SYNTHESIS AND EXTENSION OF DIALLYL TELECHELIC POLYISOBUTYLENES TO HIGHER MOLECULAR WEIGHTS AND NETWORKS BY THIOL-ENE CHEMISTRY

by

Elif KURNAZ

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To my dearest mother and father

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ABSTRACT

SYNTHESIS AND EXTENSION OF DIALLYL TELECHELIC POLYISOBUTYLENES TO HIGHER MOLECULAR WEIGHTS AND NETWORKS BY THIOL-ENE CHEMISTRY

In this research, the focus is on the use of the thiol-ene click chemistry for the preparation of high molecular weight linear rubbery or crosslinked polyisobutylenes from lower molecular weight liquid polyisobutylene precursors for the first time. Radical thiol-ene addition reactions were found to successfully connect polymer blocks together with the purpose of chain extension. The synthetic strategy followed comprises three stages: (i) synthesis of a difunctional carbocationic initiator,5-tert-butyl-1,3-bis(2-chloro-2-propyl)benzene (t-Bu-m-DiCumCl) from 5-tert-butyl-1,3-dicarboxybenzene in three steps; (ii) synthesis of well-defined polyisobutylenes via quasiliving carbocationic polymerization and following in-situ end-capping reactions with allyltrimethylsilane; (iii) utilization of UV light initiated thiol-ene reactions in order to obtain high molecular weight products and networks in the presence of 2,2-dimethoxy-2-phenyl acetophenone (DMPA) as photoinitiator in dichloromethane under inert atmosphere. In a complementary study, the effect of thermal initiation on the efficiency of radical thiol-ene addition reactions in chain extension reactions was also investigated. The intermediates and the final products were characterized by ^{1}H NMR spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR) and Size Exclusion Chromatography (SEC) in terms of molecular structure and molecular weight, respectively. Increase in the molecular weight of the chain extended linear polymers was monitored by SEC. The crosslinked networks were characterized by Raman spectroscopy which confirmed the formation of C-S bonds. The network properties were evaluated by swelling and extraction studies.

ÖZET

DİALİL TELEKELİK POLİİZOBÜTİLENLERİN SENTEZİ VE TİYOL-EN KİMYASI İLE YÜKSEK MOLEKÜLER AĞIRLIKLARA UZATILMASI VE AĞ YAPILARININ ELDESİ

Bu araştırmada, düşük moleküler ağırlıklı sıvı poliizobütilen başlangıç polimerlerinden yüksek moleküler ağırlıklı kauçuksu doğrusal veya çapraz bağlı poliizobütilenlerin tiyol-en klik kimyası kullanılarak eldesi ilk kez gerçekleştirilmiştir. Radikal tiyol-en eklenme reaksiyonlarının zincir uzatma amacıyla polimer bloklarını başarıyla bağlayabildiği saptanmıştır. İzlenilen sentetik strateji üç aşamadan oluşmaktadır: (i) çift fonksiyonlu katyonik başlatıcının, 5-tersiyer-butil-1,3-bis(2-kloro-2-propil)benzen (t-Bu-m-DiCumCl), 5-tersiyer-bütil-1,3-dikarboksibenzen'den üç adımda sentezi; (ii) yaşayan katyonik polimerizasyon yöntemi ile iyi tanımlanmış poliizobütilenlerin sentezi ve aliltrimetilsilan ile zincir uçlarının fonksiyonlandırılması; (iii) UV ışığı ile başlatılmış tiyol-en reaksiyonlarının 2,2-dimetoksi-2-fenil asetofenon fotobaşlatıcı varlığında diklorometan içinde inert ortamda yüksek moleküler ağırlıklı ürünler ve ağ yapılarının eldesinde kullanımı. Tamamlayıcı bir çalışma olarak, termal yolla başlatma metodunun tiyol-en kimyası ile zincir uzatma reaksiyonlarındaki verimliliği de çalışılmıştır. Ara maddeler ve son ürünler ^{1}H NMR spektroskopisi, Fourier Transform Kızılötesi Spektroskopisi (FTIR) ve Büyüklükçe Ayırma Kromatografisi (SEC) ile moleküler yapısı ve moleküler ağırlığı açısından karakterize edilmiştir. Doğrusal polimerlerin moleküler ağırlığındaki artış SEC ile izlenmiştir. Çarpraz bağlı ağ yapılar Raman spekroskopisi ile karakterize edilmiş ve C-S bağlarının oluşumu doğrulanmıştır. Ağ yapılarının özellikleri şişme ve ekstraksiyon çalışmaları ile değerlendirilmiştir.

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-b-	Block copolymer
C_n	Characteristic ratio of polymer
E_p	Activation energy of propagation
E_{tr}	Activation energy of chain transfer
g	Gram
h	Hour
l	Average bond length
ml	Milliliter
mmHg	Millimeter of Mercury
$\bar{\bar{M}}_c$	Average molecular weight between crosslinks
M_n	Number Average Molecular Weight
M_w	Weight Average Molecular Weight
M_w/M_n	Polydispersity Index
M_r	Molecular weight of the repeating unit
m_d	Dry weight of network
m_{ex}	Dry weight of network after extraction
m_s	Equilibrium weight of swollen network
mW	Milliwatt
n	Number of bonds in crosslink
nm	Nanometer
V_1	Molar volume of solvent
β	Beta
δ	Chemical shift
ΔE	Activation energy difference
µL	Microliter
q_w	Equilibrium weight swelling ratio
ρ_c	Crosslink density

ξ	Mesh size
$V_{2,s}$	Equilibrium polymer volume fraction
ρ_p	Density of crosslinked polymer
ρ_{cyc}	Density of cyclohexane
$\bar{v}$	Specific volume of polymer
χ	Polymer-solvent interaction parameter

LIST OF ACRONYMS/ABBREVIATIONS

AIBN	2,2′-azobis(2-methylpropionitrile)
AllylBr	Allyl bromide
ATMS	Allyltrimethylsilane
Ar	Argon
BCl_3	Boron trichloride
BP	Benzophenone
$CDCl_3$	Deuterated chloroform
CQ	Camphorquinone
CuOAc	Cumyl acetate
DCM	Dichloromethane
DMPA	2,2-dimethoxy-2-phenylacetophenone
DP_n	Degree of Polymerization
DtBP	di-tert-butylpyridine
EDT	1,2-ethanedithiol
$EtAlCl_2$	Ethylaluminum dichloride
Equiv.	Equivalent
FTIR	Fourier Transform Infrared Spectroscopy
HCl	Hydrogen chloride
HDT	1,6-hexanedithiol
IB	Isobutylene
LiBr	Lithium bromide
MA	Methyl acrylate
mCPBA	m-Chloroperoxybenzoic acid
MeMgBr	Methylmagnesium bromide
MMA	Methyl methacrylate
MPA	3-mercaptopropionic acid
MWD	Molecular Weight Distribution
N_2	Nitrogen

n-Bu_4NCl	tetra-n-butylammonium chloride
NMR	Nuclear Magnetic Resonance Spectroscopy
PIB	Polyisobutylene
PEO_m-b-PIB-b-PEO_n	poly(ethylene oxide)-b-polyisobutylene-b-tri(ethylene oxide)
PSt-Allyl	Alkene end functionalized polystyrene
PSt-SH	Thiol end functionalized polystyrene
PTFE	Polytetrafluoroethylene
RAFT	Reversible Addition-Fragmentation Chain Transfer
SEC	Size Exclusion Chromatography
t-BuCl	tert-butyl chloride
t-Bu-m-DiCumCl	5-tert-butyl-1,3-bis(2-chloro-2-propyl)benzene
t-Bu-m-DiCumOH	5-tert-butyl-1,3-dicumyl alcohol
t-BuOAc	t-butyl acetate
TIBCl	2-chloro-2,4,4,6,6-pentamethylheptane
$TiCl_4$	Titanium tetrachloride
TMDPO	(2,4,6,-trimethylbenzoyl)diphenylphosphine oxide
TMPOAc	2,4,4-trimethylpenthyl-2-acetate
TMPCl	2-chloro-2,4,4-trimethylpentane
TX	Thioxanthone
UV	Ultraviolet
$ZnBr_2$	Zinc bromide

1. INTRODUCTION

1.1. Polyisobutylene

Polyisobutylene (PIB) is an industrially valuable polymer of isobutylene. PIBs varying from low molecular weight oligomers to high molecular weight polymers have found a broad field of application area due to their unique properties [1, 2]. Low molecular weight PIBs with functional end groups are widely used as intermediates in the synthesis of fuel and lubricating oil additives, sealants and adhesives. Examples of commercial products are allyl telechelic PIB based EPION and succinic anhydride telechelic PIB based PIBSA [3, 4]. High molecular weight PIBs copolymerized with a few percent isoprene called butyl rubber are tough elastomers. Butyl rubber together with homopolymers of isobutylene constitute the vast majority of commercial applications of carbocationic polymerization [1]. They are used broadly in areas where gas impermeability, high damping characteristics and environmental and chemical stability are required; such as tire inner liners (halogenated butyl rubbers), vibration proof materials and engine mounts, tank liners, pharmaceutical stoppers and so forth [5]. PIB has also found some special applications in biomaterial science. In this aspect, triblock copolymer of isobutylene with styrene (SIBS) is used as drug eluting coating on the TAXUS coronary stent (trademark of Boston Scientific Co.). On account of absence of any polar bonds in the polymer chains, these thermoplastic elastomers exhibit excellent biostability and biocompatibility [6].

With the discovery of butyl rubber, isobutylene became an important monomer for the industry and scientific community. Isobutylene is a nonpolar hydrocarbon monomer that can only be polymerized by carbocationic polymerization. The reactivity of isobutylene in carbocationic polymerization is due to the ability of two methyl substituents in stabilizing the resulting tertiary carbocation via inductive effect (or/and hyperconjugation) [2, 7]. Other carbocationic monomers of interest include N-vinylcarbazole, vinyl ethers and styrenes. Kennedy group has pioneered the way through living carbocationic polymerization of isobutylene. After their report of first living isobutylene polymerization in 1980s [8], kinetic

and mechanistic aspects of polymerization have been extensively investigated [9]. By combining living carbocationic polymerization with different synthetic methodologies, PIB based products with a variety of topologies, compositions and functionalities have been obtained [10].

1.2. Quasiliving Carbocationic Polymerization

The concept of "living" polymerization is introduced by Szwarc in 1956 and used for anionic polymerization of styrene initiated by complex of naphthalene-sodium initiator. In a system free of oxygen and water, red color of polystyryl anion persists through polymerization indicating the stability of polystyryl anion [11, 12]. Further supply of styrene to the system results in an increase in the viscosity of the solution and a consequent increase in molecular weight of the initial polymer [11, 12]. This polymerization illustrates the two criteria of living polymerization: absence of transfer and termination reactions and ability of resulting polymer chains adding subsequent portions of monomer [13].

Transfer and termination reactions are a challenging task to deal with as they inevitably occur in real polymerization systems. However, they have to be prevented in order to obtain well defined polymers with desired architectures and functionalities such as stars, networks, block copolymers, telechelic polymers, etc. On the other hand, it is also possible to obtain well defined polymers with a limited extent of these reactions; as long as fast initiation and fast exchange between active and dormant species exist in ionic polymerizations [2]. Thus, a modified definition of livingness is considered [13, 14]. According to this viewpoint, polymer chains that keep their activity during the achievement of a synthetic task are named as "living". Three diagnostic criteria of the livingness are linear increase of the number average molecular weight with conversion (DP_n vs. Conversion), first order kinetic plot (ln[M] vs. time) and narrow molecular weight distribution (Poisson MWD). The first criterion is the indicator of the constant number of chains (absence of transfer), while the second one proves constancy of the number of active species (absence of termination) [15].

In the early stage of carbocationic polymerizations, these criteria were thought to be unachievable considering the highly reactive nature of carbocations; which Kennedy mentions as a fundamental strength and weakness of cationic polymerization [1]. As a result,

cationic polymerizatons are considered as complex since they are more prone to undergo above mentioned reactions than anionic polymerizations [1]. Side reactions including β proton elimination, carbocationic rearrangements and Friedel-Crafts alkylation of aromatic rings take place during carbocationic polymerizations (Figure 1.1). It is known that β protons share the positive charge of the propagating active center and thus are acidic in character which makes them open to elimination reactions leading to terminal unsaturations [2]. In conventional isobutylene polymerizations a variety of olefinic end groups are detected including endo-, exo-, tri- and tetra-substituted olefins and the mechanisms governing the formation of these unsaturations are investigated [16, 17]. β proton elimination together with carbenium ion rearrangements via hydride and methide shifts and chain scissions are thought to be responsible for the unsaturations. These reactions hinder chain end functionalizations as they may result in more stable interior carbocations which means termination of the kinetic chain. Besides, the eliminated protons initiate new propagating chains which result in uncontrolled molecular weights and broad polydispersities [2]. However, these reactions contribute more at higher polymerization temperatures [16]. In a study by Faust *et al*., activation energy for β proton elimination is calculated to be higher than that of propagation which has negligible enthalpic barrier (E_{tr}-E_p = ~20kcal/mol. Therefore, the contribution of transfer reactions decreases at cryogenic polymerization temperatures [18].

In carbocationic polymerization of styrene, side reactions due to Friedel Crafts alkylation of aromatic rings are known to occur via inter and intramolecular pathways. While intermolecular alkylation yields branching, intramolecular alkylation results in terminal indanyl rings [19]. Likewise, indan formation is also significant in isobutylene polymerization when cumyl derivatives are used as the initiator. It results in consumption of initiator and impedes formation of telechelic polymers. However, indanyl formation is very dependent on sterics and thus can be prevented by substituents at meta positions (Figure 1.2) [2].

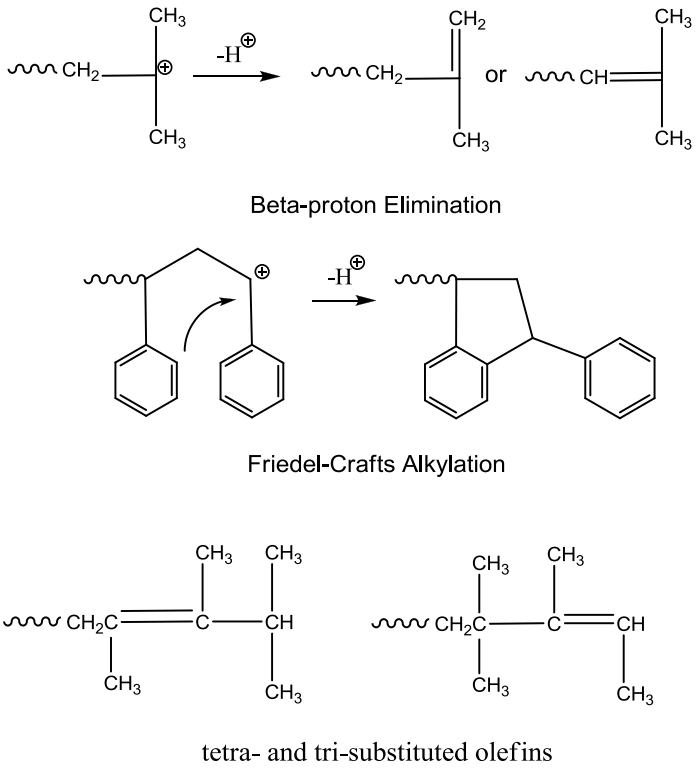

Figure 1.1. Side reactions in carbocationic polymerization.

Additionally, purity of the polymerization medium has high importance. Nucleophiles may be present in an insufficiently purified systems. They may be involved in β proton elimination if they are basic or may react with growing carbocations irreversibly to cause termination. Also, they may complex with Lewis acids and affect their activity [2]. As a result carbocationic polymerizations are typically done under inert atmosphere (dry N_2 or Ar atmosphere) with highly purified reagents at cryogenic temperatures in order to suppress transfer and termination reactions mentioned above.

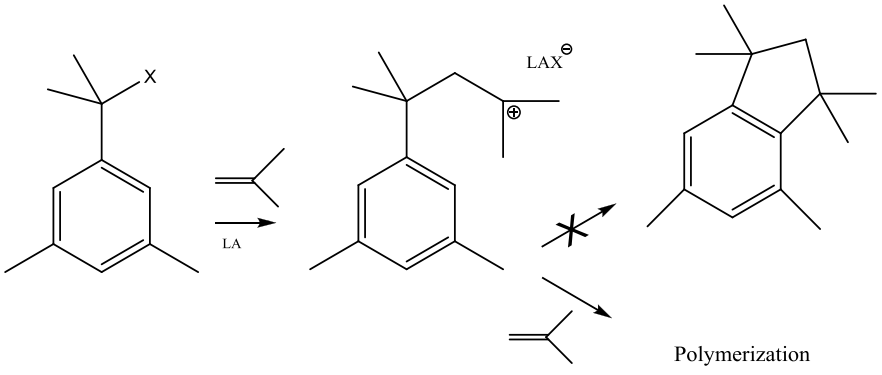

Figure 1.2. Substituent effect on indanyl formation.

The term “Quasiliving” is used to denote the existence of a dynamic equilibrium between reversibly terminated chain ends (dormant species) and growing carbocationic chain ends (active species) [20]. Kennedy emphasizes that the idea of reversible termination is a milestone in the progress of carbocationic polymerizations [4]. Since such polymerization systems have higher rate of exchange than that of propagation (rapid dynamic equilibrium), the lifetime of growing species is extended. That is, the growing species are active only for a small fraction of time, whereas during the vast majority of time they are in dormant state and hence do not undergo any transfer and termination reaction [2]. Therefore, this kind of mechanisms are frequently called living or controlled/living in literature [20].

The most important initiating system for isobutylene polymerization is a two component system of Friedel-Crafts acid (Lewis acid) and carbocation source (initiator). The efficiency of an initiating system depends on two parameters: the structure of the initiator and the strength of the Lewis acid which are chosen considering the reactivity of the monomer. For isobutylene, cumyl and 2,4,4-trimethylpentane derivatives (halides, alcohols, esters and ethers) in conjunction with Lewis acids such as BCl_3, $TiCl_4$ and organoaluminum compounds are the preferred initiating systems [21].

Initiators should ionize faster than the dormant chain ends and also provide carbocations which are similar to active chain ends in structure and reactivity [22]. This increases initiation efficiency and makes simultaneous growth of all polymer chains possible. Therefore, in the absence of chain transfer and termination reactions - or at least in their suppressed existence - these chains would have equal probability of growth which is required to achieve monodisperse polymers [22]. Concerning this issue, cumyl esters, ethers and halides are widely studied in isobutylene polymerization as they enable comparable rates of initiation and propagation.

First example of living isobutylene polymerization is reported by Kennedy group in 1987 [8]. The initiating systems studied are aromatic and aliphatic tertiary esters including cumyl acetate (CuOAc), t-butyl acetate (t-BuOAc) and 2,4,4-trimethylpentyl-2-acetate (TMPOAc). The polymerizations are done typically with BCl_3 in polar solvents such as dichloromethane and methyl chloride in the range of temperatures between -10 °C and -50

°C. The living nature of these polymerizations are attributed to tertiary ester/BCl_3 initiating complexes which generate counteranions that do not involve in any transfer and termination reactions (Figure 1.3) [8].

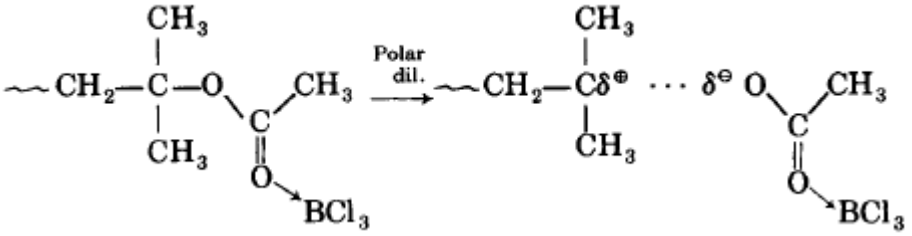

Figure 1.3. Tertiary ester/BCl_3 initiating complex.

In 1999, Storey and coworkers studied the effect of widely used aromatic difunctional initiator, 5-tert-butyl-1,3-bis(2-chloro-2-propyl)benzene (t-Bu-m-DiCumCl) and aliphatic initiators: 2-chloro-2,4,4-trimethylpentane (TMPCl), 2-chloro-2,4,4,6,6-pentamethylheptane (TIBCl) and tert-butyl chloride (t-BuCl) on $TiCl_4$ catalyzed isobutylene polymerization. The results indicated that t-Bu-m-DiCumCl had higher ionization equilibrium constant relative to chlorine terminated chain ends and showed an initial reaction exotherm. On the other hand, aliphatic initiators do not have initial exotherm and they are slower initiators than t-Bu-m-DiCumCl e.g. t-BuCl results in slow and incomplete initiation [23].

Lewis acid acts as a catalyst and activates the carbocation source and sustains a dynamic equilibrium between dormant covalent species and active ion pairs. Two important features of this equilibrium are: the rate of deactivation and the equilibrium position which are governed by a combined effect of polymerization parameters including the initiation system, the solvent polarity and the temperature [22]. The rate of deactivation is an important kinetic feature as it determines the molecular weight distributions. Lewis acid complexes with the leaving group of the initiator and forms complex counteranions. The stability of the counteranions determines the rates of deactivation. A well recognized fact is that the rate of exchange reactions between the active and dormant species must be fast compared to that of propagation. Otherwise, polymodal molecular weight distribution is obtained [22]. For

instance, very strong Lewis acids are unable to provide fast rate of deactivation as they result in very stable counteranions and this leads to uncontrolled polymerizations. Therefore, weaker Lewis acids are preferred as long as they are not too weak otherwise incomplete ionization occurs and the rate of propagation decreases [24].

