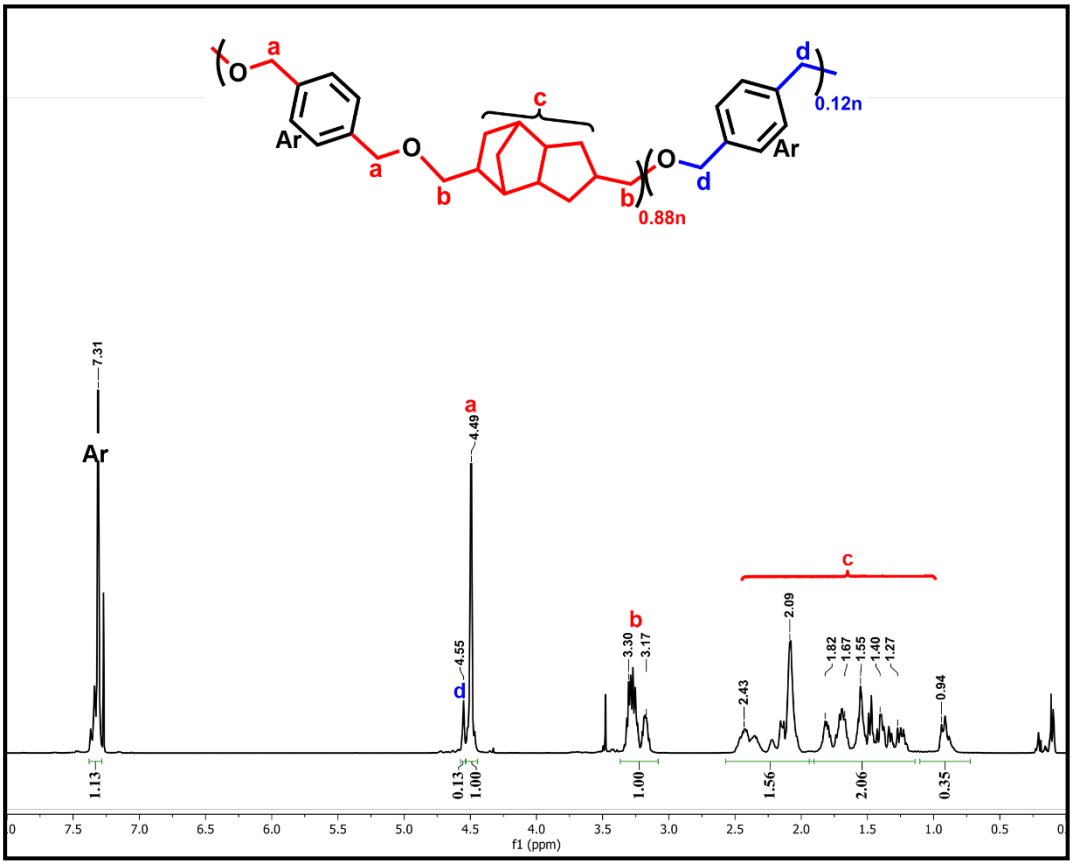


Figure 3.42 : ^{1}H NMR spectrum of P13 in $CDCl_3$ (500 MHz).

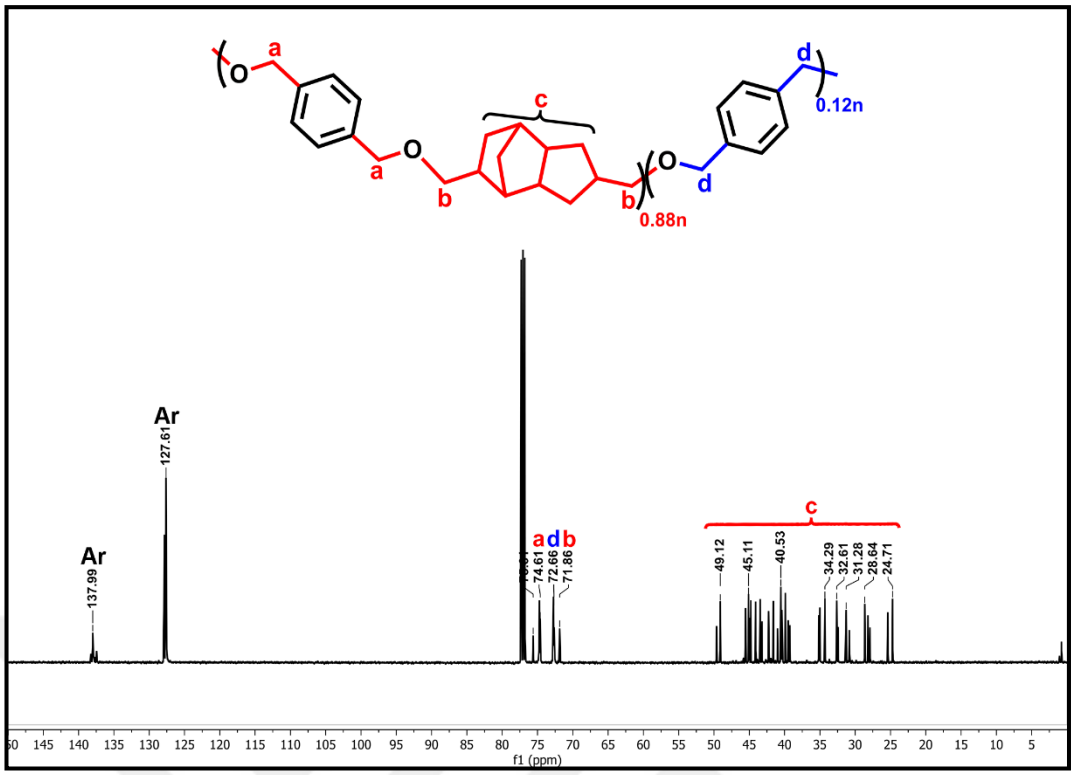


Figure 3.43 : ^{13}C NMR spectrum of P13 in $CDCl_3$ (125 MHz).

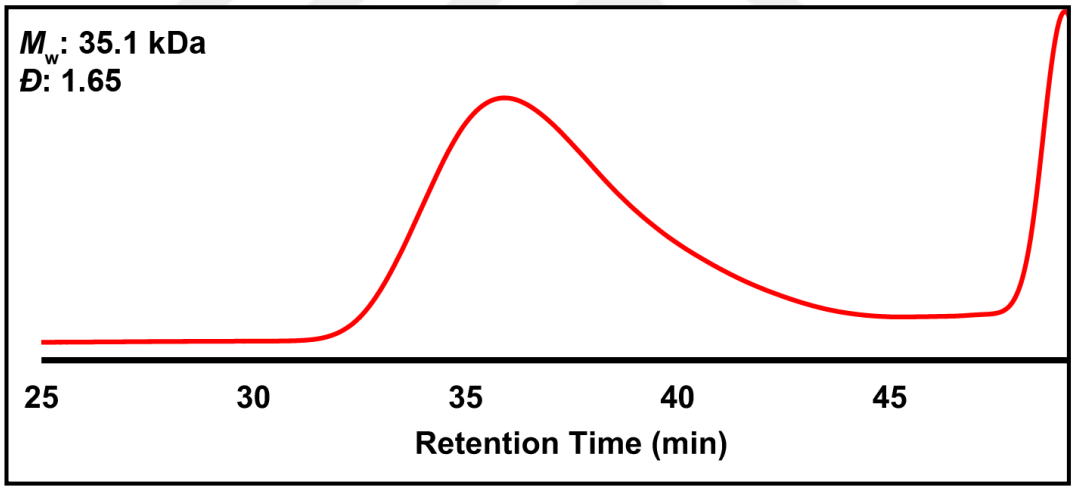


Figure 3.44 : GPC chromatogram of P13.

3.4.3.14 Synthesis of P14

General procedure was followed. TPA (0.443 g, 0.33 mmol), 2,5-hexanediol (0.354 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction mixture was observed to be slurry during the course of the reaction. P14 was obtained as a transparent sticky solid. (Yield = 561 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33-7.31 (4H, Ar*H*), 4.53 (4H, ArCH_2O), 4.45 (4H, ArCH_2O), 3.49 (2H, OC*H*(CH_3)CH_2CH_2C*H*(CH_3)O), 1.60 (4H, OCH(CH_3)CH_2CH_2CH(CH_3)O) 1.18 (6H, OCH(CH_3)CH_2CH_2CH(CH_3)O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 138.23 (Ar*C*),

127.64 (Ar*C*), 74.99 (Ar*C*H_2O), 70.11 (O*C*H(CH_3)CH_2CH_2*C*H(CH_3)O), 32.67/32.14 (OCH(CH_3)*C*H_2*C*H_2CH(CH_3)O), 19.70 (OCH(*C*H_3)CH_2CH_2CH(*C*H_3)O) ppm.

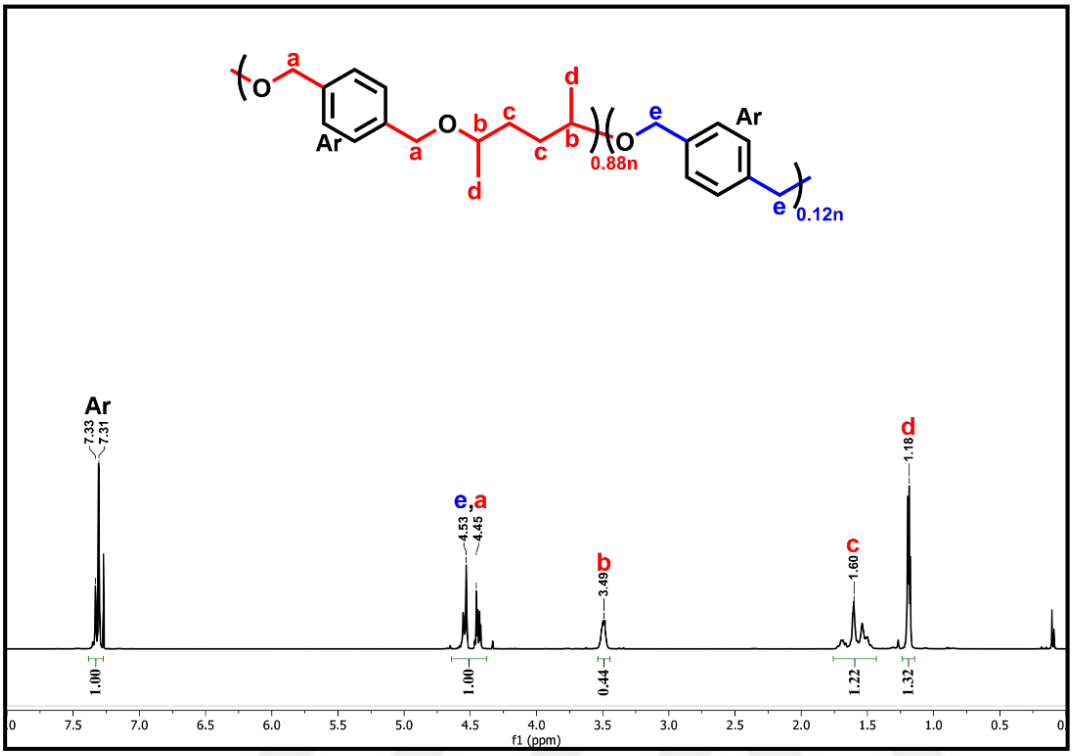


Figure 3.45 : ^{1}H NMR spectrum of P14 in $CDCl_3$ (500 MHz).

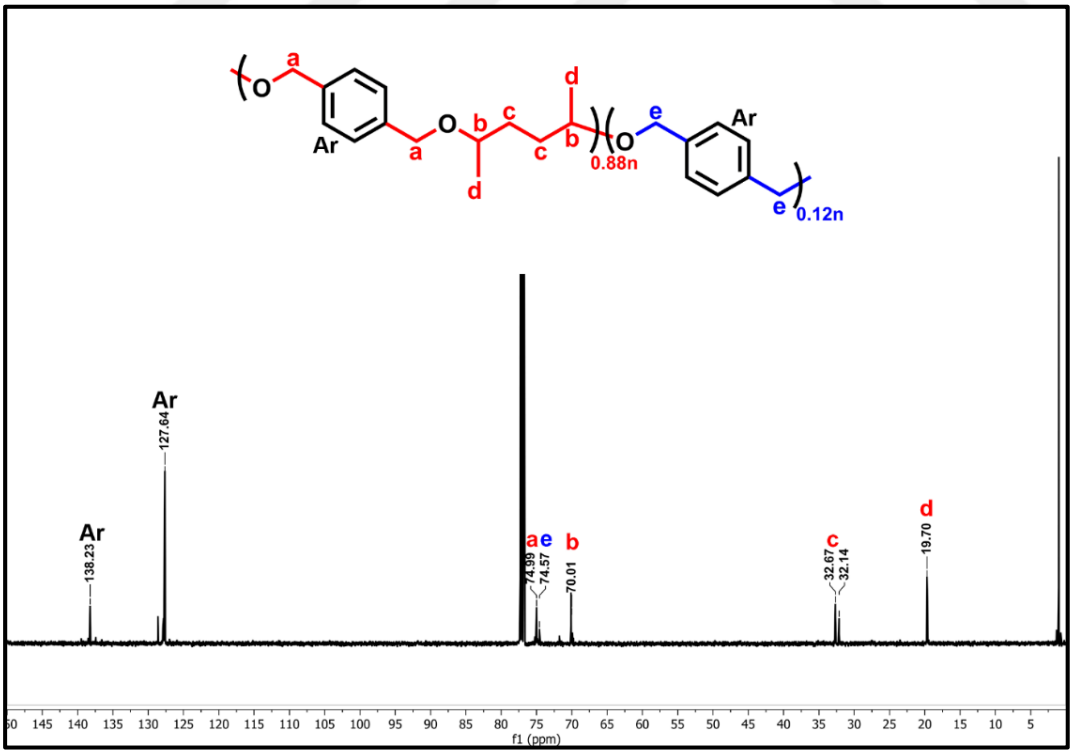


Figure 3.46 : ^{13}C NMR spectrum of P14 in $CDCl_3$ (125 MHz).

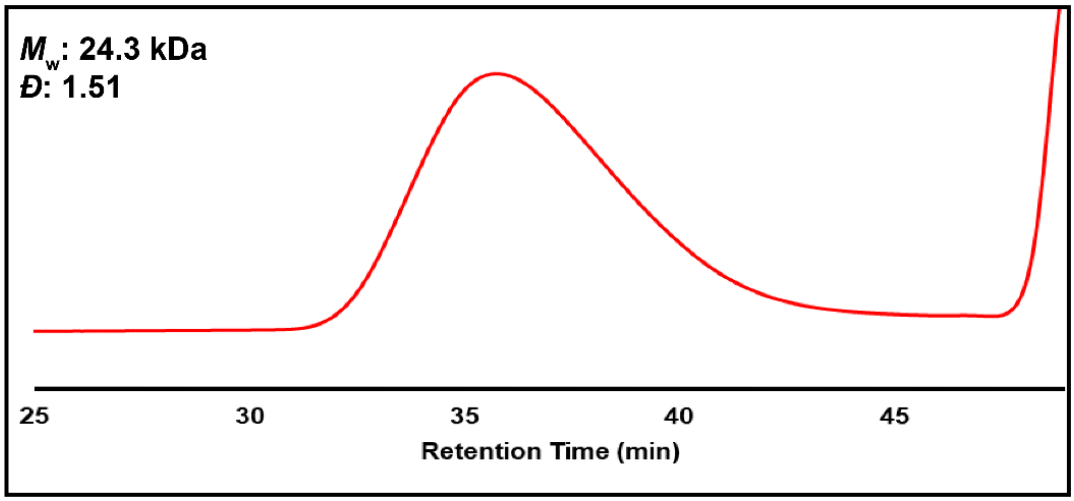


Figure 3.47 : GPC chromatogram of P14.

3.4.3.15 Synthesis of P15

General procedure was followed. TPA (0.443 g, 0.33 mmol), 1,5-hexanediol (0.354 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction mixture was found to be slurry during the course of the reaction. P15 was obtained as a transparent sticky solid. (Yield = 541 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31 (4H, Ar*H*), 4.54-4.44 (8H, ArC*H*$_2$O), 3.51-3.45 (3H, OC*H*(CH_3)$CH_2CH_2CH_2CH_2$O), 1.63-1.47 (6H, OCH(CH_3)C*H*$_2$C*H*$_2$C*H*$_2$$CH_2$O). 1.18 (3H, OCH(C*H*$_3$)$CH_2CH_2CH_2CH_2$O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 137.78 (Ar*C*), 127.66 (Ar*C*), 74.81 (Ar*C*H$_2$O), 72.68 (Ar*C*H$_2$O), 70.09 (O*C*H(CH_3)$CH_2CH_2CH_2CH_2$O), 36.46 (OCH(CH_3)*C*H$_2$$CH_2CH_2CH_2$O), 29.84 (OCH($CH_3$)$CH_2$*C*H$_2$$CH_2CH_2$O), 22.20 (OCH($CH_3$)$CH_2CH_2$*C*H$_2$$CH_2$O), 19.61 (OCH(*C*H$_3$)$CH_2CH_2CH_2CH_2$O) ppm.

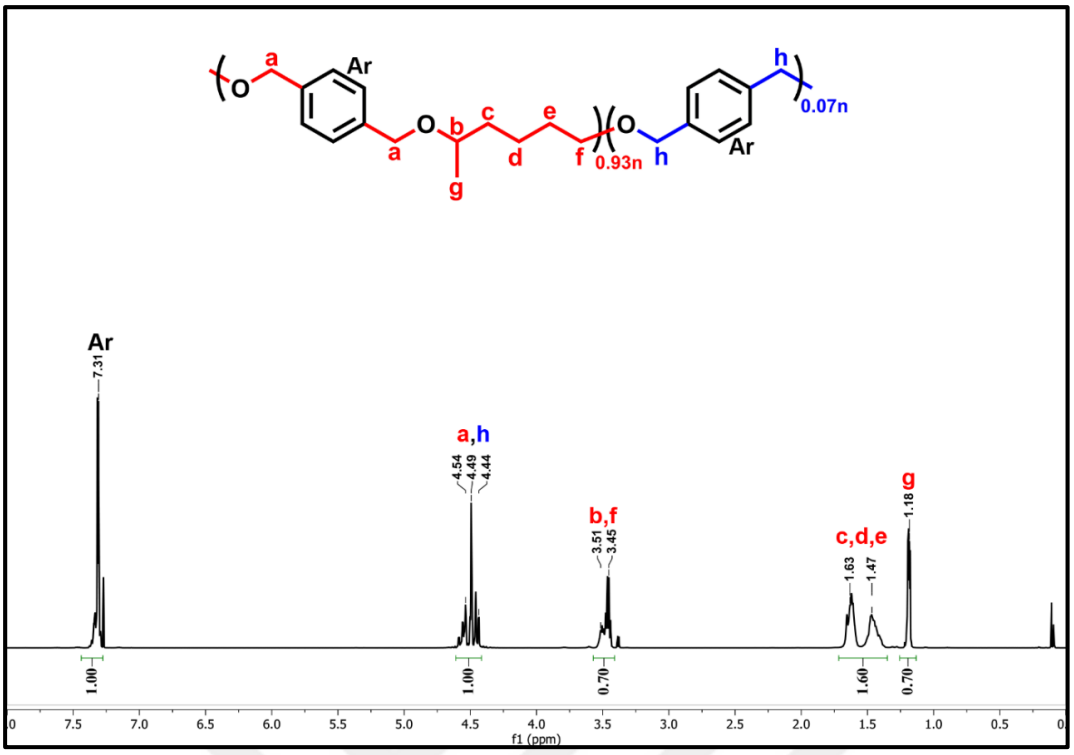


Figure 3.48 : ^{1}H NMR spectrum of P15 in $CDCl_3$ (500 MHz).

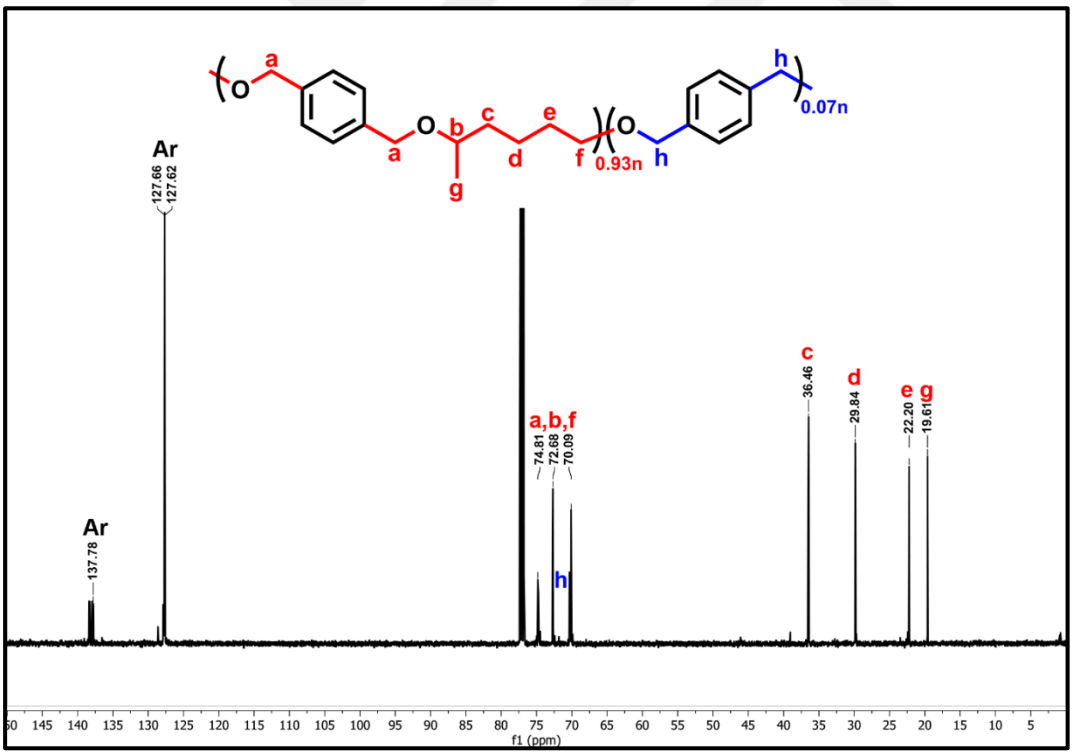


Figure 3.49 : ^{13}C NMR spectrum of P15 in $CDCl_3$ (125 MHz).

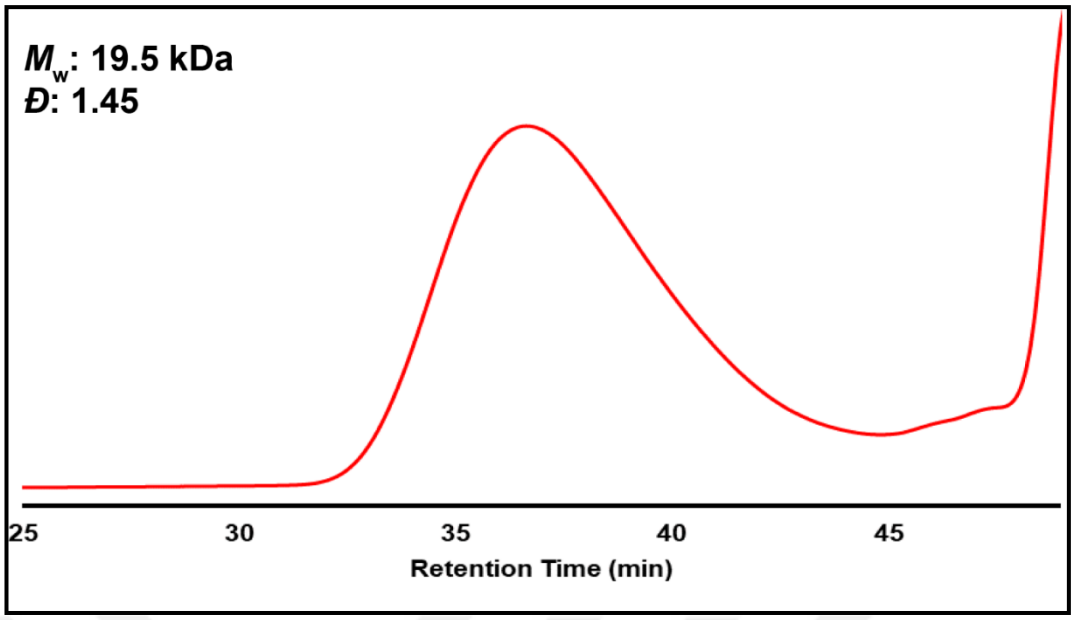


Figure 3.50 : GPC chromatogram of P15.

3.4.3.16 Synthesis of P16

General procedure was followed. Isophtalaldehyde (0.443 g, 0.33 mmol), 1,4-butanediol (0.27 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction mixture was found to be slurry during the course of the reaction. P16 was obtained as a pale yellow solid. (Yield = 507 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38-7.26 (4H, Ar*H*), 4.59 (4H, ArC*H*$_2$O), 4.55 (4H, ArC*H*$_2$O), 3.49 (4H, OC*H*$_2$CH$_2$CH$_2$C*H*$_2$O), 1.70 (4H, OCH$_2$C*H*$_2$C*H*$_2$CH$_2$O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.73 (Ar*C*), 128.44 (Ar*C*), 126.77 (Ar*C*), 72.79 (Ar*C*H$_2$O), 72.15 (Ar*C*H$_2$O), 70.23 (O*C*H$_2$CH$_2$CH$_2$*C*H$_2$O), 26.51 (OCH$_2$*C*H$_2$*C*H$_2$CH$_2$O) ppm.

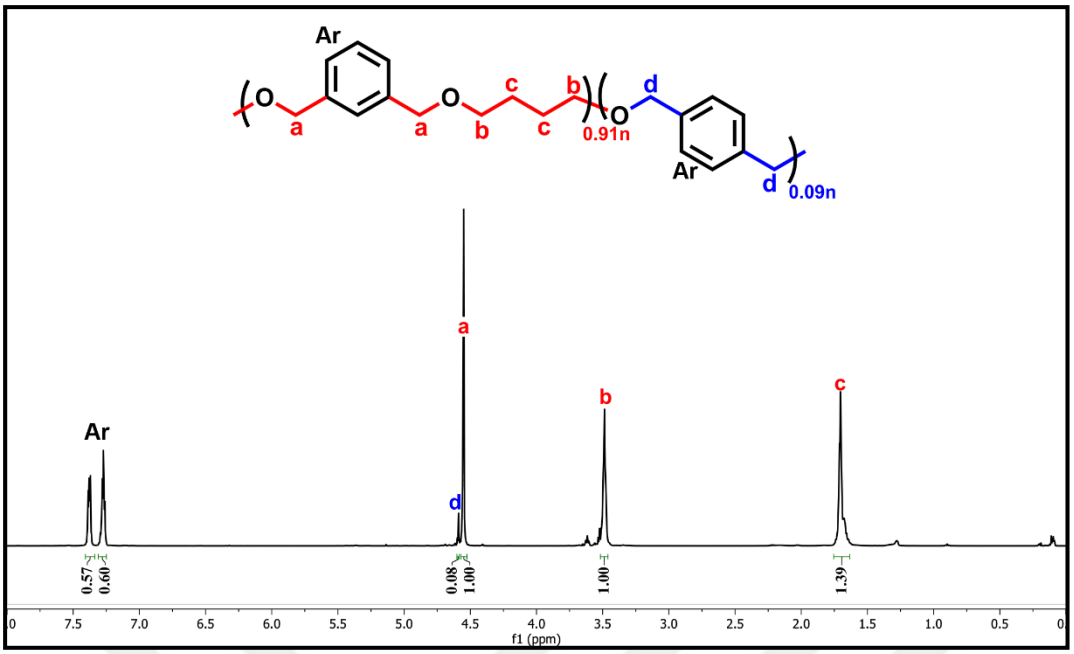


Figure 3.51 : ^{1}H NMR spectrum of P16 in $CDCl_3$ (500 MHz).

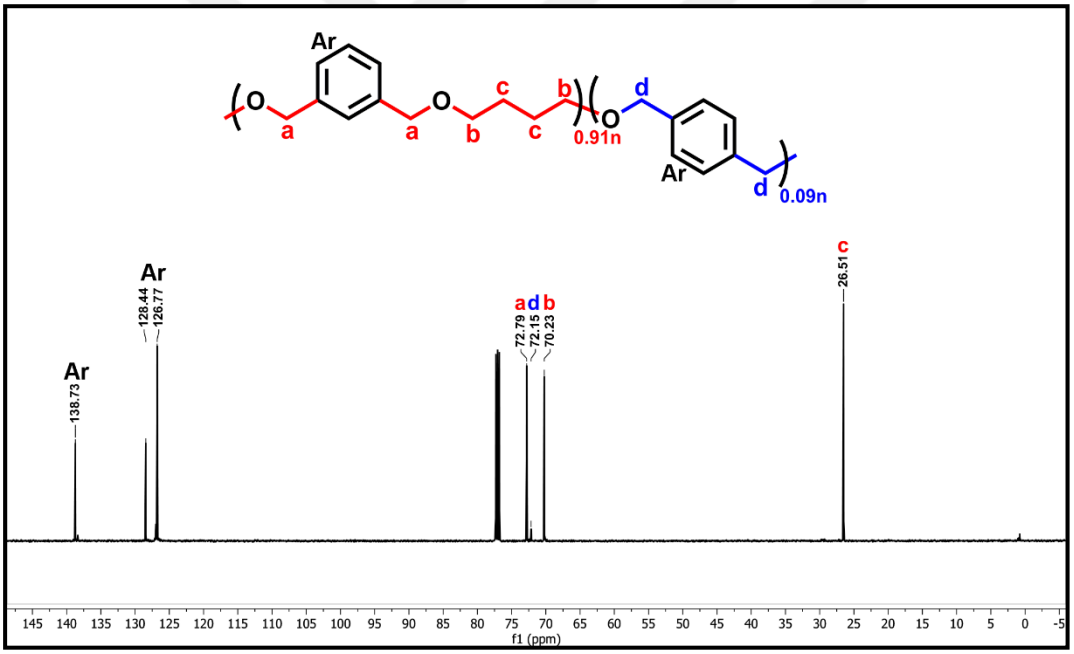


Figure 3.52 : ^{13}C NMR spectrum of P16 in $CDCl_3$ (125 MHz).

