ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

EXTREMELY RAPID POSTFUNCTIONALIZATION OF POLYESTERS IN THE PRESENCE OF TBD

M.Sc. THESIS

Buse ÖZCAN

Department of Chemistry

Chemistry Programme

JULY 2020

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TBD VARLIĞINDA POLİESTERLERİN HIZLI BİR ŞEKİLDE FONKSİYONLANDIRILMASI

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To my family

FOREWORD

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ABBREVIATIONS

^{1}H NMR	**:** Proton Nuclear Magnetic Resonance
GPC	**:** Gel Permeation Chromatography
HPLC	**:** High Pressure Liquid Chromatography
DSC	**:** Differential Scanning Calorimetry
$CHCl_3$	**:** Chloroform
$CDCl_3$	**:** Deuterated Chloroform
THF	**:** Tetrahydrofuran
DMF	**:** N,N-dimethylformamide
MeOH	**:** Methanol
mmol	**:** Milimole

SYMBOLS

Đ	**:** Dispersity of polymer
kDa	**:** Kilodalton
h	**:** Hour
M_w	**:** Molecular weight
MHz	**:** Mega Hertz
µL	**:** Microliter
µm	**:** Micrometre

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EXTREMELY RAPID POSTFUNCTIONALIZATION OF POLYESTERS IN THE PRESENCE OF TBD

SUMMARY

Unsaturated polyesters (UP) as commercially important polymers have been used remarkably for wide range applications due to their double bond nature provides a site for subsequent cross-linking or functionalization using postpolymerization modification. UP scaffold, P1 possessing an electron-deficient double bond in the main chain was synthesized via a simple condensation polymerization between maleic anhydride and 1,4-butanediol in high yield and then the precursor polymer was utilized for thiol- Michael addition reactions. From a detailed catalyst search (amidine and guanidine bases), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) proved to be the most efficient catalyst because of owing to highly basic for thiol-Michael addition reactions since pendant thioether functional polyesters were achieved quantitatively within 1 min. These experiments were occured in minimal scales. P1 (0.880 mmol) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. Thiol (1.06 mmol) and TBD (0.0880 mmol) were added to the solution, respectively. The mixture was stirred at room temperature for 1 min and precipitated in 20 mL of MeOH followed by removing excess solvent via decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times and the recovered yellow sticky product was dried in a vacuum oven for 24 h. From ^{1}H NMR spectra of thioether functional polyesters, characteristic maleate C*H*=C*H* protons at 6.25 ppm entirely vanished and new multiplet signals appeared at around 3.65 and 3.00-2.70 ppm assignable to the characteristic main chain C*H* proton attached to the S and it's neighbor CH_2 protons, respectively. NMR results, it is obvious that thiol-Michael addition reactions occurred with 100% efficiencies, indicating that the thiols used, in terms of the nucleophilic power, were not important in the presence of TBD. GPC traces of all polymers displayed unimodal curves with broader dispersity (*Đ*). GPC analysis of the resulting polyesters indicated the molecular weight increase after the postfunctionalization.

TBD VARLIĞINDA POLİESTERLERİN HIZLI BİR ŞEKİLDE FONKSİYONLANDIRILMASI

ÖZET

Kimyasal sentezlerde "klik" kimyası, biyo-konjügasyonda yaygın olarak kullanılan ve uygun substratların spesifik biyomoleküllerle birleştirilmesine izin veren bir biyo-uyumlu küçük molekül reaksiyonları sınıfında yer alır. Klik kimyası tek bir spesifik reaksiyon olmamakla beraber, ancak doğada örnekleri izleyen ve aynı zamanda küçük modüler birimlere katılarak yeni seztez ürünlerinin elde edilmesini sağlayan reaksiyon metodlarıdır. Birçok uygulamada, klik reaksiyonları bir biyomoleküle katılır; ancak, klik kimyası biyolojik koşullarla sınırlı değildir: Klik reaksiyonu kavramı farmakolojik ve çeşitli biyomimetik uygulamalarda da kullanılmıştır. Bununla birlikte, biyomoleküllerin saptanması, lokalizasyonu ve nitelendirilmesinde özellikle yararlı hale getirilmiştir. Bu reaksiyonlar yüksek verimli, geniş kapsamlı, stereospesifik, gerçekleştirmesi kolay ve yan ürünleri reaksiyon ortamından kolayca uzaklaştırabilir olduğundan dolaylı diğer reksiyon çeşitlerine göre bu alanda önem kazanmıştır ve tercih edilir hale gelmiştir. Epoksitlerin ve aziridinlerin nükleofilik halka açılma reaksiyonları, hidrazonların ve heterosiklikerin oluşumu gibi aldol tipi olmayan karbonil reaksiyonları, katılma reaksiyonları gibi özellikle bir ürüne yol açan termodinamik olarak tercih edilen reaksiyon çeşitleri tanımlanmıştır. Michael katılma reaksiyonları da klik kimyasının içerisinde bulunan önemli bir yere sahip reaksiyon çeşididir. Michael katılma reaksiyonları tarihsel olarak her zaman organik sentezde kullanılmış olsa da, bunlara ek olarak malzeme uygulamalarında, yüzey modifikasyonunda, polimer modifikasyonunda aynı zamanda polimer sentezlerinde uygulanması, büyük ölçüde materyallerde, klik kimyasının uygulanmasına paralel olarak ortaya çıkmıştır.

Michael katılma reaksiyonlarının, geniş başlangıç materyalleri, hafif reaksiyon koşulları ve yüksek fonksiyonel grup toleransının yanı sıra çeşitli fonksiyonel materyaller yapmak için reaksiyonların yüksek dönüşümlerle gerçekleşmesi nedeniyle sentetik polimer kimyasında büyük avantajlara sahip olduğu düşünülmektedir. Michael katılması, β-doymamış karbonil bileşiğine bir nükleofilin (veya bir karbanyonun) nükleofilik katılması olarak tanımlanabilir ve karbon-karbon bağlarının oluşumunda çok etkili olduğu düşünülen bir reaksiyon çeşididir. α,β-doymamış keton, nitril, nitro ve ester bileşikleri gibi aktif olefin veya alkin grupları ile C,N,O ve S atomları içeren nükleofiller arasında gerçekleşen konjuge katılmalar Michael katılma reaksiyonları olarak adlandırılır. Michael katılmalarının mekanizması, β-doymamış karbonil bileşiğinin baz tarafından α-hidrojeninin koparılamsıyla başlar. Elektron çekici karbonil gruplarından dolayı stabil bir karbanyon enolat rezonansları oluşturur. Enolat iyonu ve Michael akseptörü reaksiyon göstererek yeni bir karbon-karbon bağının oluşmasını sağlar. Böylece, enolat iyonu α,β-doymamış karbonil bileşiği üzerinde 1,4 ilavesini tamamlar. α, β -doymamış karbonil bileşiği üzerindeki 1,4 enolat ilavesinden oluşan bileşik potolanlanarak istenilen sonuç ürünü verir. Eğer reaksiyon S atomu içeren nükleofil üzerinden gerçekleşiyorsa bu katılma tiyol-Micheal katılması olarak adlandırılır.

Bazik katalizör kükürt atomu içeren bileşikte kükürtün protonunu kopartarak nükleofilik hale getirir. Nükleofil, elektron çekiçi grup içeren bileşiğe saldırır ve katılma gerçekleşir. Bazik katalizörün protonlamasıyla ürün elde edilir.

Yeşil Kimya'nın önem kazanmasıyla birlikte son dönemde yapılan çalışmaların basit,enerji ve atom tasarruflu, ekonomik ve çevre sağlığı açısından zararlı olmayan yöntemlerin geliştirilmesi aynı değerde önem kazanmıştır. Bu amaçla reaksiyonun katalizörsüz, düşük sıcaklık ve çözücüsüz ortamda gerçekleştirilmesi için yöntemler geliştirilmektedir. Aynı şekilde bu amaçlar göz ününde bulundurularak, bu çalışmada atom (100% dönüşümlü) ve enerji tasarruflu (ısı kullanılmadan ve bir dakika içerisinde) sentez metodu geliştirilmesi hedeflenmiştir.

Sahip oldukları çift bağ yapıları nedeniyle, ticari olarak önemli özelliklere sahip olan polimerler, özellikle doymamış polyesterler (DP), postpolimerizasyon modifikasyon yöntemleri kullanılarak cross-link veya fonksiyonelleştirme için uygun olduklarından geniş çaplı uygulama alanlarına sahiptir. Doymamış polyester reçineleri, doymamış asitlerin veya anhidritlerin ve diollerin diasit içeren / içermeyen kondenzasyon ürünleridir. doymamış polyesterler geniş bir uygulama yelpazesi için dikkat çekici bir şekilde kullanılmaktadır, bu da onları büyük önem taşıyan bir termoset sistem haline getirmektedir. Bu polimerler, başlatıcılar ve diğer katkı maddelerinin seçimine bağlı olarak çok çeşitli kimyasal ve mekanik özelliklere sahip birçok termoset ürünlerin elde edilmesinde kullanılabilir.

Ana zincirde elektronca eksik bir çift bağa sahip olan doymamış polimer zinciri (P1), yüksek verimde maleik anhidrit ve 1,4-bütandiol kullanılarak basit bir kondenzasyon polimerizasyon yöntemi ile Dean-Stark aparatı kullanılarak sentezlendi ve daha sonra tiyol-Michael modifikayson reaksiyonları için bu ham polimer kullanıldı.Ana polimerin saflaştırılmasında, THF ile balondan alınan polimer metanole çöktürüldü. Çöz-çöktür ile bu aşama bir kez daha tekrarlandı. Elde edilen yapışkan kahverengi polimer 24 saat boyunca vakumlu fırında kurutuldu. Ayrıntılı bir katalizör (amidin ve guanidin bazları: 1,4-diazabisiklo[2.2.2]octan (DABCO), 1,5,7-triazabisiklo[4.4.0]dec-5-en (TBD), 7-metil-1,5,7-triazabisiklo[4.4.0]dec-5-en (MTBD), trietilamin (Et_3N), 1,8-diazabisiklo[5.4.0]undec-7-en (DBU), 1,5-diazabisiklo[4.3.0]non-5-en (DBN), ve 1,1,3,3-tetrametilguanidin (TMG)) araştırmasından sonra, tiyol-Michael katılma reaksiyonları için güçlü bazikliğinden dolayı en verimli katalizörün 1,5,7-triazabisiklo [4.4.0] dec-5-en (TBD) olduğu bulundu..

Bu deneylerde minimal ölçeklerde çalışıldı. Pl (0.880 mmol), 3 mL $CHCl_3$ içerisinde çözüldü ve çözelti 10 mL'lik bir balona aktarıldı. Çözünmüş ana polimerin bulunduğu balona sırasıyla tiyol (1.06 mmol) ve TBD (0.0880 mmol) ilave edildi. Karışım oda sıcaklığında 1 dakika karıştırıldıktan sonra 20 mL MeOH içerisine çöktürülerek reaksiyon sonlandırıldı. MeOH içerisine çöktürülürek aynı zamanda saflaştırma prosedürüne başlanmış olundu. Fazla çözücü dekante edilerek ortamdan uzaklaştırıldı. Elde edilen polimer $CHCl_3$ ile çözüldükten sonra safsızlıklardan tamamen kurtulmak için tekrar MeOH içerisine çöktürüldü ve geri kazanılan sarı yapışkan sonuç polimer, 24 saat boyunca vakumlu bir fırında kurutuldu. Primer ve sekonder olmak üzere çeşitli alifatik ve aromatik tiyoller ile çalışıldı. Çalışılan tiyoller: 1-propantiyol, siklopentantiyol, 2-furanmetantiyol, benzilmerkaptan, 2-naftalentiyol, *N*-asetil-*L*-sistein, 1-oktantiyol, 2-merkaptoetanol, metiltiyoglikolat ve tiyofenol. Bu deneylere ek olarak, aynı reaksiyon şartları uygulanarak ve aynı balon içerisinde gerçekleştirilmek kaydıyla polimer 1 dk içerisinde iki farklı tiyol ile

modifiye edildi. Bu deney için benzil metkaptan ve 1-propantiyol seçildi. Bu tiyollerin seçilme sebebi, proton NMR sonuçlarında alifatik ve aromatik bölgede farkları daha net gözlemleyip dönüşüm yüzdelerinin daha kolay ve doğru yorumlanmasını sağlamaktır.

Fonksiyonlandırılmış polimerlerin analizleri şu cihazlar kullanılarak yapılmıştır: ^{1}H spektrumları Agilent VNMR 500 Hz spektrometre ile, iç standart olarak $Si(CH_3)_4$ ve çözücü olarak $CDCl_3$ içinde kayıt edilmiştir, jel geçirgenlik kromatografisi (GPC) Agilent Cihazı (Model 1100) pompa, refraktif indeks (RI) ve ultraviolet detektörlerden ve 4 adet Waters Styragel klonlardan oluşan (guard, HR 5E, HR 4E, HR3 ve HR 2) (46 mm iç yarıçap, 300 mm uzunluk) ile yapıldı, efektif molekül ağırlığı dağılımı 2000-4,000,000, 50-100,000, 500-30,000, ve 500-20,000, çözücü olarak THF ve toluen 0.3 mL/min akış hızında 30 °C kullanıldı, molekül ağırlıkları (Mn,GPC ve Mw,GPC) ve polidispersitler (Mw/Mn) lineer PS standartlarına göre Polymer Laboratories'den PL Caliber Software kullanılarak hesaplandı, Diferansiyel Taramalı Kalorimetri (DSC), DSC Q1000 (TA Instruments) ve Diamond DSC (Perkin-Elmer) ile 10 ^{o}C/dakika ısıtma hızıyla ve N2 ortamında yapıldı, tüm veriler ikinci ısıtma döngüsünden, camsı geçiş sıcaklığı (Tg) ve erime sıcaklığı (Tm), orta noktası ve termogramın maksimum pik noktası olarak hesaplandı.

Fonksiyonlandırılmış polyesterlerin proton NMR spektrumlarına bakıldığında, maleat C*H* = C*H* protonlarının 6.25 ppm'de verdikleri karakteristik pikin tamamen kaybolduğu ve tiyolün bağlı olduğu karbona ait protonun 3.65 ppm civarında ve tiyolün bağlı olduğu karbonun komşu kabonundaki protonların 3.00-2.70 ppm'de pik verdikleri gözlemlenmiştir. Ayrıca, tüm polimerlerin ^{13}C NMR spektrumları, tiyol-Michael ilave reaksiyonlarının, 130 ppm civarında *C*H = *C*H sinyalinin tamamen kaybolduğu ve tiyoeter fonksiyonelliğine ilişkin karşılık gelen *C* sinyallerinin beklenen bölgelerde göründüğü ve kantitatif verimliliklerle gerçekleştirildiğini de destekledi. Destekleyici bilgilerde, tüm polimerlerin ^{13}C NMR spektrumlarından, 165 ppm'de P1'in C=O sinyallerinin, post-fonksiyonelleştirmeden sonra 170 ppm üzerine kaydırıldığı açıkça tespit edilmiştir.

NMR sonuçları, tiyol-Michael katılma reaksiyonlarının % 100 verimlilikle meydana geldiğini kanıtlamışır, bu da kullanılan tiyollerin nükleofilik güç açısından TBD varlığında önemli olmadığını gösterir. Benzil merkaptoetanol ile modifiye edilmiş polimerin GPC sonuçları hariç, tüm tiyoller ile fonksiyonlandırılmış polimerler daha geniş dağılımlı (*Đ*) tek-modlu eğriler göstermiştir. Elde edilen polyesterlerin GPC analizi, fonksiyonelleştirmeden sonra elde edilen polimerlerin molekül ağırlıkları ile teorik olarak uyumlu moleküler ağırlık artışı gösterdiği incelenmiştir. DSC verilerinin incelenmesiyle, düşük *Tg* değerleri gösteren tamamen amorf ve tüm polimerlerin yapışkan olduğu olduğu belirtilmektedir.

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1. INTRODUCTION

General-purpose unsaturated polyesters (UPs) are synthesized by employing maleic anhydride, phthalic anhydride, and diol [1]. UPs as commercially important polymers have been used remarkably for wide range applications due to their double bond nature provides a site for subsequent cross-linking or functionalization using postpolymerization modification [1]. The cross-linking reactions of these UPs having major importance are carried out by blending vinyl monomers (e.g. styrene), fillers, and reinforcements and then curing by free radical initiators to yield thermoset articles with a wide variety of chemical and mechanical properties [1].

Moreover, the unsaturation in the main chain of this type of polyesters offers a suitable position for efficient chemical reactions to produce well-defined functional materials. It is thought that Michael addition reactions have great advantages in synthetic polymer chemistry due to extensive starting materials, mild reaction conditions, and high functional group tolerance as well as high conversions to make diverse functional materials [2-21].

1.1 Literature Review and Purpose of Thesis

Recently, Daglar and colleagues investigated that aza- and thiol-Michael addition reactions on polyesters with electron-deficient alkyne units in the main chain [22]. Thus, this polyester scaffold was successfully reacted with a variety of primary and secondary amines as well as various thiols within a reasonably short time (2 min). The heterofunctionalization on the polyester backbone was also investigated using a mixture of different amines, or a mixture of amine and thiol compounds. According to this study, a series of nucleophilic thiol-Michael addition reactions were realized on this polyester backbone to result in monofunctional products (vinyl thioether structure) using 1,4-diazabicyclo[2.2.2]octane (DABCO) as the most efficient nucleophilic catalyst. The reaction efficiencies using DABCO were high as much as 87-91% with *Z*-stereoisomer as the major product. After that, homo and mixed double functionalizations through the thiol-Michael addition reactions were studied

using a variety of organocatalysts. Finally, highly basic as well as nucleophilic catalyst namely, 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), demonstrated higher efficiencies in terms of the double addition, and almost complete double functionalization was observed when 0.25 equiv of TBD per alkyne unit was employed in the reactions.

Recently, Michael addition reactions on UPs have gained popularity in the literature owing to that aliphatic polyesters are well known biodegradable and biocompatible platform [7, 9, 12, 14]. Du and Li group reported the synthesis of thermally degradable polyesters through the postpolymerization modification of an aliphatic UP via thiol-Michael addition reaction with β-amino mercaptans [23]. Aliphatic UP was synthesized from maleic acid and 10-undecenol followed by the acyclic diene metathesis (ADMET) polymerization. Takasu group combined two sequential routes: aza-Michael addition and UV-initiated free radical polymerization of vinyl monomers for one-pot synthesis of polyester-based double network gels by chemoselective cross-linking at room temperature [24]. When acrylamide was used as a vinyl monomer, polyester double network hydrogel was readily obtained. More recently, Wei group prepared UPs with a wide range of well-controlled *cis*- (maleate) and *trans*- (fumarate) isomer compositions [25]. Inspired by these studies, an extremely rapid postfunctionalization of the unsaturated polyester backbone with maleate unit catalyzed by TBD through thiol- Michael addition reactions at room temperature in 1 min was investigated.

2. EXPERIMENTAL

2.1 Materials

Maleic anhydride (99%, Aldrich), 1,4-butanediol (99% Aldrich), *p*-toluenesulfonic acid monohydrate (99%, Aldrich), 1-propanethiol (99%, Aldrich), benzyl mercaptan (99%, Aldrich), methyl thioglycolate (95%, Aldrich), 1-octanethiol (99%, Aldrich), 2-furanmethanethiol (98%, Aldrich), *N*-acetyl-*L*-cysteine methyl ester (90%, Aldrich), cyclopentanethiol (97%, Aldrich), thiophenol (97%, Aldrich), 2-naphthalenethiol (99%, Aldrich), 2-mercaptoethanol (99%, Aldrich), 1,4-diazabicyclo[2.2.2]octane (DABCO, 95%, Aldrich), 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD, 98%, Aldrich), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene (MTBD, 98%, Aldrich), triethylamine (Et_3N, 99.5%, Aldrich), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%, Aldrich), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN, 98%, Aldrich), and 1,1,3,3-tetramethylguanidine (TMG, 99%, Aldrich) were used as received. Tetrahydrofuran (THF, 99%, Aldrich) was distilled immediately prior to use under nitrogen from sodium benzophenone ketyl. Chloroform ($CHCl_3$, 99%, Aldrich), dichloromethane (DCM), diethyl ether, and benzene were of HPLC grade and anhydrous, used without further purification. Methanol was of reagent grade and used as received.