Ionic polymerizations are characterized by the existence of equilibrium between a variety of ionic species as visualized in Winstein spectrum (Figure 1.4) [25, 26]. Their coexistence complicates the propagation step as there is a probability that both ion pairs and free ions may propagate. Although the reactivities of ion pairs and free ions in carbocationic polymerization are found to be similar in contrast to anionic polymerizations, the difference in their lifetimes results in a bimodal molecular weight distribution with the higher molecular weight fraction belonging to free cations [27, 28, 29].

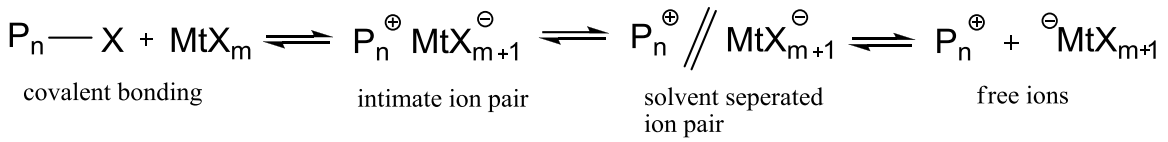

Figure 1.4. Winstein spectrum of ionic species.

However, salts with common ions, e.g. tetra-n-butylammonium chloride (n-Bu_4NCl), are reported to prevent the propagation on free cations by shifting the equilibrium to the side of ion pair. Besides; di-tert-butylpyridine, a widely used sterically hindered proton trap, reacts with protic impurities (e.g. H_2O) present in inadequately dried systems and prevents undesired initiation. Similar to salts, it is proposed that $Ti_2Cl_9^-$ counteranions are generated upon reaction of di-tertbutylpyridine with protons in the presence of $TiCl_4$. For such a system the ion pairs are the only propagating species and their propagation results in narrow molecular weight distributions [30].

A typical carbocationic polymerization is a very fast reaction with high propagation rate constant and hence chain transfer and termination reactions dominate throughout the polymerization yielding uncontrolled polydispersities and molecular weights. On the other hand, in living carbocationic polymerization the overall polymerization rate is decreased by keeping the concentration of active ion pairs low [2]. In a study of Faust *et al.*, lower rate of deactivation at decreasing temperatures and higher solvent polarity are reported to shift the

position of the ionization equilibrium towards growing species. As a result, increased overall rate of polymerizations are observed [9].

For isobutylene polymerization the most studied solvent system includes hexane/DCM mixture (60/40, v/v). The effect of solvent polarity on ionization and propagation is opposite. While polar DCM component enhances the rate of ionization, nonpolar hexane component accelerates propagation and provides homogeneous polymerization medium for nonpolar PIB.

1.3. Telechelic Polyisobutylenes

Early examples of telechelic PIBs date back to 1980s. Kennedy group reports the synthesis of chloride telechelic PIBs by using para-dicumylchloride initiator in conjuction with BCl_3 in a polar solvent medium at low temperatures *ca.* -50 °C [31]. The same group realizes that indanyl ring formation occurs with unhindered dicumyl chloride initiator at higher temperatures. On the other hand, with tri-functional cumyl chloride initiator indanyl ring formation does not occur even at higher temperatures *ca*. -30 °C. Therefore, if a dicumyl chloride initiator with meta position substituted with tert-butyl group is used, indanyl ring formations can be suppressed and perfect telechelic PIBs can be achieved at higher temperatures [32]. The success of this initiator is attributed to its sterically hindered structure.

In another study of Kennedy group, the synthetic yield of sterically hindered dicumyl chloride initiator is found to be low. Therefore, its ether derivative is studied in order to obtain chloride telechelic PIBs (Figure 1.5) [33].

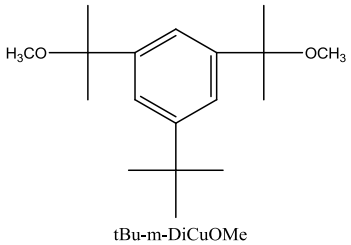

Figure 1.5. Sterically hindered dicumyl ether initiator.

Telechelic PIBs are synthesized using this initiator with BCl_3 in dichloromethane or methyl chloride at -30 °C/ -10 °C (Figure 1.6) [33].

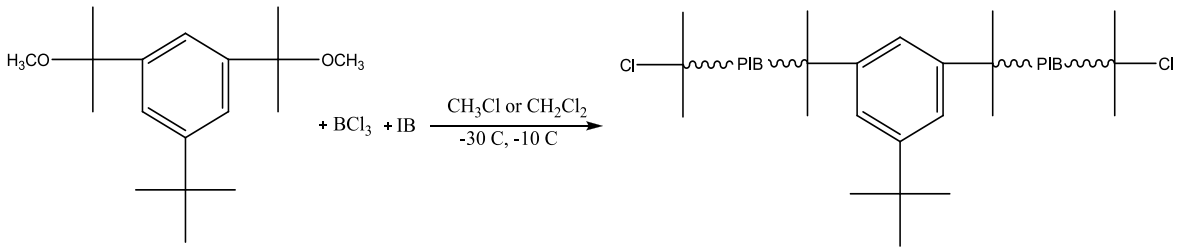

Figure 1.6. Carbocationic polymerization of isobutylene with sterically hindered dicumyl ether.

At the beginning of 1980s, tert-chloride telechelic PIBs are subjected to a series of modifications in order to synthesize the first examples of hydroxy, epoxy and aldehyde telechelic PIBs. These modifications involve telechelic exo-olefin terminal intermediate that is obtained upon dehydrochlorination of tert-chloride chain ends with potassium tert-butoxide. Further hydroboration and oxidation reactions yield hydroxy telechelic PIB, whereas reaction with m-Chloroperoxybenzoic acid (mCPBA) gives epoxy telechelics. In addition, aldehyde telechelic PIBs are prepared via subsequent isomerization reaction of epoxide telechelic PIBs with $ZnBr_2$ [34, 35]. However, this methodology has deficiencies such as long reaction times in dehydrochlorination step or costly hydroboration reagents [36]. Therefore, in the following years new methodologies involving in situ quenching are developed.

In this context, various nucleophiles are investigated and considering the possible reaction between the Lewis acids and the nucleophiles the most efficients are limited to nonhomopolymerizable olefins e.g. allytrimethylsilane and reactive aromatic compounds e.g. N-substituted pyyroles and alkoxybenzenes [37].

Allytrimethylsilane quencher first utilized by Kennedy group results in quantitative allyl terminal telechelics which are modified to epoxy and hydroxy telechelics (Figure 1.7) [38]. Quantitative allyl terminal telechelic PIBs are first reported by Wilczek and Kennedy

in a “one pot two steps” system with polar media using allyltrimethylsilane quencher and excess $TiCl_4$ relative to end groups at -70 °C [39].

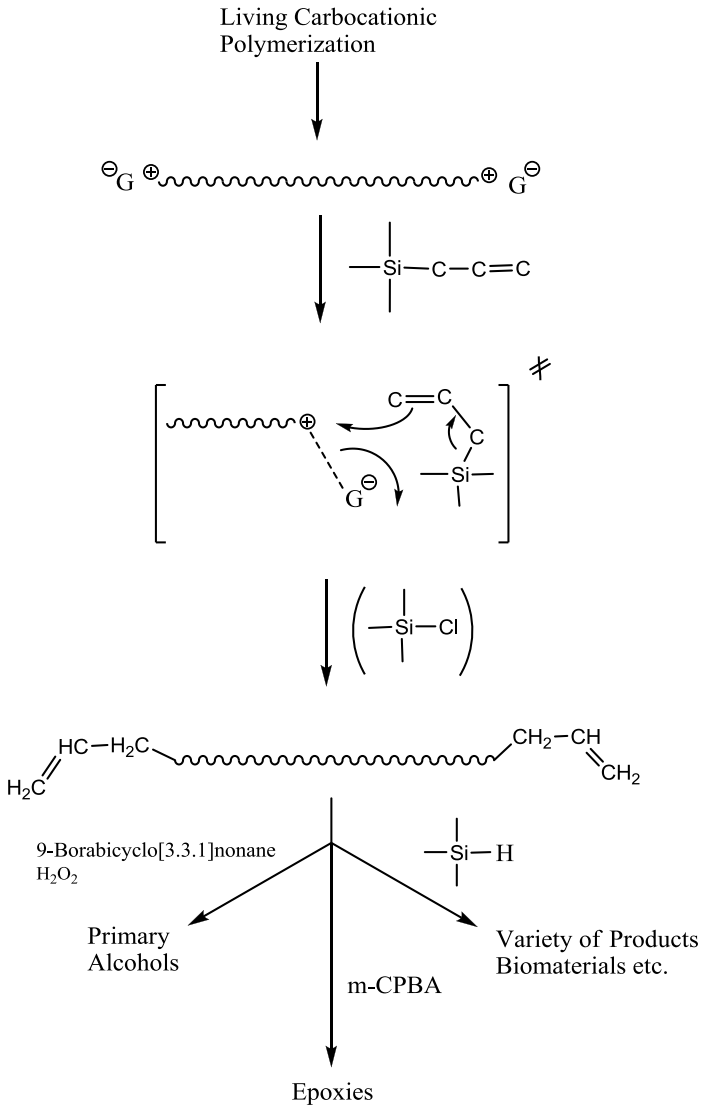

Figure 1.7. Allyl functionalization and further derivatization (G^-: counter ion) [38].

The importance of allyl functional end groups is that they can be quantitatively converted to primary bromides by well known anti-Markovnikov hydrobromination reaction [36]. Primary bromide terminals, on the other hand, are of great concern as they can be converted to a variety of functionalities which can be used as building blocks in PIB based products [37]. In a 2008 study, 100% primary hydroxy, amine and methacrylate functionalized telechelic PIBs are obtained by substitution reactions of primary bromide telechelic PIBs with corresponding nucleophiles as illustrated in Figure 1.8 [36].

Furthermore, primary amine telechelic PIBs are used as soft segments of polyurea elastomers in order to improve their hydrolytic and oxidative stabilities [40]. The success of this methodology bases on the fact that primary bromide terminals are readily undergo nucleophilic substitution reactions [41].

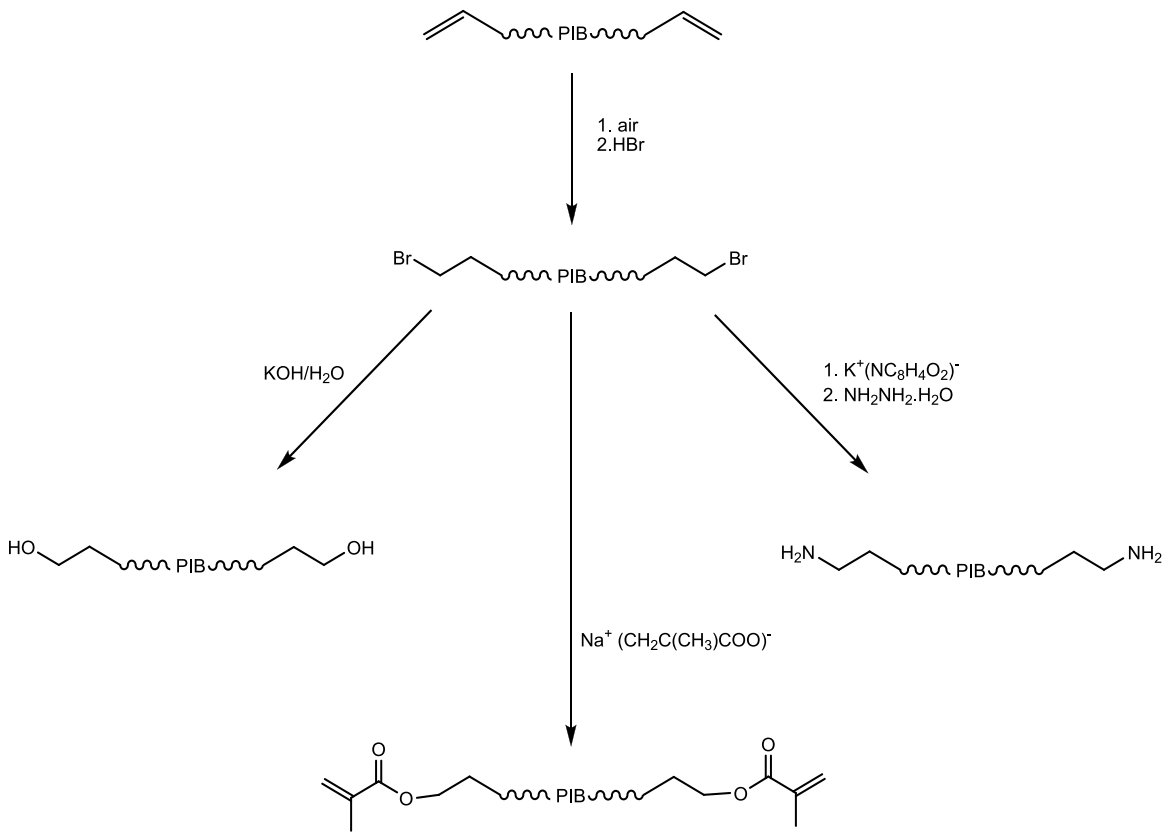

Figure 1.8. Strategy for the synthesis of –Br, –OH, –NH_2 and Methacrylate Telechelic PIB.

In a similar approach developed by Faust *et al*., allyl chloride terminals are obtained via 1,3-butadiene quencher. Then, these terminals are exposed to halogen exchange reactions with LiBr leading allyl bromide terminals. Further substitution reactions are successfully used to yield various functionalities including mono allyl azides, propargyl ethers, amines and methyl ethers [42]. Other examples of telechelic PIBs by this approach are polymerizable acrylates, methacrylates, vinyl ether and epoxy macromonomers [43].These macromonomers are potential intermediates for PIB based polymeric materials exhibiting the desired characteristics of PIB (Figure 1.9).

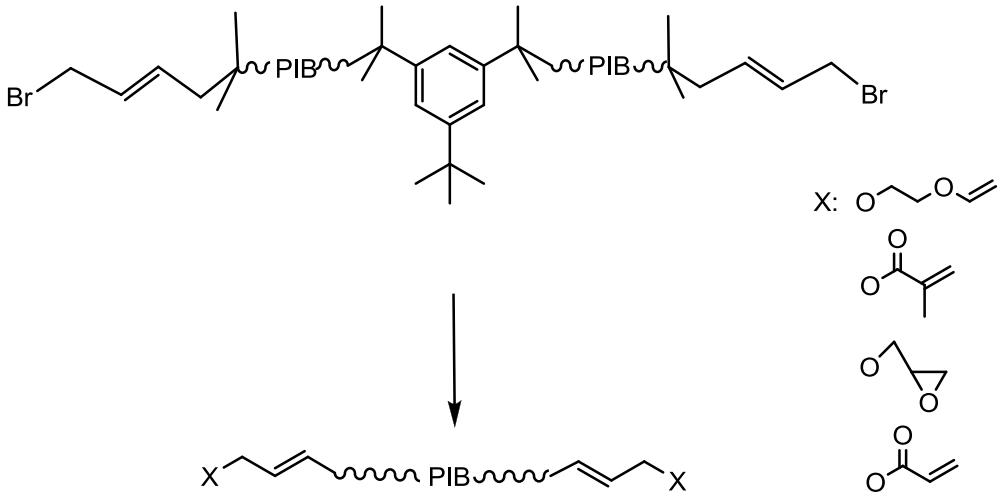

Figure 1.9. Synthesis of Vinyl ether, Methacrylate, Epoxy and Acrylate telechelic PIB.

In a series of studies of Storey *et al.*, a new synthetic approach is utilized to successfully obtain bromide and hydroxyl telechelic PIBs with direct addition reactions using reagents such as bromoethylpyrrole and N-(2-tert-Butoxyethyl)pyrrole, respectively [41,44]. These techniques differ from the previous methods by a quenching agent with its functional groups already in its structure. A key point for the hydroxy functionalities is to use of a protected quencher. The need for protection stems from the susceptibility of hydroxy groups to react with Lewis acid present as an internal component of the polymerization medium. Thus, unwanted consumption of the quencher and the Lewis acid can be prevented. In this case a deprotection step in the presence of $EtAlCl_2$ and sulfuric acid is eventually required in order to remove tert-butyl protection on the pyrrole quencher [44]. In addition, telechelic azidoalkylpyrrolyl PIB is reported. This functionality enables to combine living carbocationic polymerization with click reactions, broadening the scope of macromolecular modifications. A set of new functional groups incorporated to polymer chain ends are listed as glycidyl, acrylate, hydroxyl and dimethylamino; using propargyl glycidyl ether, propargyl acrylate, propargyl alcohol and 3-dimethylamino-1-propyne, respectively [45]. Alkoxybenzenes quenchers provide another method to achieve one-step reactions that offer functionalization with ease. 3-bromopropoxybenzene capped telechelic PIBs are converted to primary azides efficiently with sodium azide. Azides are precursors to amine groups which are the products of palladium-catalyzed hydrogenation of the former moieties [37]. 3-bromopropoxybenzene terminated telechelic PIB is also used in a multi-step reaction with

thiourea and following transformations in order to obtain thiol telechelic PIBs [47]. In a recent study of the same group amine telechelic PIBs are utilized in supramolecular copolymers with sulfonated polystyrene via ionic interactions. Sulfonate and amine groups undergo sufficient interactions to achieve a successful supramoleular structure [48].

There is a possibility of building nonsymmetric telechelic PIBs by starting with an epoxide initiator to synthesize a functional alkoxybenzene terminated PIB which is followed by click reactions [49]. In a more recent study of Binder *et al*., speciality products of PEO_m-b-PIB-b-PEO_n triblock copolymers are obtained via the same reaction pathways [50].

1.4. Thiol-ene Chemistry

Thiol based reactions are widely utilized in organic synthesis, as well as in polymer chemistry. In organic chemistry thiols are involved in synthetic transformations. For example, they are used in protection of carbonyl groups as dithioacetals which are intermediates in Raney Nickel assisted reduction of carbonyl groups to desired saturated hydrocarbon or olefin final product [51]. In polymer chemistry thiols have found numerous applications due to high efficiency of the reactions with a variety of functional groups namely alkyl halides, epoxides, acrylates, maleimides, carbon disulfide, isocyanates, carbon-carbon double and triple bonds and so on, which are grouped under Thiol-X chemistry [52]. The reactivity of thiols can be explained by the relatively long and weak S-H bond that makes H atom rather labile in ionic and radical reactions. In general terms, the bond dissociation energy of S-H bond is known to be less than that of corresponding O-H bond and as a result of this thiols are more acidic and better nucleophiles than alcohols in nucleophilic reactions [53]. Due to the same reason, H abstraction by radicals occurs with ease for S-H bond generating thiyl radicals reactive in addition reactions [53, 54].

Addition of sulfur to unsaturated hydrocarbons has been known since Goodyear's discovery of vulcanized rubber, which forms the basis of tire industry. The first report on the addition of mercaptans to alkenes producing thioethers was reported by Posner in 1905 [55]. Posner realizes that the mercapto group of phenyl mercaptan adds to the carbon of the double bond that has the higher number of hydrogen atom contrary to Markovnikov's rule.

Later it has been clarified that the addition is catalyzed by peroxides and accelerated by light [56-60]. Accordingly, in the absence of peroxides or upon addition of sulfur catalyst mercaptan addition to alkenes is reported to follow the Markovnikov's rule [58]. In 1938 Kharasch elucidated the mechanism of peroxide catalyzed addition of thioglycolic acid to styrene and isobutylene and showed that the addition is a chain reaction mediated by free radicals [59]. In the middle of 20th century Marvel and Chambers utilized the thiol-ene reaction in polymer synthesis. They synthesized linear poly(hexamethylene sulfide) from UV initiated polymerization of hexamethylenedithiol and 1,5-hexadiene in cyclohexane [60]. In 1970's most of the research focused on crosslinked network formation by UV-induced curing of polythiols and polyenes [61]. Initial studies on mechanism and kinetics of crosslinking reactions in the presence of a photoinitiator were done by Morgan *et al*.. They showed the mechanism of thiol-ene addition reaction in the presence of a variety of ketonic photoinitiators and investigated the substituent effects on curing rates [61]. Thiol-ene based networks have found commercial value in UV-radiation curing applications, some of which are protective coatings (optical fiber, electrical wire coatings etc.) and photocurable adhesives [62].

The generally accepted mechanism of UV-initiated radical thiol-ene addition reaction is shown in Figure 1.10 [63]. For an ene that is not homopolymerizable, a typical insertion process occurs through radical addition of a thiol to an ene via consecutive propagation and chain transfer reactions in a stepwise manner [64]. The process starts with the irradiation of a photoinitiator of either cleavage type (Type I) or H-abstraction type (Type II) to generate an excited triplet state. Following the generation of excited triplet states, cleavage type photoinitiators, e.g. 2,2-dimethoxy-2-phenylacetophenone (DMPA), undergo scission at α-carbon of the aromatic ketone forming initiator-derived radicals [64]. These radicals abstract a hydrogen from a thiol molecule, producing thiyl radicals (Figure 1.11) [63]. Thiyl radicals are inserted into a carbon-carbon double bond regioselectively in an anti-Markovnikov fashion in order to form thioether bond and carbon centered radicals (propagation). The process completes when the resulting carbon radicals abstract a hydrogen from another thiol molecule forming the addition product and thiyl radicals (chain transfer). In the case of Type II photoinitiators, a hydrogen donor is required which could be amines, alcohols or thiols. The photoinitiator, e.g. benzophenone, in excited triplet state abstracts hydrogen atom of a thiol producing unreactive aromatic ketyl radicals in addition to reactive thiyl radicals

(Figure 1.12) [63, 66]. In this respect it differs from the cleavage type that decompose by unimolecular reaction creating two reactive radicals capable of both abstracting hydrogen from a thiol and adding to a double bond as a side reaction [66]. The insertion process may be impeded by any radical-radical coupling reactions.