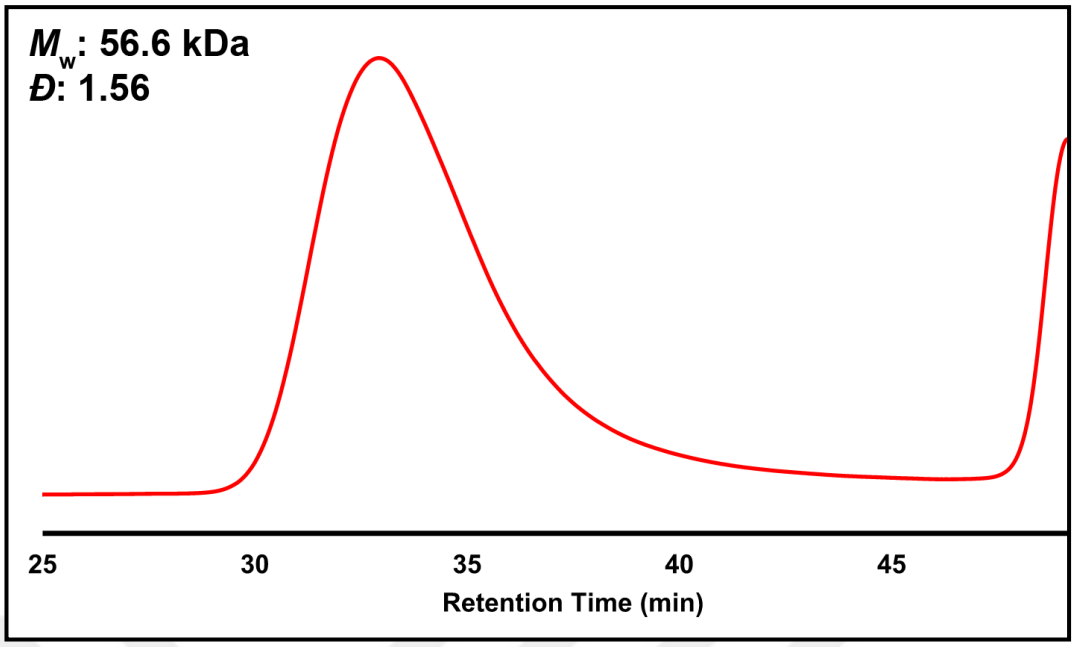


Figure 3.53 : GPC chromatogram of P16.

3.4.3.17 Synthesis of P17

General procedure was followed. Phtalaldehyde (0.443 g, 0.33 mmol), 1,4-butanediol (0.27 g, 0.30 mmol), CDMS (2 mL, 1.80 mmol) and 1 mL of CH_3NO_2 were used. The reaction mixture was found to be slurry during the course of the reaction. P17 was obtained as a white sticky solid. (Yield = 461 mg, 80%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.33-7.25 (4H, Ar*H*), 4.56 (4H, ArC*H*$_2$O), 4.50 (4H, ArC*H*$_2$O), 3.50 (4H, OC*H*$_2$CH$_2$CH$_2$C*H*$_2$O), 1.72 (4H, OCH$_2$C*H*$_2$C*H*$_2$CH$_2$O) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 136.57 (Ar*C*), 128.50 (Ar*C*), 127.62 (Ar*C*), 70.51 (ArCH$_2$O), 70.41 (ArCH$_2$O), 70.31 (OCH$_2$CH$_2$CH$_2$CH$_2$O), 26.63 (OCH$_2$CH$_2$CH$_2$CH$_2$O) ppm.

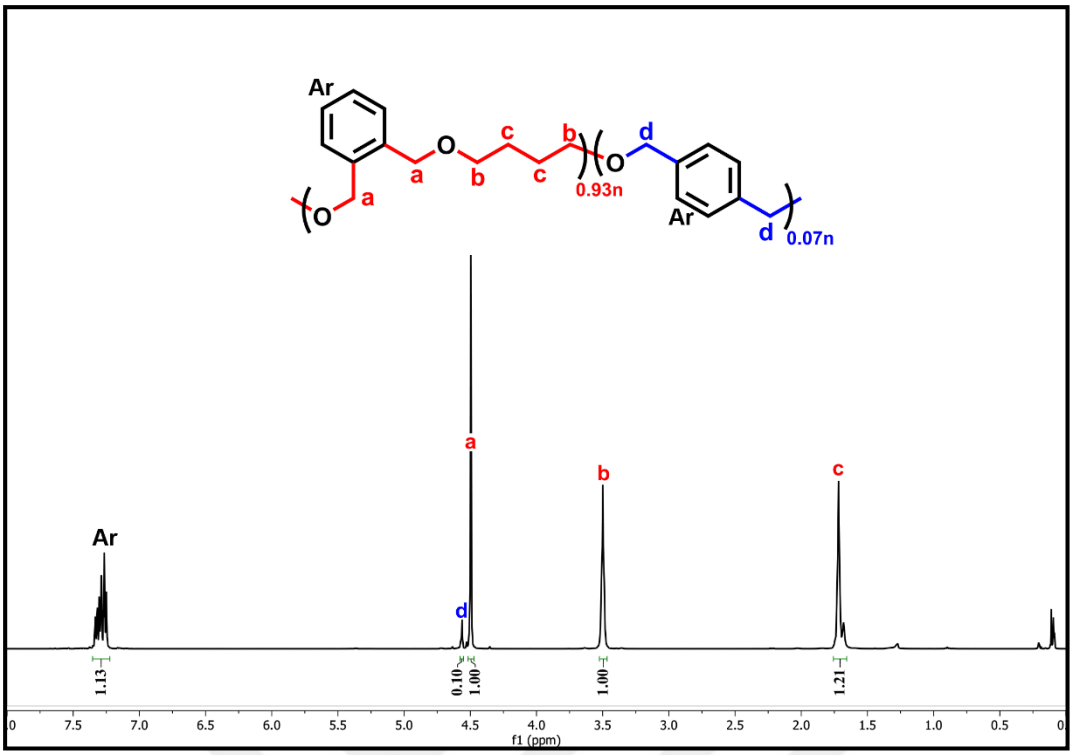


Figure 3.54 : ^{1}H NMR spectrum of P17 in $CDCl_3$ (500 MHz).

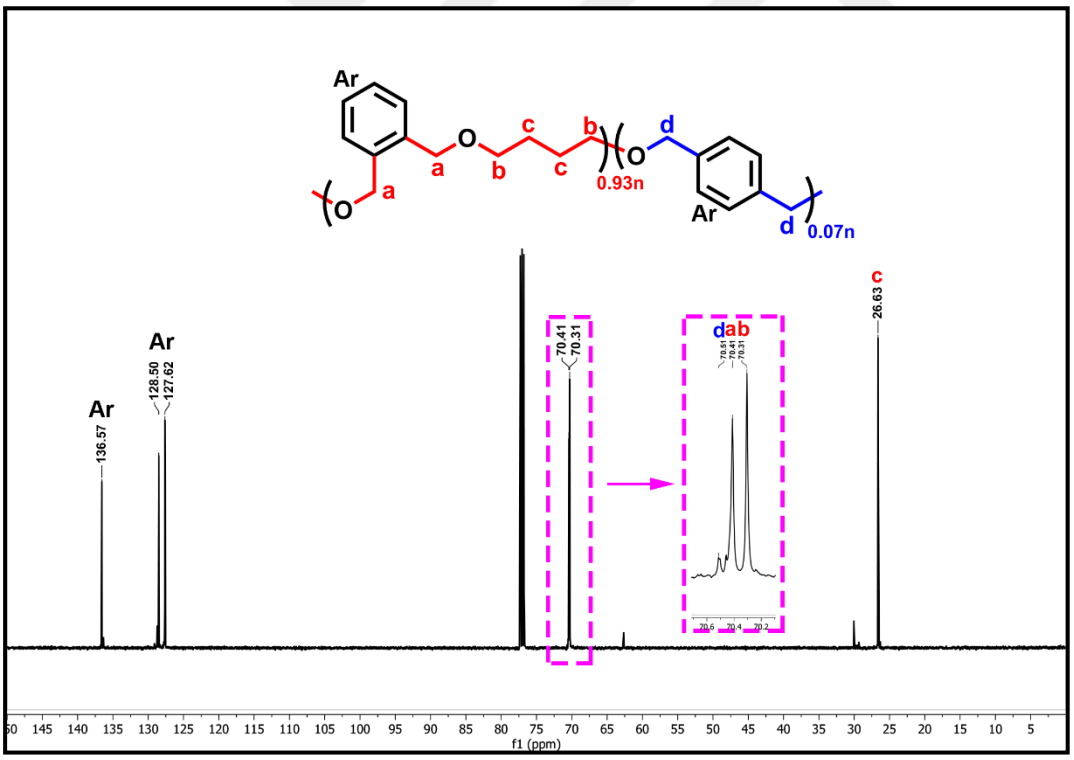


Figure 3.55 : ^{13}C NMR spectrum of P17 in $CDCl_3$ (125 MHz).

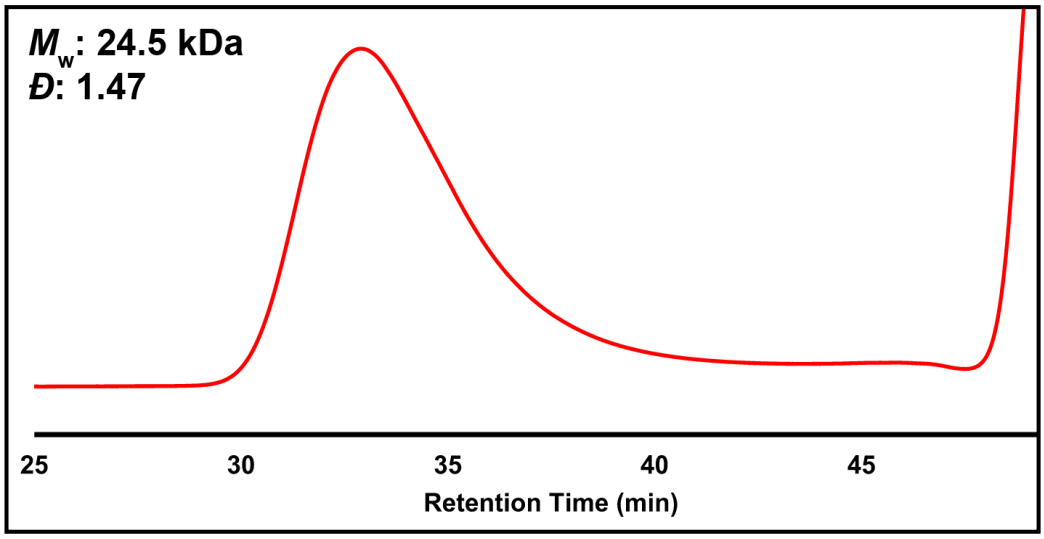


Figure 3.56 : GPC chromatogram of P17.

3.4.3.18 End-Group Modification Reaction of P1

P1 [(run 12, Table 1), 450 mg)] was added to a 50 mL round bottom flask and dissolved in 10 mL of DCM. Then, Et_3N (1.30 mL, 9.36 mmol) was added to this polymer solution, and the reaction mixture was cooled to 0 ^oC using an ice bath. Acryloyl chloride (0.189 mL, 4.68 mmol) dissolved in 5 mL of DCM was added dropwise to this solution. After the addition was complete, the reaction mixture was stirred at 0 ^oC for 15 min, then the ice bath was removed and the reaction stirred at room temperature for 24 h. After that, excess of CH_2Cl_2 was evaporated and the mixture was precipitated into 50 mL of CH_3OH. The dissolution-precipitation procedure ($CHCl_3$-CH_3OH) was repeated two times. Finally, the obtained polymer was dissolved in 5 mL of $CHCl_3$ and transferred to a glass vial and the solvent was evaporated to yield a white solid. ^1H NMR (500 MHz, $CDCl_3$): δ = 7.30 (4H, Ar*H*), 6.38, (1H, CH_2=C*H*C(=O)OCH_2) 6.13/5.81 (2H, C*H*$_2$=CHC(=O)OCH_2), 4.49 (4H, ArC*H*$_2$O), 4.19 (4H, CH_2=CHC(=O)OC*H*$_2$), 3.48 (4H, OC*H*$_2$$CH_2$$CH_2$C*H*$_2$O), 1.70 (4H, O$CH_2$C*H*$_2$C*H*$_2$$CH_2$O) ppm.

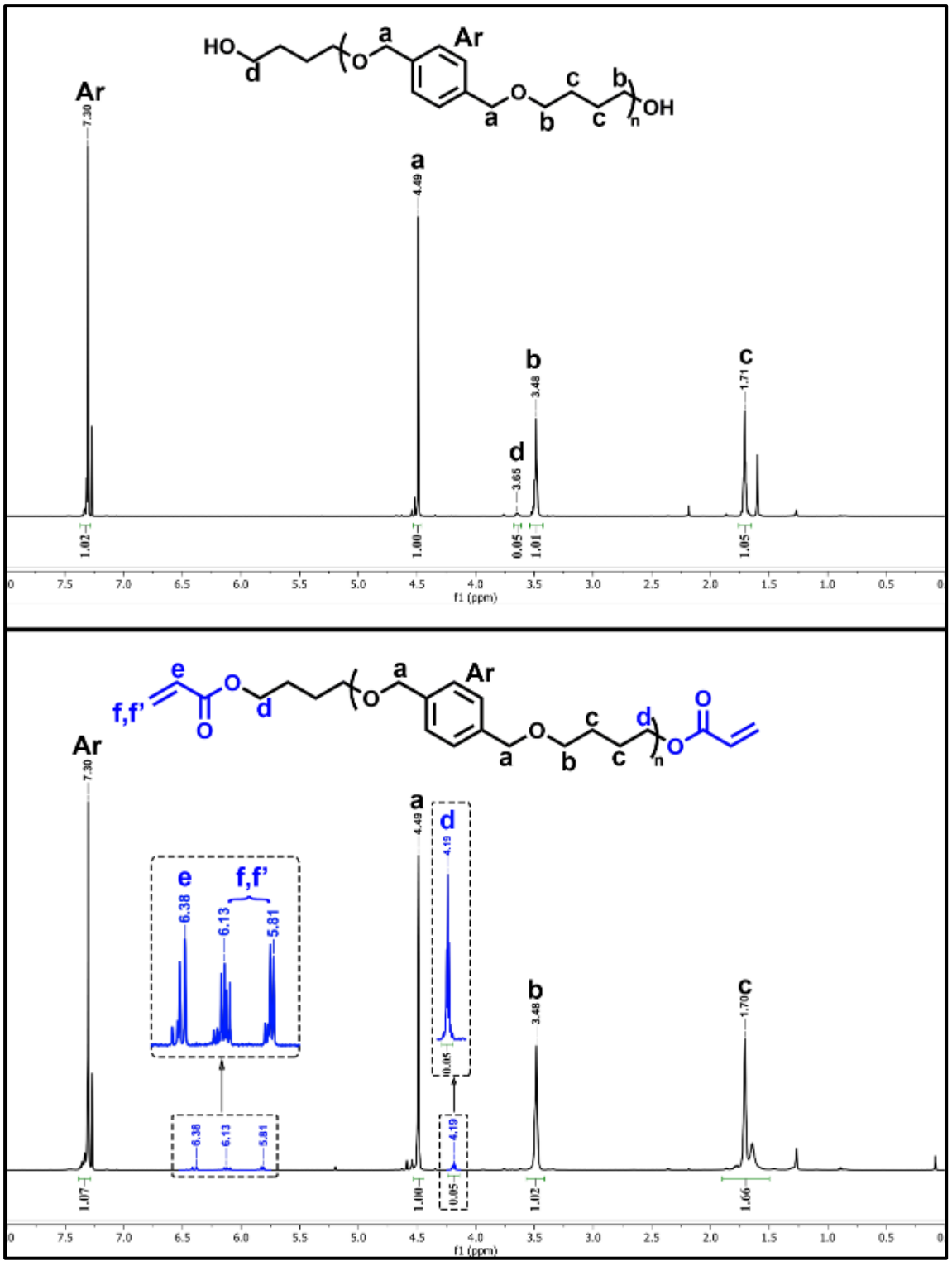


Figure 3.57 : ^{1}H NMR spectra of P1 (run 12, Table 1) before (top) and after (bottom) end-group modification reaction in $CDCl_3$ (500 MHz).

4. A STRAIGHTFORWARD AND RAPID PROTOCOL FOR THE SYNTHESIS OF POLY(THIOACETAL)S: THE BEAUTY OF CHLORODIMETHYLSILANE AS A CATALYST[3]

4.1 Introduction

Thioacetals are one of the very renowned functional groups in organic chemistry as they can be used as Umpolung reagent [74]. However, their polymeric analogues, polythioacetals (PTA) have not been widely explored in polymer science. PTAs are special polymers comprising thioacetal units that can be synthesized by reacting an aldehyde or a ketone with a dithiol in the presence of an acid catalyst [75-77]. The first example of PTA was achieved by the reaction of pentaerythritol and 1,4-cyclohexadione to yield a spiran type of polymer by Fisher and Wiley [78, 79]. Then, linear PTA synthesis was employed by Marvel and co-workers, using various carbonyl compounds and dithiols in the presence of dry $HCl_{(g)}$ [78, 79]. More recently, *p*-toluenesulfonic acid (PTSA) cataylzed linear PTA synthesis was employed to obtain PTA-based vitrimers as well [80].

PTAs differ from their oxygen analogues by their strong stability in acidic and basic conditions [81, 82]; however, the bond is labile in the presence of reactive oxygen species (ROS), making them attractive for applications where controlled degradation is desired, such as targeted drug delivery and tissue engineering. To this end, Wilson and co-workers have synthesized polymeric thioacetals, using 1,4-benzenedimethandithiol and 2,2-dimethoxypropane, to load with small interfering (siRNA) against the proinflammatory cytokine tumour necrosis factor-alpha (TNFα) to inhibit gene expression in the intestines [83]. Cinnamaldehyde-based PTAs were developed as a vehicle to be used in immunocancer therapy and also in wound healing in many different based mainly on their ROS responsiveness [76, 83-87].

Reductive etherification reaction (RER) is a straightforward strategy to obtain symmetric or asymmetric ethers in the presence of a reducing silane agent in an acid

[3] In Preparation

catalyst [21, 23, 24, 28-34, 67]. Amongst the reducing agents used, chlorodimethylsilane (CDMS) was found to have both characteristics of a reducing agent, and a Lewis acid character [38]. The RER and CDMS-mediated RER protocol can also be adapted to polymer science in order to synthesize linear polymers, as well as a PPM method [35-37, 58, 71-73, 88, 89]. From one of our group's last works, a pendant aldehyde group containing polymer was subjected to CDMS-mediated RER in order to obtain pendant ether and thioether groups using alcohols and thiols, respectively. Strikingly, along with side chain thioether groups, thioacetal formation was also reported in this work [88]. From here, we envisoned that turning this side reaction to our advantage to a new protocol with a particular focus on the synthesis of PTAs in the presence of CDMS; hence, in this paper, we aim to provide an in-depth overview of CDMS-mediated PTA synthesis. Optimization of the polymerization was carried out in multiple aspects in order to reveal the ideal conditions. Then, a wide range of aldehydes and dithiols, a total of 19, were used to create a polymer library and reported that moderate to high molecular weights and yields could be achieved (Scheme 1). Additionally, a mechanistic approach was also highlighted for polymerization. Finally, to show the degradability of the polymer, degradation of the PTA was studied in the presence of H_2O_2.

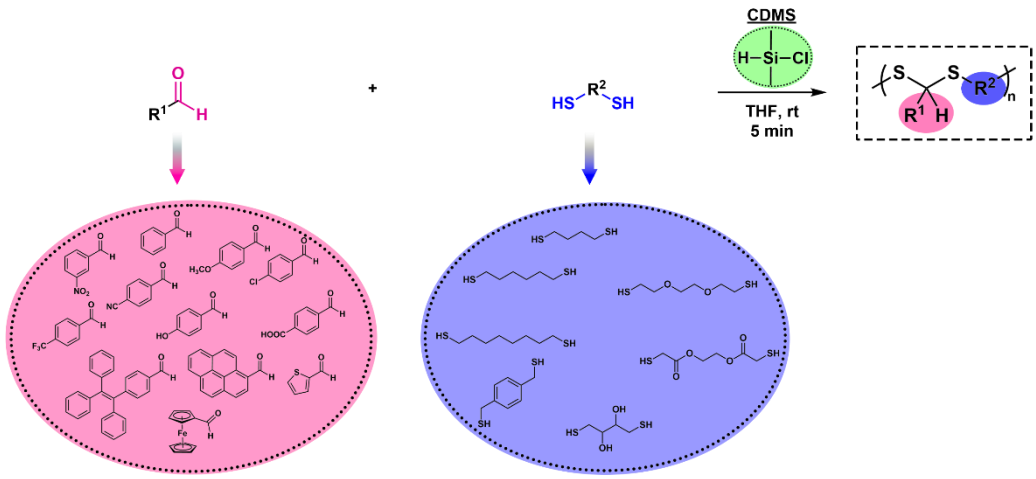


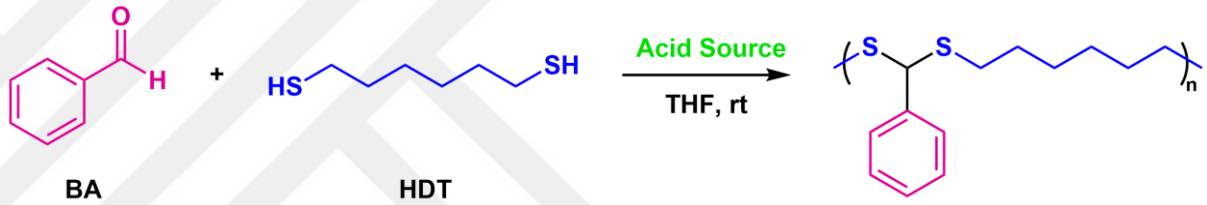
Figure 4.1 : Synthetic route for the synthesis of PTAs in the presence of CDMS.

4.2 Results and discussion

Optimization of the polymerization conditions for PTA (P1) was carried out in multiple aspects. During these studies, BA and HDT were chosen as the model monomers for the polymerization, and the reaction was performed in THF at room

temperature. It is a known fact that PTA synthesis can be carried out in the presence of Brønsted acids. For this purpose, the effects of different acids, H_2SO_4, PTSA, and MSA, along with CDMS, on polymerization were initially compared and summarized in Table 1. Initially, polymerization was carried out by using equimolar BA and HDT, in the presence of 0.01 equiv of the acids in 1 mL of THF, at room temperature, and the reaction was monitored over 72 h. In all cases, polymerization was observed starting from 1 h with increasing molecular weights over 72 h, in which H_2SO_4, PTSA, MSA, and CDMS resulted in molecular weights of 3.93 kDa, 4.00 kDa, 4.25 kDa, and 8.21 kDa, respectively (run 1,4,7 and 10, Table 1). When the acid ratios were increased to 0.10 equiv, an improvement on the molecular weight of the P1 was also observed as well (runs 2,5,8 and 11, Table 1), especially when PTSA, MSA and CDMS were used, in which the molecular weights were notably increased to 17.7 kDa, 17.8 kDa and 22.6 kDa over the course of the reaction, respectively (runs 5,8 and 11, Table 1). Finally, when the equiv of the acids was further increased to 0.25; H_2SO_4 and PTSA were increased up to 25.5, and 40.5 kDa, respectively (runs 3 and 6, Table 1). An increment in the ratio of MSA to 0.25 equiv had no significant effect when compared to the former (run 9, Table 1). However, when 0.25 equiv of CDMS was used, the molecular weight was increased dramatically, up to 69.9 kDa over 3 days, when compared to both other acids and other ratios of CDMS (run 12, Table 1). This difference can be attributed to the polymerization mechanism, which will be explained in detail later on. From these results, CDMS found to be the better alternative as an acid source, and all the other studies were carried out using CDMS. It should also be noted here that with the addition of the catalysts, an exothermic reaction occurs and the reaction medium turns into a turbid solution during the course of the polymerization.

Table 4.1 : Effect of the Acid Sources on Polymerization[a]



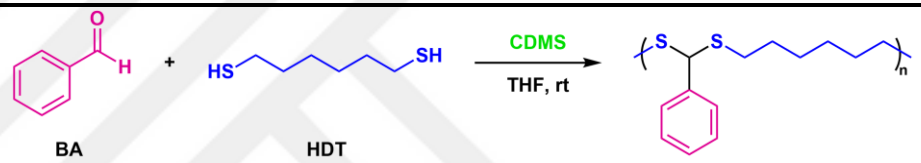
M_w (kDa)[b]/$Đ$[b]

run	Acid source	equiv	1h	4h	8h	24h	48h	72h
1		0.01	2.29/2.63	2.58/2.39	3.36/3.39	3.79/2.75	3.83/2.87	3.93/2.73
2	H_2SO_4	0.10	2.88/3.17	3.14/2.98	4.41/2.85	5.11/2.53	6.34/2.46	7.26/2.23
3		0.25	5.68/3.16	10.1/2.23	11.1/2.11	16.2/1.77	20.6/1.52	25.5/1.51
4		0.01	1.55/2.04	2.23/2.34	3.21/3.04	3.30/2.68	3.86/3.45	4.00/3.17
5	PTSA	0.10	2.96/2.59	3.51/2.62	7.52/2.54	10.6/1.87	15.7/1.42	17.7/1.58
6		0.25	7.22/3.25	14.0/2.95	21.3/1.58	28.9/1.41	37.3/1.51	40.5/1.66
7		0.01	2.08/3.39	2.31/3.14	2.44/3.23	2.91/3.14	4.19/3.41	4.25/3.25
8	MSA	0.10	2.78/2.99	3.55/2.66	6.52/2.53	10.7/2.12	14.5/1.71	17.8/1.42
9		0.25	4.61/3.55	6.39/2.99	10.1/2.66	17.3/2.83	17.8/3.21	19.0/2.97
10		0.01	3.27/2.35	3.56/2.90	4.31/2.49	5.20/2.25	5.71/2.60	8.21/2.93
11	CDMS	0.10	3.69/2.61	4.00/3.21	4.87/3.01	9.91/2.17	18.3/1.88	22.6/ 1.68
12		0.25	12.5/2.39	18.9/1.42	34.5/1.54	43.6/1.50	57.4/1.52	69.9/1.55

[a]All reactions were carried out using BA:HDT at a mole ratio of 1:1 in 1 mL of THF at room temperature. [b]Determined by GPC calibrated based on linear PS standards in THF.