2.2 Instrumentation

^1H (500 MHz) and ^{13}C (125 MHz) spectra were recorded using an Agilent VNMRS 500 instrument in $CDCl_3$. Gel permeation chromatography (GPC) measurements were performed with an Agilent instrument (Model 1100) with a pump, refractive index and UV detectors and four Waters Styragel columns (HR 5E, HR 4E, HR 3, HR 2), (4.6 mm internal diameter, 300 mm length, packed with 5 µm particles). The effective molecular weight ranges of columns were 2000-4,000,000, 50-100,000, 500-30,000, and 500-20,000 g/mol, respectively. THF was used as an eluent at a flow rate of 0.3 mL/min at 30 ^oC and toluene was used as an internal standard. The weight-average molecular weight (M_w) and the dispersity ($Đ$) of polymers were

calculated based on linear polystyrene (PS) standards (Polymer Laboratories). Differential scanning calorimetry (DSC) experiments were carried out under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} with a DSC-7020 calorimeter (Hitachi High-Tech Science Corp., Tokyo, Japan) recording data from the second heating cycle.

2.3 Synthetic Procedures

2.3.1 Synthesis of poly(butylene maleate) (P1)

Maleic anhydride (3.00 g, 30.5 mmol) was added to 100 mL of a round-bottom flask and dissolved in 30 mL of benzene. 1,4-Butanediol (2.76 g, 30.5 mmol) and then p-toluenesulfonic acid monohydrate (0.580 g, 3.05 mmol) were added to the solution. The mixture was gradually heated in a round-bottomed flask attached with a Dean-Stark apparatus in an oil bath set to 100 °C and stirred overnight. After that time, the solvent was removed under reduced pressure, THF was added to the residue and the resulting polymer solution was finally precipitated in methanol. The dissolution–precipitation (THF-MeOH) procedure was repeated two times. The obtained highly sticky brown polymer was dried in a vacuum oven for 24 h (Yield = 3.9 g, 75%, M_w = 26.8 kDa, $Đ$ = 2.01). ^{1}H NMR (Figure 2.1) ($CDCl_3$, δ) 6.25 (s, 2H, O=CC*H*C*H*C=O), 4.22 (s, 4H, OCH_2), 1.78 (s, 4H, OCH_2CH_2); ^{13}C NMR (Figure 2.2) ($CDCl_3$, δ) 165.17, 129.83, 64.67, 25.07. T_g value of P1 is -45.9^{o}C. (Figure 2.3)

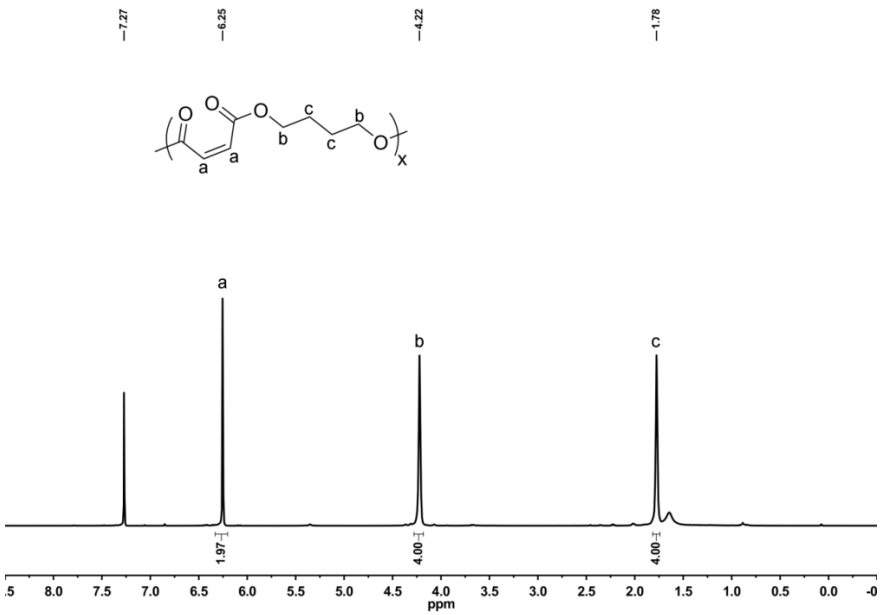

Figure 2.1: ^{1}H NMR spectrum of P1 in $CDCl_3$ (500 MHz).

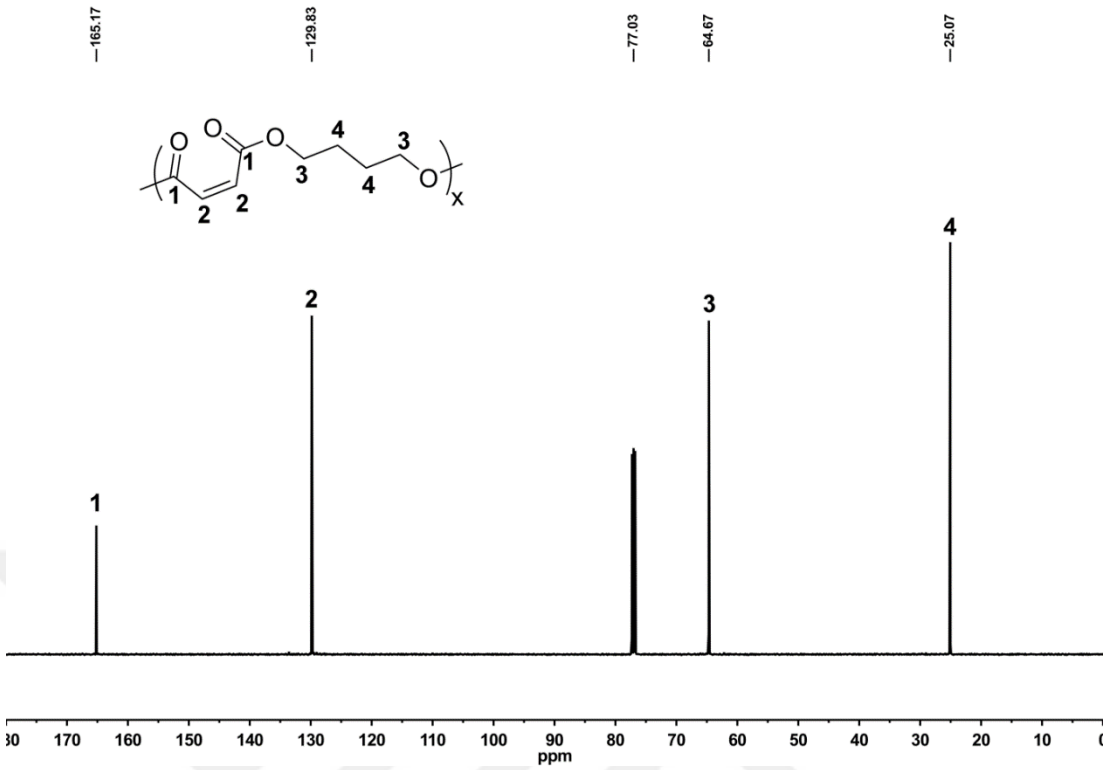

Figure 2.2: ^{13}C NMR spectrum of P1 in $CDCl_3$ (125 MHz).

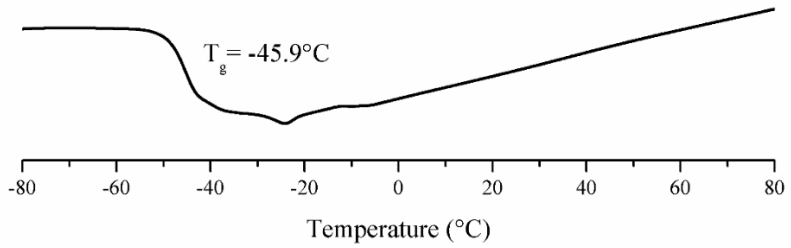

Figure 2.3: DSC thermogram of P1 at a heating rate of 10 °C/min under nitrogen (second run).

2.3.2 A General procedure to reveal the catalyst performance for thiol-Michael addition reactions

P1 (0.15 g, 0.88 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. 1-propanethiol (98.3 µL, 1.06 mmol), and

organocatalyst (0.088 mmol) were added to the solution, respectively. The reaction mixture was stirred at room temperature for 1 min, precipitated in 20 mL of MeOH, and the solvent was removed by decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times. The purified polymer was finally dried in a vacuum oven for 24 h.

2.3.3 Procedure for 1-propanethiol addition (P2)

P1 (0.15 g, 0.88 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. 1-propanethiol (98.3 µL, 1.06 mmol) and TBD (12.3 mg, 0.0880 mmol) were added to the solution, respectively. The mixture was stirred at room temperature for 1 min and precipitated in 20 mL of MeOH followed by removing excess solvent via decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times and the recovered yellow sticky polymer P2 was dried in a vacuum oven for 24 h (Yield = 0.17 g, 80%). ^{1}H NMR ($CDCl_3$, δ) 4.19 (m, 4H, OCH_2), 3.64 (m, 1H, SCH), 2.99-2.67 (m, 4H, SCH_2 and CH_2C=O), 1.74-1.58 (m, 6H, aliphatic CH_2), 0.99 (t, 3H, CH_3); ^{13}C NMR (Figure 2.4) ($CDCl_3$, δ) 171.80, 170.74, 64.69, 41.42, 36.47, 33.53, 25.16, 22.59, 13.40. T_g value of P2 is -37.7^{o}C (Figure 2.5). GPC trace of P2 is observed higher molecular weight region than GPC trace of P1 (Figure 2.6).

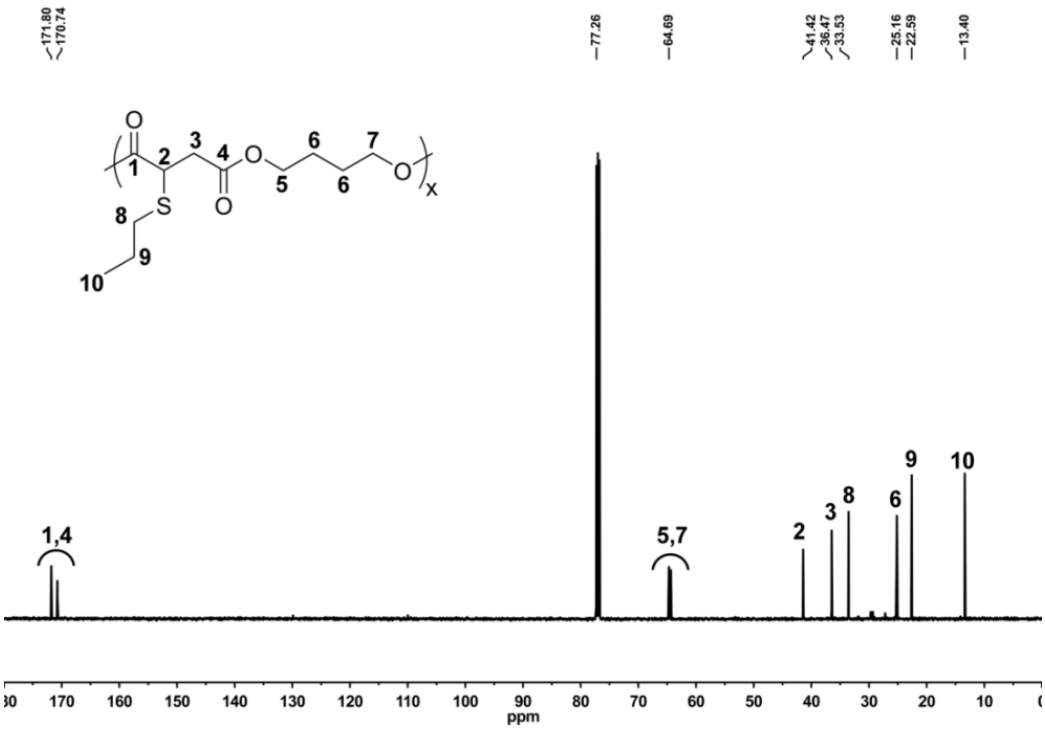

Figure 2.4: ^{13}C NMR spectrum of P2 in $CDCl_3$ (125 MHz).

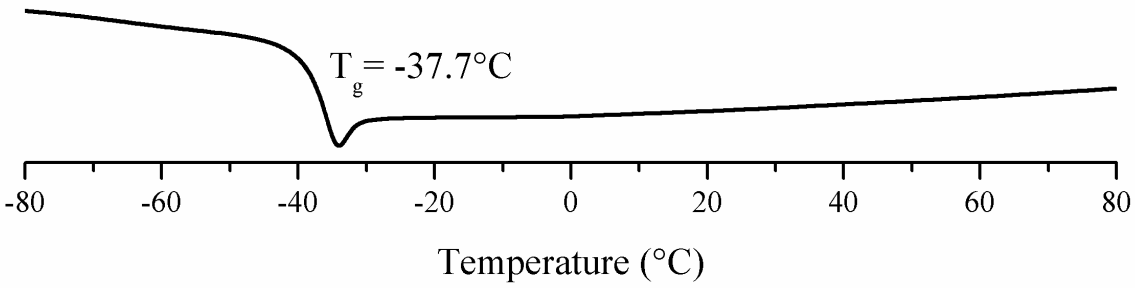

Figure 2.5: DSC thermogram of P2 at a heating rate of 10 °C/min under nitrogen (second run).

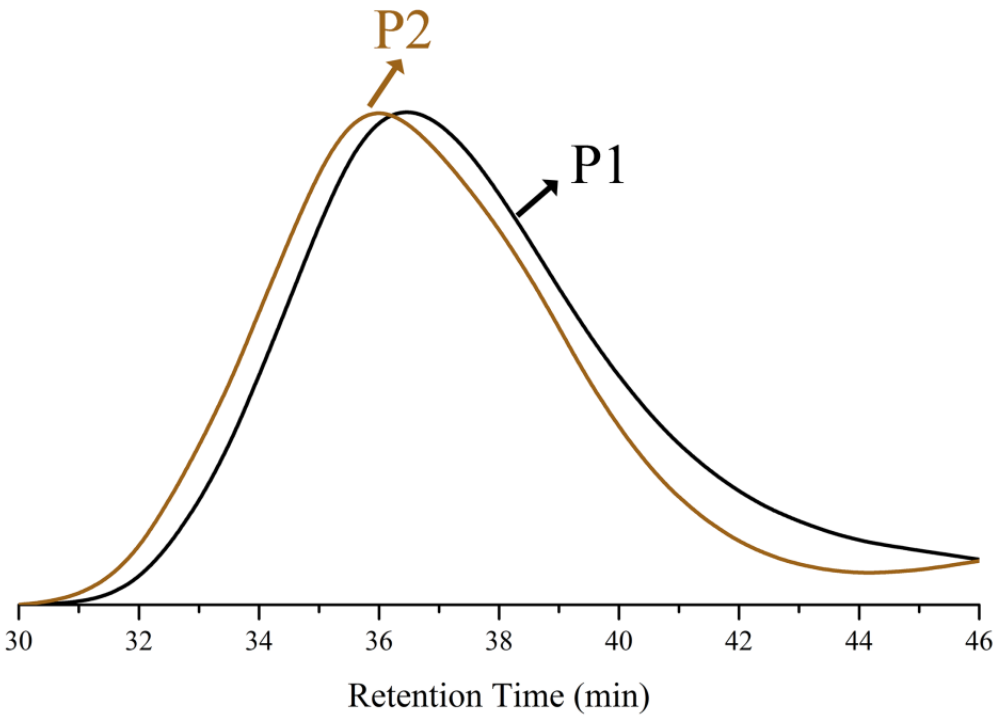

Figure 2.6: Overlaid GPC traces of P1 and P2 (at 30 °C in THF).

2.3.4 Procedure for cyclopentanethiol addition (P3)

P1 (0.15 g, 0.88 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. Cyclopentanethiol (113.3 µL, 1.060 mmol) and TBD (12.3 mg, 0.0880 mmol) were added to the solution, respectively. The mixture was stirred at room temperature for 1 min and precipitated in 20 mL of MeOH followed by removing excess solvent via decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times and the recovered yellow sticky polymer

P3 was dried in a vacuum oven for 24 h (Yield = 0.24 g, 76%). ^{1}H NMR ($CDCl_3$, δ) 4.18 (m, 4H, OCH_2), 3.67 (m, 1H, C=OSCH), 3.29 (m, 1H, CH(CH_2)$_2$,cyclopentane), 2.99-2.70 (m, 2H, CH_2C=O), 2.03-1.58 (m, 12H, cyclic and aliphatic CH_2); ^{13}C NMR (Figure 2.7) ($CDCl_3$, δ) 172.10, 170.76, 64.65, 244.12, 41.97, 36.75, 34.10, 24.66. T_g value of P3 is -31.1^{o}C (Figure 2.8). GPC trace of P3 is observed higher molecular weight region than GPC trace of P1 (Figure 2.9).

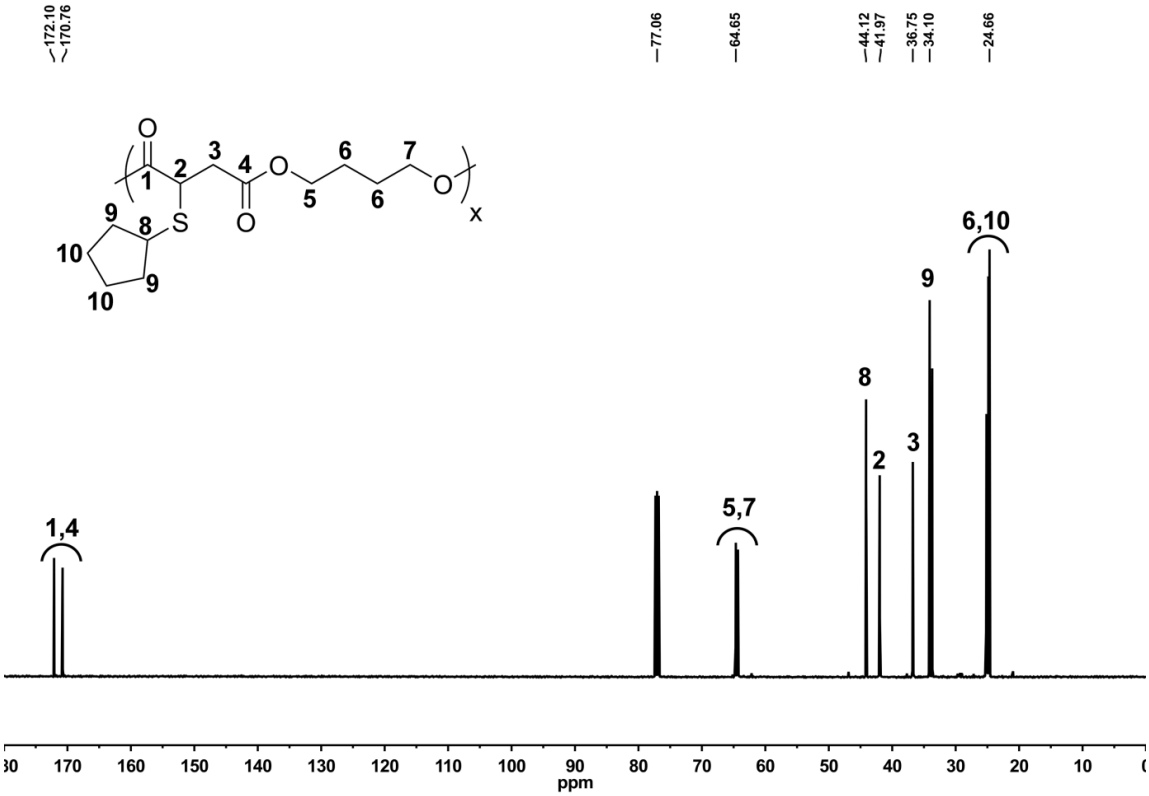

Figure 2.7: ^{13}C NMR spectrum of P3 in $CDCl_3$ (125 MHz).

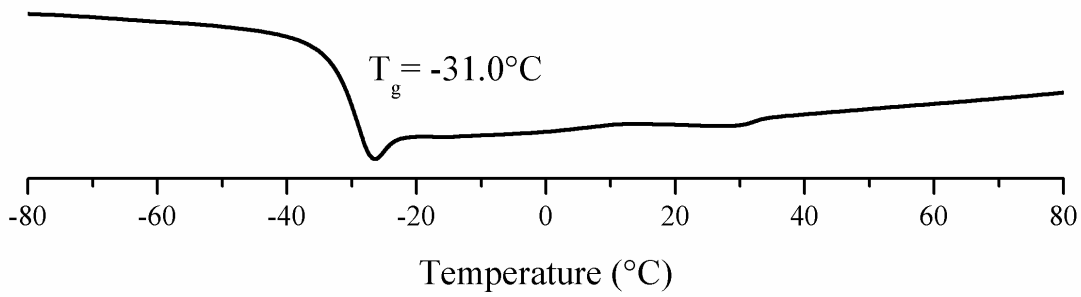

Figure 2.8: DSC thermogram of P3 at a heating rate of 10 °C/min under nitrogen(second run).