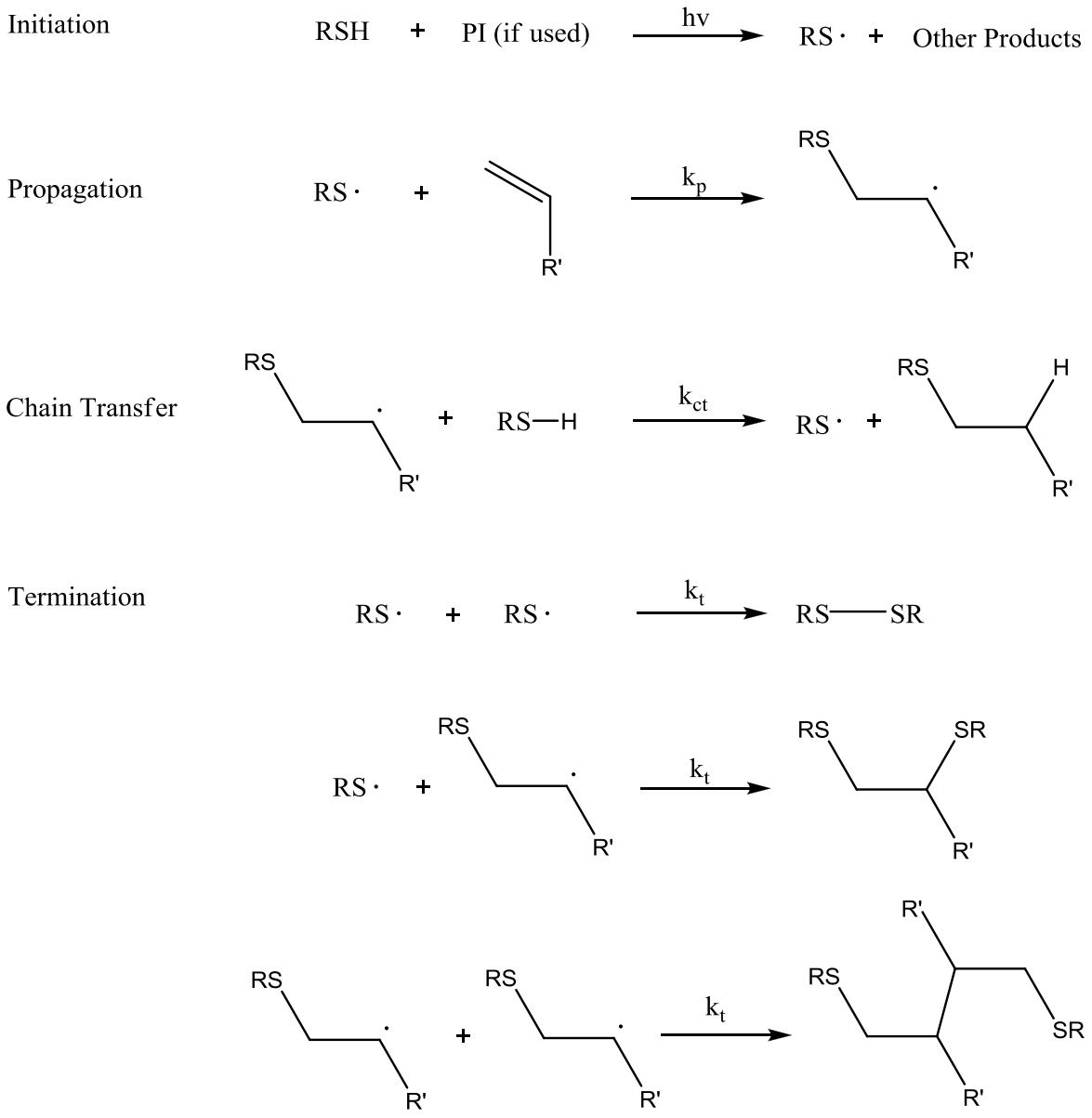

Figure 1.10. UV-initiated chain mechanism of thiol-ene reaction.

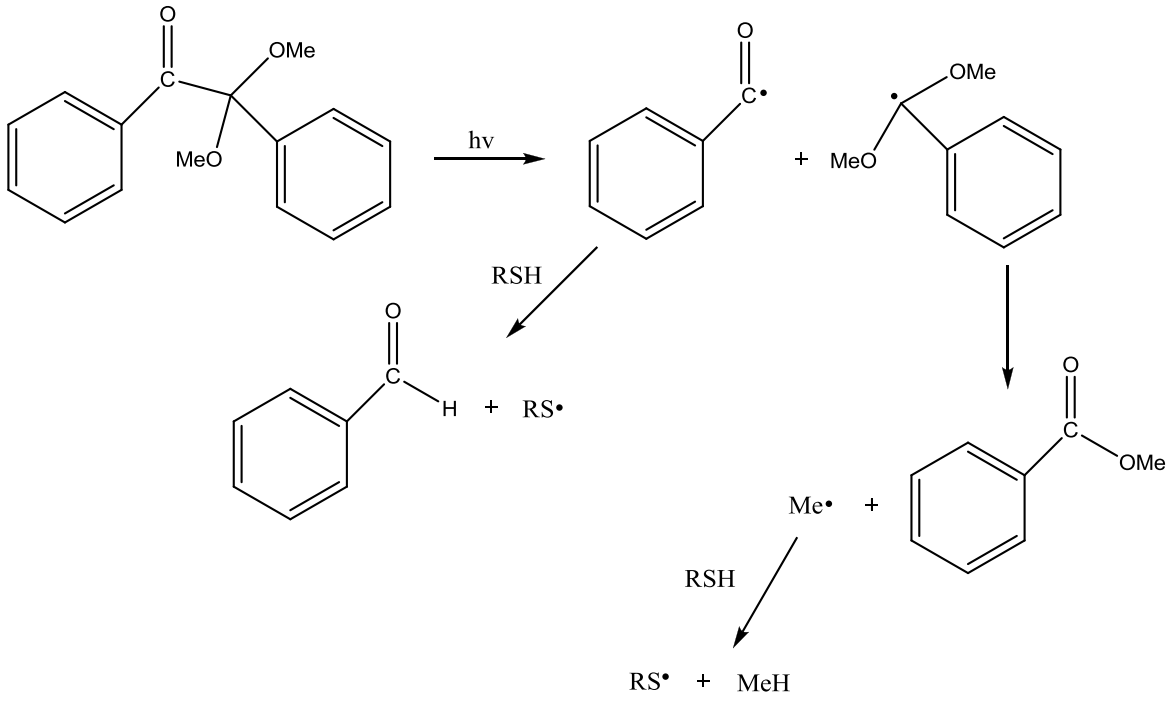

Figure 1.11. Photoinitiation with cleavage type photoinitiator (Type I).

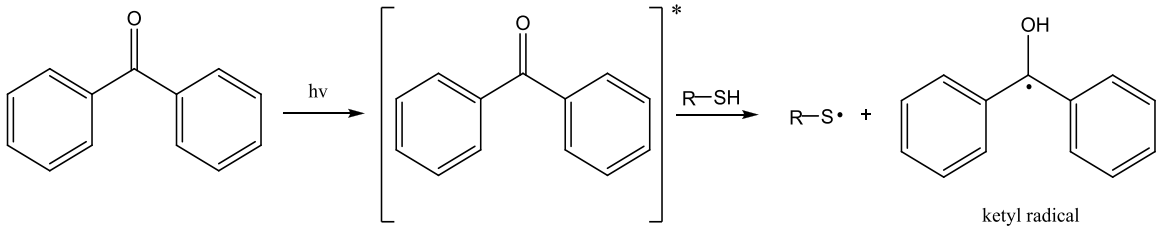

Figure 1.12. Photoinitiation with H-abstraction type photoinitiator (Type II).

In a comprehensive study by Yagcı *et al.*, efficiency of a variety of photoinitiators including Type I ((2,4,6,-trimethylbenzoyl)diphenylphosphine oxide (TMDPO) and 2,2,dimethoxy-2-phenyl acetophenone (DMPA)) and Type II (benzophenone (BP), thioxanthone (TX) and camphorquinone (CQ)) in thiol-ene reactions are compared. For this purpose several ene-thiol combinations are studied such as small molecule enes (allyl bromide (AllylBr), methyl acrylate (MA) and methyl methacrylate (MMA)) and polymeric thiol (PSt-SH) or small molecule thiol (3-mercaptopropionic acid (MPA)) and polymeric ene (PSt-Allyl). In addition to the photoinitiation, thermal initiation is also studied using 2,2′-azobis(2-methylpropionitrile) (AIBN). Almost quantitative conversions are reported with

the highest yields belonging to Type I and the lowest ones belonging to the thermal initiator [66].

Thiol-ene reactions are widely utilized in synthesis of networks and construction of an array of macromolecular structures, e.g. dendrimers, stars, hyperbranched structures and so forth, as well as in polymer modifications. Regarding such a wide utilization area, thiol-ene reactions are proven to be versatile reactions taking place in a simple reaction set up at ambient temperature, without a requirement of an inert atmosphere, i.e. they are not inhibited by oxygen, yielding quantitative products with known regioselectivity. Furthermore, UV-initiated thiol-ene reactions have an additional advantage of possibility of controlling reaction rate by simply adjusting the intensity and time of irradiation [67].

A great deal of research on thiol-ene photopolymerization was conducted by Hoyle and Bowman groups. Their research is a source of inspiration for applications of thiol-ene crosslinking in various fields, in which well defined network formation with reduced shrinkage stress and narrow glass transition temperature range are desirable such as hydrogels [68], dental restorative materials [69], soft imprint lithography [70] and shape memory polymers [71, 72, 73]. Besides, thiol-ene reaction is widely implemented in synthesis of complex macromolecular architectures like dendrimers. The harsh reaction conditions and multi step protection deprotection reactions required in the synthesis of dendrimers are challenging for researchers [72]. On the other hand, click reactions, especially photo-induced thiol-ene addition reactions are simple alternatives with the above-mentioned favorable properties. Additionally, polymer backbones and chain ends can be modified with ease via thiol-ene reactions. For examples, Schlaad and coworkers demonstrated the modification of 1,2-polybutadiene backbone with various mercaptans such as methy-3-mercaptopropionate and 3-mercaptopropionic acid [74].

Although there are numerious examples for modification of a wide variety of (co)polymers with thiol-ene chemistry, studies on polyisobutylenes are limited in number. In those initial studies commercial monofunctional PIBs such as Glissopal and Ultravis with high methyl vinylidene (exo-olefin) content were modified with an array of thiols [75,76]. Gorski *et al*. modify Glissopal with mercaptoethanol and mercaptophenol in order to introduce hydroxy functionalities which are subjected to further reactions to obtain

macromonomers. However, the model reaction with 2,4,4-trimethyl-1-pentene shows high reaction times [75]. Similarly, Blackborrow *et al*. functionalize Ultravis with an array of thiols with various functionalities like hydroxy and organosilane and it is concluded that the reaction conversions are low and must be improved [76]. In a 2010 study of Storey, high conversions are obtained while the reaction times are kept low providing click features using quantitatively functionalized low molecular weight mono- and di-functional exo-olefin PIBs [77].

In a very recent patent of Nugay and Kennedy, 1,3-di(2-methoxy-2-propyl)-5-tert-butyl-benzene, a sterically hindered difunctional ether initiator, is synthesized using a novel method. This initiator is used to synthesize ally-, exo- and endo-olefin functionalized telechelic PIBs which are modified with mercapto alcohols via radical thiol-ene addition reactions (Figure 1.13) [78].

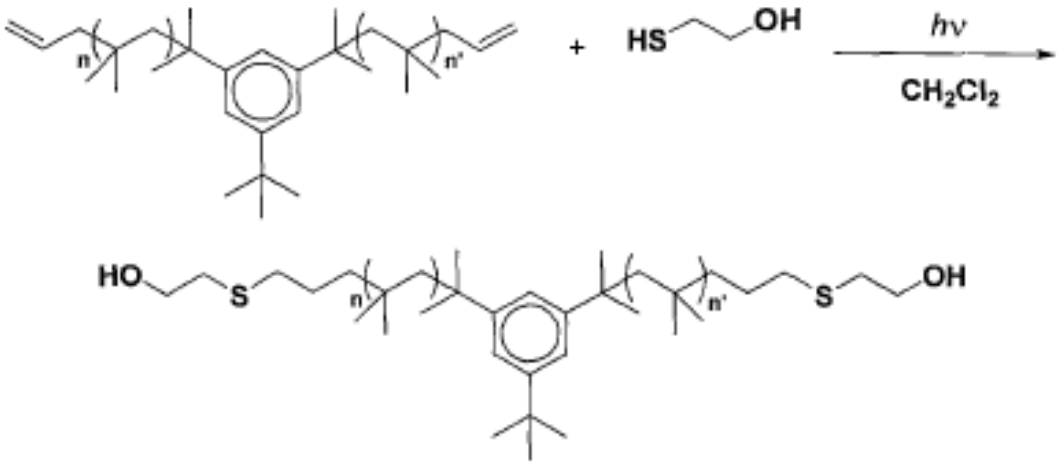

Figure 1.13. Functionalization of diallyl telechelic PIBs via radical thiol-ene chemistry.

When coupling polymeric blocks in a simple reaction set up with high yields is desired; copper catalyzed azide and alkyne 1,3-dipolar cycloaddition reactions [79], Raft-Hetero Diels-Alder cycloaddition [80], thiol-Michael [81] and thiol-ene [82] reactions are frequently used in literature. Among them photoinitiated thiol-ene reactions come forward as a valuable means of conjugation due to the convenient use of UV-light and mild reaction conditions [82]. In a collaborative study of Du Prez and Barner-Kowollik, radical thiol-ene coupling is utilized in synthesis of star polymers and block copolymers. Star polymers are

obtained from Butyl acrylate macromonomers reacting with trifunctional thiol core. Block copolymers of polystyrene-b-polyvinylacetate are synthesized by coupling each block via thiol-ene chemistry (Figure 1.14).

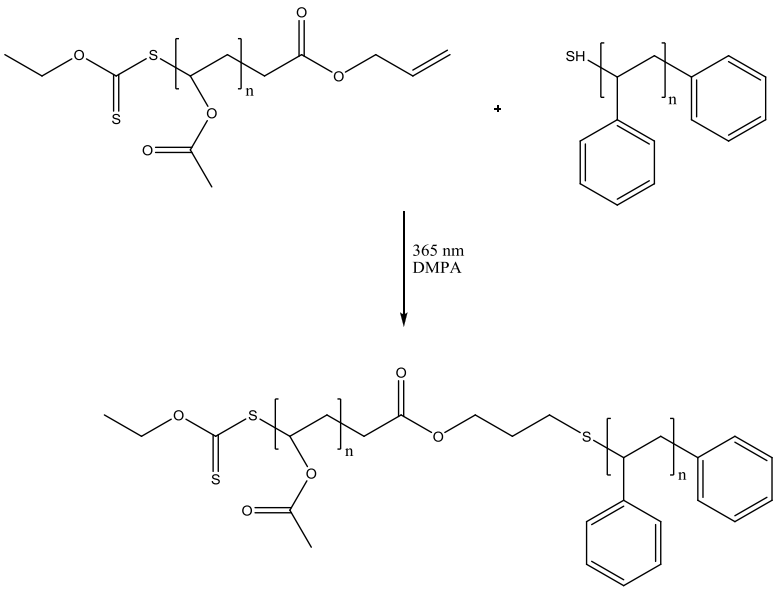

Figure 1.14. Block copolymer synthesis via radical thiol-ene chemistry.

The authors conclude that radical thiol-ene coupling reaction fails as a polymer-polymer conjugation tool in both cases when equimolar reactants are used. The low coupling efficiencies (around 23% for block copolymers) are attributed to radical-radical termination reactions and the addition of initiator derived radicals to the polymeric enes [82].

On the light of the previous findings, in our project we accomplished coupling of homopolymer blocks via radical thiol-ene coupling reactions with the aim of chain extension to higher molecular weights for the first time.

2. AIM OF THE STUDY

The overarching objective of this research is to use the thiol-ene click reactions for the preparation of high molecular weight linear rubbery or crosslinked PIBs from lower molecular weight liquid PIB precursors. For this purpose, di-telechelic PIBs carrying allyl terminal unsaturations are synthesized and reacted with bi- and multifunctional thiols via UV irradiation. The first task is to prepare a difunctional initiator, 5-tert-butyl-1,3-bis(2-chloro-2-propyl)benzene (t-Bu-m-DiCumCl) from 5-tert-butyl-1,3-dicarboxybenzene in three steps followed by the polymerization of isobutylene and in-situ end capping reaction with allyltrimethylsilane. Then the thiol-ene reactions are performed to obtain high molecular weight products and networks in the presence of 2,2-dimethoxy-2-phenyl acetophenone (DMPA) as photoinitiator in dichloromethane or using 2,2′-azobis(2-methylpropionitrile) AIBN as thermal initiator in toluene under inert atmosphere. The intermediates and the final products are all characterized in terms of molecular structure and weight, and network properties.

3. EXPERIMENTAL

3.1. System

The syntheses conducted in the project require the use of a vacuum system providing an inert reaction medium free of impurities like moisture, peroxides and atmospheric gases. The impurities might be introduced into the reaction medium via the reagents and the solvents used or via the glassware itself. Therefore, the solvents and some of the reagents must be rigorously purified by distilling over necessary desiccants. Besides, the glassware must be dried by heating under vacuum in order to get rid of adsorbed water from the surface of the glass and the inert gas (high purity grade nitrogen gas) must be further purified by passing it through desiccants and oxygen scavengers. Otherwise, the very active reagents (i.e. Grignard reagent, sodium hydride etc.) react violently upon contact with moisture and the other impurities which might also interfere with the reactions including polymerizations.

The vacuum system used in our laboratory is a dual manifold consisting of a vacuum and an inert gas line made of Pyrex glass (Figure 3.1). The vacuum line is connected to a vacuum pump system including an oil diffusion pump working in conjunction with a mechanical pump. The system is capable of reducing the pressure to 10^{-3} mmHg which is measured with a vacuum gauge (the Pirani). A liquid nitrogen cooled vacuum trap condenses water or organic vapors before they reach the pump. As an inert gas source high purity grade nitrogen gas is used after further purification by passing it through the traps containing active molecular sieves and mineral oil containing lithium metal. In this process nitrogen gas is dried and deoxygenated before introducing it into the reaction medium. The rate of the gas flow is controlled by using a needle valve.

All glassware, syringes and capillaries are dried in oven at 90 °C and removed prior to use. The distillations are done under reduced pressure. The vacuum distillation apparatus, equipped with a magnetic stirrer bar and three way glass stopcock valves with a septum and hose connection, is assembled. The ground glass joints are greased with Apiezon H grease. The apparatus is connected to the vacuum line, evacuated, checked with Tesla coil for any

leakage and then flamed. After the glassware cools down, nitrogen gas is introduced into the apparatus while controlling the rate of gas flow by bubbling it into the mineral oil containing lithium metal. Following that, the desiccant is added into the round bottom flask of the apparatus by opening it for a short time while providing a nitrogen flush through the system. The apparatus is carefully evacuated and refilled with nitrogen gas. The material to be purified is transferred onto the desiccant via syringe or capillary technique. Afterwards, freeze-pump-thaw cycles are conducted in the following way. The round bottom flask is frozen by immersing into liquid nitrogen Dewar and then evacuated. The side arm and the graduated part of the apparatus where the distillate will be collected is flamed again and the system is open to vacuum again until bubbling is observed. This process is repeated several times in order to degas the material and recover any evaporated material by condensing it back. The distillation is started upon immersion of the graduated part into the liquid nitrogen Dewar leading a pressure difference between the two parts of the apparatus enabling the distillation process. The process can also be aided by gentle warming the distillation flask via a hair dryer. Following the completion of distillation, the liquid nitrogen Dewar is removed and the frozen distillate is allowed to equilibrate to room temperature for a while and then purged with nitrogen gas.

Transfer of the liquid distillate to a previously flamed and nitrogen filled round bottom flask is done via capillary technique. Prior to use, the steel capillary is flamed under nitrogen gas flow with the aim of removing impurities that might be present in it. The technique is based on the pressure difference between the distillation apparatus and the round bottom flask. The pressure difference required to force the distillate to flow through the capillary to the flask is generated by the continuous flow of nitrogen gas through the distillation apparatus. Upon completion of the transfer process, the distillate is kept under nitrogen atmosphere.

For the UV system, a set of Philips TL 8W Blacklight Blue low-pressure mercury-vapor fluorescent 8 Watt lamps having an emission maximum at 365nm wavelength are assembled in a closed UV chamber (Figure 3.2). In both thiol-ene chain extension reactions and crosslinking reactions the intensity of light is adjusted to 6.5 mW/cm^2 and measured by using UVA/B Light Meter 850009 (Sper Scientific). The reactions are carried out at room temperature. A fan attached at the back side of the UV chamber circulates air through the

chamber and prevents increase of temperature owing to the exothermic nature of the reaction and the heat generated by the lamps. For the chain extension reactions, the lamps are positioned in such a way enabling irradiation from two facing sides of the chamber and the reactions are carried out in crimp sealed vials under nitrogen atmosphere. For the crosslinking reactions, the lamps are positioned at the top of the chamber and the reactions are carried out over Teflon mold (3 cm x 1 cm x 0.5 cm) in air.

