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Investigation of Novel Quasiliving Polyisobutylene Chain-end Functionalization (Quenching) Methods

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INVESTIGATION OF NOVEL QUASILIVING POLYISOBUTYLENE CHAIN-END FUNCTIONALIZATION (QUENCHING) METHODS

by

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ABSTRACT

INVESTIGATION OF NOVEL QUASILIVING POLYISOBUTYLENE CHAIN-END FUNCTIONALIZATION (QUENCHING) METHODS

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This volume recounts efforts toward the development and understanding of chain functionalization techniques involving the direct addition of nucleophiles to quasiliving polyisobutylene (PIB). Nucleophiles included in the study were sterically hindered organic bases, (di)sulfides, *N*-substituted pyrroles, and alkoxybenzenes. A kinetic investigation of the end-quenching of $TiCl_4$-catalyzed quasiliving PIB with sterically hindered amines was used to determine the mode of interaction with $TiCl_4$ and the active species responsible for β-proton abstraction. 2,5-disubstituted-*N*-hydropyrroles formed pyrrole-$TiCl_3$ adducts that were active in formation of *exo*-olefin chain ends; whereas, with other sterically hindered amines, only an equilibrium fraction of the amine that did not complex with $TiCl_4$ remained available for proton abstraction. Low-temperature-stable sulfonium ion adducts were generated by addition of mono- and disulfides to $TiCl_4$-catalyzed quasiliving PIB. At temperatures less than or equal to -60 ^{o}C, quantitative 1:1 adducts were formed between the (di)sulfides and the oligo-isobutylenes. When a more reactive nucleophile such as an alcohol or amine was added to the reaction, the adducts were destroyed, and both elimination and substitution products were obtained. *N*-(2-*tert*-Butoxyethyl)pyrrole was used to end-quench $TiCl_4$-catalyzed quasiliving PIB and resulted in near quantitative end-capping, except for the formation of <5% *exo*-olefin chain ends, with alkylation occurring in both the C-3 (57%) and C-2

(38%) position on the pyrrole ring. Further treatment with acids and warming resulted in alkylation via the residual olefin and rapid cleavage of the terminal *tert*-butyl group of the *N*-(2-*tert*-butoxyethyl)pyrrole-capped PIB to provide hydroxyl end group functionality *in situ*. Alkoxybenzenes were also used to end-quench $TiCl_4$-catalyzed quasiliving isobutylene polymerizations. Successfully alkylated alkoxybenzenes included those with alkyl tethers, such as anisole and isopropoxybenzene, those with haloalkyl tethers, such as (3-bromopropoxy)benzene and (2-chloroethoxy)benzene, and even those with hydroxyl and amine functionality, such as 4-phenoxybutanol and 6-phenoxyhexylamine. Alkylation occurred exclusively in the *para* position of alkoxybenzenes, and multiple alkylations were not observed. The alkylation reactions were tolerant of temperatures ranging from -70 to -30 ^{o}C and were unimpeded by the presence of *endo*- or *exo*-olefin termini. Terminal ether cleavage for polyisobutylenes capped with anisole and isopropoxybenzene allowed single-pot synthesis of phenol telechelics.

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CHAPTER I

INTRODUCTION

Isobutylene Polymerization

The acid-induced polymerization of isobutylene was discovered well over 100 years ago; however, the demand for synthetic rubber in the early 1900s ignited great interest in achieving high-molecular weight polyisobutylenes. The initial reports of M. Otto and M. Muller-Cunradi of I.G. Farbenindustrie AG[1,2] in the 1930s demonstrated that Friedel-Crafts catalysts such as aluminum trichloride, high purity monomer, and low temperatures were required to achieve "solid" polyisobutylenes. With the help of R. M. Thomas of Standard Oil Development, the polymerizations were refined to achieve molecular weights in excess of 100,000 g/mol.[3] These polymers were not immediately considered useful because they did not contain the unsaturations required for vulcanization. The problem was solved by copolymerizing isobutylene with a small quantity of conjugated diene, and eventually led to the formulation of "butyl rubber", a copolymer of isobutylene and isoprene.[4,5]

After the development of butyl rubber, much effort went into further understanding the fundamentals of cationic polymerization.[6] However, unlike emerging technologies involving Ziegler-Natta and anionic polymerization of olefins, high levels of control in cationic polymerization were lagging.[7] It was widely known that lower temperatures favored higher molecular weight materials by suppressing chain transfer to monomer, but "living" systems with adequate stability to prevent chain breaking reactions were slow in developing. In a movement largely led by J. P. Kennedy in the early 1980s, the conditions for the "quasiliving" polymerization of isobutylene were

finally realized.[8] These so called quasiliving polymerizations involved controlled initiation, and propagation proceeded in the absence of termination or chain transfer over the lifetime of monomer consumption. This effectively allowed for the synthesis of low molecular weight polyisobutylenes of predictable molecular weight having well defined end groups ("telechelics").

The focus of the current volume of work is on chain end functionalization of low molecular weight (< 5,000 g/mol) isobutylene homopolymers, and more specifically, the *in situ* functionalization of quasiliving polyisobutylene. Relevant for review are the currently practiced "conventional" and "quasiliving" cationic polymerizations of isobutylene as well as end group functionalities derived therefrom.

Conventional Polymerization of Isobutylene

Most commercially available low molecular weight polyisobutylenes (polybutenes) are manufactured under non-living conditions where chain-transfer by proton expulsion dominates, resulting in a mixture of unsaturated termini.[9] These conventional polymerizations involve aluminum trichloride ($AlCl_3$) or boron trifluoride (BF_3) catalysis and protic initiators, e.g., water or an alcohol. $AlCl_3$-catalyzed isobutylene polymerizations yield high levels of tri- and tetra-substituted olefinic end groups with relatively small amounts of the more highly reactive *exo*-olefin (methyl vinylidene) end group. For BF_3/alcohol[10] and BF_3/etherate[11] initiating systems, 70-90% of the chain ends bear the more highly reactive methyl vinylidene end groups. Such highly reactive polyisobutylenes having one end fitted with 80-85% methyl vinylidene, have been marketed by BASF under the trade name Glissopal®. BASF also markets the fuel additive Kerocom®, a polyisobutylene bearing primary amine end groups, produced from

Glissopal® by hydroformylation and subsequent reductive amination. No commercially available polybutenes are quantitatively end-functionalized, and most are limited to a single reactive end group due to protic initiation.

Quasiliving Polymerization of Isobutylene

Progress toward "living" isobutylene polymerization occurred primarily in Kennedy's group at The University of Akron. The initial systems involved bifunctional *ini*tiator-trans*fer* agents (inifers)[12], primarily *p*-dicumyl chloride, co-initiated with boron trichloride (BCl_3). These systems were free of chain transfer to monomer, but re-initiation of terminated chains was very slow, and reaction rates were too fast for adequate synthetic control. Later, systems offering better control were developed, based upon tertiary ether[13] and ester[8] initiators. Termination of these $TiCl_4$ or BCl_3 catalyzed polymerizations invariably led to *tert*-chloride chain ends, and this eventually led to the realization that Lewis acids react with ether and ester moieties to generate "electron donating" species[14] *in situ*. It was proposed that the presence of such electron donating species somehow stabilizes the growing chain ends and thus increases the livingness of the system. This prompted the deliberate addition of external electron donors to gain greater control over the polymerizations.[14] Later it was found that the addition of common ion salts could also convert a conventional polymerization to a living one. For example, isobutylene polymerizations catalyzed by $TiCl_4$ may be controlled by adding tetrabutyl ammonium chloride.[15] The chloride ion of the added salt combines with $TiCl_4$ to produce $Ti_2Cl_9^-$ and shifts the chain end equilibrium towards lower ionicity. After much debate over the role of electron donors, Storey *et al.*[16] showed that common ion salts and electron donating species have the same general effect on polymerization

control by suppressing the generation of free ions via the formation of suitable common counter ions. For Lewis bases such as substituted pyridines, this easily occurs through the scavenging of protic impurities or water in the system, which has the added benefit of suppressing protic initiation.

The two most commonly used Lewis acid catalysts for quasiliving isobutylene polymerization are titanium tetrachloride ($TiCl_4$) and boron trichloride (BCl_3). Of these, $TiCl_4$ has received the most attention due to its usefulness in the synthesis of block copolymers via sequential addition of monomers, i.e. isobutylene followed by addition of, for example, styrene[17] or indene.[18] As an alternative, aluminum based catalysts have been explored. Cheradame *et al.*[19] were first to demonstrate quasiliving isobutylene polymerization catalyzed by diethyl aluminum chloride. The polymerization required use of a tertiary azide initiator, from which the azide participated in reversible termination of the propagating chains. Nucleophilic additives were not required to achieve living polymerization kinetics because initiation by adventitious moisture was not a problem. Unfortunately, living character was only observed for molecular weights less than 50,000; above that a slight deviation was observed. Another polymerization system based on diethyl aluminum chloride was developed based on tertiary alkyl halide initiators and use of an 80/20 (v/v) nonpolar/polar solvent mixture, for example, polymerization using diethyl aluminum chloride at -75 °C in 80/20 (v/v) methylcyclohexane/methylene chloride.[20] However, the use of the highly nonpolar solvent mixture precluded the synthesis of block copolymer such as those based on sequential addition of isobutylene and styrene due to solubility problems; this is especially so with block copolymers having a high styrene content. Moreover, this

system was also displayed non-living behavior at high monomer conversions and broadening of the molecular weight distribution was observed upon incremental monomer addition. Non-living behavior was attributed to termination, most like due to alkylation and hydridation.[21]

Dimethyl aluminum chloride is a poorer alkylating agent than diethyl aluminum chloride and cannot participate in hydridation because it lacks β-hydrogens.[22] Adventitious moisture is a poor initiator with dimethyl aluminum chloride, as it is with other dialkylaluminum chlorides.[23,21] These traits make dimethyl aluminum chloride an attractive alternative as an aluminum-based Lewis acid for living isobutylene polymerizations. Bahadur *et al.* demonstrated quasiliving isobutylene polymerization with dimethyl aluminum catalysis in 60/40 (v/v) hexane/methylene chloride for molecular weights near 100,000 without the use of nucleophilic additives.[24] Later, Faust *et al.*[25] observed lower polymerization rates with dimethylaluminum chloride compared to Bahadur *et al*,[24] and attributed this result to their use of the proton trap, 2,6-di-*tert*-butyl pyridine.[26] They found the latter necessary to scavenge protic impurities that otherwise lead to possible formation of methyl aluminum dichloride, a much strong Lewis acid. Their work also indicated that very rapid quasiliving isobutylene polymerizations could be catalyzed by methylaluminum sesquichloride or methyl aluminum dichloride in hexanes/CH_3Cl 60/40 (v/v) at -80 °C. Faust *et al.* made further use of aluminum alkyl halide catalysts by using methyl aluminum bromides for quenching reactions with butadiene.[27] Kennedy *et al.* have reported on isobutylene polymerizations catalyzed by trivinyl aluminum[28,29] and triphenyl aluminum.[30,31,32] Though these polymerizations were non-living, termination was dominated by ligand

exchange with the catalyst, yielding vinyl and phenyl telechelics. Attempts at controlled/living polymerizations with $AlCl_3$ catalysis have been made, [33] but with little success.

Solvent-ligated manganese(II) complexes have been used to polymerize isobutylene above room temperature.[34] Low and medium molecular weight polyisobutylenes were obtained containing a high fraction (70-80%) of *exo*-olefin end groups. Highly reactive polyisobutylenes with 60-92% *exo*-olefin termini have also been synthesized at room temperature using an ethyl zinc chloride/*tert*-butyl chloride initiating system.[35] Weakly coordinating anions, such as those generated from chelating diborane and cumyl chloride have also been used to polymerize isobutylene.[36]

Polyisobutylene Functionalization

Post-Polymerization Derivatization

The commercial availability of olefin terminated polybutenes and early development of procedures for post-polymerization dehydrochlorination of *tert*-chloride telechelic PIB have made the olefin end group the most prevalent starting point for chain end functionalization and further derivatization. The largest use of methyl vinylidene polybutene is in the manufacture of polybutenylsuccinic anhydride (PIBSA), a precursor for lubricant additives. PIBSA is obtained by the thermally driven Alder ene addition of maleic anhydride to the olefin chain end. The reaction is facile with "highly reactive" *exo*-olefin terminated PIB, but lower yields are obtained from tri- and tetra-substituted olefins[37] and *tert*-chloride terminated PIB.[38] The PIBSA itself may be used as a corrosion inhibitor, or it may be further reacted with oligo(iminoethylene) to form

polybutenylsuccinimide, an ashless dispersant that prevents the buildup of sludge and varnish on engine surfaces.

In Kennedy's synthetic scheme for telechelic *exo*-olefin PIB, *tert*-chloride terminated PIB was first synthesized using the "inifer" technique.[12] The isolated product was then regio-specifically dehydrochlorinated with an excess of the hindered base, potassium *tert*-butoxide, under refluxing tetrahydrofuran.[39] This expensive and laborious approach requires long reaction times (20 h) and clean-up of the intermediate polymer. Later, the less expensive base, sodium ethoxide, in THF/ethanol was also shown to quantitatively dehydrochlorinate PIB.[40]

Storey *et al.* have shown the usefulness of olefin-terminated[41] and *tert*-chloride terminated[42] PIB in the synthesis of ionomers via direct sulfonation. Alternatively, multiple sulfonate groups can be added by reacting triphenyl silyl chloride or triphenyl carbenium ion with lithiated olefinic PIB and subsequent sulfonation of the aromatics and the residual olefin.[43]

Kennedy *et al.* [44] synthesized Si-Cl and Si-H functional PIB by hydrosilylation of *exo*-olefin end groups with silyl chlorides; reduction with $LiAlH_4$ provided silyl hydrides. The hydrosilylation reaction of *exo*-olefin telechelic PIB has also been used to synthesize crosslinked networks.[45]

Attempts at synthesis of aldehyde capped polyisobutylene began with hydroformylation of commercially available olefinic PIB, which contains a large number of internal, tri- and tetra-substituted double bonds.[46] These internal double bonds were unreactive toward hydroformylation and quantitative chain end conversion could not be obtained. When telechelic *exo*-olefin PIB became available, quantitative rhodium

catalyzed hydroformylation of this material to aldehyde telechelic was reported by Kennedy *et al.*[47] Zsuga *et al.* [48] reacted aldehyde functional PIB with the organic oxidant, dimethyldioxirane, to produce carboxylic acid end groups, or alternatively, a β-hydroxy carboxylic acid end group by reaction of the aldehydes with an acetic acid double anion. Kummer *et al.* [49] in an extension of the "oxo" process obtained amino functional PIB by reductive amination of the hydroformylated PIB.

Kennedy *et al.*[50] synthesized telechelic primary hydroxyl PIB by hydroboration-oxidation of the *exo*-olefin end groups. Commercially produced PIB with high *exo*-olefin content has also served as a substrate for hydroboration-oxidation;[51] however, on an industrial scale hydroformylation-hydrogenation of the olefin would be preferred.[52]

Kennedy *et al.* [53] have subjected the *exo*-olefin end group to epoxidation, and hydroxyl functionality was obtained by acid catalyzed isomerization of the epoxide to an aldehyde and subsequent reduction of the aldehyde.[54] Terminally and centrally amine functionalized telechelics were obtained by ring opening of epoxide functional polyisobutylene with excess methyl amine.[55] Regioselective attack of the amine on a given epoxide end group resulted in a secondary amine which could subsequently ring open another epoxide end group to provide centrally functionalized polyisobutylene.

As shown by Storey *et al.*, [56] ozonolysis of the *exo*-olefin end groups and subsequent reduction of the ozonide with trimethylphosphite yields methyl ketone end groups, that can be converted to hydroxyl or carboxylic acid end groups by reduction or oxidation, respectively. Oxidation of the methyl ketone end group with hypobromite (haloform reaction) required very long reaction times. [57] As an alternative, tetrachloromethane oxidation provided much faster conversion to carboxylic acid end

groups, especially with use of a phase transfer catalyst or CCl_4 solvent.[58] An alternative method of producing carboxylic acid end groups from olefin was disclosed by Ohno *et al.*[59] and involved reaction of the olefin with an aluminum hydride and subsequently carbon dioxide.

Kennedy *et al.* [60,61] lithiated e*xo*-olefin and *tert*-chloride terminated PIB with BuLi/TMEDA. The metalated PIB macroanions were oxyethylated using ethylene oxide to provide hydroxy-functional PIB, but the functionality was 5% higher than theoretical due to dilithiation. An improved procedure required use of *n*-butyl lithium and potassium *tert*-butoxide to simultaneously dehydrochlorinate and lithiate the chain ends. [62] The metalated chain ends have also been carbonated to afford carboxylic acid end groups[62] and reacted with 2-chloro ethyl vinyl ether to obtain vinyl ether telechelics.[63]

Hydroxyl telechelic PIB has been used as a starting point for many other chain end functionalities. Kennedy *et al.*[64] converted the hydroxyl end groups to allyl by reaction with allyl bromide or monoallyl phthalic acid chloride. Carboxylic acid end groups were obtained by reaction of hydroxyl functional PIB with excess dicarbxylic acid chlorides followed by hydrolysis.[65] Binder *et al.*[66] chloromethylated hydroxyl PIB using paraformaldehyde and HCl gas. The chloromethylether terminated polymers were then reacted with various silylated nucleobases to produce polyisobutylenes for hydrogen bonded supramolecular chemistry. Kennedy *et al.*, [67] in an attempt to obtain isocyanate telechelics, reacted PIB glycols with toluene diisocyanate. Predictably, this method led to small amounts of chain extension. Later, a method with more control and the advantage of a product with a more reactive oxycarbonyl isocyanate endgroup was achieved by reacting the PIB glycols with *N*-chlorocarbonyl isocyanate.[68] Percec *et al.*[69]

obtained primary and tertiary amino functional PIB by a Gabriel synthesis method that first involved tosylating or mesylating the hydroxy functional chain ends.[70] These activated esters were then diplaced by phthalamide as well as the potassium salts of ethanol amines and cyanoethanol. The phthalamide and cyanoethanol chain ends required additional reaction with hydrazine and $LiAlH_4$, respectively, to yield the amine functionality. Keki *et al.*[71] made primary amine telechelics through reaction of hydroxy functional polyisobutylene with carbonyldiimidazole to yield imidazole-1-carboxylate esters that were then reacted with ethylene diamine. A relatively large excess of ethylene diamine was required to prevent chain coupling.

PIB glycols have been used for synthesis of a number of block copolymers. For example, step growth polymerizations have provided model urethane networks,[72,73] flexible polyurethane foams,[74] polyurethanes with enhanced oxidative stability,[75,76,77,78] polyesters,[79] and amphiphilic networks.[80] Wondraczek and Kennedy[67] made polyisobuytylene–*b*-nylons by reacting hydroxyl functional PIB with diisocyanates, N-chlorocarbonyl diisocyanates, and oxalyl chloride. These polymers were used as macroactivators for the anionic polymerization of caprolactam. Kennedy *et al.*[81] also converted the terminal hydroxyl group of PIB to a silylketene acetal, yielding a macroiniator for group transfer polymerization of methyl methacrylate. Hatada *et al.*[82,83] reacted the hydroxyl end group with isobutyroyl chloride in the presence of triethylamine, then lithiated with lithium diisopropylamide LDA to produce α,ω-di-anionic polyisobutylene for intiation of a methyl methacrylate polymerization. Kennedy and Hiza radically polymerized α-methacryloyloxy PIB to high molecular weight[84] and α,ω-di(methacryloyloxy)PIB to a highly crosslinked network.[85] The methacarylate

telechelics were also combined and polymerized with dimethylacrylamide to produce amphiphilic networks.[86,87] Welch and Gaymans used anhydride capped PIBs to synthesize poly(butylene terephthalate)-*b*-polyisobutylene.[88] Sipos *et al.*[89] converted α,ω-dihydroxyl PIB to the postassium alcoholate for ring opening polymerization of L-lactide to produce block copolymers that are both thermoplastic and partially biodegradable.

The olefin terminus of PIB has served in a number of Friedel-Crafts alkylation reactions. With the commercially available methyl vinylidene PIB, alkylation of aromatics such as phenol using BF_3 catalysis has been demonstrated.[90] Kennedy *et al.* reported successful post polymerization alkylation of phenol,[91] anisole,[92] benzene, toluene, and xylene[93] in the presence of BF_3-OEt_2 with both *tert*-chloride and *exo*-olefin telechelic polyisobutylenes derived from a quasiliving polymerization process. Reactions were slow using BF_3-etherate; for example, phenolic end groups were obtained by reacting *exo*-olefin with phenol in the presence of BF_3-OEt_2 at 50-55 ^oC for 30 h.[91] Kennedy *et al.* claimed alkylation of less reactive arenes such as benzene, toluene, and 2-bromoethyl benzene with *tert*-chloride terminated PIB in fewer than 5 h using aluminum trichloride catalysis at temperatures between -50 and -80 ^oC.[94] Kennedy *et al.*[95] converted phenolic PIB to the corresponding glycidyl ether by reaction with epichlorohydrin, and the di- and tri-functional polymers were cured with triethylene tetraamine.[96] Rooney used phenolic PIB in the synthesis of ethylene oxide-isobutylene block copolymers.[97] Kennedy *et al.* also reacted phenolic PIB with 2-chloroethyl vinyl ether to produce vinyl ether end groups.[64]

Functionalization of polyisobutylene with phenolic and hydroxyl end-groups through thiol-ene addition reactions became of interest with the commercial availability of the highly reactive methyl vinylidene terminated polymers.[98,99] The free radical induced anti-Markovnikov addition is selective toward the presence of the di-substituted terminal unsaturation, and conversions as high as 90% may be achieved in open air with UV or organic peroxide induced radical generation.[100]

Halide terminated PIB has also been a product of significant interest because of its use in nucleophilic displacement reactions. Simple addition of a hydrogen halide to olefin terminated PIB leads to tertiary halide end groups, which are not very reactive. Alternate halogenation routes that provide a more reactive halide at the chain terminus involve free radical induced additions. For example, Wagenaar[101] disclosed the iodine promoted addition of chlorine to di- and tri-substituted olefin terminated PIB resulting in allyl chloride and methallyl chloride end groups, respectively. The anti-Markovnikov hydrobromination to olefin terminated PIB in the presence of oxygen has also been reported, first by Couturier *et al.*[102] and then by Kennedy *et al.*[103] Kennedy and co-workers observed rapid hydrobromination by first bubbling air through a mixture of the polymer in refluxing THF or hexane, followed by cooling to 0 ^{o}C, and finally bubbling HBr through the mixture. Primary hydroxyl terminated PIB obtained by hydroxide displacement of bromide was converted to methacrylate functionality using enzymatic catalysis.[104] Conversion of the bromide functional PIB to primary amine telechelics was accomplished by conversion to the corresponding phthalimide with subsequent hydrazinolysis (Gaberial synthesis), and these were later used for improved synthesis of polyisobutylene based polyureas.[105]

in situ Functionalization of Polyisobutylene

Since the advent of quasiliving isobutylene polymerizations, much effort has gone into *in situ* functionalization methods, which theoretically provide a more direct route to the desired functionality. In general there are two approaches for *in situ* synthesis of end-functionalized polymers via living addition polymerization techniques; the initiator can be used to incorporate a latent functionality, or the polymerization may be quenched in order to cap or modify the living chain end.

Functional initiators. A number of functional initiators have been developed for isobutylene polymerization, and early efforts were aimed at synthesis of asymmetric telechelics. Kennedy *et al.* synthesized asymmetric telechelic PIB with a tri-substituted olefin at one end by initiating from 1-chloro-3-methyl-2-butene.[106,107] or *cis*-2-pinanol.[108] It was also found that chlorine in combination with BCl_3 could initiate isobutylene polymerization and produce polymers with a primary chloride at the initiating site. [109] The α-primary-chloro-ω-*tert*-chloropolyisobutylenes provided a method to produce block copolymers that included converting the primary halide at the initiating site into a Grignard reagent for the polymerization of methyl methacrylate.

Kennedy *et al.*[110] reported isobutylene polymerization from an acetate functionalized cumyl initiator (3-*tert*-butyl-5-(1-chloro-1-methyl-ethyl)-benzoic acid methyl ester); the acetate moiety was later converted to carboxylic acid by treatment with potassium *tert*-butoxide, followed by acid wash and rehydrochlorination. Strictly speaking, the ultimate functionality was not obtained *in situ* since the intermediate polymer product was purified. As an alternative, the acid catalyzed ring opening of *tert*-lactone initiators can provide acid or ester groups at the initiation site.[111]

Balogh *et al.*[112] found that isobutylene in the absence of a cation source undergoes haloboration by BCl_3 to generate a tertiary chloride initiating species *in situ*. The asymmetric telechelic polyisobutylene produced from such an initiating species bears a tertiary chloride at one end and dimethoxyboron functionality at the other after termination with methanol. Later, the dichloroboron endgroup that persists during polymerization was used to generate more useful functionality, such as amine and hydroxyl. Koroskenyi and Faust[113] found that alkyl azides react with the dichloroborane end group resulting in loss of nitrogen (and boron after hydrolysis) to form di- or tri-alkyl amines. Primary amines in 80% yield were obtained by quenching the polymerization with benzyl azide and subsequent debenzylation of the polymer via Pd catalyzed hydrogenolysis.[114] Hydroxyl groups were obtained by oxidation of the methoxy-boron chain ends with hydrogen peroxide.

Asymmetric silicon functional initiators were developed by Kennedy *et al.*,[115] and subsequent work by Faust *et al.* [116,117,118] showed that silylchlorides can survive conditions of $TiCl_4$-catalyzed quasiliving isobutylene polymerization. Silyl functional initiators included dichloro-{2-[3-(1-chloro-1-methylethyl)-phenyl]propyl}methylsilane and 1-methyldichlorosilyl-3,3,5-trimethyl-5-chlorohexane. Upon terminating the reaction with methanol dimethoxysilyl end groups were obtained.

Cheradame *et al.* [119] found that partial azide and nitrile functional polyisobutylene could be obtained *in situ* by initiation of isobutylene polymerization with $HN_3/TiCl_4$ and $HCN/TiCl_4$, respectively, but little control over the functionality was demonstrated. Later, azide functionality was obtained by initiation from 1,4-*bis*(1-azido-1-methylethyl)benzene and catalysis by $TiCl_4$[120] or BCl_3[121]. Depending on the

experimental conditions the chain ends exhibited different amounts of *tert*-butyl, *tert*-chloride, di- and tri-substituted olefins, as well as tertiary azide end groups. Quasiliving polymerization and quantitative azide telechelics were not obtained until diethyl aluminum chloride catalyst was used in conjunction with the 1,4-*bis*(1-azido-1-methylethyl)benzene intiaitor.[19,122] Quantitative azide functionality was observed at -50 ^{o}C in dichloromethane; lower temperatures resulted in increased amounts of terminal di- and tri-substituted olefins.

Puskas *et al.*[123] have worked with initiators containing latent hydroxyls masked as epoxides. Hydroxyl functionality at the initiation site was obtained by acid induced ring opening of the epoxide moiety. Quasiliving isobutylene polymerizations were demonstrated, but initiator efficiency remained low. For example, maximum initiator efficiencies of 40% where reported for α-methyl styrene epoxide, and apparently lower efficiencies were obtained for molecular weight targets under 4000 g/mol.[124] The low initiator efficiencies were caused epoxide rearrangement (e.g. formation of aldehydes) and formation of polyethers,[125] the extent of such side reactions being determined by the initiator structure.[126]

Weisberg *et al.*[127] initiated $TiCl_4$-catalyzed isobutylene polymerization from a secondary benzylic chloride also bearing two *tert*-butyldimethylsilyl protected hydroxyls (1-chloro-1-[3,4-di(*tert*-butyldimethylsiloxy)phenyl]ethane). Initiator efficiency remained low, but after deprotection, α,α′-dihydroxypolyisobutylene macromonomer was obtained in high enough yields for use in comb polyurethaneurea synthesis.

Jamois *et al.*[128] reported the polymerization of isobutylene from 4-(1-hydroxy-1-methylethyl)phenol. The intent was to produce an α,ω-telechelic polybutene with a

phenolic functionality at one end and a *tert*-chloride functionality at the other. The polymerization was catalyzed by BCl_3 and three distinct products were found. One was the intended product (55-65%), but the two others consisted of the initiator with only one unit of isobutylene added (5-20%) and oligomers initiated from a proton source (20-35%). The proton source was deduced to be the phenol functionality.

A novel synthesis of isocyanate and methacrylate functional PIB was presented by Toman *et al.*[129,130] Isobutylene was copolymerized with 3-isopropenyl-α,α-dimethyl benzyl isocyanate leading to a random copolymer bearing pendant isocyanate groups. The polymerization was catalyzed by $SnCl_4$ in CH_2Cl_2 at -50 ^oC. The isocyanate groups were transformed *in situ* to methacrylate functionality by the dibutyl tin dilaurate catalyzed reaction with hydroxyethyl methacrylate. Polymers with broad molecular weight distributions and ill defined end groups were obtained. However, since an average isocyanate functionality of approximately four was achieved, these results were deemed acceptable by the authors since the objective was synthesis of amphiphilic networks by further radical polymerization of the methacrylate endgroups with hydrophilic monomers.

End-quenching. Because quasiliving polymerization of isobutylene proceeds with minimal chain transfer or termination, for chain end concentrations equal to or greater than about 10^{-3} M, the chain ends remain viable for reaction even after complete monomer consumption. This presents the possibility for direct functionalization of the chain ends by *in situ* quenching with a nucleophilic reagent. Unfortunately, functionalization of quasiliving polyisobutylene in this manner is an inherently difficult task due to the stability imparted by the low number of active or ionized chain ends. The ionized chain

end concentration is typically $10^{-11} – 10^{-12}$ times the Lewis acid concentration; hence only a very small fraction of the chain ends are ionized at any given time. When a nucleophile is purposefully added to a polymerization in attempt to modify the chain ends, the intended reaction is often unavailing due to depletion of the Lewis acid through rapid and overwhelming interaction and/or reaction with the nucleophile. Thus, most attempts at reacting so called "hard" σ-nucleophiles with the quasiliving polyisobutylene chain end have only resulted in a *tert*-chloride terminus.[131,132] Reaction with the polyisobutylene carbenium ion chain end can only occur when a nucleophilic agent does not significantly and/or irreversibly react with the Lewis acid catalyst.