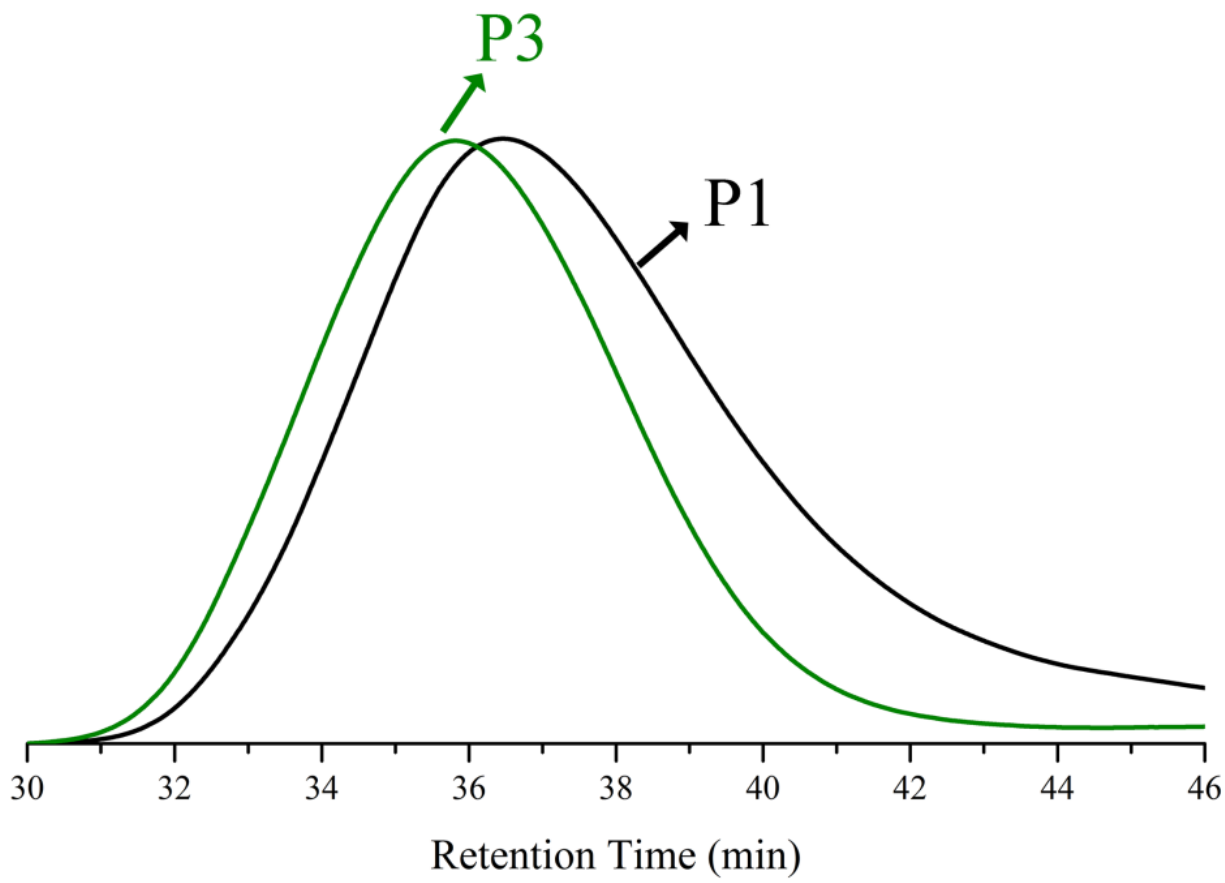

Figure 2.9: Overlaid GPC traces of P1 and P3 (at 30 °C in THF).

2.3.5 Procedure for 2-furanemethanethiol addition (P4)

P1 (0.15 g, 0.88 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. 2-furanmethanthiol (106.8 µL, 1.060 mmol) and TBD (12.3 mg, 0.0880 mmol) were added to the solution, respectively. The mixture was stirred at room temperature for 1 min and precipitated in 20 mL of MeOH followed by removing excess solvent via decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times and the recovered yellow sticky polymer P4 was dried in a vacuum oven for 24 h (Yield = 0.23 g, 92%). ^{1}H NMR ($CDCl_3$, δ) 7.37 (s, 1H, C*H*=C, furan), 6.31-6.25 (m, 2H, OC*H*=C*H*, furan), 4.16 (m, 4H, OCH_2), 3.93-3.84 (m, 2H, SCH_2) 3.67 (m, 1H, SC*H*), 2.96-2.64 (m, 2H, CH_2C=O), 1.71 (m, 4H, aliphatic CH_2); ^{13}C NMR (Figure 2.10) ($CDCl_3$, δ) 171.43, 170.55, 150.26, 142.48, 110.55, 108.37, 64.85, 41.10, 36.05, 28.28, 25.07. T_g value of P4 is -19.1^{o}C (Figure 2.11). GPC trace of P4 is observed higher molecular weight region than GPC trace of P1 (Figure 2.12).

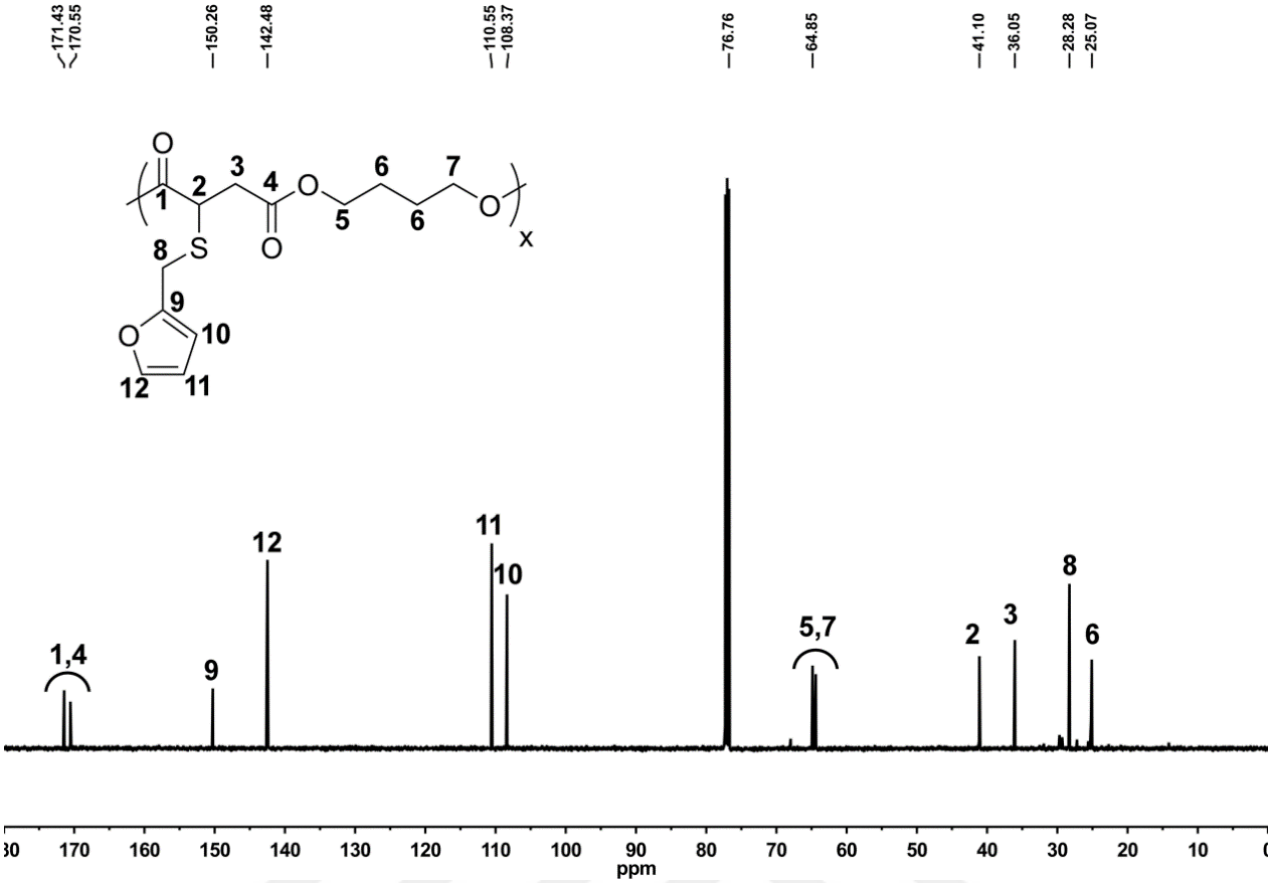

Figure 2.10: ^{13}C NMR spectrum of P4 in $CDCl_3$ (125 MHz).

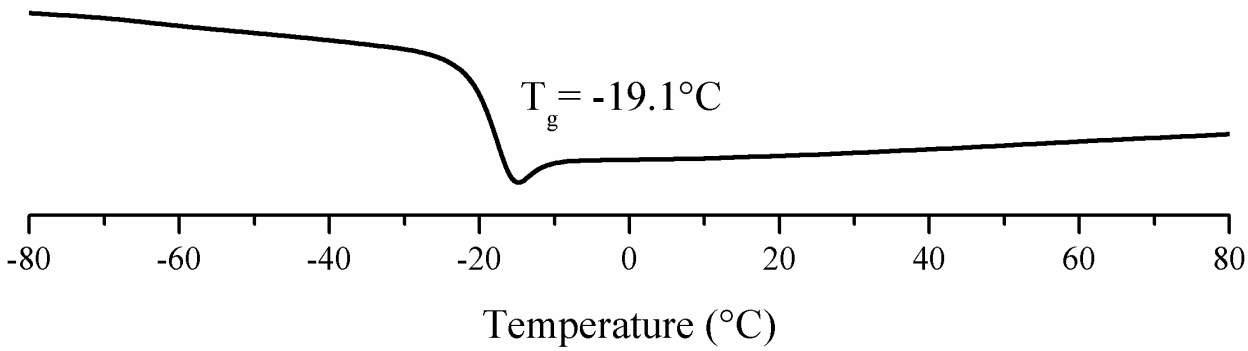

Figure 2.11: DSC thermogram of P4 at a heating rate of 10 °C/min under nitrogen (second run).

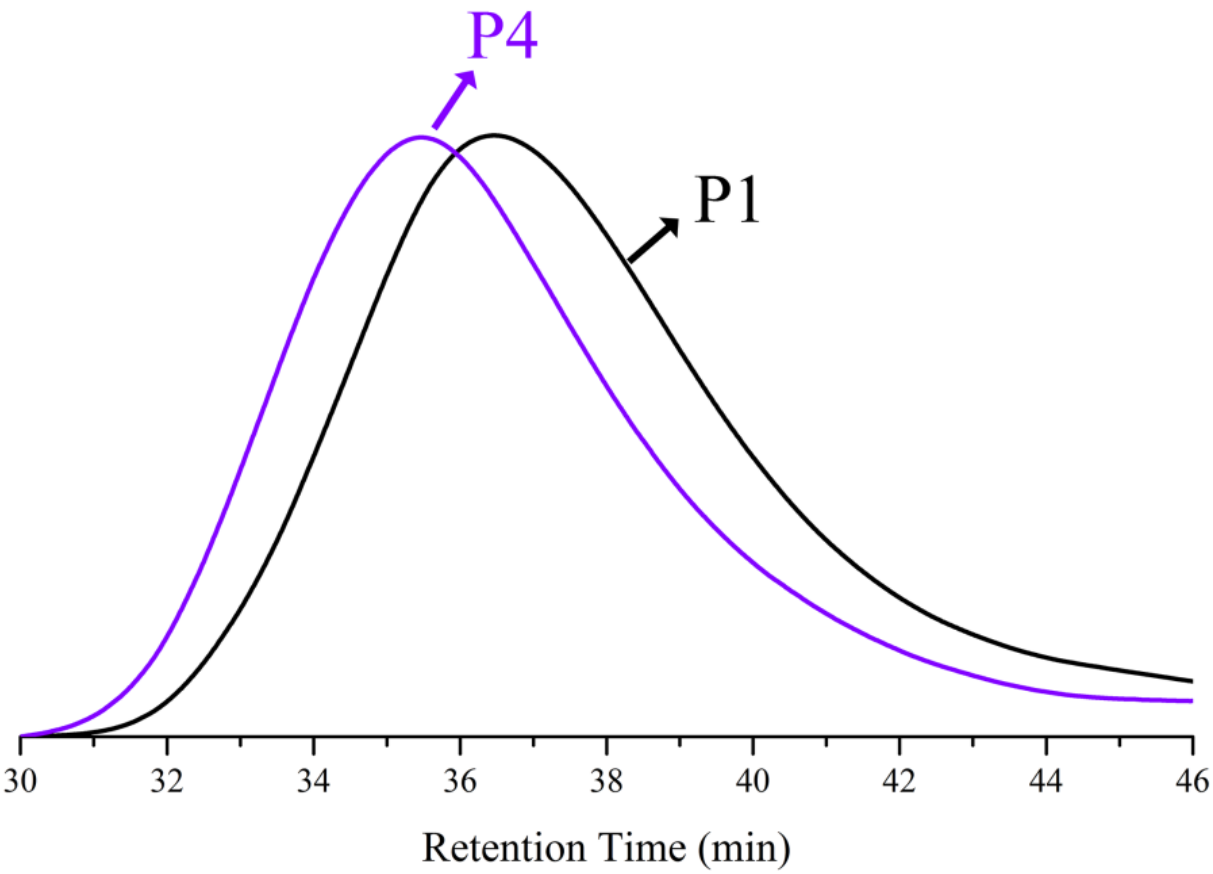

Figure 2.12: Overlaid GPC traces of P1 and P4 (at 30 °C in THF).

2.3.6 Procedure for benzyl mercaptan addition (P5)

P1 (0.15 g, 0.88 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. Benzyl mercaptan (124.3 μL, 1.060 mmol) and TBD (12.3 mg, 0.0880 mmol) were added to the solution, respectively. The mixture was stirred at room temperature for 1 min and precipitated in 20 mL of MeOH followed by removing excess solvent via decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times and the recovered yellow sticky polymer P5 was dried in a vacuum oven for 24 h (Yield = 0.22 g, 84%). ^{1}H NMR ($CDCl_3$, δ) 7.32-7.27 (m, 5H, Ar*H*), 4.14 (m, 4H, OCH_2), 3.87 (m, 2H, benzyl-CH_2) 3.57 (m, 1H, SC*H*), 2.95-2.61 (m, 2H, CH_2C=O), 1.70 (m, 4H, aliphatic CH_2); ^{13}C NMR (Figure 2.13) ($CDCl_3$, δ) 171.54, 170.53, 137.02, 129.05, 128.60, 127.39, 64.76, 41.00, 36.03, 25.08. T_g value of P5 is -13.9^{o}C (Figure 2.14). GPC trace of P5 is observed higher molecular weight region than GPC trace of P1 (Figure 2.15).

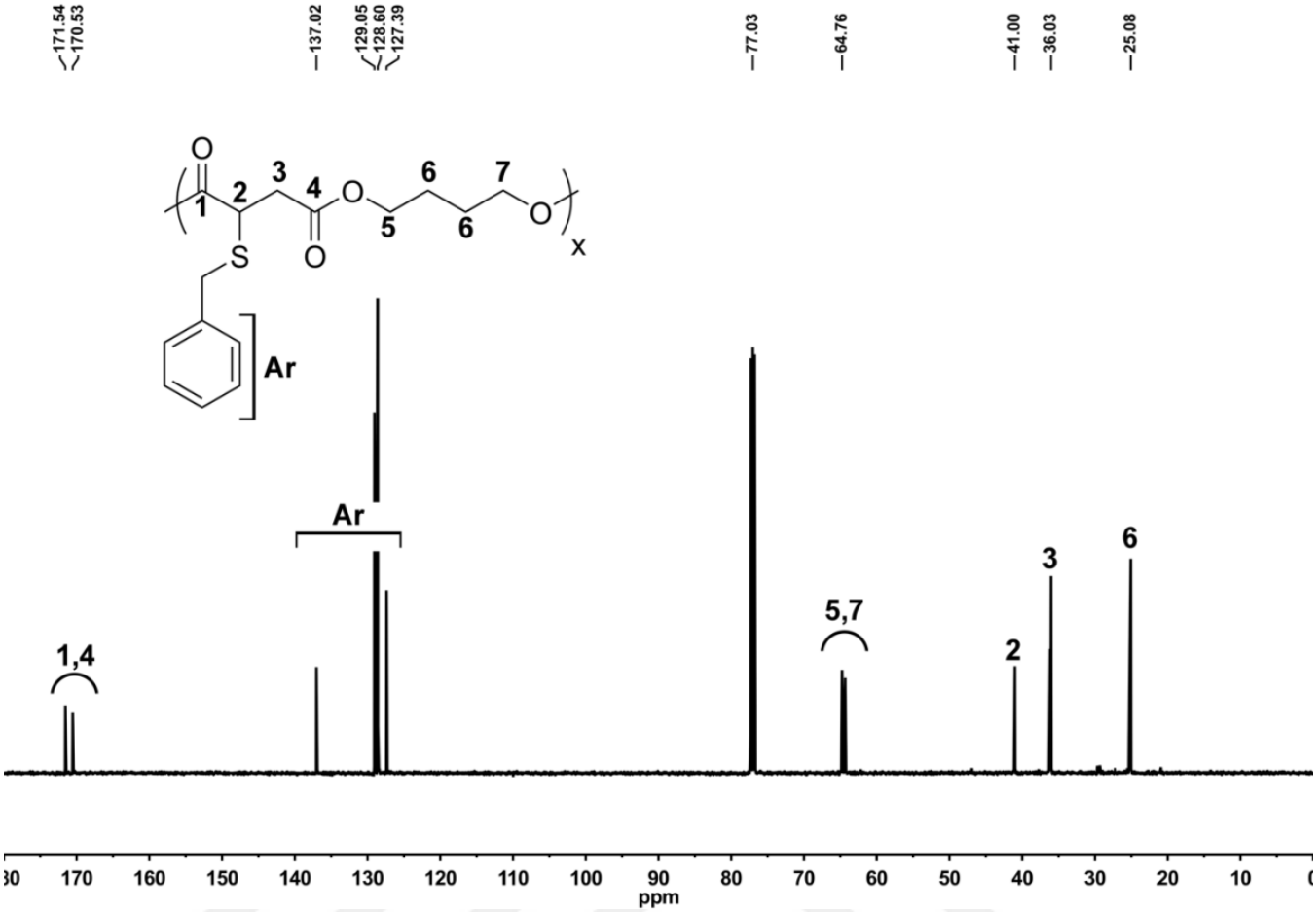

Figure 2.13: ^{13}C NMR spectrum of P5 in $CDCl_3$ (125 MHz).

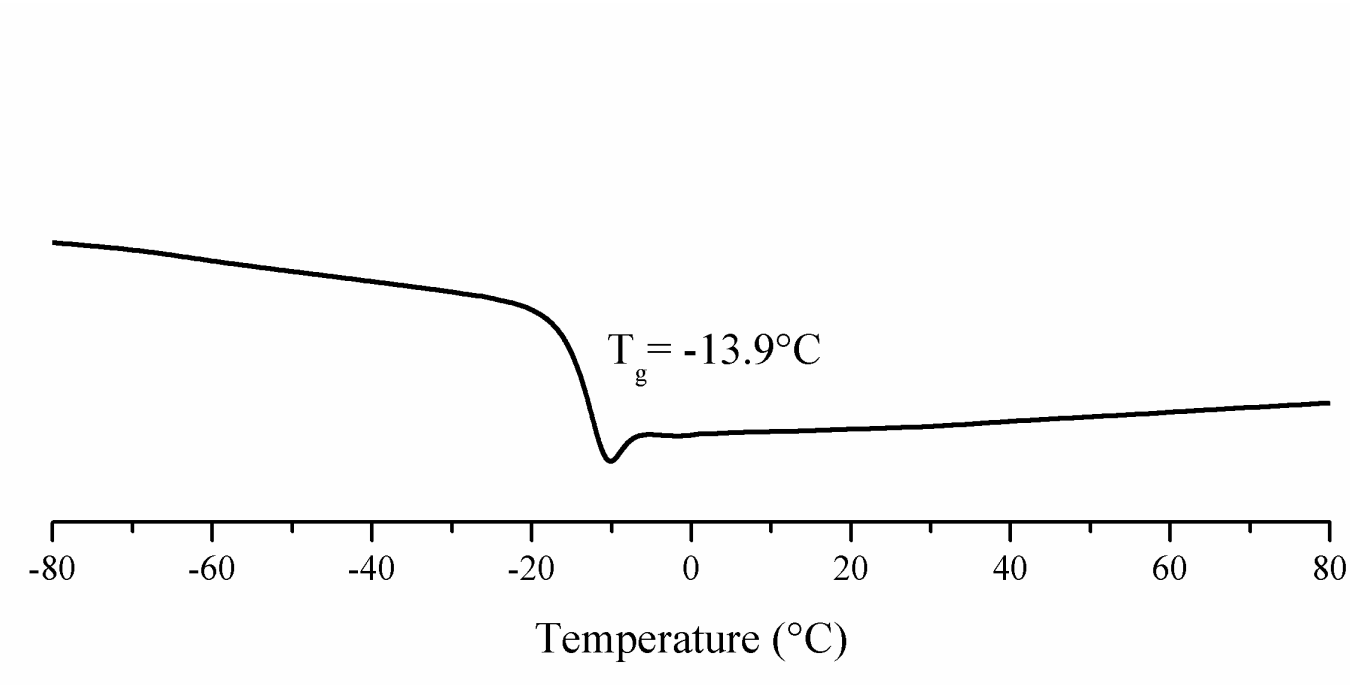

Figure 2.14: DSC thermogram of P5 at a heating rate of 10 °C/min under nitrogen (second run).