3.2. Materials

Methanol (MeOH), sulfuric acid (H_2SO_4), diethyl ether (DEE), sodium bicarbonate ($NaHCO_3$), ammonium chloride (NH_4Cl), magnesium sulfate ($MgSO_4$), di-phosphorous pentoxide, dichloromethane (DCM), n-hexane, tetrahydrofuran (THF), titanium tetrachloride ($TiCl_4$), calcium hydride (CaH_2), sodium chloride (NaCl), 1,2-ethanedithiol and benzophenone were all purchased from Merck. 2,6-di-tert-butylpyridine (DtBP), allyltrimethylsilane (ATMS) (97%), and trimethylolpropane tris(3-mercaptopropionate) were purchased from Sigma Aldrich. Methylmagnesium bromide (MeMgBr, 3M in DEE solution), 1,6-hexanedithiol (%97), and 2,2-Dimethoxy-2-phenylacetophenone (DMPA) were purchased from Across. Na metal was purchased from Alfa Aesar. Calcium chloride anhydrous was purchased from J.T. Baker 2,2′-azobis(2-methylpropionitrile) (AIBN), and Trimethylolpropane tris(3-mercaptopropionate) were purchased from Acros. Isobutylene (IB) was purchased from Scott Speciality Gases.

3.2.1. Purification of Solvents and Reagents

Isobutylene was dried by passing through a column containing anhydrous calcium sulfate, cobalt chloride, moisture sensitive color indicator and silica gel. It was condensed into a flamed and nitrogen filled graduated cylinder immersed into an acetone-dry ice bath at -40 °C.

Allytrimethylsilane (ATMS) was purified by distillation over calcium hydride (CaH_2). Into a previously flamed and nitrogen filled distillation apparatus, CaH_2 was added by

opening it for a short time while providing a nitrogen flush through the apparatus. The system was carefully opened to vacuum, evacuated and refilled with nitrogen gas. The required amount of ATMS was transferred onto CaH_2 by means of a syringe equipped with a long steel capillary. After degassing the liquid via consecutive freeze-pump-thaw cycles, the distillation was started by immersing the graduated part of the apparatus into liquid nitrogen. Following the completion of the distillation, the apparatus was backfilled with nitrogen gas.

2,6-di-tert-butylpyridine (DtBP) was purified by the same procedure applied to ATMS.

DCM was washed with 5% NaOH and then water in order to get rid of stabilizers and impurities like alcohols. Then it was pre-dried with anhydrous $CaCl_2$ and refluxed over CaH_2 under nitrogen atmosphere. For polymerizations DCM was freshly distilled from phosphorous pentoxide. Phosphorous pentoxide was added to the previously flamed and nitrogen filled distillation apparatus by opening it for a short time while providing a nitrogen flush through the apparatus. Then the system was carefully open to vacuum, evacuated and refilled with nitrogen gas. The required amount of DCM was transferred to the distillation apparatus via capillary technique. After degassing the liquid via consecutive freeze-pump-thaw cycles, the distillation was started by immersing the graduated part of the apparatus into liquid nitrogen. Following the completion of the distillation, the apparatus was backfilled with nitrogen gas.

n-Hexane was refluxed over CaH_2 under nitrogen atmosphere and freshly distilled from sodium mirror prior to use. A piece of sodium metal with shiny surfaces is cut and placed in a previously flamed and nitrogen filled distillation apparatus by opening it for a short time while providing a nitrogen flush through the apparatus. Then, the apparatus was opened to vacuum and evacuated. Under vacuum the flask is flamed gently until the metal melts. Finally a homogeneous sodium mirror forms on the surface of the distillation flask. The required amount of n-hexane was transferred onto sodium mirror via capillary technique. After degassing the liquid via consecutive freeze-pump-thaw cycles, the distillation was started by immersing the graduated part of the apparatus into liquid nitrogen. Following the completion of the distillation, the apparatus was backfilled with nitrogen gas.

THF was purified by distillation over sodium and benzophenone. The required amount of THF was transferred into a previously flamed and nitrogen filled distillation apparatus via capillary technique. A few pieces of sodium metal with shiny surfaces and two teaspoons of benzophenone were added to the distillation flask by opening the apparatus for a short time while providing nitrogen flush through the system. The mixture was allowed to stir until the colorless solution turns to dark blue. This color indicates to the formation of sodium-benzophenone ketyl species, a radical anion acts as a water and oxygen scavenger. Afterwards, the distillation flask was frozen and degassed via consecutive freeze-pump-thaw cycles mentioned above. Then distillation was started upon immersion of the collection flask into isopropyl alcohol bath at around -60 °C. Following the completion of the distillation, the apparatus was backfilled with nitrogen gas.

3.3. Synthesis of Carbocationic initiator

Sterically hindered di-functional chloroinitiator, 5-tert-butyl-1,3-bis(2-chloro-2-propyl)benzene (t-Bu-m-DiCumCl), is prepared from the starting compound 5-tert-butylisophthalic acid in three steps. Initially dimethyl-5-tert-butyl-1,3-benzyl dicarboxylate is synthesized and then converted to 5-tert-butyl-1,3-dicumyl alcohol, t-Bu-m-DiCumCl is obtained in the final step.

3.3.1. Synthesis of dimethyl-5-tert-butyl-1,3-benzyl dicarboxylate

25 g 5-tert-butylisophthalic acid was esterified by refluxing for 2 days in 700 ml CH_3OH in the presence of 47.5 ml H_2SO_4 (Figure 3.3). The resultant colorless and transparent mixture was then cooled to room temperature and stored at 0 °C overnight. The white diester precipitated at the bottom of the round bottom flask was filtered and washed with water a few times in order to make the filtrate acid free. Then the filtrate (the diester) was dissolved in DEE and 100 ml 2% $NaHCO_3$ was added to the diester dissolved in DEE. After extraction, the DEE phase was dried over $MgSO_4$ and filtered through the sintered glass followed by solvent evaporation on rotary evaporator. The product was further dried on the high vacuum line and weighed as 21.9606 g (yield= 87.8%).

^{1}H NMR ($CDCl_3$): δ= 1.37 (s, 9H, $C(CH_3)_3$), 3.94 (s, 6H, OCH_3), 8.20-8.55 (m, 3H, Ar-CH)

3.3.2. Synthesis of 5-tert-butyl-1,3-dicumyl alcohol (t-Bu-m-DiCumOH)

10.02 g (0.04 mol) dimethyl-5-tert-butyl-1,3-benzyl dicarboxylate was dissolved in 50 ml freshly distilled THF. Grignard reaction was carried out by drop wise addition of 66.6 ml (0.2 mol) MeMgBr (3M in DEE) to the solution of the ester at 0 °C under N_2 atmosphere. After a few drops of MeMgBr were added a dusty rose color is observed. Then the color became brownish orange (Figure 3.4). After overnight reaction (Figure 3.5), the solid product was dissolved in 50 ml DEE and the solution was added to a stirred ice-NH_4Cl mixture. Following to extraction with DEE, the DEE phase was dried over $MgSO_4$ and the solids were filtered off. The solvent was evaporated on rotary evaporator and the product was further dried on the high vacuum line. Yield =94 %

^{1}H NMR ($CDCl_3$): δ= 1.34 (s, 9H, $C(CH_3)_3$), 1.60 (s,12H, $C(CH_3)_2$),7.35-7.50 (m,3H, Ar-CH)

3.3.3. Synthesis of 5-tert-butyl-1,3-bis(2-chloro-2-propyl)benzene (t-Bu-m-DiCumCl)

5 g (0.02 mol) 5-tert-butyl-1,3-dicumyl alcohol was dissolved in DCM under nitrogen atmosphere and transferred into a previously flamed reactor with $CaCl_2$ via capillary technique. HCl gas was generated by the drop wise addition of sulfuric acid onto sodium chloride and introduced into the reactor by passing through polytetrafluoroethylene (PTFE) capillary tubing under continuous nitrogen flush (Figure 3.6). During the reaction, HCl gas was bubbled through the alcohol solution at 0 °C for six hours. The excess of HCl gas was neutralized by bubbling through sodium hydroxide solution.

The solution was filtered through a fine sintered glass, concentrated on rotary evaporator and extracted with DEE and $NaHCO_3$ solution. The DEE layer was dried over $MgSO_4$. Following to filtration, the solvent was evaporated on rotary evaporator and the product was further dried on the high vacuum line. Next, it was dissolved in hexane and recrystallized in deep freeze. Afterwards, hexane was evaporated on rotary evaporator and

the product was purified on the high vacuum line. Finally, it was kept under nitrogen atmosphere.

^{1}H NMR ($CDCl_3$): δ= 1.35 (s, 9H, $C(CH_3)_3$), 2.01 (s, 12H, $C(CH_3)_2$), 7.52-7.62 (M, 3H, Ar-CH)

3.4. Polymerizations

3.4.1. Synthesis of di-Allyl Telechelic Polyisobutylenes by Carbocationic Polymerizations

A representative polymerization and in-situ end-quenching procedure for PIB-A-3 is carried out as following. A 500 ml one neck round bottom flask equipped with a magnetic stirrer bar and a rubber septum was connected to the vacuum line and flamed under vacuum and charged with nitrogen gas. The polymerization was carried out in freshly distilled n-hexane/DCM (60:40 %) solvent mixture at -80 °C under nitrogen atmosphere. t-Bu-m-DiCumCl/$TiCl_4$ initiating system was used in the carbocationic polymerization process. DtBP was utilized as the proton trap. 51 ml Hexane, 33 ml DCM and 0.4765 g (1.66×10^{-3} mol) t-Bu-m-DiCumCl were transferred into the reactor via capillary. 0.2 ml (8.3×10^{-5} mol) of a 5 ml stock solution of DtBP in hexane was added via syringe equipped with steel capillary and then the reactor was immersed into methanol bath at -80 °C. 8 ml isobutylene was condensed into a previously flamed and nitrogen filled graduated cylinder at -40 °C and charged to the reactor via capillary. Afterwards, the polymerization was started by transferring 3.66 ml (3.33×10^{-2} mol) $TiCl_4$ equilibrated to -80 °C into the reactor via capillary. After one hour, the polymerization was quenched by the drop wise addition of 8 ml (0.05 mol) ATMS. Following the quenching process for 30 min, 5 ml methanol was added to the reaction mixture.

The reactor was removed from the methanol bath and allowed to warm to room temperature. Next, the polymer solution was concentrated on rotary evaporator and precipitated into methanol. The methanol was decantated and the polymer was dissolved in hexane. The polymer solution was extracted with water and the organic layer was dried over

magnesium sulfate, filtered through a fine sintered glass. Subsequently, the solvent was evaporated on rotary evaporator and the polymer was further dried on high vacuum line.
^{1}H NMR ($CDCl_3$): δ= 0.77-0.88 (s, 12H, $C(CH_3)_2$), 1.03-1.22 (br, 2H, CH_2), 1.35-1.46 (br, 6H, $C(CH_3)_2$), 7.15 (s, 3H, Ar-H)

FTIR: 2949.31 and 2892.99 (C-H stretch), 1470.04, 1388.18 and 1364.97, 1229.56 (C-H bend), 948.78 and 911.08 (C-C stretch)

Five sets of polymerizations were carried out with the reaction conditions given in Table 3.1. In syntheses of PIB-A-1 and PIB-A-2, a second portion of $TiCl_4$ was added to the polymerization medium before end-quenching with ATMS. Synthesis of PIB-A-4 was conducted without the use of DtBP.

Table 3.1. Reaction Conditions for Quasiliving Carbocationic Polymerization of IB and End-Quenching with ATMS.

Name	IB (mol)	t-Bu-m-DiCumCl ($mol/10^{-3}$)	$TiCl_4$ ($mol/10^{-2}$)		DtBP ($mol/10^{-3}$)	ATMS (mol)
			Initiation step	Quenching step		
PIB-A-1	0.086	1.70	3.33	3.33	2.23	0.041
PIB-A-2	0.086	1.65	3.33	3.33	2.23	0.044
PIB-A-3	0.092	1.66	3.33	_	0.083	0.050
PIB-A-4	0.064	1.64	3.33	_	_	0.053
PIB-A-5	0.45	12.5	3.75	_	1.25	0.31

3.4.2. Chain Extension Reactions via Thiol-ene Chemistry

Radical thiol-ene chain extension reactions were initiated either by UV light or heating. UV initiated reactions were carried out in the UV chamber equipped with 365 nm lamps. The details of the UV chamber were as described in Section 3.1. Crimp sealed vials were used as the reactors. The vials were exposed to UV light from sideways and the light intensity was 6.5 mW/cm^2. The reactions were done under nitrogen atmosphere at room temperature. A set of reactions were carried out with 1,6-hexanedithiol at specified photoinitiator concentrations (0.1, 0.25, 0.5 and 1 equivalent per alkene) for 10 hours as shown in Table 3.2. Another set of reactions were carried out with 1 equivalent of aliphatic thiols, namely 1,6-hexanedithiol and 1,2-ethanedithiol, at given time intervals for 0.5 equivalent of DMPA per alkene as shown in Table 3.3 and Table 3.4. The products of 1,2-ethanedithiol were named as PIB-A-3-EDT-1, PIB-A-3-EDT-5, PIB-A-3-EDT-10 and PIB-

A-3-EDT-20; whereas the products of 1,6-hexanedithiol were named as PIB-A-3-HDT-1, PIB-A-3-HDT-5, PIB-A-3-HDT-10 and PIB-A-3-HDT-20 for 1, 5, 10 and 20 h reaction times, respectively.

In a typical UV light activated chain extension reaction, 0.1 g (2.94×10^{-5} mol) diallyl telechelic polymer, 4.6×10^{-3} g (2.94×10^{-5} mol) 1 equivalent of 1,6-hexanedithiol and 7.5×10^{-3} g (2.94×10^{-5} mol) 0.5 equivalent of 2,2-Dimethoxy-2-phenylacetophenone (DMPA) with respect to alkene functional group were weighed into a vial and dissolved in a minimal amount of DCM. The vial was sealed and the reaction mixture was purged with nitrogen for a minute. The vial was placed into the UV chamber and irradiated for ten hours while stirring. At the end of the reaction, the vial was opened to air and DCM was evaporated. The resulting polymer was dissolved in hexane and precipitated into methanol. Finally, methanol was decantated and the polymer was dried in vacuum oven at 30 °C.

Table 3.2. Reaction conditions for UV light initiated chain extension reactions with 1,6-hexanedithiol for 10 hours.

Name	PIB-A-3 ($mol/10^{-5}$)	1,6-hexanedithiol ($mol/10^{-5}$)	DMPA ($mol/10^{-5}$)
PIB-A-3-0.1	2.94	2.94	0.59
PIB-A-3-0.25	2.94	2.94	1.47
PIB-A-3-0.5	2.94	2.94	2.94
PIB-A-3-1	2.94	2.94	5.88

Table 3.3. Reaction conditions for UV light initiated chain extension reactions with 1,6-hexanedithiol using 0.5 equivalent DMPA.

Name	PIB-A-3 (mol/10^{-5})	1,6-hexanedithiol (mol/10^{-5})	DMPA (mol/10^{-5})	Time (h)
PIB-A-3-HDT-1	2.94	2.94	2.94	1
PIB-A-3-HDT-5	2.94	2.94	2.94	5
PIB-A-3-HDT-10	2.94	2.94	2.94	10
PIB-A-3-HDT-20	2.94	2.94	2.94	20

Table 3.4. Reaction conditions for UV light initiated chain extension reactions with 1,2-ethanedithiol using 0.5 equivalent DMPA.

Name	PIB-A-3 (mol/10^{-5})	1,2-ethanedithiol (mol/10^{-5})	DMPA (mol/10^{-5})	Time (h)
PIB-A-3-EDT-1	2.94	2.94	2.94	1
PIB-A-3-EDT-5	2.94	2.94	2.94	5
PIB-A-3-EDT-10	2.94	2.94	2.94	10
PIB-A-3-EDT-20	2.94	2.94	2.94	20

A typical thermal initiation of radical thiol-ene chain reaction at 60 °C was carried out as following; 0.1 g (3.59 x 10^{-5} mol) of diallyl telechelic polymer (PIB-A-5), 5.57 x 10^{-3} g (3.59 x 10^{-5} mol) 1,6-hexanedithiol and 5.9 x 10^{-3} g (3.59 x 10^{-5} mol) 0.5 equivalent of 2,2′-azobis(2-methylpropionitrile) (AIBN) with respect to alkene functionality were weighed into a vial, dissolved in 1 ml toluene and purged with nitrogen for 5 minutes. The vial was immersed into a silicon bath and allowed to react for 20 h while stirring. At the end of the

reaction, the resulting polymer was precipitated into methanol. Finally, methanol was decantated and the polymer was dried in vacuum oven at 30 °C.

3.4.3. Crosslinking reactions via Thiol-ene Chemistry

Into a vial 0.2120 g (7.62×10^{-5} mol) PIB-A-5, 0.02023 g (5.08×10^{-5} mol) trimethylolpropane tris(3-mercaptopropionate) 1 equivalent with respect to alkene functional group and 0.0195 g (7.62×10^{-5} mol) 2,2-Dimethoxy-2-phenylacetophenone (DMPA) 0.5 equivalent with respect to alkene functional group were weighed into a vial and dissolved in 0.5 ml DCM. The homogenized reaction mixture was poured into a Teflon mold and then the polymer was subjected to UV irradiation at 365 nm from above for 10 hours. The resulting crosslinked polymer was dried in vacuum oven at 30 °C. Following that it was post-cured in the UV chamber for 24 hours. The light intensities were 6.5 mW/cm^2 for both curing and post-curing reactions.

3.5. Characterization of Samples

3.5.1. Spectroscopic Analysis

Structural analysis of samples were performed using ^1H nuclear magnetic resonance (NMR) spectroscopy on Varian Gemini 400 MHz spectrometer at room temperature with deuterated chloroform (δ $CDCl_3$: 7.26 ppm) as solvent.

Fourier Transform Infrared (FTIR) spectra were recorded using a Thermo Scientific Nicolet 380 FTIR Spectrometer with a diamond ATR accessory. The result was evaluated by EZ Omnic. The number of scans was 32.

Raman spectrum was collected using Renishaw inVia Raman microscope with the following operation parameters: 785 nm 300 mW diode laser as the excitation source; laser intensity 15 mW; 5 s acquisition time; a total of 5 accumulations per spectrum.

3.5.2. Chromatographic Analysis

The number average molecular weights (Mn) and polydispersities of the polymers were determined by Size Exclusion Chromatography (SEC) at 30 °C using Waters Isocratic HPLC Pump with Waters 2414 Refractive Index Detector and four Waters Styragel columns HR 3, HR 4, HR 4E and HR 5E. Distilled THF was used as the mobile phase at a flow rate of 0.35 mL THF/min. Polystyrene standards used for calibration were in the range of 400-180000. Samples were injected using 100 µL Hamilton syringe.

3.5.3. Swelling and Extraction Studies

Swelling studies of vacuum-dried sample of crosslinked network were performed by gravimetric measurements. Approximately 45 mg samples were weighed and immersed in cyclohexane at room temperature. At regular time intervals the samples were taken out, excess cyclohexane was removed by gently blotting with a Kim-wipe and weighed until equilibrium swelling was reached.

The equilibrium weight swelling ratio (q_w) was calculated according to Equation 3.1 [83] and used in the calculation of the average molecular weight between crosslinks ($\bar{M}_c$), the crosslink density (ρ_c) and the mesh size (ξ).

$$q_w = \frac{m_s}{m_d} \tag{3.1}$$

In the equation, m_s is the equilibrium weight of the swollen network and m_d is the dry weight of the network. The equilibrium polymer volume fraction ($v_{2,s}$) is related to q_w by the following Equation 3.2 [83]

$$v_{2,s} = \left[1 + \frac{(q_w - 1)\,\rho_p}{\rho_{cyc}}\right]^{-1} \tag{3.2}$$

where ρ_p is the density of the crosslinked polymer (0.6894 g/cm^3) and ρ_{cyc} is the density of cyclohexane (0.78 g/cm^3). From the obtained value of $v_{2,s}$, the average molecular weight between crosslinks ($\bar{\bar{M}}_c$) was calculated according to Equation 3.3 [84]

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{(\bar{v}/V_1)[\ln(1-v_{2,s}) + v_{2,S} + \chi v_{2,s}^2]}{v_{2,S}^{1/3} - \frac{v_{2,S}}{2}} \quad (3.3)$$

where $\bar{M}_n$ is the number average molecular weight of the uncrosslinked polymer, $\bar{v}$ is the specific volume of polymer (1.1 cm^3/g for PIB) [85], V_1 is the molar volume of the solvent (108.7 cm^3/mol for cyclohexane) [86] and χ is the polymer-solvent interaction parameter (0.403 for PIB – cyclohexane) [87]. The obtained value of $\bar{M}_c$ was put into the Equations 3.4 and 3.5 in order to determine the crosslink density (ρ_c) [88] and the root mean square end to end distance of polymer chain in the unperturbed state ($(\bar{r}_0^2)^{1/2}$) [84], respectively.

$$\rho_c = \frac{1}{\bar{v}\,\bar{M}_c} \quad (3.4)$$

$$(\bar{r}_0^2)^{1/2} = \mathrm{l}\, C_n^{1/2} n^{1/2} \quad (3.5)$$

In Equation 3.5, l is the average bond length (0.154 nm) [89], C_n is the characteristic ratio of polymer (6.73 for PIB) [90], and n is the number of bonds in the crosslink which was calculated according to Equation 3.6 [91]

$$n = 3\frac{\bar{M}_c}{M_r} \quad (3.6)$$

where M_r is the molecular weight of the repeating unit (56.11 g/mol). The mesh size (ξ) was then obtained by Equation 3.7 [84]

$$\xi = v_{2,s}^{-1/3}(\bar{r}_0^2)^{1/2} \quad (3.7)$$

Extraction study of the vacuum dried sample of crosslinked networks was performed in cyclohexane. Approximately 45 mg samples were weighed and immersed in 30 ml cyclohexane which was refreshed every day. The samples were left for removal of the sol fraction for 3 days at room temperature. The extracted samples were taken out, vacuum dried for 24 h at 30 °C and weighed. The weight percent sol fraction was calculated by

$$sol\ fraction\ (\%) = \frac{(m_{dry} - m_{ex})}{m_{dry}} \times 100\% \quad (3.8)$$

where m_{dry} is the weight of the dried sample before extraction and m_{ex} is the weight of the dried sample after extraction [92].