For the cationic polymerization of monomers other than isobutylene, for example, vinyl ethers, direct quenching reactions have been easier. After the discovery of the living polymerization of vinyl ethers Higashimura *et al.*[133,134,135] found that sodium malonic esters and phenyl carbanions were able to effectively end cap these vinyl ether polymerizations. The "soft" carbanions were able to react with the carbenium ion chains without inducing β-proton elimination. Hard carbanions such as butyl lithium were found ineffective and led to olefinic chain ends.[136] Other examples of successful capping agents for vinyl ether polymerization include, anilines substituted with amines, carboxylic acids and esters,[137] and dimethyl(trimethylsilyl)methyl ketone, and living polymethylmethacrylate synthesized by group transfer polymerization.[138] Quenching with the small molecule silyl ketene acetal appeared to provide quantitative ester functionality at the chain end, and coupling with the silyl ketene acetal terminated poly(methylmethacrylate) provided block copolymers. Coupling was also achieved with bifunctional silyl enol ethers[139] and polystyryllithium.[140] Direct addition of *n*-butyl amine

to a living ethyl vinyl ether polymerization resulted in capping of the chain ends, but the resulting α-amino ether is a fairly weak linkage.[141] An alternative approach involves capping the living polyvinyl ether chain ends with a styrenic monomer before reaction with the amine.[142]

The seminal work on nucleophilic quenching of carbocationic isobutylene polymerization was reported by Wilczek and Kennedy.[143,144,145] They found that the addition of a 1-3 fold molar excess of allyltrimethylsilane and $TiCl_4$ to a living BCl_3 co-initiated polymerization of isobutylene produced a quantitative yield of allyl terminated chains. This reaction was later[146] used to produce telechelic polyisobutylene with allylic functionality that was further derivatized to form primary hydroxy or epoxy end groups. Allyl telechelic PIBs (faster than *exo*-olefin PIBs) have also been crosslinked by hydrosilylation[147] and used to introduce reactive dimethylsilyl groups to the chain end that crosslink on exposure to moisture.[148]

Roth and Mayr,[149] during a study of propagation kinetics, found that an analogous reaction with methallyltrimethylsilane resulted in polyisobutylene with *exo*-olefin termini. Nielsen *et al.*[150] later described the direct use of methallyltrimethylsilane as a quenching agent to obtain *exo*-olefin chain ends. Unfortunately, the authors did not demonstrate complete conversion of chain ends to *exo*-olefin using an *in situ* quenching process. The major problem was chain-chain coupling, as indicated by their molecular weight distributions. Coupling occurs when a carbenium ion chain end reacts with an olefin that has already been formed. Successful reaction conditions were achieved only when previously synthesized *tert*-chloride terminated polyisobutylene was reinitiated and then quenched.

As an alternative method for direct functionalization to *exo*-olefin, Storey *et al.*[151,152] have disclosed the deliberate addition of hindered amines to quasiliving polyisobutylene, which leads to quantitative regioselective β-proton elimination. Addition of oxazoles to the polymerization has also been found produce high levels of *exo*-olefin end groups.[153] A number of prior studies had indicated that certain basic and/or nucleophilic additives actually induce unwanted olefin formation (termination) during the polymerization.[154,155] In particular, 2,6-di-*tert*-butylpyridine (proton trap) has been shown to lead to increased amounts of chain coupling. Since coupling occurs when a carbenium ion chain end reacts a with preformed olefin chain end, it was thought that the proton trap might be acting as a nucleophile and abstracting a proton from a small number of active chain ends. When Bae and Faust[156] noticed a significant amount of olefin formation for polymerizations involving the proton trap, 2,6-di-*tert*-butylpyridine, they attributed the elimination to a less hindered impurity (estimated at 0.2%). They suggested that this was most likely the case in other reports, as the proton trap was consistently reported as being "used as received." The impurity was modeled using 2-*tert*-butylpyridine, and further study indicated that the latter was indeed able to affect β-proton elimination. Faust *et al.* taught avoidance of such elimination reactions; however, Storey *et al.* sought to exploit them.

Another electrophilic addition reaction useful for end functionalization of polyisobutylene involves reaction with a non-polymerizable monomer such as 1,1-diphenylethlyene or 1,1-ditolylethylene. As shown by Faust and co-workers[157], addition of either of these monomers to a living isobutylene polymerization under certain conditions results in quantitative mono-addition. The diphenyl chain end is well suited

for further reaction with nucleophiles, since significant resonance stabilization results in near complete ionization of all the chain ends, simultaneously. If the reaction is quenched with methanol, a methylether end group is formed, as opposed to the usual *tert*-chloride end group formed when most of the chain ends are dormant (not ionized). Functionalizations were also made by direct addition of silyl enol ethers or allyltrimethylsilane.[158] Direct addition of a silyl ketene acetal such as 1-methoxy-1-trimethylsiloxypropene led to methoxy carbonyl functionality that could easily be hydrolyzed to a carboxylic acid.[159,160,161]

Feldthusen *et al.*[162] also quenched their isobutylene polymerizations with diphenyl ethylene and were able to terminate the reaction to olefinic and chloride functionality. The chloride functional end groups easily eliminated with potassium *tert*-butoxide to yield quantitative olefin functionality. The olefin functionality could then be metalated and used for anionic polymerization of methacrylates.[163] Binder *et al.*[164] demonstrated the approach of tethering a useful functionality to a quencher using a non-homopolymerizable olefin; these authors attached a primary bromide to 1,1-diphenylethylene via a three-carbon tether and used the resulting monomer to quench an isobutylene polymerization to a primary bromide terminus. The diphenyl vinyl end group, as well as the allyl end group, have been used to obtain carboxylic acid functionality through thermal decomposition of their corresponding ozonides formed via ozonolysis.[165] Presence of the β-protons in these structures was critical, leading to the intermediate formation of an aldehyde which oxidized *in situ*.

The ionized diphenyl carbenium ions are also well suited to enhance cross-over efficiency with the direct addition of a second, more reactive, cationically polymerizable

monomer such as *p*-methyl styrene[166,167] α-methylstyrene.[168,169], methyl vinyl ether[170] and isobutyl vinyl ether[171,172]. In these systems, the living chain ends were converted todiphenylalkylcarbenium ions followed by attenuation of the Lewis acidity with titanium alkoxides or alkyl ammonium chloride salts. *Bis*-diphenyl ethylenes, such as 2,2-*bis*[4-(1-phenylethenyl)phenyl]-propane and 2,2-*bis*[4-(1-tolylethenyl)phenyl]propane have also been used for coupling agents[173] where the living ionized chain ends may be reacted further with second monomer to producing mikto-arm star morpholgies.[174,175]

Unfortunately, the use of diphenylethylenes is limited due to difficultly in achieving complete capping at higher temperatures. At temperatures above -40 ^{o}C for $TiCl_4$ and -80 ^{o}C for BCl_3, the equilibrium constants of capping and decapping are unfavorable.[176,177,178]

Knoll *et al.*[179] first demonstrated the *in situ* synthesis of allyl chloride-terminated PIB by charging 1,3-butadiene to BCl_3-catalyzed isobutylene polymerizations. Later, Faust *et al.* [180,181] also obtained allyl chloride-terminated PIB by the *trans*-1,4-monoaddition of butadiene to $TiCl_4$-catalyzed quasiliving PIB. However, the allylchloride end group was insufficiently reactive for certain synthetic procedures, e.g., for quantitative reaction with poly(methyl methacrylate) living anions to create well defined block copolymers, due to the relatively strong carbon-chlorine bond, and it was necessary to utilize allylbromide end groups to obtain quantitative nucleophilic substitution.[182] Consequently, Faust *et al.* developed synthetic procedures to produce PIB-allylbromide, including post-polymerization halogen exchange with LiBr as well as the more complicated approach of wholesale replacement of the $TiCl_4$ polymerization

catalyst with a totally brominated Lewis acid system produced from mixtures of trimethyl aluminum and $TiBr_4$.[27]

The haloallyl functional polybutenes were later subjected to post polymerization nucleophilic substitution reactions to obtain hydroxyl, primary amine, alkyne, azide, and carboxylic acid end groups.[181] Hydroxyl end groups were obtained by reaction of the chloro- and bromoallyl terminated polybutenes with 1% KOH or tetrabutylammonium hydroxide in refluxing THF. Reaction of the bromide was significantly faster than the chloride, requiring only 3 h versus 24 h, and when using the more readily organic soluble tetrabutyl ammonium hydroxide, the bromoallyl end groups were hydrolyzed in only 1 h. Primary amines were obtained by first reacting the chloroallyl PIB with phthalimide, then subjecting this material to hydrazinolysis. The indirect route was chosen to avoid the formation of a mixture of primary, secondary, and teriatry species as would occur upon reaction with ammonia. Alkyne and azido functional polymer was obtained by reacting the chloroallyl functional polymers with propargyl alcohol and sodium azide. Finally, the carboxylate functionality was obtained by alkylation of dimethyl malonate, followed by decarboxylation of the malonic ester.

Quenching $TiCl_4$-catalyzed isobutylene with α-olefins, including 1,9-decadiene[183] and 9-decen-1-ol,[184] has been reported by Chiba *et al.* Surprisingly, with 9-decen-1-ol hydroxyl functionality as high as 95% was obtained, but the process was complicated by reaction of the bare hydroxyls with $TiCl_4$ and competitive hydrochlorination of the 9-decen-1-ol α-olefin moiety.

Schaffer disclosed a method of direct quenching of $TiCl_4$-catalyzed isobutylene polymerizations with alkylsilyl pseudohalides.[185] In particular, addition of azido

trimethylsilane to a $TiCl_4$-catalyzed quasiliving PIB resulted in exchange at the tertiary chloride end group to provide azide functionality.

Friedel-Crafts alkylation of aromatic quenching agents has been reported as a means of functionalizing quasiliving PIB. This has primarily involved heterocyclic aromatics such as pyrrole,[186] furan,[187] and thiophene.[188] These are rational choices in comparison to benzene or activated benzenes since a hetero-atom in the ring produces a higher electron density and allows the positive charge of the reactive intermediate to exist as a stabilized onium ion. In fact, Ivan and De Jong[189] postulated that five to seven membered heterocyclic aromatics, both unsubstituted and substituted with amino and hydroxyl moieties, would be effectively alkylated with quasiliving polyisobutylene. However, the position of the substituent group on the ring can have profound effects on reactivity. In addition, incorporation of certain nucleophilic moieties such as amino and hydroxyl can deactivate the catalyst.

Hadjikyriacou and Faust,[187] in a study of furan derivatives, were the first of several groups to thoroughly investigate heterocyclic aromatic quenchers. Furans substituted at the C-2 position, which cannot homopolymerize, were found to quantitatively add to the polyisobutylene chain at the C-5 position. The allylic cation generated upon addition is stabilized by the unshared electron pairs on the adjacent oxygen atom and can be trapped with tributyl hydride, yielding a dihydrofuran. Quenching with methanol re-aromatizes the furan functionality. *Bis*-furanyl compounds such as 2,5-*bis*-(2-furyl-2-propyl)furan were found to be excellent coupling agents and more easily prepared than *bis*-arylethylene coupling agents, and they can be used with weaker Lewis acids at higher temperatures. [190]

Storey *et al.*[186] later investigated more reactive *N*-methylpyrroles. They were able to obtain quantitative mono-addition of living polyisobutylene (C-2 and C-3 isomers in near equal proportions) using $TiCl_4$ as the co-initiator. Only 5-10% excess of the pyrrole relative to the number of chain ends was required for complete end-capping. Similar reactions involving BCl_3 as a co-initiator were less successful. Later, it was demonstrated that the *N*-alkyl group can be exploited as an alkylene tether for the attachment of more useful functional groups to PIB, such as primary halogen.[191]

There have been few reports on direct quenching of isobutylene polymerizations with less reactive arenes. Zhang *et al.*[192] performed Friedel-Crafts alkylation of triphenylamine at elevated temperatures (50 ^{o}C) on a mixture of *tert*-chloride and *exo*-olefin functional polyisobutylene that had been synthesized from an $H_2O/TiCl_4$ initiating system at -40 ^{o}C. The alkylations were performed both *in situ* and post-polymerization on a purified polymer. In either case, the maximum capping efficiency was in the 70 to 80% range, and the process was plagued by competitive *exo*-olefin formation. Fujisawa *et al.*[193] have disclosed the $SnCl_4$ catalyzed alkylation of vinylalkoxybenzenes with both *tert*-chloride and olefin terminated PIB. The alkylation reactions were performed in methylene chloride from -30 ^{o}C to room temperature, and vinyl end group functionalities from 76-90% were obtained.

Preview

The current volume of work involves *in situ* chain end functionalization of quasiliving polyisobutylene and builds from research initiated over 20 years previously. As outlined above, much effort has gone into the pursuit of operable nucleophiles that can quantitatively modify the quasiliving PIB chain end to a useful functionality. Though

efficacy has been demonstrated for a number of technologies, functionalization of the PIB chain end is still considered a challenge and this obstacle, among others, has largely relegated quasiliving PIB to laboratory scale preparations. The necessity for an efficient, robust and economical process for producing functional PIBs has been the impetus for the developments recounted in the following chapters. Chapter II focuses on further elucidation of the mechanism involved with the deliberate addition of hindered amines to quasiliving PIB, which induces β-proton elimination and provides quantitative *exo*-olefin chain end functionality. Kinetic measurements highlight the significant difference in interaction of the $TiCl_4$ catalyst with 2,5-disubstituted-*N*-hydropyrroles compared with other sterically hinder amines. Chapter III examines direct addition of sulfides and disulfides to $TiCl_4$-catalyzed quasiliving PIB. Low temperature NMR experiments were used to identify the sulfonium ion adduct intermediate structures. Selective decomposition of the sulfide-PIB adducts provided high yields of *exo*-olefin; whereas selective decomposition of functional disulfide-PIB adducts resulted in cleavage of the disulfide and retention of the functional fragment on the end of the polymer chain. Chapter IV expands on previous work with *N*-substituted pyrroles, and a protected *N*-(ω-hydroxyalkyl)pyrrole was used for single-pot synthesis of PIB with primary hydroxyl end groups. Chapter V describes the direct addition of alkyl phenyl ethers to $TiCl_4$-catalyzed quasiliving isobutylene polymerizations. The phenoxy moiety, though less reactive than a heterocyclic aromatic, was found to quantitatively cap the PIB chain ends via electrophilic aromatic substitution. While the alkylations were faster at lower temperatures, they were also tolerant of higher temperatures where olefinic chain ends often arise and are detrimental to other functionalization reactions. Many highly sought

after functionalities were obtained directly at the PIB chain end from placement on the alkyl tether of the alkyl phenyl ether quenching agent, including primary halide, silyl chloride, alkynyl, primary hydroxyl and primary amine.

CHAPTER II

KINETICS AND MECHANISM OF END-QUENCHING OF $TiCl_4$-CATALYZED QUASILIVING POLYISOBUTYLENE WITH STERICALLY HINDERED AMINES

Introduction

We recently reported that direct addition of certain sterically hindered organic bases to $TiCl_4$-catalyzed quasiliving polyisobutylene (PIB) leads to quantitative *exo*-olefin chain end formation.[151] This regioselective elimination at the carbenium ion chain end occurred via reaction with a small fraction of the base that remained uncomplexed with $TiCl_4$ due to steric hindrance. The degree of complexation with $TiCl_4$ determined the nominal amount of base necessary in the reaction to provide a concentration of "free" base sufficiently high to scavenge carbenium ion chain ends and prevent chain coupling. The examples of 2-*tert*-butylpyridine (2TBP) and 1,2,2,6,6-pentamethylpiperidine (PMP) were provided, the former of which apparently complexed with $TiCl_4$ to a greater extent, and therefore led to greater chain coupling under the same set of reaction conditions. Quenching to *exo*-olefin was also demonstrated with the base, 2,5-dimethylpyrrole (25DMP), which worked surprising well and was thought to have fundamentally different behavior. Here we provide a more detailed analysis of the kinetics and mechanism for quenching $TiCl_4$-catalyzed quasiliving PIB with sterically hindered amines, as well as delineate the mechanism of reaction between simple tertiary and second amines and that of 2,5-disubstituted-*N*-hydropyrroles.

Experimental

Materials

Hexane (anhydrous, 95 %), titanium tetrachloride ($TiCl_4$) (99.9 %,), 2,6-lutidine (redistilled, 99.5%), 2,5-dimethylpyrrole (25DMP) (98%), 2-*tert*-butylpyridine (2TBP) (98%), 1,2,2,6,6-pentamethylpiperidine (PMP) (97%), 2,2,6,6-tetramethylpiperidine (TMP) (99%), cyclohexane (anhydrous, 99.5%), methanol (anhydrous, 99.8%) and chloroform-*d* ($CDCl_3$) were purchased from Sigma-Aldrich Co. and used as received. Methyl chloride from Alexander Chemical Corp. was dried by passing the gas through columns of $CaSO_4$/molecular sieves/$CaCl_2$ and condensed within a N_2-atmosphere glove box immediately prior to use. Monofunctional *tert*-chloride-terminated PIB (2.0×10^3 g/mol) was prepared via BCl_3-catalyzed polymerization of isobutylene from TMPCl in methyl chloride[194] at -60 ^{o}C.

Instrumentation

Nuclear magnetic resonance (NMR) spectra were obtained using a 300 MHz Varian Mercury^{plus} NMR spectrometer. Standard ^{1}H and ^{13}C pulse sequences were used. Composite pulse decoupling was used to remove proton coupling in ^{13}C spectra. All ^{1}H chemical shifts were referenced to TMS (0 ppm), and all ^{13}C shifts were referenced to the residual $CDCl_3$ solvent resonance (77.0 ppm). PIB samples were prepared by dissolving the polymer in $CDCl_3$ (20-50 mg/mL) and charging the solution to 5 mm o.d. NMR tubes.

Kinetics of Quenching

The kinetics for β-proton abstraction from quasiliving PIB were determined by addition of amines to *tert*-chloride PIB in 60/40 (v/v) hexane/methylchloride at -60 ^{o}C

and subsequent activation with $TiCl_4$. Within a N_2-atmosphere glove box, 1.6 g (8×10^{-4} mol) monofunctional *tert*-chloride-terminated PIB (2.0×10^3 g/mol) was dissolved in 480 mL of hexane at room temperature. The mixture was chilled to -60 ^oC in a 4-neck round bottom flask equipped with an overhead stirrer, and 320 mL of methylchloride was then added. To this solution were added 0.47 mL (4×10^{-3} mol) of 2,6-lutidine and various amounts of the amine quenchers, ranging from 0.5 to 8 equiv per chain end ($4 – 64 \times 10^{-4}$ mol). After thermal equilibration, $TiCl_4$ was charged to the reactor in amounts ranging from 25 to 40 equiv per chain end ($2.0 – 3.2 \times 10^{-2}$ mol). Aliquots of 100 mL were taken from the reaction and poured into beakers containing 25 mL of chilled methanol. Conversion from *tert*-chloride to *exo*-olefin chain ends was estimated by integration of the ^1H NMR spectra of aliquots taken from the reactions. *tert*-Chloride chain ends are characterized by resonances at 1.69 (methyl) and 1.96 ppm (methylene) and *exo*-olefin chains ends by resonances at 1.78 (methyl), 2.00 (methylene) and 4.82 and 4.84 ppm (vinyl).[195] No resonances were observed at 5.15 ppm due to *endo*-olefin chain ends or 4.82 ppm due to chain coupling.[196]

Pyrrole-$TiCl_3$ Adduct Formation

25DMP was reacted with $TiCl_4$ in the presence of 2,6-lutidine for spectroscopic identification of a pyrrole-$TiCl_3$ adduct. Within a N_2-atmosphere glove box, 0.1 mL (9.3×10^{-4} mol) of cyclohexane (as an internal reference), 0.108 mL (1.0×10^{-3} mol) of 25DMP and 0.116 mL (1.0×10^{-3} mol) of 2,6-lutidine were added to 10 mL of $CDCl_3$ at -60 ^oC. Adduct formation was achieved by addition of 0.658 mL (6.0×10^{-3} mol) of $TiCl_4$. The reaction produced HCl, resulting in the immediate formation of a brown precipitate consisting of 2,6-lutidinium $Ti_2Cl_9^-$ salt . Aliquots were taken before and after

addition of $TiCl_4$ (once the solids had settled) and charged directly to 5 mm o.d. NMR tubes for analysis.

Results and Discussion

In our previous report[151] we proposed that end quenching of $TiCl_4$-catalyzed quasiliving PIB with certain amines, e.g., 2TBP or PMP, proceeded according to the mechanism shown in Figure 2-1. Complexation of these amine bases with $TiCl_4$ is incomplete due to steric hindrance, resulting in a finite concentration of free base in solution; the free base regio-specifically abstracts a β-proton from the PIB carbenium ion to produce exclusively *exo*-olefin chain ends. It was further proposed that the hindered base may be regenerated when a stronger, fully complexed base such as 2,6-lutidine is present and capable of acting as a proton sink. We also showed that 25DMP was an effective quencher, but suggested that it might operate through a different mechanism.

To further elucidate the mechanism of quenching by sterically hindered amines, reaction kinetics were investigated in 60/40 (v/v) hexane/methyl chloride at -60 ^{o}C. In general, the rate of disappearance of *tert*-chloride chain ends, [PIBCl], is directly proportional to concentration of carbenium ion chains, [PIB^+], and the concentration of the species, [*Q*], responsible for β-proton extraction from the ionized chain end.

$$-\frac{d[PIBCl]}{dt} = k_{-H}[PIB^+][Q] \qquad (1)$$

Assuming that ionization involves two equivalents of $TiCl_4$ to form $Ti_2Cl_9^-$ counterions[197] and is fast and unperturbed by proton abstraction, we may reduce eq 1 to a more accessible form,

$$-\frac{d[PIBCl]}{dt} = k_{-H}K_{eq}[PIBCl][TiCl_4]^2[Q] \qquad (2)$$

where K_{eq} is the ionization equilibrium constant. Integration of eq 2 in terms of conversion (p) of *tert*-chloride chain ends yields

$$\ln\left(\frac{1}{1-p}\right) = k_{-H}K_{eq}[TiCl_4]^2[Q]t \quad (3)$$

Plots of ln(1/1-p) versus time (t) should be linear, and the quenching reaction should exhibit first-order kinetics provided that $k_{-H}K_{eq}[TiCl_4][Q]$ remains constant during measurement. Unfortunately, $[TiCl_4]$ is expected to decrease over the course of the reaction via the formation onium salts, and [Q] may also decrease in the absence of a stronger base such as 2,6-lutidine. 2,6-Lutidine is not capable of proton extraction under conditions common for $TiCl_4$-catalyzed quasiliving isobutylene polymerization;[16] however, protons may be transferred from weaker bases to 2,6-lutidine. The potential variation of [Q] and $[TiCl_4]$ can be readily dealt with by considering only initial rates. However, we chose to use somewhat dilute reaction systems to enable the more useful integral analysis. The chain end concentration was lowered to 0.001 M, and the nominal $TiCl_4$ concentration set to $[TiCl_4]_0 = 20[PIBCl]_0$.

First-order kinetic plots for end-quenching of $TiCl_4$-catalyzed quasiliving PIB with 2TBP are shown in Figure 2-2. The plots are linear in accordance with eq 3, and plots similar to Figure 2-2 were obtained for quenching with TMP, PMP and 25DMP. Figure 2-3 shows the observed first-order rate constants for the various amines as a function of nominal concentration. For 2TBP, TMP and PMP the plotted data are more or less linear, monotonically increasing over the range of 4 to 8 equiv per chain end. In contrast, the observed first-order rate constant for 25DMP is proportional to nominal quencher concentration only at low quencher concentrations; it then reaches a maximum

and finally decreases with increasing concentration. The early appearance of this maximum for 25DMP suggests a significant difference in the mechanism of reaction, a difference attributable to the manner of interaction with $TiCl_4$.

As suggested in Figure 2-1, for amine bases such as 2TBP, the mode of interaction with $TiCl_4$ is formation of a reversible 1:1 complex. The complex that forms is unreactive toward β-proton abstraction at the carbenium ion chain end. However, if the steric hindrance around nitrogen prevents exhaustive complexation, then residual free base is available to react with the carbenium ion to produce *exo*-olefin chain ends.[156] We may revise eqs 1-3 to account for complexation in terms of a complexation equilibrium constant (K_{com}),

$$K_{com} = \frac{[Q:TiCl_4]}{[Q][TiCl_4]} = \frac{[Q]_0 - [Q]}{[Q][TiCl_4]} \qquad (6)$$

where $[Q]_0$ is the initial, nominal concentration of quencher and $[Q:TiCl_4]$ is the concentration of the complex. The concentration of $TiCl_4$ is decreased by 1:1 complexation with base, and assuming near complete complexation of the quencher ($1 << K_{com}[TiCl_4]$), eq 3 becomes:

$$\ln\left(\frac{1}{1-p}\right) = k_{-H}\frac{K_{eq}}{K_{com}}[TiCl_4]_{effective}[Q]_0\, t \qquad (7)$$

The effective $TiCl_4$ concentration is approximately $[TiCl_4]_{effective} = [TiCl_4]_0 - [2,6\text{-lutidine}] - [Q]_0$, where $[TiCl]_0$ is the nominal $TiCl_4$ concentration charged to the reactor. Eq 7 predicts that the rate of the quenching rises linearly at low $[Q]_0$, but a maximum will occur and the rate will eventually fall with increasing $[Q]_0$ (a parabolic dependence on $[Q]_0$). As more quencher is used, the rate initially increases due to higher amounts of free base; however, the rate is simultaneously retarded due to a decrease in available $TiCl_4$

because of complexation with the quencher. A maximum rate is predicted from the kinetic model at $[Q]_0 = ([TiCl_4]_0 - [2,6\text{-lutidine}])/2$. In Figure 2-3, the maximum should appear at $[Q]_0 = 0.01$ M, a value outside the experimental space; hence the maximum is not observed. The rates of quenching with the piperidines in Figure 2-3 were faster than that with 2TBP, and this observation can be explained by higher free base concentration for the piperidines caused by increased steric hindrance around nitrogen that prevents complexation with $TiCl_4$. The fastest rates of proton abstraction, other than with 25DMP, were observed with the extremely hindered PMP. Figure 2-4 shows a plot of the first-order rate constants for quenching with 2TBP as a function of $[TiCl_4]_{effective}$. The slope of the plot indicates a first order dependence on the effective concentration of $TiCl_4$ as predicted by eq 7.

For 25DMP in Figure 2-3 the rate of quenching for a given nominal concentration of quencher is fast compared with the other amines and it is unlikely that such a relatively fast rate could be due to only a minute concentration of the free quencher available for proton abstraction. In fact, using a calculated value[198] for K_{eq} under these conditions of 5.5×10^{-8} M^{-2}, for the first few data points for 25DMP in Figure 2-3, eq 3 predicts a value of k_{-H} that is approximately at the diffusion limit even when [Q] is set to the nominal concentration of charged quencher. In addition, the maximum rate of proton abstraction for 25DMP in Figure 2-3 occurs at a lower $[Q]_0$ than predicted by eq 7, and as discussed later, ^{1}H NMR spectroscopy showed that reaction of 25DMP and $TiCl_4$ appears to be irreversible, in contrast to a reversible complexation with $TiCl_4$ that is typical of other amines. These observations indicate that interaction between $TiCl_4$ and 25DMP is not happening to the extent or in the manner outlined in Figure 2-1. Thus we propose an

alternative mechanism shown in Figure 2-5, in which the proton on nitrogen is displaced to form a 25DMP-$TiCl_3$ adduct with HCl as a byproduct. According to Dias *et al.*[199] the expected adduct for 25DMP is an η^5 coordination complex with titanium rather than the more energetic σ complex in which titanium is bonded directly to nitrogen. The HCl generated results in onium salts and further loss of $TiCl_4$. According to this mechanism, the correct form of eq 3 for 25DMP then becomes

$$\ln\left(\frac{1}{1-p}\right) = k_{-H} K_{eq} [TiCl_4]^2_{effective} [Q]_0 \, t \qquad (8)$$

where $[TiCl_4]_{effective} = [TiCl_4]_0 - [2,6\text{-lutidine}] - 2[Q]_0$. According to Figure 2-5, a net consumption of two molecules of $TiCl_4$ occurs for every 25DMP-$TiCl_3$ adduct formed, when $[2,6\text{-lutidine}] > [Q]_0$. If the concentration of 25DMP exceeds that of 2,6-lutidine, the consumption of $TiCl_4$ is higher, and the rate will decrease even faster, as some fraction of 25DMP or 25DMP-$TiCl_3$ adduct will precipitate from the reaction due to formation of onium salts. Again, a maximum rate is predicted by the model, but at a much lower $[Q]_0$, namely at $[Q]_0 = ([TiCl_4]_0 - [2,6\text{-lutidine}])/6$. In Figure 2, the maximum occurs at approximately $[Q]_0 = 0.003$ M as predicted from eq 8. The dependence of the rate on $[TiCl_4]_{effective}$ is illustrated in Figure 3 for the case of 25DMP, and the slope of approximately two indicates a second order dependence on $[TiCl_4]_{effective}$, again, consistent with eq 8.