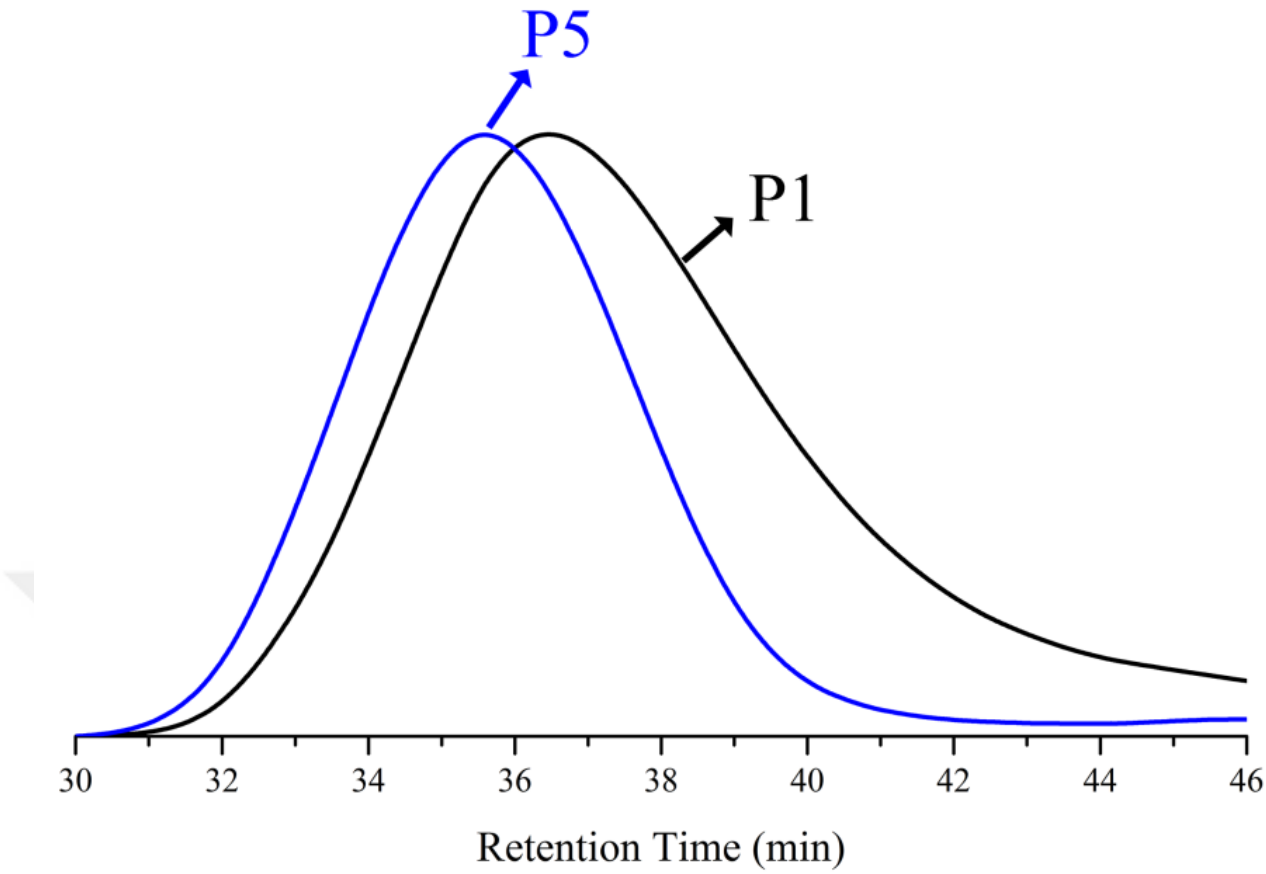

Figure 2.15: Overlaid GPC traces of P1 and P5 (at 30 °C in THF).

2.3.7 Procedure for 2-naphthalenethiol addition (P6)

P1 (0.15 g, 0.88 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. 2-naphthalenethiol (169.7 mg, 1.060 mmol) and TBD (12.3 mg, 0.0880 mmol) were added to the solution, respectively. The mixture was stirred at room temperature for 1 min and precipitated in 20 mL of MeOH followed by removing excess solvent via decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times and the recovered yellow sticky polymer P6 was dried in a vacuum oven for 24 h (Yield = 0.29 g, 99%). ^{1}H NMR ($CDCl_3$, δ) 7.98-7.49 (m, 7H, Ar*H*), 4.08 (m, 5H, SC*H* and OCH_2), 2.97-2.77 (m, 2H, CH_2C=O), 1.64 (m, 4H, aliphatic CH_2); ^{13}C NMR (Figure 2.16) ($CDCl_3$, δ) 171.16, 170.56, 133.45, 130.34, 128.77, 127.72, 126.77, 125.65, 64.85, 64.42, 45.56, 36.38, 25.11. T_g value of P6 is -37.7^{o}C (Figure 2.17). GPC trace of P6 is observed higher molecular weight region than GPC trace of P1 (Figure 2.18).

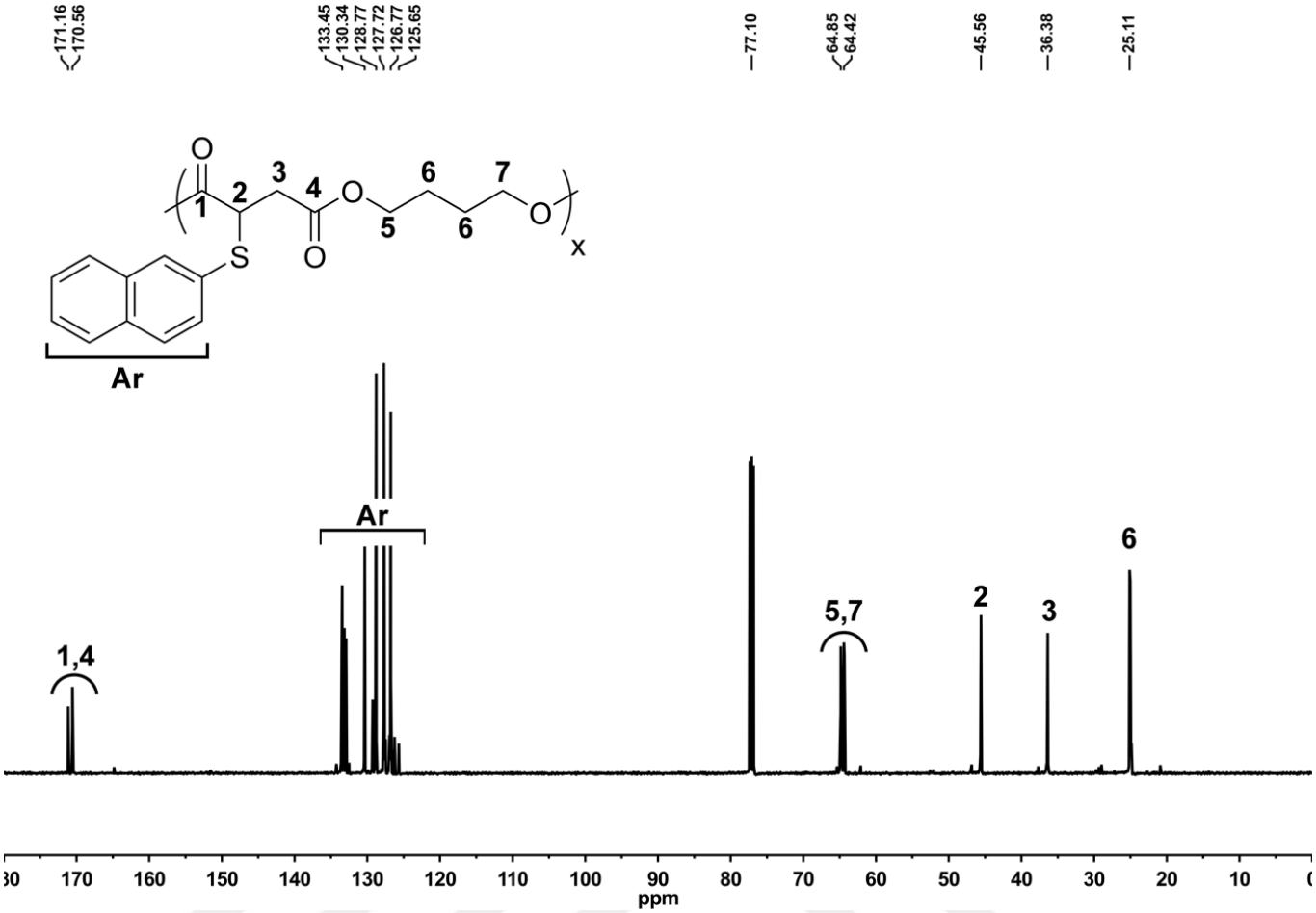

Figure 2.16: ^{13}C NMR spectrum of P6 in $CDCl_3$ (125 MHz).

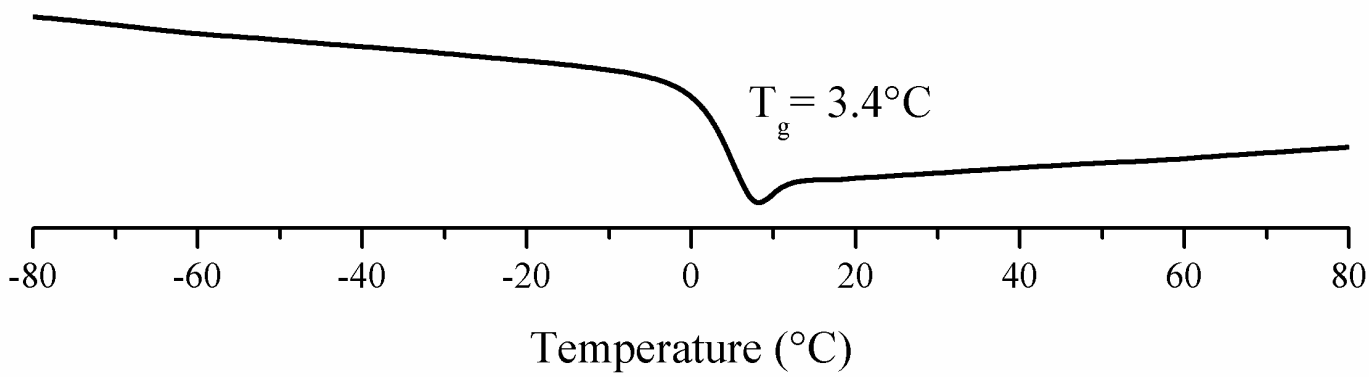

Figure 2.17: DSC thermogram of P6 at a heating rate of 10 °C/min under nitrogen (second run).

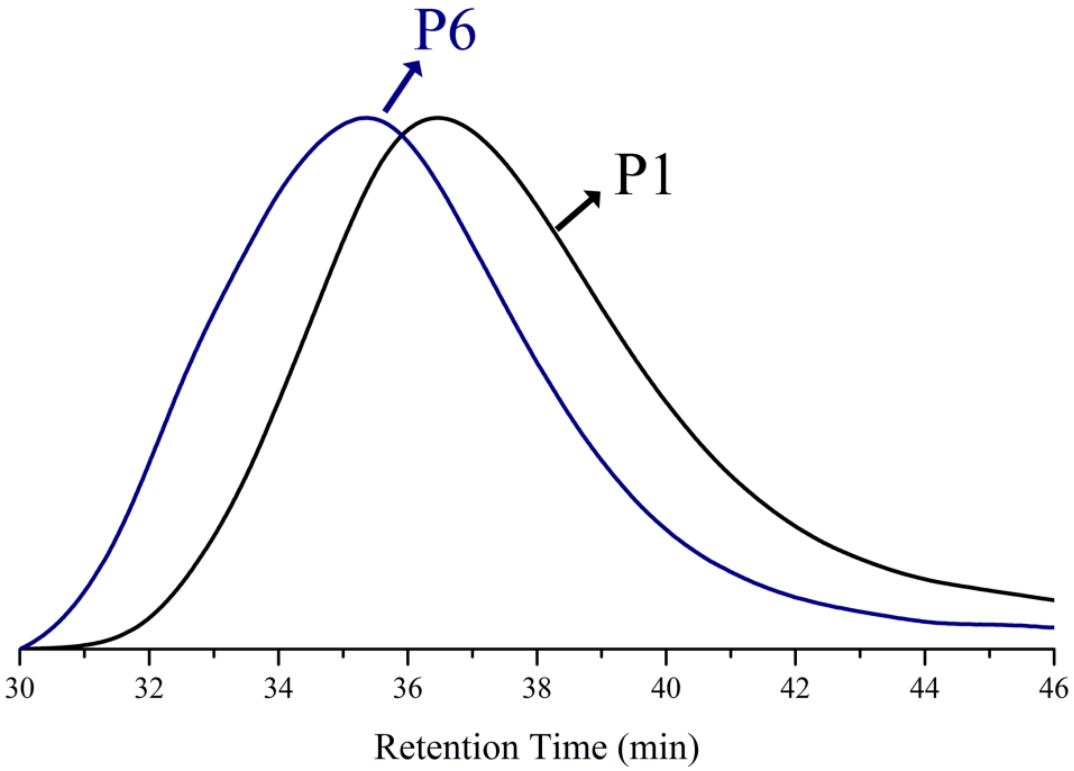

Figure 2.18: Overlaid GPC traces of P1 and P6 (at 30 °C in THF).

2.3.8 Procedure for *N*-Acetyl-*L*-cysteine methyl ester addition (P7)

P1 (0.15 g, 0.88 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. *N*-acetyl-*L*-cysteine methyl ester (188 mg, 1.06 mmol) and TBD (12.3 mg, 0.0880 mmol) were added to the solution, respectively. The reaction mixture was stirred at room temperature for 1 min, precipitated in 20 mL of diethyl ether followed by removing excess solvent via decantation. Then the polymer residue was dissolved in 20 mL of DCM and washed with distilled water two times. The organic phase was dried with Na_2SO_4 and filtered, then concentrated to obtain a yellow sticky polymer. The purified polymer was finally dried in a vacuum oven for 24 h (Yield = 205 mg, 67%). ^{1}H NMR ($CDCl_3$, δ) 6.90 (br, N*H*), 4.92 (d, 1H, C*H*NH), 4.18 (m, 4H, OCH_2), 3.75-3.65 (m, 4H, SC*H* and OCH_3), 3.25-3.04 (m, 2H, SCH_2), 2.97-2.65 (m, 2H, CH_2C=O), 2.07 (d, 3H, CH_3C=O), 1.73 (m, 4H, OCH_2CH_2); ^{13}C NMR (Figure 2.19) ($CDCl_3$, δ) 171.44, 170. 76, 65.00, 52.73, 41.97, 35.97, 33.93, 25.08, 22.95. T_g value of P7 is -4.8^{o}C (Figure 2.20). GPC trace of P7 is observed higher molecular weight region than GPC trace of P1 (Figure 2.21).

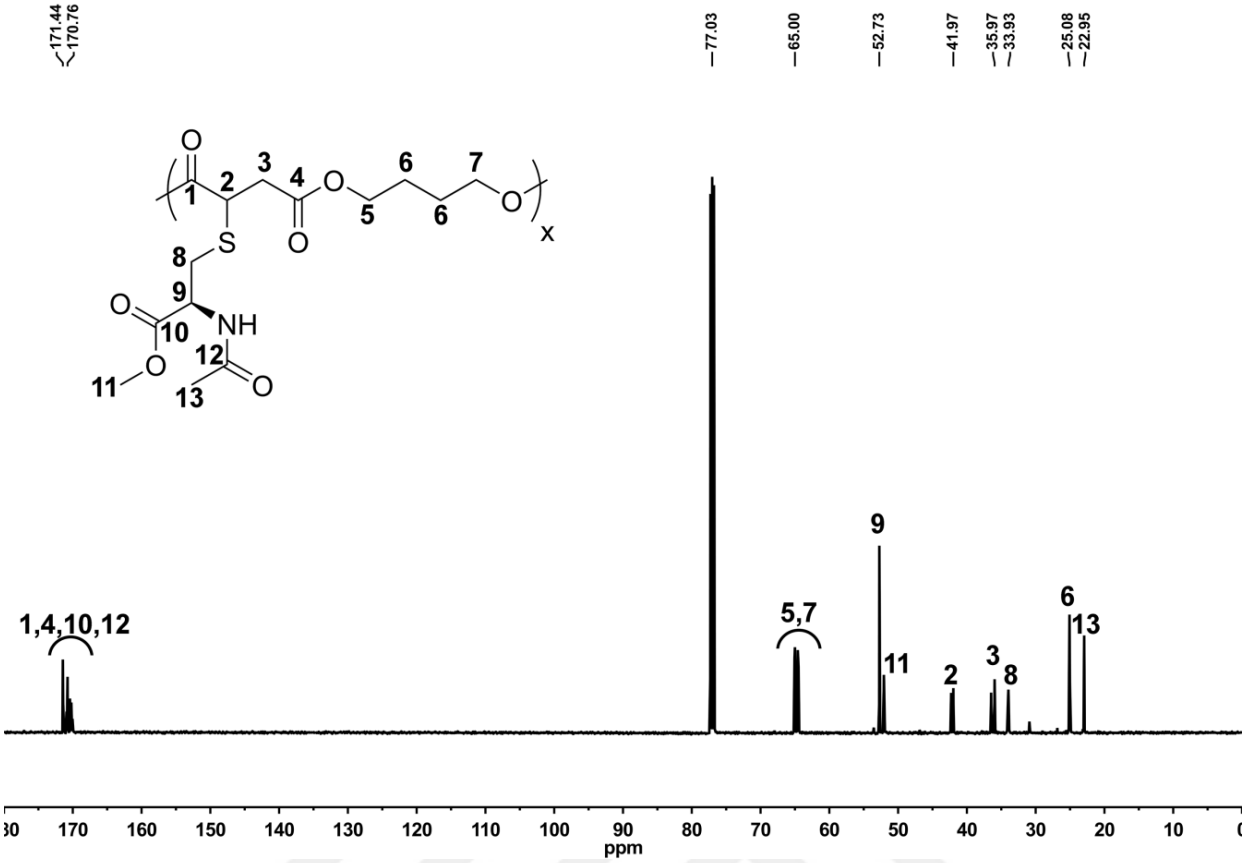

Figure 2.19: ^{13}C NMR spectrum of P7 in $CDCl_3$ (125 MHz).

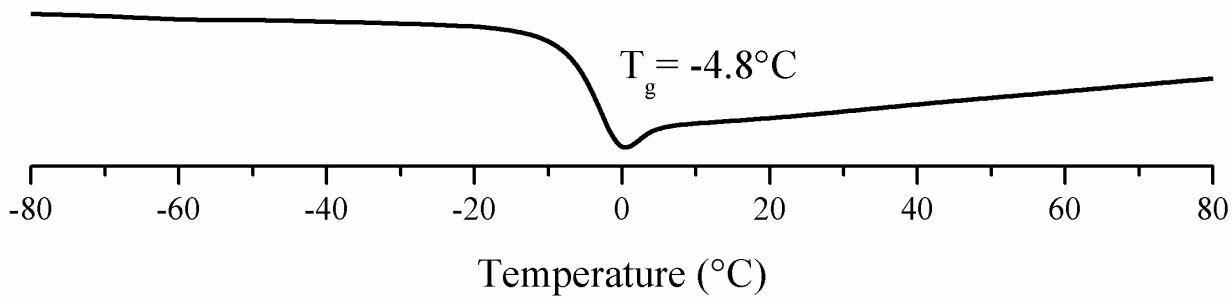

Figure 2.20: DSC thermogram of P7 at a heating rate of 10 °C/min under nitrogen (second run).