Figure 3.1. The system used in quasiliving carbocationic polymerizations.

Figure 3.2. UV chamber used in the experiments.

Figure 3.3. Synthesis of dimetyl-5-tert-butyl-1,3-benzyl dicarboxylate.

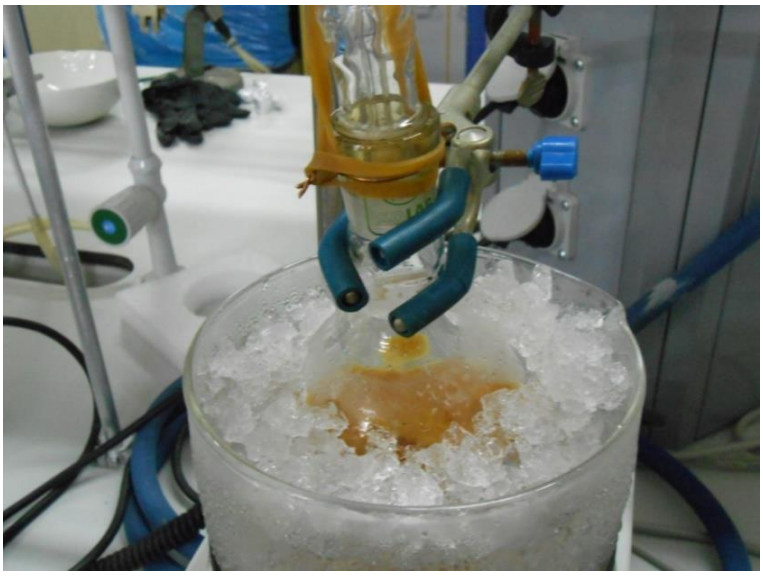

Figure 3.4. Synthesis of 5-tert-butyl-1,3-dicumyl alcohol (t-Bu-m-DiCumOH).

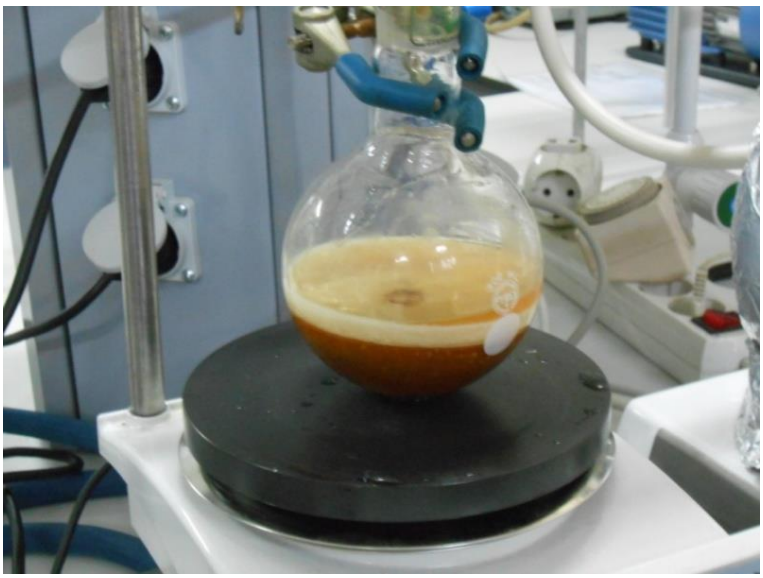

Figure 3.5. Reaction medium after Grignard reaction.

Figure 3.6. Synthesis of 5-tert-butyl-1,3-bis(2-chloro-2-propyl)benzene (t-Bu-m-DiCumCl).

4. RESULTS AND DISCUSSION

4.1. Synthesis of carbocationic initiator (t-Bu-m-DiCumCl)

4.1.1. Synthesis of dimethyl-5-tert-butyl-1,3-benzyl dicarboxylate

The synthesis of dimethyl-5-tert-butyl-1,3-benzyl dicarboxylate was done according to the literature procedure as shown in Figure 4.1 [33].

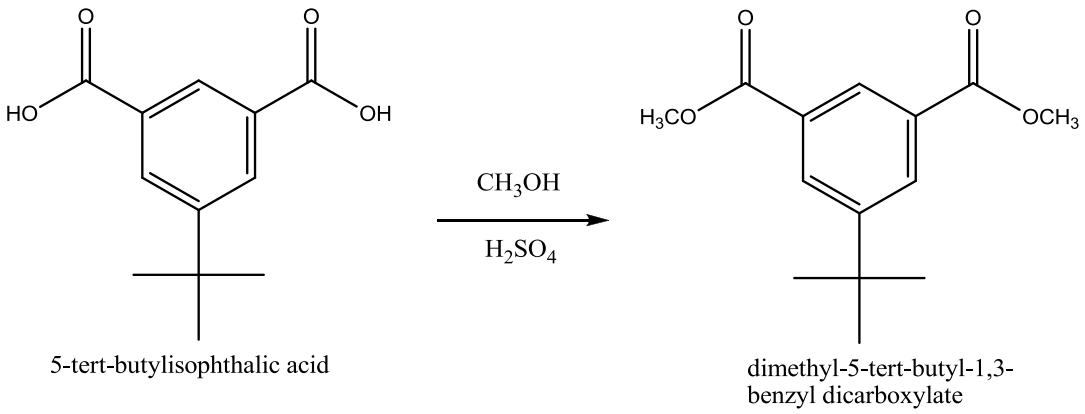

Figure 4.1. Esterification reaction of 5-tert-butylisophthalic acid.

The ^{1}H NMR spectrum in Figure 4.2 shows methyl protons of t-butyl group at 1.37 ppm (s), methyl protons of ester groups at 3.94 ppm (s) and aromatic protons between 8.2 and 8.5 ppm (m).

Quantitative conversion of the diacid compound to the corresponding diester was confirmed by an integration ratio of 3:2 for the methyl protons of t-butyl and ester groups.

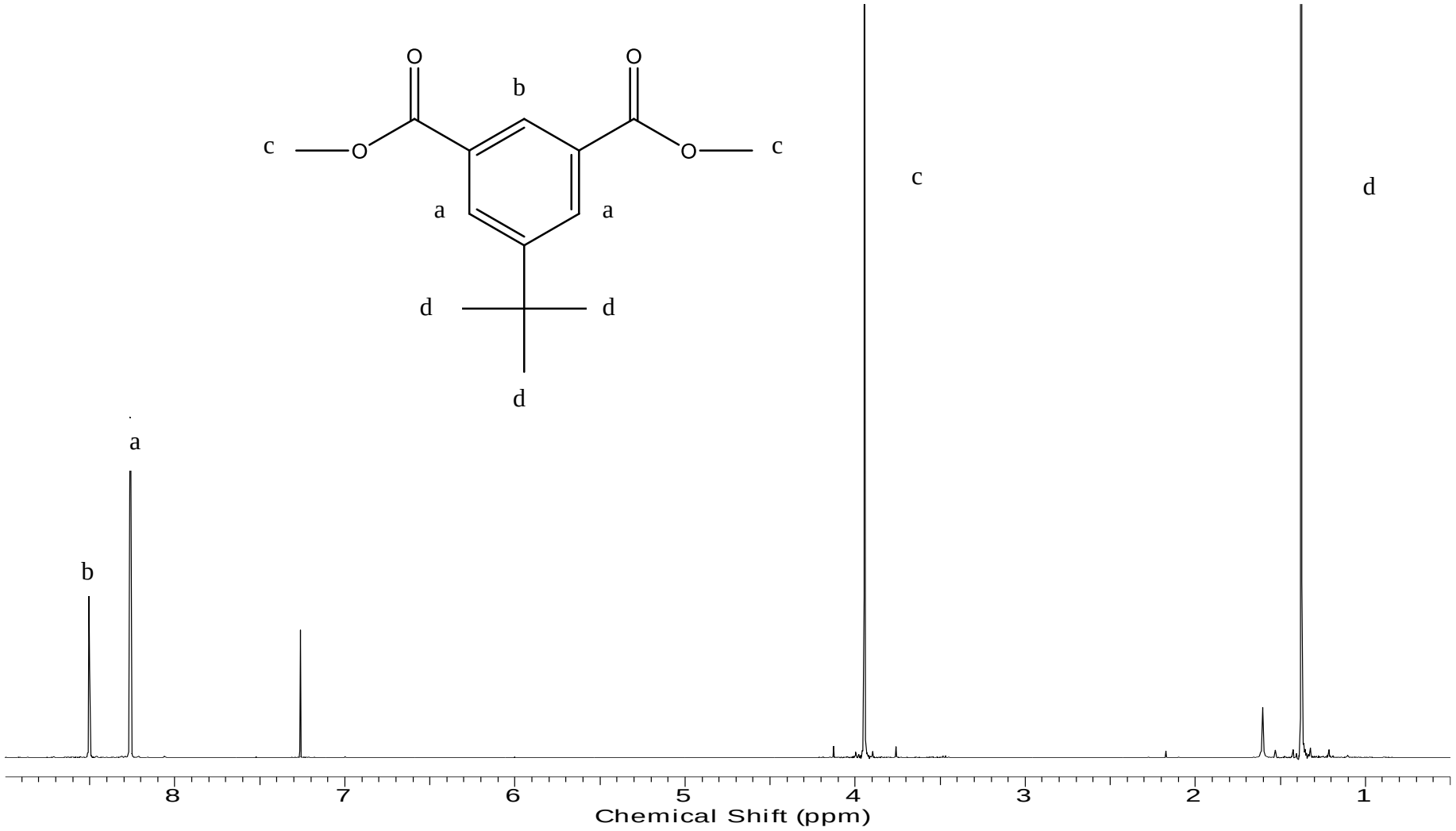

Figure 4.2. ^{1}H NMR spectrum of dimethyl-5-tert-butyl-1,3-benzyl dicarboxylate.

4.1.2. Synthesis of 5-tert-butyl-1,3-dicumyl alcohol (t-Bu-m-DiCumOH)

5-tert-butyl-1,3-dicumyl alcohol was synthesized as described in literature (Figure 4.3) [33].

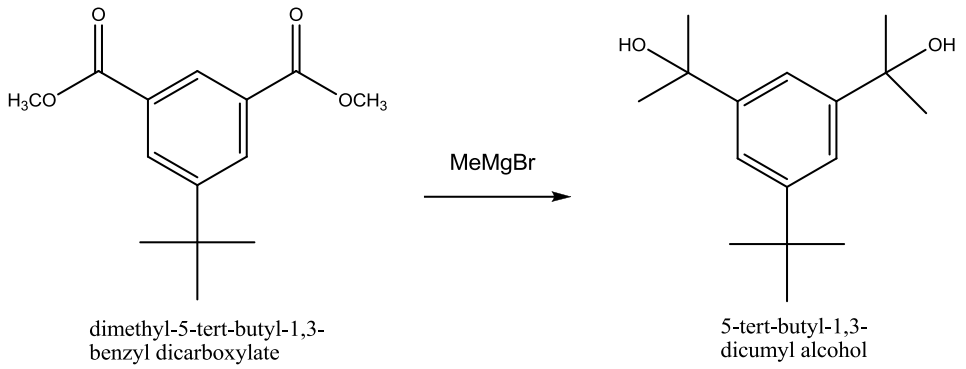

Figure 4.3. Synthesis of t-Bu-m-DiCumOH.

Figure 4.4 shows the ^{1}H NMR spectrum of dicumyl alcohol after Grignard reaction of the corresponding diester. In the spectrum, methyl protons of ester groups at 3.94 ppm were replaced by methyl protons of isopropyl groups at 1.60 ppm (s) and aromatic protons shifted upfield considerably and appeared between 7.35 and 7.50 ppm (m).

Quantitative conversion was confirmed by an integration ratio of 4:3 for methyl protons of isopropyl and t-butyl groups.

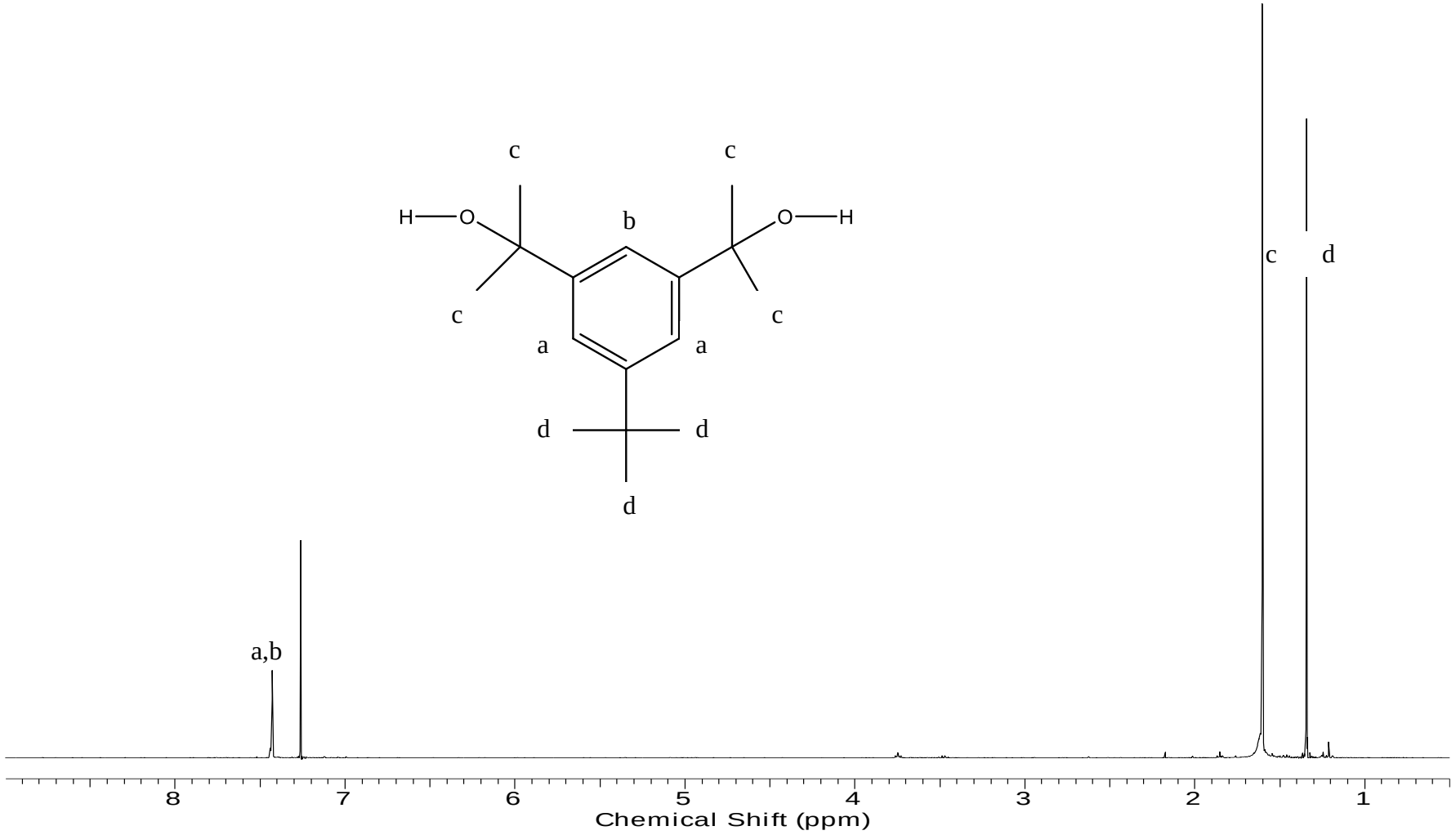

Figure 4.4. ^{1}H NMR spectrum of 5-tert-butyl-1,3-dicumyl alcohol (t-Bu-m-DiCumOH).

4.1.3. Synthesis of 5-tert-butyl-1,3-bis(2-chloro-2-propyl)benzene (t-Bu-m-DiCumCl)

The synthesis of 5-tert-butyl-1,3-bis(2-chloro-2-propyl)benzene was done in a similar manner to the literature (Figure 4.5) [93].

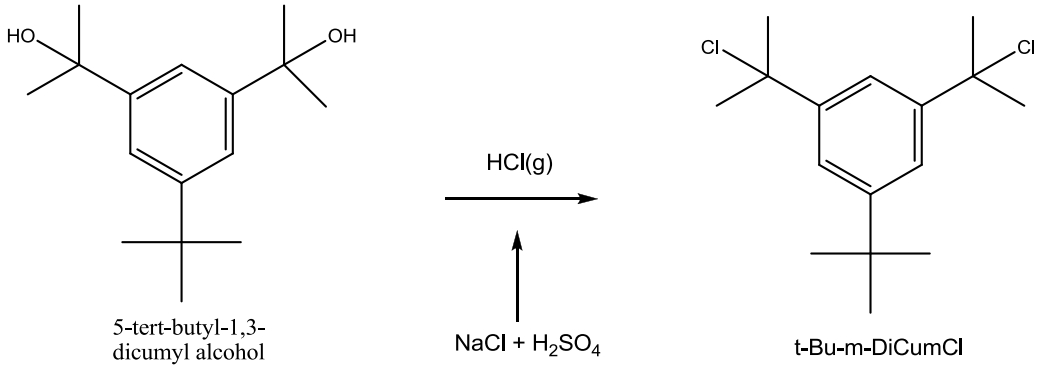

Figure 4.5. Chlorination reaction of t-Bu-m-DiCumOH.

The possibility of formation of undesired exo-olefin groups complicates the chlorination reaction of the dicumyl alcohol. If this was case the vinylic hydrogens would be observed at 5 and 5.35 ppm. The absence of these proton peaks in the ^{1}H NMR spectrum of the product indicates that the aforementioned side reaction did not occur (Figure 4.6). Methyl protons of isopropyl groups shifted downfield to 2 ppm upon chlorination.

Quantitative conversion was confirmed by an integration ratio of 4:3 for the methyl protons of isopropyl and t-butyl groups. The product was obtained with high purity and yield.

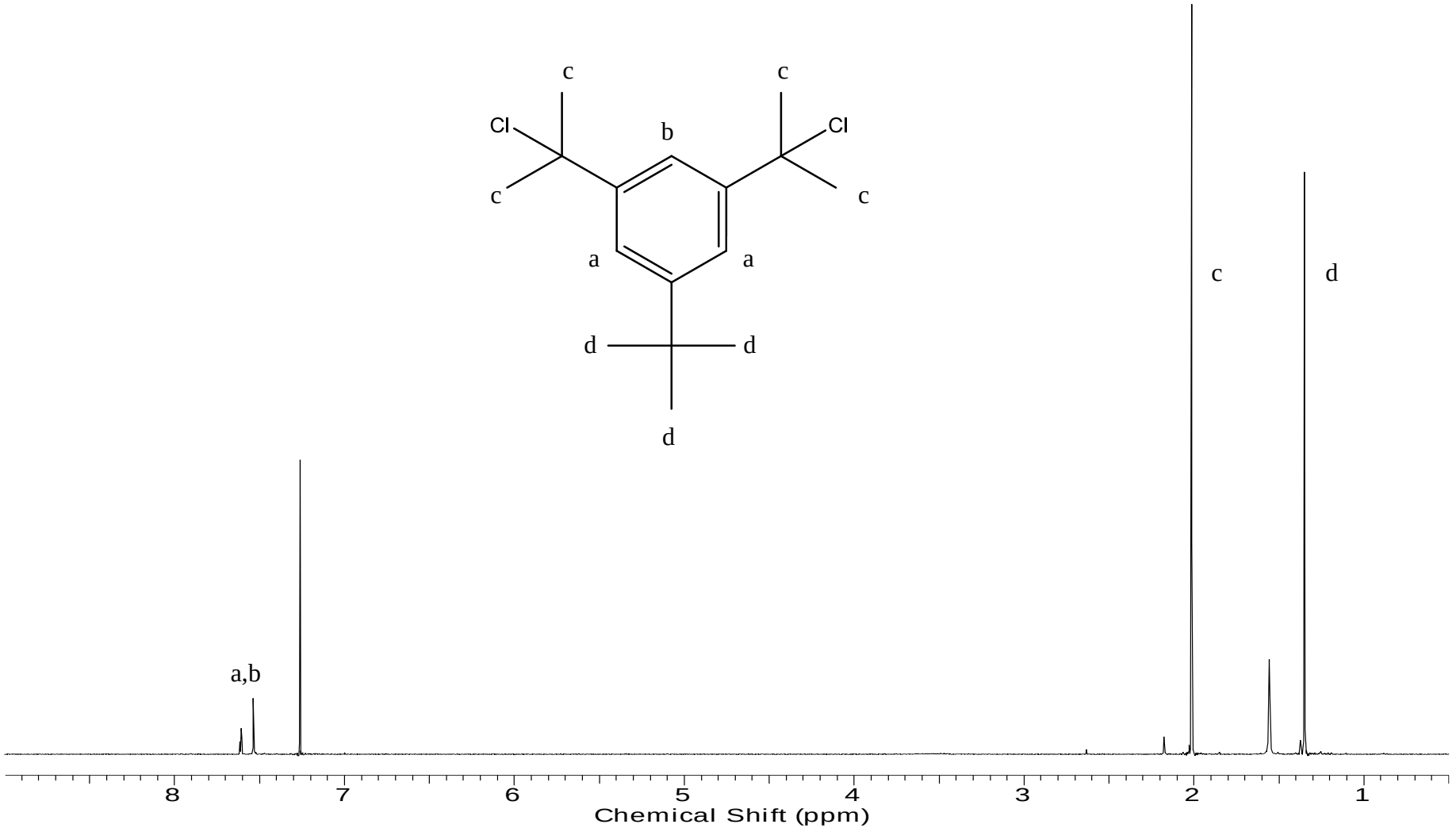

Figure 4.6. ^{1}H NMR spectrum of 5-tert-butyl-1,3-bis(2-chloro-2-propyl)benzene (t-Bu-m-DiCumCl).