The 25DMP -$TiCl_3$ adduct is formed immediately upon charging 25DMP to the reactor, and when 2,6-lutidine is present in the reaction system in excess, essentially all of the 25DMP-$TiCl_3$ adduct remains in solution and is capable of β-proton abstraction from the carbenium ion chain end. 2,6-Lutidine (pKa = 6.75)[200] is more basic than

25DMP (pKa = -0.71),[201] and is certainly expected to be more basic than the 25DMP-$TiCl_3$ adduct. Direct evidence for the 25DMP-$TiCl_3$ adduct was obtained by adding $TiCl_4$ to an approximately equimolar mixture of 25DMP and 2,6-lutidine in $CDCl_3$ at -60 ^oC. Upon addition of $TiCl_4$ to the mixture, precipitation of onium salts immediately occurred. Once the precipitate settled, an aliquot was taken, and the room temperature ^1H NMR spectrum of the aliquot is shown in Figure 2-6 B. The spectrum in Figure 2-6 A is of the solution before addition of $TiCl_4$ and is included as a reference. Note that the solution also contained a small quantity of cyclohexane as an internal reference for ^1H NMR integration. In Figure 2-6 B, the resonances due to the pyrrole moiety have an intensity approximately equal to that before addition of $TiCl_4$, indicating that the 25DMP-$TiCl_3$ adduct remains in solution. The resonances have been shifted down field from their original values at 2.22 and 5.75 ppm for 25DMP to 2.80 and 7.02 ppm for the 25DMP-$TiCl_3$ reaction product. This downfield shift would be expected from the deshielding effect of the $TiCl_3$ ligand. The resonances due to 2,6-lutidine are also shifted down field from their original values at 2.52, 9.94 and 7.45 ppm to 2.97, 7.67 and 8.35 ppm due to complexation with $TiCl_4$. However, the signal intensity for 2,6-lutidine has diminished significantly due to formation of onium salts that have precipitation from solution. A ^{13}C NMR spectrum of the sample of Figure 2-6 B exhibits resonances due to pyrrole at 19.7, 126.6 and 157.1 ppm, consistent with the formation of an η^5 adduct.[199]

Additional support for the formation of the pyrrole-$TiCl_3$ η^5 complex and its activity as a quenching agent comes from the fact that 1,2,5-trimethylpyrrole proved ineffective as a quencher of $TiCl_4$-catalyzed isobutylene polymerizations;[202] this quencher returned only *tert*-chloride chain ends. With the *N*-methyl substituent present

the pyrrole-$TiCl_3$ adduct cannot form; electrophilic aromatic substitution also does not occur apparently due to the methyl substituents at the C-2 and C-5 positions.[186] 2,3,4,5-Tetramethylpyrrole, which has the requisite replaceable hydrogen on nitrogen, and due to greater electron density in the ring, is expected to form an η^5 titanium complex even more readily than 25DMP, was also shown to be a highly effective quencher, returning exclusively *exo*-olefin chain ends.

Quenching reactions involving 2,5-disubstituted-*N*-hydropyrroles, such as 25DMP or 2,3,4,5-tetramethylpyrrole, are able to proceed rapidly at low $[Q]_0/[TiCl_4]_0$ ratios because most or all of the pyrrole charged to the reaction, once complexed with $TiCl_4$, can actively extract protons from the carbenium ion chain end. For strongly basic, sterically hindered amines, such as 2TBP, a dominant fraction of the base is complexed with $TiCl_4$ and therefore unavailable for reaction at the carbenium ion chain end. As shown previously,[151] the nominal concentration of hindered amine, especially for those that complex with $TiCl_4$ to the greatest extent, must be adjusted upward to reduce chain coupling. The rate of coupling (r_c) is proportional to the concentration of ionized chain ends as well as the concentration of *exo*-olefin chain ends [PIB=].

$$r_c = k_c K_{eq}[PIBCl][TiCl_4]^2[PIB=] \tag{9}$$

Taking the ratio of the rate of quenching (proton abstraction, r_{-H}) relative to the rate of coupling for sterically hindered amines involved in 1:1 complexation with $TiCl_4$,

$$\frac{r_{-H}}{r_c} = \frac{k_{-H}}{k_c K_{com}} \frac{[Q]_0}{[TiCl_4][PIB=]} \tag{10}$$

it is evident that coupling can be minimized using lower chain end concentrations, lower $TiCl_4$ concentrations and higher nominal quencher concentrations. To optimize the ratio

r_{-H}/r_c at a given chain end concentration, the ratio $[Q]_0/[TiCl_4]$ should be maximized, and this is most easily accomplished by an increase in $[Q]_0$, which will also lead to a decrease in $[TiCl_4]$ due to complexation. For amines such as 25DMP, the ratio of the rate of quenching to that of coupling is expressed differently:

$$\frac{r_{-H}}{r_c} = \frac{k_{-H}}{k_c}\frac{[Q]_0}{[PIB =]} \qquad (11)$$

From eq 11 it is evident that elimination of coupling is easier with 25DMP because the concentration of active quencher is not reduced by complexation with $TiCl_4$; however, the amount of $TiCl_4$ must be adjusted to account for pyrrole-$TiCl_3$ adduct formation.

Conclusion

Using controlled kinetic experiments we were able to demonstrate a fundamentally different mode of interaction of $TiCl_4$ with 2,5-disubstituted-*N*-hydropyrroles as compared to other sterically hindered amines during end-quenching of quasiliving isobutylene polymerizations. With strongly basic, sterically hindered tertiary and secondary amines, the mode of interaction is simple 1:1 complexation; however, with pyrrole such as 25DMP, reaction occurs with $TiCl_4$ to form a pyrrole-$TiCl_3$ adduct. The adduct is capable of extracting β-protons from the PIB carbenium ion chain end, effectively producing *exo*-olefin terminated PIB with rates faster than can be attained with other sterically hindered amines at low quencher/$TiCl_4$ ratios.

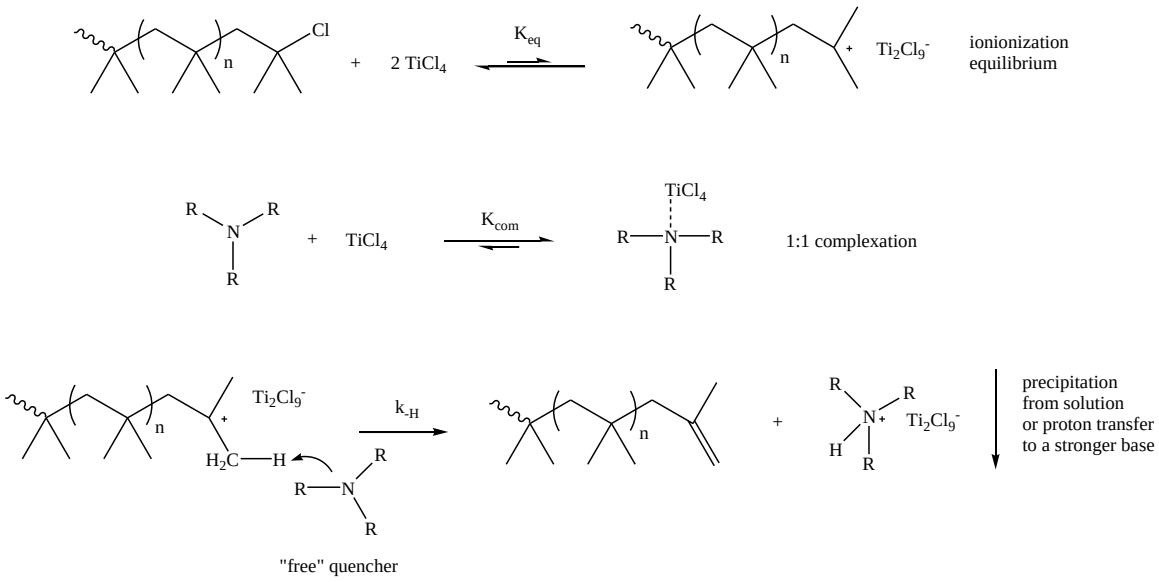

Figure 2-1. Mechanisms for β-proton abstraction from the PIB carbenium ion chain end when using either sterically hindered amines that undergo 1:1 complexation with $TiCl_4$.

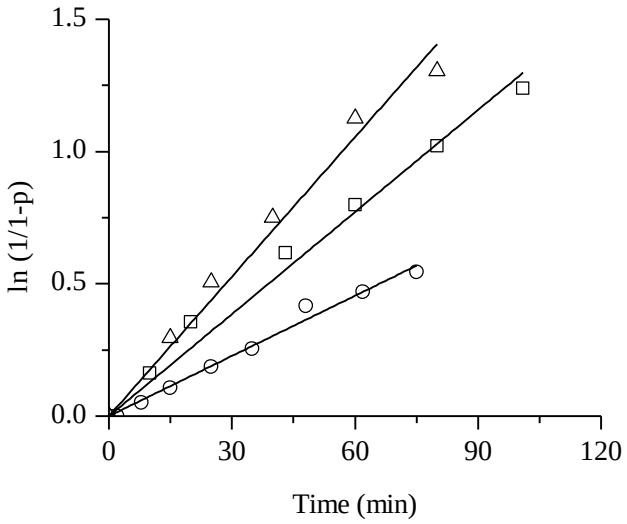

Figure 2-2. First-order kinetic plots for quenching of $TiCl_4$-catalyzed quasiliving PIB with 2TBP at -60 ^oC in 60/40 (v/v) hexane/methylchloride. $[PIBCl]_0$ = 0.001 M, [2,6-lutidine] = 0.005 M, $[TiCl_4]_0$ = 0.025 M and $[Q]_0$ = 0.00325 (○), 0.005 (□) and 0.007 M (△).

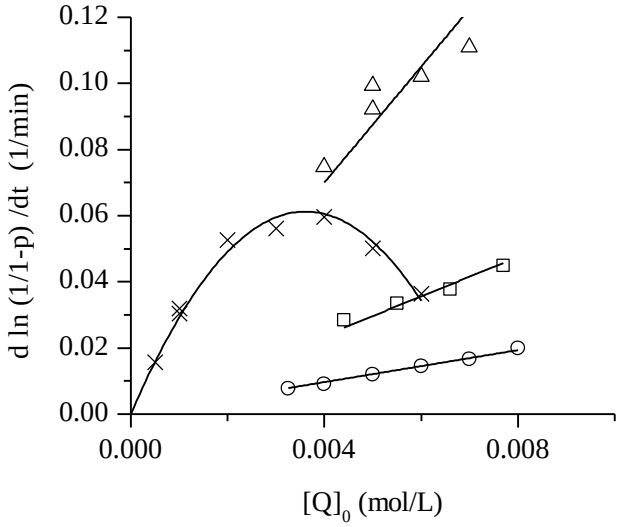

Figure 2-3. Plot of the apparent rate constant for quenching of $TiCl_4$-catalyzed quasiliving PIB as a function of the nominal amine concentration, $[Q]_0$. Reactions were carried out at -60 ^oC in 60/40 (v/v) hexane/methyl chloride with $[PIBCl]_0$ = 0.001 M, [2,6-lutidine] = 0.005 M, $[TiCl_4]_0$ = 0.025 M. 25DMP (×), 2TBP (○), TMP (□) and PMP (△).

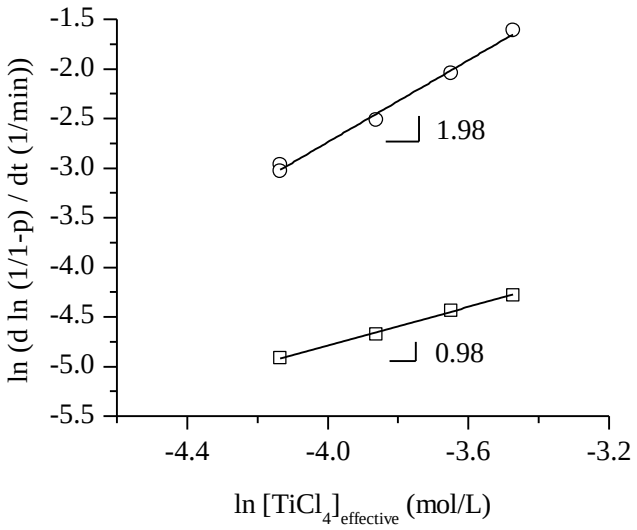

Figure 2-4. ln-ln plot of the apparent rate constant for quenching vs. $[TiCl_4]_{effective}$ for $TiCl_4$-catalyzed quasiliving PIB at -60 ^oC in 60/40 (v/v) hexane/methyl chloride, with $[PIBCl]_0$ = 0.001 M, [2,6-lutidine] = 0.005 M, and $[TiCl_4]_0$ = 0.025, 0.030, 0.035, and 0.040 M. 2TBP (□): $[Q]_0$ = 0.004, $[TiCl_4]_{effective} = [TiCl_4]_0 - [2,6\text{-lutidine}] - [Q]_0$. 25DMP (○): $[Q]_0$ = 0.002 M and $[TiCl_4]_{effective} = [TiCl_4]_0 - [2,6\text{-lutidine}] - 2[Q]_0$.

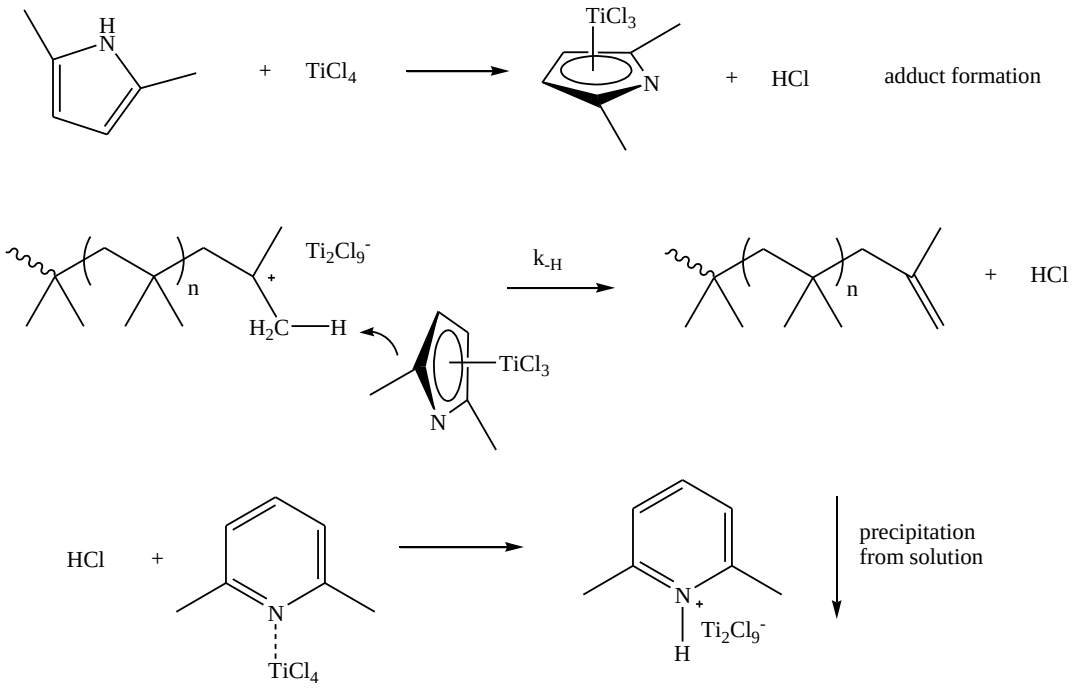

Figure 2-5. Mechanisms for β-proton abstraction from the PIB carbenium ion chain end when using 2,5-disubstituted-*N*-hydropyrroles that form pyrrole-$TiCl_3$ adducts.

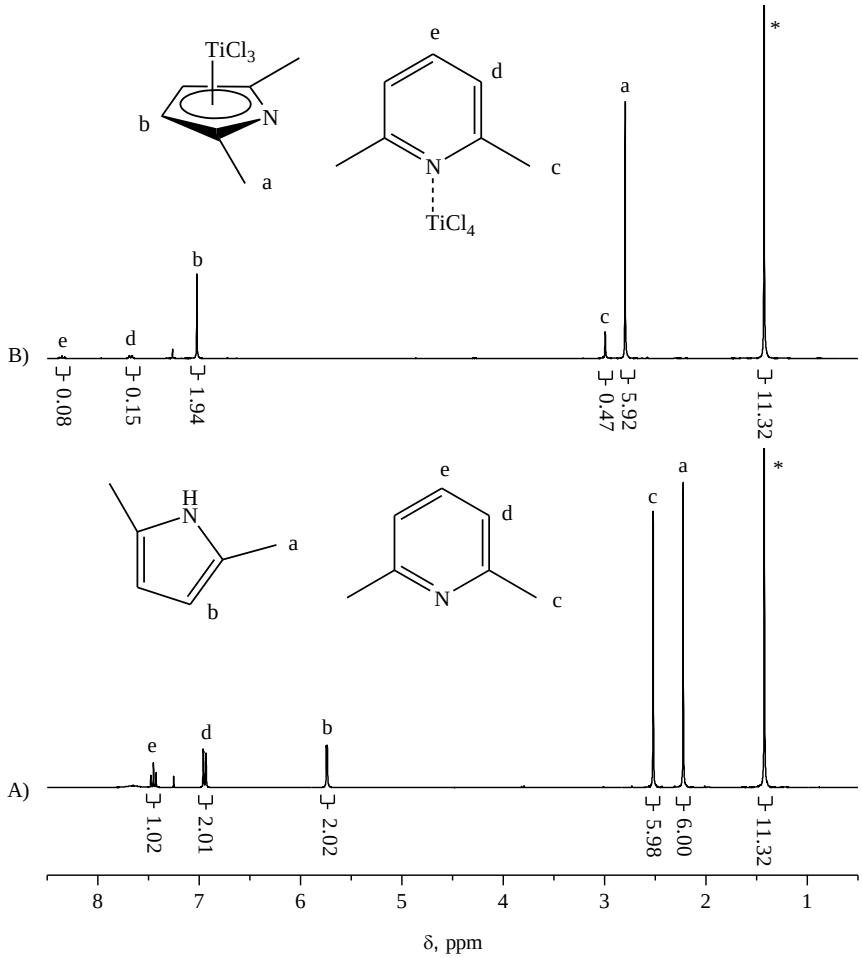

Figure 2-6. ^{1}H NMR (300 MHz, $CDCl_3$, 22 ^{o}C) of 25DMP and 2,6-lutidine A) before and B) after addition of excess $TiCl_4$ at -60 ^{o}C. Cyclohexane (*) included as an internal reference.

CHAPTER III

SULFONIUM ION ADDUCTS FROM QUASILVING POLYISOBUTYLENE AND MONO- OR DI-SULFIDES

Introduction

In situ functionalization of quasiliving polyisobutylene (PIB) is an inherently difficult task due to the stability imparted by the low number of active or ionized chain ends. For a typical isobutylene polymerization catalyzed by $TiCl_4$, the dormant-active equilibrium constant is very low,[203] near 10^{-7} M^{-2}. When a nucleophilic quenching or capping agent is deliberately added to the polymerization, it is more likely to be rapidly consumed by interaction with the Lewis acid rather than reacting with the carbenium ion chain ends. The result is ion-pair collapse and production of unmodified *tert*-chloride terminated PIB. To date, only a few successful quenching reactions have been reported, including capping by non-polymerizing olefins,[162,157,149,150,146,180] substitution at highly reactive aromatic substrates,[176,186,188] and those that lead to β-proton elimination.[151]

Here we report on a use of sulfides and disulfides as quenching/capping agents for $TiCl_4$-catalyzed isobutylene polymerizations. We show that when a (di)sulfide is added to an isobutylene polymerization, consumption of monomer ceases and a low-temperature-stable sulfonium ion adduct is formed. When a more reactive nucleophile is then added, such as an alcohol or amine, both substitution (ether or thioether) and elimination (*exo*-olefin) products are obtained at the PIB chain end. The stability of sulfonium ions has been used previously in other cationic polymerization systems to impart control but not as a means for chain end functionalization. For example, during the polymerization of epoxides[204], styrenics[205] or vinyl ethers[206,207] the carbenium or oxonium ions may be

trapped as more stable trivalent sulfonium ions, either slowing or stopping monomer consumption.

The formation of small molecule alkyl sulfonium salts and subsequent nucleophilic decomposition was originally studied by Hughes, Ingold, and Maw.[208] They formed alkyl dimethylsulfonium iodides by reacting alkyl thiols with two equivalents of methyl iodide. The primary, secondary, and tertiary alkyl dimethyl sulfide adducts were reacted with sodium ethoxide in ethanol at or above room temperature. Typically, adduct decomposition resulted in elimination accompanied by nucleophilic substitution. When substitution occurred, either a methyl group of the sulfide moiety was displaced, creating a thioether, or the entire sulfide moiety was replaced with ethoxide, creating an ether.

Experimental

Materials

Titanium (IV) tetrachloride (99.9%), hexane (95%, anhydrous), 2,6-lutidine (26Lut, 99+%, redistilled), carbon disulfide (99.9%), and d_2-dichloromethane (99.9% D) were used as received from Sigma-Aldrich. Isobutylene (IB) from BOC and methyl chloride (MeCl) from Alexander Chemical Corp. were passed through columns of $CaSO_4$/molecular sieves/$CaCl_2$ and condensed within a N_2-atmosphere glove box immediately prior to use.

Initiators, Oligo-isobutylenes, and tert-Chloride PIB Masterbatch

2-Chloro-2,4,4-trimethylpentane (TMPCl), 2-chloro-2,4,4,6,6,8,8-heptamethylnonane (C_{16}PIBCl), and 2-chloro-2,4,4,6,6,8,8,10,10-nonamethylundecane (C_{20}PIBCl) were prepared by bubbling HCl gas through neat 2,4,4-trimethyl-1-pentene (Sigma-Aldrich), 2,4,4,6,6,8,8-heptamethyl-1-nonene (Chevron Oronite) in CH_2Cl_2, and

2,4,4,6,6,8,8,10,10-nonamethyl-undec-1-ene (Chevron Oronite) in CH_2Cl_2, respectively, at 0 °C. The HCl-saturated TMPCl was stored at 0 °C, and immediately prior to use it was neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered. The HCl-saturated C_{16}PIBCl and C_{20}PIBCl were neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under vacuum and the product stored at 0 °C. Low molecular weight polyisobutylene ($\overline{M}_n$ = 2.0 x10^3 g/mol, $\overline{M}_w / \overline{M}_n$ = 1.03 by GPC-MALLS) with *tert*-chloride end groups ("*tert*-chloride PIB masterbatch") was prepared via the BCl_3-catalyzed polymerization of isobutylene from TMPCl in methyl chloride[194] at -60 °C.

Sulfides, Ddisulfides, and Nucleophilic Terminators

Dimethyl sulfide (99%), diisopropyl sulfide (99%), dimethyl disulfide (99%), diethyl disulfide (99%), di-*tert*-butyl disulfide (97%), *n*-butylamine (99.5%), triethylamine (99.5%), 1,2,2,6,6-pentamethylpiperidine (97%), 2,6-di-*tert*-butylpyridine (>97%), and 2,5-dimethylpyrrole (98%) were used as received from Sigma-Aldrich. Diisopropyl disulfide (96%), di-*p*-tolyl disulfide (98%), and ethanol (99.5%) were used as received from Acros Organics. *Bis*(2-chloroethyl) disulfide was prepared using a published procedure.[209]

Bis(2-bromoethyl) disulfide was prepared using a variation of a published procedure.[210] To a round-bottom flask at room temperature were added 113 mL (1.0 mol) of 48% hydrobromic acid, followed by 13 mL of concentrated sulfuric acid, in portions with stirring. Using a syringe, 30.85 g (0.20 mol) of *bis*(2-hydroxyethyl) disulfide (Sigma-Aldrich, technical grade) was charged to the reactor, followed by an additional 11 mL of concentrated sulfuric acid, in portions with stirring. The resulting

biphasic mixture was refluxed for 2-3 h. Upon cooling, the organic layer was taken up into 200 mL of diethyl ether. The ether solution was washed with saturated $NaHCO_3$ solution and then with distilled water, dried by stirring over $MgSO_4$, filtered, and finally concentrated on a rotary evaporator to yield 52.72 g (94%) of crude *bis*(2-bromoethyl) disulfide. The product was dissolved in hexane and passed through a silica gel column. Removal of the hexane on a rotary evaporator afforded 44.47 g (79%) of a clear, oily liquid; ^{1}H NMR δ 3.10 (t, 4H, SCH_2), δ 3.62 (t, 4H, CH_2Br).

Isobutylene Polymerization and (Di)Sulfide Quenching

PIBs with various end-functionalities (Table 3-1) were obtained from isobutylene polymerization and quenching reactions carried out within a N_2-atmosphere glove box fitted with a cryostated heptane bath. Polymerizations were conducted in stirred round-bottom flasks at -60 ^{o}C using a co-solvent mixture of hexane/methyl chloride 60/40 (v/v) unless otherwise indicated. Isobutylene polymerizations were initiated from TMPCl and catalyzed by $TiCl_4$. The base, 2,6-lutidine, was used as water scavenger/common ion generator. In some cases, consumption of monomer was followed in real time via ATR-FTIR spectroscopy, as previously described,[211] by monitoring the diminution of the absorbance at 887 cm^{-1} due to the $=CH_2$ wag of isobutylene. ATR-FTIR reaction monitoring was not always available, and in those cases, the required polymerization time was estimated from previous kinetic measurements. The (di)sulfide quenching agent of interest was added (1.1 - 2 equiv per chain end) to the reactor at the desired monomer conversion (typically >98%) and allowed to react for 10-20 min. Then, excess chilled alcohol or amine terminating agent was added to finish/terminate the reaction. Preliminary experiments indicated that PIB-sulfonium ion adduct formation was rapid

and quantitative at low temperature (e.g. -60 °C) and thus the exact time allowed before subsequent addition of nucleophiles to terminate the reaction was not critical and could be dictated by convenience. In some cases, the polymerization mixture was quenched with a (di)sulfide and then divided into glass tube reactors so that a common PIB-sulfonium ion adduct could be terminated with different nucleophiles (Condition A). In another case, the mixture was divided prior to quenching so that a common quasiliving PIB could be quenched with different (di)sulfides (Condition B). Two preparative-scale reactions were conducted to produce larger quantities of primary halogen-terminated PIB (Conditions C and D). Finally, *tert*-chloride-terminated PIB ("*tert*-chloride PIB masterbatch") prepared in a separate BCl_3-catalyzed reaction was divided into tubes, re-activated with $TiCl_4$, and quenched with various disulfides and terminating agents (Condition MB). The various conditions used were dictated by the objectives of the experiments; for example, in the preparative-scale experiments, to achieve appropriate reaction rates both during polymerization and quenching, total $TiCl_4$ was added in two separate charges, a first charge to catalyze the polymerization and a second charge, after addition of the (di)sulfide, to catalyze the sulfonium ion formation. Details of the conditions used for the samples in Table 3-1 were as follows:

Condition A (Table 3-1). Polymerization reaction mixtures were quenched with a (di)sulfide and then divided into several glass tube reactors, each of which received a different terminating nucleophile. Reaction concentrations were as follows: [IB] = 0.82 M; [TMPCl] = 0.021 M; [26Lut] = 0.010 M; $[TiCl_4]/[TMPCl] = 5.0$; [(di)sulfide]/[TMPCl] = 1.5. Condition A is representative of those polymerization reactions divided into glass tubes and is therefore described in detail for the case of

quenching with diisopropyl sulfide: A four-necked 500 mL round-bottom flask, equipped with an overhead mechanical stirrer and platinum resistance thermometer, was charged with 165 mL of hexane (-60°C), 110 mL of methyl chloride (-60°C), 1.06 mL of TMPCl (RT, 6.2 mmol), 0.35 mL of 26Lut (RT, 3.0 mmol), and 19.9 mL of IB (-60°C, 0.244 mol). The contents were stirred and equilibrated at -60°C. Then, with continued stirring, 3.42 mL of $TiCl_4$ (RT, 31.1 mmol) was charged to the flask to initiate polymerization. The reaction was allowed to proceed for 17 min, and then 1.36 mL (9.3 mmol) of diisopropyl sulfide was charged to the reactor. After 30 s, 35 mL of the polymerization solution was charged to each of several 60 mL test tubes. The tubes were sealed with threaded caps and immersed in the heptane bath maintained at -60°C. Quenching was allowed to proceed for 17 min. Then, into individual tubes were added one of the following terminating nucleophiles, pre-equilibrated to -60°C and at approximately 60-fold excess relative to chain ends: 2.55 mL of ethanol (43.7 mmol), 3.34 mL of isopropanol (43.6 mmol), or 4.53 mL of *n*-butylamine (45.8 mmol). The terminated reaction mixtures were allowed to warm to RT, and low boiling components were volatilized. A volume of hexane (2-3 mL) was added to each sample to dissolve the PIB, and then the polymers were precipitated into methanol. Finally, the isolated PIBs were washed with fresh methanol to remove any remaining salts and dried by vacuum stripping.

Condition B (Table 3-1). Polymerization reaction mixtures were catalyzed (*vide supra*), divided into several glass tube reactors, and after 26 min, each tube was quenched with a different (di)sulfide. After 15 min quenching time, each tube was charged with a large excess of methanol. Reaction concentrations were as follows: [IB] = 1.03 M;

[TMPCl] = 0.014 M; [26Lut] = 0.010 M; [$TiCl_4$]/[TMPCl] = 9.8; [(di)sulfide]/[TMPCl] = 2.0.