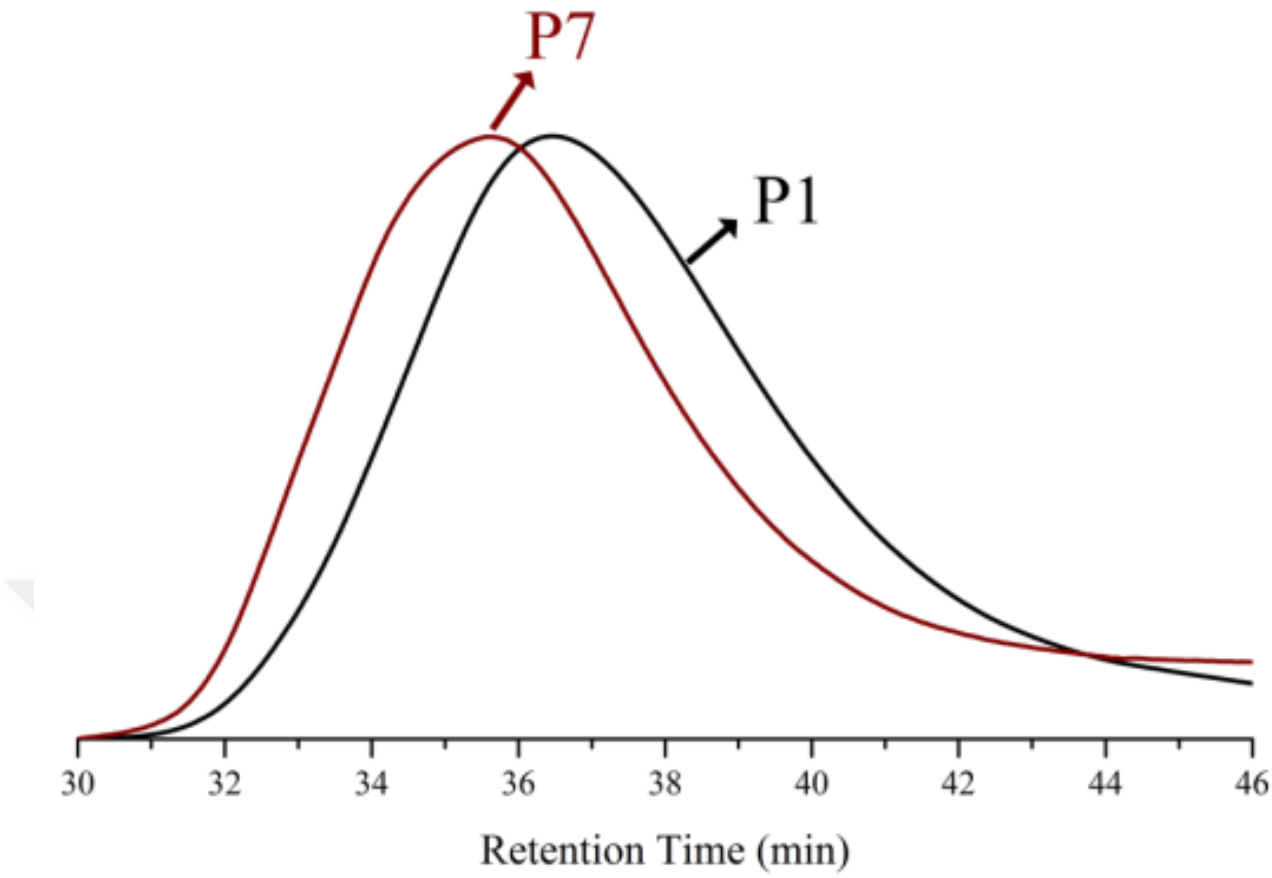

Figure 2.21: Overlaid GPC traces of P1 and P7 (at 30 °C in THF).

2.3.9 Procedure for 1-octanethiol addition (P8)

P1 (0.15 g, 0.88 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. 1-octanethiol (183.7 µL, 1.060 mmol) and TBD (12.3 mg, 0.0880 mmol) were added to the solution, respectively. The mixture was stirred at room temperature for 1 min and precipitated in 20 mL of MeOH followed by removing excess solvent via decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times and the recovered yellow sticky polymer P8 was dried in a vacuum oven for 24 h (Yield = 0.24 g, 87%). ^{1}H NMR (Figure 2.22) ($CDCl_3$, δ) 4.18 (m, 4H, OCH_2), 3.64 (m, 1H, SCH), 2.99-2.66 (m, 4H, SCH_2 and CH_2C=O), 1.74-1.28 (m, 16H, aliphatic CH_2), 0.89 (t, 3H, CH_3); ^{13}C NMR (Figure 2.23) ($CDCl_3$, δ) 171.75, 170.73, 64.66, 41.45, 36.43, 31.77, 29.14, 25.15, 22.62, 14.08. T_g value of P8 is -53.3^{o}C (Figure 2.24). GPC trace of P8 is observed higher molecular weight region than GPC trace of P1 (Figure 2.25).

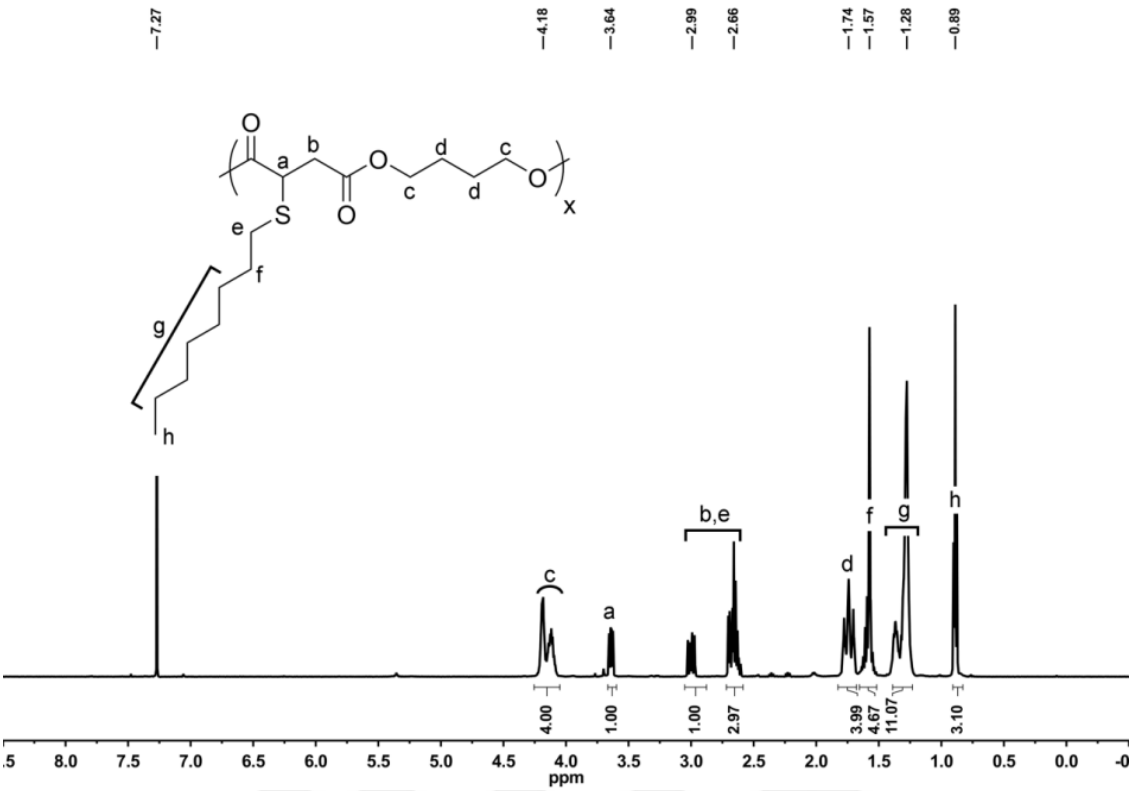

Figure 2.22: ^{1}H NMR spectrum of P8 in $CDCl_3$ (500 MHz).

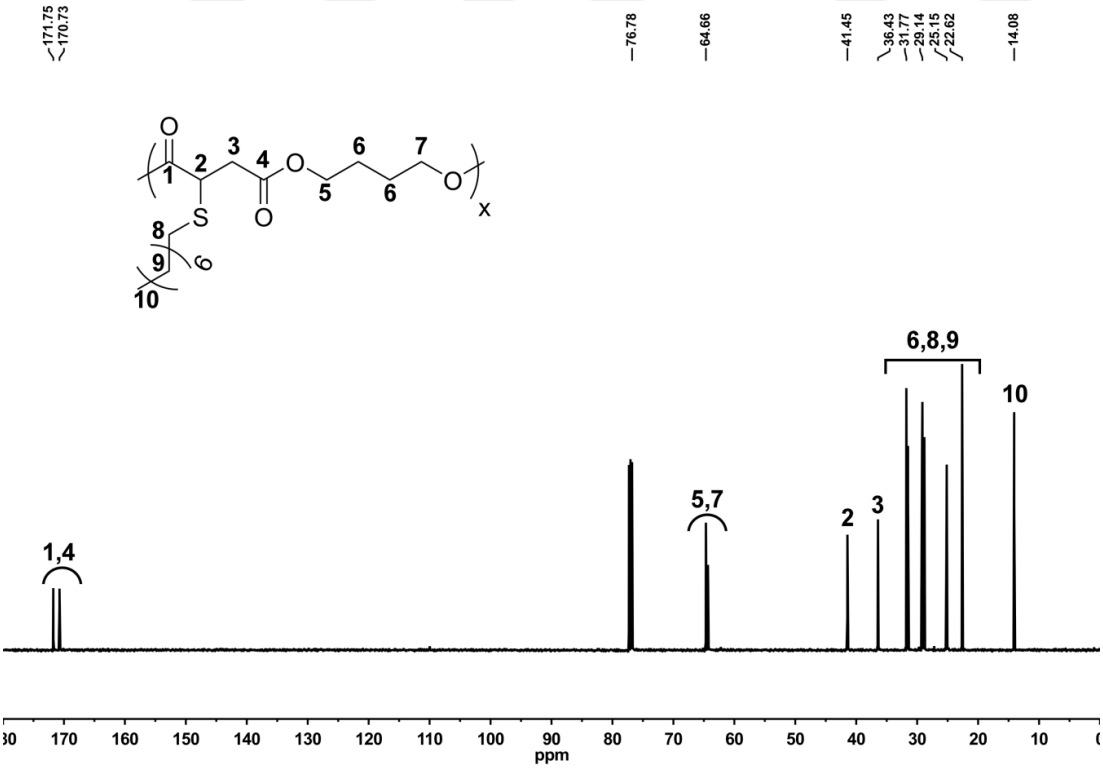

Figure 2.23: ^{13}C NMR spectrum of P8 in $CDCl_3$ (125 MHz).

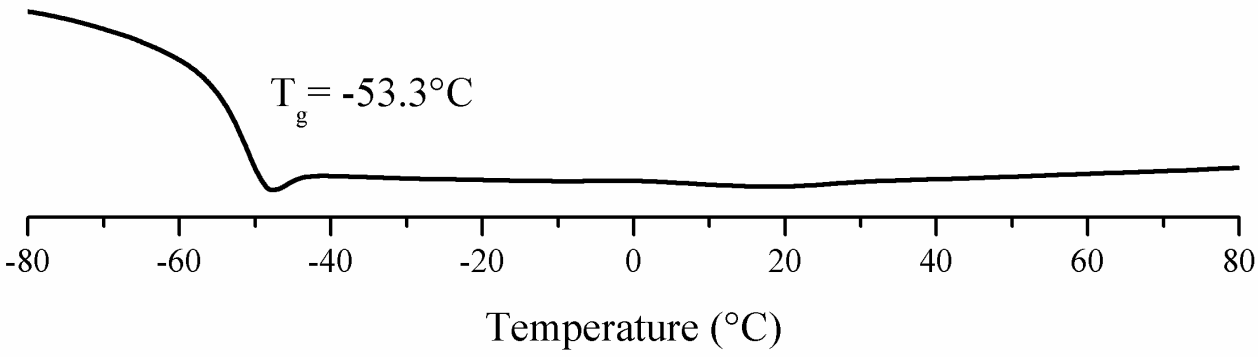

Figure 2.24: DSC thermogram of P8 at a heating rate of 10 °C/min under nitrogen (second run).

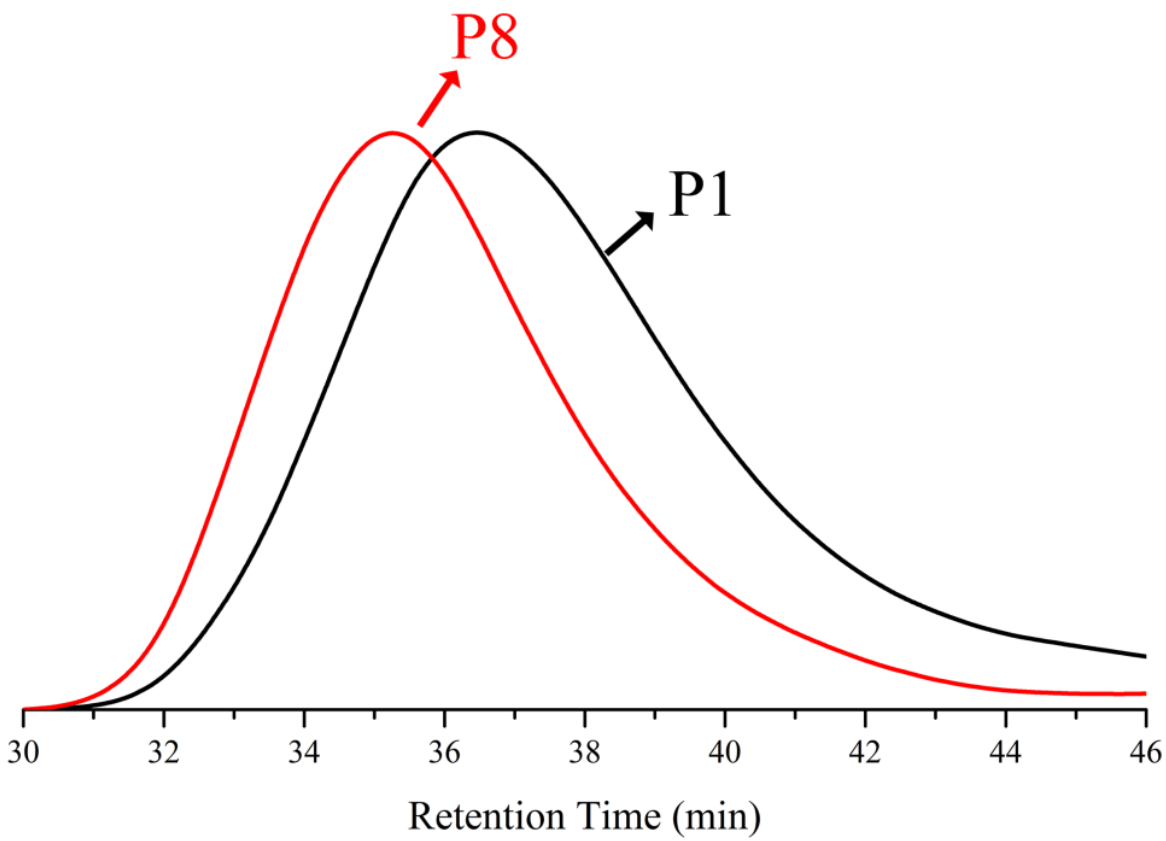

Figure 2.25: Overlaid GPC traces of P1 and P8 (at 30 °C in THF).

2.3.10 Procedure for 2-mercaptoethanol addition (P9)

P1 (0.15 g, 0.88 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. 2-mercaptoethanol (74.2 μL, 1.06 mmol) and TBD (12.3 mg, 0.0880 mmol) were added to the solution, respectively. The mixture was stirred at room temperature for 1 min and precipitated in 20 mL of MeOH followed by removing excess solvent via decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times and the recovered yellow sticky polymer P9 was dried in a vacuum oven for 24 h (Yield = 0.16 g, 45%). ^{1}H NMR (Figure 2.26) ($CDCl_3$, δ) 4.21 (m, 4H, OCH_2), 3.79 (m, 3H, CH_2OH and SCH), 2.97-2.75 (m, 4H, SCH_2 and CH_2C=O), 1.75 (m, 4H, aliphatic CH_2); ^{13}C NMR (Figure 2.27) ($CDCl_3$, δ) 171.91, 170.82, 128.59, 64.57, 61.20, 41.43, 36.47, 34.81, 25.13. T_g value of P9 is -31.7^{o}C (Figure 2.28). GPC trace of P9 is observed higher molecular weight region than GPC trace of P1 (Figure 2.29).

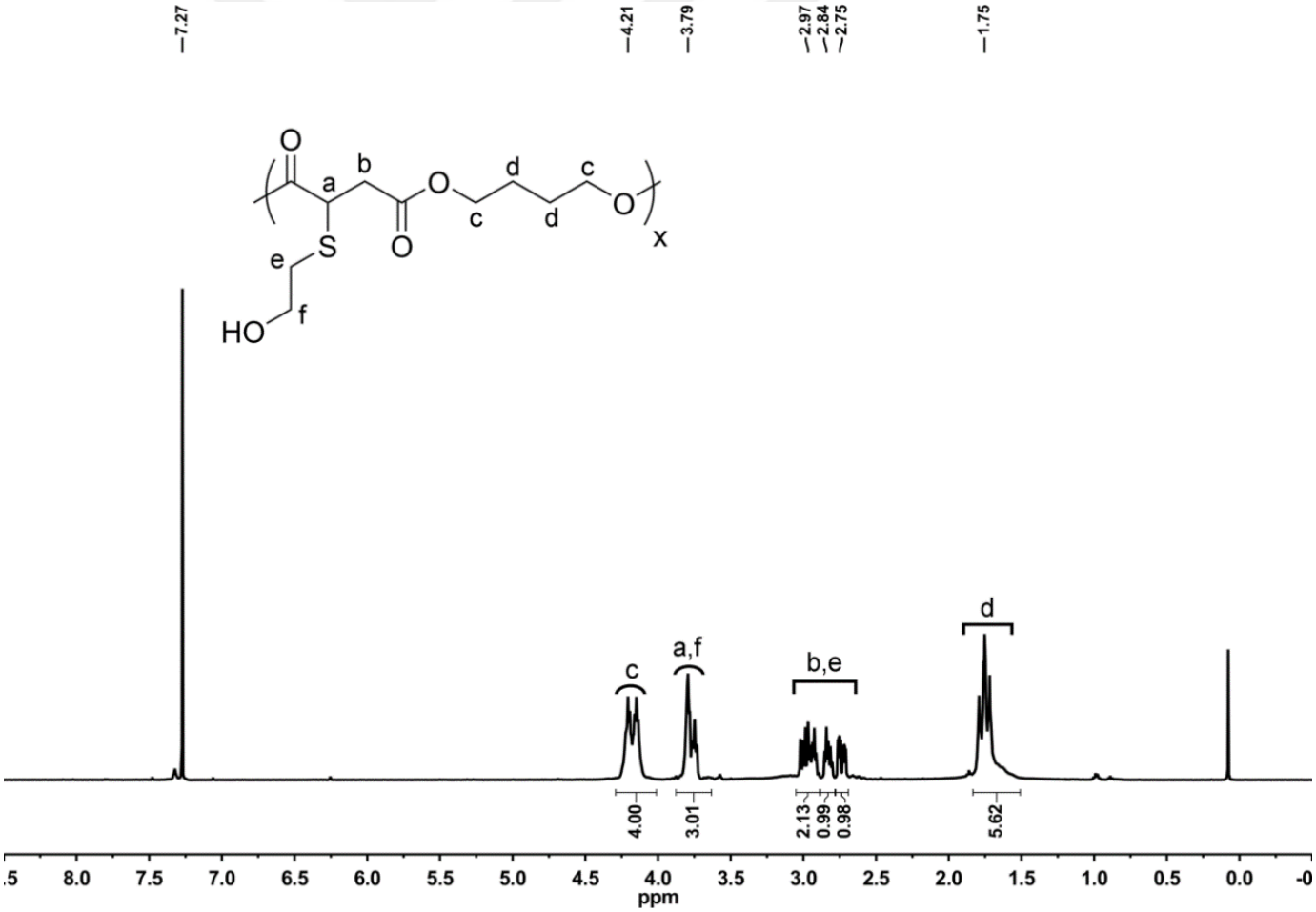

Figure 2.26: ^{1}H NMR spectrum of P9 in $CDCl_3$ (500 MHz).