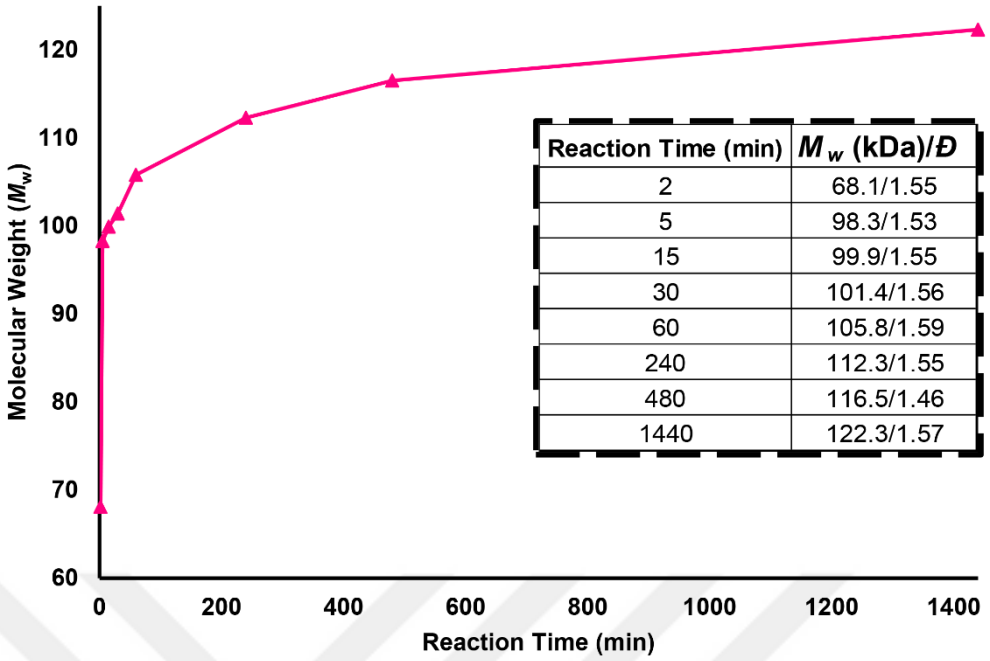
Next, the effect of the CDMS ratio and monomer concentration on polymerization was progressively monitored by taking samples from the reaction medium at regular intervals to determine the ideal polymerization duration. Upon closer examination, when 0.25 equiv of CDMS was used, it was found that the formation of P1 started very early, within 2 min, with a molecular weight of 5.73 kDa and progressively increased over 24 h to 43.6 kDa (run 1, Table 1). When the CDMS amount was increased to 0.5 equiv, the reaction rate was found to be increased, in addition, the obtained molecular weights were also increased from 13.7 kDa in 2 mins to 65.5 kDa in 24h (run 2, Table 1). Finally, when CDMS was increased to 1 equiv, the reaction progression was found to be somewhat similar to the 0.50 equiv, yet, after 24h the molecular weight was slightly lower than the former (run 3, Table 2). This can be attributed to the increased acidity of the medium due to CDMS, hence could degrade the resulting PTA. As a result, 0.5 equiv was chosen to continue to the next stage, which was to use different monomer concentrations. When the monomer concentration was increased to [4M] (with respect to HDT), the reaction rate and the molecular weight increased tremendously; a molecular weight of 21.7 kDa was observed in 2 min and found to be increased to 85.1 kDa over 24 h (run 4, Table 2). On the other hand, reducing the monomer of the concentration by half resulted in a dramatic loss of both the polymerization rate and the molecular weight of the resulting polymer (run 5, Table 2). Another part that should be highlighted is that in the presence of CDMS, an aldehyde can reduce to its alcohol analogue via RER, which could easily cause an equivalent imbalance within the reactants. For this purpose, another iteration was made by increasing the BA amount by 10%, resulting in a dramatic increase in both the reaction rate and the molecular weight of the P1. As shown in Figure 1, in 2 min, the molecular weight of the polymer was found to be 68.1 kDa, rose to 98.3 kDa in 5 min and somewhat slightly increased to 122.3 kDa over 24 h (run 6, Table 2). Yet, further increment in the amount of BA resulted in a lower molecular weight over 24 h (M_w = 89.3 kDa) which can be attributed to a new equivalent imbalance between the two monomers (run 7, Table 2). In summary, the ideal equivalents for BA:HDT:CDMS were found to be 1.1:1:0.5 in 1 mL of THF and the polymerization duration for the proposed strategy was set to 5 min and these conditions were used in the next studies

Table 4.2 : Effect of different parameters on polymerization[a]



			M_w (kDa)[b]/$Đ$[b]							
run	[BA]:[HDT]:[CDMS]	[HDT] (M)	2 min	5 min	15 min	30 min	60 min	240 min	480 min	1440 min
1	1:1:0.25	2	5.73/1.78	8.21/1.56	9.98/1.77	11.1/1.68	12.5/2.39	18.9/1.42	34.5/1.54	43.6/1.50
2	1:1:0.50	2	13.7/1.95	27.4/1.48	29.6/1.59	33.2/1.44	36.2/1.51	37.9/1.49	41.2/1.59	65.5/1.53
3	1:1:1	2	17.7/1.66	23.1/1.58	34.3/1.44	39.5/1.45	47.6/1.47	49.4/1.47	50.2/1.55	57.3/1.46
4	1:1:0.50	4	21.7/1.54	49.3/1.48	51.6/1.52	53.6/1.56	55.6/1.47	56.8/1.48	65.4/1.65	85.1/1.56
5	1:1:0.50	1	4.51/1.95	5.44/1.91	6.22/2.58	6.64/1.88	7.74/2.21	8.12/2.21	8.55/2.25	8.61/2.11
6	1.1:1:0.50	4	68.1/1.55	98.3/1.53	99.9/1.55	101.4/1.56	105.8/1.59	112.3/1.55	116.5/1.46	122.3/1.57
7	1.2:1:0.50	4	69.7/1.61	73.1/1.53	79.3/1.54	81.3/1.58	82.2/1.49	85.5/1.66	88.8/1.58	89.3/1.58

[a]All reactions were carried out using 1 mL of THF at room temperature. [b]Determined by GPC calibrated based on linear PS standards in THF.



Reaction Time (min)	M_w (kDa)/Đ
2	68.1/1.55
5	98.3/1.53
15	99.9/1.55
30	101.4/1.56
60	105.8/1.59
240	112.3/1.55
480	116.5/1.46
1440	122.3/1.57

Figure 4.2 : Molecular weight growth of P1 (run 6, Table 2) vs time.

Among the solvents that were trialed for the polymerization, THF afforded PTAs with high molecular weights along with high yields (run 1, Table 3). When chlorinated solvents, such as $CHCl_3$ and DCE were also found to be suitable for the proposed polymerization, resulted in relatively high yields and molecular weights, 75.2 and 81.1 kDa, respectively (runs 2 and 3, Table 3). In addition, different etheric solvents, such as 1,4-dioxane and 2-MeTHF were also found to be as effective as THF, resulted in very similair fashion in terms of both molecular weights (M_w = 87.7 kDa and 95.3 kDa) and yields (runs 4 and 5, Table 3). However, carbonyl unit containing solvents, such as DMF, NMP and DMAc was not the ideal choice for the synhtesis of PTAs. When DMF and NMP (runs 6 and 7, Table 3) was used, the molecular weights were found to be quite low (M_w = 5.22 kDa and 5.81 kDa) when compared to the other solvents, even further, in the presence of DMAc (run 8, Table 3) there was no polymerization observed. Theses results could be attributed to the CDMS' affinity towards carbonyl units in the solvent, hence causing side reactions to prevent polymerization progression. Consequently, THF was continued to used with the aforementioned conditions for the rest of this study.

Table 4.2 : Effect of Solvent on Polymerization[a]

run	solvent	M_w[b] (kDa)	$Đ$[b]	Yield (%)[c]
1	THF	98.3	1.53	98
2	$CHCl_3$	75.2	1.74	89
3	DCE	81.1	1.50	90
4	1,4-Dioxane	87.7	1.46	90
5	2-MeTHF	95.3	1.54	96
6	DMF	5.22	3.64	54
7	NMP	5.81	3.32	52
8	DMAc		No reaction	

[a]All reactions were carried out using BA:HDT:CDMS at a mole ratio of 1.1:1:0.5 in 1 mL of solvent at room temperature for 5 min. [b]Determined by GPC calibrated based on linear PS standards in THF

Before examining the scope of reactants, P1 was characterized in detail by various spectroscopic measurements. To this end, when ^{1}H NMR of P1 was closely inspected, the methine proton of the PTA backbone can be seen at 4.85 ppm. In addition, the aromatic protons of P1 are detected between 7.41 and 7.25 ppm and the methylene protons regarding HDT resonated at 2.49, 1.50, and 1.29 ppm (Figure 2A). From the ^{13}C NMR spectrum of P1, it was found that the methine carbon of the PTA backbone was assigned at 53.29 ppm. Also, aromatic carbons of P1 resonated at 140.52, 128.52, 127.82, and, 127.68 ppm; together with the methylene carbons located at 32.16, 28.95, and 28.38 ppm (Figure 2B). Furthermore, from the FT-IR spectrum of P1, a strong C–S thioether stretching at around 750 cm^{-1} was observed, indicating the PTA backbone's formation (Figure 2C). Finally, the GPC chromatogram of P1 showed a monomodal distribution curve with a relatively low polydispersity index of 1.53, indicating smooth polymerization (Figure 2D).

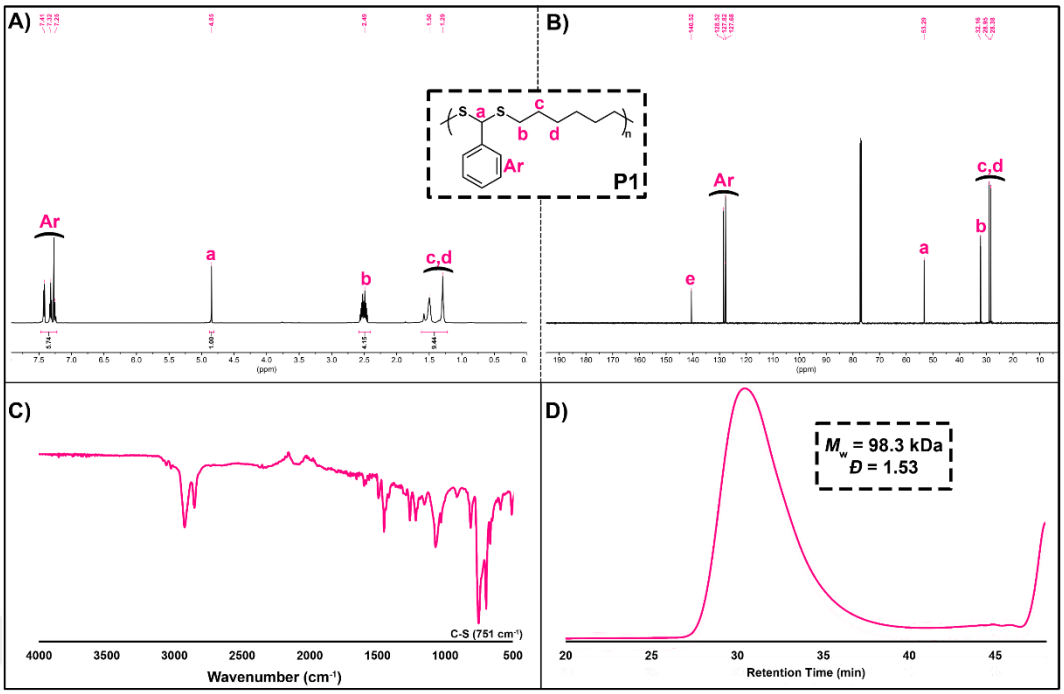


Figure 4.3 : ^{1}H NMR spectrum (A, $CDCl_3$ 500 MHz), ^{13}C NMR spectrum (A, $CDCl_3$ 125 MHz), FT-IR spectrum (C), and GPC chromatogram (D) of P1.

A variety of aldehydes and dithiols were then reacted to generate a library of PTAs using the optimized conditions, and the results achieved are collected in Table 4. The final structures of the obtained polymers and the ^{1}H NMR spectra of some selected polymers confirming the chemical structure of precursor monomers that are used in polymerizations can be seen in Figures 3 and 4. While examining the aldehyde scope, HDT was used as the model dithiol. Firstly, the electronic effects of different substituents on polymerization were trialed. When electron-withdrawing substituent containing aldehydes were used, such as 3-nitrobenzaldehyde (P2, M_w = 35.7 kDa) and 4-cyanobenzaldehyde (P3, M_w = 18.9 kDa) moderate molecular weighted PTAs with high yields were obtained. On the other hand, when 4-formylbenzoic acid (P4, M_w = 28.4 kDa) was used, a relatively high polydispersity value ($Đ$ = 3.17) was observed which can be attributed to an increase in the hydrodynamic volume due to the pendant carboxylic acid groups. The lower molecular weights could be the result of the –(M) effect of the electron-withdrawing substituents on the aromatic ring, hence decreasing the reactivity of the aldehyde group to some extent. Interestingly, when 4-(trifluoromethyl)benzaldehyde (P5, M_w = 2.54 kDa) was used, the resulting PTA has one of the lowest molecular weights in the library, indicating that, when compared with the –(M) effect, the –(I) effect of the trifluoromethyl group has dramatically decreased the aldehyde reactivity. When electron-donating substituent containing

aldehydes, such as *p*-anisaldehyde (P6, M_w = 24.3 kDa) and 4-hydroxylbenzaldehyde (P7, M_w = 19.9 kDa); and a halo-substitued aldehyde, 4-chlorobenzaldehyde (P8, M_w = 12.7 kDa) was used, moderate molecular weights were found as well. Essentially, these results could indicate that the –(I) effect of the substituent is far more dominant to decrease the reactivity of the aldehyde than the mesomeric effect of the same substituent, resulting in a decrease in the molecular weight.

To introduce different functionalities to the PTA backbone, a series of different functional aldehydes were also used. When an organosulphur compound, 2-thiophenecarboxyaldehyde was used corresponding PTA (P9) was observed to have a moderately high molecular weight (M_w = 48.7 kDa) with good yields. Similar results were obtained when 1-pyrenecarboxyaldheyde was used (P10, M_w = 32.2 kDa). Sterically congested aldehyde, 4-(1,2,2-triphenylethenyl)benzaldehyde afforded the corresponding PTA (P11) with a high molecular weight (M_w = 97.9 kDa) in a high yield. This result was particularly striking since lower activity was expected from this aldehyde. In addition, this protocol could be a useful tool to achieve luminogenic materials starting from tetraphenylethene building blocks since there is an increasing interest in two-photon absorption and aggregation-induced emission. In addition, ferroncenecarboxyaldehyde was also used to achieve the corresponding PTA (P12) and resulted in a moderate molecular weight (M_w = 22.0 kDa). This was another remarkable result since the ferrocene unit was found to be intact after the polymerization.

The dithiol scope was also examined to explore the scope of the polymerization. BA was used as the model aldehyde. Similar to P1, high molecular weights were observed when linear aliphatic dithiols such as 1,4-butanedithiol (P13, M_w = 111.3 kDa) and 1,8-octanedithiol (P14, M_w = 108.9 kDa) were used. To add more, 2,2'-(ethylenedioxy)diethanethiol was resulted in a similar fashion to P1 as well (P15, M_w = 96.7 kDa). When an aromatic dithiol, 1,4-benzenedimethanethiol, was used to perform the polymerization, the resulting PTA (P16) was found to be moderate molecular weight (M_w = 23.2 kDa). Also, ethylene glycol bis-mercaptoacetate resulted in a PTA (P17), similar terms to P16 (M_w = 32.0 kDa). Relatively lower nucleophilicities of these dithiols could result in moderate molecular weight of the corresponding PTAs. Finally, when DL-Dithiothreitol was used, obtained PTA (P18) was found to have a very low molecular weight (M_w = 1.23 kDa). This could be due to

the low nucleophilicity of the dithiol, as well as the hydrodynamic volume change of the PTA backbone due to the pendant hydroxyl groups.

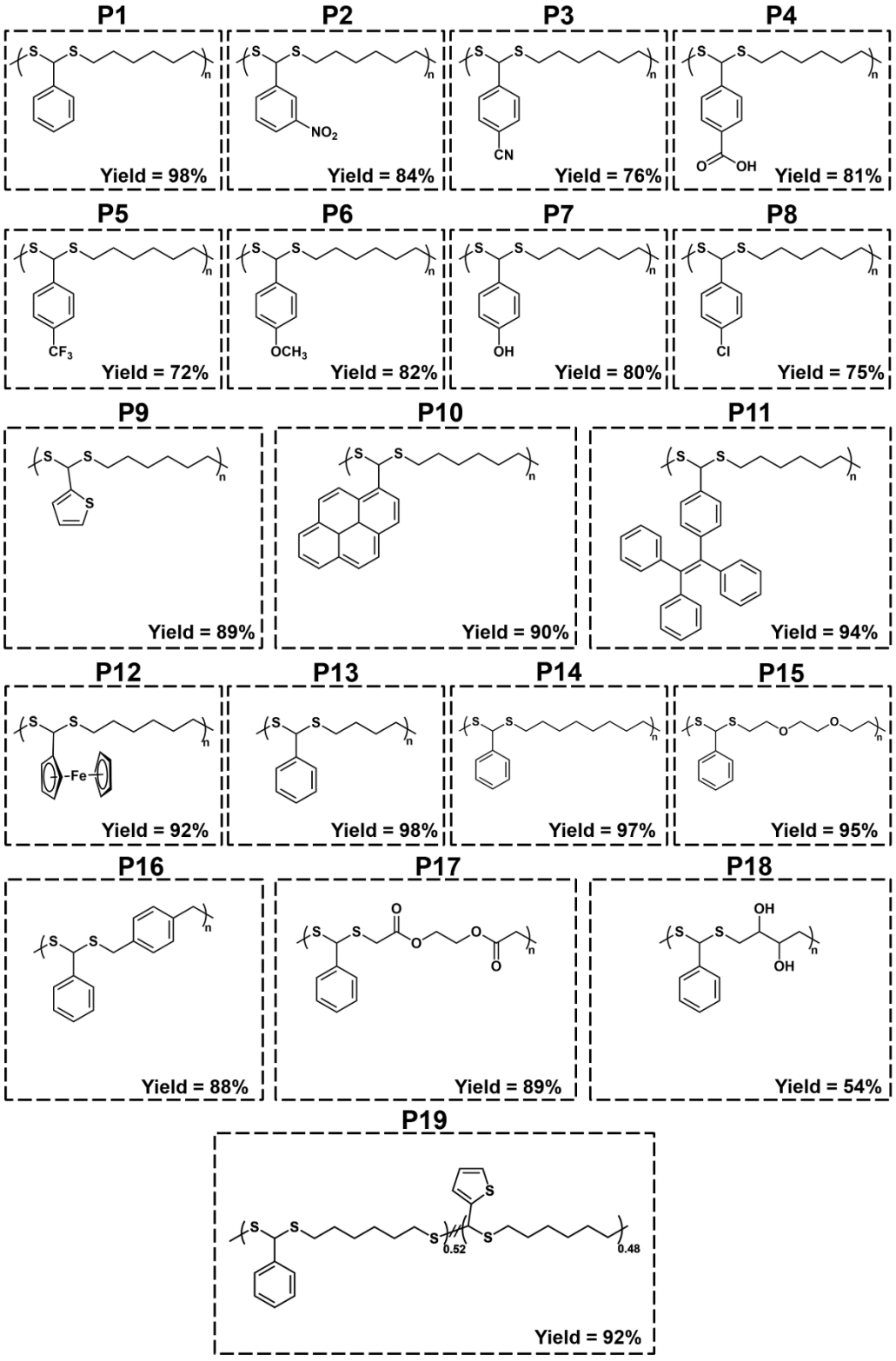


Figure 4.4 : Final structures of the resulting polymers. Yields were calculated after the second precipitation.

Table 4.4 : Reactant scope and obtained PTAs results[a]

Polymer	Aldehyde	Dithiol	M_w (kDa)[b]	$Đ$[b]	Yield (%)[d]
P1	BA	HDT	98.3	1.53	98
P2	3-nitrobenzaldehyde	HDT	35.7	2.00	84
P3	4-cyanobenzaldehyde	HDT	18.9	2.16	76
P4	4-formylbenzoic acid	HDT	28.4	3.17	81
P5	4-(trifluoromethyl)benzaldehyde	HDT	2.54	1.98	72
P6	*p*-anisaldehyde	HDT	24.3	1.58	82
P7	4-hydroxybenzaldehyde	HDT	19.9	2.57	80
P8	4-chlorobenzaldehyde	HDT	12.7	2.07	75
P9	2-thiophenecarboxaldehyde	HDT	48.7	1.62	89

Table 4.4 (continued) : Reactant scope and obtained PTAs results[a]

Polymer	Aldehyde	Dithiol	M_w (kDa)[b]	$Đ$[b]	Yield (%)[d]
P10	1-pyrenecarboxaldehyde	HDT	32.2	1.97	90
P11	4-(1,2,2-triphenylethenyl)benzaldehyde	HDT	97.9	2.09	94
P12	Ferrocenecarboxaldehyde	HDT	22.0	1.62	92
P13	BA	1,4-butanedithiol	111.3	1.69	98
P14	BA	1,8-octanedithiol	108.9	1.88	97
P15	BA	2,2'-(ethylenedioxy)diethanethiol	96.7	1.65	95
P16	BA	1,4-benzenedimethanethiol	23.2	1.67	88
P17	BA	ethylene glycol bis-mercaptoacetate	32.0	2.25	89
P18	BA	DL-Dithiothreitol	1.23	1.91	54
P19[e]	BA/2-thiophenecatboxyaldehyde	HDT	80.1	1.63	92

[a]All reactions were carried out using Aldehyde:Dithiol:CDMS at a mole ratio of 1.1:1:0.5 in 1 mL of THF at room temperature for 5 min. [b]Determined by GPC calibrated based on linear PS standards in THF [c] DSC [d]Isolated yields were calculated after the second precipitation. [e]Aldehydes were used at a mole ratio of 0.55/0.55.

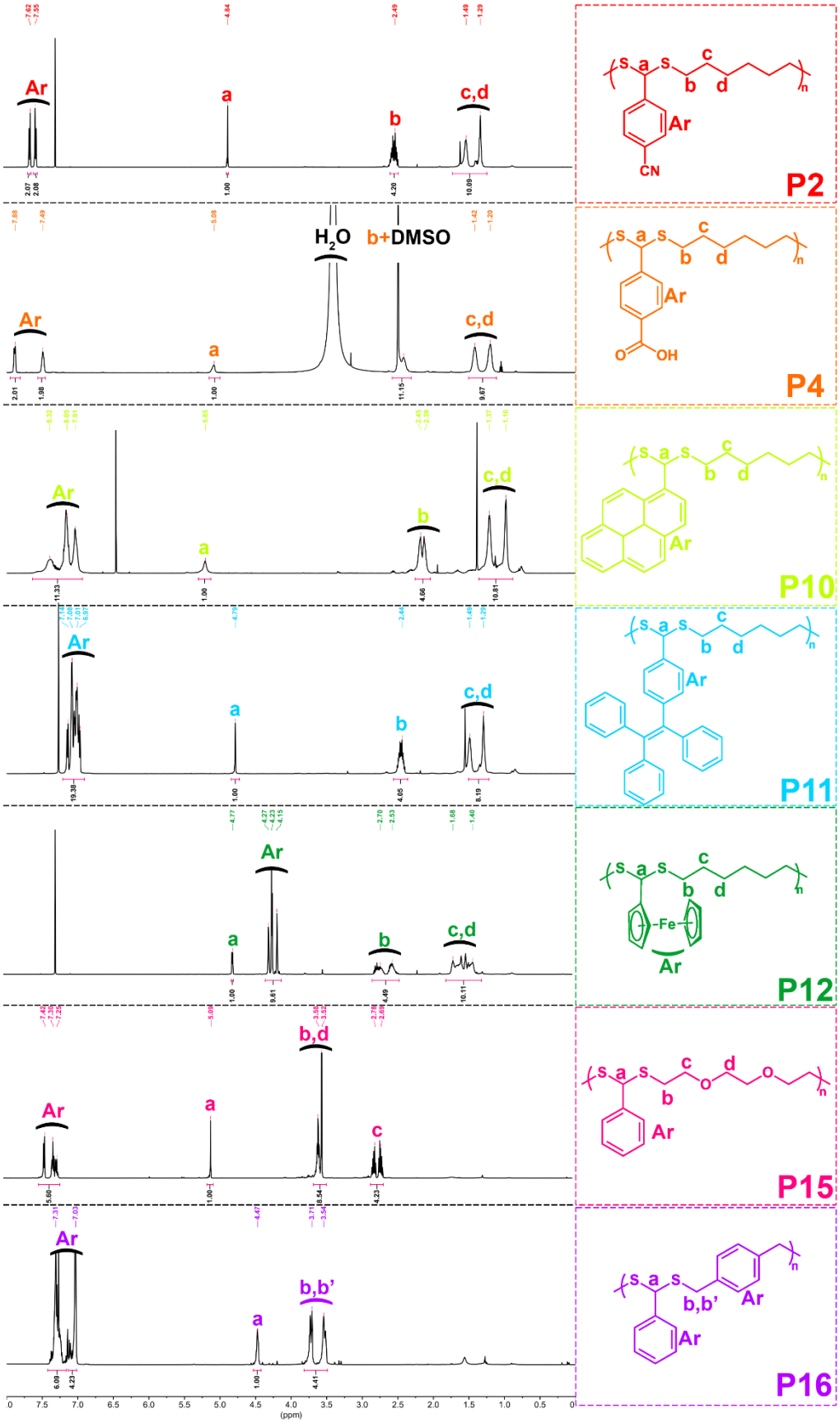


Figure 4.5 : ^{1}H NMR spectra of representative polymers in $CDCl_3$ and d_6-DMSO (500 MHz).

To extend the polymerization scope, a copolymerization was also trialed, as decipated in Scheme 3, by mixing equal amounts of BA:2-thiophenecarboxyaldehyde, using HDT as the dithiol, in the same polymerization conditions to yield corresponding copolymer PTA (P19) with a high molecular weight (M_w = 80.1 kDa) (Figure 6B). When the ^{1}H NMR spectrum of P19 was examined the comparison of the integral areas of methine protons regarding BA/2-thiophenecarboxyaldhyde resulted in a nearly equal distribution (0.52/0.48) within the PTA backbone which indicates that different copolymeric backbones can be achieved with the desired feed ratio of the starting materials by employing this protocol (Figure 6A).

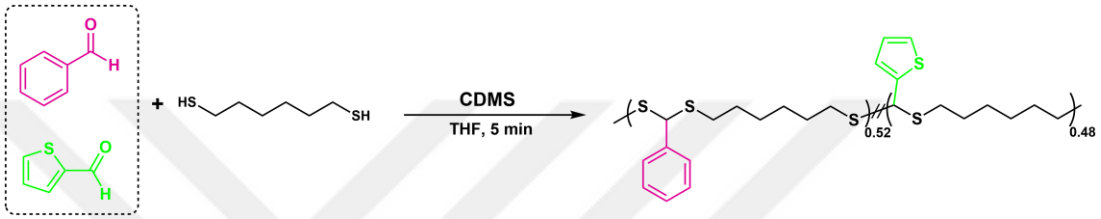


Figure 4.6 : Synthetic pathway for the copolymer PTA (P19).

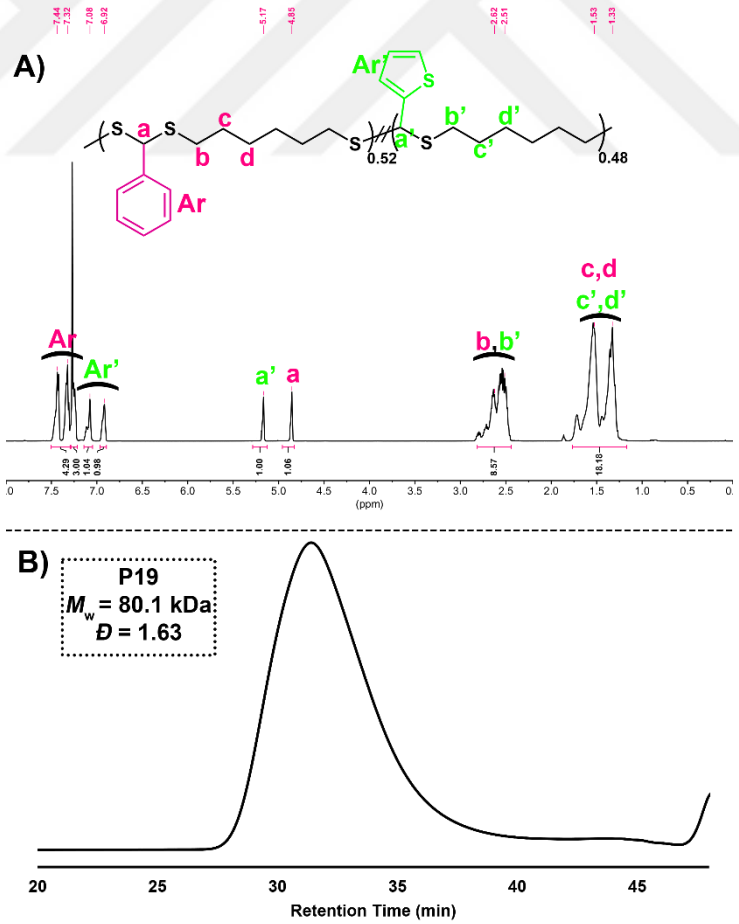


Figure 4.7 : ^{1}H NMR spectrum (A, $CDCl_3$, 500 MHz) and GPC chromatogram (B) of P19.

The CDMS-catalyzed PTA described in this study was then examined in terms of mechanistic aspects. Figure 7 exhibits the proposed mechanism for the polymerization protocol. Since CDMS acts as a Lewis acid, but during the course of the reaction, it also generates HCl in situ, it is most likely to expect a Brønsted acid character. To this end, we envisioned two mechanisms working along during the polymerization. For the Lewis acid route, as explained in our previous works [29,30], the reaction starts with the silylation of the aldehyde unit in the presence of CDMS, where the chlorine ion acts as the leaving group, in order to form the silylated aldehyde (**I**). Then, **I** is attacked by the dithiol, resulting in a hemithioacetal-type of an intermediate **II**, followed by a protonation step to yield **III**, then silanol leaving from the structure and attack of another dithiol to form **IV**. Finally, polymerization takes place condensation reaction between **III** and **IV**.

As mentioned before, the Brønsted acid route can also be expected during the reaction since in situ HCl formation was observed hence, aldehyde can also be protonated with HCl to form a hemithioacetal intermediate (**V**). From there, the reaction is expected to follow the traditional acid-catalyzed thioacetal formation mechanism, where **V** is then attacked by a dithiol to form **VI**, followed by the protonation step to lose the water from this intermediate (**VII**) and attack from another dithiol to form **VIII**. Finally, **VII** and **VIII** condensation will result in the formation of PTA. Since polymerization takes place with two possible mechanisms, it is most likely to expect that CDMS resulted in much higher molecular weights when compared to other acids that were trialed during this study.