Condition C (Table 3-1). Primary bromide-terminated PIB was prepared using the following concentrations: [IB] = 3.02 M; [TMPCl] = 0.076 M; [26Lut] = 0.007 M; [$TiCl_4$] (pzn.) = 0.034 M; [$TiCl_4$] (quench) = 0.500 M; [disulfide]/[TMPCl] = 1.2; 47/53 (v/v) hexane/methyl chloride. Condition C is representative of a preparative-scale batch reaction and is therefore described in detail: A four-necked 1 L round-bottom flask, equipped with an overhead mechanical stirrer and platinum resistance thermometer, was charged with 189 mL of hexane (-60 °C), 216 mL of methyl chloride (-60 °C), 6.25 g of TMPCl (42.0 mmol), 0.48 mL of 26Lut (RT, 4.1 mmol), and 135 mL of IB (-60 °C, 1.66 mol). The contents were mixed and equilibrated at -60 °C. Then, 2.03 mL of $TiCl_4$ (RT, 18.5 mmol) was charged to the flask to initiate polymerization. The polymerization was allowed to proceed for 90 min (conversion > 0.98), at which time 14.13 g of *bis*(2-bromoethyl) disulfide (50.5 mmol) and an additional 30.24 mL of $TiCl_4$ (RT, 0.275 mol) were charged to the reactor. The mixture was allowed to react 22 min and was then terminated by addition of 29.3 mL of triethylamine (0.21 mol) pre-equilibrated at -60 °C. The mixture was stirred for 10 min, and then 73.2 mL of methanol, pre-equilibrated at -60°C, was slowly charged to the reactor. The flask was removed from the glove box, and the volatile components were allowed to evaporate under ambient conditions. The hexane/polyisobutylene layer was washed with 5% HCl (aq) and then deionized H_2O until the extracts were neutral. The hexane solution was dried over $MgSO_4$, filtered, and concentrated using rotary evaporation.

Condition D (Table 3-1). Primary chloride-terminated PIB was prepared in a preparative-scale batch reaction (*vide supra*) using the following concentrations: [IB] = 2.02 M; [TMPCl] = 0.091 M; [26Lut] = 0.008 M; [$TiCl_4$] (pzn.) = 0.033 M; [$TiCl_4$] (quench) = 0.744 M; [disulfide]/[TMPCl] = 1.2; 52/48 (v/v) hexane/methyl chloride.

Condition MB (Table 3-1). tert-Chloride PIB masterbatch was prepared in a separate BCl_3-catalyzed reaction, divided into tubes, re-activated with $TiCl_4$ and quenched with various (di)sulfides and terminating agents. Pre-formed *tert*-chloride terminated PIB re-activated in this manner yielded chain end functionality identical to that of the $TiCl_4$-catalyzed isobutylene polymerizations. The detailed procedure was as follows: Individual tubes were charged with 20 mL of a 0.015 M solution of *tert*-chloride PIB masterbatch in 60/40 (v/v) hexane/methyl chloride and allowed to equilibrate at -60°C. Into each tube was charged 0.60 mmol of a (di)sulfide (i.e., dimethyl sulfide, diisopropyl sulfide, dimethyl disulfide, diisopropyl disulfide), followed by 0.16 mL (1.5 mmol) of $TiCl_4$. Quenching was allowed to proceed for 15 min, after which time, a large excess of a terminating nucleophile (i.e., methanol, triethylamine, 2,6-di-*tert*-butylpyridine, 1,2,2,6,6-pentamethylpiperidine, 2,5-dimethylpyrrole) was charged to each tube. The terminated mixtures were allowed to warm to room temperature, and low boiling components were volatilized. The polymers were precipitated twice from hexane into methanol, and residual solvents were removed under vacuum.

^{1}H-NMR spectra of the purified polymers in $CDCl_3$ (20-50 mg/mL) at room temperature were recorded on a 300 MHz Varian Mercury^{plus} NMR spectrometer. Relative molar quantities of the various chain end functionalities were determined using peak integration and converted to absolute percentages by assuming that the following

constitute 100% of the chain ends: *tert*-chloride, *exo* olefin, *endo* olefin, coupled, and if appropriate, methoxy (or ethoxy) and/or thio ether (methyl, isopropyl, *p*-tolyl, 2-bromoethyl, or 2-chloroethyl). The various resonances integrated were: *tert*-chloride, δ 1.69 (s, 6H, terminal *gem*-dimethyl); *exo*-olefin, δ 4.64 (m, 1H, olefin); *endo*-olefin, δ 5.15 (s, 1H, olefin); coupled, δ 4.82,[196] obtained as the difference between the 4.85 and 4.64 *exo*-olefin resonances; methoxy, δ 3.17 (s, 3H, OCH_3); ethoxy, δ 3.37 (m, 2H, OCH_2); methyl thio ether, δ 2.03 (s, 3H, SCH_3); isopropyl thio ether, δ 2.93 (m, 1H, SCH)), *p*-tolyl thio ether, δ 2.36 (s, 3H, methyl), δ 7.13 (d, 2H, *ortho* phenyl), or δ 7.40 (d, 2H, *meta* phenyl); 2-bromoethyl thio ether, δ 3.10 (t, 2H, SCH_2) or δ 3.62 (t, 2H, CH_2Br); 2-chloroethyl thio ether, δ 3.03 (t, 2H, SCH_2) or δ 3.77 (t, 2H, CH_2Cl).

Low-Temperature in situ NMR Investigation of Sulfonium Ion Adducts

Sulfonium ion adducts were formed by reacting TMPCl or oligo-isobutylenes with (di)sulfides in the presence of $TiCl_4$. A 0.02 M solution of TMPCl (or oligo-isobutylene) in a 50/50 (v/v) mixture of CS_2/CD_2Cl_2 was prepared within a N_2-atmosphere glove box and chilled to -60 °C. The *tert*-chloride groups were then activated by the addition of 5 equiv of $TiCl_4$ (RT, neat). A portion of the activated solution was charged to a 5 mm o.d. NMR tube fitted with a screw-on septum cap. The sealed tube was placed in a spinner, removed from the dry box and transported at dry-ice temperature (approximately -78 °C) to the probe of a Varian Inova 500 MHz spectrometer. The (di)sulfide was added to the tube through the septum with a microliter syringe to achieve the necessary concentration, and the contents of the tube were briefly mixed by swirling and inverting before inserting the tube into the probe. The tube was equilibrated at the desired temperature (calibrated with a methanol standard) before recording spectra. All

chemical shifts were referenced to the residual solvent resonances of CD_2Cl_2, i.e. 5.32 ppm for ^{1}H and 53.8 ppm for ^{13}C.

Results and Discussion

When a sulfide or disulfide is charged to an active $TiCl_4$-catalyzed isobutylene polymerization in an equivalent or excess amount relative to the number of chain ends, consumption of monomer immediately ceases, as shown in Figure 3-1 for diisopropyl disulfide. This occurs as the sulfide or disulfide immediately complexes $TiCl_4$, and the complex reacts with the carbenium ion chain ends to form sulfonium ion adducts as outlined in Figure 3-2. Lewkebandara *et al.*[212] found that sulfide-$TiCl_4$ complexes in solution likely exist as a 6-coordinate $TiCl_4$ having two sulfide ligands. However, disulfide-$TiCl_4$ complexes were different, consisting of dimeric Ti_2Cl_8 and a single disulfide ligand. The difference was thought to occur because the η^2-disulfide ligand cannot bind strongly in bidentate fashion to the small titanium center; rather it coordinates with two faces of Ti_2Cl_8 forming a bridge. Regardless of the exact (di)sulfide-$TiCl_4$ complexation stoichiometry, there appears to be minimal effect on the overall PIB-(di)sulfide adduct formation when excess $TiCl_4$ is present. Under typical polymerization conditions with temperatures between -60 ^{o}C and -80 ^{o}C, adduct formation is quantitative even when only one equivalent of (di)sulfide relative to chain chains is present.

The sulfonium ion at the PIB chain end, though unreactive with isobutylene under typical quasiliving polymerization conditions, represents an excellent leaving group for reaction with stronger nucleophiles such as alcohols or amines. As illustrated in Figure 3-2, when sulfonium ion adducts are contacted with excess alcohol or amine a mixture of

elimination and substitution products results. The predominant decomposition pathway for PIB-sulfide adducts is elimination to form *exo*-olefin PIB; however, in some cases alcohols can displace the sulfide moiety resulting in concomitant formation of ether endgroups. With PIB-disulfide adducts high yields of *exo*-olefin are also possible, but the situation is complicated by an additional reaction pathway where the sulfur-sulfur linkage of the disulfide moiety is cleaved to provide thioether endgroups.

Sulfonium Ion Adducts

Low-temperature *in situ* NMR was used to investigate the sulfonium ion adducts. The initiator, 2-chloro-2,4,4-trimethylpentane (TMPCl), was chosen as a model for the polyisobutylene chain to provide more lucid spectra. Figure 3-3 shows ^{1}H NMR spectra of sulfonium ion adducts formed from the 1:1 reaction of alkyl monosulfides with TMPCl in the presence of $TiCl_4$ at -60 ^{o}C. Included in Figure 3-3 are spectra of $TiCl_4$-activated TMPCl and sulfide-$TiCl_4$ complexes to serve as comparators. Complexation of the sulfides with $TiCl_4$ results in a downfield shift of their respective resonances. However, adduct formation with TMPCl is evident by further downfield shift of the sulfide moiety resonances as well as a downfield shift in the 2,4,4-trimethylpentyl (TMP) resonances. Formation of a 1:1 adduct was quantitative as seen by the lack of any resonance due to excess sulfide or residual TMPCl.

Figure 3-4 shows the ^{1}H NMR spectra of sulfonium ion adducts formed from the reaction of various disulfides with TMPCl in the presence of $TiCl_4$ at -60 ^{o}C. The disulfide adducts are similar to the sulfide adducts in that resonances of the TMP moiety are shifted downfield; however, the *gem*-dimethyl protons (c) now appear non-equivalent due to the asymmetric sulfonium ion and hindered rotation about the newly formed

carbon-sulfur bond. In the spectrum for the dimethyl disulfide adduct the methylene protons of the TMP moiety are equivalent. As the size of the groups attached to sulfur increases, rotation about the carbon-carbon bond between the neopentyl moiety of TMP and the remainder of the adduct is further hindered. In the spectra for diisopropyl, di-*tert*-butyl, and di-*p*-tolyl disulfide, the methylene protons of the TMP moiety (b) appear as a doublet of doublets indicating that they, in addition to the *gem*-dimethyl protons (c), are also non-equivalent. Evidently, the neopentyl group of TMP cannot easily swing past the diisopropyl, di-*tert*-butyl, or di-*p*-tolyl disulfide moieties. For all of the disulfides shown in Figure 3-4, formation of asymmetric sulfonium ions results in differing chemical shifts for the otherwise identical disulfide moieties. For example, resonances of the methyl protons from the dimethyl disulfide adduct appear at 3.12 and 2.94 ppm with the furthest downfield being due to the methyl closest to the electron deficient onium ion. Disulfides with very bulky alkyl groups produce less stable adducts, and hence a lower equilibrium concentration of adduct at a given temperature. In Figure 3-4, even when di-*tert*-butyl disulfide is present in excess to TMPCl, as seen by the resonance at 1.65 ppm (f), unreacted TMPCl remains. For the given conditions, the temperature must be dropped to -75^{o}C to convert all the TMPCl to the di-*tert*-butyl disulfide-TMP adduct.

Figure 3-5 shows the ^{13}C NMR spectra of the sulfonium ion adducts formed from the reaction of dimethyl, diisopropyl, and di-*p*-tolyl disulfide with TMPCl in the presence of $TiCl_4$ at -60 ^{o}C. These ^{13}C spectra more clearly show the non-equivalence imparted by hindered rotation from steric bulk and asymmetry in the disulfide moiety.

To confirm that equivalent sulfonium ion adducts are formed with higher molecular weight oligo-isobutylenes, a series of *tert*-chloride functional oligo-

isobutylenes was reacted with dimethyl disulfide in the presence of $TiCl_4$ at -60 ^oC. Figure 3-6 shows the resulting ^1H NMR spectra. As with the TMPCl-dimethyl disulfide adduct, the ultimate dimethyl resonances of the oligo-isobutylenes are split and shifted downfield. Also, the methyl resonances of the disulfide moiety are split, consistent with asymmetric sulfonium ion formation.

Sulfonium ion adduct formation has a significant dependence on temperature. Figure 3-7 illustrates this temperature dependence for the 1:1 TMPCl/dimethyl disulfide (MDS) adduct. In the range of -60 to -20 ^oC adduct formation is essentially quantitative. Above -20 °C, adduct formation becomes reversible, and with increasing temperature, increasing amounts of MDS-$TiCl_4$ complex and TMPCl are observed in equilibrium with the adduct (e.g., see 10 ^oC or 20 ^oC spectrum). Over the temperature range where the sulfonium ion adduct, TMPCl, and $(MDS)\cdot(TiCl_4)_2$ species coexist, the ^1H NMR resonances for each species are resolved indicating a slow rate of exchange in reference to the NMR time scale.[206,213] If the system is further warmed, for example, to room temperature or above, irreversible side reactions begin to occur and the adduct cannot be fully recovered by cooling. Figure 3-7 also shows that the *gem*-dimethyl resonances of TMP that appeared non-equivalent below -20 ^oC begin to coalesce into a single resonance at higher temperatures, indicating increased rotation about the carbon-sulfur bond between the TMP and disulfide moiety.

Adduct formation between TMPCl and MDS is governed by both the apparent TMPCl ionization equilibrium (K_i) and the adduct formation equilibrium (K_a).

$$TMPCl + 2\ TiCl_4 \overset{K_i}{\rightleftharpoons} TMP^+Ti_2Cl_9^- \qquad (1)$$

$$TMP^{+}Ti_2Cl_9^{-} + (MDS)\cdot(TiCl_4)_2 \overset{K_a}{\rightleftharpoons} TMP-MDS^{+}Ti_2Cl_9^{-} + 2\ TiCl_4 \quad (2)$$

Combining these two equilibria, and assuming quantitative complexation of the disulfide in the presence of excess $TiCl_4$ (i.e., no free MDS) and equimolar charges of TMPCl and MDS, i.e. $[TMPCl]_0 = [MDS]_0$, the overall adduct formation equilibrium constant may be written as

$$K_aK_i = \frac{\left[TMP-MDS^{+}Ti_2Cl_9^{-}\right]}{\left[TMPCl\right]\left[(MDS)\cdot(TiCl_4)_2\right]} = \frac{1}{\left[TMPCl\right]_0}\frac{\varepsilon}{(1-\varepsilon)^2} \quad (3)$$

where the concentrations of TMPCl, $(MDS)\cdot(TiCl_4)_2$, and the adduct TMP-$MDS^{+}Ti_2Cl_9^{-}$ are written in terms of the initial TMPCl concentration, $[TMPCl]_0$, and the extent of adduct formation, ε, defined as

$$\varepsilon = \frac{\left[TMP-MDS^{+}Ti_2Cl_9^{-}\right]}{\left[TMPCl\right]_0} \quad (4)$$

The apparent equilibrium constant (K_aK_i) can be estimated by integration of the methyl resonances of $(MDS)\cdot(TiCl_4)_2$ versus those of the adduct in Figure 6 and assuming $[TiCl_4]$ remains roughly constant and equal to its initial nominal concentration, $[TiCl_4]_0$. This assumption becomes valid for $[TiCl_4]_0 >> [TMPCl]_0$. Calculated values of the apparent equilibrium constant (K_aK_i) are shown in Table 3-2. The values are quite large and increase with decreasing temperature, indicating energetically favorable formation of the sulfonium ion adduct. The data from Table 3-2 are shown as a van't Hoff plot in Figure 3-8. The apparent standard enthalpy change for adduct formation is estimated from the slope of the plot to be -24.7 kcal/mol.

Decomposition of Sulfonium Ion Adducts

To be useful as an *in situ* PIB functionalization method, addition of the sulfide or disulfide should be timed to coincide with approximately full monomer conversion, and the terminating nucleophile should be selected to yield exclusively one type of chain end. As shown in Table 3-1, the product distribution is effected by both the (di)sulfide and the terminating nucleophile. In general, sulfides can be used to obtain high yields of *exo*-olefin PIB, and disulfides produce high yields of thioether-capped PIB.

For PIB-monosulfide adducts, when methanol or ethanol is used as the terminating nucleophile, the major product is *exo*-olefin, but some substitution occurs to yield alkoxy chain end functionality. Figure 3-9 B, shows a ^{1}H NMR spectrum of PIB obtained through methanol termination of a PIB-diisopropyl sulfide adduct (Entry 2, Table 3-1); a *tert*-chloride-terminated PIB spectrum is shown for comparison (spectrum A). Switching to a bulkier alcohol, such as isopropanol (Entry 4, Table 3-1), eliminates the substitution product. Amines are also efficient at converting monosulfide-capped chain ends to *exo*-olefin; however, in some cases reformation of *tert*-chloride chain ends is observed (e.g., Entry 6, Table 3-1) suggesting competitive complexation/reaction with $TiCl_4$, leading to collapse of the sulfonium ion adduct. The best results are obtained with highly hindered amines such as 2,6-di-*tert*-butylpyridine, which in combination with diisopropyl sulfide results in near-quantitative formation of *exo*-olefin chain ends (Entry 7, Table 3-1).

For a PIB-disulfide adduct, the terminating nucleophile can attack the sulfonium ion, rupture the sulfur-sulfur linkage, and yield a potentially useful thioether end group. For example, Figures 3-9 C and 3-9 D show isopropyl thioether and primary bromide-

terminated PIB, respectively, obtained through triethylamine termination of the PIB-diisopropyl disulfide adduct (Entry 15, Table 3-1) and the PIB-*bis*(2-bromoethyl) disulfide adduct (Entry 17, Table 3-1). As shown in Table 3-1, cleavage of the sulfur-sulfur linkage to produce thioether is the dominant decomposition pathway for PIB-disulfide adducts; it fails to occur only for bulky disulfides such as diisopropyl disulfide in combination with a weakly nucleophilic and/or bulky terminator (Entries 11-13, Table 3-1). For these cases, *exo*-olefin is the major product. One principle exception to this generalization is that decomposition to thioether can also fail even for slender disulfides when an alcohol is used for termination in the absence of a proton trap/electron donor, such as 2,6-lutidine (compare Entry 8, with 26Lut, to Entry 9, without 26Lut, Table 3-1). This suggests that 2,6-lutidine, if present, may be the actual nucleophile responsible for decomposition of the adduct. Even in the presence of 2,6-lutidine, the fraction of thioether produced by methanol termination drops from 0.75 to 0.55 to zero when the bulkiness of the disulfide is systematically changed from methyl to ethyl to isopropyl (compare Entries 8, 10, and 11, Table 3-1). In general, nucleophilic amines such as triethylamine and 2,5-dimethylpyrrole provide very high yields of thioether without inducing chain coupling (see GPC trace for primary bromide functionalized PIB in Figure 3-10). Non-nucleophilic proton traps, such as 2,6-di-*tert*-butylpyridine and 1,2,2,6,6-pentamethylpiperidine, are presumably too bulky to attack the disulfide moiety directly, and therefore yield mostly olefin.

Conclusions

Sulfonium ion adducts are quantitatively produced when a mono- or disulfide is added to $TiCl_4$-catalyzed quasiliving polyisobutylene. The adducts are stable at -60 °C

and lower, and they possess a well defined structure as elucidated by low-temperature NMR spectroscopy. PIB-sulfide and PIB-disulfide adducts provide an excellent platform for chain end functionalization. Near-quantitative yield of *exo*-olefin functionalized polyisobutylene can be obtained by addition of 2,6-di-*tert*-butylpyridine to the PIB-diisopropyl sulfide adduct. In this regard, the sulfonium ion adducts may offer significant advantage in terms of *exo*-olefin functionalization because they may reduce chain coupling at high chain end concentrations. Addition of an amine such as triethylamine to a PIB-disulfide adduct gives near-quantitative yield of the corresponding thioether functionalized PIB. This latter reaction is tolerant of the presence of other functional groups on the disulfide, including halogen, thus offering a method for introducing other useful functionality onto the PIB chain end.

Table 3-1. Polyisobutylene chain end compositions obtained after addition of various nucleophiles to PIB-sulfide and PIB-disulfide onium ion adducts

				fractional end group functionality					
entry	conditions[a]	sulfide	terminating nucleophile[b] (excess)	*tert*-Cl	*endo*-olefin	*exo*-olefin	coupled	ether	thioether
1	MB	dimethyl sulfide	methanol	0.03	0.19	0.69	-	0.09	-
2	MB	diisopropyl sulfide	methanol	0.01	0.02	0.90	-	0.07	-
3	A		ethanol	0.03	0.03	0.90	0.03	0.01	-
4	A		isopropanol	0.03	0.03	0.91	0.03	-	-
5	A		*n*-butylamine	0.05	0.03	0.88	0.04	-	-
6	MB		triethylamine	0.12	0.02	0.85	0.01	-	-
7	MB		2,6-di-*tert*-butylpyridine	0.01	0.02	0.97	-	-	-
		disulfide							
8	B	dimethyl disulfide	methanol	0.01	0.01	0.23	-	-	0.75
9	MB			0.22	0.05	0.52	-	0.21	-
10	B	diethyl disulfide	methanol	0.01	0.02	0.40	0.02	-	0.55
11[c]	A	diisopropyl disulfide	methanol	0.09	0.03	0.79	0.01	0.08	-
12	MB		1,2,2,6,6-pentamethyl piperidines	0.20	-	0.80	-	-	-
13	MB		2,6-di-*tert*-butylpyridine	0.03	0.13	0.84	-	-	-
14	MB		2,5-dimethylpyrrole	-	-	-	-	-	1.0
15	MB		triethyl amine	-	-	-	-	-	1.0
16	A	di-*p*-tolyl disulfide		-	-	0.15	-	-	0.85
17[d]	C	*bis*(2-bromoethyl) disulfide	triethylamine	-	-	0.03	-	-	0.97
18[e]	D	*bis*(2-chloroethyl) disulfide		-	-	0.03	-	-	0.97

[a]See experimental section for specific reaction conditions A, B, C, D, and MB. All reactions conducted at -60 °C.
[b]2,6-lutidine included as an additional nucleophile at low concentration, except for reactions with *tert*-chloride PIB masterbatch (MB).
[c] [diisopropyl disulfide]/[TMPCl] = 2.0.
[d]Number average molecular weight $\overline{M}_n$ = 2,450 g/mol; polydispersity $\overline{M}_w / \overline{M}_n$ = 1.1.
[e] $\overline{M}_n$ = 1,505 g/mol; $\overline{M}_w / \overline{M}_n$ = 1.19.

Table 3-2. Estimated apparent equilibrium constant (K_aK_i) for adduct formation between dimethyl disulfide (MDS) and TMPCl based on integration of the ^{1}H NMR spectra of Figure 6 and $[TMPCl]_0 = 0.02$ M

Temperature (°C)	Reciprocal Temperature (K^{-1})	Extent of Adduct Formation, ε	Equilibrium Constant, $K_aK_i \times 10^{-2}$ (M^{-1})	$\ln(K_aK_i)$
-20		1.00		
-10	0.00380	0.94	130.6	9.5
0	0.00366	0.87	25.7	7.9
10	0.00353	0.74	5.5	6.3
20	0.00341	0.50	1.0	4.6

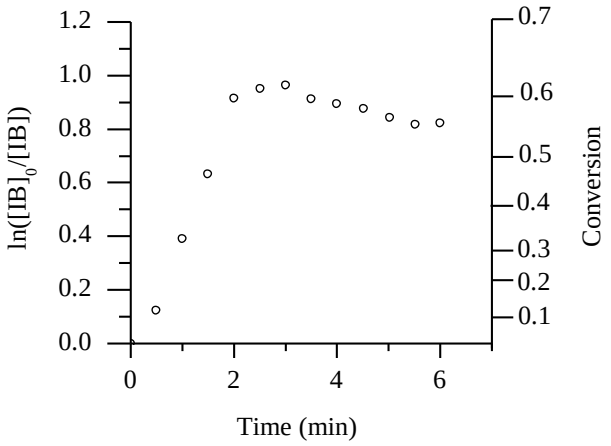

Figure 3-1. 1st order kinetic plot of an isobutylene polymerization in which diisopropyl disulfide was added at approximately 60% monomer conversion. Conditions were: -60 ^{o}C in 60/40 (v/v) hexane/methyl chloride, [TMPCl] = 0.015 M, [IB] = 0.5 M, [26Lut] = 0.005 M, [$TiCl_4$] = 0.09 M, [diisopropyl disulfide] = 0.03 M.

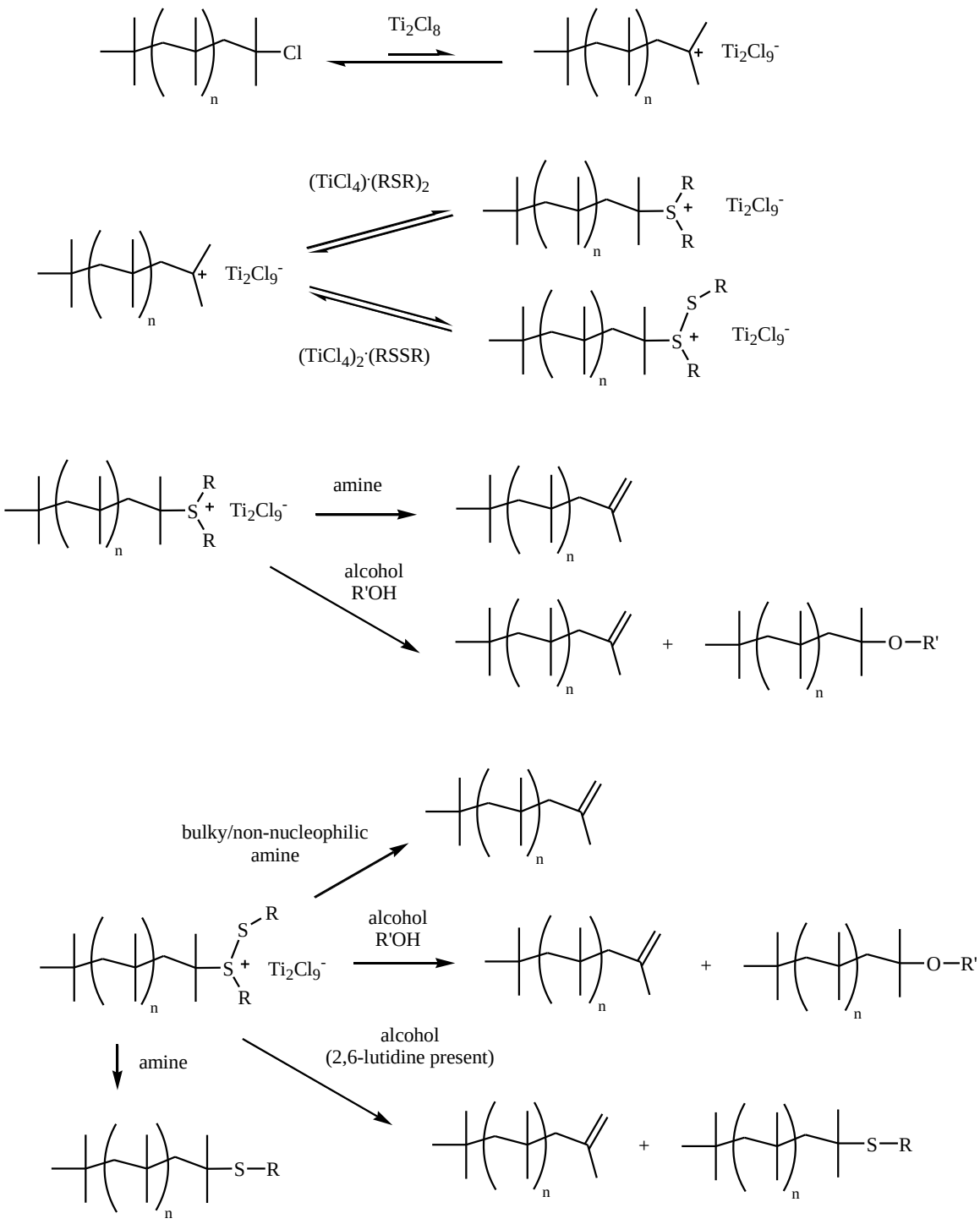

Figure 3-2. Chain end functionalities that can be obtained upon decomposition of polyisobutylene-(di)sulfide onium ion adducts by contact with excess alcohol and/or amines.

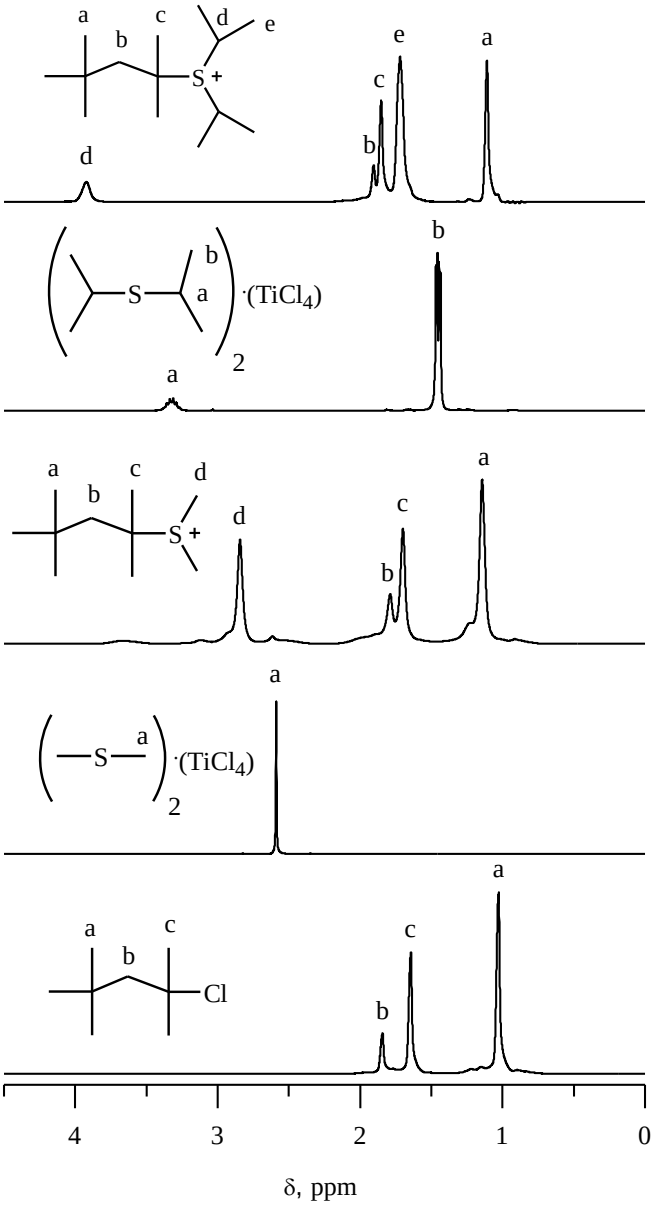

Figure 3-3. 500 MHz ^{1}H NMR spectra of TMPCl and TMPCl/monosulfide adducts with dimethyl sulfide and diisopropyl sulfide in the presence of 5 equiv of $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 at -60 ^{o}C. Spectra of dimethyl sulfide and diisopropyl sulfide complexes with $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 at 20 ^{o}C are also shown for comparison. $Ti_2Cl_9^-$ counterions are not shown with the sulfonium ions for simplicity.