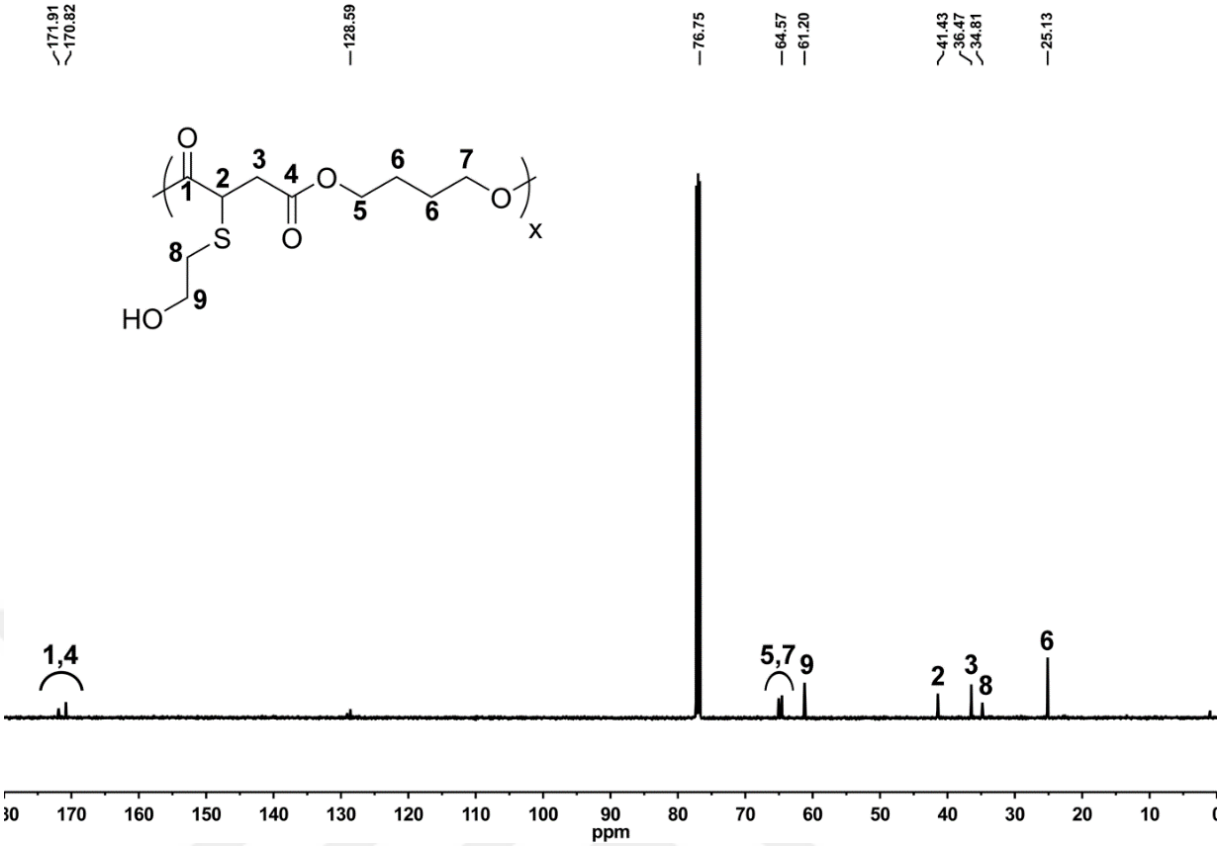

Figure 2.27: ^{13}C NMR spectrum of P9 in $CDCl_3$ (125 MHz).

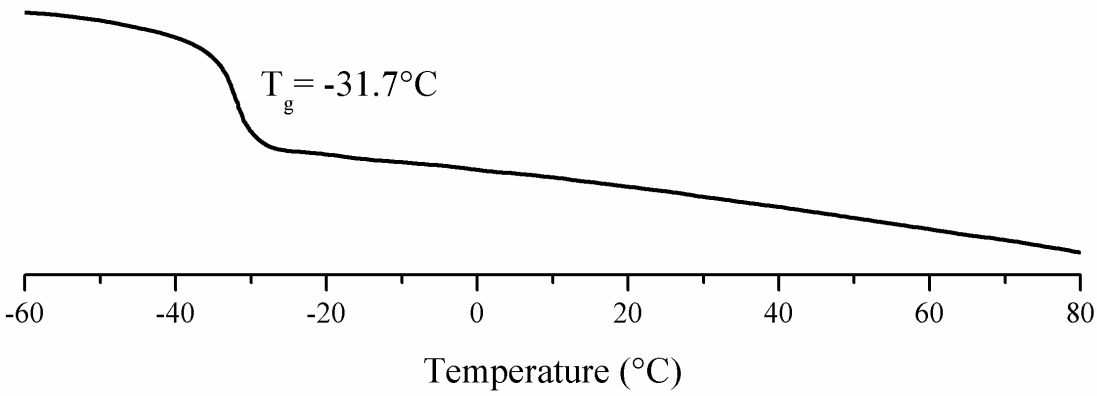

Figure 2.28: DSC thermogram of P9 at a heating rate of 10 °C/min under nitrogen (second run).

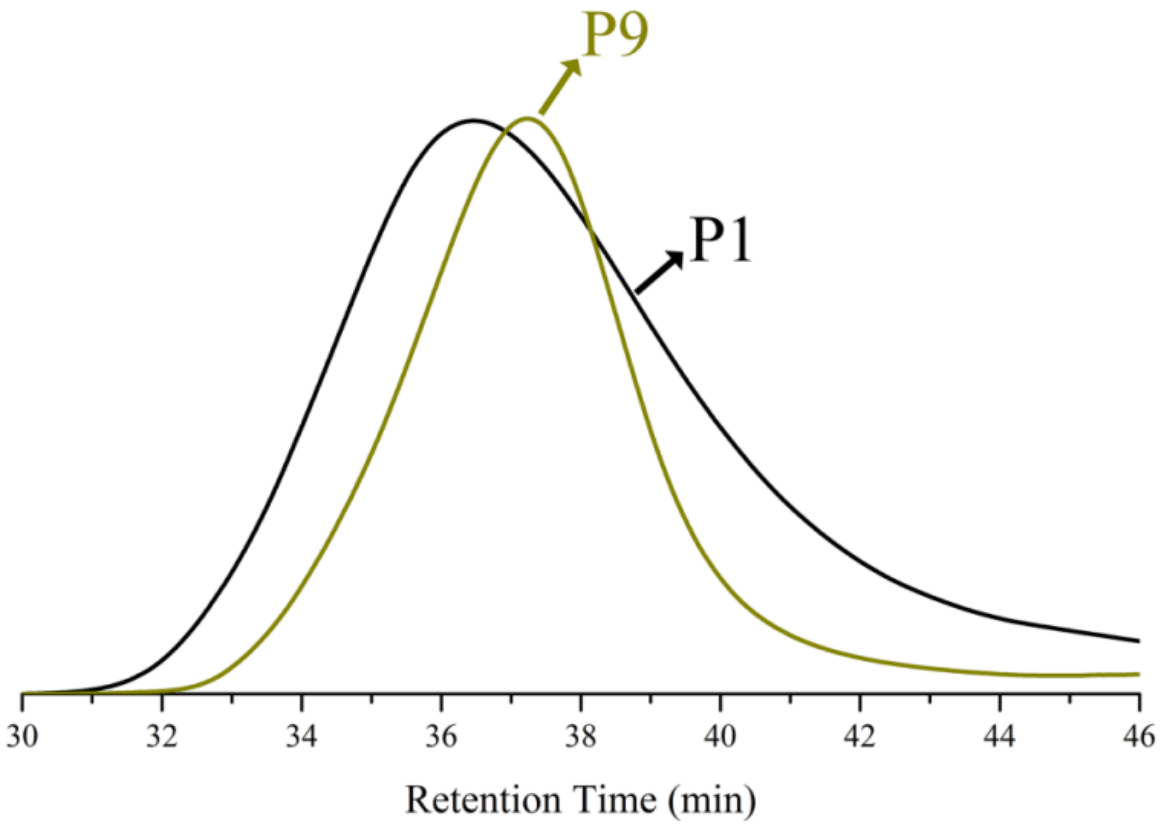

Figure 2.29: Overlaid GPC traces of P1 and P9 (at 30 °C in THF).

2.3.11 Procedure for methyl thioglycolate addition (P10)

P1 (0.15 g, 0.88 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. Methyl thioglycolate (94.6 μL, 1.06 mmol) and TBD (12.3 mg, 0.0880 mmol) were added to the solution, respectively. The mixture was stirred at room temperature for 1 min and precipitated in 20 mL of MeOH followed by removing excess solvent via decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times and the recovered yellow sticky polymer P10 was dried in a vacuum oven for 24 h (Yield = 0.18 g, 62%). ^{1}H NMR (Figure 2.30) ($CDCl_3$, δ) 4.14 (m, 4H, OCH_2), 3.78 (m, 1H, SCH) 3.71 (s, 3H, C=OOCH_3), 3.47-3.36 (m, 2H, SCH_2), 2.94-2.72 (m, 2H, CHCH_2C=O), 1.69 (m, 4H, aliphatic CH_2); ^{13}C NMR (Figure 2.31) ($CDCl_3$, δ) 171.05, 170.35, 64.97, 52.62, 41.66, 35.99, 33.04, 25.07. T_g value of P10 is -25.0^{o}C (Figure 2.32). The GPC trace of P10 is observed higher molecular weight region than the GPC trace of P1 (Figure 2.33).

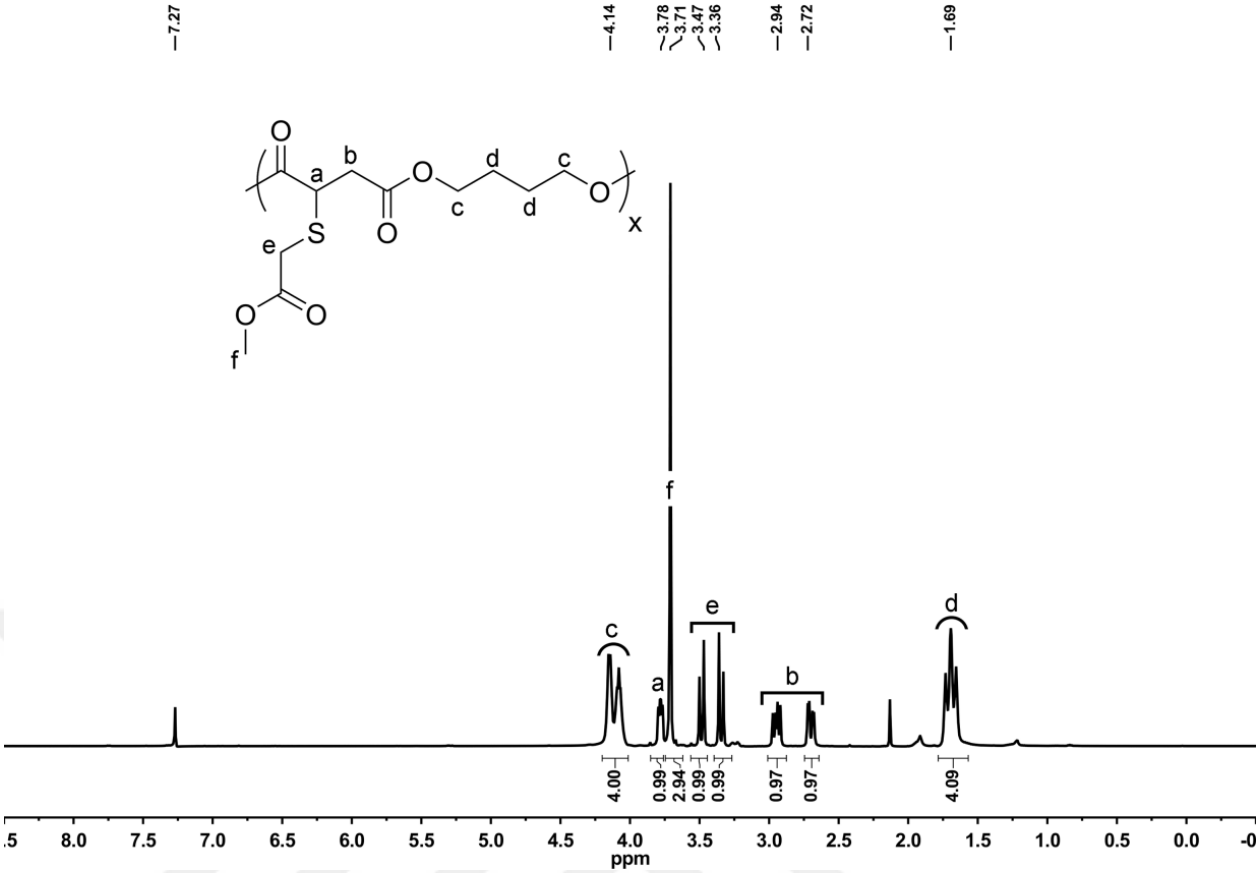

Figure 2.30: ^{1}H NMR spectrum of P10 in $CDCl_3$ (500 MHz).

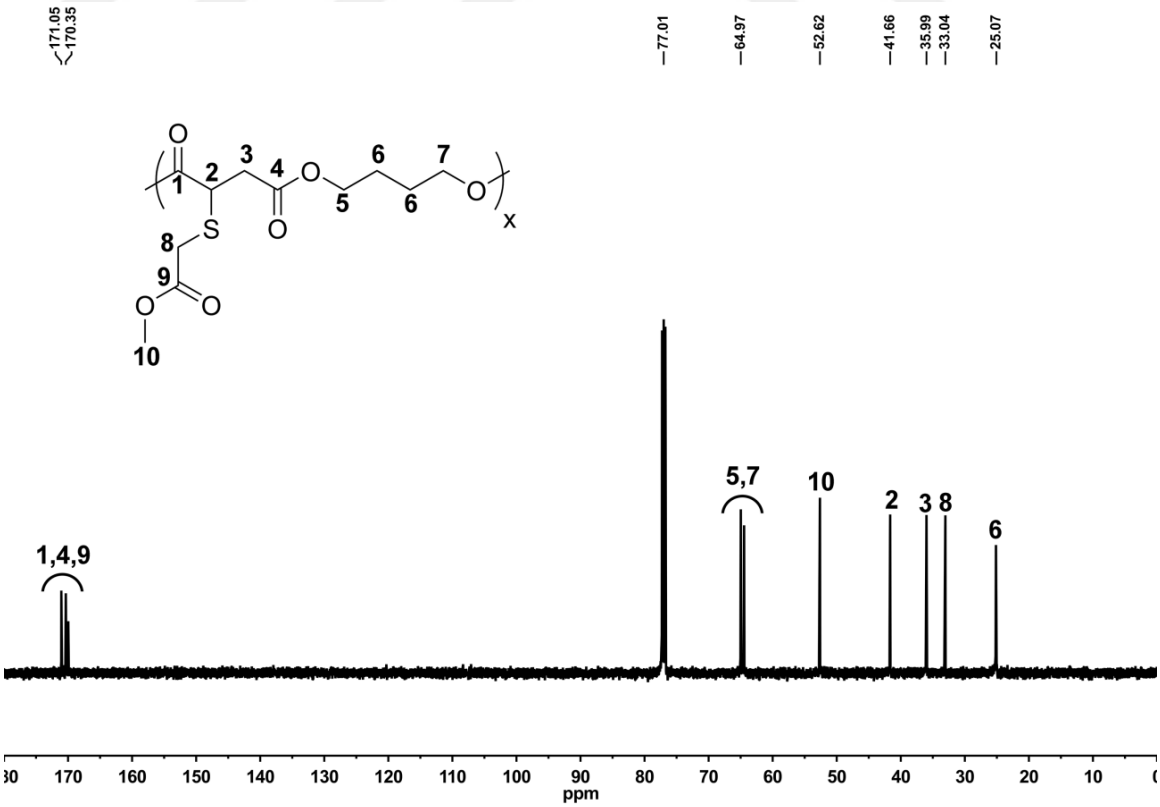

Figure 2.31: ^{13}C NMR spectrum of P10 in $CDCl_3$ (125 MHz).

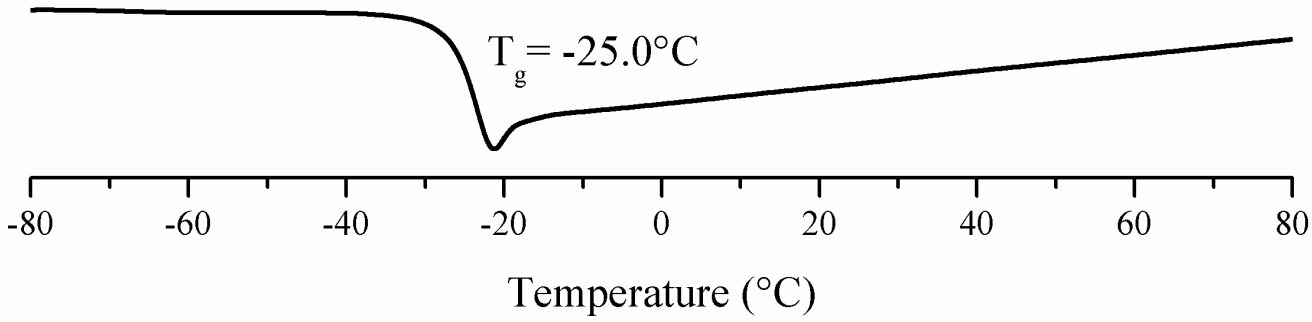

Figure 2.32: DSC thermogram of P10 at a heating rate of 10 °C/min under nitrogen (second run).

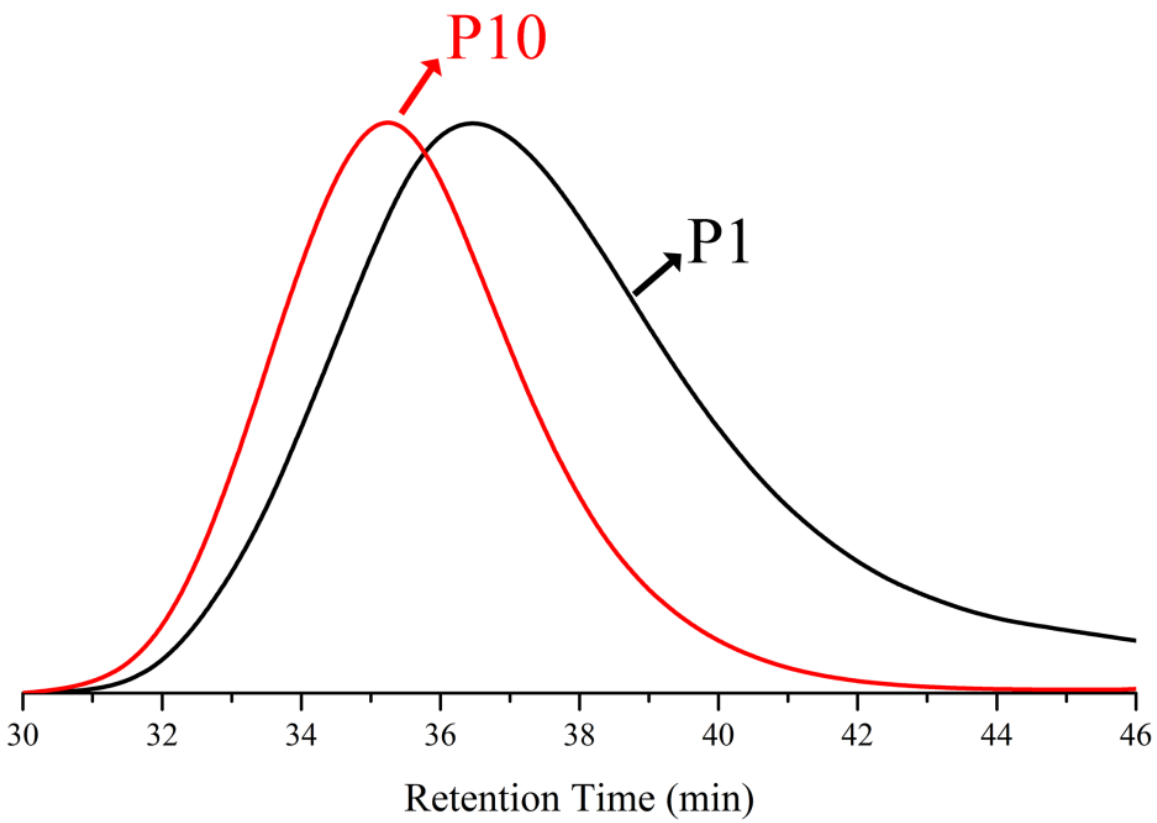

Figure 2.33: Overlaid GPC traces of P1 and P10 (at 30 °C in THF).

2.3.12 Procedure for thiophenol addition (P11)

P1 (0.15 g, 0.88 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. Thiophenol (108.7 µL, 1.060 mmol) and TBD (12.3 mg, 0.0880 mmol) were added to the solution, respectively. The mixture was stirred at room temperature for 1 min and precipitated in 20 mL of MeOH followed by removing excess solvent via decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times and the recovered yellow sticky polymer P11 was dried in a vacuum oven for 24 h (Yield = 0.28 g, 85%). ^{1}H NMR (Figure 2.34) ($CDCl_3$, δ) 7.47-7.33 (m, 5H, Ar*H*), 4.08 (m, 5H, SC*H* and OCH_2), 2.94-2.75 (m, 2H, CH_2C=O), 1.66 (m, 4H, aliphatic CH_2); ^{13}C NMR (Figure 2.35) ($CDCl_3$, δ) 170.56, 133.86, 131.81, 129.10, 64.40, 45.51, 36.36, 25.12. T_g value of P11 is -17.1^{o}C (Figure 2.36). The GPC trace of P11 is observed higher molecular weight region than the GPC trace of P1 (Figure 2.37).