4.2. Cationic Polymerizations

4.2.1. Synthesis of di-Allyl Telechelic Polyisobutylenes by Carbocationic Polymerization

Polyisobutylenes were synthesized by using t-Bu-m-DiCumCl/$TiCl_4$ initiating system via Quasiliving carbocationic polymerization. Ally functionalities were introduced into the chain ends by quenching with allytrimethylsilane as illustrated in Figure 4.7.

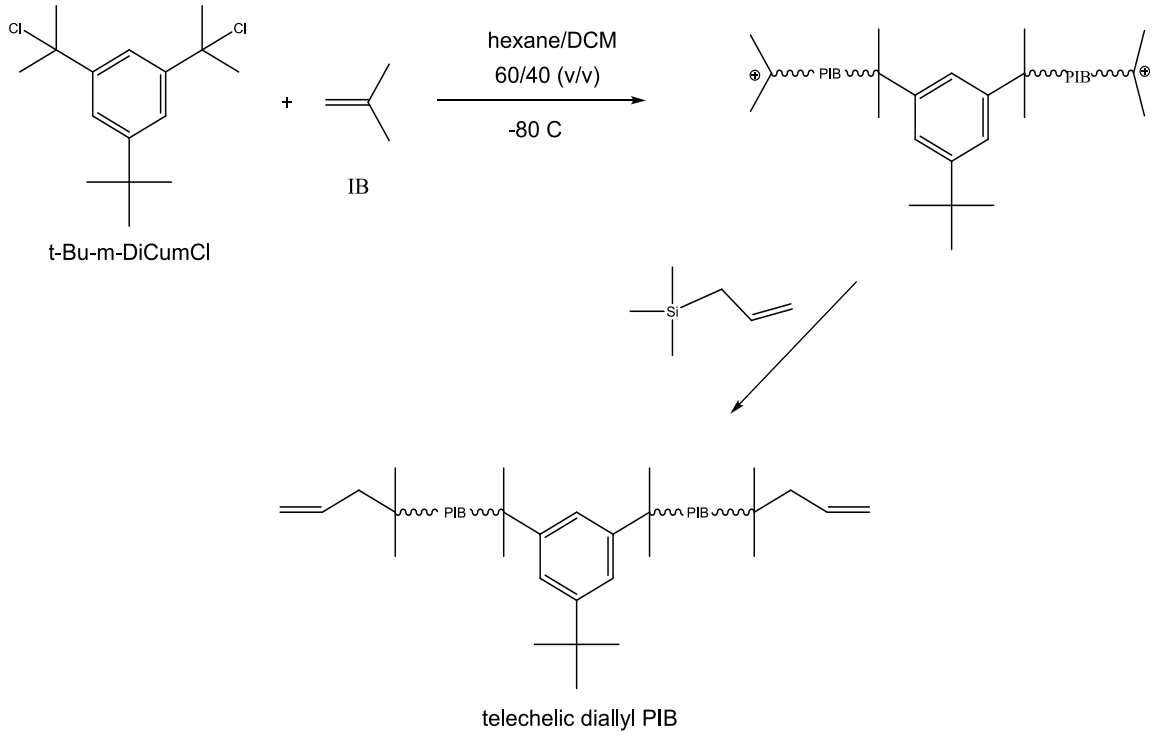

Figure 4.7. Quasiliving carbocationic polymerization of isobutylene and in-situ quenching with ATMS.

The representative ^{1}H NMR spectrum shows characteristic peaks of polyisobutylene (Figure 4.8). The peaks between 1.03-1.22 ppm correspond to the methyl protons and the peaks between 1.35-1.46 ppm correspond to the methylene protons of the backbone. Aromatic hydrogens of the initiator appear at 7.15 ppm. The two distinct peaks appearing between 5.6-6.0 and 4.75-5.20 ppm correspond to allylic hydrogens, which indicate the successful end functionalization.

In the FTIR spectrum of PIB-A-3 stretching and bending peaks typical of PIB were observed. C-H bond stretching at 2949.56 cm^{-1} and 2892.99 cm^{-1}, C-H bond bending at 1470.04, 1388.18, 1364.97, 1229.56, 948.78 and 911.08 cm^{-1} were clearly seen in Figure 4.9. [94]. In literature C=C bond is generally reported at 1636 cm^{-1} [95]. However, these bonds cannot be distinguished from the background noise (Figure 4.9). Moreover, these peaks have very low intensity with respect to dominant PIB backbone peaks due to very low content of allylic groups; which diminish their visibility. Therefore, ^{1}H NMR spectrum is more suitable to detect the presence of these bonds.

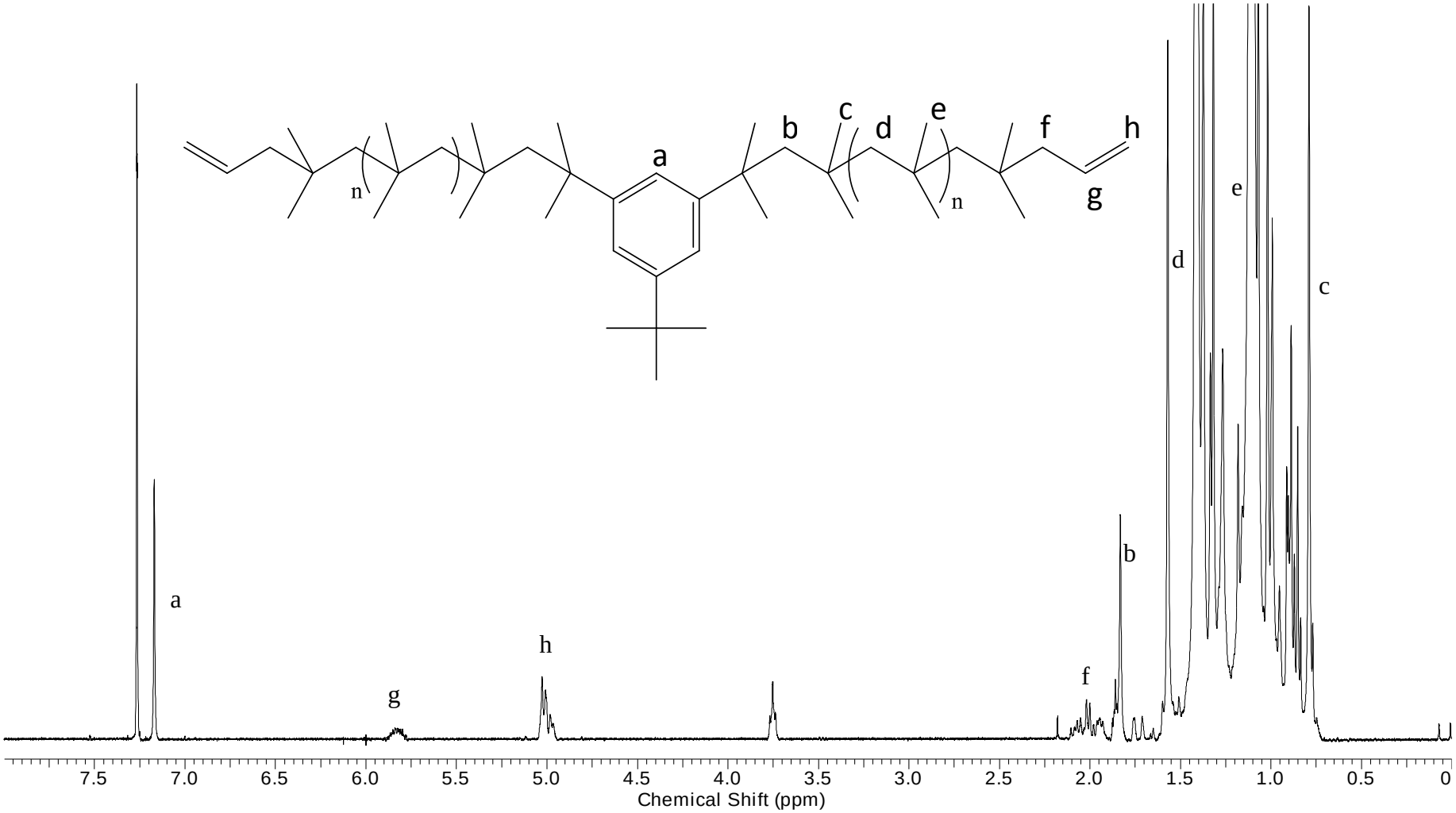

Figure 4.8. ^{1}H NMR spectrum of PIB-A-3.

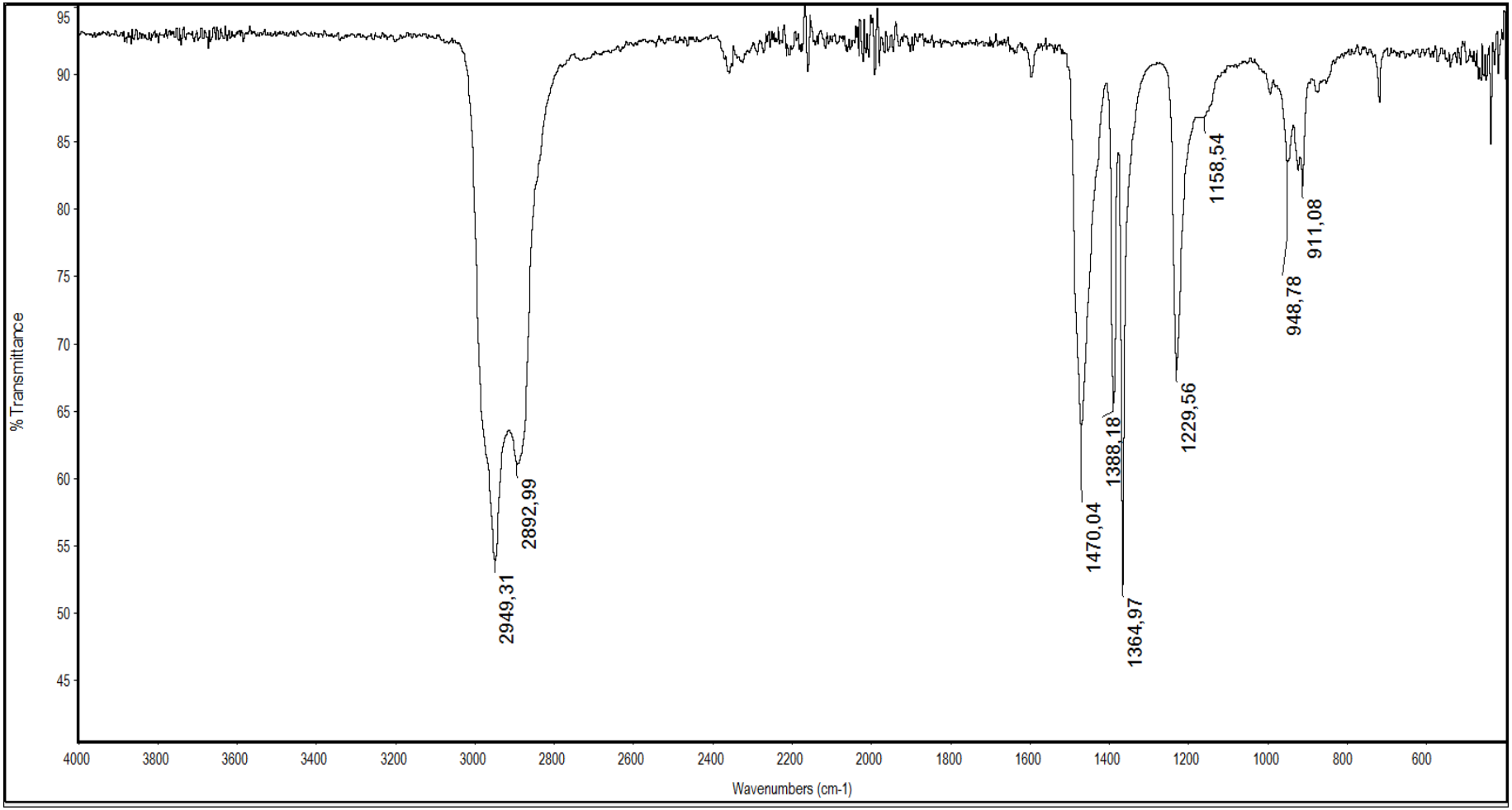

Figure 4.9. FTIR spectrum of PIB-A-3.

Table 4.1. Molecular Weight Analysis data of allyl end-capped PIBs.

Name	M_n *a*	M_n *b*	M_w *b*	M_w/M_n *b*
PIB-A-1	3394	9490	16718	1.76
PIB-A-2	2732	8222	15327	1.86
PIB-A-3	3400	5500	6462	1.17
PIB-A-4	1822	3695	6909	1.87
PIB-A-5	2783	3506	4571	1.30

a calculated from ^{1}H NMR

b calculated from SEC

The molecular weights and polydispersity indices of allyl end capped PIBs calculated by using ^{1}H NMR spectra and SEC were indicated in Table 4.1. The methyl protons of the polymer backbone (1.03-1.22 ppm) and the methyl protons of the first isobutylene units attached to the bifunctional initiator (0.78 ppm) were used to calculate the M_n values. A poor correlation between ^{1}H NMR and SEC results may be attributed to two factors. First, PIB molecular weight determination was done by using calibration curve prepared by polystyrene standards which may lead to deviation from theoretical results. Secondly, poor resolution of ^{1}H NMR baseline prevents making accurate calculations leading to variations in calculated molecular weights. The quality of the baseline could not be improved by increasing the acquisition time or repetition of scans.

The SEC data of PIB-A-3 shows a small high molecular weight shoulder (Figure 4.10). This may be attributed to some free ion formation during the polymerization. Additionally, a possible disruption of the initiator structure by elimination of chloro leaving group may also lead to high molecular weight product. This undesired reaction would lead to formation of double bond on the initiator which could be detected by ^{1}H NMR spectroscopy. Our

spectrum in Figure 4.6 indicates that such vinylic protons are not present and our initiator was pure prior to the polymer synthesis. However, occurrence of this type of elimination reactions is thought to be possible even in low temperature storage conditions. This might affect the activity of initiator overtime. However, it can be safely concluded that the molecular weight distributions are in well agreement with the ones reported in the literature (33).

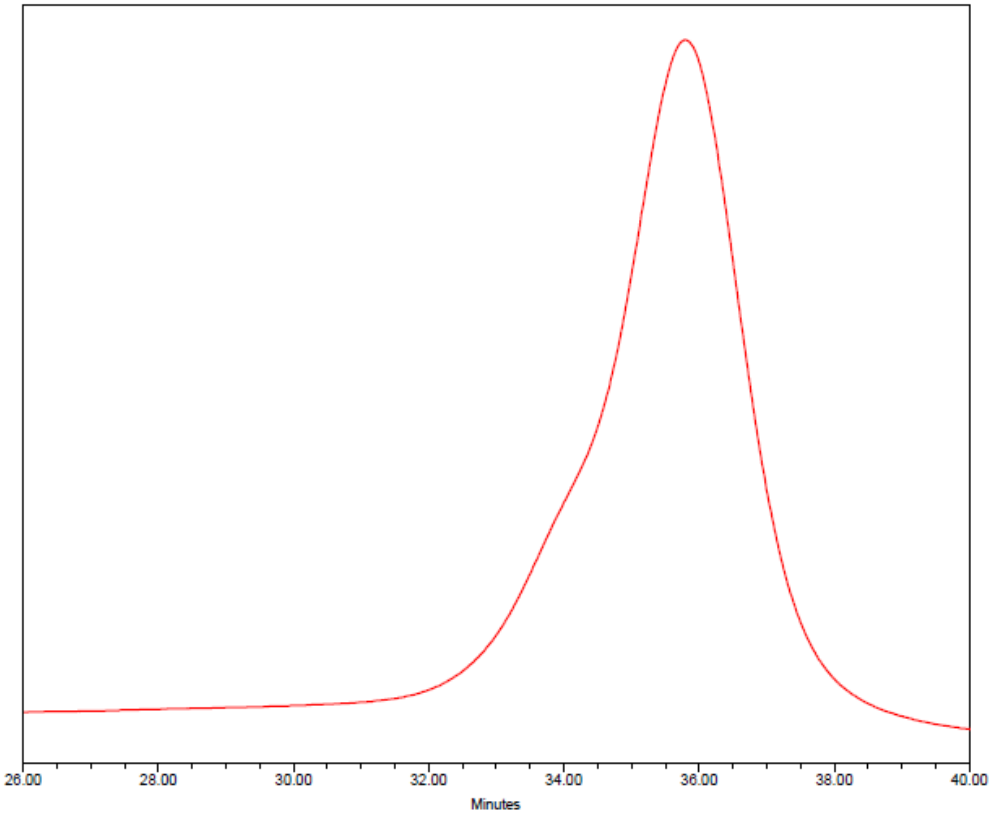

Figure 4.10. SEC data of PIB-A-3.

4.3. Thiol-ene chain extension reactions

Up to date there has been limited application of radical thiol-ene chemistry on polymers produced via quasiliving carbocationic polymerization [73]. These studies concentrate mainly on functionalization of the chain ends. However, radical thiol-ene polymer-polymer coupling reactions have not been utilized to polymers synthesized by quasiliving carbocationic polymerization [82]. The only example as a polymer-polymer

conjugation tool was investigated in a collaborative study of Du Prez and Barner-Kowollik. The polymeric products were obtained via RAFT technique. It was certainly stated that radical thiol-ene chemistry cannot be regarded as a click reaction in order to join two polymer blocks from their chain ends [82].

The reasons for failure of polymer-polymer coupling are examined in a 2013 study of kinetic modeling [96]. It is revealed that low concentration of ene and thiol functional chain ends lead to a decrease in addition and transfer rates for polymer-polymer systems compared to small molecule systems. Radical-radical recombination reactions are unavoidable and moreover photoinitiators use up ene functionalities which prevents formation of desired insertion products and hence reduce coupling efficiencies. The effect of diffusional limitations on addition and transfer rates is also questioned. It is concluded that the low coupling efficiencies cannot be attributed limitations on addition and transfer reactions which already have very low rate coefficients due to their chain length dependencies [96].

It is worth to say the coupling of homopolymer blocks via radical thiol-ene chemistry for chain extension to higher molecular weights was achieved for the first time in our study. This creates an opportunity to synthesize desired molecular weight linear polyisobutylenes by simply exposing the mixture of polymer, thiol, and photoinitiator to UV irradiation.

The reaction path which was followed in our experiments was given in Figure 4.11.

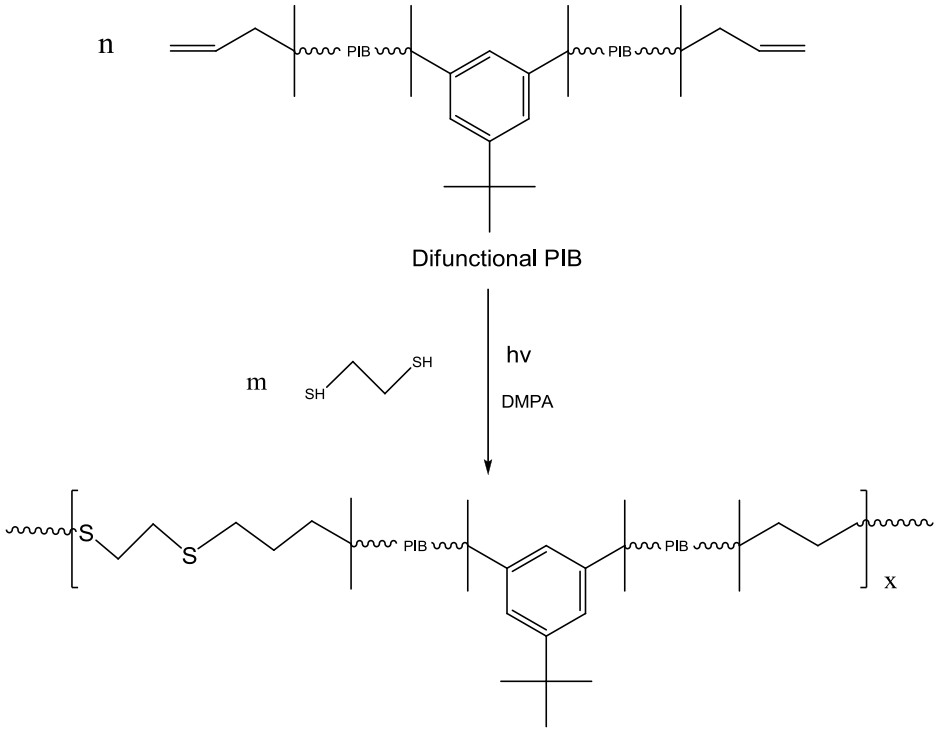

Figure 4.11. Radical thiol-ene chain extension reaction of diallyl telechelic PIB with dithiol.