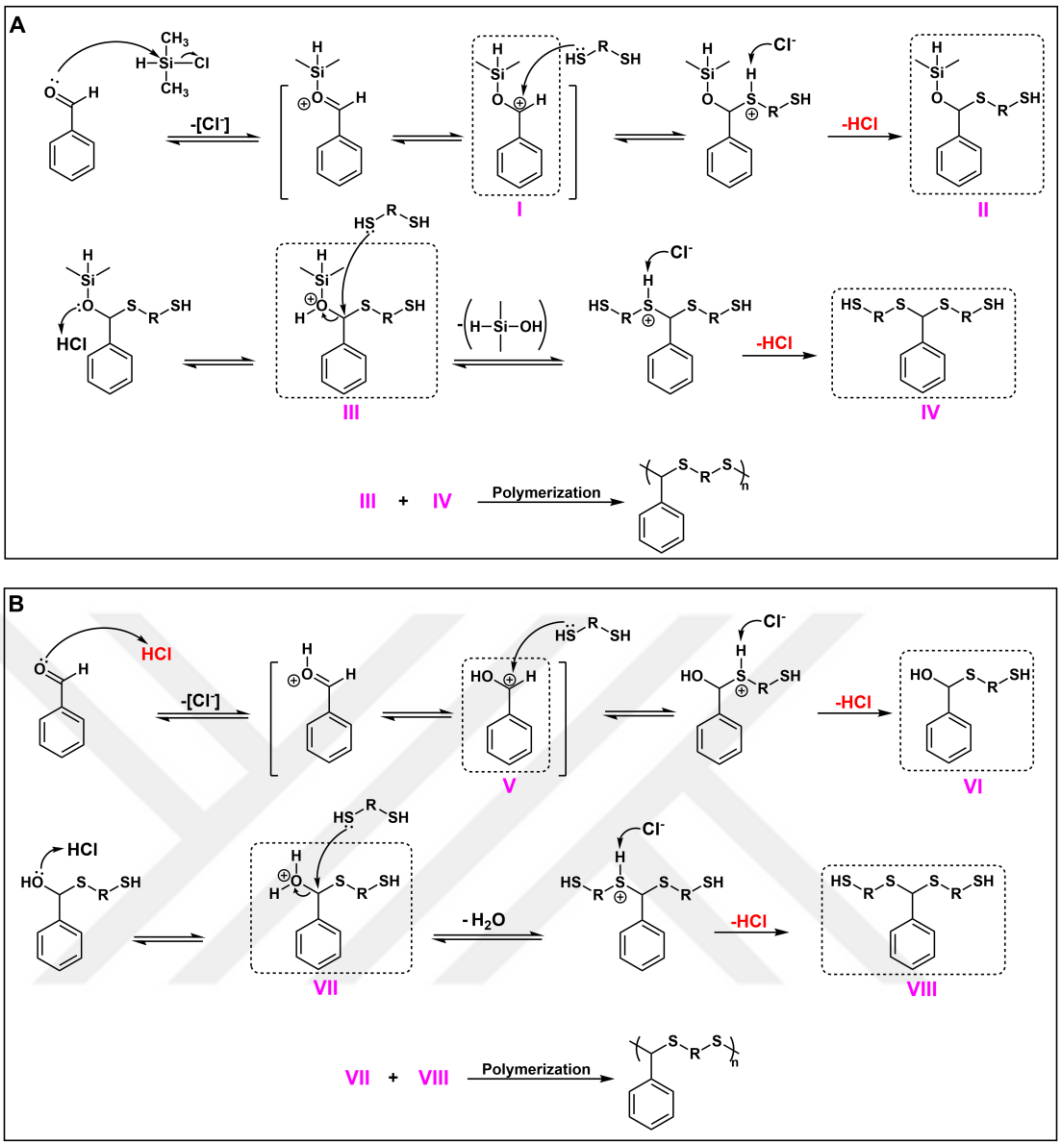


Figure 4.8 : Proposed mechanism for CDMS-catalyzed PTA formation: (A) Lewis acid route, (B) Brønsted acid route.

As mentioned before, one of the most important features of thioacetal bonds is their cleavage in the ROS medium. In this regard, P1 was subjected to degradation using H_2O_2 as the ROS source, and the progress of the reaction was monitored kinetically by taking a sample from the reaction medium at regular intervals and analysed by GPC (Scheme 3). As seen in Figure 8, the degradation of the polymer started within 1 h, continued over time and was largely turned into an oligomeric form after 24 h. Also, from the ^{1}H NMR, the methine peak of P1 at 4.85 ppm completely disappeared after 24 h and the aldehyde proton at 10.05 ppm reappeared, hence further complementing the degradation of the polymer.

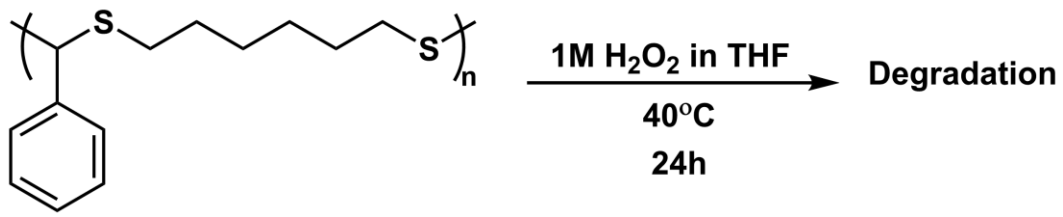


Figure 4.9 : Degradation of P1 (run 6, Table 2) in the presence of H_2O_2.

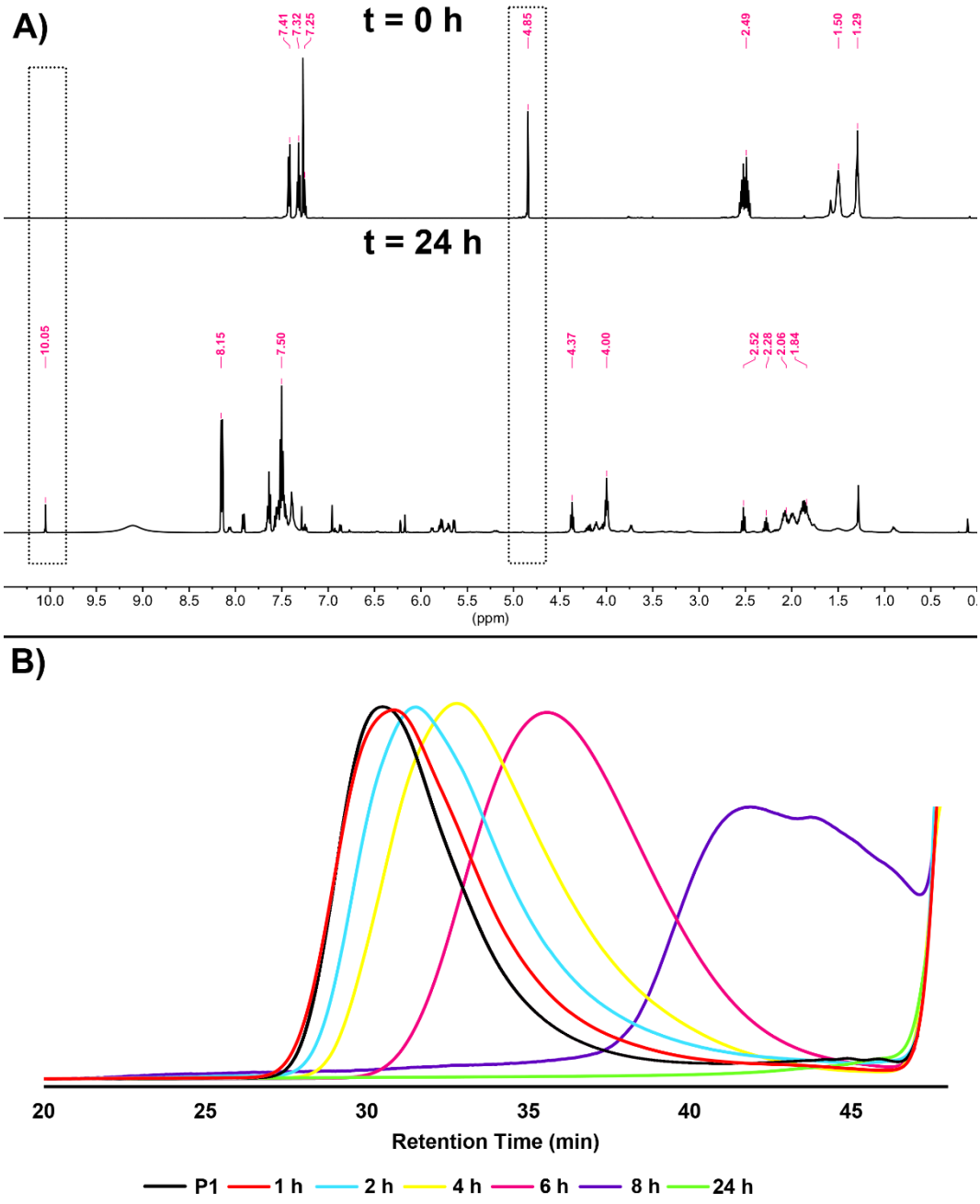


Figure 4.10 : ^{1}H NMR spectrum (A, $CDCl_3$, 500 MHz) and overlaid GPC traces (B) of degradation of P1.

4.3 Conclusions

We have successfully synthesized various PTAs using CDMS as a catalyst. Optimization studies that took place between BA and HDT revealed that slight excess of BA (1.1 equiv) together with 0.25 equiv of CDMS is essential to obtain relatively high molecular weight polymers. The proposed protocol proceeded in a straightforward fashion under mild conditions and resulted in PTAs having high isolated yields in just 5 minutes and molecular weights between 1.23 and 111.3 kDa. PTA backbone was tailored with the selection of different aldehydes and dithiols, forming a huge polymer library. Also, a degradation study on a model PTA (P1) was performed and a complete degradation was observed over 24 h. Although PTA synthesis is known in polymer chemistry literature, a detailed work was performed to investigate many different polymerization parameters. More importantly,.

It is believed that a straightforward and rapid PTA synthesis method has been revealed in this study, which promises circumventing the harsh conditions required in a classical PTA synthesis. We believe that this work will pave a new way in PTA synthesis, we aim to inspire further research in this field and facilitate the development of PTA-based materials with tailored properties for diverse applications.

4.4 Experimental

4.4.1 Materials

Benzaldehyde (BA, purified by redistillation, ≥99.5%, Sigma-Aldrich), 3-nitrobenzaldehyde (99%, Sigma-Aldrich), 4-cyanobenzaldehyde (95%, Sigma-Aldrich), 4-formylbenzoic acid (97%, Sigma-Aldrich), 4-(trifluoromethyl)benzaldehye (98%, Sigma-Aldrich), *p*-anisaldehyde (98%, Sigma-Aldrich), 4-hydroxybenzaldehyde (98%, Sigma-Aldrich), 4-chlorobenzaldehyde (98%, Sigma-Aldrich), 2-thiophenecarboxaldehyde (98%, Sigma-Aldrich), 1-pyrenecarboxaldehyde (99%, Sigma-Aldrich), 4-(1,2,2-triphenylethenyl)benzaldehyde (Sigma-Aldrich), ferrocenecarboxaldehye (98%, Sigma-Aldrich), 1,4-butanedithiol (%98, Sigma-Aldrich), 1,6-hexanedithiol (HDT, 96%, Sigma-Aldrich), 1,8-octanedithiol (97%, Sigma-Aldrich), ethylene glycol bismercaptoacetate (≥95.0%, Sigma-Aldrich), 2,2′-(ethylenedioxy) diethanethiol (95%, Sigma-Aldrich), DL-dithiothreitol (≥98% (HPLC), Sigma-Aldrich), sulfuric

acid (H_2SO_4, 99.999%, Sigma-Aldrich), *p*-toluenesulfonic acid monohydrate (PTSA, ACS reagent, ≥98.5%, Sigma-Aldrich), methanesulfonic acid (MSA, ≥99.0%, Sigma-Aldrich) and CDMS (98%, Aldrich) were used as received. Tetrahydrofuran (THF, 99%, Sigma-Aldrich), chloroform ($CHCl_3$, 99%, Sigma-Aldrich), 1,2-dichloroethane (DCE, 99.8%, Aldrich), 1,4-dioxane (for liquid chromatography LiChrosolv®, Supleco), 2-methyltetrahydrofuran (2-MeTHF, ≥99%, Sigma-Aldrich), *N*,*N*-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), 1-methyl-2-pyrrolidone (NMR, for liquid chromatography LiChrosolv®, Supleco) and *N*,*N*-dimethylacetamide (DMAc, 99.8%, Aldrich) were anhydrous and were of HPLC quality and used without further purification. Methanol was of reagent grade and used as received.

4.4.2 Instrumentation

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded using an Agilent VNMRS 500 instrument in $CDCl_3$. Gel permeation chromatography (GPC) measurements were carried out with Agilent Instrument (series 1100), using a refractive index detector, loaded with 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 the columns are 2000–4,000,000, 50–100,000, 500–30,000, and 500–20,000 g/mol, respectively. THF was used as an eluent at a flow rate of 0.3 mL/min at 30 °C, and 2,6-di-*tert*-butyl-4-methylphenol was used as an internal standard. The weight-average molecular weight (M_w) and dispersity ($Đ$) of the polymers were calculated based on narrow linear polystyrene (PS) standards (Polymer Laboratories) ranging between 2300 and 3,050,000 g/mol. FT-IR spectra were recorded on an Agilent Technologies Cary 630 FT-IR instrument over the range of 4000–400 cm $^{-1}$.

4.4.3 General Procedure for the Synthesis of Poly(dithioacetal)s (Synthesis of P1)

BA (224 μL, 2.20 mmol) was added to a 10 mL round-bottomed flask, and dissolved in 500 μL of THF. Then, with continuous stirring, HDT (306 μL, 2.00 mmol) and CDMS (111 μL, 1.00 mmol) were added to this solution, respectively. Upon the addition of CDMS to the mixture, an exothermic reaction occurs, and within 2 min, the reaction medium became a slurry. The reaction was allowed to stir for a total of 5 min, dissolved in 2 mL of additional THF, then precipitated into 50 mL of MeOH. The dissolution-precipitation procedure (THF–CH_3OH) was repeated two times. Finally,

the obtained polymer, P1, was dissolved in 5 mL of $CHCl_3$ and transferred to a glass vial, and the solvent was evaporated to yield a white sticky solid.

(Yield = 513 mg, 98%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41, 7.32, 7.25 (5H, Ar*H*), 4.85 (1H, ArSC*H*S), 2.49 (4H, SC*H*$_2$(CH_2)$_4$C*H*$_2$), 1.50-1.29 (8H, SCH_2(C*H*$_2$)$_4$$CH_2$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 140.52 128.52 127.82 127.68 53.29 32.16 28.95 28.38

4.4.4 Synthesis of P2

General procedure was followed. 3-nitrobenzaldehyde (332 mg, 2.20 mmol), HDT (306 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P2 was obtained as a white sticky solid (Yield = 475 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29-7.51 (4H, Ar*H*), 4.92 (1H, ArC*H*S), 2.59-2.47 (4H, SC*H*$_2$(CH_2)$_4$C*H*$_2$S), 1.51-1.31 (8H, SCH_2(C*H*$_2$)$_4$$CH_2$S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.30, 142.77, 133.99, 129.63, 122.97, 122.82, 50.90, 31.84, 28.64, 28.02.

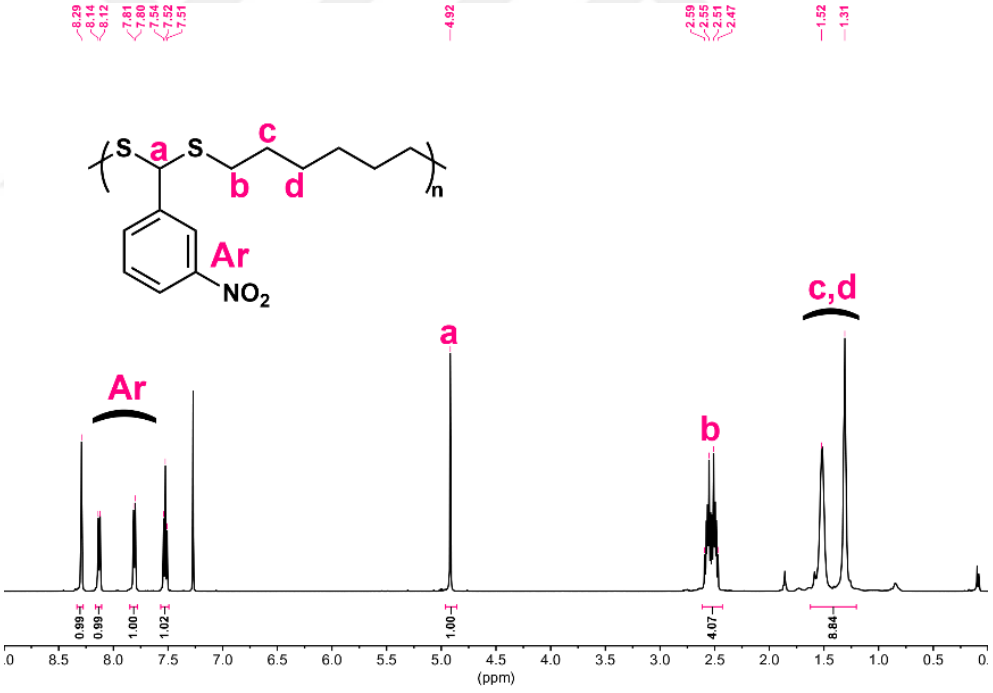


Figure 4.11 : ^{1}H NMR spectrum of P2 ($CDCl_3$, 500 MHz).

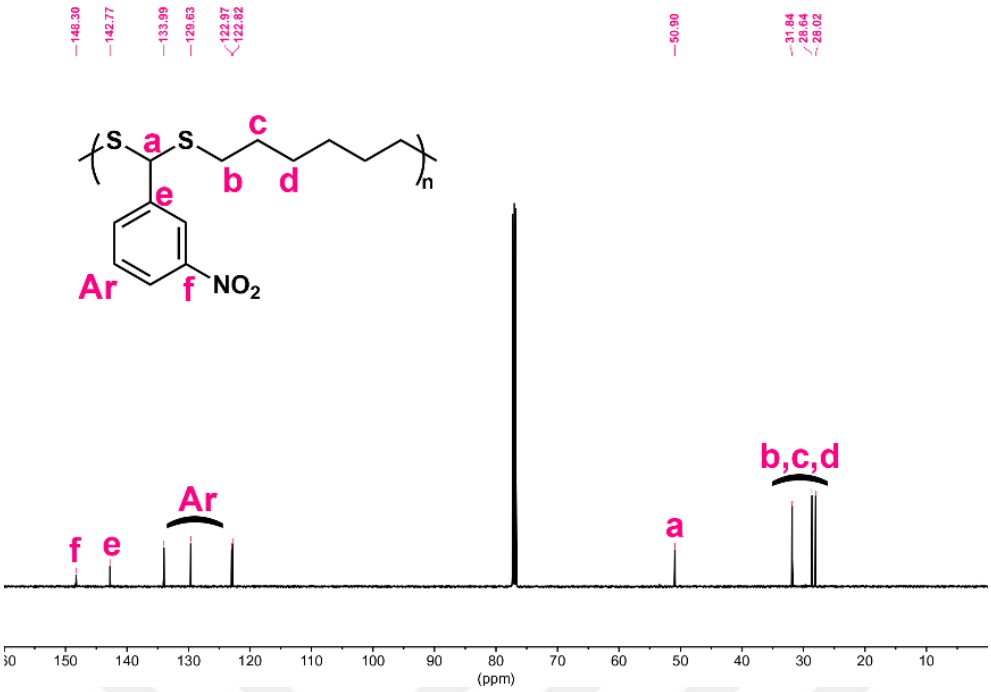


Figure 4.12 : ^{13}C NMR spectrum of P2 ($CDCl_3$, 125 MHz).

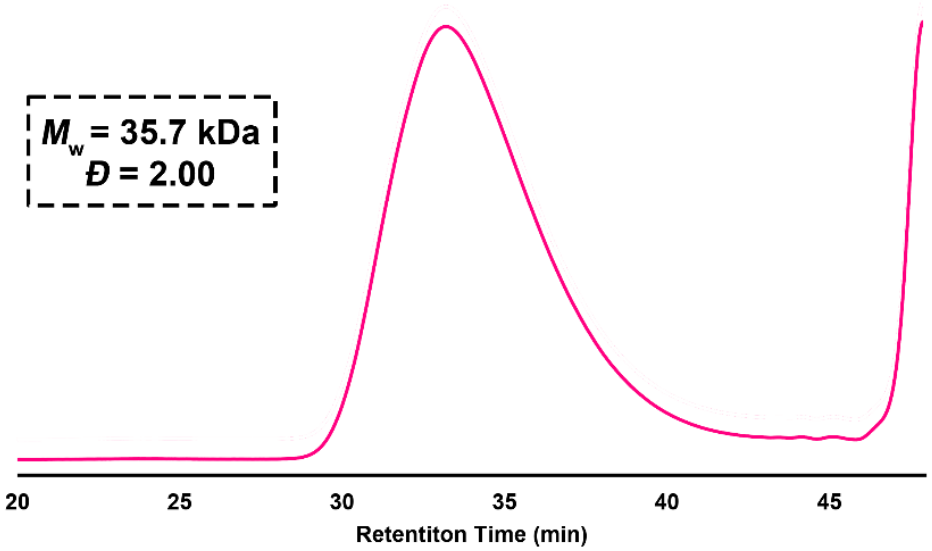


Figure 4.13 : GPC chromatogram of P2.

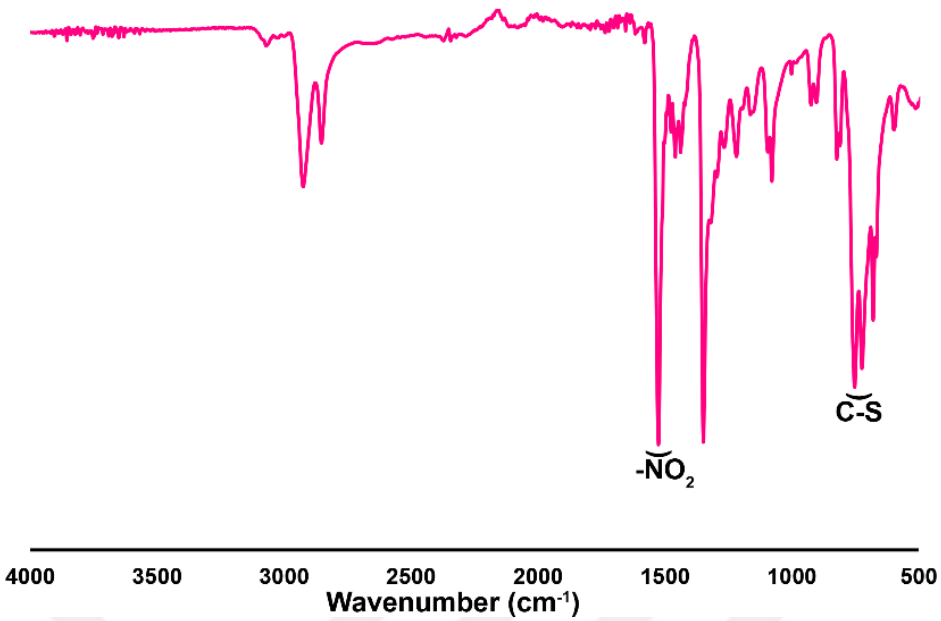


Figure 4.14 : FT-IR spectrum of P2.

4.4.5 Synthesis of P3

General procedure was followed. 3-cyanobenzaldehyde (288 mg, 2.20 mmol), HDT (306 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P3 was obtained as a white sticky solid (Yield = 400 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62, 7.55 (4H, Ar*H*), 4.84 (1H, ArC*H*S), 2.49 (4H, SC*H*$_2$(CH_2)$_4$C*H*$_2$S), 1.49-1.29 (8H, SCH$_2$(C*H*$_2$)$_4$CH$_2$S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.09, 132.42, 128.49, 118.56, 111.59, 52.93, 32.19, 28.81, 28.29.

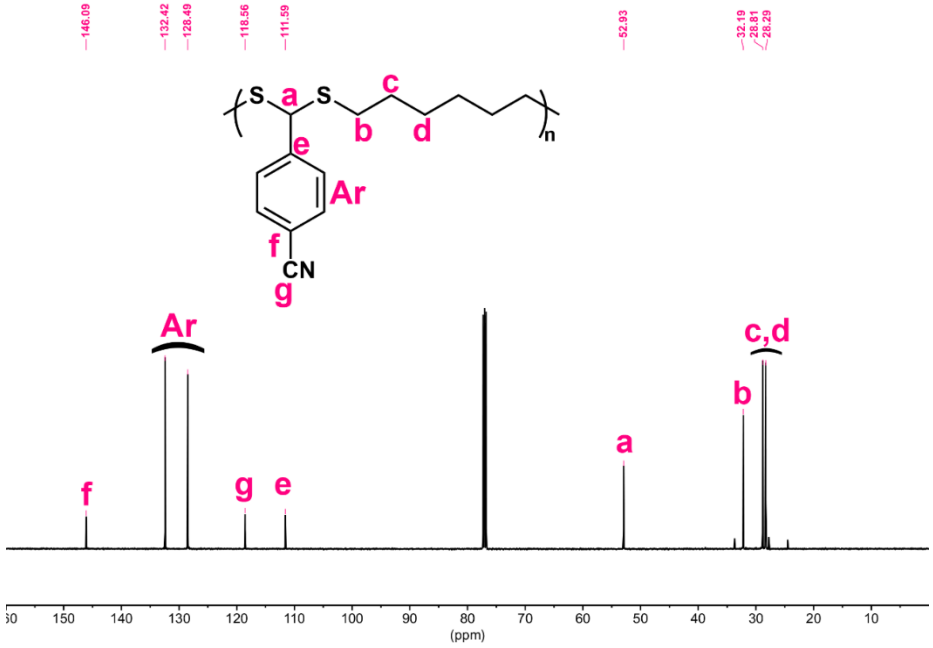


Figure 4.15 : ^{13}C NMR spectrum of P3 ($CDCl_3$, 125 MHz).

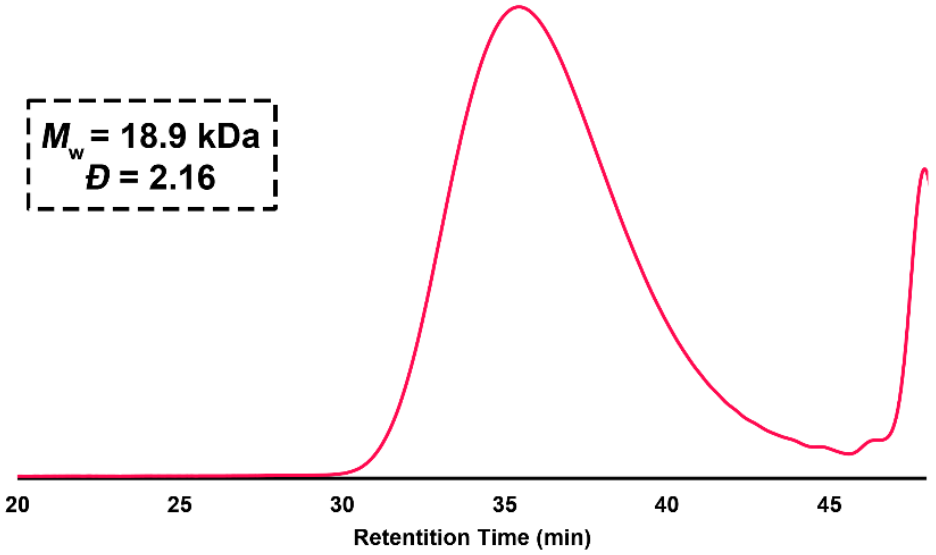


Figure 4.16 : GPC chromatogram of P3.

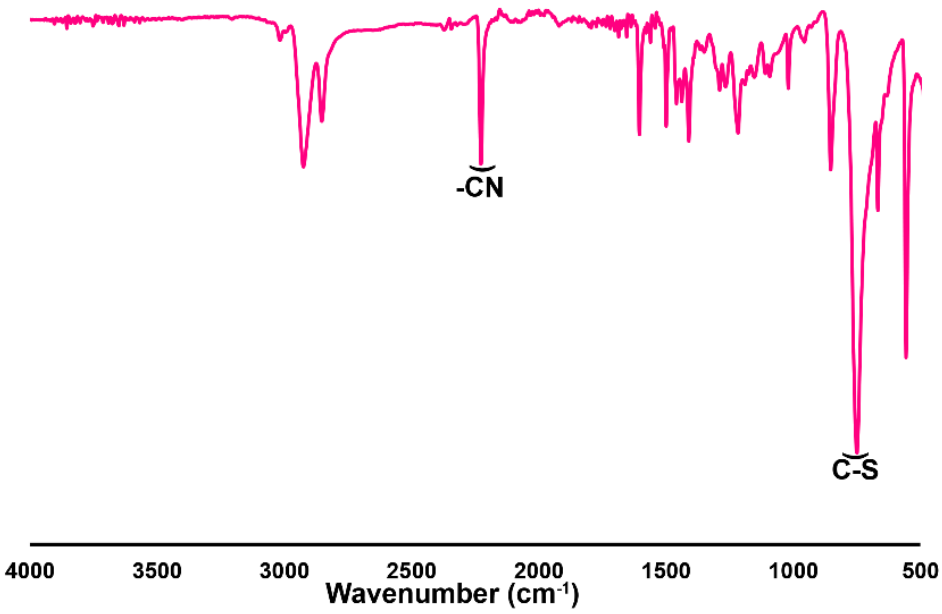


Figure 4.17 : FT-IR spectrum of P2.

4.4.6 Synthesis of P4

General procedure was followed. 3-formylbenzoic acid (330 mg, 2.20 mmol), HDT (306 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P4 was obtained as a white sticky solid (Yield = 447 mg, 76%). ^{1}H NMR (500 MHz, d_6-DMSO): δ 7.88, 7.49 (4H, Ar*H*), 5.08 (1H, ArC*H*S), 2.42 (4H, SC*H*$_2$(CH$_2$)$_4$C*H*$_2$S), 1.42-1.20 (8H, SCH$_2$(C*H*$_2$)$_4$CH$_2$S) ppm. ^{13}C NMR (125 MHz, d_6-DMSO): δ 167.39, 130.53, 129.96, 128.04, 79.59, 32.02, 28.87, 28.09.