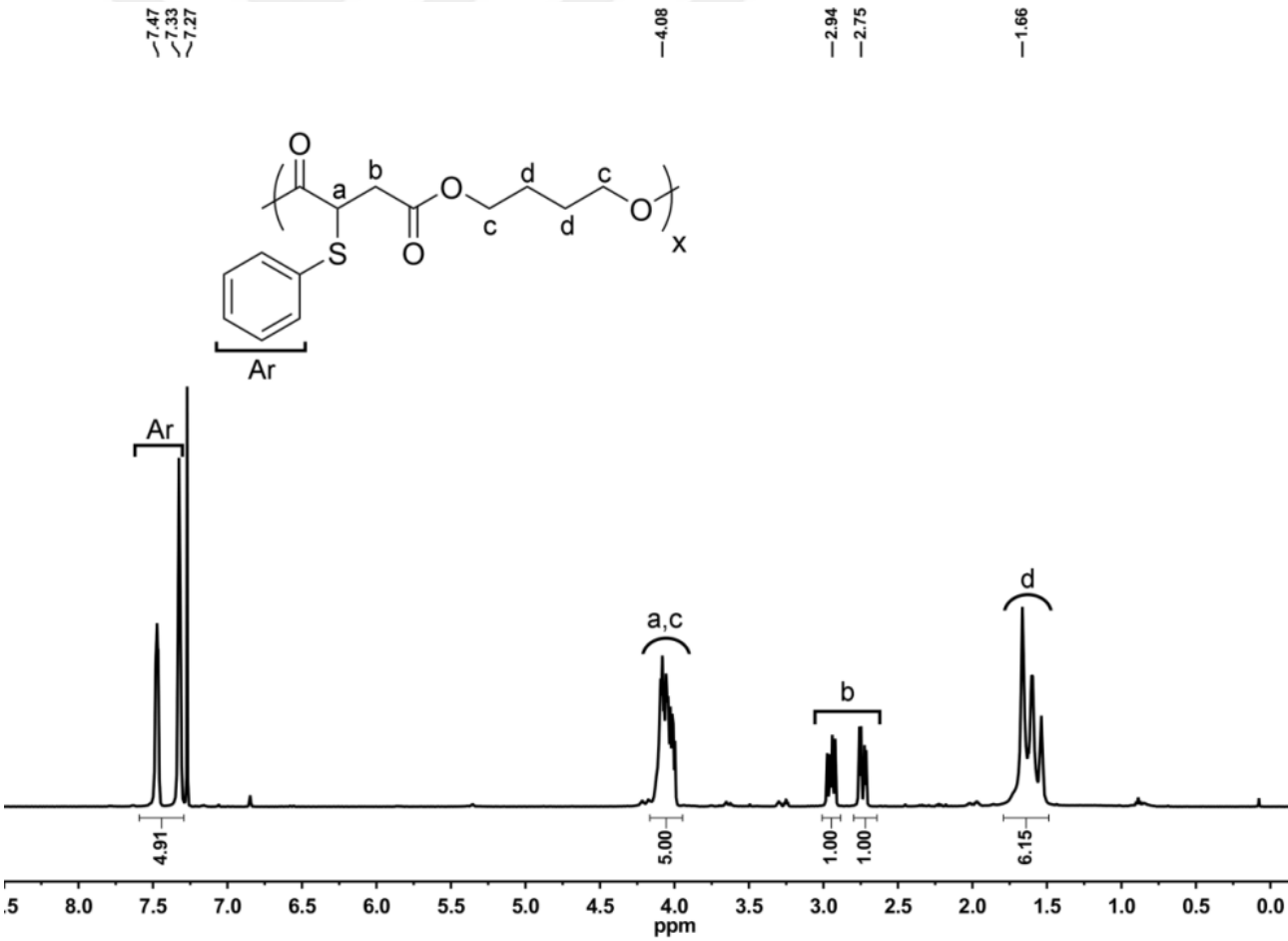

Figure 2.34: ^{1}H NMR spectrum of P11 in $CDCl_3$ (500 MHz).

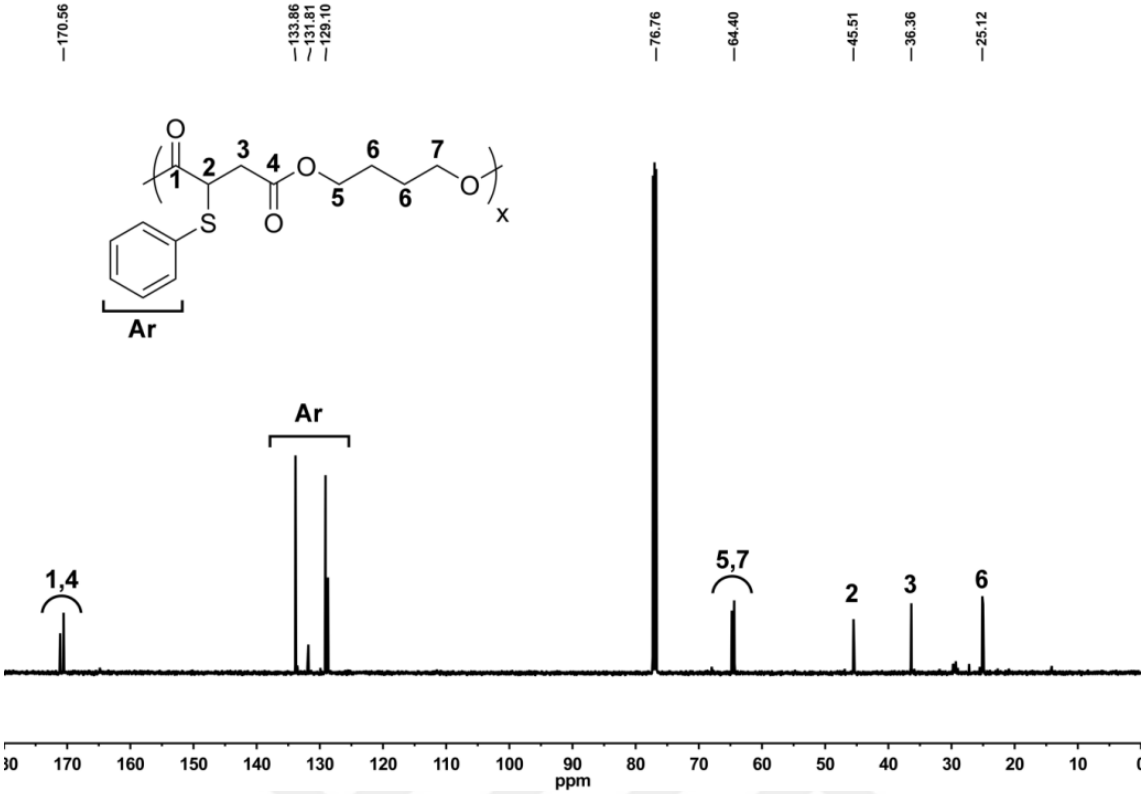

Figure 2.35: ^{13}C NMR spectrum of P11 in $CDCl_3$ (125 MHz).

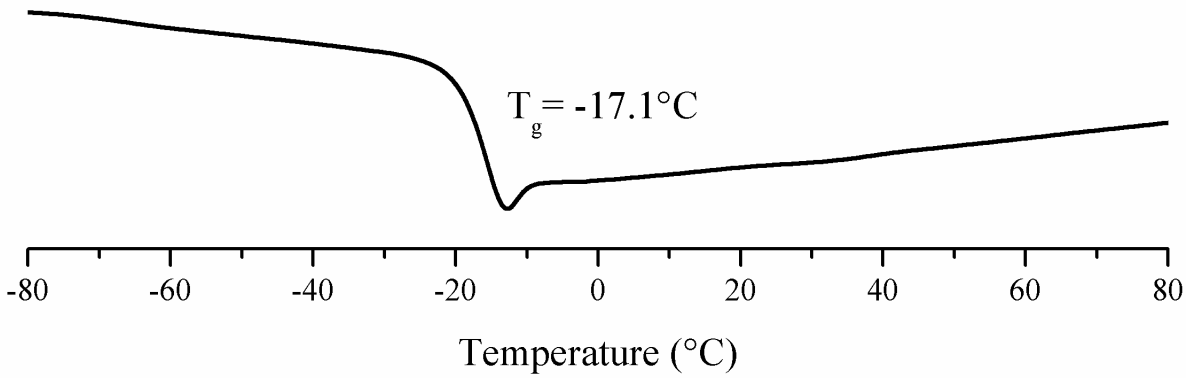

Figure 2.36: DSC thermogram of P11 at a heating rate of 10 °C/min under nitrogen (second run).

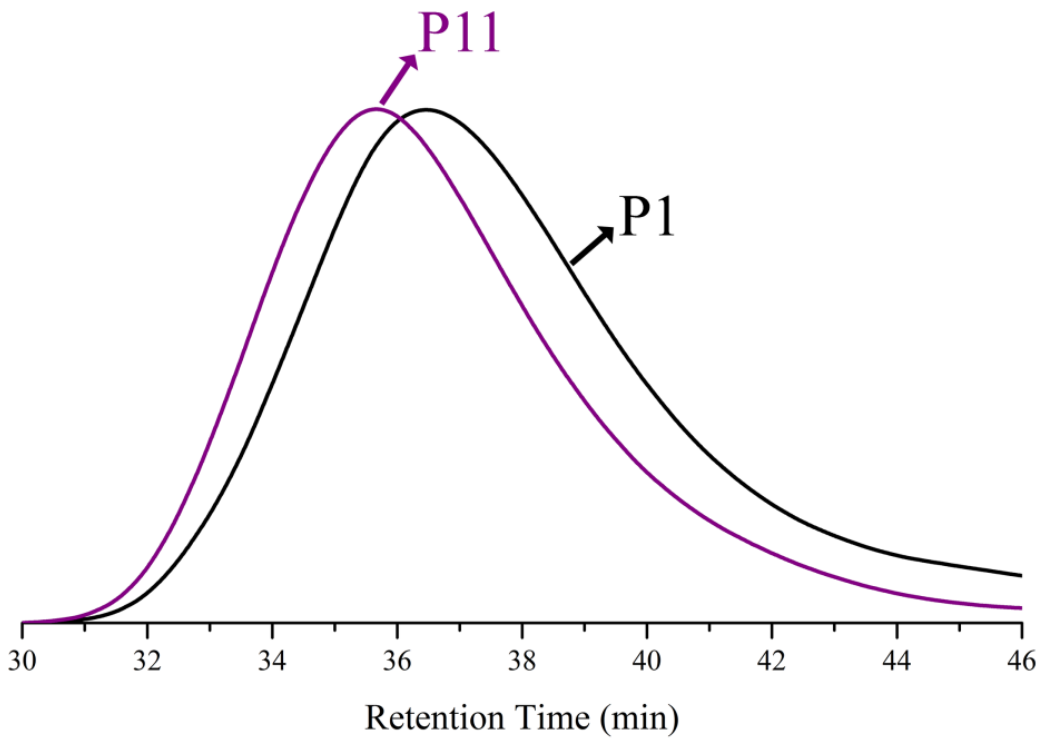

Figure 2.37: Overlaid GPC traces of P1 and P11 (at 30 °C in THF).

2.3.13 Procedure for mixed thiol addition (P12)

P1 (0.200 g, 1.18 mmol of alkene) was dissolved in 3 mL of $CHCl_3$ and transferred to 10 mL of a round-bottom flask. Benzyl mercaptan (82.9 µL, 0.710 mmol) and 1-propanethiol (65.5 µL, 0,710 mmol), TBD (163.7 mg, 0.1180 mmol) were added to the solution, respectively. The mixture was stirred at room temperature for 1 min and precipitated in 20 mL of MeOH followed by removing excess solvent via decantation. The dissolution–precipitation ($CHCl_3$-MeOH) procedure was repeated two times and the recovered yellow sticky polymer P12 was dried in a vacuum oven for 24 h (Yield = 0.23 g, 73%). ^{1}H NMR (Figure 2.38) ($CDCl_3$, δ) 7.32-7.27 (m, 5H, Ar*H*), 4.17 (m, 4H, OCH_2), 3.88 (m, 2H, benzyl-CH_2) 3.58 (m, 1H, SC*H*), 2.99-2.62 (m, 4H, SCH_2 and CH_2C=O), 1.70 (m, 6H, aliphatic CH_2), 0.98 (m, 3H, CH_3); ^{13}C NMR (Figure 2.39) ($CDCl_3$, δ) 171.53, 170.52, 137.03, 128.59, 127.38, 64.35, 41.04, 36.04, 33.53, 25.19, 22.59, 13.39. T_g value of P12 is -19.1^{o}C (Figure 2.40). The GPC trace of P12 is observed higher molecular weight region than the GPC trace of P1 (Figure 2.41).

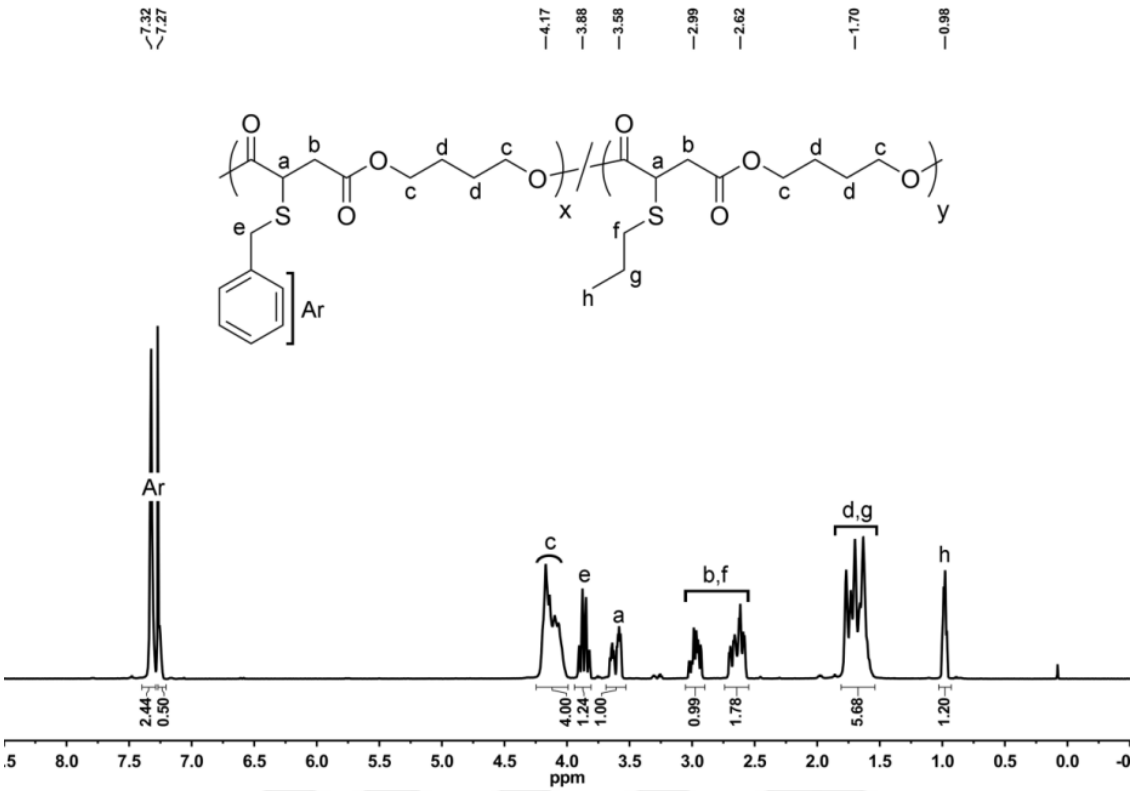

Figure 2.38: ^{1}H NMR spectrum of P12 in $CDCl_3$ (500 MHz).

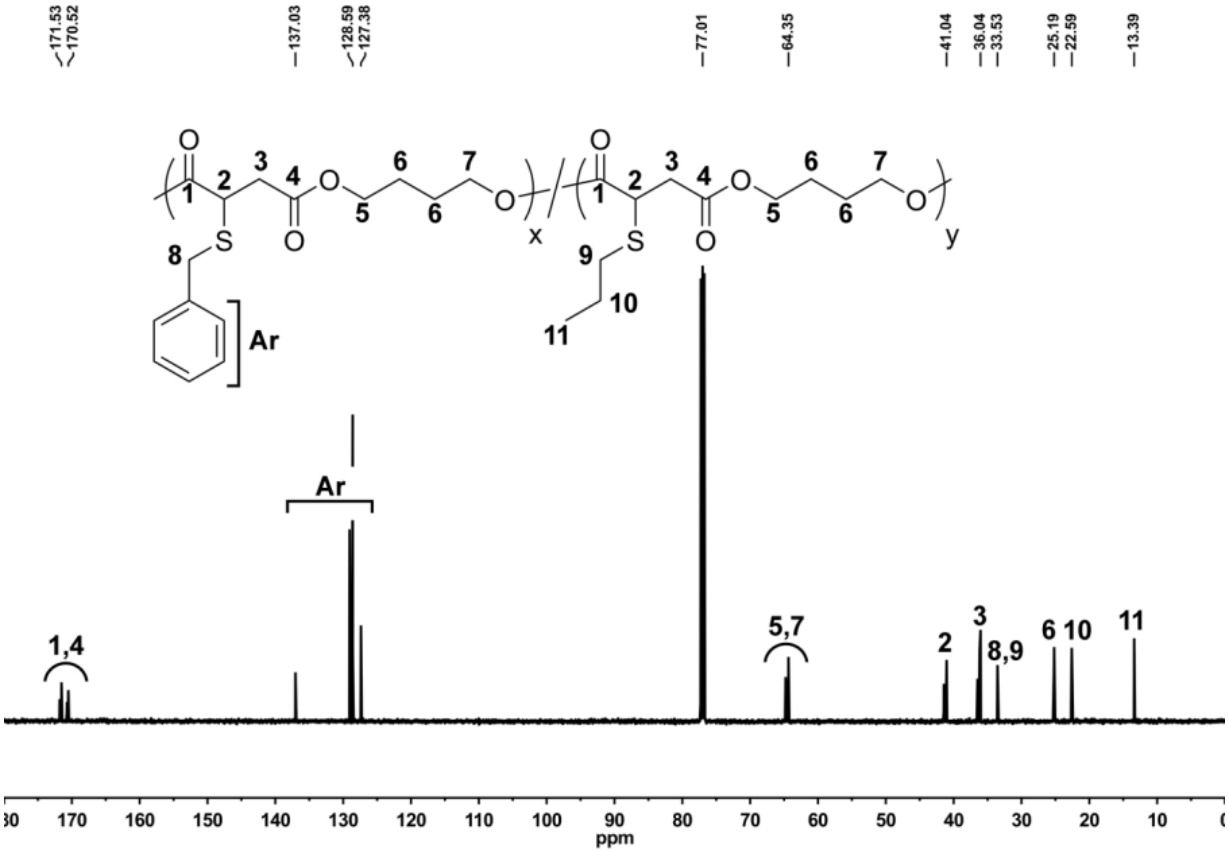

Figure 2.39: ^{13}C NMR spectrum of P12 in $CDCl_3$ (125 MHz).

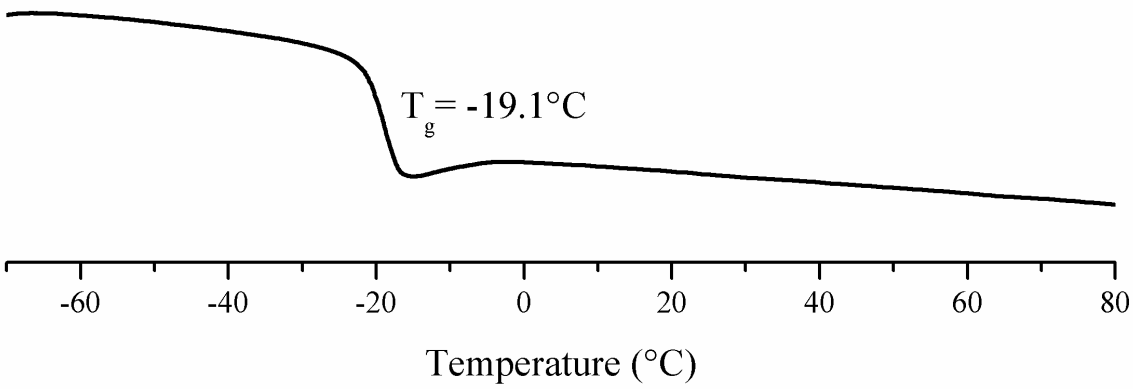

Figure 2.40: DSC thermogram of P12 at a heating rate of 10 °C/min under nitrogen (second run).