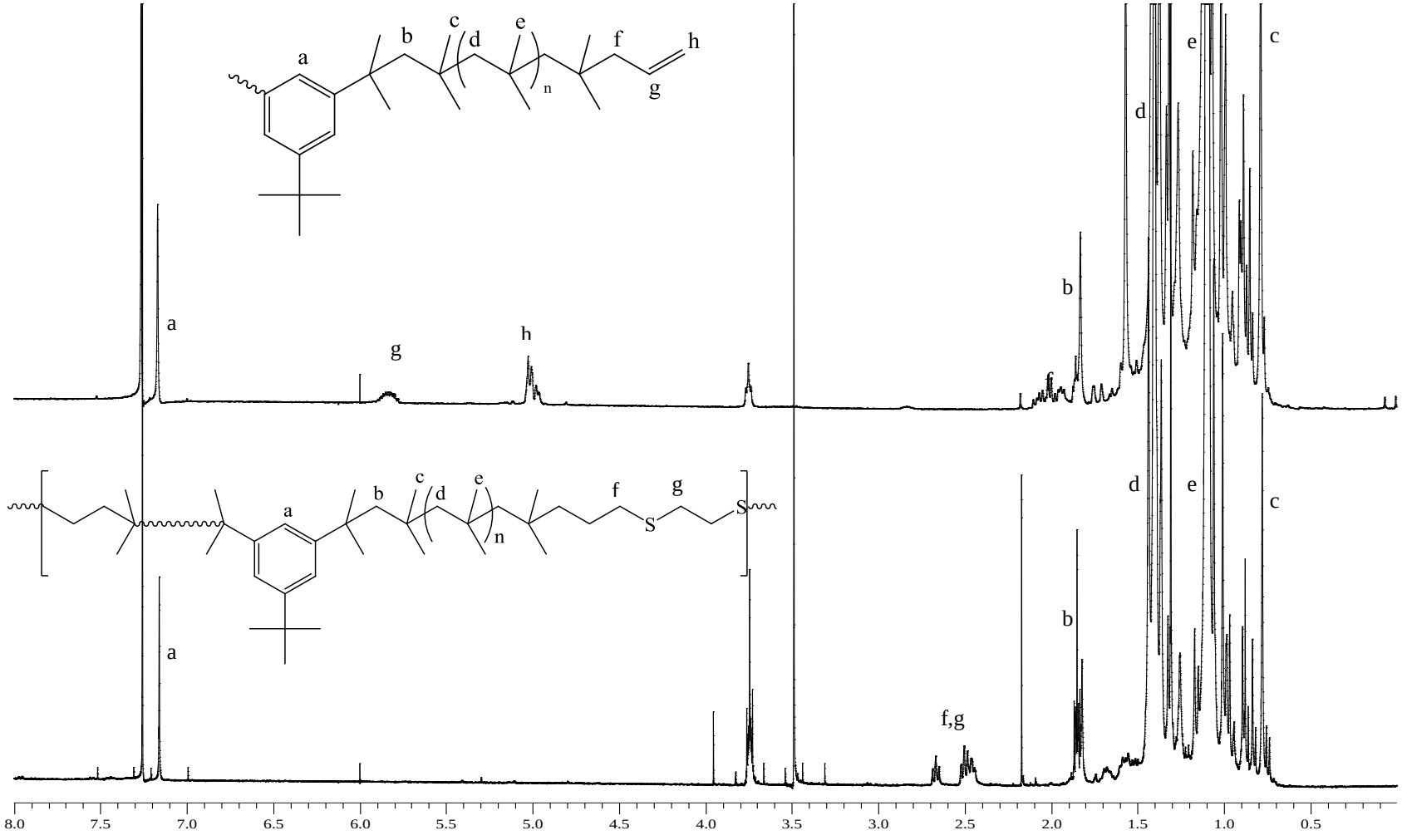

Figure 4.12. ^{1}H NMR spectra of a) PIB-A-3 and b) PIB-A-3-HDT-20.

In Figure 4.12, the overlay of ^{1}H NMR spectrum of PIB-A-3, and PIB-A-3-HDT-20, which is the result after thiol-ene chain extension reaction, is given. The disappearance of characteristic two peaks appearing between 5.6-6.0 and 4.75-5.20 ppm correspond to allylic hydrogens and the formation of new thioether peaks between 2.4-2.7 ppm are an indication of successful conjugation.

4.3.1. Effect of Photoinitiator concentration

Effect of photoinitiator concentration on chain extension efficiency was monitored by using SEC technique. Figure 4.13 shows the SEC traces of the starting polymer PIB-A-3 and chain extended products obtained by radical thiol-ene addition of HDT to PIB-A-3 with different amounts of photoinitiator DMPA for 10 h reaction time. The products were named as PIB-A-3-0.1, PIB-A-3-0.25, PIB-A-3-0.5 and PIB-A-3-1 for 0.1, 0.25, 0.5 and 1 equivalent of DMPA with respect to alkene functionality, respectively.

Examination of the SEC data (Figure 4.13) reveals that polymer molecular weights can be extended to desired values by adjusting the concentration of DMPA. The variation in the molecular weights is summarized in Table 4.2.

An increase in photoinitiator concentration results in a regular shift of molecular weight distribution curve to higher molecular weight side up until 0.5 equivalent of DMPA and further increase in photoinitiator results in a decrease in molecular weights. This result is consistent with literature since the occurrence of side reactions becomes significant beyond the optimum amount of DMPA [96]. Under the given reaction conditions, it can be clearly seen that in order to reach maximum molecular weight average it is sufficient to use 0.5 equivalent photoinitiator.

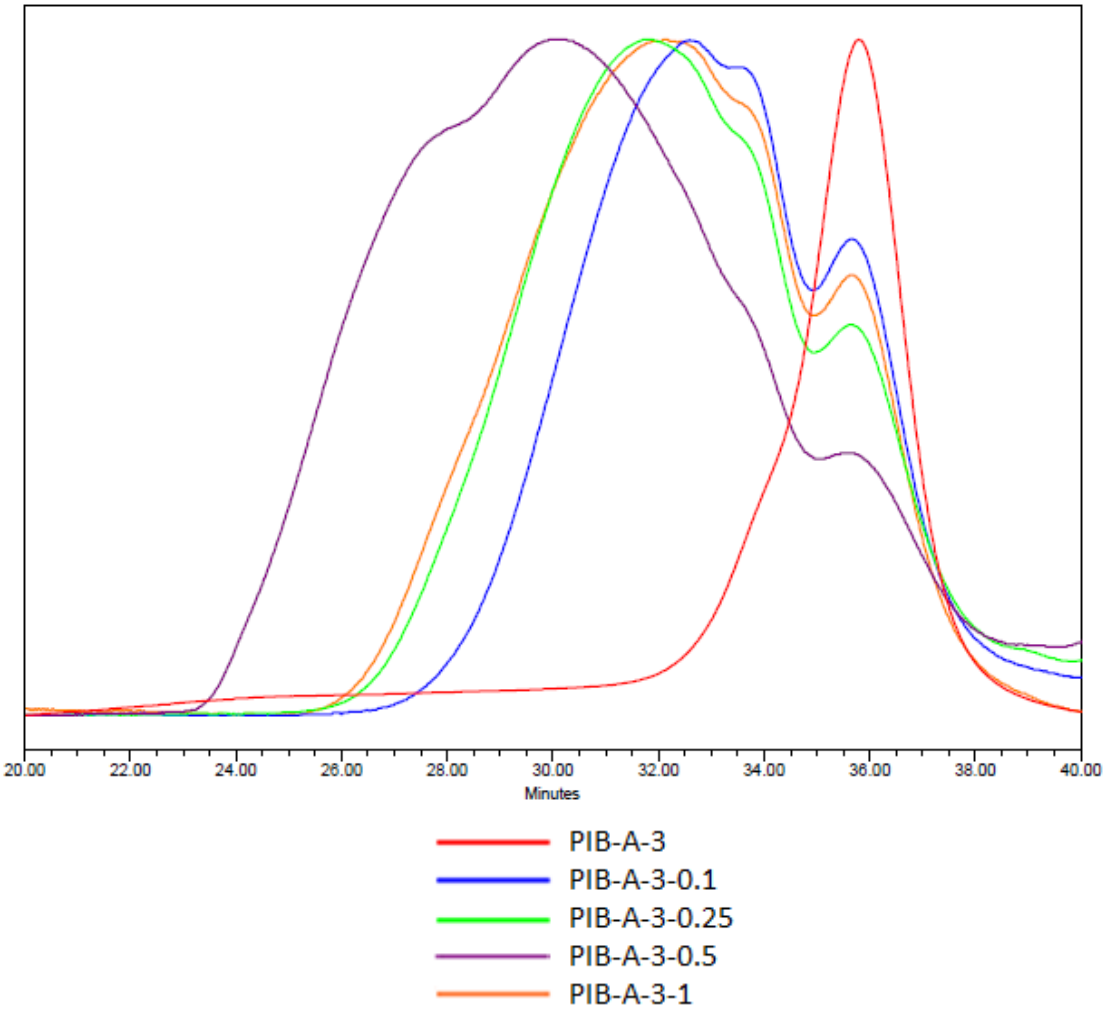

Figure 4.13. SEC data of PIB-A-3 and chain extended polymers obtained using varied amounts of DMPA.

Table 4.2. Summary of SEC analyses of chain extended polymers prepared using varied amounts of DMPA.

Name	DMPA (equiv.)	M_n	M_w	M_w/M_n
PIB-A-3	-	5500	6462	1.17
PIB-A-3-0.1	0.1	10889	19309	1.77
PIB-A-3-0.25	0.25	13225	26157	1.98
PIB-A-3-0.5	0.5	21490	71291	3.32
PIB-A-3-1	1	12778	26837	2.10

4.3.2. Effect of Reaction Time and Dithiol Nature

It was thought that the solubility of the dithiol in the nonpolar PIB based reaction medium would be a determinative effect on the success of the extension reactions. It is also known that thiols with the short alkyl chain would have a lower solubility in above mentioned medium. Therefore, two types dithiols having short and long alkyl groups namely ethanedithiol (EDT) and 1,6 hexanedithiol (HDT) were examined in the chain extension reactions in different time intervals.

The SEC traces of the starting polymer PIB-A-3 and chain extended products obtained by radical thiol-ene addition of EDT to PIB-A-3 at specific time intervals are given in Figure 4.14. The products were named as PIB-A-3-EDT-1, PIB-A-3-EDT-5, PIB-A-3-EDT-10 and PIB-A-3-EDT-20 for 1, 5, 10 and 20 h reaction time, respectively. The variation of the molecular weights is summarized in Table 4.3.

Upon examination of the SEC data (Figure 4.14), it is obvious that the prominent increase in molecular weight occurs within the initial 5 hour period. The intensity of the low molecular weight shoulder decreases as the low molecular weight fragments get involved in chain extension. The coupling efficiency continues to improve up to 10 hours. As the reaction was allowed to continue until 20 h, the increase in molecular weight was ceased. Several factors could be responsible for the observed trend. As the polymer chain lengths become greater with conversion, functional groups at the chain ends get trapped and their ability to interact diminishes considerably. Besides, the concentration of the active groups decreases overtime due to the step-growth mechanism of the reaction. Therefore, it is stated that maximum conversions were reached within 10 h reaction time.

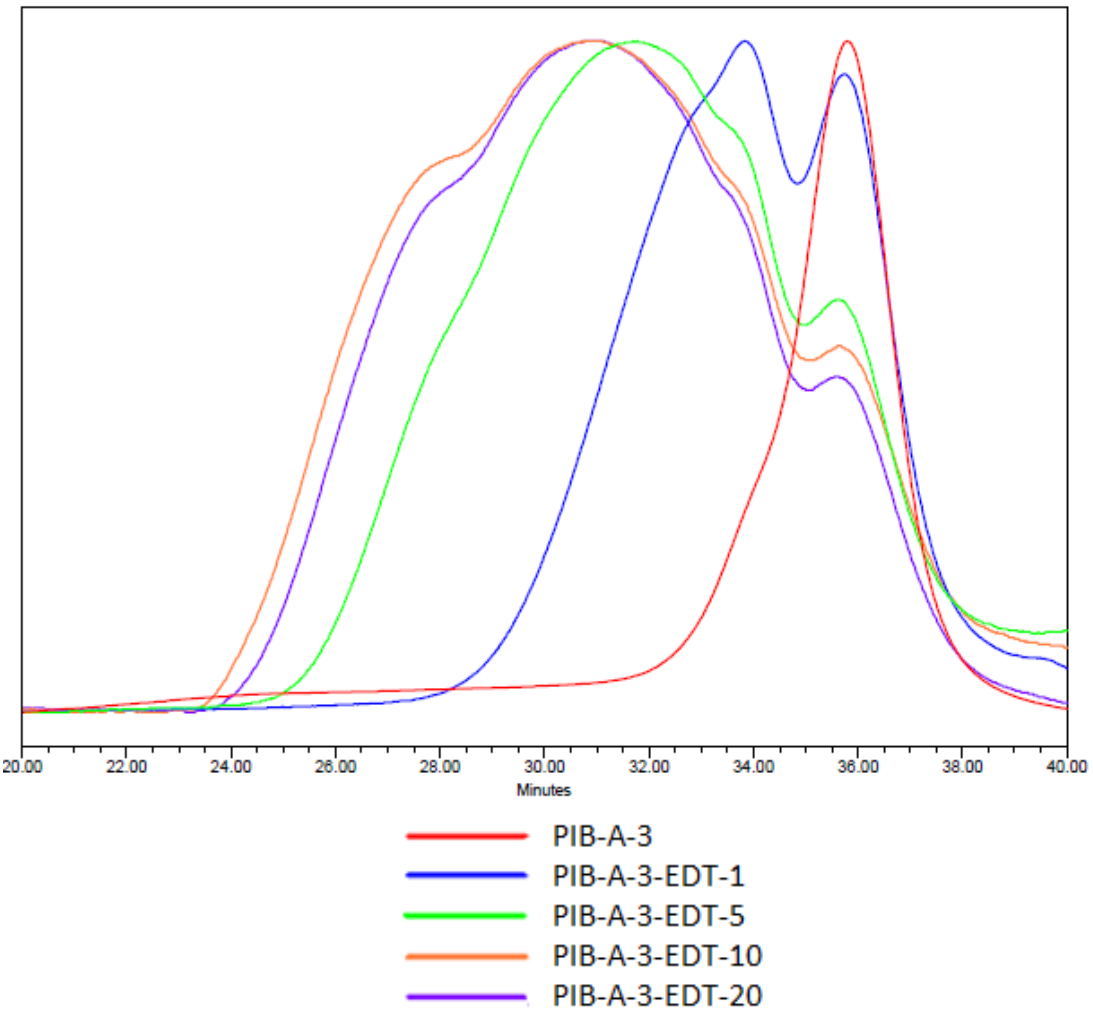

Figure 4.14. SEC data of PIB-A-3 and chain extended polymers prepared with EDT at specific time intervals.

Table 4.3. Summary of SEC analyses of chain extended polymers prepared with EDT at specific time intervals.

Name	M_n	M_w	M_w/M_n
PIB-A-3	5500	6462	1.17
PIB-A-3-EDT-1	8538	13884	1.63
PIB-A-3-EDT-5	14726	34275	2.33
PIB-A-3-EDT-10	17344	59867	3.45
PIB-A-3-EDT-20	17000	51885	3.05

The products of conjugation using HDT were named as PIB-A-3-HDT-1, PIB-A-3-HDT-5, PIB-A-3-HDT-10 and PIB-A-3-HDT-20 for 1, 5, 10 and 20 h reaction time, respectively (Table 4.4). SEC analysis results are demonstrated in Figure 4.15.

The increase in molecular weight using HDT is much faster with respect to EDT usage (Figure 4.16). Number average molecular weight reached with EDT is 17344 whereas a higher result of 21490 with HDT is achieved within the same reaction time of 10 hours. Even within the first hour, low molecular fragments participate in chain extension and high viscosity polymers are achieved faster.

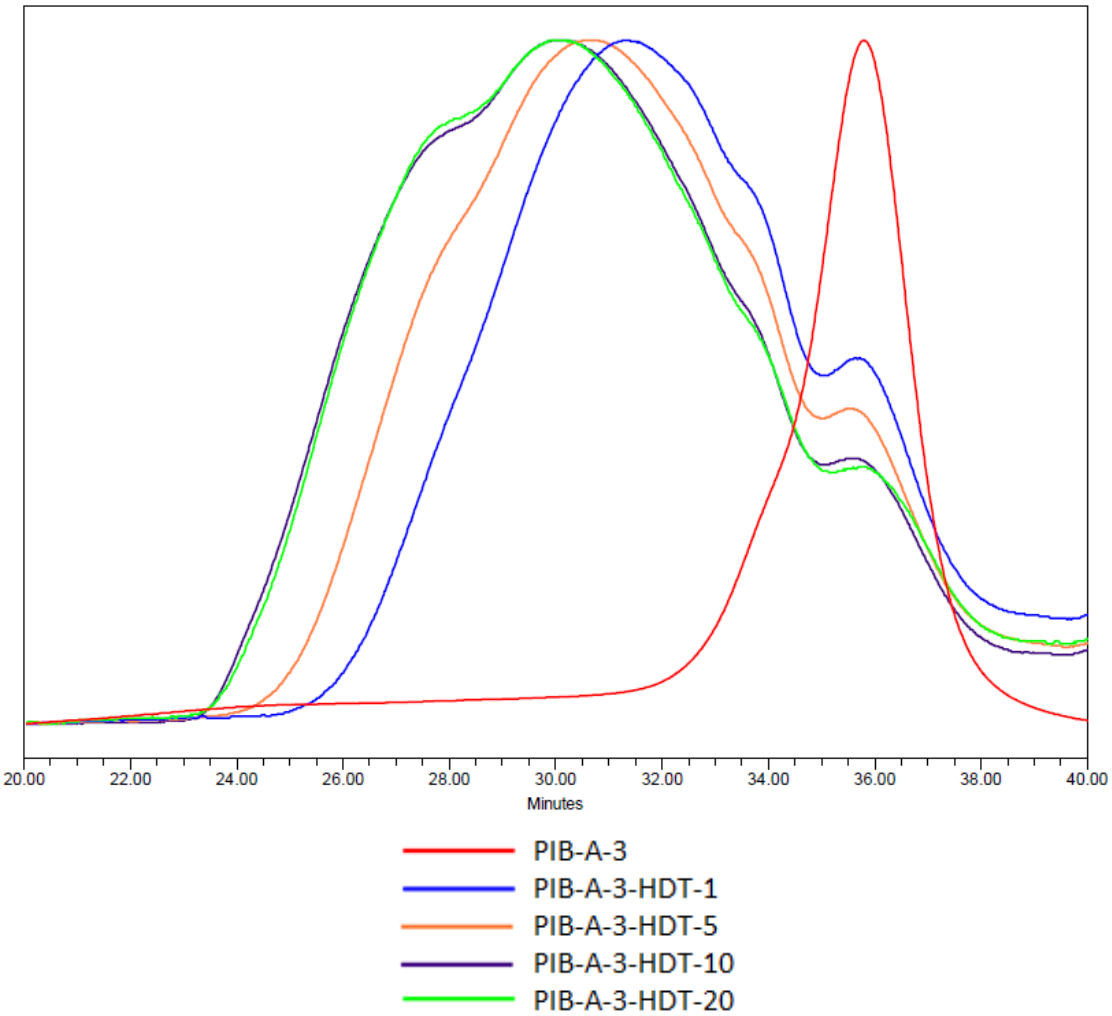

Figure 4.15. SEC data of PIB-A-3 and chain extended polymers prepared with HDT at specific time intervals.

Table 4.4. Summary of SEC analyses of chain extended polymers prepared with HDT at specific time intervals.

Name	M_n	M_w	M_w/M_n
PIB-A-3	5500	6462	1.17
PIB-A-3-HDT-1	14797	32059	2.17
PIB-A-3-HDT-5	17676	45064	2.55
PIB-A-3-HDT-10	21490	71291	3.32
PIB-A-3-HDT-20	21852	69131	3.16

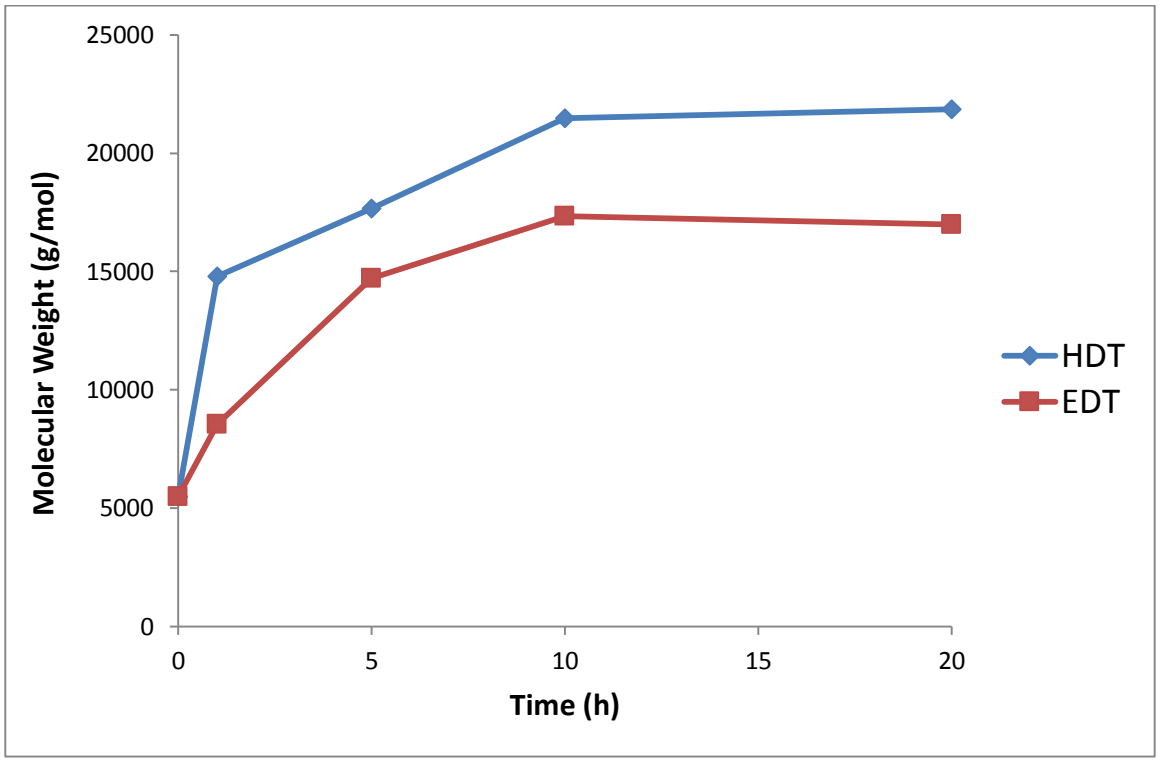

Figure 4.16. The difference between molecular weight increments by time for the two dithiols.