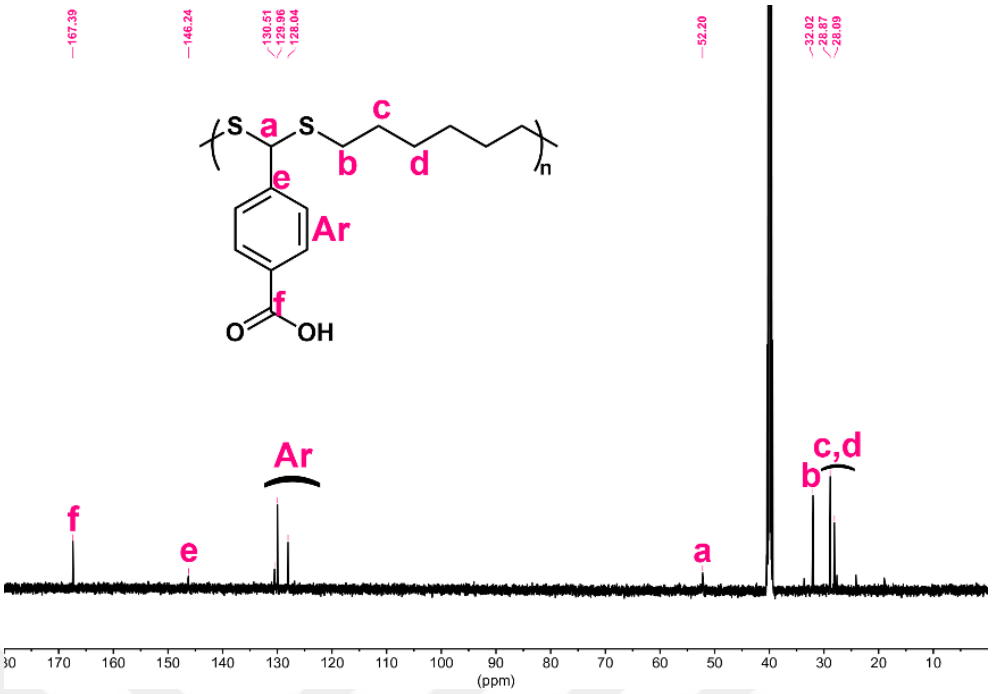


Figure 4.18 : ^{13}C NMR spectrum of P4 (d_6-DMSO, 125 MHz).

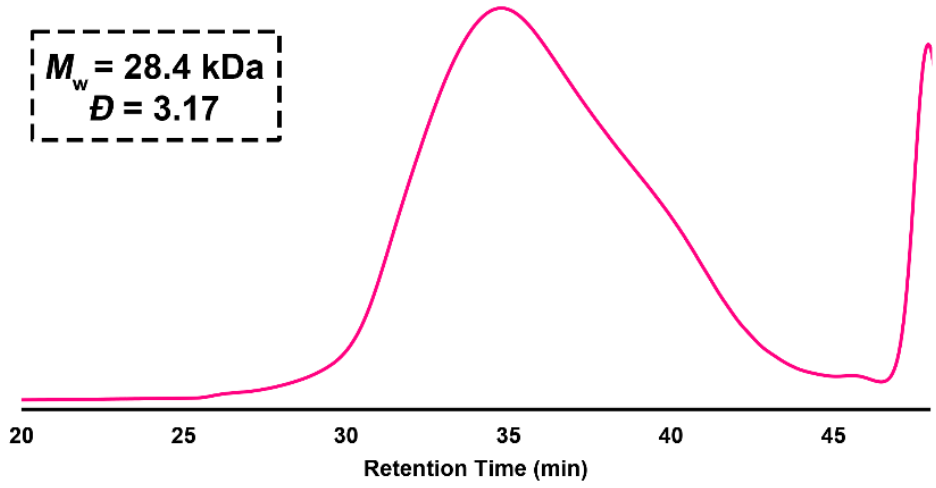


Figure 4.19 : GPC chromatogram of P4.

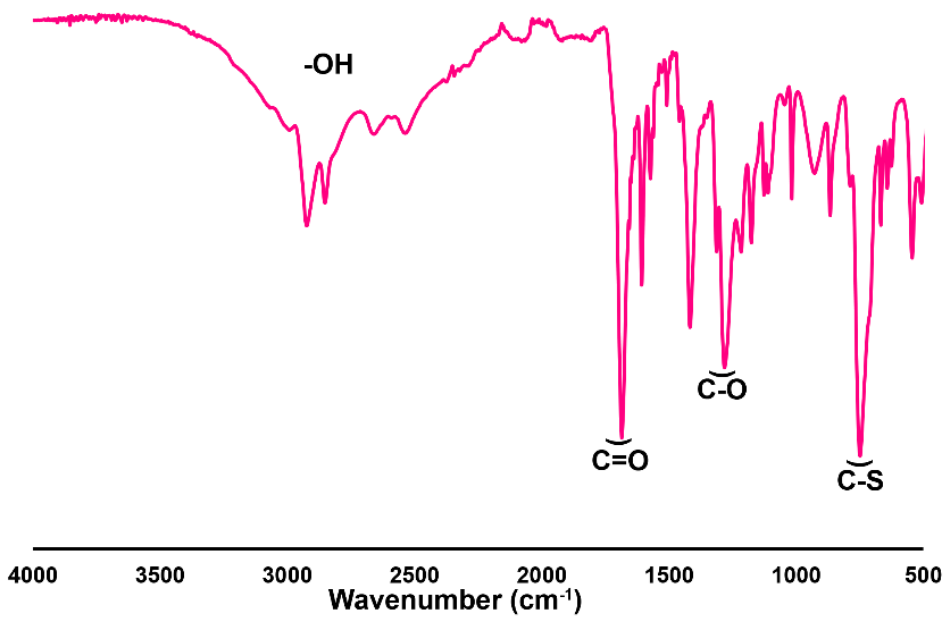


Figure 4.20 : FT-IR spectrum of P4.

4.4.7 Synthesis of P5

General procedure was followed. 4-(trifluoromethyl)benzaldehyde (383 mg, 2.20 mmol), HDT (306 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P5 was obtained as a white sticky solid (Yield = 441 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59-7.54 (4H, Ar*H*), 4.88 (1H, ArC*H*S), 2.52 (4H, S*CH*$_2$(CH_2)$_4$*CH*$_2$S), 1.56-1.31 (8H, SCH$_2$(*CH*$_2$)$_4$CH$_2$S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.69, 128.06, 125.53, 52.77, 33.73, 32.17, 28.85, 28.33, 27.81, 24.50.

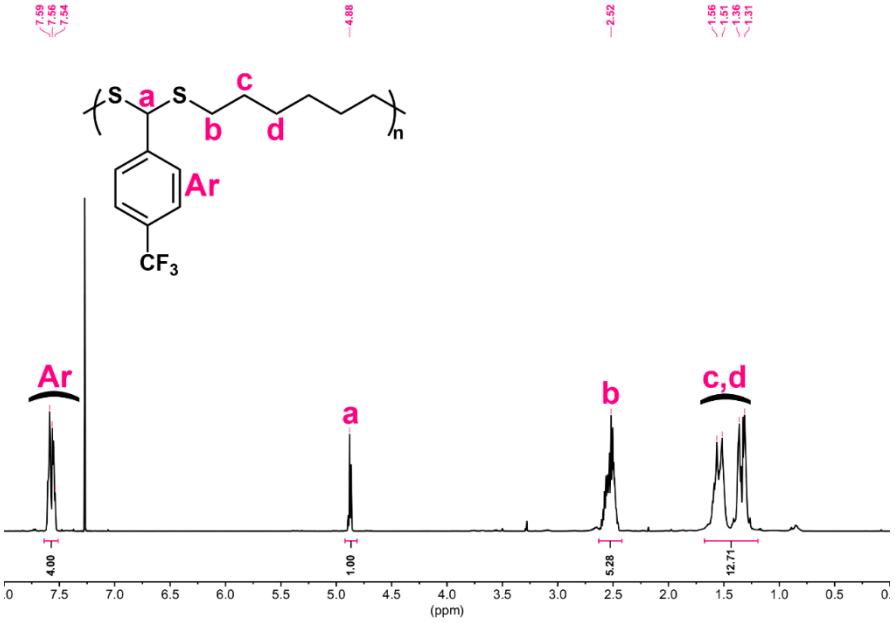


Figure 4.21 : ^{1}H NMR spectrum of P5 ($CDCl_3$, 500 MHz).

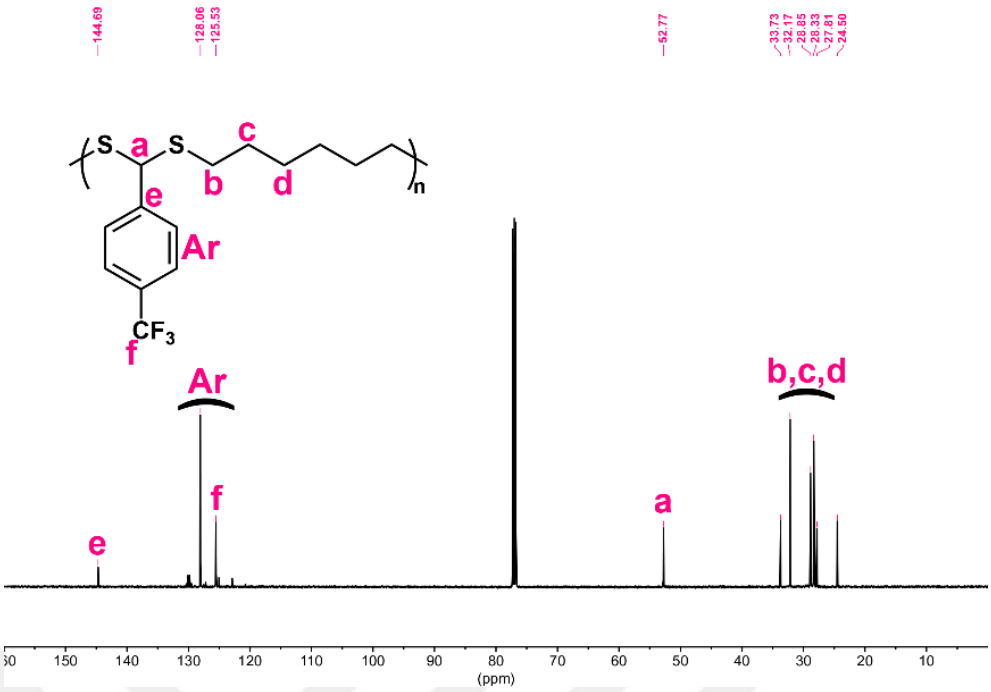


Figure 4.22 : ^{13}C NMR spectrum of P5 ($CDCl_3$, 125 MHz).

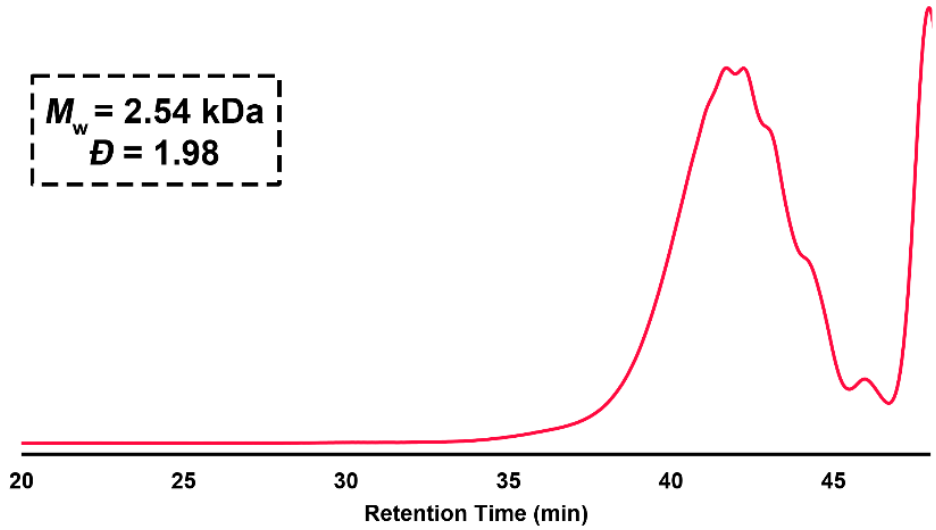


Figure 4.23 : GPC chromatogram of P5.

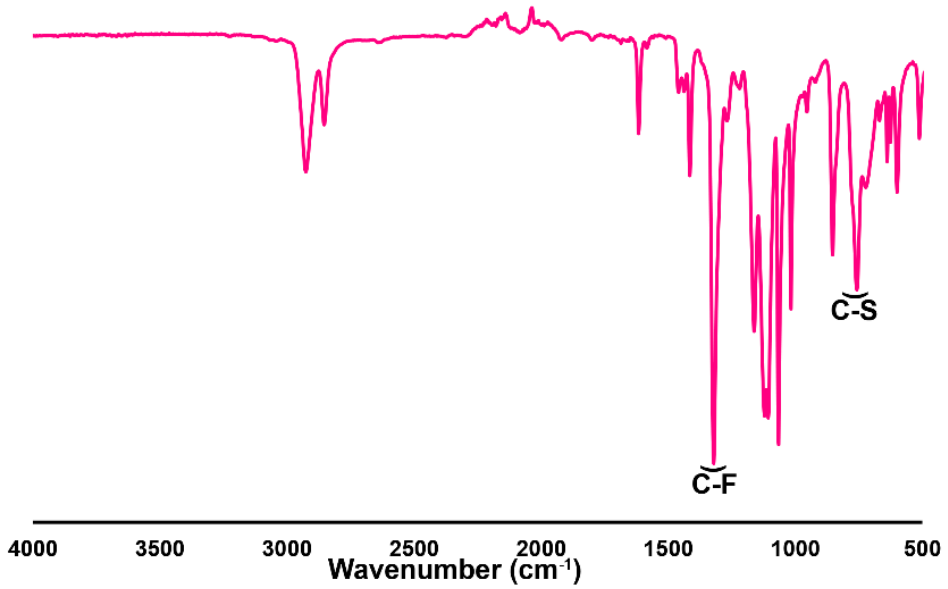


Figure 4.24 : FT-IR spectrum of P5.

4.4.8 Synthesis of P6

General procedure was followed. *p*-Anisaldehyde (268 µL, 2.20 mmol), HDT (306 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P6 was obtained as a white sticky solid (Yield = 483 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36, 7.34, 6.86, 6.84 (4H, Ar*H*), 4.83 (1H, ArC*H*S), 3.80 (3H, ArOCH_3), 2.49 (4H, SCH_2(CH_2)$_4$CH_2S), 1.50-1.30 (8H, SCH_2(CH_2)$_4$CH_2S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.10, 132.48, 128.83, 113.84, 55.31, 52.68, 32.18, 29.00, 28.43.

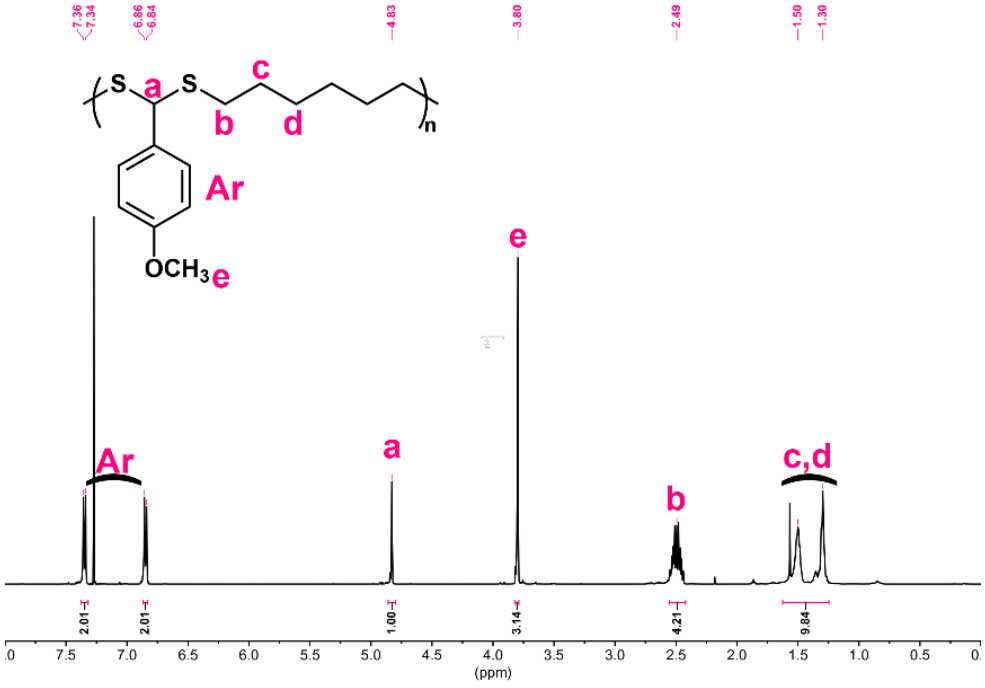


Figure 4.25 : ^{1}H NMR spectrum of P6 ($CDCl_3$, 500 MHz).

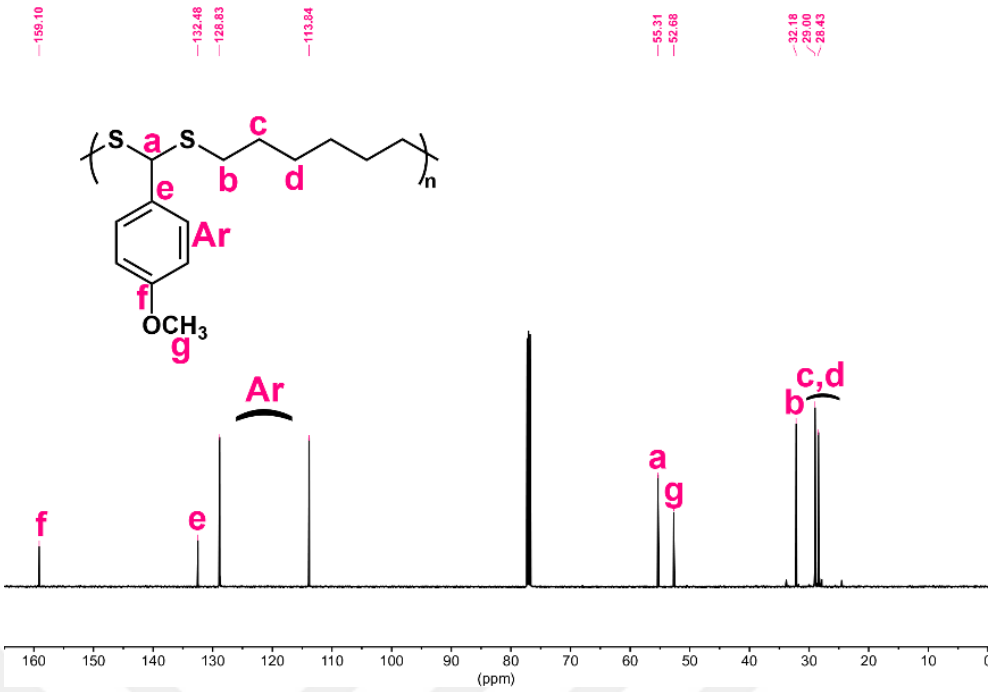


Figure 4.26 : ^{13}C NMR spectrum of P6 ($CDCl_3$, 125 MHz).

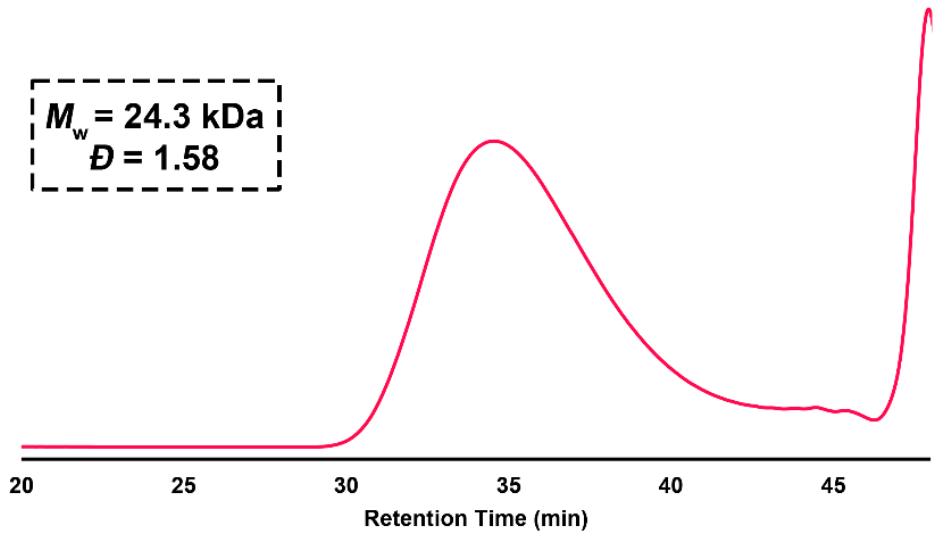


Figure 4.27 : GPC chromatogram of P6.

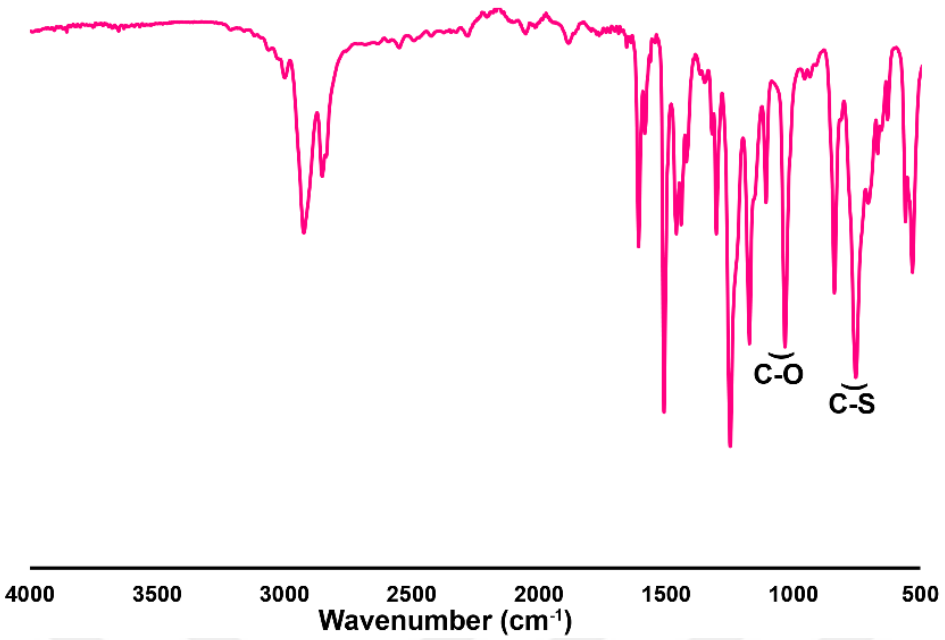


Figure 4.28 : Figure 1. FT-IR spectrum of P6.

4.4.9 Synthesis of P7

General procedure was followed. *p*-hydroxybenzaldehyde (269 mg, 2.20 mmol), HDT (306 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P7 was obtained as a white sticky solid (Yield = 447 mg, 80%). ^{1}H NMR (500 MHz, d_6-DMSO): δ 9.46 (1H, ArO*H*) 7.17, 6.69 (4H, Ar*H*), 4.92 (1H, ArC*H*S), 2.49-2.40 (4H, SCH_2(CH$_2$)$_4$CH_2S), 1.42-1.22 (8H, SCH$_2$(CH_2)$_4$CH$_2$S) ppm. ^{13}C NMR (125 MHz, d_6-DMSO): δ 157.25, 131.26, 129.11, 115.46, 52.30, 31.99, 29.00, 28.23.

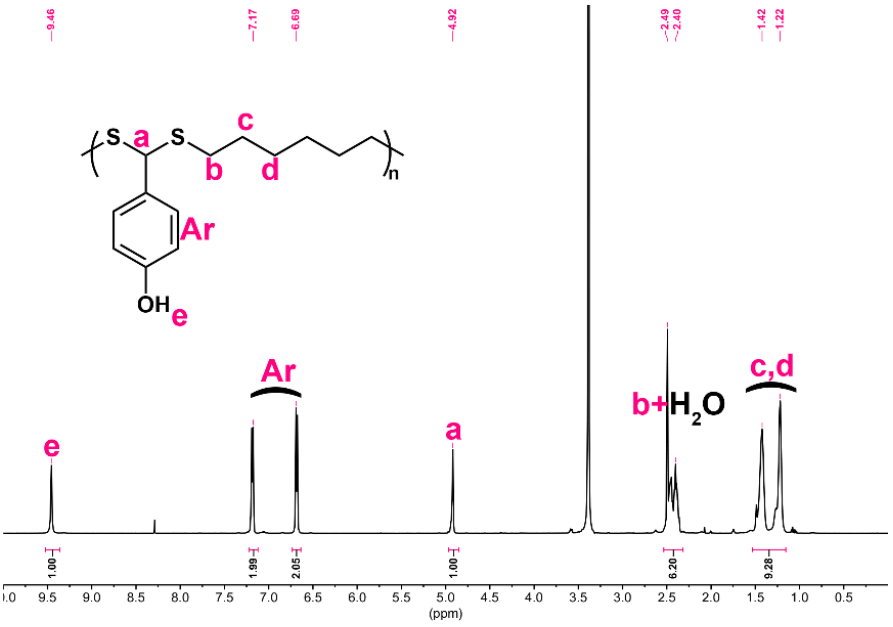


Figure 4.29 : ^{1}H NMR spectrum of P7 (d_6-DMSO, 500 MHz).

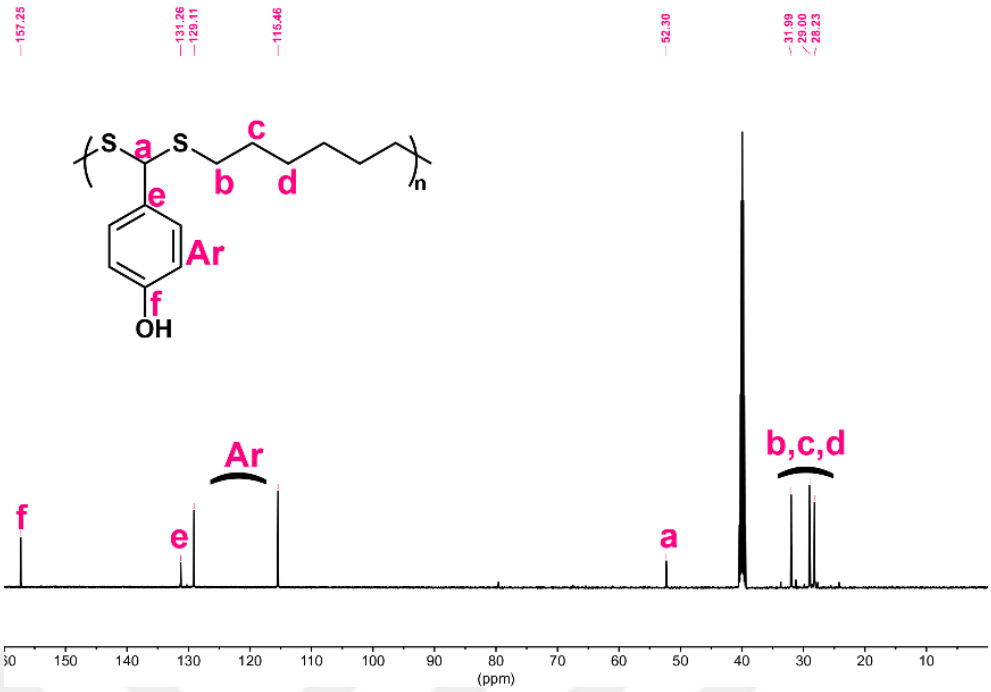


Figure 4.30 : ^{13}C NMR spectrum of P7 (d_6-DMSO, 125 MHz).

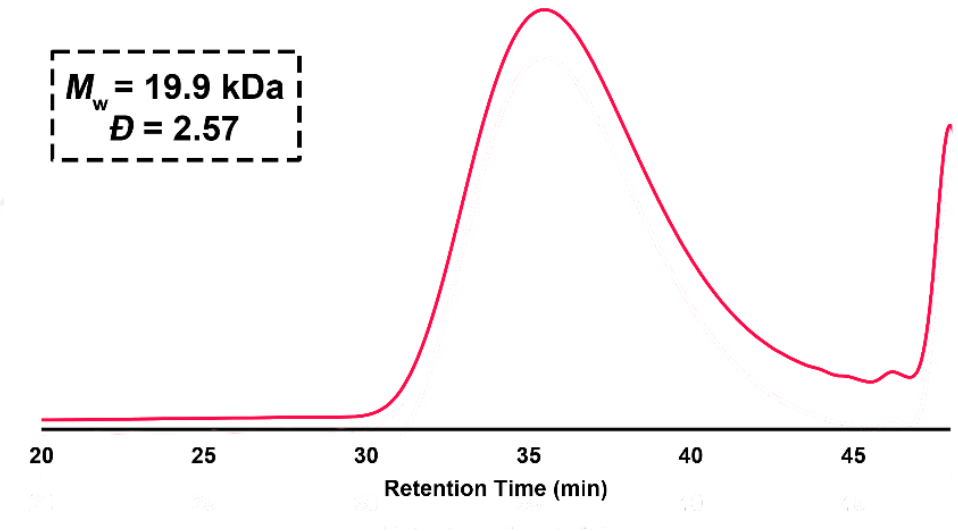


Figure 4.31 : GPC chromatogram of P7.