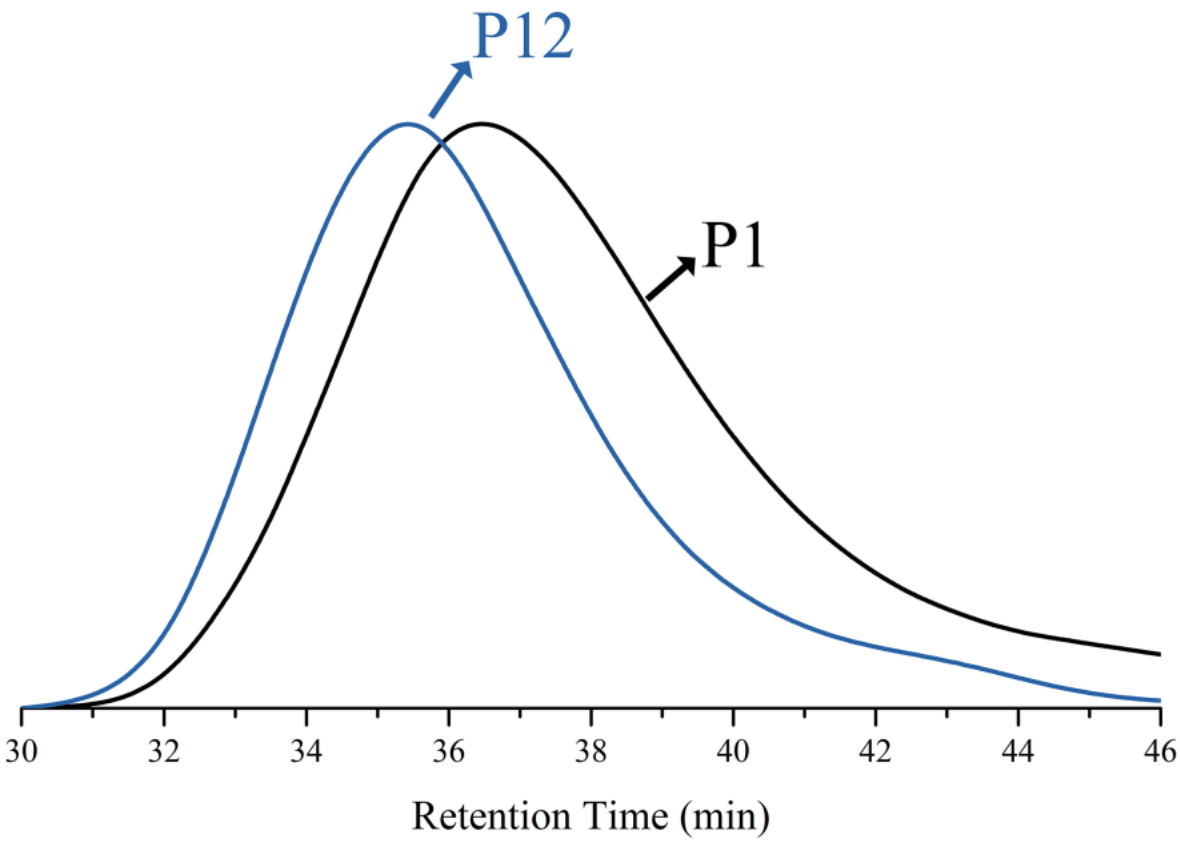

Figure 2.41: Overlaid GPC traces of P1 and P12 (at 30 °C in THF).

3. RESULTS AND DISCUSSIONS

In this work, TBD provided the highest efficiency between amidine- and guanidine-based catalysts, when utilized as 0.25 equiv per alkyne in the presence of 2.5 equiv thiol per alkyne in $CHCl_3$ at room temperature. Very recently, Daglar and co-workers developed that a novel and extremely fast method for polythioether synthesis based on the reaction of dialkyl acetylenedicarboxylates and dithiols in $CHCl_3$ using an organobase TBD at room temperature [26]. Thus, a series of polythioethers with molecular weight up to ~50 kDa was quantitatively achieved in 1 min, under the optimum experimental conditions.

Inspired of the postfunctionalization of polymer which has alkyne moieties, postfunctionalization on UP was studied in the presence of an organobase in an extremely rapid way through thiol-Michael addition reaction. For this purpose, poly(butylene maleate) (P1) was prepared via a simple condensation polymerization between maleic anhydride and 1,4-butanediol in high yield. NMR confirmed the formation of the polymer by displaying the expected signals (Figure 2.1 and 2.2). Polyester P1 was then reacted with 1-propanethiol in $CHCl_3$ in the presence of various organocatalysts to reveal the suitable catalyst for postfunctionalization studies, utilizing the following reactions conditions: P1 (1 equiv), 1-propanethiol (1.2 equiv per alkene), and catalyst (0.1 equiv per alkene) in 3 mL of $CHCl_3$ at room temperature (Table 3.1). The reaction efficiencies depending on the remaining double bonds in the main backbone were calculated by ^{1}H NMR spectra of resulting polyesters comparing an integrated area ratio of two ester CH_2 at 4.22 by a distinctive signal at 6.25 ppm regarding the C*H*=C*H* of the maleate unit. Among the studied catalysts, TBD afforded a remarkable effect in terms of the postfunctionalization and produced pendant thioether functional polyester with 100% efficiency in 1 min. It is worth to mention here that amidine and guanidine bases tested in this study exhibited good to excellent efficiencies under short durations, attributable to their high basicities. On the other hand, very low efficiencies were found when mild bases DABCO and Et_3N were utilized as catalysts even the reaction time was extended to 16 h.

Table 3.1 : Effect of various organocatalysts on thiol-Michael addition reactions[a].

Catalyst	Efficiency(%)[b]	pKa[e]
TBD	100	26.0
MTBD	85/99[c]	25.5
DBU	79/94[c]	24.3
DBN	55/78[c]	23.9
TMG	37/75[c]	23.3
Et_3N	0/16[d]	18.8
DABCO	0/26[d]	18.3

[a]Reaction conditions: P1 (1 equiv), 1-propanethiol (1.2 equiv per alkene), catalyst (0.1 equiv per alkene) in $CHCl_3$ at rt for 1 min; [b]Determined by ^{1}H NMR; [c]Reaction proceeded for 5 min; [d]Reaction proceeded for 16 h; [e]See ref [27].

As could be seen in Table 3.1, we decided to use TBD as a catalyst for thiol-Michael addition reactions since it exhibited the highest efficiency within 1 min period under the given reaction conditions. Thus, P1 was allowed to react with a wide variety of thiols to yield pendant thioether functional polyesters, P2-P11, using TBD in $CHCl_3$ for 1 min at room temperature (Figure 3.1 and 3.2). It should be noted that ^{1}H NMR spectra and the molecular weight data of thioether functional polyesters together with T_gs were displayed in Figure 2.1 and Table 3.2, respectively. Notably, from ^{1}H NMR spectra of thioether functional polyesters (Figure 3.3), characteristic maleate C*H*=C*H* protons at 6.25 ppm entirely vanished and new multiplet signals appeared at around 3.65 and 3.00-2.70 ppm assignable to the characteristic main chain C*H* proton attached to the S and it's neighbor CH_2 protons, respectively. The signals of the main chain polyester and the thioether functionals could also be detected along with the characteristic signals mentioned above. Moreover, ^{13}C NMR spectra of all polymers also supported that the thiol-Michael addition reactions were carried out with quantitative efficiencies, in which *C*H=*C*H signal around 130 ppm completely disappeared while the corresponding *C* signals regarding the thioether functionals appeared in the expected regions. In the supporting information, it was clearly detected from ^{13}C NMR spectra of all polymers that the C=O signals of P1 at 165 ppm shifted to over 170 ppm after the postfunctionalization. Given the NMR results , it is obvious that thiol-Michael addition reactions occurred with 100% efficiencies, indicating that the thiols used, in terms of the nucleophilic power, were not important in the presence of TBD. GPC traces of all polymers displayed unimodal curves with broader dispersity (*Đ*). GPC analysis of the resulting polyesters indicated the molecular weight increase after the postfunctionalization except for P9, which

displayed lower molecular weight and *Đ* values than those of P1. Extracting DSC data, it is noted that all polymers are sticky and completely amorphous displaying low T_g values.

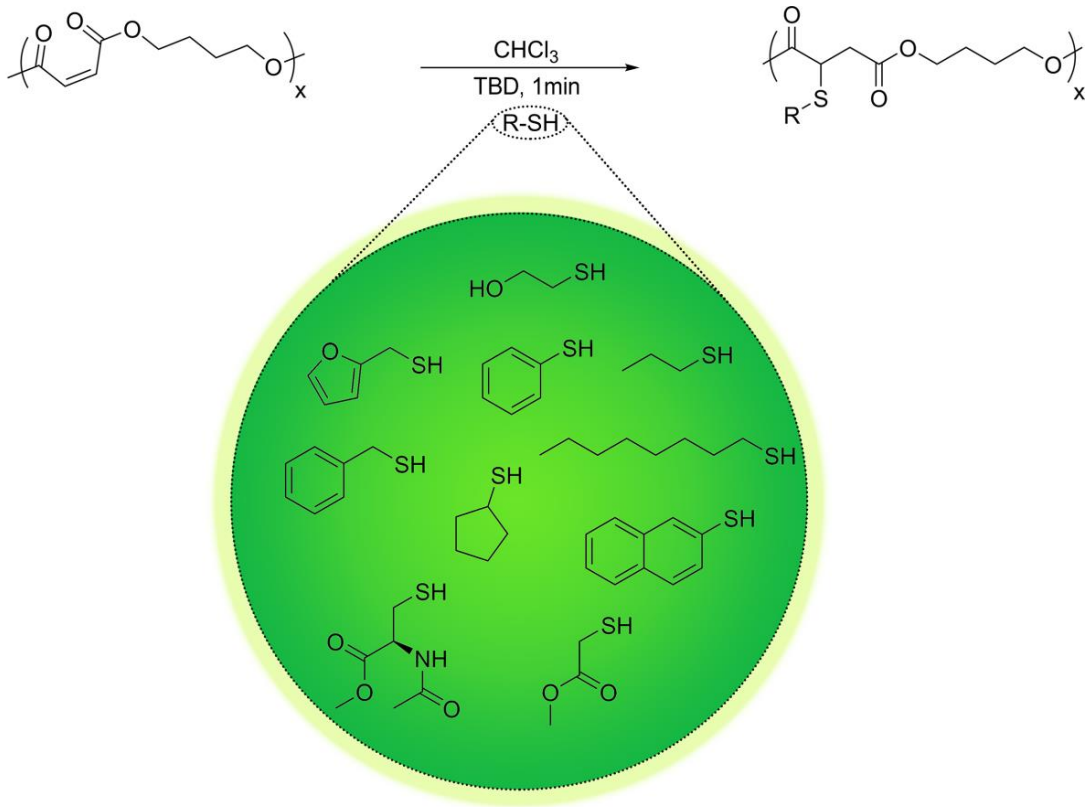

Figure 3.1: Synthetic route for the postfunctionalization of P1 via thiol-Michael addition reactions and variety of thiols used.

Moreover, for a mixed thioether functionalization of P1, two different thiols, benzyl mercaptan, and 1-propanethiol, were charged equimolarly to the reaction mixture of P1 and TBD (10% mol per alkene) catalyst in $CHCl_3$ at room temperature for 1 min. Synthesized polymer P12 demonstrates the benzyl mercaptan (0.60) and propanethiol (0.40) functional segments based on the integrated area ratio for the benzyl-CH_2 at 3.88 ppm and CH_3 of propanethiol at 0.98 ppm.

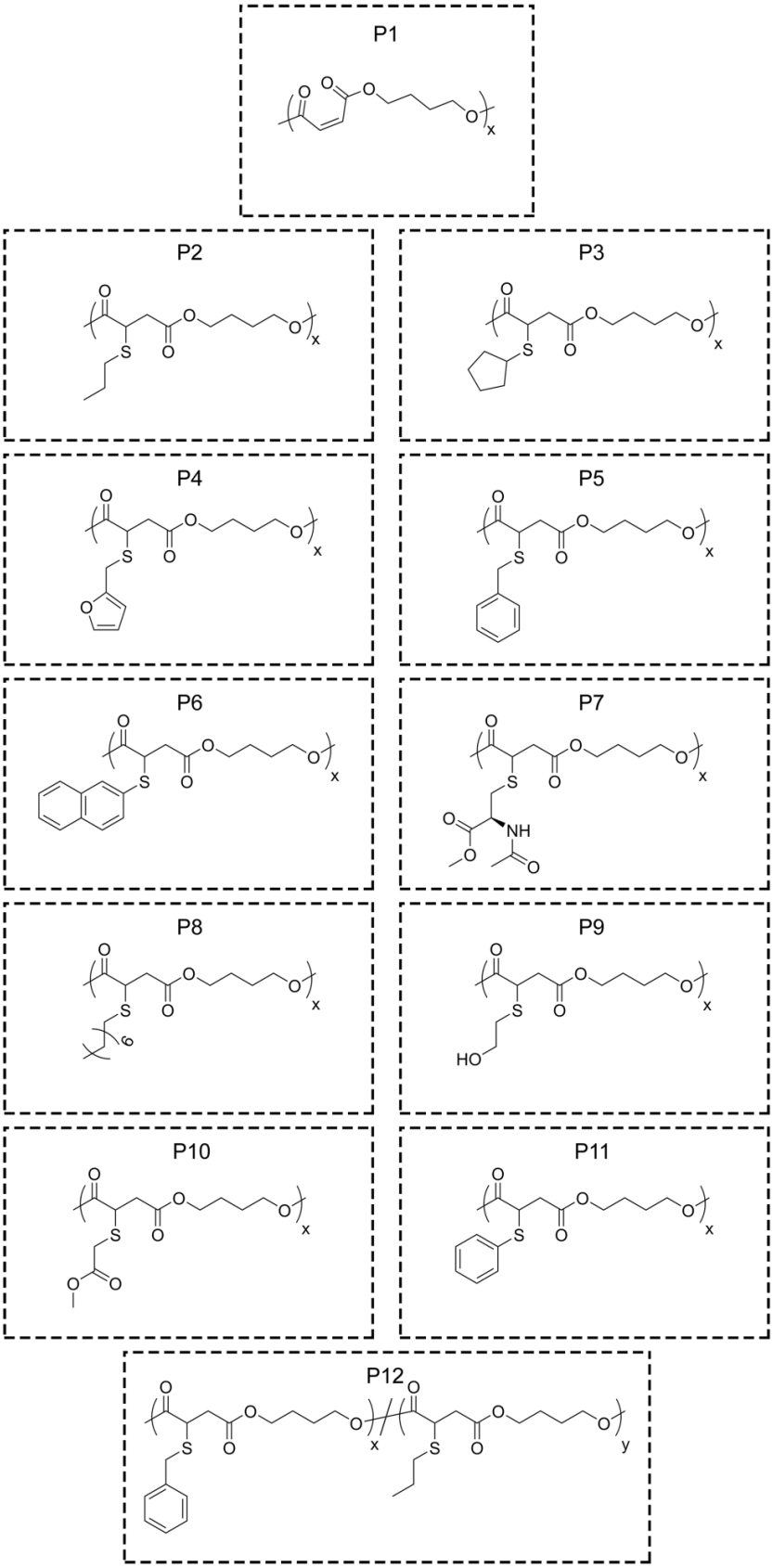

Figure 3.2: The final structures of the resulting polyesters after thiol-Michael addition reactions.

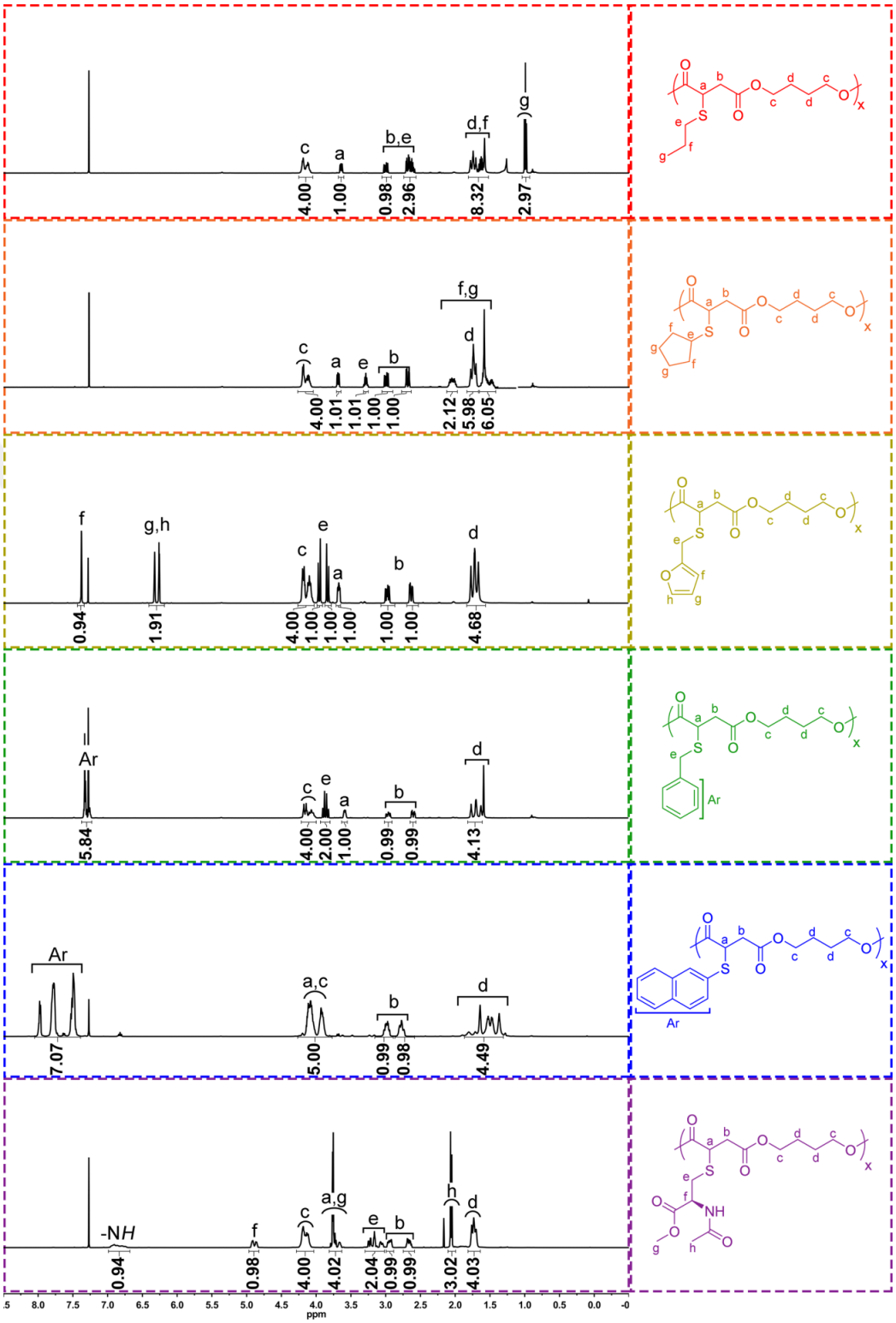

Figure 3.3: ^{1}H NMR spectra of P2-P7 (from top to down) in $CDCl_3$ (500 MHz).

Table 3.2 : Results of polyesters after postfunctionalization reactions between P1 and thiols[a].

Polymer	M_w (kDa)[b]	$Đ$ (M_w/M_n)[b]	T_g (°C)[c]
P1	26.8	2.01	-45.9
P2	33.5	1.80	-37.7
P3	40.0	1.67	-31.0
P4	40.3	2.06	-19.1
P5	54.7	2.09	-13.9
P6	53.1	2.20	3.4
P7	39.0	1.81	-4.8
P8	41.1	1.81	-53.3
P9	24.8	1.37	-31.7
P10	43.0	1.60	-25.0
P11	36.4	2.03	-17.1
P12	40.3	2.15	-19.1

[a]Reaction conditions: P1 (1 equiv), thiol (1.2 equiv per alkene), TBD (0.1 equiv per alkene) in $CHCl_3$ at rt for 1 min; [b]Determined by GPC; [c]Determined by DSC from a second heating cycle.

4. CONCLUSION

In the concept of the postfunctionalization of the UP backbone using thiols via thiol-Michael addition reactions, we tested a vast range of organocatalysts. We found that TBD is the best organocatalyst for the postfunctionalization of thiols with P1 since it is stronger base than other organobases studied in this study. In the presence of TBD (10% mol per alkene), P1 reacted quantitatively with a variety of thiols within 1 min reaction period in $CHCl_3$ at room temperature, resulting in pendant thioether functional polyesters to form. As a result, we have made a complementary study on a simple and highly atom economical modification on the polyester scaffold with electron-deficient maleate moieties in the main chain through thiol-Michael addition reactions. We believe the functionalization strategy described in this study is highly time-saving, which is nowadays the most desirable condition for a post-polymerization study.

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