In conclusion, both dithiols cause an increase in molecular weight by time. It seems that the molecular weight reaches to a plateau after the reaction times longer than 10 hrs most probably due to the low diffusibility of the active chain ends. On the other hand, as expected, due to its lower solubility, ethanethiol exhibited slower chain extension reaction than hexanedithiol. Moreover, the higher flexibility of hexyl thiol group than that of ethyl thiol group at the chain end after the first thiol-ene reaction can be considered as an another issue which must be further studied in detail.

4.3.3. Thermal initiation effect

The influence of thermal initiation method for radical thiol-ene chain extension reactions was investigated as a complementary study to the photoinitiated counterpart. For this purpose a series of reactions were conducted for varying amounts of AIBN concentrations ranging from 2 to 0.10 equivalents (with respect to alkene functionality) at a temperature range of 60-80 °C. Figure 4.17 and Table 4.5 show the SEC traces of the starting polymer PIB-A-5 and chain extended products obtained by radical thiol-ene addition of HDT to PIB-A-5 at 60 °C.

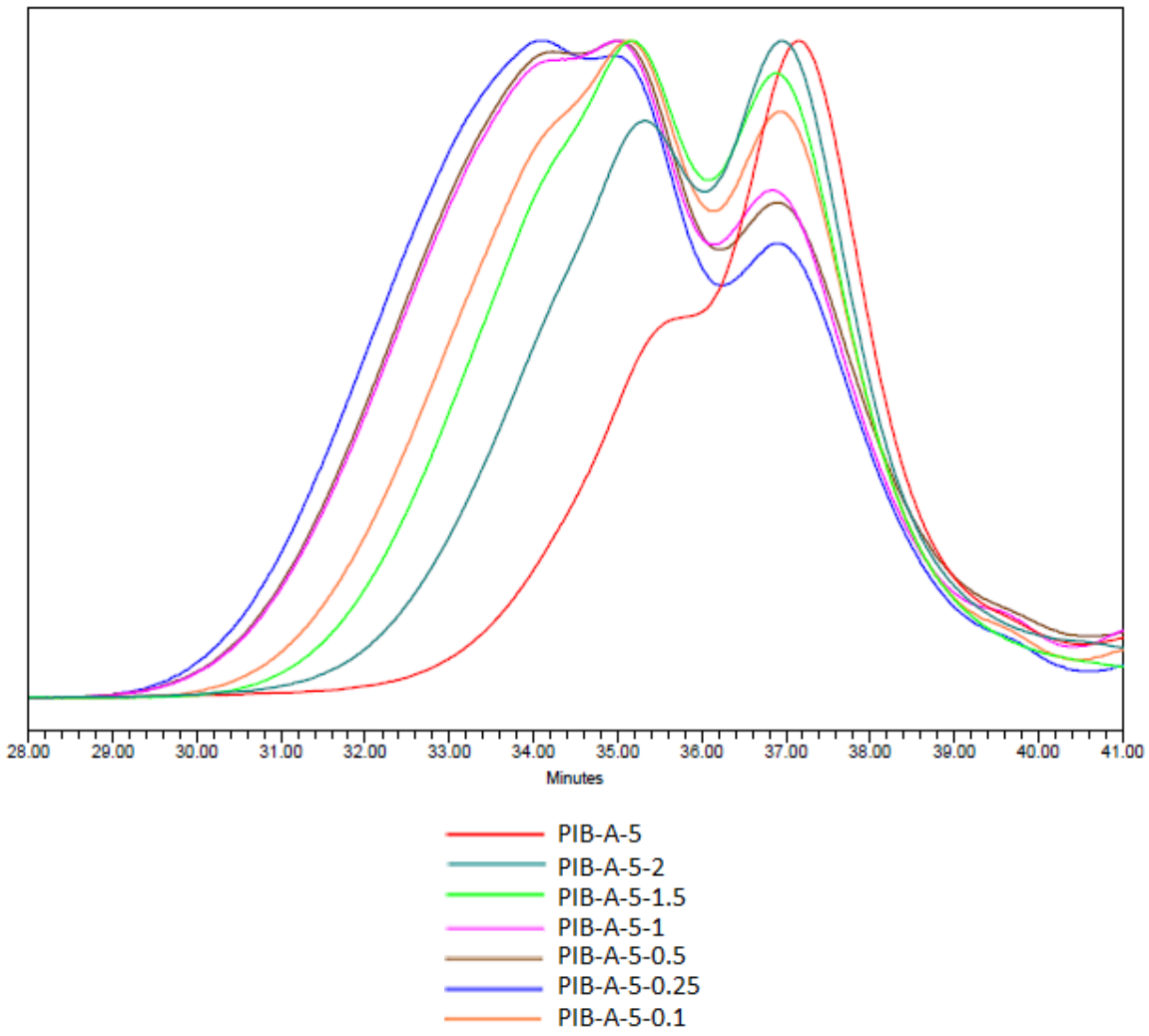

Figure 4.17. SEC data of PIB-A-5 and chain extended polymers prepared by thermal initiation at 60 °C.

Table 4.5. Summary of SEC analyses of chain extended polymers prepared by thermal initiation at 60 °C.

Name	M_n	M_w	M_w/M_n
PIB-A-5	3506	4571	1.30
PIB-A-5-2	4372	6207	1.42
PIB-A-5-1.5	4837	7350	1.52
PIB-A-5-1	5769	9642	1.67
PIB-A-5-0.5	5766	9678	1.68
PIB-A-5-0.25	6017	10375	1.72
PIB-A-5-0.1	5120	8057	1.57

The increase in the molecular weights for the experiments conducted at 70 °C and 80 °C was not as high as for those conducted at 60 °C (Figure 4.18). The highest molecular weight was reached for 0.25 equivalent of AIBN at 60 °C. Generally speaking better results were obtained for lower equivalents of AIBN for each reaction temperature. Actually this result is consistent with the literature. The occurrence of side reactions associated with the initiator was known to decrease the efficiency of formation of the insertion product. These side reactions consume the ene [96]. It is probable that, in our case, the occurrence of side reactions became more prominent as the initiator concentration and temperature increase. Hence the lowest yields were obtained for two equivalents AIBN.

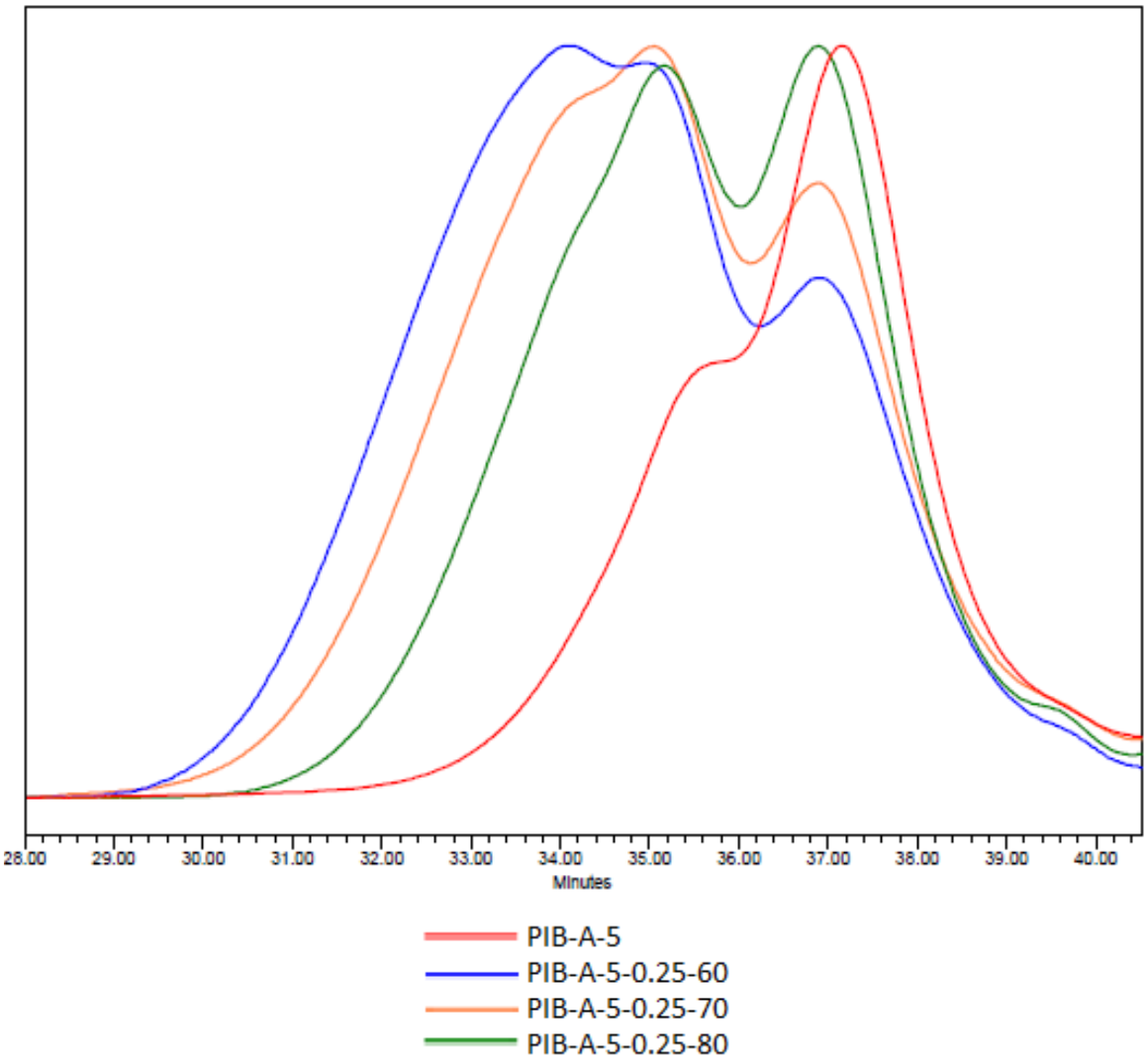

Figure 4.18. SEC data of PIB-A-5 and chain extended polymers for 0.25 equivalent of AIBN at 60, 70 and 80 °C.

SEC analyses indicate that the coupling efficiency could not be improved in the case of thermal process as much as the photo-initiated counterpart. Under these reaction conditions, it was concluded that the photochemical method showed superiority over thermally initiated reactions in thiol-ene addition reactions.

4.3.4. Thiol-ene crosslinking reactions

Figure 4.19 shows the formation thiol-ene network structure by the reaction of diallyl telechelic PIBs with the trifunctional thiol trimethylolpropane tris(3-mercaptopropionate).

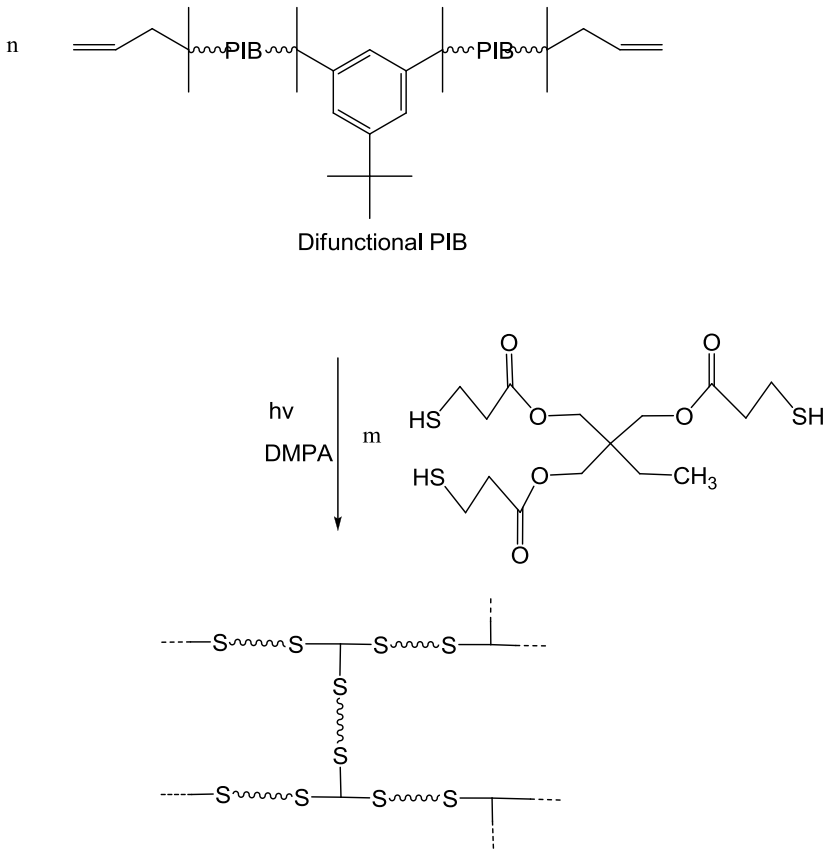

Figure 4.19. The path followed in the synthesis of network structures.

Characterization of the network structure was performed by Raman Spectroscopy, which is a powerful technique in providing vibrational information of S-S and C-S bonds and hence frequently used in analysis of polymers containing sulfur species.

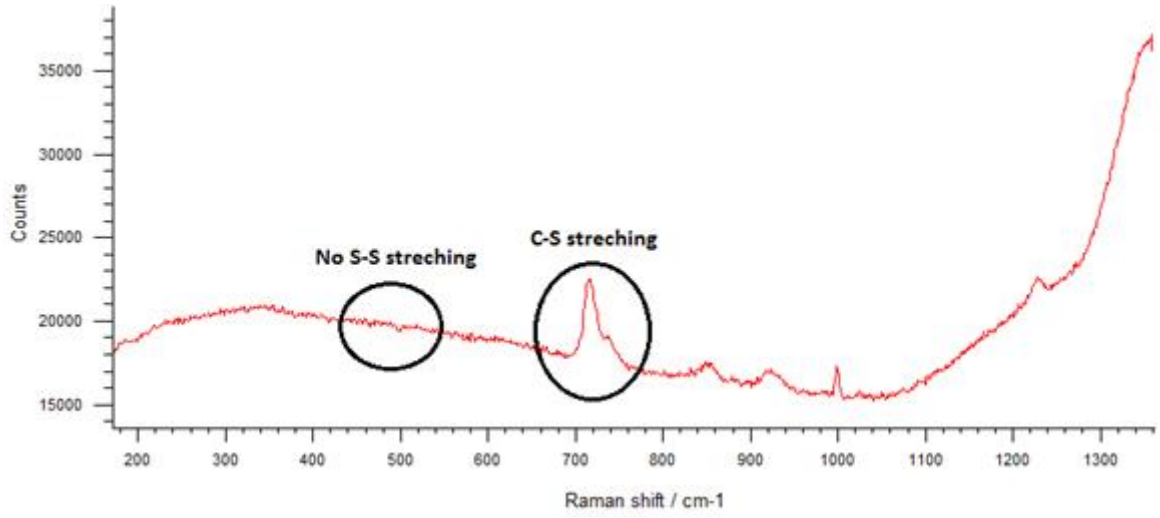

Figure 4.20. Raman analysis of the crosslinked polymer.

The Raman spectrum of the crosslinked samples in 200-1300 cm^{-1} spectral range was given in Figure 4.20. The Raman band observed in 680-760 cm^{-1} region was attributed to C-S stretching. Most importantly, the absence of characteristic S-S stretching band located in 430-550 cm^{-1} region is an indication of non existence of disulfide formation.

4.3.5. Swelling and extraction studies

Swelling behavior of the chemically crosslinked network in cyclohexane was followed gravimetrically in order to be able to evaluate the network properties e.g. the average molecular weight between crosslinks ($\bar{M}_c$), crosslink density (ρ), and mesh size (ξ), which were calculated by the equations listed in Part 3.5.3 and summarized in Figure 4.21 and Table 4.6.

The crosslinking process was very fast and even gelation started to occur while the mixture was being stirred for homogenization before subjected to UV irradiation. However, in order to reach fully crosslinked network, the samples were irradiated for 10 hours.

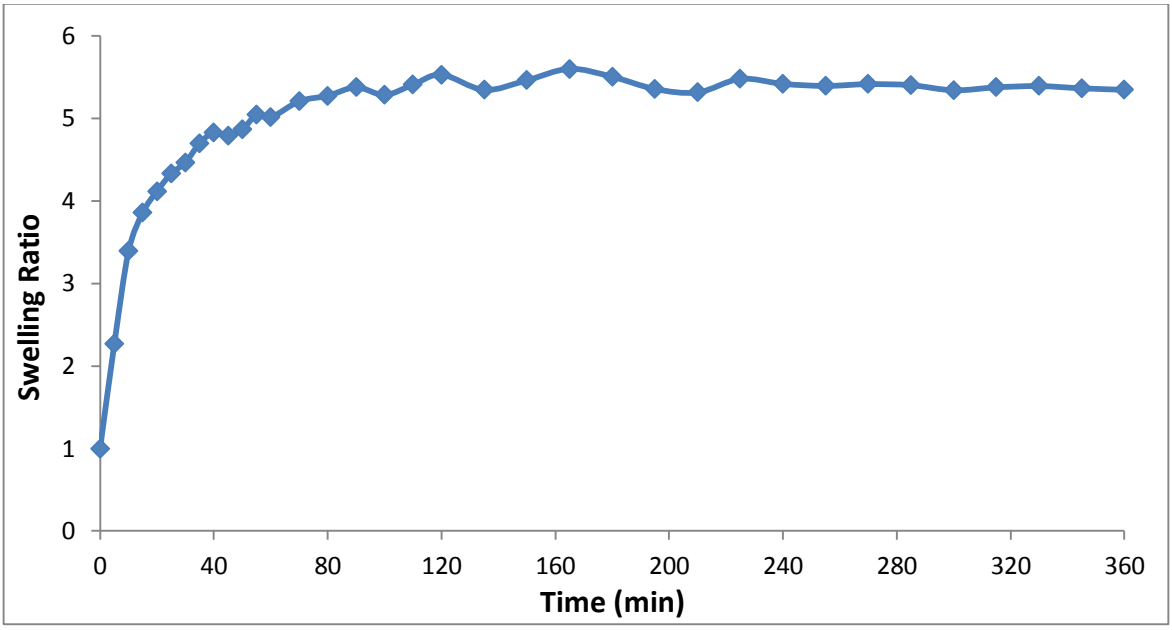

Figure 4.21. Swelling ratio versus time graph of the crosslinked polymer network.

Table 4.6. Average molecular weight between crosslinks ($\bar{M}_c$), equilibrium swelling ratio (q_w), crosslink density (ρ), and mesh size (ξ) data of network obtained from swelling studies.

Name	$\bar{M}_c$ (g/mol)	q_w	ρ_c (x10^{-4})	ξ (nm)
PIB-A-3 Network	1141	5.35	7.96	5.28

The fast and high swelling behavior of the PIB network is successfully experimented. The weight percent of extractables, i.e. starting materials not involved in the network structure, was found to be 17.8 % by taking the average of data collected from different samples of the network.

5. CONCLUSION

In this research, a sterically hindered chloro initiator, 5-tert-butyl-1,3-bis(2-chloro-2-propyl)benzene (t-Bu-m-DiCumCl), is successfully synthesized with high efficiency in three steps to be used in quasiliving carbocationic polymerizations of low molecular weight allyl terminal liquid polyisobutylenes. ^{1}H NMR and SEC analyses were used to determine molecular weights of intermediates and polymeric products.

For chain extension of polyisobutylenes, thiol-ene addition reactions via photo or thermal initiation using aliphatic thiols such as EDT and HDT were investigated. In the photoinitiated method; effect of photoinitiator concentration (DMPA), reaction time and thiol type were all examined. The results were monitored by SEC and the optimum was obtained when using HDT, 0.5 equivalent DMPA initiator and a reaction time of 10 hours. Whereas, in thermal initiation, even with the best results obtained using HDT, 0.25 equivalent AIBN initiator and at a reaction temperature of 60 °C, the increase in molecular weight was not as high as in that of photoinitiated process.

In examining the network structure, the well-defined telechelic polyisobutylenes were crosslinked via the photoinitiation method using a trifunctional thiol trimethylolpropane tris(3-mercaptopropionate). Raman Spectroscopy showed the formation of C-S bonds and confirmed the absence of unwanted disulfide bonds. The swelling behavior was experimented by gravimetric analysis. The average molecular weight between crosslinks ($\bar{M}_c$), crosslink density (ρ), and mesh size (ξ) data were calculated successfully as 1141 g/mol, 7.96 x 10^{-4}, and 5.28 nm, respectively. The weight percent of extractables was determined as 17.8 %.

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