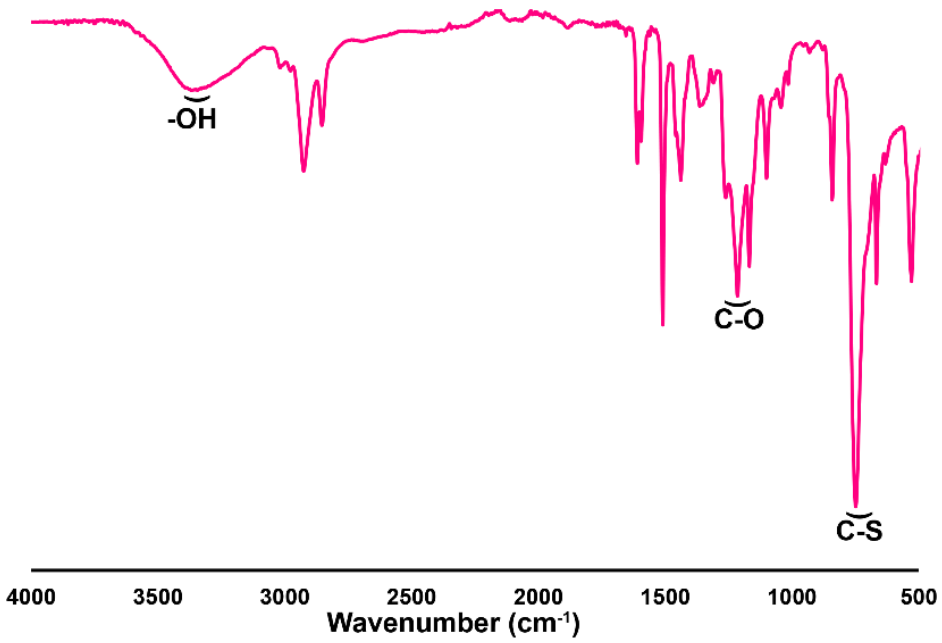


Figure 4.32 : FT-IR spectrum of P7.

4.4.10 Synthesis of P8

General procedure was followed. *p*-chlorobenzaldehyde (309 mg, 2.20 mmol), HDT (306 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P8 was obtained as a white sticky solid (Yield = 449 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36, 7.30 (4H, Ar*H*), 4.81 (1H, ArC*H*S), 2.57-2.48 (4H, SCH_2(CH_2)$_4$CH_2S), 1.50-1.30 (8H, SCH_2(CH_2)$_4$CH_2S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.14, 133.44, 129.08, 52.60, 32.16, 28.90.

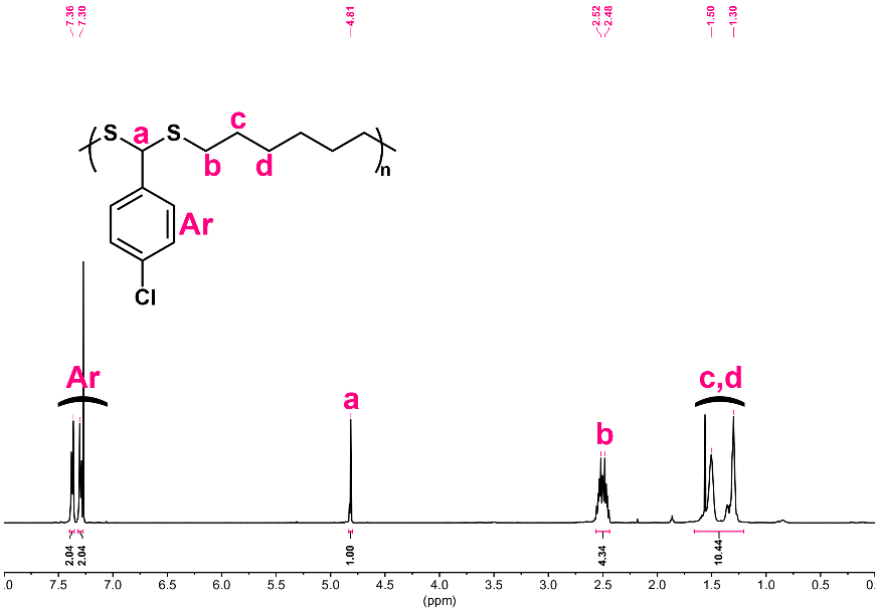


Figure 4.33 : ^{1}H NMR spectrum of P8 ($CDCl_3$, 500 MHz).

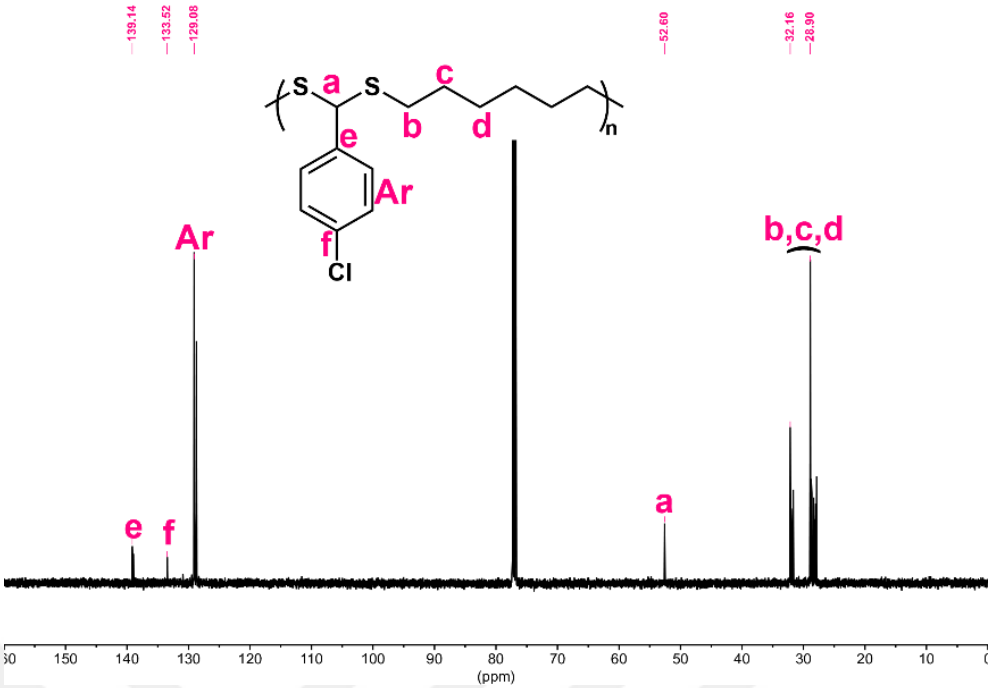


Figure 4.34 : ^{13}C NMR spectrum of P8 ($CDCl_3$, 500 MHz).

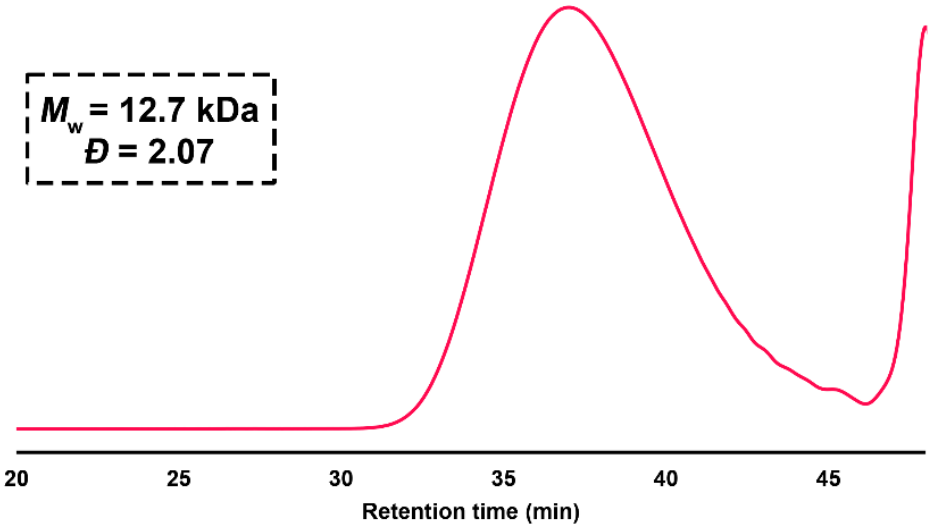


Figure 4.35 : GPC chromatogram of P8.

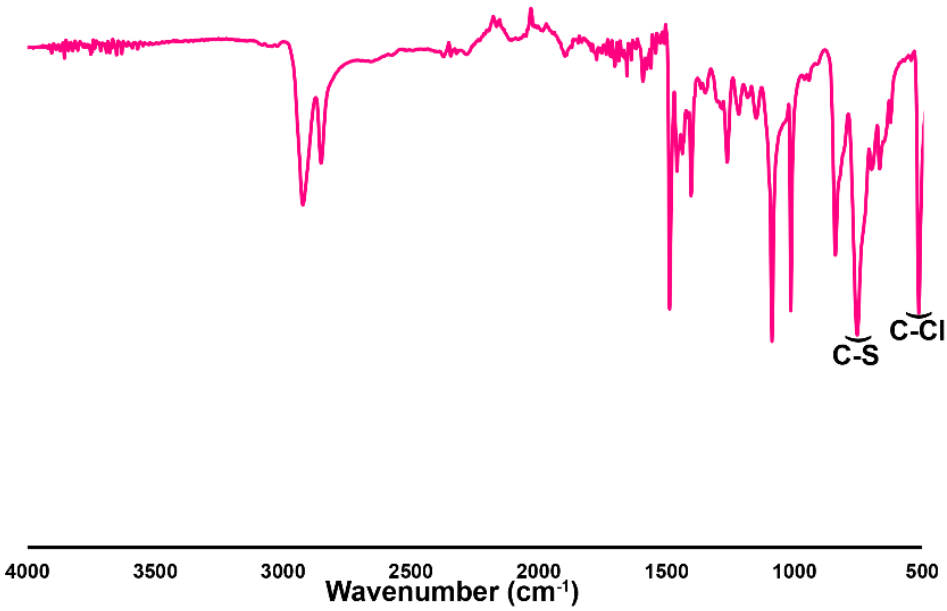


Figure 4.36 : FT-IR spectrum of P8.

4.4.11 Synthesis of P9

General procedure was followed. 2-thiophenecarboxaldehyde (223 µL, 2.20 mmol), HDT (306 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P9 was obtained as a white sticky solid (Yield = 450 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25, 7.07, 6.92 (3H, Ar*H*), 5.17 (1H, ArC*H*S), 2.64-2.58 (4H, SC*H*$_2$(CH$_2$)$_4$C*H*$_2$S), 1.56-1.35 (8H, SCH$_2$(C*H*$_2$)$_4$CH$_2$S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.15 126.44 125.76 125.45 48.41 32.01 28.90 28.45.

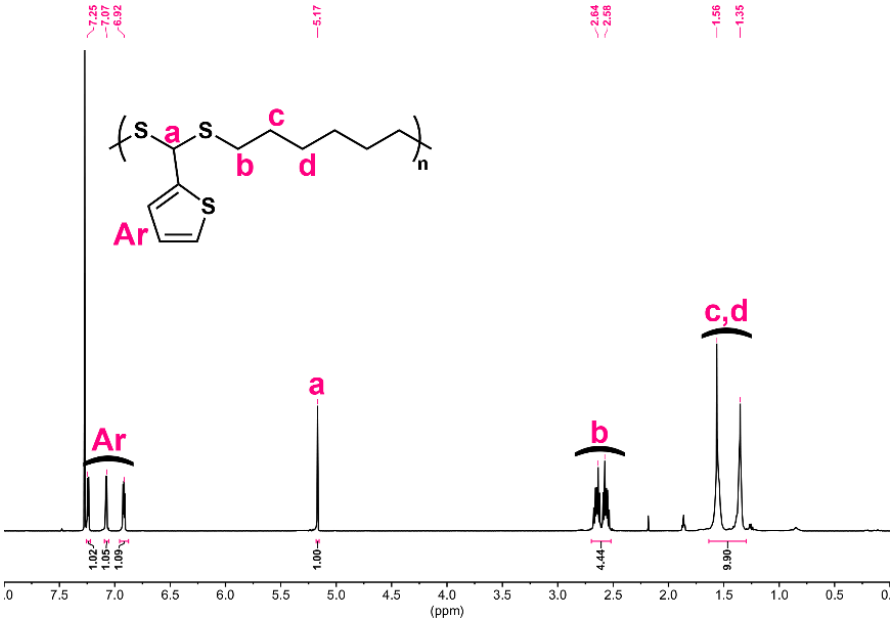


Figure 4.37 : ^{1}H NMR spectrum of P9 ($CDCl_3$, 500 MHz).

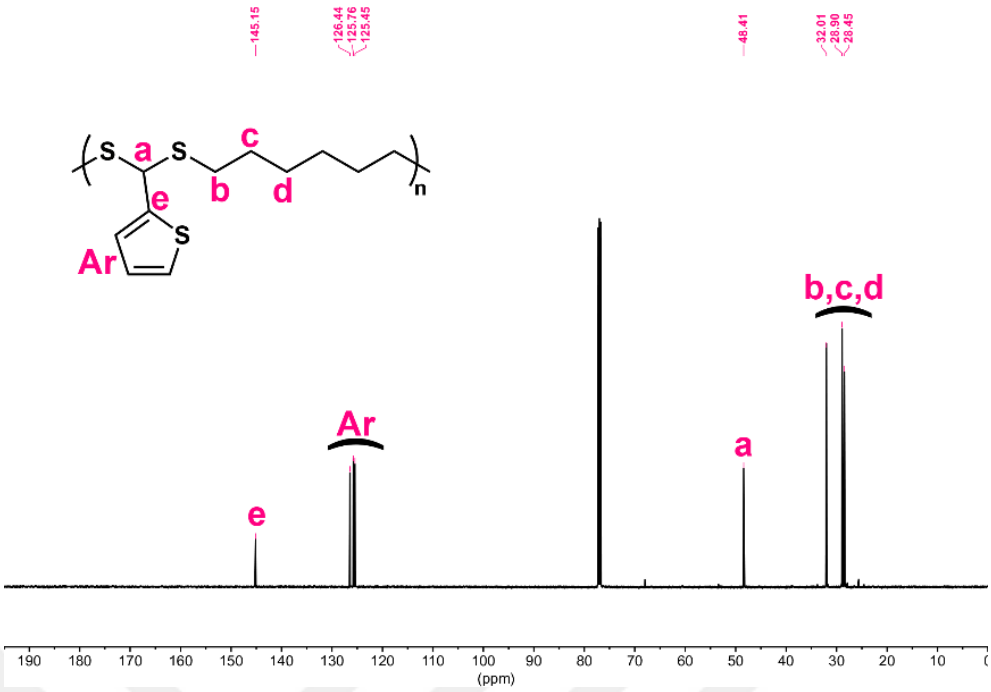


Figure 4.38 : ^{13}C NMR spectrum of P9 ($CDCl_3$, 125 MHz).

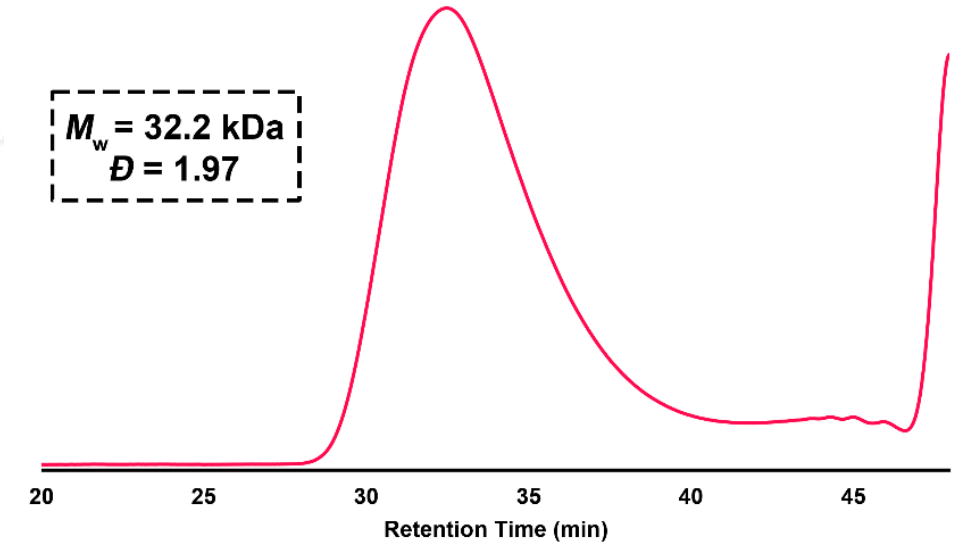


Figure 4.39 : GPC chromatogram of P9.

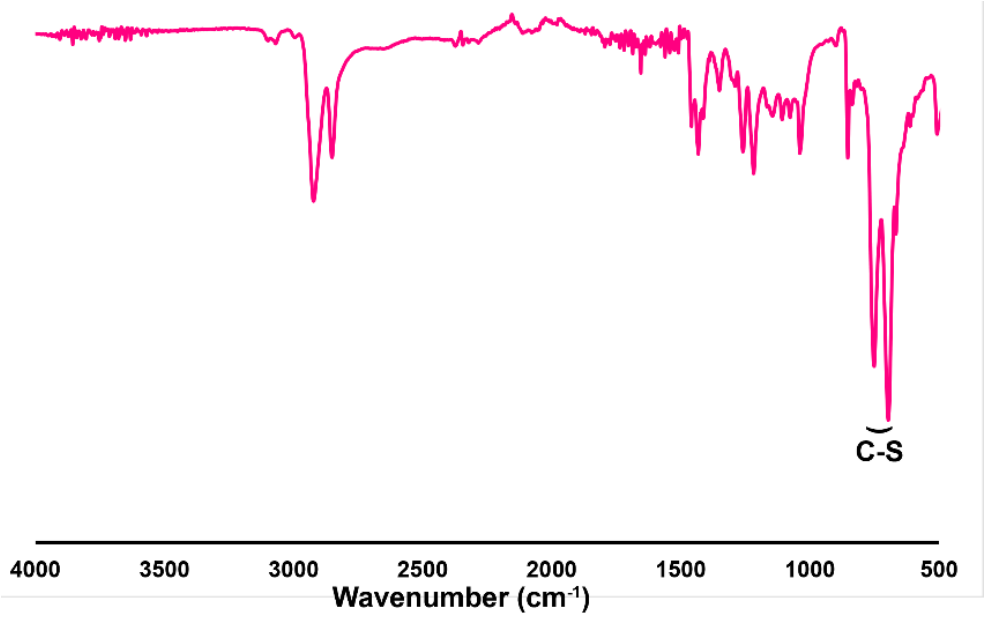


Figure 4.40 : FT-IR spectrum of P9.

4.4.12 Synthesis of P10

General procedure was followed. 1-pyrenecarboxaldehyde (507 mg 2.20 mmol), HDT (306 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P10 was obtained as a white sticky solid (Yield = 717 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.32-7.91 (9H, Ar*H*), 5.85 (1H, ArC*H*S), 2.45-2.39 (4H, SC*H*$_2$(CH$_2$)$_4$C*H*$_2$S), 1.37-1.10 (8H, SCH$_2$(C*H*$_2$)$_4$CH$_2$S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 133.29 130.72 127.44 126.08 124.94 50.08 28.97 28.06.

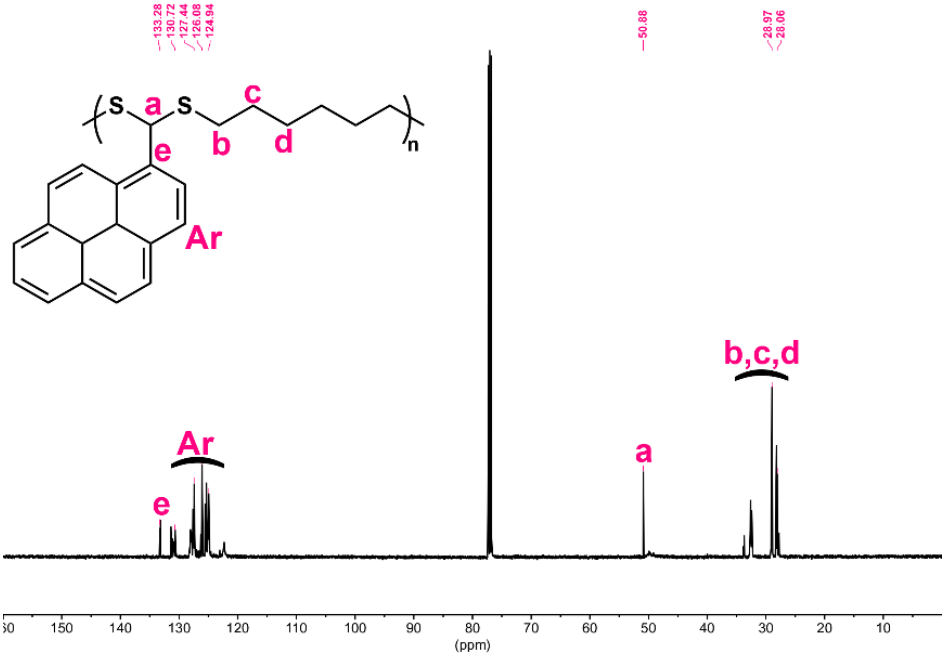


Figure 4.41 : ^{13}C NMR spectrum of P10 ($CDCl_3$, 125 MHz).

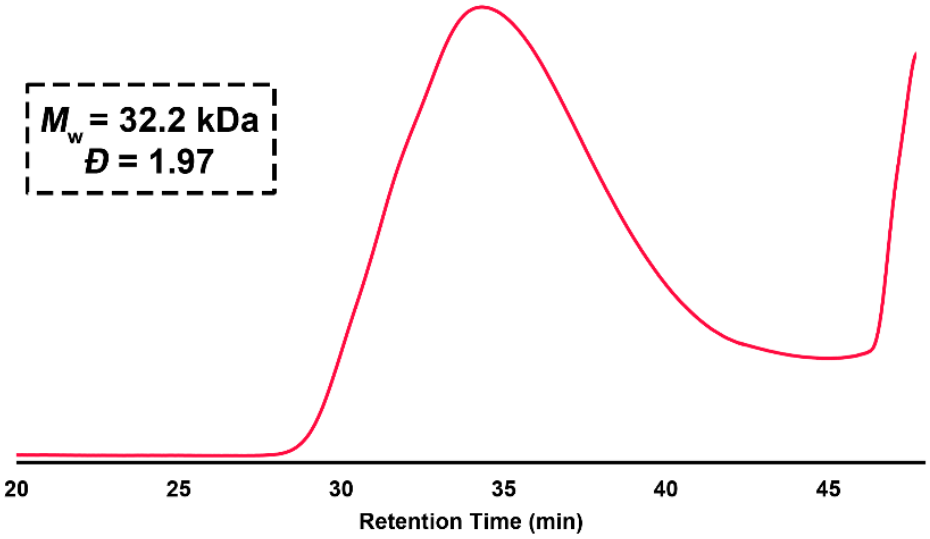


Figure 4.42 : GPC chromatogram of P10.

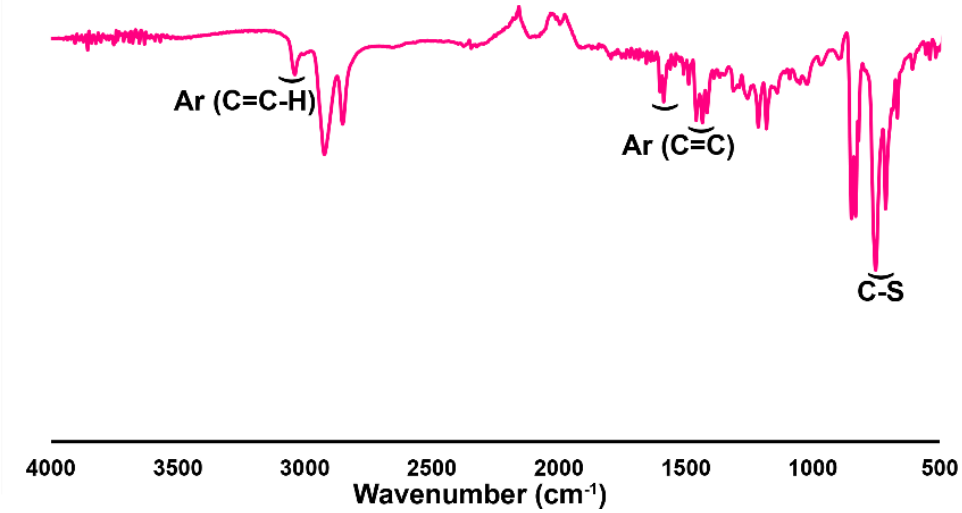


Figure 4.43 : FT-IR spectrum of P10.

4.4.13 Synthesis of P11

General procedure was followed. 4-(1,2,2-triphenylethenyl)benzaldehyde (396 mg 1.11 mmol), HDT (153 µL, 1.00 mmol), CDMS (56 µL, 0.50 mmol) and 500 µL of THF were used. P11 was obtained as a white sticky solid (Yield = 509 mg, 94%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14-6.97 (14H, Ar*H*), 4.79 (1H, ArC*H*S), 2.44 (4H, SCH_2(CH_2)$_4$CH_2S), 1.49-1.29 (8H, SCH_2(CH_2)$_4$$CH_2$S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.64 143.52 143.34 141.27 140.47 138.29 131.31 127.68 127.08 126.47 53.00 32.05 29.05 28.54.

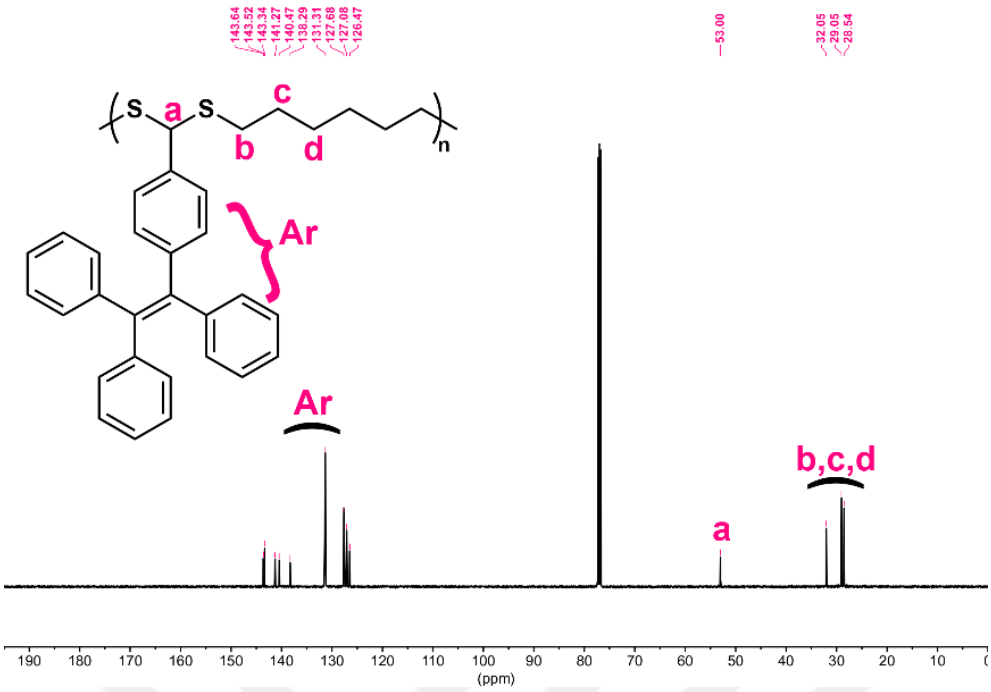


Figure 4.44 : ^{13}C NMR spectrum of P11 ($CDCl_3$, 125 MHz).

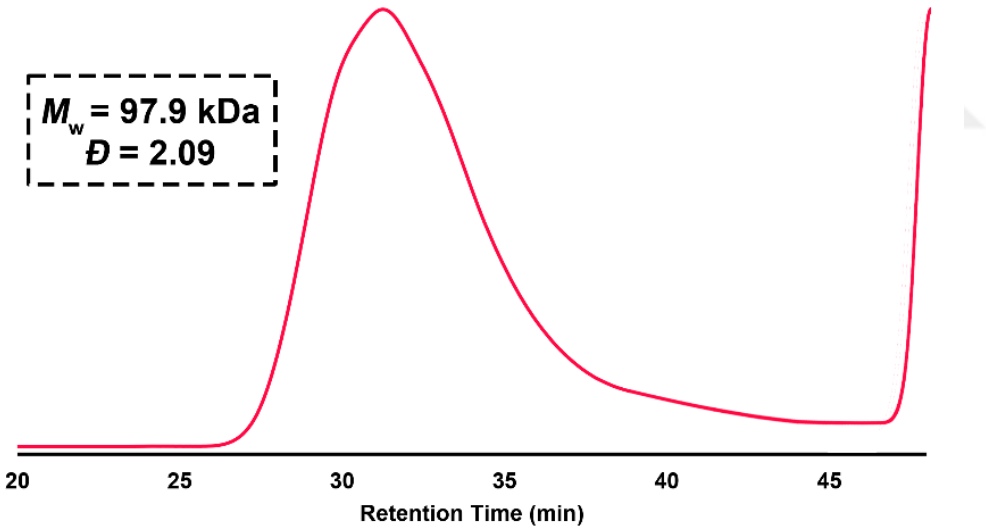


Figure 4.45 : GPC chromatogram of P11.