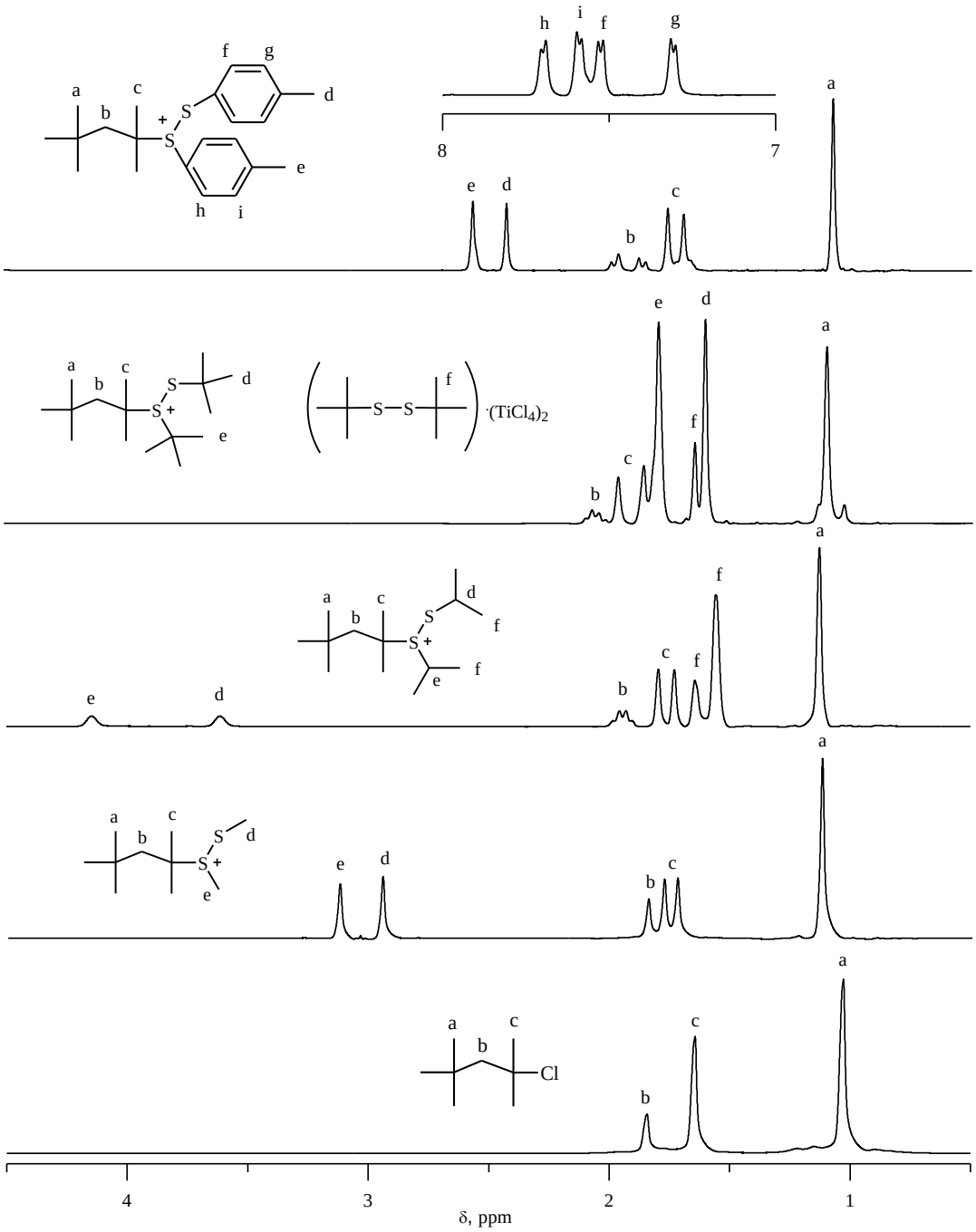

Figure 3-4. 500 MHz ^{1}H NMR spectra of TMPCl and TMPCl/disulfide adducts in the presence of 5 equiv of $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 at -60 ^{o}C. Shown are adducts from dimethyl disulfide, diisopropyl disulfide, di-*tert*-butyl disulfide, and di-*p*-tolyl disulfide.

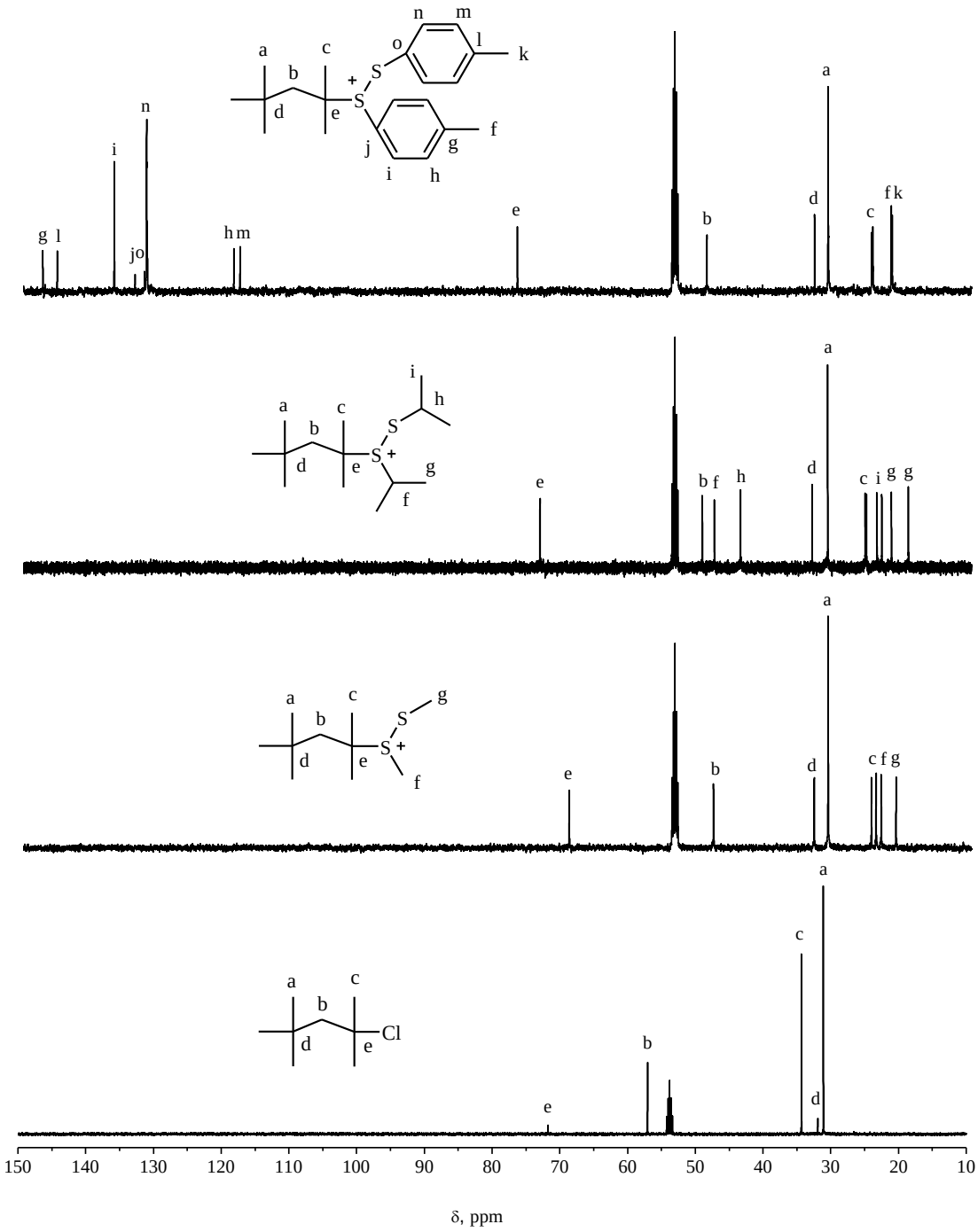

Figure 3-5. 125 MHz ^{13}C NMR spectra of TMPCl and its adducts with dimethyl disulfide, diisopropyl disulfide, and di-*p*-tolyl disulfide in the presence of 5 equiv of $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 at -60 ^oC.

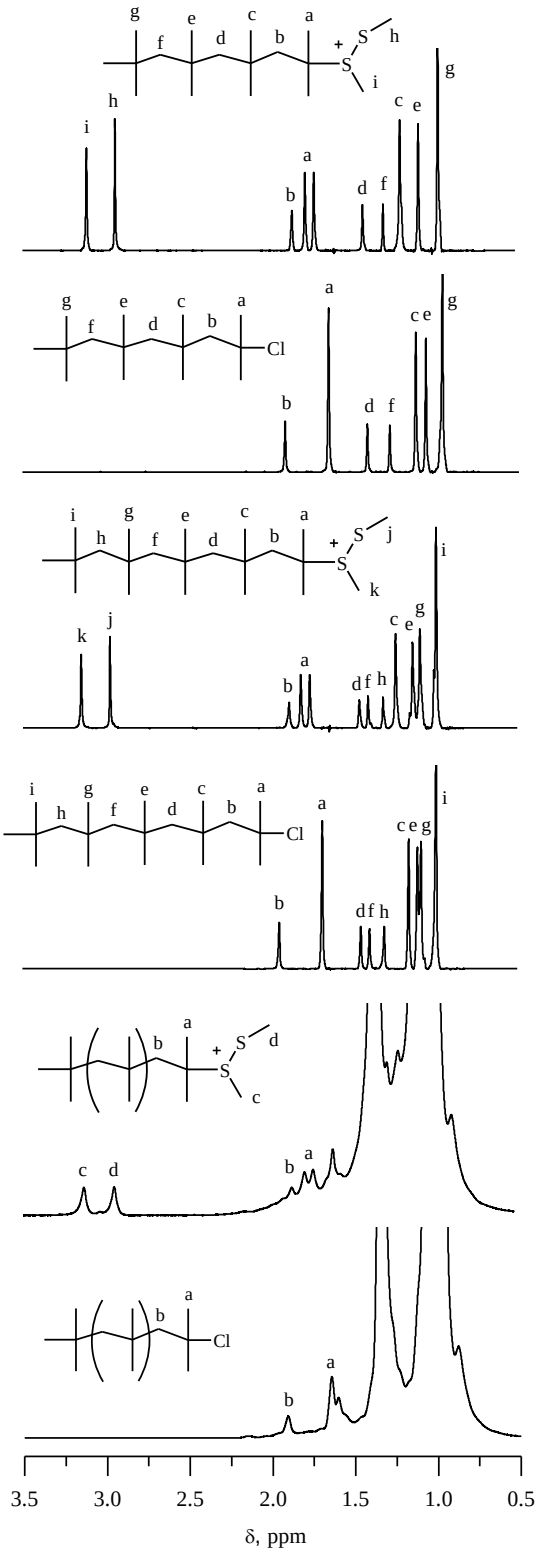

Figure 3-6. 500 MHz ^{1}H NMR spectra of dimethyl disulfide adducts in the presence of 5 equiv of $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 at -60 ^{o}C. Shown are adducts of dimethyl disulfide with *tert*-chloride PIB masterbatch, C_{16}PIBCl and C_{20}PIBCl.

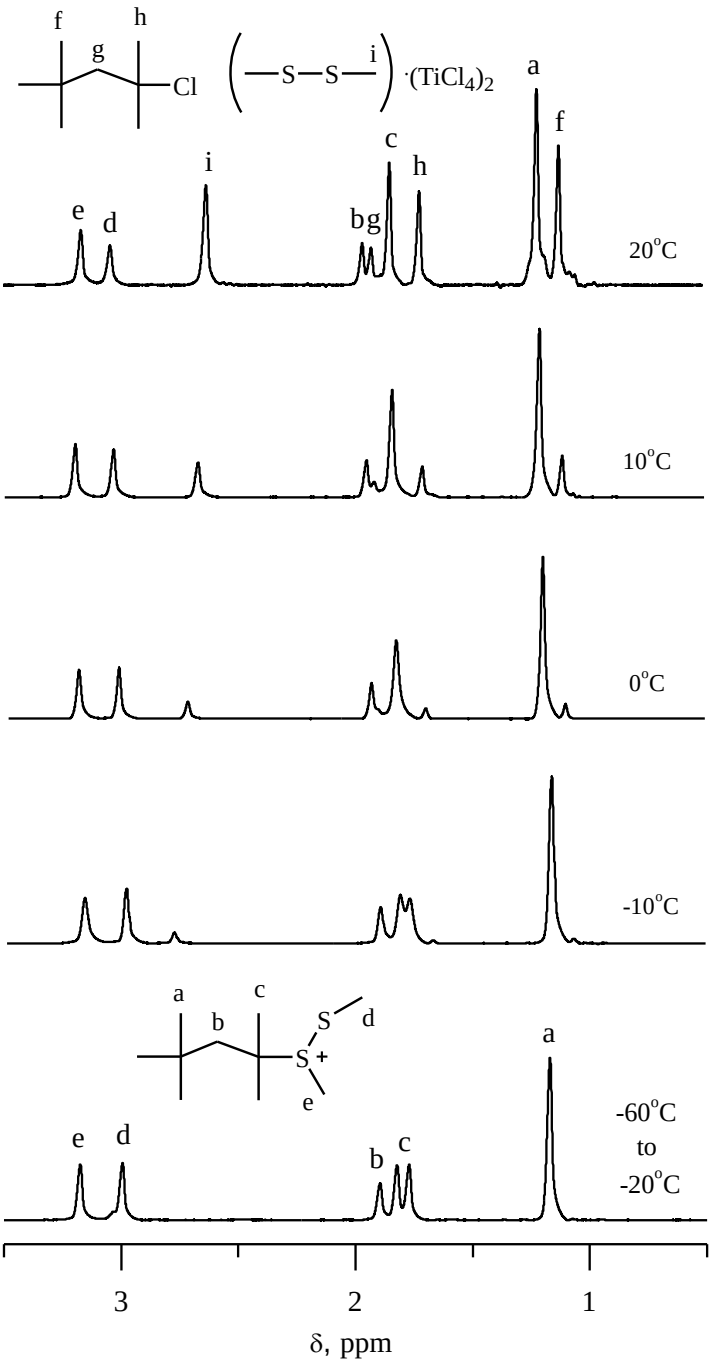

Figure 3-7. 500 MHz ^{1}H NMR spectra of the TMPCl/dimethyl disulfide adduct in the presence of 5 equiv of $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 from -60 ^{o}C to 20 ^{o}C.

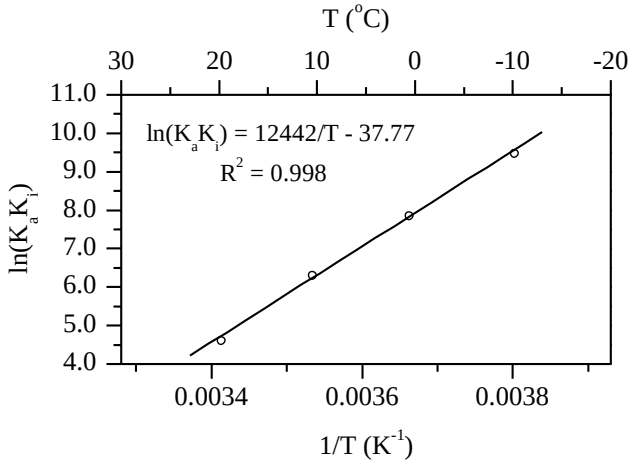

Figure 3-8. van't Hoff plot of TMPCl-dimethyl disulfide adduct formation reaction.

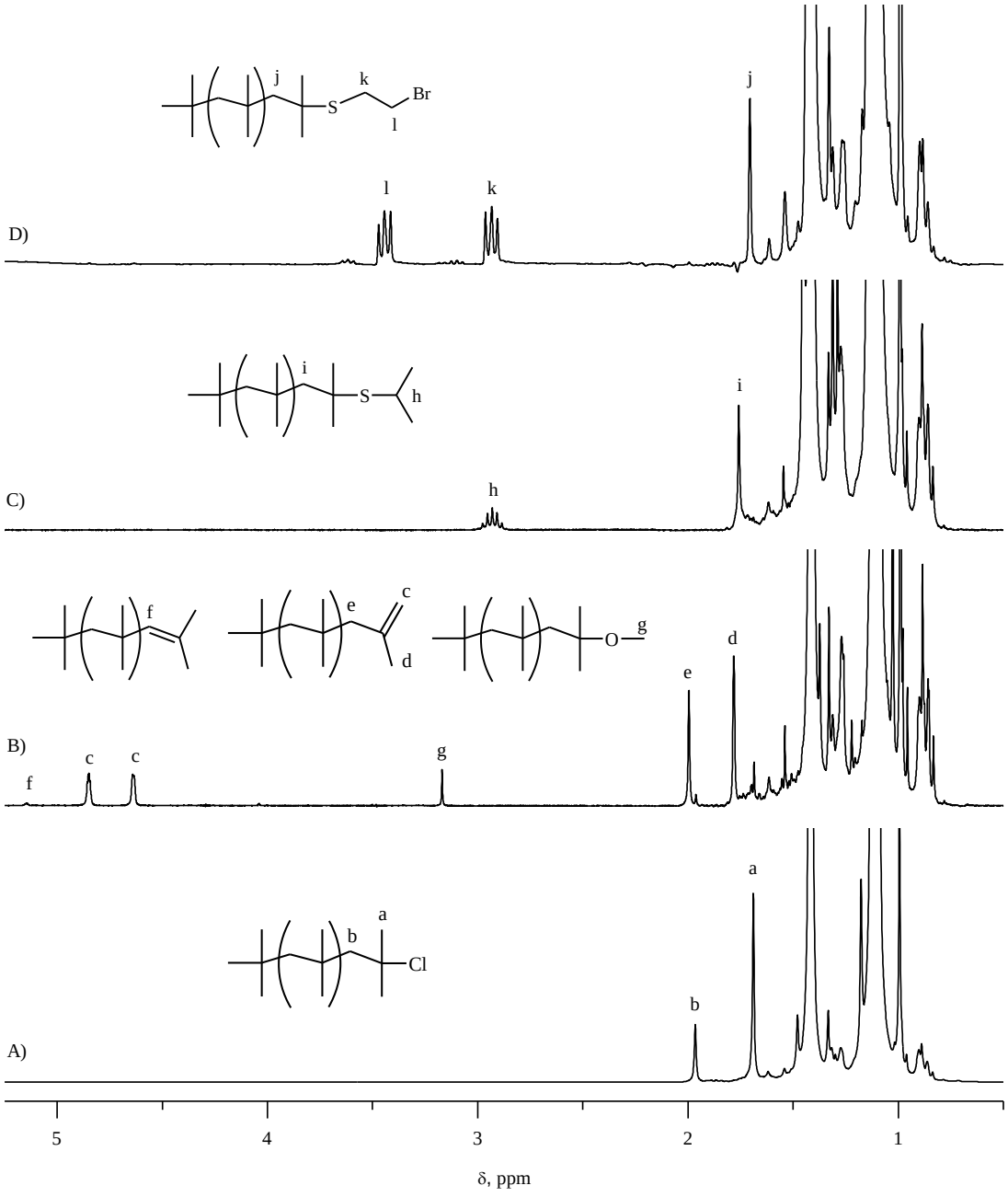

Figure 3-9. 300 MHz ^{1}H NMR spectra of polyisobutylene with representative chain end functionalities at 25^{o}C in $CDCl_3$. Shown are A) *tert*-chloride chain ends, B) *exo*-olefin, *endo*-olefin, and methoxy chain ends from termination of the PIB-diisopropyl sulfide adduct with methanol, C) isopropyl thioether chain ends from termination of the PIB-diisopropyl disulfide adduct with triethylamine, and D) 2-bromoethylsulfanyl chain ends from termination of the PIB-*bis*(2-bromoethyl) disulfide adduct with triethylamine.

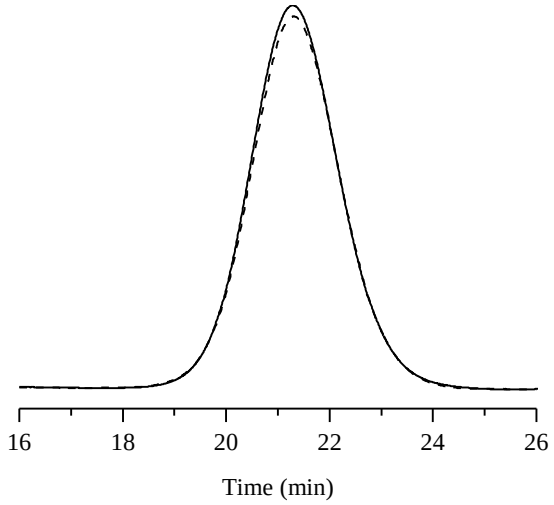

Figure 3-10. Differential refractive index traces for GPC of PIB immediately before addition of *bis*(2-bromoethyl) disulfide (---) and of the final primary bromide functional polymer (—) obtained from triethylamine decomposition of the PIB- *bis*(2-bromoethyl) disulfide adduct.

CHAPTER IV

PRIMARY HYDROXY-TERMINATED POLYISOBUTYLENE VIA END-QUENCHING WITH A PROTECTED *N*-(ω-HYDROXYALKYL)PYRROLE

Introduction

There has been significant interest in telechelic polyisobutylene (PIB) bearing primary hydroxyl groups,[214] and there is a need for a quantitative and efficient one-pot synthetic approach for obtaining the hydroxyl terminus. The traditional, multi-step route to hydroxy-functional PIB has involved post-polymerization derivatization of telechelic PIB obtained through quasiliving polymerization processes or commercially available, high methyl vinylidene (*exo*-olefin) functional PIB.

Ivan, Kennedy and Chang[50] were the first to synthesize telechelic primary hydroxy-functional PIB through a multi-step process involving an *exo*-olefin-terminated intermediate. This was accomplished by preparing the *tert*-chloride terminated polymer via the "inifer" technique, followed by regio-specific dehydrochlorination of the isolated product with potassium *tert*-butoxide,[39] and finally hydroboration-oxidation of the *exo*-olefin end groups. Commercially available PIB with high *exo*-olefin content has also served as a substrate for hydroboration-oxidation;[51] however, on an industrial scale hydroformylation-hydrogenation of the olefin would be preferred.[52] An alternative route to hydroxyl functionality via olefinic PIB, with an even greater number of steps, involves epoxidation[53] followed by acid-catalyzed isomerization of the epoxide to an aldehyde and subsequent reduction of the aldehyde.[54] Kennedy *et al.*[62] have also demonstrated a somewhat more direct approach to hydroxyl functionality involving simultaneous dehydrochlorination and lithiation of telechelic *tert*-chloride PIB using *n*-butyl lithium

and potassium *tert*-butoxide, followed by oxyethylation of the macro-anions with ethylene oxide.

Synthesis of hydroxy-telechelic PIB was simplified with the discovery of *in situ* functionalization/quenching techniques that provided a direct route to olefin chain ends. As shown by Kennedy *et al.*,[144,146] addition of allyltrimethylsilane to a $TiCl_4$-catalyzed quasiliving isobutylene polymerization leads to quantitative formation of allyl end groups. Similarly, Ivan *et al.*[150] described quenching with methallyltrimethylsilane to obtain PIB with *exo*-olefin end groups. As an alternative, Storey *et al.*[151] have shown that deliberate addition of hindered amines to a $TiCl_4$-catalyzed isobutylene polymerization induces β-proton elimination at the chain end for quantitative *exo*-olefin formation.

An efficient method for transformation of olefinic termini to primary hydroxyl involves anti-Markovnikov hydrobromination and subsequent nucleophilic displacement reactions.[102] Kennedy *et al.*[103] achieved rapid hydrobromination of commercial, "highly-reactive" PIB (Glissopal ®) and allyl terminated PIB[144,146] by bubbling air through a solution of the polymer in boiling THF or hexane, followed by bubbling of HBr at 0 ^{o}C. The primary bromide termini formed from the allylic PIB were displaced by hydroxide after 8-12 h in a refluxing mixture of THF and 25-35 wt% 1-methyl-2-pyrrolidone. The same procedure was not as effective with the hydrobrominated *exo*-olefin PIB (Glissopal ®), which required displacement of the bromide by benzoate, then hydrolysis of the resulting ester with potassium hydroxide.

Synthetic routes not involving unsaturated PIB intermediates have also been reported. Puskas *et al.*[123] have worked with initiators containing latent hydroxyl groups masked as epoxides. Hydroxyl functionality at the initiation site was obtained by acid-

induced ring opening of the epoxide moiety. Quasiliving isobutylene polymerizations were demonstrated, but initiation efficiency remained low. For example, maximum initiation efficiencies of 40% where reported for α-methylstyrene epoxide, and apparently lower efficiencies were obtained for molecular weight targets under 4000 g/mol.[124] The low initiation efficiencies were caused by epoxide rearrangement (e.g. formation of aldehydes) and formation of polyethers,[125] the extent of such side reactions being determined by the initiator structure.[126] Knoll *et al.*[179] demonstrated the *in situ* synthesis of allyl chloride-terminated PIB by charging 1,3-butadiene to BCl_3-catalyzed isobutylene polymerizations. Later, Faust *et al.*[181] also obtained allyl chloride-terminated PIB by the 1,4-addition of butadiene to $TiCl_4$-catalyzed quasiliving PIB, and subsequently achieved hydroxyl end groups by post-polymerization nucleophilic displacement of the terminal allyl chlorides by hydroxide in THF. These authors showed that reaction of a PIB allyl bromide with KOH in THF at 130 ^{o}C under pressure was significantly faster than reaction of the allyl chloride, the former requiring only 3 h versus 24 h for the latter; however, formation of the allyl bromide terminus required use of brominated alkyl aluminum catalysts[27] or post-polymerization halide exchange.[182] Quenching to hydroxyl functionality by direct addition of 9-decen-1-ol to $TiCl_4$-catalyzed isobutylene polymerizations was reported by Chiba *et al.*[184] Surprisingly, hydroxyl functionality as high as 95% was obtained, but the process was complicated by reaction of the bare hydroxyls with $TiCl_4$ and competitive hydrochlorination of the 9-decen-1-ol α-olefin moiety.

As a further alternative, the traditional synthetic routes to low molecular weight PIB may be circumvented completely, and PIB macro-glycols can be obtained through

ozonolysis and reduction of isobutylene-isoprene copolymers (e.g., butyl rubber).[215,216] Unfortunately, oxidative cleavage of isobutylene-diene copolymers may provide polydisperse oligomers with more or less than the desired functionality. For example, a hydroxyl functionality greater than two would arise upon ozonolysis and subsequent reduction of butyl rubber that contains significant levels of 1,2 or 3,4 isoprene enchainment.

We recently reported that quasiliving PIB reacts quantitatively with *N*-methylpyrrole to yield an isomeric mixture of 2- and 3-PIB-*N*-methylpyrroles, with no detectable di-substitution (coupled) products.[186] In addition, we have demonstrated that the *N*-alkyl group can be exploited as an alkylene tether for the attachment of more useful functional groups to PIB, such as primary halogen.[191] Herein, we report the *in situ* functionalization of PIB with pyrroles bearing a protected hydroxyl group attached via an *N*-alkylene tether as a means for single-pot synthesis of primary hydroxy-functional PIB (Figure 4-1).

Experimental

Materials

Hexane (anhydrous, 95%), $TiCl_4$ (99.9%,), 2,6-lutidine (2,6Lut) (redistilled, 99.5%), ethyl aluminum dichloride ($EtAlCl_2$) (97%), *tert*-butyl acetic acid (98%), phenyl isocyanate (98%), butyl isocyanate (98%), 4,4′-methylene*bis*(phenyl isocyanate) (MDI) (98%), dimethylsulfoxide (DMSO) (anhydrous, 99.9%), sodium hydride (95%), pyrrole (98%), 2-chloroethanol (99%), dibutyltin dilaurate (DBTDL) (95%) and chloroform-*d* ($CDCl_3$) were purchased from Sigma-Aldrich and used as received. Isobutylene from BOC Gases and methyl chloride from Alexander Chemical Corp. were dried by passing

the gases through columns of $CaSO_4$/molecular sieves/$CaCl_2$ and condensed within a N_2-atmosphere glove box immediately prior to use. The monofunctional initiator, 2-chloro-2,4,4-trimethylpentane (TMPCl), was prepared by bubbling HCl gas through neat 2,4,4-trimethyl-1-pentene (Sigma-Aldrich) at 0°C. The HCl-saturated TMPCl was stored at 0 ^{o}C, and immediately prior to use, neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered. The difunctional initiator, 5-*tert*-butyl-1,3-di(1-chloro-1-methylethyl)benzene (*t*-Bu-*m*-DCC), was synthesized as previously reported[217] and stored at 0 ^{o}C. Monofunctional *tert*-chloride-terminated PIB (2.0 x 10^3 g/mol) was prepared via BCl_3-catalyzed polymerization of isobutylene from TMPCl in methyl chloride[194] at -60 ^{o}C.

Instrumentation

NMR spectra of polymer samples (20-100 mg/mL in $CDCl_3$) were obtained using a 300 MHz Varian Mercury^{plus} NMR spectrometer. Composite pulse decoupling was used to remove proton coupling in ^{13}C spectra. All ^{1}H chemical shifts were referenced to tetramethylsilane (0 ppm), and all ^{13}C shifts were referenced to the residual $CDCl_3$ solvent resonance (77.01 ppm). NMR resonance assignments were made with the assistance of standard ^{1}H-^{13}C correlation experiments. Single bond ^{1}H-^{13}C connectivity was established using gradient-enhanced heteronuclear single-quantum coherence (gHSQC) spectra, and multiple bond connectivity was established using gradient-enhanced heteronuclear multiple bond coherence (gHMBC) spectra.

Number average molecular weights ($\overline{M}_n$) and polydispersities (PDI = $\overline{M}_w / \overline{M}_n$) of the polymeric materials were estimated using a gel permeation chromatography (GPC) system consisting of a Waters Alliance 2695 separations module, an on-line multi-angle

laser light scattering (MALLS) detector fitted with a gallium arsenide laser (power: 20 mW) operating at 658 nm (miniDAWN TREOS, Wyatt Technology Inc.), an interferometric refractometer (Optilab rEX, Wyatt Technology Inc.) operating at 35°C and 685 nm, and two PLgel (Polymer Laboratories Inc.) mixed E columns (pore size range 50-10^3 Å, 3 μm bead size). Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were *ca.* 15-20 mg of polymer/mL of THF, and the injection volume was 100 μL. The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology Inc.), and absolute molecular weights were determined by MALLS using a *dn/dc* calculated from the refractive index detector response and assuming 100% mass recovery from the columns.

Real-time ATR-FTIR analysis was performed using a ReactIR 4000 (Mettler-Toledo) integrated with a N_2 atmosphere glove box.[211] Isobutylene conversion during polymerization was determined by monitoring the area, above a two-point baseline, of the absorbance centered at 887 cm^{-1}, associated with the $=CH_2$ wag of isobutylene.

Synthesis of N-(2-tert-butoxyethyl)pyrrole

N-(2-*tert*-butoxyethyl)pyrrole was prepared in two steps. First, 2-(2-chloroethoxy)-2-methylpropane was synthesized by addition of isobutylene to 2-chloroethanol. Typically, 50 mL of 2-chloroethanol and 140 mL (2 equiv) of isobutylene were combined at -25 ^oC under a N_2 atmosphere. While stirring vigorously, 10 mL (0.25 equiv) of concentrated H_2SO_4 was added to catalyze the reaction. After 30 min, the flask was removed from the cooling bath and allowed to warm to room temperature for 2 h as the excess isobutylene boiled off. The reaction mixture was immediately washed and neutralized with aqueous $NaHCO_3$. The organic layer was dried over $MgSO_4$ and filtered

to yield 83 g (85%) of a colorless liquid. ^{1}H NMR ($CDCl_3$) δ 1.21 (s, *tert*-butyl, 9H), 3.57 (t, -C*H*$_2$Cl, 2H), 3.61 (t, -OC*H*$_2$-, 2H). ^{13}C NMR ($CDCl_3$) δ 27.3 ((*C*H$_3$)$_3$C-), 43.6 (-*C*H$_2$Cl), 62.4 (-O*C*H$_2$-), 73.5 ((CH$_3$)$_3$*C*-). The 2-(2-chloroethoxy)-2-methylpropane was then reacted with pyrrolyl sodium salt to form *N*-(2-*tert*-butoxyethyl)pyrrole. Typically, 34 mL of pyrrole in 50 mL of dimethyl sulfoxide (DMSO) was added dropwise to 12.9 g (1.1 equiv) of sodium hydride in 50 mL of DMSO under a N_2 atmosphere. After cessation of H_2 release, 70 g (1.05 equiv) of 2-(2-chloroethoxy)-2-methylpropane in 50 mL of DMSO was slowly added. After 3 h, the product was washed with water and extracted into methylene chloride. The resulting solution was dried over $MgSO_4$ and filtered, after which the solvent was removed under vacuum. Vacuum distillation of the crude product yielded 60 g (73%) of a colorless liquid, which was stored under N_2 in the absence of light. ^{1}H NMR ($CDCl_3$) δ 1.22 (s, *tert*-butyl, 9H), 3.67 (t, -C*H*$_2$O-, 2H), 4.06 (t, NC*H*$_2$-, 2H), 6.2 (t, C-3-pyrrole, 2H), 6.78 (t, C-2-pyrrole, 2H). ^{13}C NMR ($CDCl_3$) δ 27.3 ((*C*H$_3$)$_3$C-), 50.3 (NCH$_2$-), 62.2 (-*C*H$_2$O-), 73.3 ((CH$_3$)$_3$*C*-), 107.8 (C-3-pyrrole), 121.1 (C-2-pyrrole).

Polymerization and Quenching

Quasiliving isobutylene polymerizations from mono- and difunctional initiators and end-quenching of those polymerizations were carried out as follows (see Table 4-1, polymers 1 and 2): Within a N_2-atmosphere glove box, 105 mL of hexane and 70 mL of methyl chloride were chilled to -60 ^{o}C and charged to a 4-neck round bottom flask equipped with an overhead stirrer, thermocouple, and ReactIR probe. To the 60/40 (v/v) mixture of hexane and methyl chloride, were added 0.109 mL of 2,6-lutidine and either 0.65 mL of TMPCl (Table 4-1, polymer 1) or 0.537 g of *t*-Bu-*m*-DCC (Table 4-1,

polymer 2) to yield a chain end concentration ([CE]) of 0.02 M. A final molecular weight of 2,000 g/mol was targeted for the monofunctional PIB by charging the reactor with 9.8 mL of isobutylene; whereas, a final molecular weight of 3,000 g/mol was targeted for the difunctional PIB by charging the reactor with 7.0 mL of isobutylene. After thermal equilibration, the polymerizations were initiated with 1.23 mL (3 equiv per chain end) of $TiCl_4$. At complete monomer conversion, 3 equiv of *N*-(2-*tert*-butoxyethyl)pyrrole was charged to the reactor, and the alkylation reaction was allowed to proceed for 25-30 min. Then, the reactor was charged with 5 equiv of $EtAlCl_2$ and 2 equiv of H_2SO_4 to promote removal of the terminal *tert*-butyl blocking group residing on the pyrrole capping agent. After addition of the acids, the reaction flask was immediately removed from the cooling bath and allowed to warm to room temperature, which required approximately 4.5 h. The reaction flask was then placed on a heating mantle, fitted with a reflux condenser, and heated to reflux at 69 ^{o}C for 3-4 h. Finally, the catalysts were destroyed by addition of excess methanol. Impurities were removed by taking the polymer up in hexane and dripping the solution into excess methanol, causing polymer precipitation. After twice precipitating the polymer, residual solvents were removed under vacuum. Table 4-1 shows the molecular weights of the PIBs, as well as the chain end composition for each stage of the reaction.

Chain end compositions were estimated by integration of ^{1}H NMR spectra. The amounts of C-2 and C-3 alkylated pyrrole (*tert*-butyl group intact) were quantified by integrating the resonances at 4.10 and 3.91 ppm due the methylene units adjacent to the alkylated pyrrole nitrogen. When the *tert*-butyl group was displaced to provide hydroxyl functionality at the chain end, the relative amounts of the C-2 and C-3 alkylated pyrrole

isomer were quantified by integration of the resonance at 4.15 ppm, due to the methylene unit adjacent to the C-2 alkylated pyrrole nitrogen, and the resonance at 3.81 ppm, due the terminal methylene unit adjacent to the hydroxyl on the C-3 alkylated pyrrole. The amount of *exo*-olefin was quantified by integration of the resonance at 2.00 ppm due to the terminal PIB methylene unit, and the amount of chain coupling via di-alkylation of pyrrole was quantified by integration of the resonances at 6.28-6.35 ppm due to a single hydrogen on the di-alkylated pyrrole ring. For those polymers exhibiting partial removal of the terminal *tert*-butyl group, the fraction of the *tert*-butyl groups remaining intact was estimated by integration of the resonances at 3.56 and 3.65 ppm due the methylene units on the C-2 and C-3 alkylated pyrroles adjacent to the *tert*-butoxy group. Initiation from *t*-Bu-*m*-DCC allowed conformation of chain end functionality by integration of the resonance at 7.17 ppm due to the initiator residue.

Kinetics of Quenching and Deprotection

Kinetics of the PIB-pyrrole alkylation reactions were investigated using 0.02 M solutions of monofunctional *tert*-chloride-terminated PIB. Into a 60/40 (v/v) mixture of hexane (120 mL) and methyl chloride (80 mL) at -60 ^{o}C were dissolved 7.8 g of 2,000 g/mol *tert*-chloride terminated PIB, 0.12 mL of 2,6-lutidine, and 0.44 to 3.63 mL (1.2-10 equiv) of *N*-(2-*tert*-butoxyethyl)pyrrole. The alkylation reactions were initiated by addition of 1.34 mL (3 equiv) of $TiCl_4$. Conversion of the chain ends was monitored by integration of ^{1}H NMR spectra of aliquots taken from the reactions.

A similar method was used to monitor the *in situ* removal of the terminal *tert*-butyl blocking group following completion of the *N*-(2-*tert*-butoxyethyl)pyrrole alkylation reaction. Into a 60/40 (v/v) mixture of hexane (105 mL) and methyl chloride (70 mL) at -60 ^{o}C were dissolved 6.9 g of 2,000 g/mol *tert*-chloride terminated PIB, 0.11 mL of 2,6-lutidine, and 1.9 mL (3 equiv) of *N*-(2-*tert*-butoxyethyl)pyrrole. The alkylation reaction was initiated with the addition of 1.19 mL (3 equiv) of $TiCl_4$. After 30 min of reaction time, additional acids were charged to the reactor, and it was immediately removed from the cooling bath to promote removal of the terminal *tert*-butyl group. After 4.5 h of warming at ambient temperature, most of the methyl chloride had volatilized. The remaining contents of the reactor were heated to reflux (69 ^{o}C) for an additional 3.5 h. As in previous reactions, changes in the chain end functionality were monitored by integration of ^{1}H NMR spectra of aliquots taken from the reactions.

Post-polymerization Reaction of Hydroxy-functional PIB

Reaction of monohydroxy-functional PIB with monofunctional acid and isocyanates was carried out as follows: Under a N_2 atmosphere, vials were charged with 0.4 g samples of 2,000 g/mol [3-polyisobutyl-*N*-(2-hydroxyethyl)]pyrrole (Table 4-1, polymer 1) dissolved in 15 mL of toluene. The esterification reaction involved addition of 76 μL (3 equiv) of *tert*-butyl acetic acid along with 2 mg (0.1 equiv) of 4-dimethylamino pyridine and 46 μL (1.5 equiv) of N,N'-diisopropyl carbodiimide. The urethane-forming reactions involved addition of 68 μL (3 equiv) of butyl isocyanate or 65 μL (3 equiv) of phenyl isocyanate; both reactions were catalyzed by subsequent addition of 6 μL (0.05 equiv) of dibutyl tin dilaurate (DBTDL). The reactions were allowed to

proceed at room temperature for 4 h before concentrating the polymer solution and precipitating the polymers from toluene into methanol.

The α,ω-dihydroxy polyisobutylene (Table 4-1, polymer 2) was chain extended with 4,4'-methylene-*bis*(phenyl isocyanate) (MDI). Under nitrogen, 1.2 g of α,ω-*bis*[*N*-(2-hydroxyethyl)pyrrol-3-yl]polyisobutylene and 0.1 g (1.05 equiv per hydroxyl) of MDI were dissolved in 20 mL of toluene. The room temperature urethane-forming reaction was catalyzed by addition of 6 μL (0.5% by weight) DBTDL. The reaction was allowed to proceed for 12 h, after which time the polymer was precipitated into methanol. Residual solvents were removed under vacuum.

Results and Discussion

N-Alkyl-substituted pyrroles are highly susceptible to electrophilic attack by carbenium ions, and therefore provide a convenient platform on which to pursue *in situ* functionalization of quasiliving PIB with terminal primary hydroxyl groups. Unfortunately, direct addition of compounds bearing an unprotected hydroxyl moiety to a $TiCl_4$-catalyzed quasiliving PIB typically results in rapid reaction of the hydroxyl with the Lewis acid present in the system, often rendering the catalyst and/or quencher unreactive towards the polymer chain ends.[146] Cognizant of this fact, we sought a suitable protecting group that could be placed on the *N*-alkyloxy tether of pyrrole, and not only survive the acidic conditions of a $TiCl_4$-catalyzed isobutylene polymerization without interference, but also be easily and efficiently removed *in situ* after pyrrole alkylation. Acyl protecting groups were considered unsatisfactory due to potentially debilitating complexation reactions that occur between carbonyl groups and $TiCl_4$.[218] Silyl protecting groups may be labile under acidic conditions; however, the substituents

around silicon can be varied in bulk to increase stability.[219] Unfortunately, increasing steric bulk around silicon also makes subsequent removal difficult, often requiring fluoride-assisted hydrolysis.[220]

With these considerations in mind our choice for hydroxyl protection became a simple alkyl group, namely *tert*-butyl. *tert*-Butyl ethers are stable under a wide variety of conditions, but can be cleaved under strongly acidic conditions.[220] Thus, an *N*-(2-*tert*-butoxyalkyl)pyrrole was synthesized by the following two-step procedure. First, the *tert*-butyl group was introduced onto 2-chloroethanol by acid-catalyzed addition of isobutylene. A pyrrolyl sodium salt was then used to displace the chloride, yielding *N*-(2-*tert*-butoxyethyl)pyrrole. An ethylene tether between pyrrole and the latent hydroxyl was chosen to minimize the incremental change in the PIB molecular weight after alkylation; however, longer alkylene tethers are expected to provide similar results.

Monofunctional Primary Hydroxy-terminated Polyisobutylene

Figure 4-2 shows ^{1}H NMR spectra of aliquots (A, B, C) removed from a $TiCl_4$-catalyzed quasiliving isobutylene polymerization initiated from TMPCl and quenched with 3 equiv per chain end of *N*-(2-*tert*-butoxyethyl)pyrrole (see Table 4-1, polymer 1). Figure 4-2 A revealed the structure of the PIB immediately after the 25 min quenching reaction; approximately 95% of the PIB chains underwent electrophilic aromatic substitution (EAS) resulting in mono-alkylation of the pyrrole ring at either the C-2 or C-3 position. The C-3 alkylated isomer exhibited a resonance at 1.66 ppm due to the terminal PIB methylene unit, two triplets at 3.55 and 3.91 ppm due to the pyrrole *N*-alkylene tether, and resonances at 5.99, 6.41, and 6.55 ppm due to the pyrrole ring. The C-2 alkylated isomer exhibited a similar set of resonances: a singlet at 1.74 ppm due to

the terminal PIB methylene unit, two triplets at 3.64 and 4.09 ppm due to the pyrrole *N*-alkylene tether, and resonances at 5.87, 6.02, and 6.64 ppm due to the pyrrole ring. The C-3 alkylated isomer was the major product representing 57% of the chain ends, and the C-2 alkylated isomer was the minor product representing 38% of the chain ends. The remaining 5% of the chain ends were *exo*-olefin as evidenced by the resonances at 1.78 ($-CH_2C(=CH_2)CH_3$), 2.00 ($-CH_2C(=CH_2)CH_3$), and 4.64/4.85 ppm ($-CH_2C(=CH_2)CH_3$). The *exo*-olefin functionality did not arise due to unimolecular β-proton expulsion (it was not present in a pre-quench aliquot), but is believed to be induced by the ether linkage of the quencher.[221] Similar pyrrole-based quenchers without ether linkages do not produce the *exo*-olefin chain ends as observed here.[191]

After the 25 min quenching reaction, 5 equiv of $EtAlCl_2$ and 2 equiv of H_2SO_4 were charged to the reactor to assist in removal of the *tert*-butyl protecting group and promote further EAS reaction between the residual *exo*-olefin chain ends and residual quencher. At this time the reaction flask was also removed from the cooling bath to begin warming. After 1.5 h, the methyl chloride had boiled off, and the reaction had warmed to 0 ^oC. ^1H NMR analysis of an aliquot removed from the reactor at this time resulted in the spectrum shown in Figure 4-2 B. This spectrum indicated that the *tert*-butyl groups were quantitatively displaced. This was seen most readily by a shift in the resonances of the methylene units of the *N*-alkyl pyrrole tether. Two quartets appear at 3.81 and 3.94 ppm, due to the methylene units adjacent to the terminal hydroxyl of the C-3 and C-2 alkylated isomers, respectively. Figure 4-2 B also showed that after warming, the isomer ratio had slightly shifted towards the more thermodynamically stable C-3

isomer, and the percentage of chain ends bearing *exo*-olefin functionality was reduced by further EAS reactions.

The reduction of *exo*-olefin upon warming the reaction in the presence of the mixed acids was further exploited by heating the reaction mixture to reflux (69 ^{o}C) for approximately 3 h. ^{1}H NMR analysis of the final product after this time resulted in the spectrum shown in Figure 4-2 C. Examination of this spectrum revealed that heating caused all residual *exo*-olefin to alkylate the pyrrole quencher, resulting in quantitative formation of primary hydroxyl chain ends. Furthermore, over 98% of the chain ends were shifted to the C-3 alkylated isomer. The final hydroxy-terminated PIB exhibited a resonance at 1.66 ppm due to the terminal PIB methylene unit, resonances at 3.81 (quartet) and 3.95 ppm (triplet) due to the *N*-alkylene tether, and resonances at 6.06, 6.41 and 6.58 ppm due to the pyrrole ring.

Alkylation of pyrrole and subsequent deprotection was also confirmed by ^{13}C NMR. Figure 4-3 A shows the spectrum of the PIB immediately after the 25 min quenching reaction. Resonances at 71.9 and 35.2 ppm, representing the ultimate quaternary and *gem*-dimethyl carbons of *tert*-chloride PIB,[222] respectively, were not present after the alkylation reaction and were replaced by a new set of resonances in both the aromatic and the aliphatic regions of the spectrum; the resonances of the pyrrole moiety occurred in pairs due to the C-2 and C-3 alkylated isomers. Figure 4-3 B shows the spectrum of the final product. After refluxing the PIB alkylated pyrrole in the presence of the mixed acids for 3 h, resonances at 73.0 and 27.0 ppm due to the terminal *tert*-butyl protecting group disappeared indicating its removal. In addition, only

resonances associated with the C-3 alkylated pyrrole were observed, further indicating nearly complete isomerization of the chain ends.

Difunctional Primary Hydroxy-terminated Polyisobutylene

Figure 4-4 shows ^{1}H NMR spectra of PIB from a $TiCl_4$-catalyzed quasiliving isobutylene polymerization initiated from *t*-Bu-*m*-DCC and quenched with 3 equiv of *N*-(2-*tert*-butoxyethyl)pyrrole (see Table 4-1, polymer 2). As with the mono-functional PIB, the spectrum of Figure 4-4 A revealed that both the C-2 and C-3 alkylated pyrroles were obtained after quenching for 27 min. The C-3 alkylated isomer was the major product representing 55% of the chain ends, and the C-2 alkylated isomer was the minor product representing 38% of the chain ends. Again, a small amount (5%) of *exo*-olefin was formed during the quenching reaction. The remaining 2% of the chain ends were involved in double alkylation of a single pyrrole ring (coupling), as discussed later.

After charging the reactor with 5 equiv of $EtAlCl_2$ and 2 eq of H_2SO_4, it was allowed to warm to 0 ^{o}C and then heated to reflux (69 ^{o}C) for approximately 4 h. Figure 4-4 B shows the ^{1}H NMR spectrum of the final α,ω-*bis*[*N*-(2-hydroxyethyl)pyrrol-3-yl]polyisobutylene obtained after reflux with the mixed acids. The terminal *tert*-butyl groups were quantitatively displaced and 98% of the chain ends shifted to the C-3 alkylated isomer. The spectrum exhibited a resonance at 1.66 ppm due to the terminal PIB methylene unit, resonances at 3.81 (quartet) and 3.95 ppm (triplet) due to the *N*-alkyl pyrrole tether, and resonances at 6.06, 6.41 and 6.58 ppm due to the pyrrole ring.

Figure 4-5 shows ^{13}C NMR spectra of difunctional PIB immediately after quenching (A) with *N*-(2-*tert*-butoxyethyl)pyrrole and after reflux (B) with the mixed acids. The 2- and 3-PIB alkylated pyrroles with *tert*-butyl protecting groups intact were

observed after quenching, but after reflux with the mixed acids the resonances at 73.0 and 27.0 ppm due to the terminal *tert*-butyl protecting groups were absent, indicating removal. In addition, only resonances from the C-3 alkylated pyrrole were observed amongst the resonances for the aromatic initiator residue in Figure 4-5 B, indicating near complete isomerization of the chain ends.

Close examination of the ^{1}H NMR spectrum of difunctional PIB alkylated pyrrole in Figure 4-4 A revealed resonances at 6.28 and 5.70 ppm that were not observed with monofunctional PIB and that accounted for approximately 2% of the difunctional PIB chain ends. These resonances were assigned to pyrrole rings that had undergone double alkylation, resulting in coupling of two PIB chains. Figure 4-6 compares the GPC traces for mono- and difunctional PIB quenched with *N*-(2-*tert*-butoxyethyl)pyrrole under otherwise identical reaction conditions. Coupling was not detectable in the monofunctional PIB alkylated pyrrole sample, but the post-quench trace for the difunctional PIB exhibited a shoulder centered at roughly twice the molecular weight of the main peak. Coupling occurred during the quenching reaction because it was not observed in the pre-quench aliquot, and it increased slightly during the acid induced deprotection/isomerization at elevated temperatures.

To confirm that chain coupling occurred through the pyrrole ring, an isobutylene polymerization initiated from TMPCl was quenched with 0.5 equiv of *N*-(2-*tert*-butoxyethyl)pyrrole to deliberately induce double alkylation (see Table 4-1, polymer 3). ^{1}H NMR analysis of the resulting PIB revealed that residual *tert*-chloride and *exo*-olefin were present, as well as the expected 2- and 3-monoalkylated pyrrole isomers; a partial spectrum (aromatic region) of the resulting polymer is shown in Figure 4-7. The 2- and

3- monoalkylated pyrroles were represented by the major peaks at 5.99, 6.41, and 6.55 ppm (C-3) and 5.87, 6.02, and 6.64 ppm (C-2). In addition, a set of minor peaks offset slightly downfield from the major peaks indicated that a small fraction of the alkylated pyrroles had begun to lose the terminal *tert*-butyl group. Two additional, distinct resonances at 6.28 and 5.70 ppm were due to di-alkylated *N*-(2-*tert*-butoxyethyl)pyrrole. Di-alkylation appeared to occur exclusively in the C-2 and C-4 positions of the pyrrole ring. GPC traces for the pre- and post-quench PIB of Figure 4-7 are shown in Figure 4-8. The post-quench UV trace has a large shoulder of roughly twice the molecular weight of the main peak indicating that coupling occurred through the UV-absorbing pyrrole ring.

Stokes[223] has shown that quasiliving PIB readily di-alkylates unsubstituted pyrroles, but Storey *et al.* later demonstrated that *N*-substitution effectively prevents di-alkylation. It was concluded that steric constraints imposed by the *N*-substituent possibly prevent a second alkylation. For *N*-(2-*tert*-butoxyethyl)pyrrole steric constraints also exist, and di-alkylation is largely prevented when excess *N*-(2-*tert*-butoxyethyl)pyrrole is present, especially for monofunctional PIB (see Figure 4-6). Coupling occurs to a greater extent with difunctional PIB and *N*-(2-*tert*-butoxyethyl)pyrrole, likely due to enhanced local concentration arising from aggregation of chains bearing at least one pyrrole moiety. The exact nature of the aggregation is not known, but it apparently involves interaction of the pyrrole moieties with $TiCl_4$. After one end of a difunctional PIB chain has alkylated pyrrole and subsequently aggregated with other PIB chains bearing pyrrole, the remaining *tert*-chloride end group is exposed to an elevated concentration of pyrrole that has already undergone one alkylation. During the deblocking stage of the reaction the difunctional hydroxy-terminated polymer actually precipitates from the reaction

solvent due to formation of tri- and/or tetravalent metal alkoxide pseudo-crosslinks. Once precipitated, the PIB chain ends are further restricted from accessing the free pyrrole in solution, hence further increasing the likelihood of chain coupling.

Non-$TiCl_4$ Catalysis

Since the inadvertent formation of *exo*-olefin termini (<5%) and chain coupling with difunctional polymer were thought to arise due to interactions between *N*-(2-*tert*-butoxyethyl)pyrrole and $TiCl_4$, efforts were made to avoid the use of $TiCl_4$ during both the polymerization and quenching reactions. $EtAlCl_2$ was capable of catalyzing both the alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole and subsequent cleavage of the terminal *tert*-butyl ether to provide hydroxyl termini, unfortunately, it was too strong of a catalyst for controlled isobutylene polymerization with the given 60/40 (v/v) hexane/methyl chloride solvent system. Even diethyl aluminum chloride (Et_2AlCl) has been reported to require a highly non-polar solvent system to yield "livingness".[20] Literature reports indicated that a better choice for alkyl aluminum halide catalyzed isobutylene polymerization may be dimethyl aluminum chloride (Me_2AlCl).[24,25] However, we observed that Me_2AlCl catalyzed isobutylene polymerizations from *t*-Bu-*m*-DCC in 60/40 (v/v) hexane/methyl chloride at -75^{o}C were plagued by both tri- and di-substituted olefin formation at the chain end, as well as cyclo-alkylation at the initiation site after one isobutylene addition (indanyl ring formation) as shown in Figure 4-9. The use of boron trichloride (BCl_3) as a polymerization catalyst in methyl chloride[194] at -60 ^{o}C with subsequent addition of *N*-(2-*tert*-butoxyethyl)pyrrole and Me_2AlCl at full monomer conversion prevented olefin formation at the PIB chain end, but the mixed catalyst system was too strong, resulting in

immediate cleavage of the *tert*-butyl ether quencher moiety and incomplete capping of the PIB.

Kinetics of Quenching and Deprotection

Figure 4-10 A shows first-order kinetic plots for alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole by monofunctional *tert*-chloride PIB. The various plots represent *N*-(2-*tert*-butoxyethyl)pyrrole concentrations ranging from 1.2 to 10 times the chain end concentration of 0.02 M. For all concentrations the rates of alkylation were equal and independent of the quencher concentration, up to about 75% conversion of the chain ends. This zero-order dependence on quencher concentration indicated that the rate of quenching was limited by chain end ionization.[203] From run number measurements made under similar conditions at -60°C, Thomas and Storey[198] calculated a value of k_i = 9.1 $L^2mol^{-2}s^{-1}$ for the rate constant for ionization of PIB chain ends. The initial first-order rate constant for alkylation in Figure 4-10 A, divided by the square of the effective $TiCl_4$ concentration[197] yielded a similar value of 8.4 $L^2mol^{-2}s^{-1}$, thus supporting the conclusion that ionization was the rate limiting step for the quenching reaction. Given the fact that increasing concentration of *N*-(2-*tert*-butoxyethyl)pyrrole in Figure 4-10 A did not cause a measurable reduction in the initial rate of quenching suggests that the equilibrium constant, K_{com}, for complexation of $TiCl_4$ with *N*-(2-*tert*-butoxyethyl)pyrrole was small, or more precisely, K_{com}×[*N*-(2-*tert*-butoxyethyl)pyrrole] << 1, assuming a 1:1 complex.

The first-order kinetic plots of Figure 4-10 A are not linear, but display downward curvature. The effect became more pronounced as the initial quencher concentration was increased. Since ionization was rate limiting at the start of reaction, it certainly was expected to remain rate limiting as chain ends were depleted by capping; hence the

observed downward curvature cannot be due to a shift in the rate limiting step from ionization to capping. The observed curvature also cannot be ascribed to complexation between $TiCl_4$ and *N*-(2-*tert*-butoxyethyl)pyrrole, since initial rates were the same regardless of quencher concentration. Thus, the curvature almost certainly represents a retarding of the rate of ionization due to loss of $TiCl_4$. As alkylation of pyrrole proceeded, HCl was generated necessarily causing active $TiCl_4$ to salt out as inactive $Ti_2Cl_9^-$ counterions, effectively reducing the overall rate of ionization.

Figure 4-10 B shows that the relative amounts of alkylated pyrrole isomers and concomitantly formed *exo*-olefin remained constant regardless of the ratio of quencher to chain ends. After alkylation the PIB chain ends were consistently comprised of 57% C-3 alkylated pyrrole, 38% C-2 alkylated pyrrole and 5% *exo*-olefin. The observed isomer ratio is in the range previously found for *N*-methylpyrrole[186] (54% C-3 alkylation / 46% C-2 alkylation) and *N*-(ω-haloalkyl)pyrroles[191] (60-74% C-3 alkylation / 26-40% C-2 alkylation, depending on alkylene tether length and identity of halogen).

Deprotection of the hydroxyl terminus via removal of the *tert*-butyl group (deblocking) can be induced with or without acids supplemental to the $TiCl_4$ used to catalyze the polymerization and alkylation reactions. Figure 4-11 A shows the kinetics of deblocking in the presence of various acid combinations, including additional $TiCl_4$, $TiCl_4/H_2SO_4$, $EtAlCl_2$, and $EtAlCl_2/H_2SO_4$. In each case, the additional acids were charged to the reactor after the $TiCl_4$-catalyzed alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole; the reactor was removed from the cold bath and allowed to warm to room temperature (requiring about 4.5 h, with evolution of methyl chloride), and then actively heated to hexane reflux (69 °C) for approximately 3.5 h. Simply allowing the

reaction to warm to room temperature without supplemental acids, i.e., making use only of the $TiCl_4$ that was already present as the polymerization catalyst, resulted in very slow deblocking (not shown). Even with an additional 5 equiv of $TiCl_4$, deblocking was relatively slow and not complete by the time the reaction had reached room temperature; however, the rate increased as heat was applied and complete deblocking was achieved. The rate of deblocking by $TiCl_4$ also increased dramatically by addition of a protic acid, e.g., H_2SO_4. As shown, the $TiCl_4/H_2SO_4$ combination provided full deblocking before the reaction had warmed to 0 ^oC (about 90 min). The most rapid deblocking was achieved by the addition of a stronger Lewis acid, e.g. $EtAlCl_2$. Charging $EtAlCl_2$ to the reactor resulted in complete deprotection within about 30 min, and the combination of $EtAlCl_2$ and H_2SO_4 yielded even a slightly higher rate.