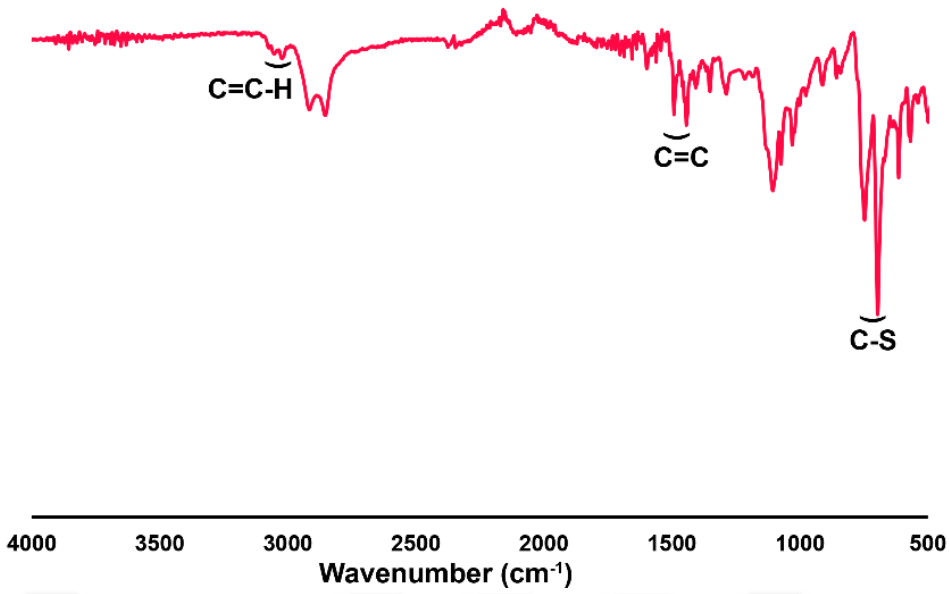


Figure 4.46 : FT-IR spectrum of P11.

4.4.14 Synthesis of P12

General procedure was followed. ferrocenecarboxaldehyde (471 mg 2.20 mmol), HDT (306 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P12 was obtained as a white sticky solid (Yield = 700 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.77 (1H, ArC*H*S), 4.27, 4.23, 4.15 (9H, Ar*H*), 2.70-2.53 (4H, SC*H*$_2$(CH_2)$_4$C*H*$_2$S), 1.68-1.40 (8H, SCH_2(C*H*$_2$)$_4$$CH_2$S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 89.17 69.45 67.69 67.41 50.30 30.73 28.64.

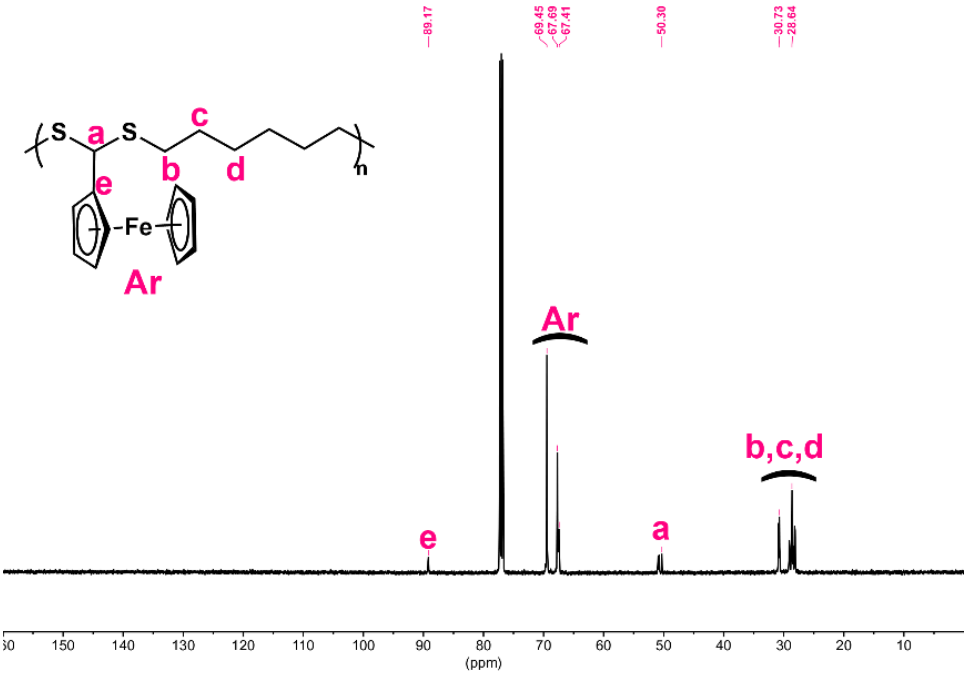


Figure 4.47 : ^{13}C NMR spectrum of P12 ($CDCl_3$, 125 MHz).

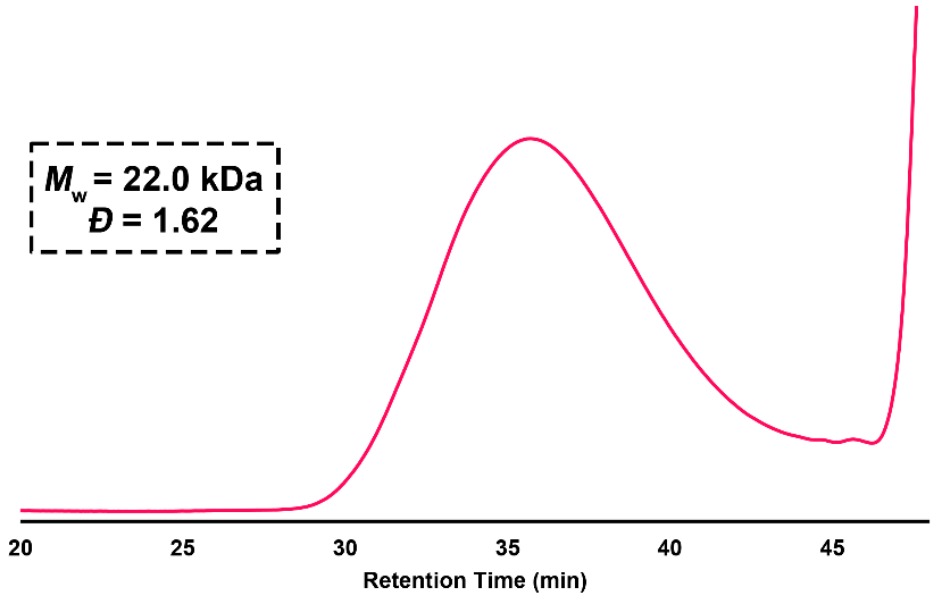


Figure 4.48 : GPC chromatogram of P12.

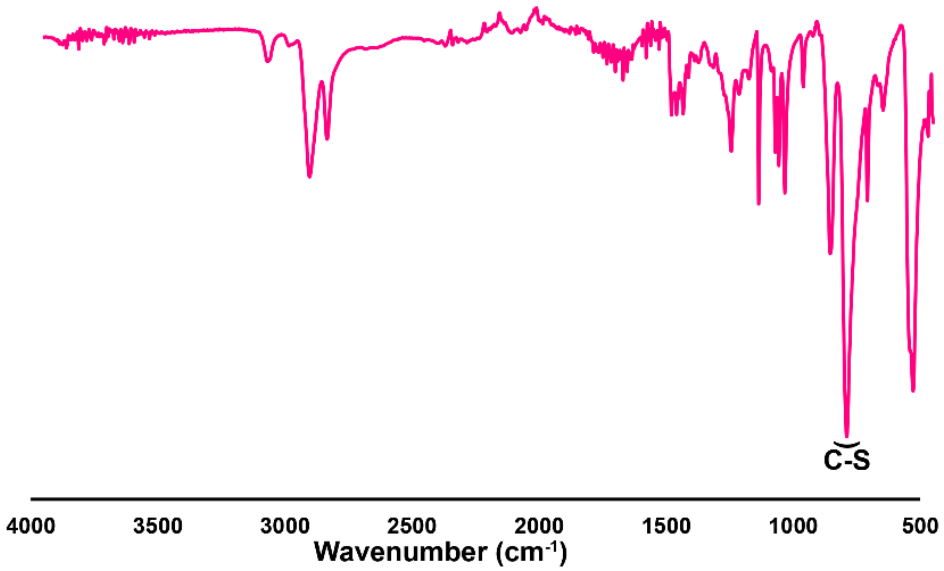


Figure 4.49 : FT-IR spectrum of P12.

4.4.15 Synthesis of P13

General procedure was followed. BA (224 µL, 2.20 mmol), 1,4-butanedithiol (235 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P13 was obtained as a white sticky solid (Yield = 439 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40, 7.33, 7.26 (5H, Ar*H*), 4.83 (1H, ArC*H*S), 2.51-2.46 (4H, S$CH_2(CH_2)_2CH_2$S), 1.58 (4H, $SCH_2(CH_2)_2CH_2S$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.82 128.61 127.46 56.84 32.61 31.72.

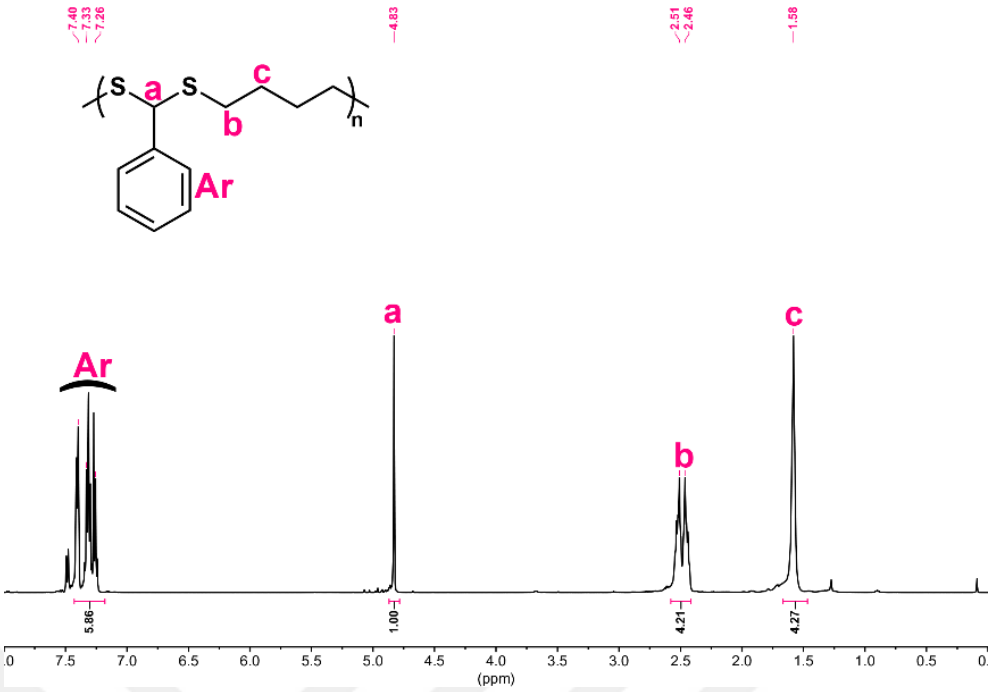


Figure 4.50 : ^{1}H NMR spectrum of P13 ($CDCl_3$, 500 MHz).

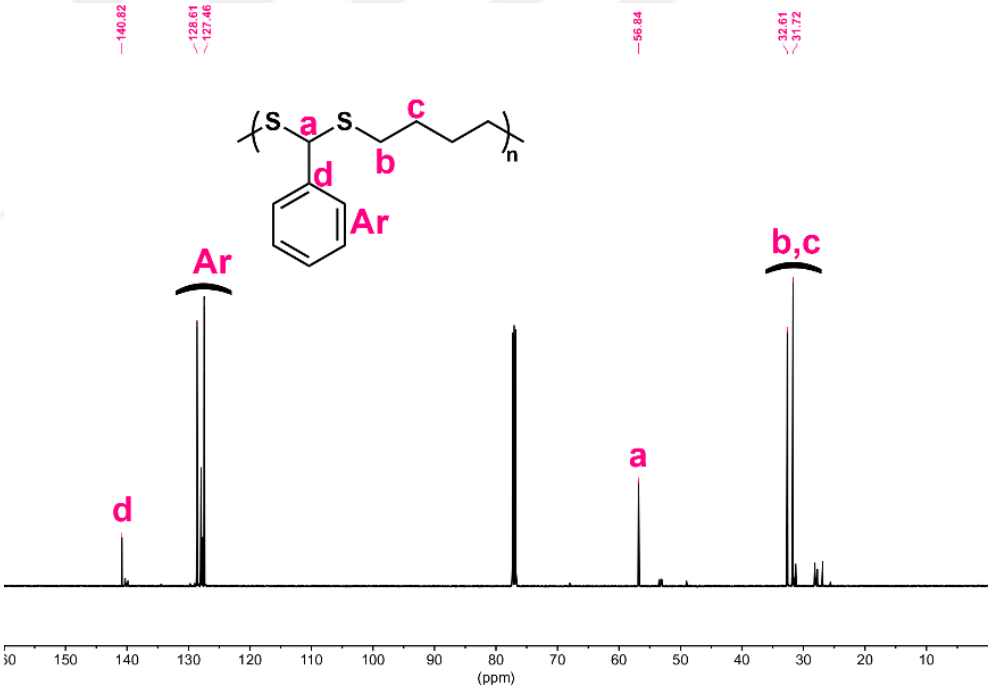


Figure 4.51 : ^{13}C NMR spectrum of P13 ($CDCl_3$, 125 MHz).

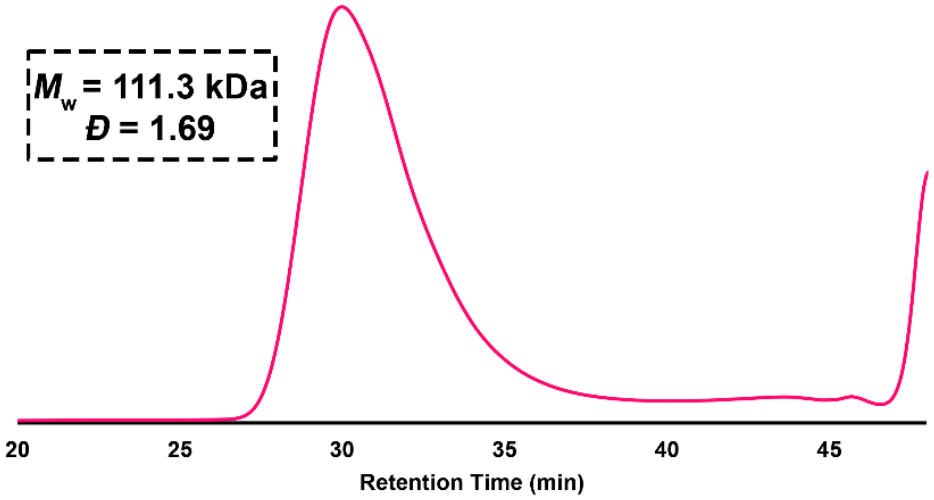


Figure 4.52 : GPC chromatogram of P13.

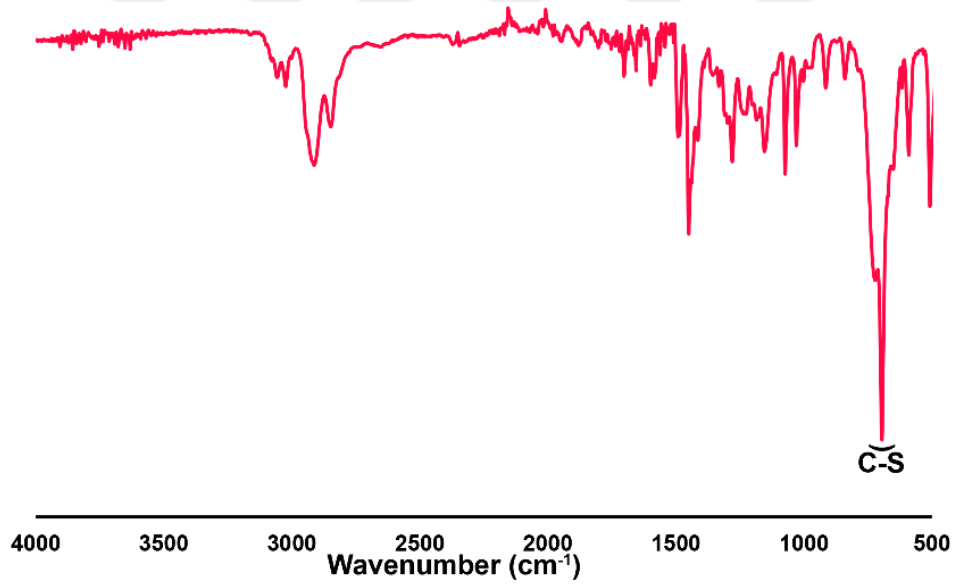


Figure 4.53 : FT-IR spectrum of P13.

4.4.16 Synthesis of P14

General procedure was followed. BA (224 µL, 2.20 mmol), 1,8-octanedithiol (368 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P14 was obtained as a white sticky solid (Yield = 568 mg, 97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45, 7.33, 7.27 (5H, Ar*H*), 4.87 (1H, ArC*H*S), 2.69, 2.51 (4H, S$CH_2(CH_2)_6CH_2$S), 1.54-1.21 (12H, S$CH_2(CH_2)_6CH_2$S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.62 128.49 127.69 53.30 32.26 29.11 28.79.

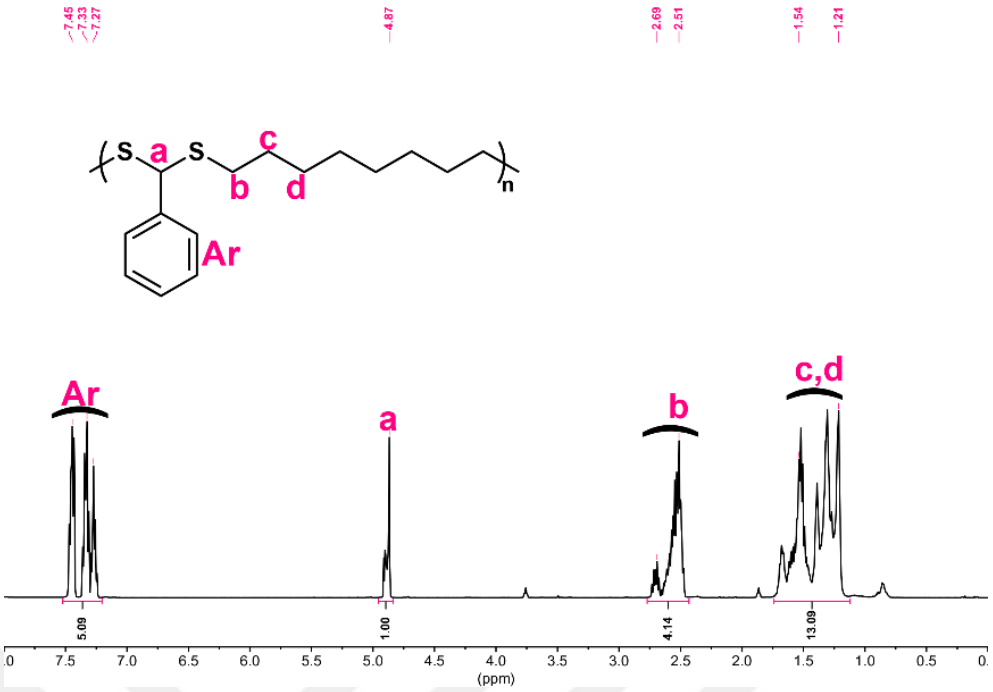


Figure 4.54 : ^{1}H NMR spectrum of P14 ($CDCl_3$, 500 MHz).

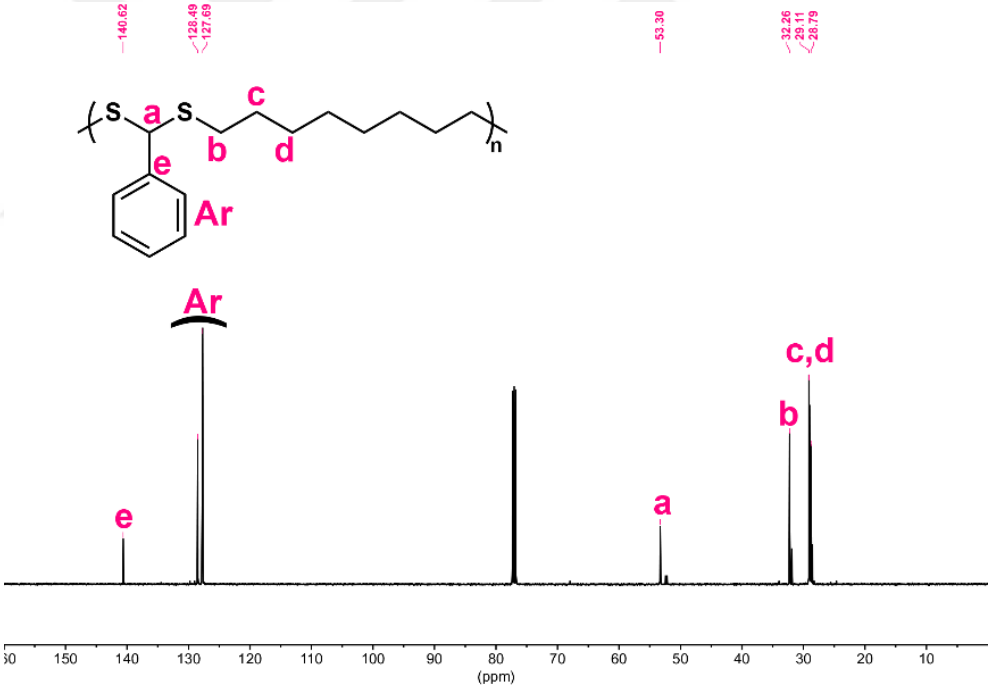


Figure 4.55 : ^{13}C NMR spectrum of P14 ($CDCl_3$, 125 MHz).

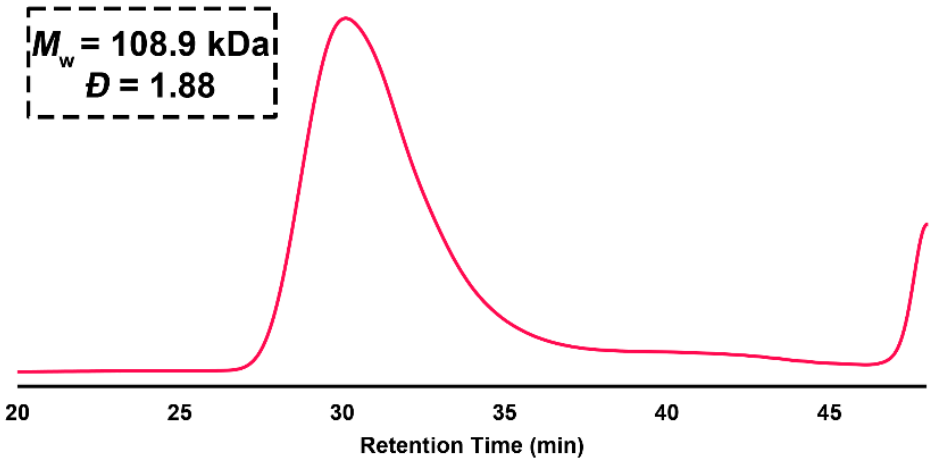


Figure 4.56 : GPC chromatogram of P14.

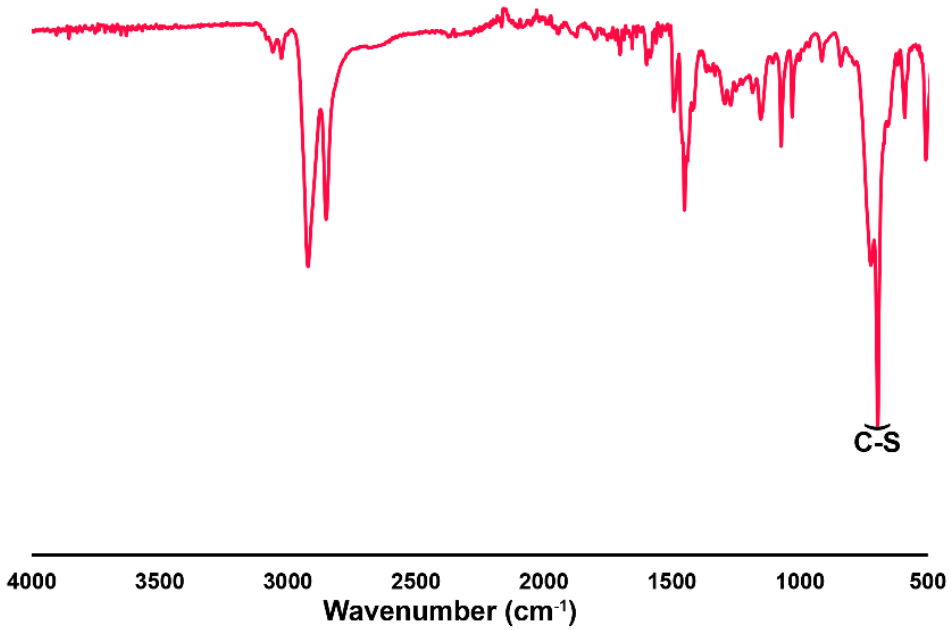


Figure 4.57 : FT-IR spectrum of P14.

4.4.17 Synthesis of P15

General procedure was followed. BA (224 µL, 2.20 mmol), 2,2'-(ethylenedioxy)diethanethiol (326 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P15 was obtained as a white sticky solid (Yield = 564 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42, 7.30, 7.25 (5H, Ar*H*), 5.09 (1H, ArC*H*S), 3.58- 3.42 (8H, SCH_2CH_2(CH_2O)$_2$CH_2CH_2S), 2.78-2.69 (8H, SCH_2(CH_2)$_4$CH_2S)

ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.84 140.94 128.52 127.87 127.67 73.74 72.01 70.21 53.46 31.78 31.39.

Figure 4.58 : ^{13}C NMR spectrum of P15 ($CDCl_3$, 125 MHz).

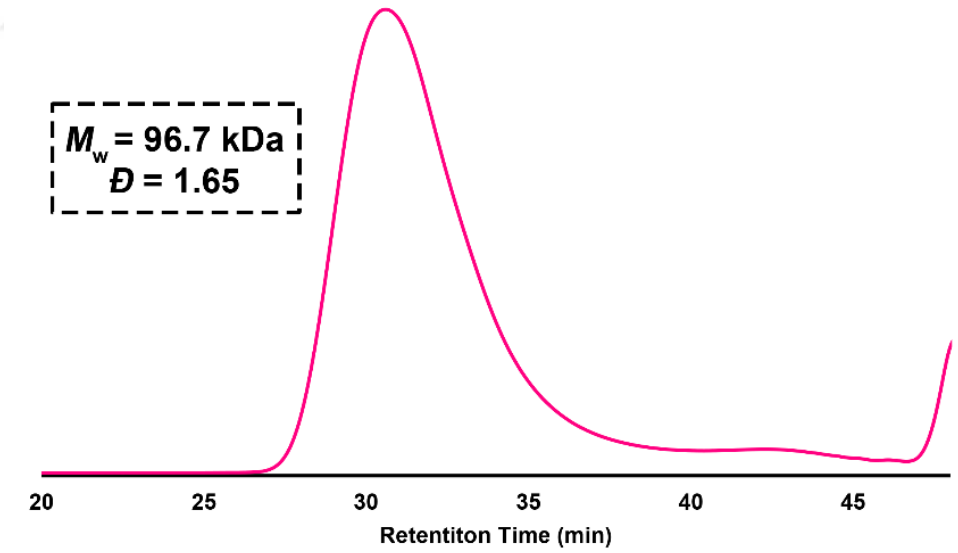


Figure 4.59 : GPC chromatogram of P15.

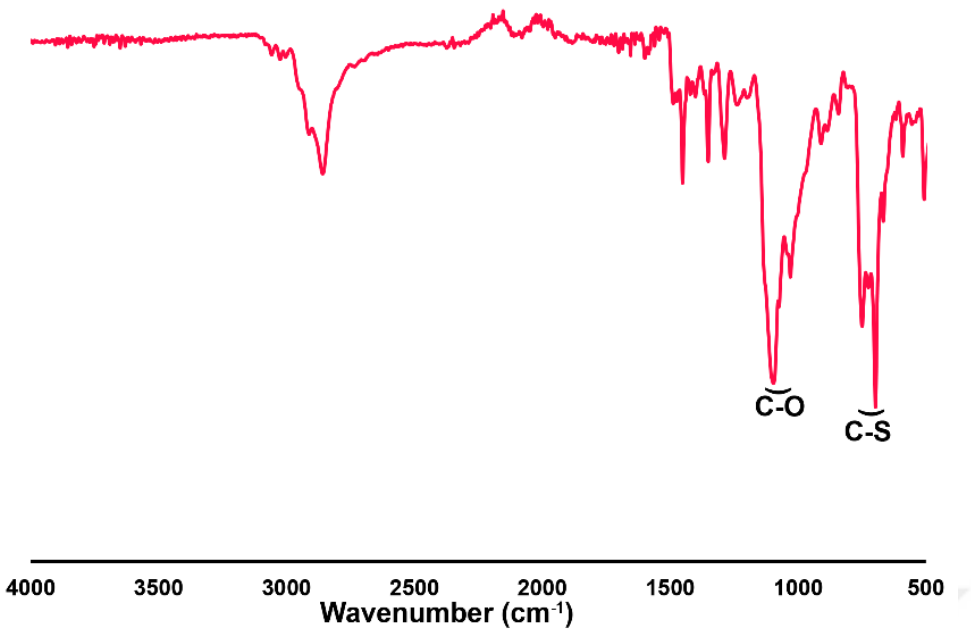


Figure 4.60 : FT-IR spectrum of P15.