In addition to the rate of deblocking, the combination of acids used for deblocking was also found to effect the overall end group composition of the PIB. ^1H NMR analysis revealed that a major drawback of the use of $TiCl_4$ as the sole Lewis acid, with or without H_2SO_4, was that it failed to promote EAS reactions between *exo*-olefin PIB and excess quencher. In addition, $TiCl_4$ induced chain coupling through the pyrrole ring (particularly when used without H_2SO_4) at elevated temperatures. Both of these issues negatively impact the overall functionality of the PIB; however, both were alleviated by addition of the stronger Lewis acid, $EtAlCl_2$. The use of $EtAlCl_2$ not only increased the rate of *tert*-butyl group removal, but it also prevented coupling. Moreover, as shown in Figure 4-11 B, when the protic acid, H_2SO_4, was used in conjunction with $EtAlCl_2$, the residual *exo*-olefin was forced to alkylate pyrrole, resulting in quantitative hydroxyl functionality.

Figure 4-11 B also illustrates isomerization of the PIB pyrrole chain ends that occurred during deblocking, principally at elevated temperature (69 ^{o}C). The C-2 alkylated pyrrole isomer was converted to the more thermodynamically stable C-3 alkylated pyrrole isomer. Isomerization occurred with all four acid combinations, but it was faster and more complete in the presence of $EtAlCl_2$. The final chain end composition in Figure 4-11 B achieved by the addition of $EtAlCl_2/H_2SO_4$, was 98% C-3 hydroxyl and 2% C-2 hydroxyl, with no detectable *exo*-olefin or coupled products.

Post-polymerization Reactions on Hydroxy-functional PIB

Difunctional hydroxy-terminated PIBs are particularly useful in the synthesis of segmented block copolymers. The aliphatic backbone of PIB exhibits outstanding thermal stability, oxidation and ozonolysis resistance, and barrier properties and has been incorporated as a soft-segment in polyesters,[79] polyurethanes,[224,225] polyamides,[226] and polycarbonates.[227] Synthesis of these copolymers typically requires reaction of hydroxy-telechelic PIBs with polyfunctional isocyanates, carboxylic acids, or esters. To demonstrate that the currently discussed hydroxy-telechelic PIBs are sufficiently reactive toward such functionalities, model reactions with isocyanates and carboxylic acids were performed, and a chain extension reaction was preformed with an aromatic diisocyanate.

Figure 4-12 shows ^{1}H NMR spectra of the products from reaction of [3-polyisobutyl-*N*-(2-hydroxyethyl)]pyrrole with *tert*-butyl acetic acid (A), butyl isocyanate (B), and phenyl isocyanate (C). For all three cases, the catalyzed room temperature reactions were quantitative after 4 h. The resonances for the methylene protons adjacent to oxygen on the pyrrole moiety were shifted downfield from 3.81 ppm after formation of the electron withdrawing ester and urethane linkages. While it has been previously

shown that isocyanates are capable of electrophilic addition to a pyrrole ring,[228] particularly in the C-2 position, reaction of isocyanate with the pyrrole ring was not observed here.

As further evidence of reactivity, the α,ω-dihydroxy polyisobutylene was chain extended in a dibutyltin dilaurate (DBTDL)-catalyzed urethane-forming reaction with 4,4′-methylene*bis*(phenyl isocyanate) (MDI) (see Table 4-1, polymer 4). Chain extension was confirmed in the ^{1}H NMR spectrum shown in Figure 4-13 by a downfield shift, from 3.81 to 4.35 ppm, of the resonance due to the ultimate methylene unit of the *N*-alkylene tether, adjacent to oxygen. The splitting pattern also changed, from a quartet to a triplet, consistent with loss of the hydroxyl proton. The aromatic resonances of the MDI residue were seen at 7-7.2 ppm, as well as the bridge methylene protons at 3.88 ppm. Chain extension was also evident in the ^{13}C NMR spectrum of Figure 4-14, most notably due to the urethane carbonyl resonance at 153.0 ppm. The number average molecular weight determined from GPC after chain extension was 3.89 x 10^4 g/mol with a polydispersity of 2.06.

Conclusion

We have shown that direct addition of excess *N*-(2-*tert*-butoxyethyl)pyrrole to a $TiCl_4$-catalyzed quasiliving isobutylene polymerization in 60/40 (v/v) hexane/methylchloride at -60 ^{o}C resulted in rapid alkylation of the pyrrole ring and concomitant formation of <5% *exo*-olefin terminated PIB . By heating the reaction mixture after quenching/alkylation in the presence of $EtAlCl_2$ and a protic acid, such as H_2SO_4, the terminal *tert*-butyl groups were successfully and expeditiously removed *in situ*. The deblocking treatment also induced alkylation of pyrrole by the residual *exo*-

olefin chain ends to yield quantitative hydroxy-functional PIB. The resulting primary hydroxy-terminated PIBs showed excellent reactivity with acids and isocyanates, and may serve as building blockings for copolymer synthesis.

Table 4-1. Experimental conditions and results of *N*-(2-*tert*-butoxyethyl)pyrrole end-quenching of $TiCl_4$-catalyzed quasiliving isobutylene polymerizations

			molecular weight	chain end composition						
						alkylated pyrrole		hydroxyl		
polymer	initiator	reaction event	$\overline{M}_n$ (PDI)	*tert*-Cl	*exo*-olefin	C-3	C-2	C-3	C-2	coupling
1[a]	TMPCl	polymerization (25 min, -60 °C)	1.9 x 10^3 (1.06)	1.0						
		alkylation (25 min, -60 °C)	2.2 x 10^3 (1.04)		0.05	0.57	0.38			
		deblocking (1.5 h, -60 → 0 °C)	2.0 x 10^3 (1.06)		0.03			0.60	0.37	
		isomerization (2.92 h, 0 → 69 °C)	2.0 x 10^3 (1.05)					0.98	0.02	
2[a]	*t*-Bu-*m*-DCC	polymerization (23 min, -60 °C)	2.7 x 10^3 (1.01)	1.0						
		alkylation (27 min, -60 °C)	3.0 x 10^3 (1.02)		0.05	0.55	0.38			0.02
		deblocking (1.5 h, -60 → 0 °C)								
		isomerization (3.83 h, 0 → 69 °C)	3.1 x 10^3 (1.05)					0.98		0.02
3[b]	TMPCl	polymerization (28 min, -60 °C)	2.0 x 10^3 (1.02)	1.0						
		alkylation (30 min, -60 °C)	2.3 x 10^3 (1.08)	0.42	0.04	0.17	0.17	0.04	0.02	0.14
4		chain extension of (2) with MDI	3.89 x 10^4 (2.06)							

[a] Polymerization/quench: 60/40 (v/v) hexane/methyl chloride, -60 °C, chain end concentration, [CE] = 0.02 M, [2,6Lut] = 0.005 M, [$TiCl_4$] = [*N*-(2-*tert*-butoxyethyl)pyrrole] = 3[CE]. Deblocking/isomerization: additionally [$EtAlCl_2$] = 5[CE], [H_2SO_4] = 2[CE]

[b] Forced coupling: conditions same as polymer 1 except [*N*-(2-*tert*-butoxyethyl)pyrrole] = 0.5[CE]

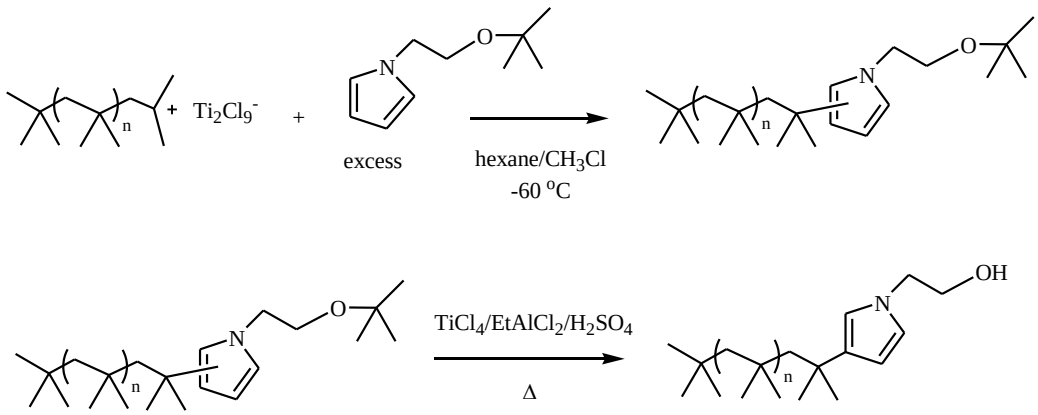

Figure 4-1. Single-pot synthesis of primary hydroxy-functional PIB from a $TiCl_4$-catalyzed quasiliving isobutylene polymerization by direct quenching with *N*-(2-*tert*-butoxyethyl)pyrrole and subsequent *in situ* cleavage of the terminal *tert*-butyl ether.

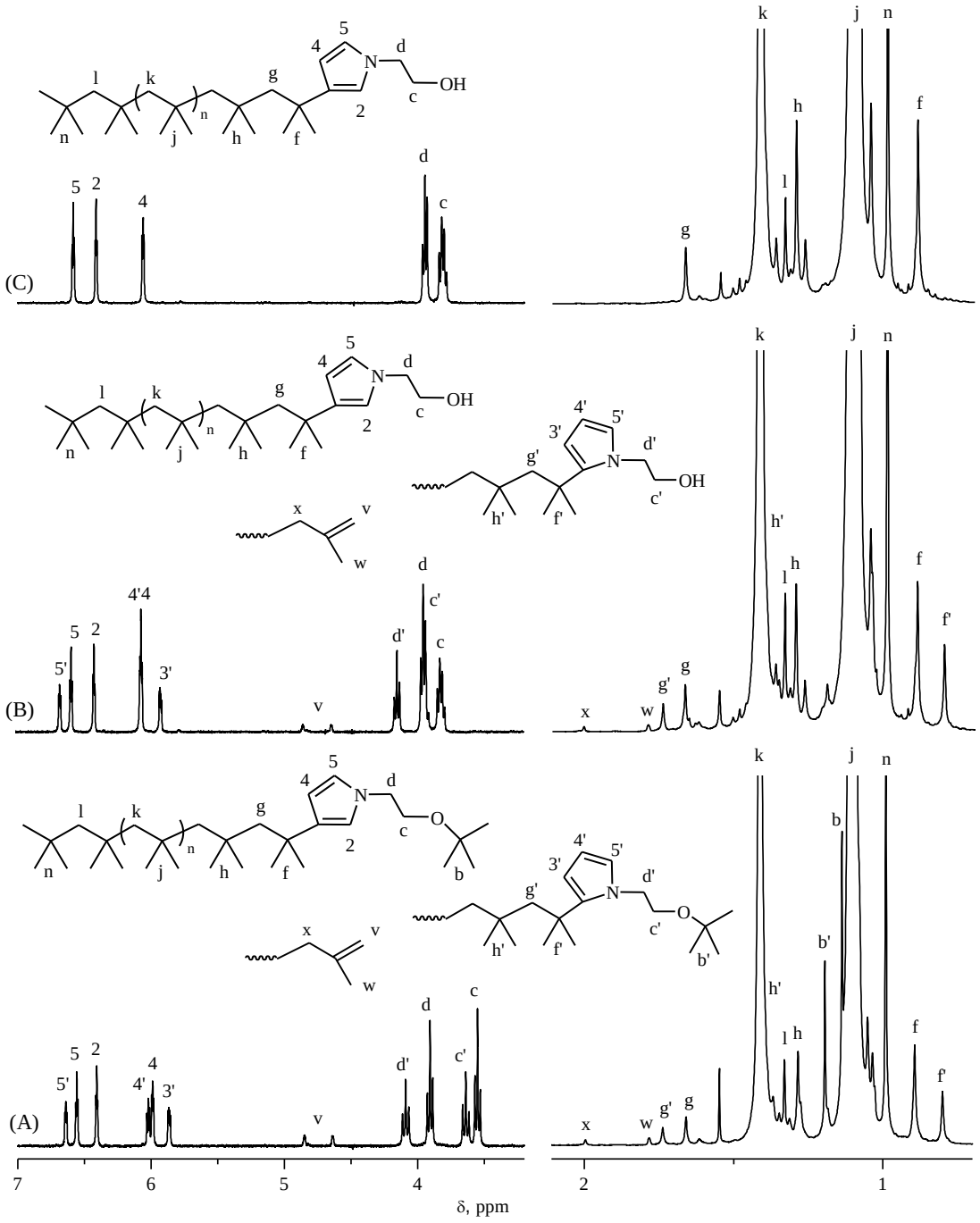

Figure 4-2. ^{1}H NMR (300 MHz, $CDCl_3$, 22^{o}C) spectra of monofunctional polyisobutylene after (A) $TiCl_4$- catalyzed alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole, (B) subsequent warming in the presence of $EtAlCl_2$ and H_2SO_4 to cleave the terminal ether, and (C) isomerization to [3-polyisobutyl-*N*-(2-hydroxyethyl)]pyrrole (see Table 4-1, polymer 1).

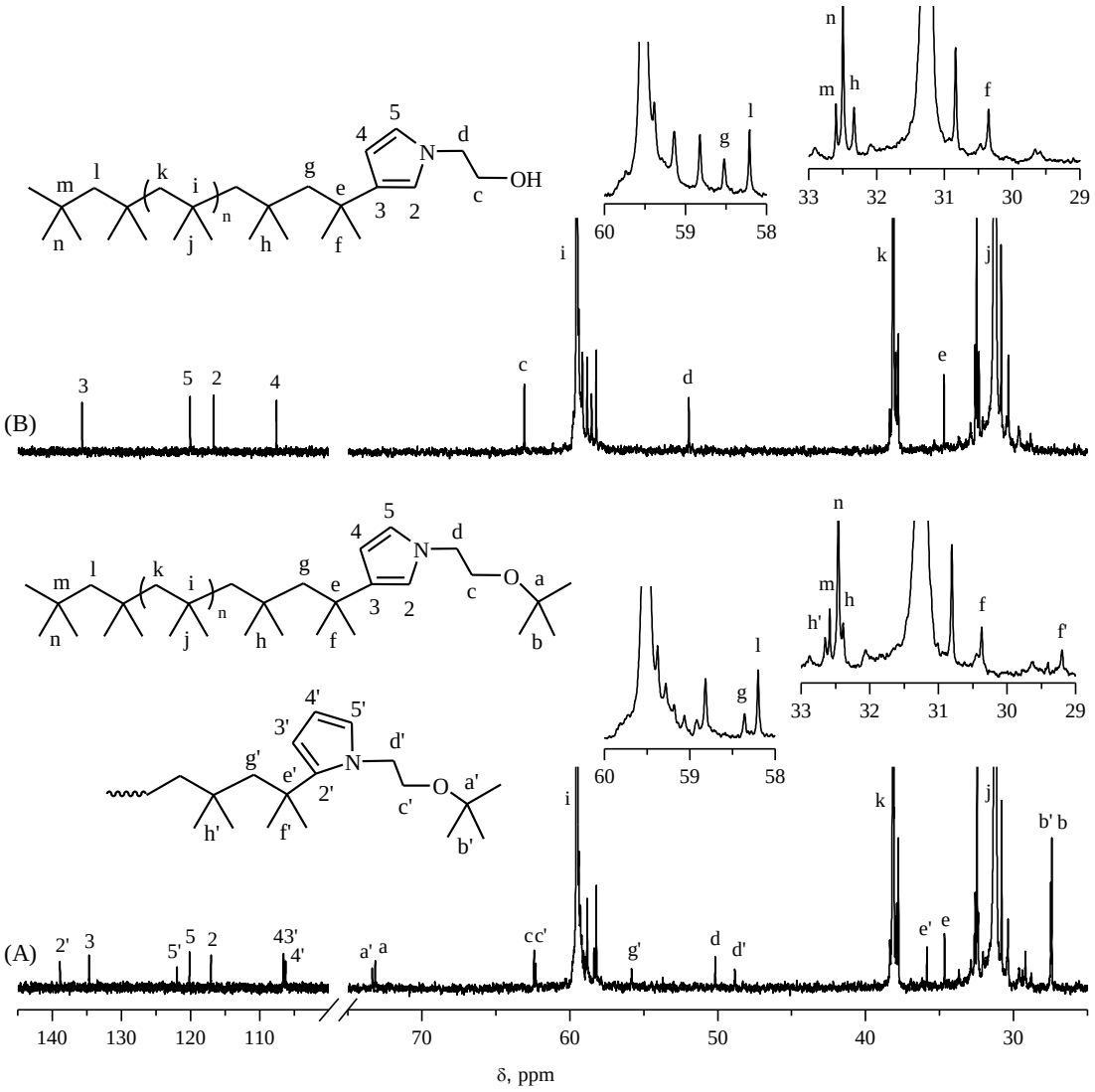

Figure 4-3. ^{13}C NMR (75 MHz, $CDCl_3$, 22 ^oC) spectra of mono functional polyisobutylene after (A) $TiCl_4$ catalyzed alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole and (B) subsequent heating to reflux in the presence of $EtAlCl_2$ and H_2SO_4 to cleave the terminal ether and induce isomerization to [3-polyisobutyl-*N*-(2-hydroxyethyl)]pyrrole (see Table 4-1, polymer 1).

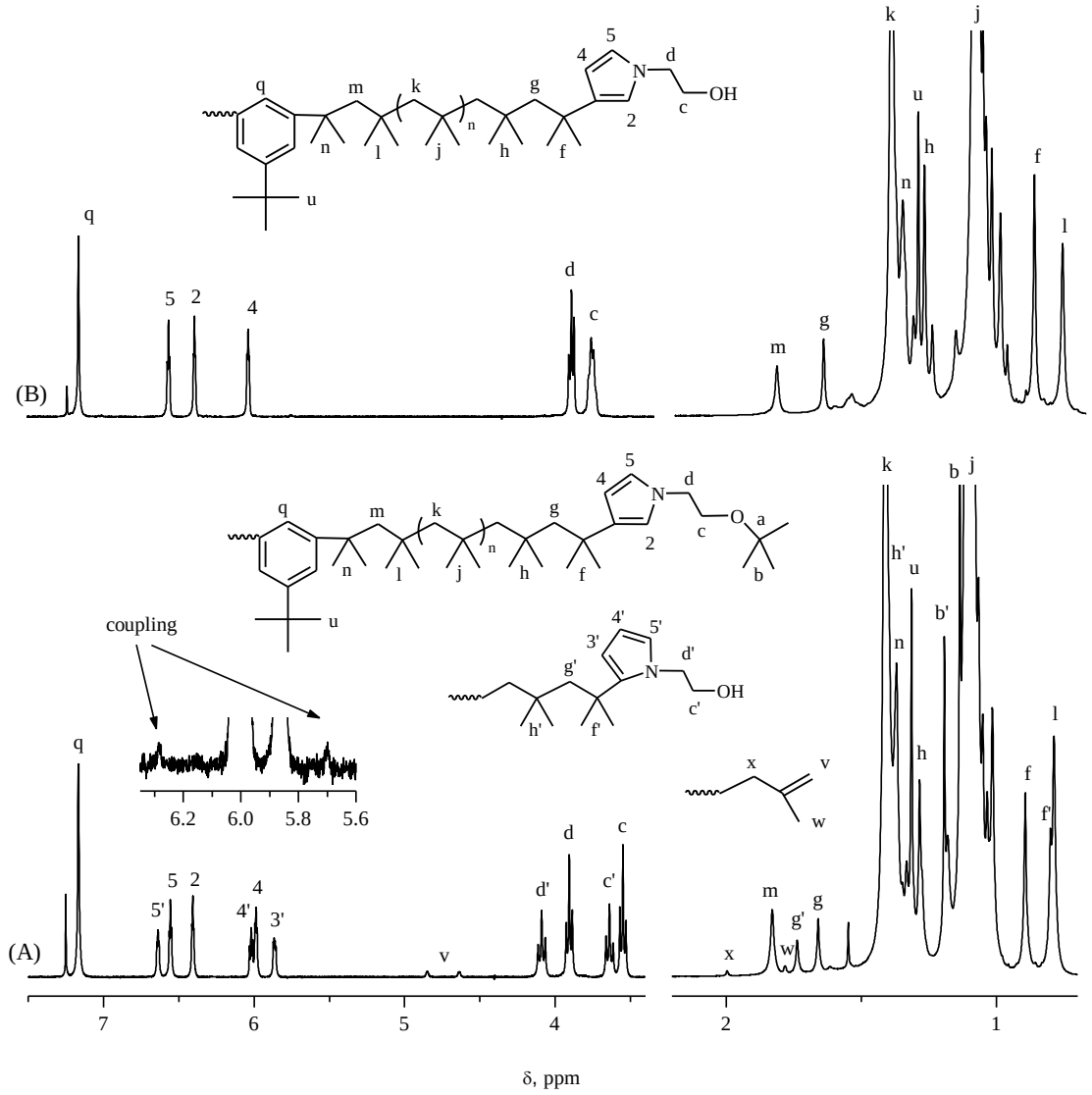

Figure 4-4. ^{1}H NMR (300 MHz, $CDCl_3$, 22^{o}C) spectra of difunctional polyisobutylene after (A) $TiCl_4$ catalyzed alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole and (B) subsequent heating to reflux in the presence of $EtAlCl_2$ and H_2SO_4 to cleave the terminal ether and induce isomerization to α,ω-*bis*[*N*-(2-hydroxyethyl)pyrrol-3-yl]polyisobutylene (see Table 4-1, polymer 2).

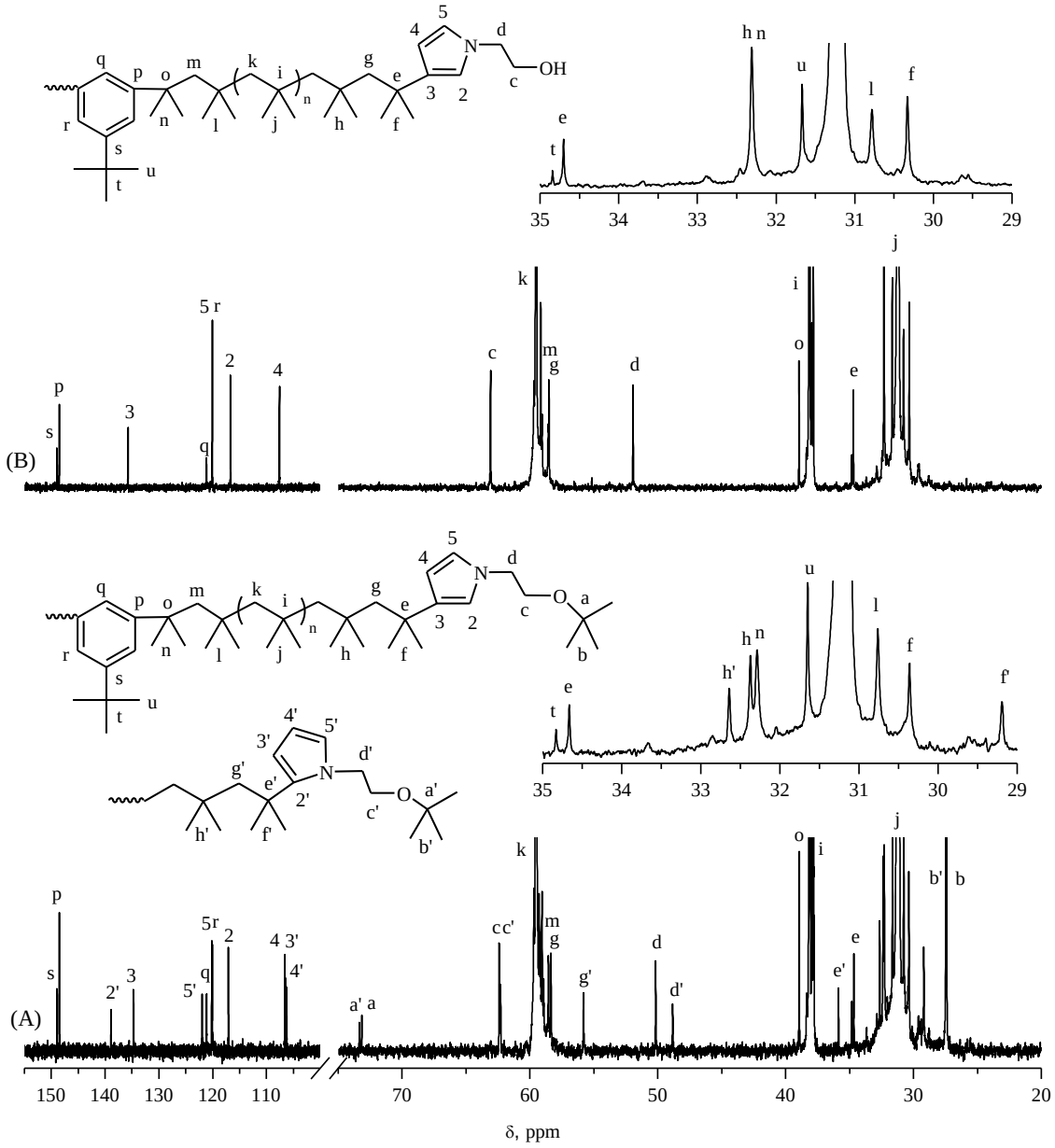

Figure 4-5. ^{13}C NMR (75 MHz, $CDCl_3$, 22°C) spectra of difunctional polyisobutylene after (A) $TiCl_4$ catalyzed alkylation of *N*-(2-*tert*-butoxyethyl)pyrrole and (B) subsequent heating to reflux in the presence of $EtAlCl_2$ and H_2SO_4 to cleave the terminal ether and induce isomerization to α,ω-*bis*[*N*-(2-hydroxyethyl)pyrrol-3-yl]polyisobutylene (see Table 4-1, polymer 2).

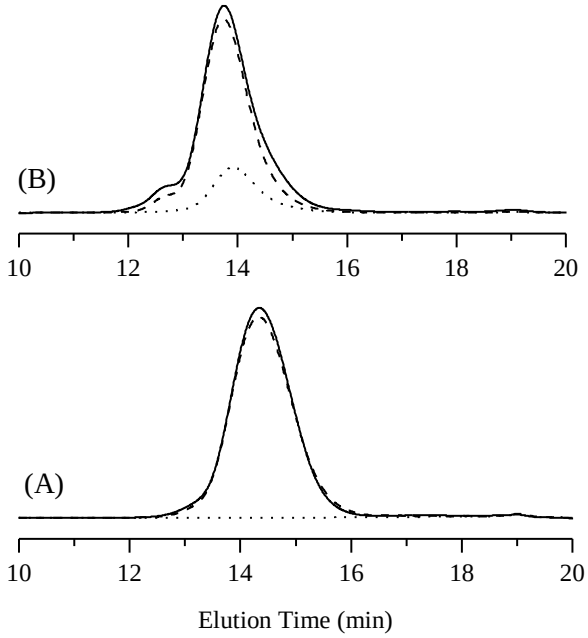

Figure 4-6. UV traces for GPC of (A) monofunctional PIB before quenching (⋯⋯), after quenching with *N*-(2-*tert*-butoxyethyl)pyrrole (---), and after deblocking (—), i.e. removal of the terminal *tert*-butyl group; and (B) difunctional PIB before quenching (⋯⋯), after quenching (---), and after deblocking (—).

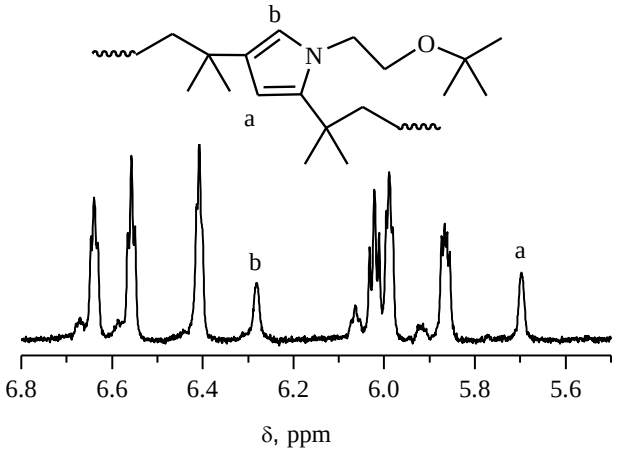

Figure 4-7. Partial ^{1}H NMR (300 MHz, $CDCl_3$, 22^{o}C) spectrum showing the di-alkylated pyrrole resonances of deliberately coupled PIB (Table 4-1, polymer 3). Unlabeled resonances are due to monoalkylated pyrrole isomers (see Figure 4-2).

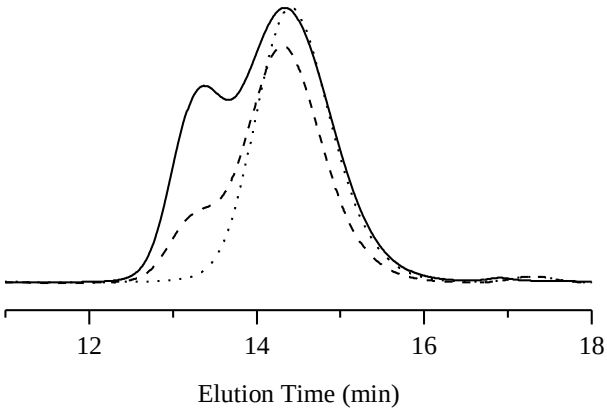

Figure 4-8. GPC traces (RI) for the PIB from Figure 6 before (·····) and after (---) quenching with 0.5 equiv per chain end of *N*-(2-*tert*-butoxyethyl)pyrrole. Coupling through the pyrrole ring is indicated by the high molecular weight shoulder in the post-quench UV trace (——).