4.4.18 Synthesis of P16

General procedure was followed. BA (224 µL, 2.20 mmol), 1,4-benzenedimethanethiol (341 mg, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P16 was obtained as a white sticky solid (Yield =499 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.03 (9H, Ar*H*), 4.47 (1H, ArC*H*S), 3.71-3.54 (4H, CH_2Ar) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.45 136.35 129.11 128.63 127.98 51.48 47.01 36.21.

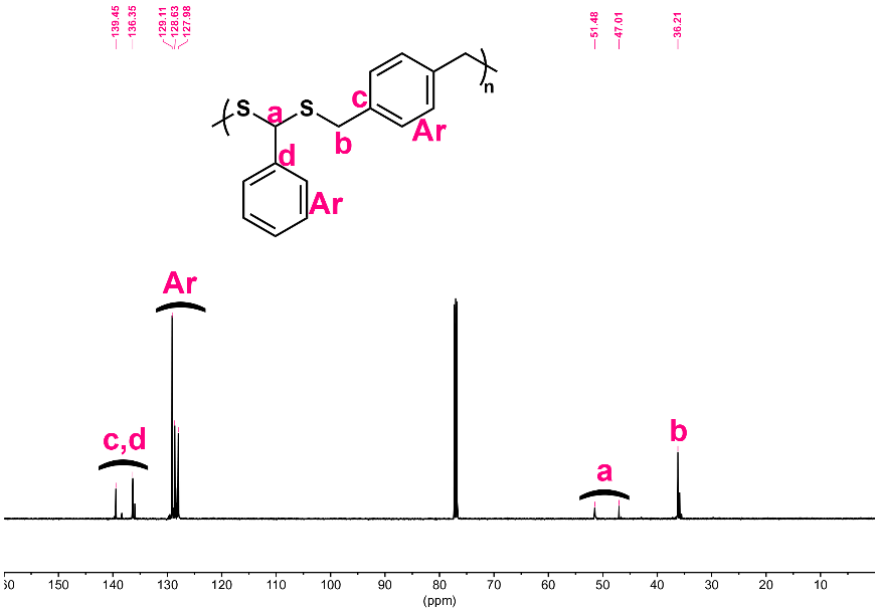


Figure 4.61 : ^{13}C NMR spectrum of P16 ($CDCl_3$, 500 MHz).

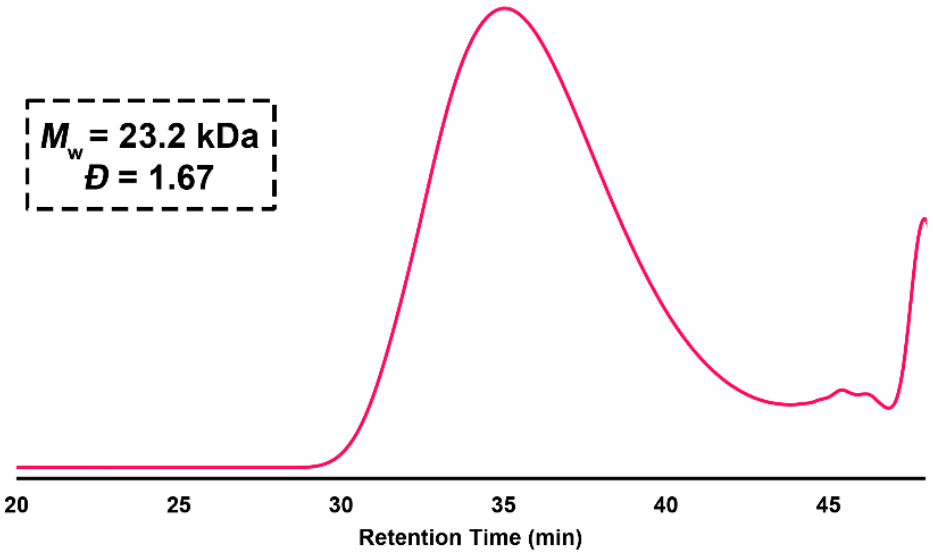


Figure 4.62 : GPC chromatogram of P16.

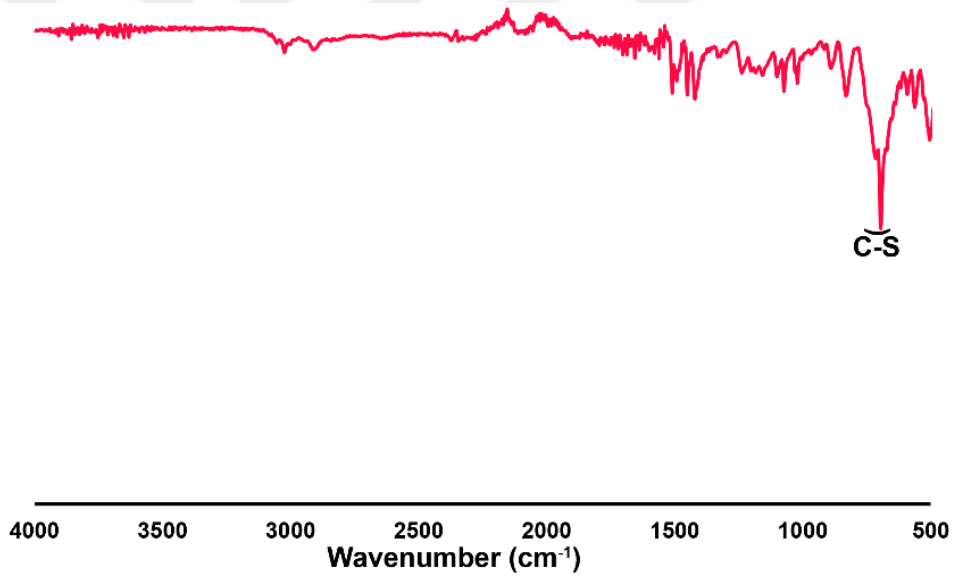


Figure 4.63 : FT-IR spectrum of P16.

4.4.19 Synthesis of P17

General procedure was followed. BA (224 µL, 2.20 mmol), ethylene glycol bis-mercaptoacetate (318 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P17 was obtained as a white sticky solid (Yield = 583 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41, 7.33 (5H, Ar*H*), 5.33 (1H, ArC*H*S), 4.27 (4H, SCH_2(C=O)(CH_2O)$_2$(C=O)CH_2), 3.42-3.21 (4H, SCH_2(C=O)(CH_2O)$_2$(C=O)CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.70 138.19 134.45 128.78 127.91 62.91 53.45 33.65.

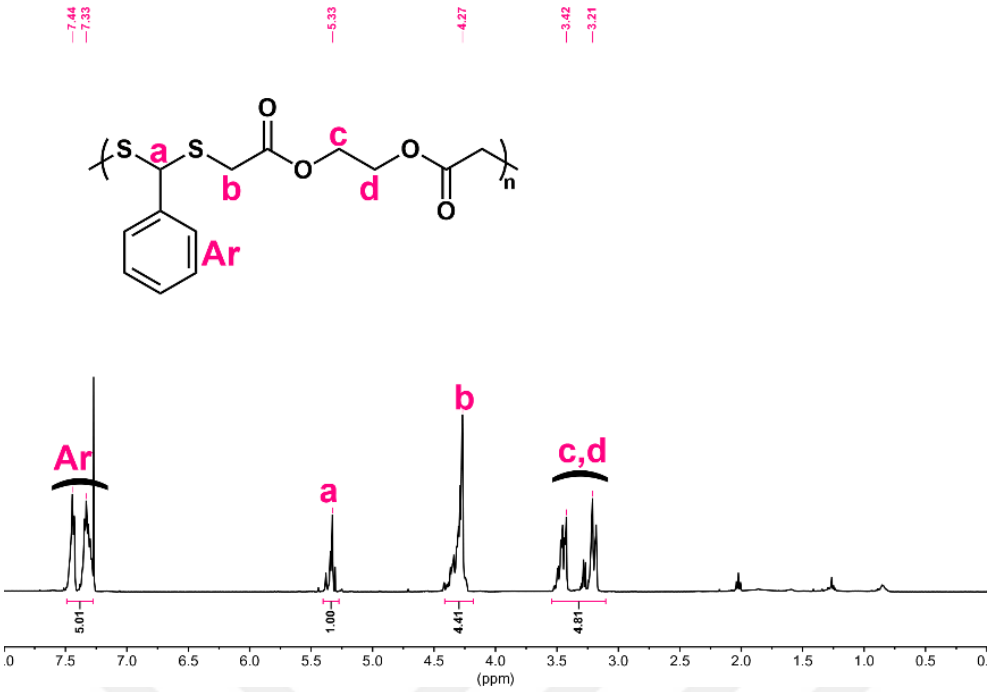


Figure 4.64 : ^{1}H NMR spectrum of P17 ($CDCl_3$, 500 MHz).

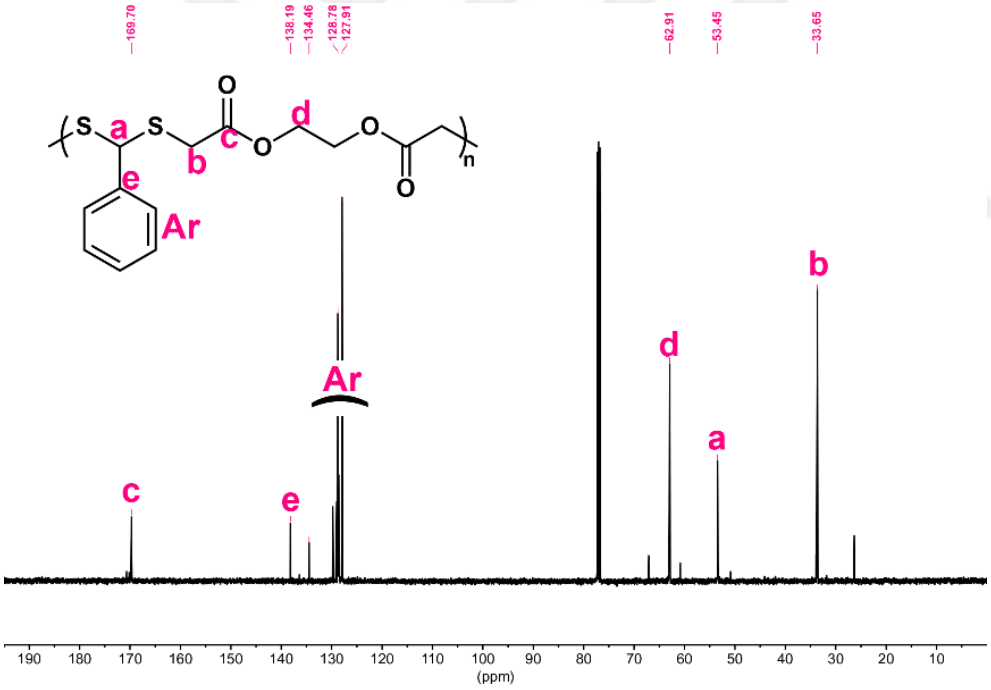


Figure 4.65 : ^{13}C NMR spectrum of P17 ($CDCl_3$, 500 MHz).

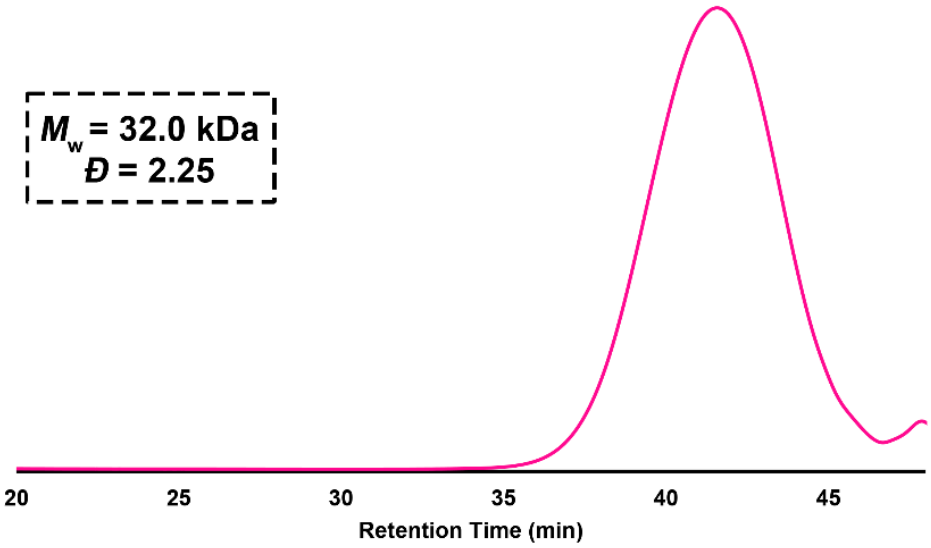


Figure 4.66 : GPC chromatogram of P17.

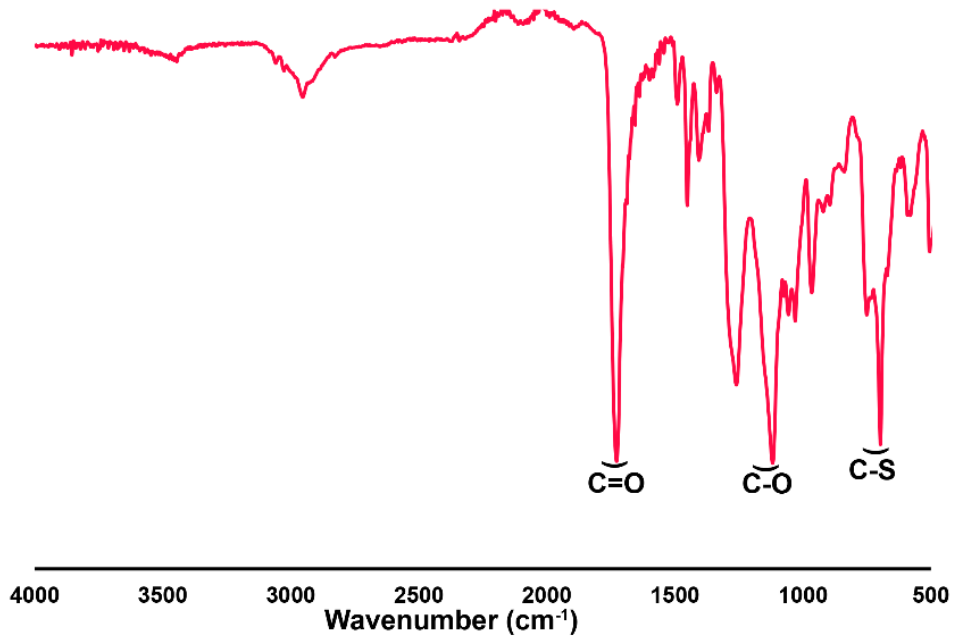


Figure 4.67 : FT-IR spectrum of P17.

4.4.21 Synthesis of P18

General procedure was followed. BA (224 µL, 2.20 mmol), DL-dithiothreitol (308 mg, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P18 was obtained as a white sticky solid (Yield = 287 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44- 7.33 (5H, Ar*H*), 5.17 (1H, ArC*H*S), 3.79 (8H, SCH_2(C*H*O*H*)$_2$CH_2S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.39 128.79 127.36 75.69 75.31 54.14 33.64.

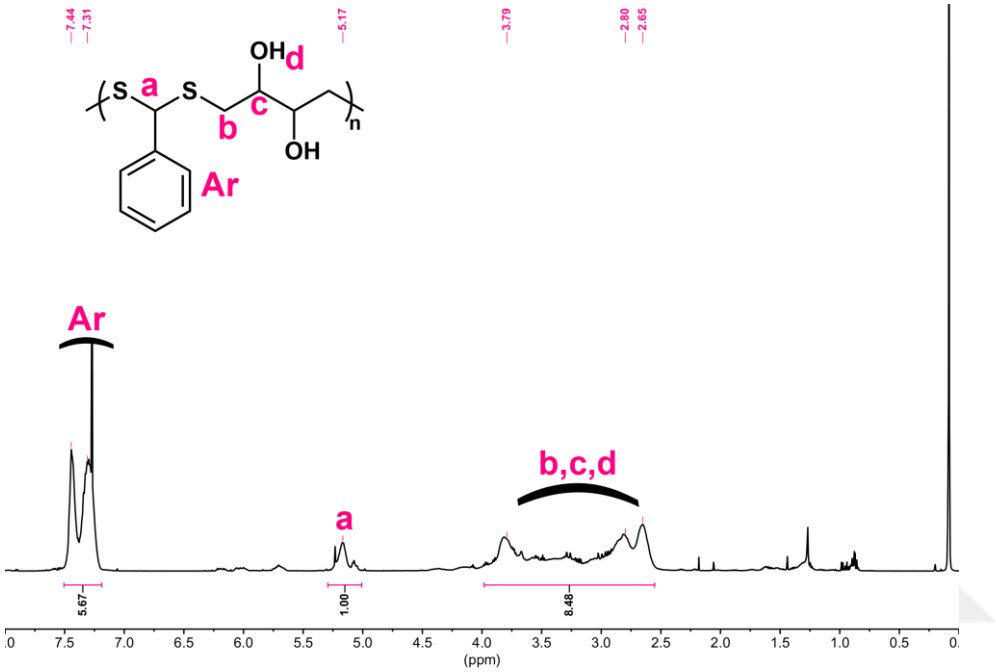


Figure 4.68 : ^{1}H NMR spectrum of P18 ($CDCl_3$, 500 MHz).

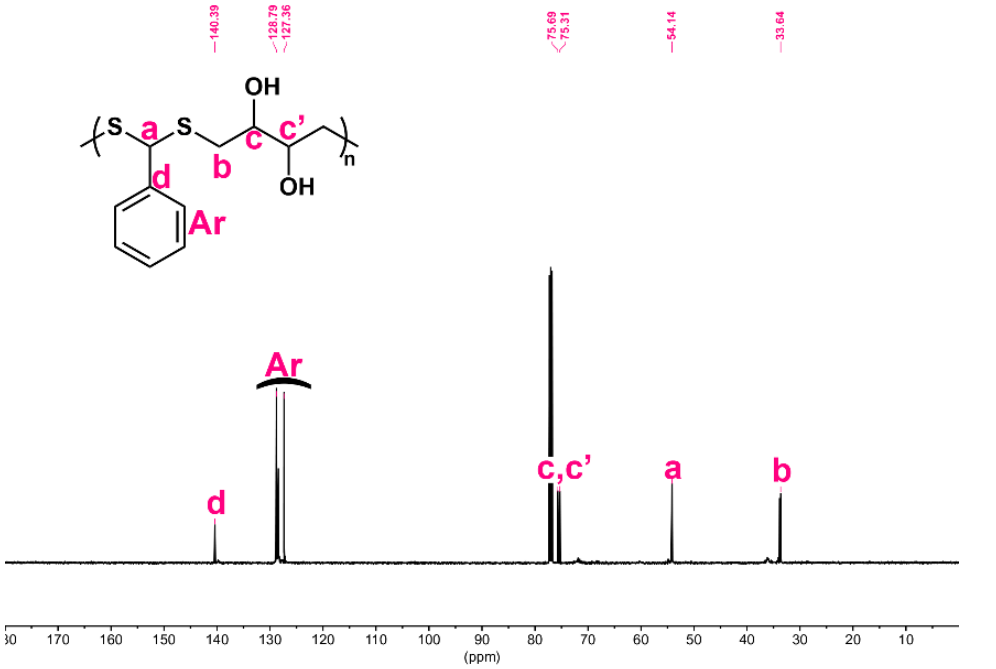


Figure 4.69 : ^{13}C NMR spectrum of P18 ($CDCl_3$, 125 MHz).

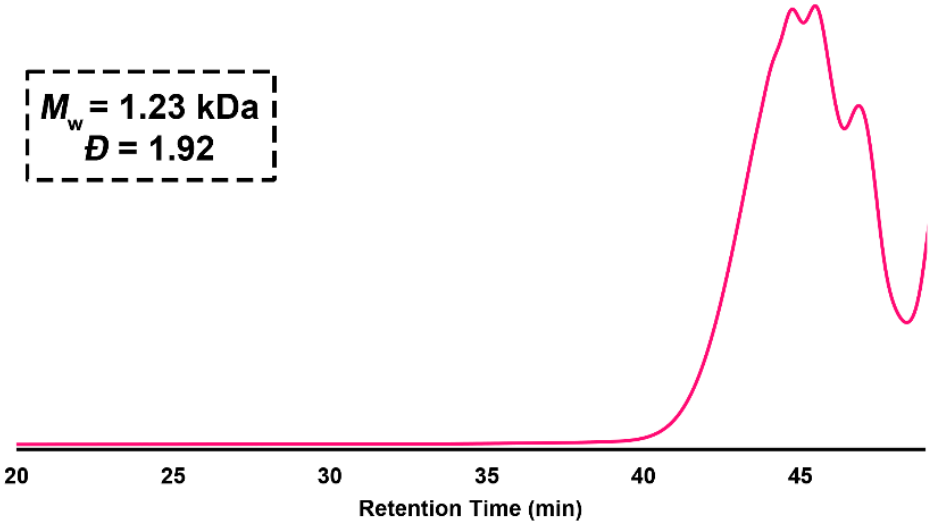


Figure 4.70 : GPC chromatogram of P18.

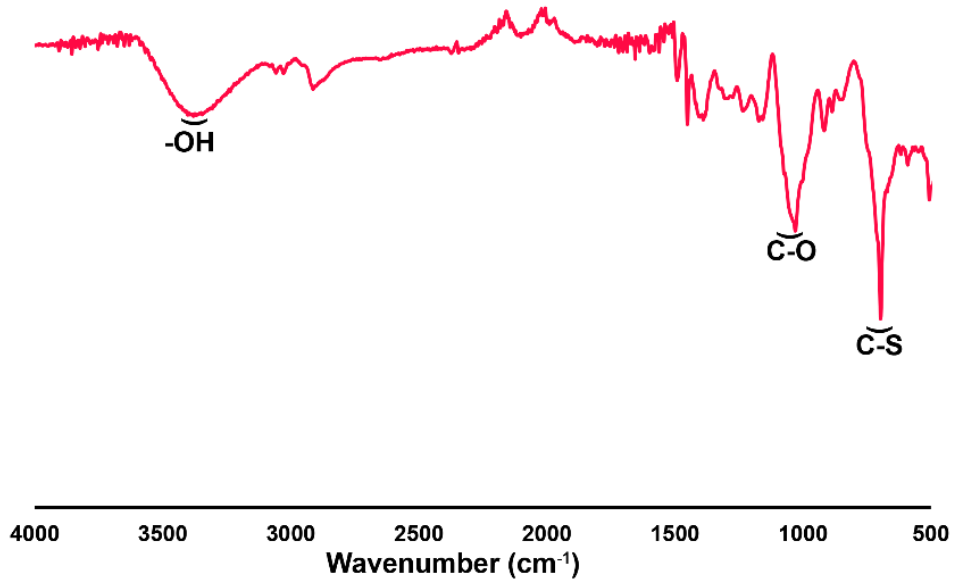


Figure 4.71 : FT-IR spectrum of P18.

4.4.22 Synthesis of P19

General procedure was followed. BA (112 µL, 1.10 mmol), 2-thiophenecarboxaldehyde (112 µL, 2.20 mmol), HDT (306 µL, 2.00 mmol), CDMS (111 µL, 1.00 mmol) and 1 mL of THF were used. P19 was obtained as a white sticky solid (Yield = 450 mg, 89%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44, 7.32 (5H, Ar*H*), 7.08, 6.92 (3H, Ar*H*), 5.17 (1H, ArC*H*S), 4.85 (1H, ArC*H*S), 2.62, 2.51 (4H, SCH_2(CH_2)$_4$CH_2S), 1.53-1.33 (8H, SCH$_2$(CH_2)$_4$CH$_2$S) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.16 140.53 128.52 127.69 126.43 125.44 53.32 48.43 32.01 28.97.

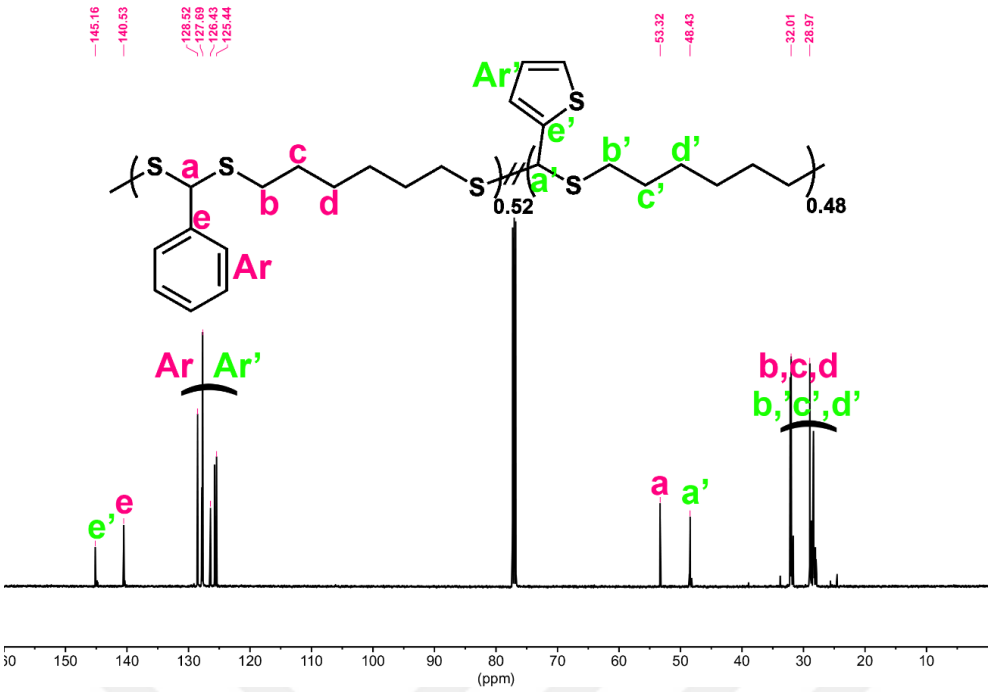


Figure 4.72 : ^{13}C NMR spectrum of P19 ($CDCl_3$, 125 MHz).

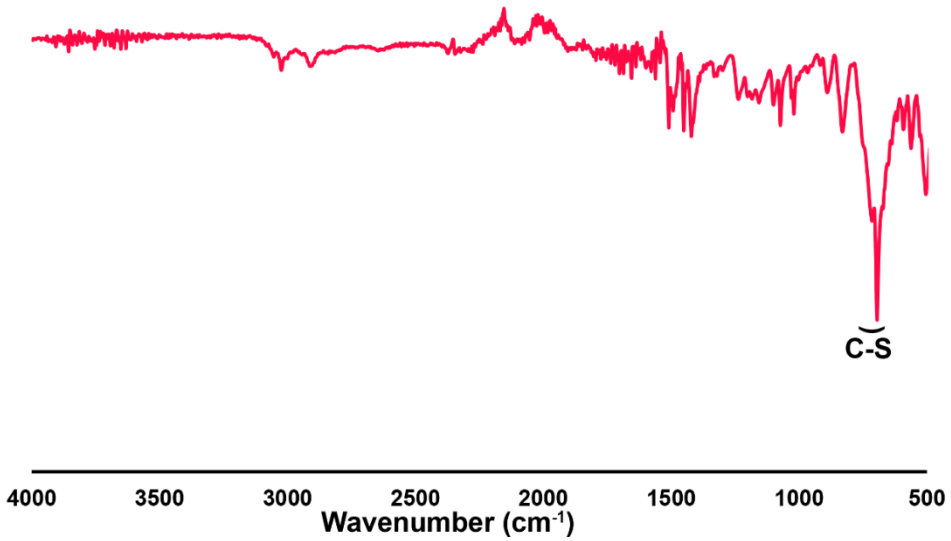


Figure 4.73 : FT-IR spectrum of P19.

5. CONCLUSION

The use of robust methods in organic chemistry has influenced the development of new, precisely defined polymers with diverse compositions and topologies. RER is a convenient method for the production of ethers from aldehyde and ketone carbonyls, and can be performed with either Brønsted or Lewis acids. RER strategy has been employed with various silane reagents and acid catalysts after it has been proposed by Doyle and co-workers in 1972. Yokozawa and co-workers has succesfully adapted this method to obtain different polyether backbones. Yet, RER has failed to come attention of polymer chemists for a long time. More recently, Lee and Morandi showed that using CDMS as both reducing agent and acid source, ether bonds can be formed effortlesly in a very straightforward concept.

Inspiring from all of these works, this thesis concludes 3 examples of the use of CDMS-mediated RER as a postpolymerization functionalization and step-growth polymerization method.

In the first study, which was given in Chapter 2, ketone carbonyl containing polymer backbone was subjected to CDMS-mediated RER in order to yield pendant alkoxyl groups. Optimization studies were carried out in order to yield the ideal reaction conditions. Various aldehydes were used to perform the reaction and finally a mechanistic approach was proposed for this PPM.

In the second study, which was given in Chapter 3, linear polyethers were synthesized via CDMS-mediated RER strategy. Optimum reagent amounts and reaction time was revealed with a systematic optimization study for the polymerization. Finally, a polyether library was created using different dialdehyde and diols.

In the final study, which was given in Chapter 4, polythioacetal synthesis were carried out using CDMS as the acid catalyst. The results for this method was compared with the traditional acid catalysts and CDMS was found to be yielding polymers in just 5 min. In addition, other reaction parameters was also studied and with the ideal

polymerization conditions in hand, a large variety of aldehyde and dithiol compounds were used to synthesize different functional PTAs.

RER strategy seems to be forgotten for a while, yet, this protocol is a very convenient and straightforward to yield ethers. We believe that with all these works, RER may have the potential to revive in upcoming years and gain the interest of the polymer chemists for many emerging and tailored applications.

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