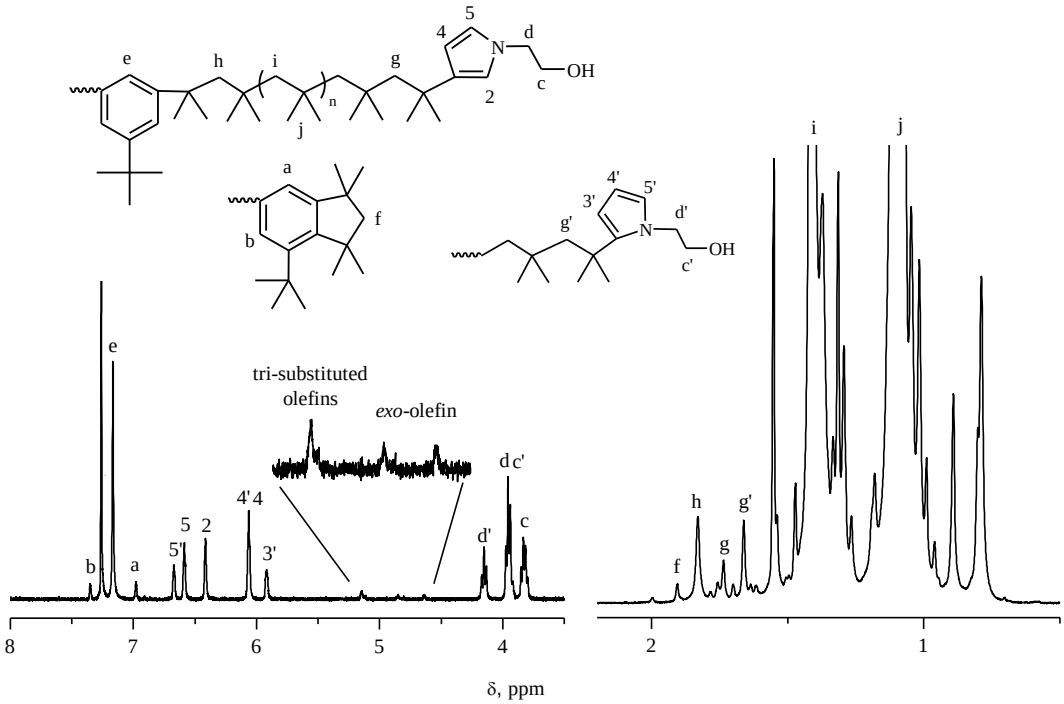

Figure 4-9. ^{1}H NMR (300 MHz, $CDCl_3$, 22 ^{o}C) spectrum of α,ω-hydroxy-terminated polyisobutylene obtained from an isobutylene polymerization catalyzed by dimethyl aluminum chloride (Me_2AlCl) (-75 ^{o}C, 55/45 (v/v) hexane/methyl chloride, [*t*-Bu-*m*-DCC] = 0.01 M, [2,6Lut] = 0.005 M, [IB] = 0.457 M, [Me_2AlCl] = 0.12 M) and quenched with *N*-(2-*tert*-butoxyethyl)pyrrole (0.05 M). Full monomer conversion was reached in 3 h, and alkylation required 8 min. Hydroxyl functionality was obtained after allowing the reaction to warm at room temperature under N_2 for 7 h. The indanyl ring structure and terminal olefins shown were also observed prior to quenching.

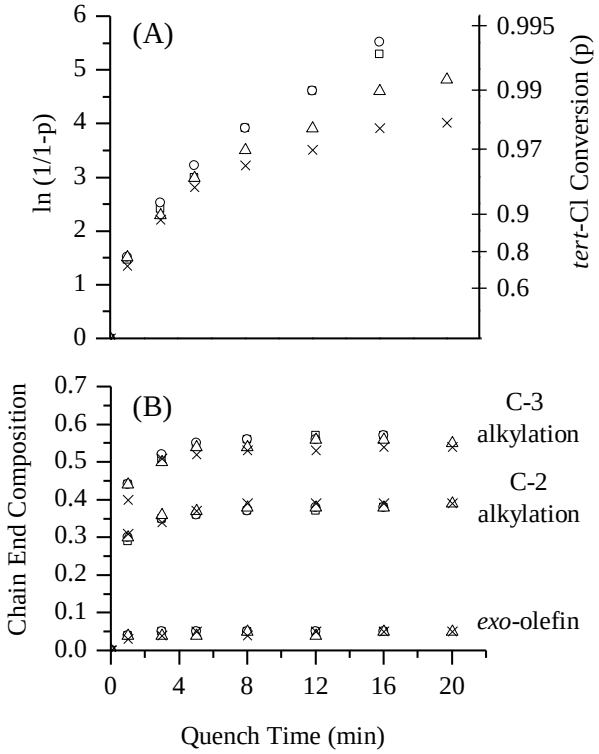

Figure 4-10. (A) Kinetics of *N*-(2-*tert*-butoxyethyl)pyrrole alkylation with monofunctional PIB (0.02 M) in 60/40 (v/v) hexane/methyl chloride at -60 ^{o}C with 2,6-lutidine (0.005 M) and 3 equiv of $TiCl_4$ using 1.2 (○), 3 (□), 6 (△) and 10 (×) equiv of *N*-(2-*tert*-butoxyethyl)pyrrole. (B) The final chain end functionality remained approximately constant over the various quencher concentrations, with 57% C-3 alkylated pyrrole, 38% C-2 alkylated pyrrole and 5% *exo*-olefin formation.

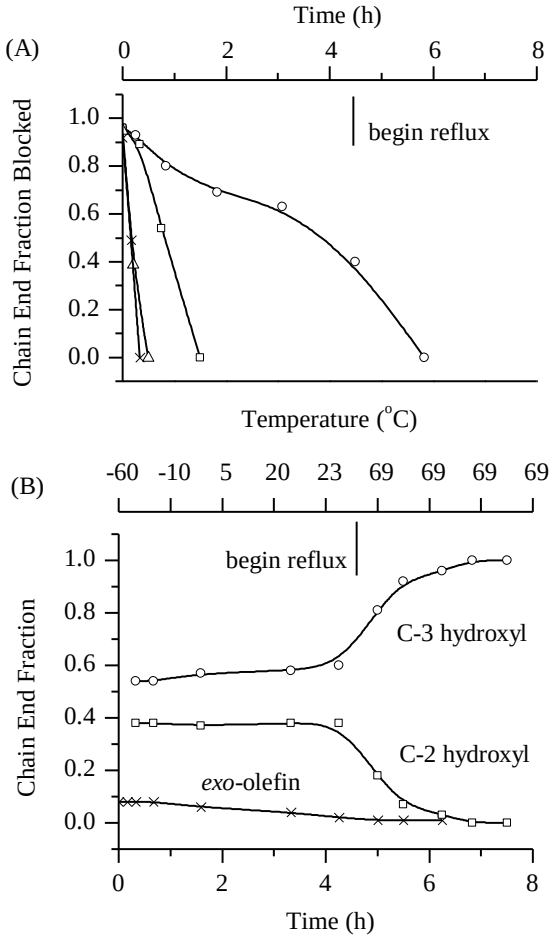

Figure 4-11. (A) Kinetics of deblocking *N*-(2-*tert*-butoxyethyl)pyrrole capped PIB (terminal *tert*-butyl ether cleavage): additional 5 equiv of $TiCl_4$ (○), 5 equiv of $TiCl_4$ and 2 equiv of H_2SO_4 (□), 5 equiv of $EtAlCl_2$ (△), or 5 equiv of $EtAlCl_2$ and 2 equiv of H_2SO_4 (×). (B) Chain end composition during deblocking with 5 equiv of $EtAlCl_2$ and 2 equiv of H_2SO_4 added: C-3 hydroxyl (○), C-2 hydroxyl (□), *exo*-olefin (×).

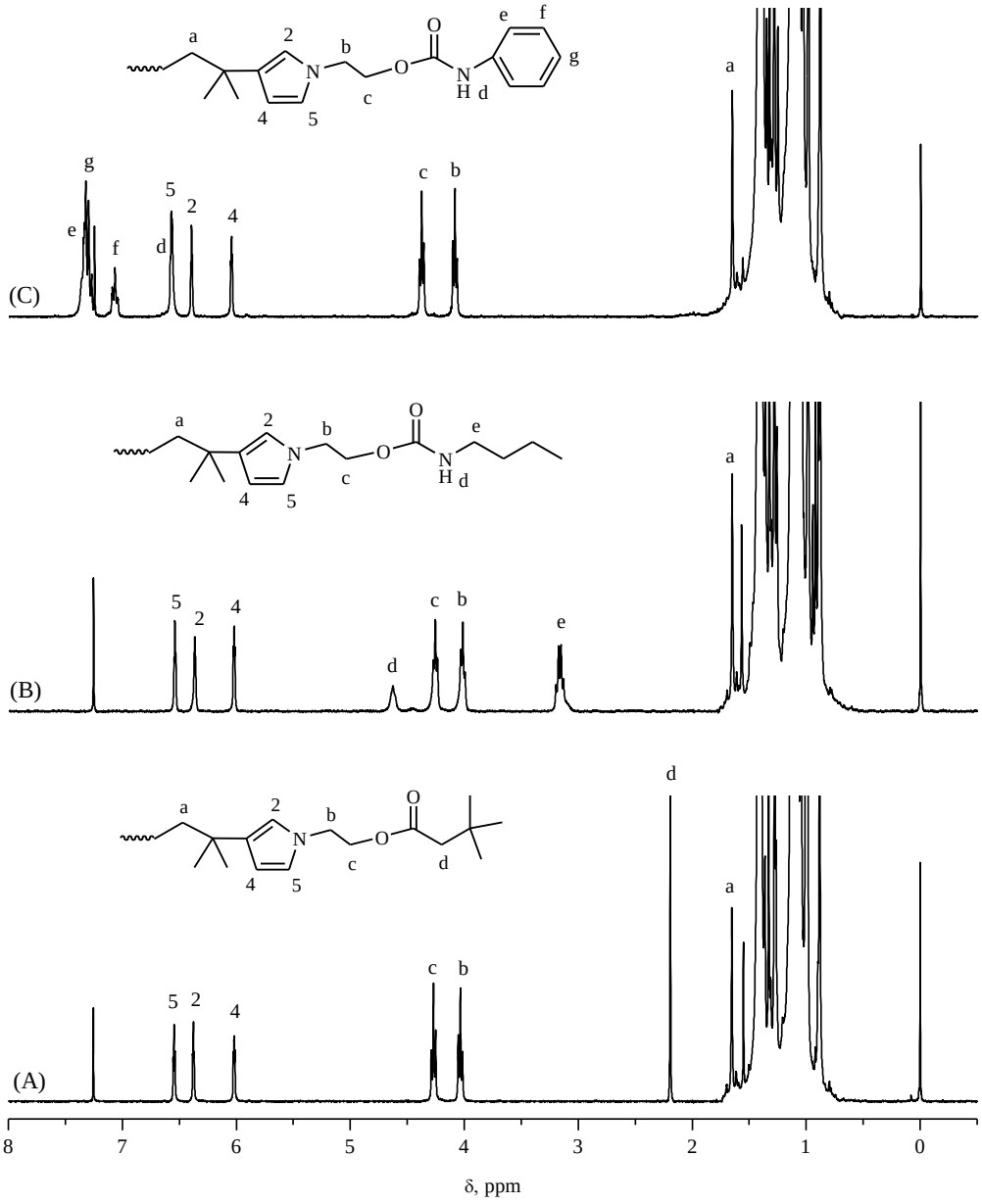

Figure 4-12. ^{1}H NMR (300 MHz, $CDCl_3$, 22^{o}C) spectra of [3-polyisobutyl-*N*-(2-hydroxyethyl)]pyrrole products of reaction with (A) *tert*-butyl acetic acid, (B) butyl isocyanate, and (C) phenyl isocyanate.

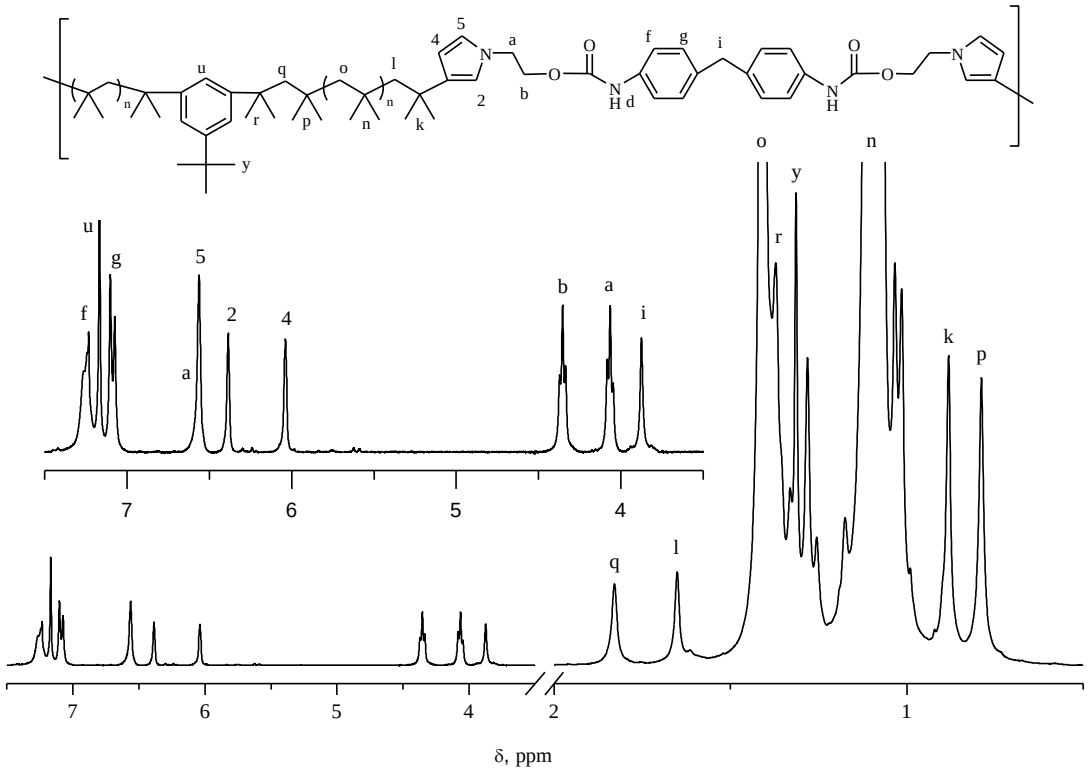

Figure 4-13. ^{1}H NMR (300 MHz, $CDCl_3$, 22^{o}C) spectrum of polymer obtained from chain extension of α,ω-*bis*[*N*-(2-hydroxyethyl)pyrrol-3-yl]polyisobutylene with 4,4'-methylene*bis*(phenyl isocyanate).

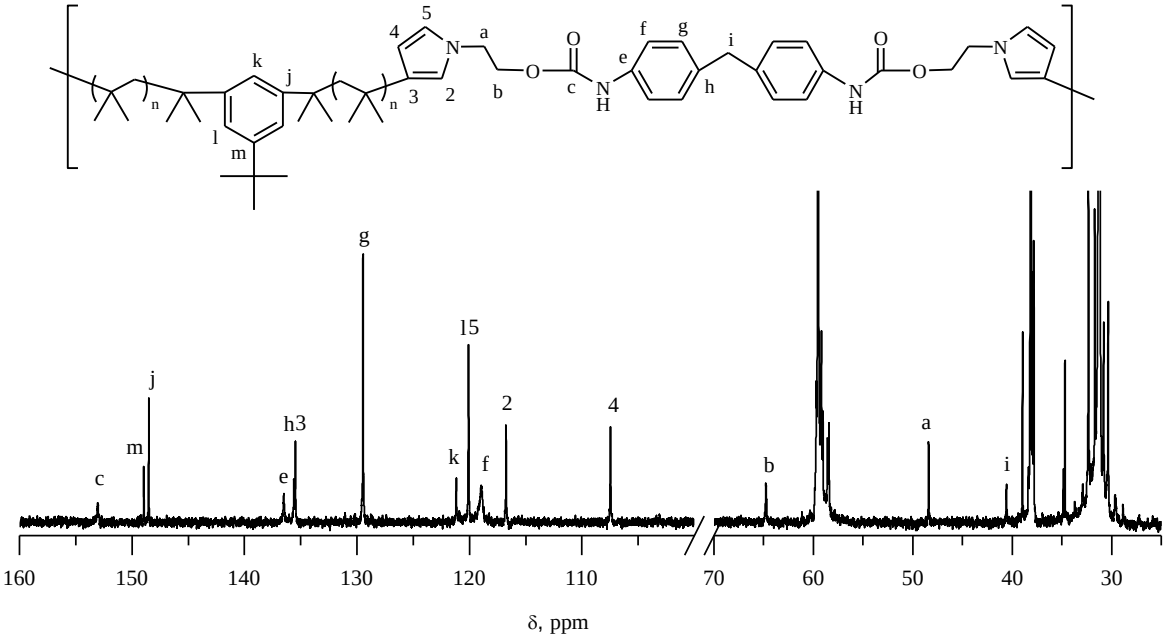

Figure 4-14. ^{13}C NMR (75 MHz, $CDCl_3$, 22^{o}C) spectrum of polymer obtained from chain extension of α,ω-*bis*[*N*-(2-hydroxyethyl)pyrrol-3-yl]polyisobutylene with 4,4'-methylene*bis*(phenyl isocyanate).

CHAPTER V

END-QUENCHING OF $TiCl_4$-CATALYZED QUASILIVING POLYISOBUTYLENE WITH ALKOXYBENZENES FOR DIRECT CHAIN END FUNCTIONALIZATION

Introduction

Polyisobutylene (PIB) is versatile material with properties desirable for applications ranging from lubricant additives[37] to biomaterials.[229] However, the use of PIB in preparation of more complex materials may require introduction of a reactive and/or polar functionality at the chain end. For most commercially produced PIBs the available starting functionality is olefin, which arises naturally from β-proton expulsion in chain transfer dominated polymerization processes. In BF_3-catalyzed polymerizations, the content of highly reactive methylvinylidene or *exo*-olefin chain ends can be as high as 70-90%; however, protic initiation requires these PIBs to contain only a single reactive terminus.[10,230] The synthesis of telechelic PIBs became possible with the development of conditions allowing quasiliving carbocationic isobutylene polymerization from multifunctional initiators. However, the dormant-active equilibrium established during such $TiCl_4$ or BCl_3-catalyzed polymerizations naturally leads to *tert*-chloride functionality at the chain end,[14] and post-polymerization dehydrochlorination would still be required to synthesize *exo*-olefin telechelic PIB.[39,40]

Olefin terminated PIB has been subjected to numerous post-polymerization transformations, including hydroboration-oxidation,[50] hydroformylation,[47] epoxidation,[53] ozonolysis,[58] lithiation,[62] sulfonation,[41] hydrosilylation,[44] and hydrobromination.[103] Terminal unsaturation has also been used as a Friedel-Crafts alkylating agent[91] and a substrate for the free radical addition of thiols.[100] These and subsequent post-

polymerization transformations provide useful chain end functionality, but often at greater difficultly and/or expensive. These problems have provided the impetus to develop technology aimed at obtaining functionalities other than *tert*-chloride and/or *exo*-olefin directly from isobutylene polymerizations. Two approaches to *in situ* functionalization have been taken: one is to begin the polymerization with a functional initiator, and the other is addition of suitable nucleophiles to the polymerization at full monomer conversion (quenching).

Functional initiators reported for isobutylene polymerization have included structures with non-polymerizable olefins,[106,107,108] acetates,[110] protected[127] and unprotected[128] phenols, and silylchlorides.[115,116,117,119] Other reported initiatiors have involved cyclic moieties such an epoxide[123] or lactone[111] that ring open in the presence of $TiCl_4$ to provide hydroxyl and ester functionality, respectively. Unfortunately, functional initiators only provide the desired functionality at the initiation site, with the PIB chain terminus remaining a *tert*-chloride unless subsequently modified or a coupling strategy is employed.

Quenching an isobutylene polymerization with a nucleophile that either adds to or modifies chain ends has been somewhat more successful because it avoids complications that could arise during initiation and propagation. However, a judicious choice of nucleophile is required because of rapid and often overwhelming interaction with the Lewis acid catalyst. Soft π-nucleophiles, such as non-polymerizable monomers[157,180,146,149] and heterocyclic aromatic substrates,[176,186,188] have been used to successfully cap $TiCl_4$-catalyzed quasiliving PIB. In addition, certain highly hindered organic bases,[151] alkoxysilanes[221] and (di)sulfides[231] have proven useful for *in situ*

transformation of the PIB chain end to olefin. Despite many advances in quenching technology, large scale practicability may be limited due to reagent expense as well as requirements for extremely low temperatures and/or dilute reaction systems.

In cationic polymerization systems, alkylation of arenes was recognized early on, but was generally regarded as a chain transfer/termination reaction only useful for controlling molecular weight. For example, Plesch *et al.* reported that polystyrene polymerizations catalyzed by $TiCl_4$ in toluene resulted in polymers with tolyl end groups[232] and that anisole may act as chain terminating agent for $TiCl_4$-catalyzed isobutylene polymerization, as evidenced by *p*-methoxyphenyl end groups.[233] Similarly, Overberger *et al.* [234,235,236] found that a wide variety of mono- and di-alkyl substituted aromatics function as chain terminating agents in $SnCl_4$ catalyzed polymerization of styrene at 0 ^oC. When Russell *et al.*[237,238,239,240,241,242] conducted $SnCl_4$-catalyzed isobutylene polymerizations in ethyl chloride at -78.5 ^oC with phenol and substituted phenols as a co-catalysts (initiators), they found evidence of phenolic end groups; however, proton expulsion was also a significant chain breaking event, leading to terminal unsaturation.[243]

The first attempts at controlled termination of carbocationic polymerizations with an arene were reported by Kennedy *et al.*[30,31,32,244] when they used a triphenylaluminum/*tert*-alkyl chloride initiating system. The arylaluminum acted as both a catalyst and chain terminating agent, yielding α,ω-diphenyl polyisobutylenes with 0.7 to 1.7 phenyl groups per chain. For polystyrene, Hunter *et al.*[245] demonstrated that 40-70% of the chain ends may be capped by alkylphenols under $AlCl_3$ catalysis. Zhang *et al.*[192] reported on the direct addition triphenylamine to PIB synthesized from an $H_2O/TiCl_4$ initiating system. The maximum capping efficiency was approximately 70 to 80%, and the

process was plagued by competitive *exo*-olefin formation due to the presence of the basic amine. Fujisawa *et al.*[193] disclosed quenching of $SnCl_4$-catalyzed isobutylene polymerizations with vinylalkoxybenzenes. The alkylation reactions were performed in methylene chloride at temperatures ranging from -30 ^oC to room temperature, and vinyl end group functionalities from 76-90% were obtained.

Due to limited success at *in situ* alkylation/incorporation of arenes, namely phenol, at the polyisobutylene chain end, much attention has been given to post-polymerization Friedel-Crafts alkylations. Conventional polyisobutylenes made from $AlCl_3$-catalysis have relatively high amounts of tri- and tetra-substituted olefin end groups, and the harsh acid catalysis required to induce alkylation via the olefin end group may also induce fragmentation of the polymer chain. Selection of appropriate alkylation catalysts[246,247] and conditions or modification of the polymer chain end[248] can minimize these problems. However, arene alkylation with the olefin terminus became more practical with the commercial availability of high methyl vinylidene (>70%) PIB. With the highly reactive isomer, alkylation can be carried out in the absence of molecular weight degradation.[90] Typical alkylation catalysts include Lewis acids (e.g. $AlCl_3$, BF_3 and BF_3 complexes), trifluoromethane sulfonic acid, and acidic molecular sieves (e.g. Amberlyst 36).

The discovery of conditions that allowed for controlled quasiliving polymerization of isobutylene also led to polymers with quantitative chain end functionality. Kennedy *et al.* made use of these telechelic polyisobutylenes and reported post-polymerization alkylation of phenol,[91,249] anisole,[92] benzene, toluene, and xylene[93] with both *tert*-chloride and *exo*-olefin terminated PIB. The Friedel-Crafts alkylations were most often catalyzed by BF_3-etherate in hexanes or aromatic/dichloromethane solvent mixtures at temperatures

from 20 to 55 ^{o}C; unfortunately, warmer temperatures, especially above 60 ^{o}C, apparently favored cracking and depolymerization. Even with the more reactive arenes, phenol and anisole, reaction times of two days were required for complete conversion of the chain ends. Bergbreiter *et al.*[51] also reported the alkylation of highly activated benzene derivatives with *exo*-olefin terminated PIB in the presence of concentrated sulfuric acid, but the reactions required 60 h for complete conversion. Marechel *et al.*[94,128] reported $SnCl_4$-catalyzed alkylation of phenol with *exo*-olefin terminated PIB at temperatures from -50 to 0 ^{o}C in dichloromethane within 1-3 h; however, polymer degradation was observed, becoming more severe at higher temperatures. Kennedy *et al.*[93,94] have claimed alkylation of less reactive arenes such as benzene, toluene, and 2-bromoethyl benzene by *tert*-chloride terminated PIB in less than 5 h using aluminum trichloride catalysis at temperatures between -50 and -80 ^{o}C. In these and all other alkylation reactions involving arenes and PIB, selection of catalyst, solvent, and reaction temperature is critical to impart sufficient solubility and prevent unwanted degradation and/or cracking of PIB. Unfortunately, the conditions necessary for the Friedel-Crafts alkylation reactions may not be synonymous with those required for quasiliving carbocationic polymerization isobutylene, and therefore, arene functionalized PIBs have predominately been prepared in a multi-step processes.

Here, we report the successful alkylation of a range of alkoxybenzene compounds with $TiCl_4$-catalyzed quasiliving PIB, leading to quantitative capping of the chain ends. Alkylation and subsequent *in situ* deprotection of simple alkyl phenols allowed single-pot synthesis of phenolic PIBs. In addition, important functionalities such as primary halide, hydroxyl and amine were incorporated at the PIB chain end in a single-step via end-

quenching of the polymerization. The alkylations were remarkably tolerant of changes in temperature, e.g. up to -30 ^{o}C, as well as the presence both *endo*- and *exo*-olefin terminated PIB.

Experimental

Materials

Hexane (anhydrous, 95 %), titanium tetrachloride ($TiCl_4$) (99.9 %,), boron tribromide (BBr_3) (99.9%), 2,6-lutidine (redistilled, 99.5%), phenol (99%), anisole (anhydrous 99.7%), (2-chloroethoxy)benzene (98%), (2-bromoethoxy)benzene (98%), (3-bromopropoxy)benzene (96%), allyl phenyl ether (99%), 2,6-di-*tert*-butylphenol (99%), 2-bromopropane (99%), phenyl propargyl ether (90%), chlorotrimethylsilane (97%), tetrahydrofuran (THF) (anhydrous, 99.9%), methyl lithium (1.6 M in diethyl ether), calcium hydride (CaH_2) (95%), 4-phenoxybutyric acid (98%), palladium (Pd) on activated carbon (10% Pd by weight dry loading), sodium azide (99.5%), phenyl isocyanate (98%), lithium aluminum hydride ($LiAlH_4$) (powder, 95%), 1,6-dibromohexane (96%), zinc (dust, 98%), butyl phenyl ether (99%), potassium benzoate (99%), potassium *tert*-butoxide (95%), tetrabutylammonium fluoride (1 M in THF) (TBAF) and chloroform-*d* ($CDCl_3$) were purchased from Sigma-Aldrich Co. and used as received. 3-Phenoxypropyldimethylchlorosilane was purchased by Gelest and used as received. Dimethylformamide (DMF) (99.8%), heptane, diethyl ether, ethyl acetate, ammonium hydroxide (NH_4OH), sodium hydroxide (NaOH), concentrated sulfuric acid (H_2SO_4), anhydrous magnesium sulfate ($MgSO_4$), anhydrous sodium sulfate (Na_2SO_4), sodium bicarbonate ($NaHCO_3$) and ammonium chloride (NH_4Cl) were purchased and used as received from Fisher Scientific. Glissopal® was provided by Chevron Oronite

Company and used as received. Isobutylene (IB) (BOC Gases) and methyl chloride (Alexander Chemical Corp.) were dried by passing the gases through columns of $CaSO_4$/molecular sieves/$CaCl_2$ and condensed within a N_2-atmosphere glove box immediately prior to use. Boron trichloride (BCl_3) purchased from Matheson was also condensed immediately prior to use. The mono-functional initiator, 2-chloro-2,4,4-trimethylpentane (TMPCl), was prepared by bubbling HCl gas through neat 2,4,4-trimethyl-1-pentene (Sigma-Aldrich) at 0°C. The HCl-saturated TMPCl was stored at 0 ^oC, and immediately prior to use it was neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered. The difunctional initiator, 5-*tert*-butyl-1,3-di(1-chloro-1-methylethyl)benzene (*t*-Bu-*m*-DCC), was synthesized as previously reported[217] and stored at 0 ^oC.

Isopropoxybenzene. Isopropoxybenzene was synthesized by reaction of phenolate with 2-brompropane. Typically, 30 g (319 mmol) of phenol, 36 mL (383 mmol) 2-bromopropane and 15.3 g (383 mmol) of NaOH were combined in 100 mL of DMF and heated to reflux in a 70 ^oC oil bath. After 16 h, the reaction was cooled, and the product was extracted into diethyl ether, washed with deionized water and dried over $MgSO_4$. Removal of solvent under reduced pressure and vacuum distillation from CaH_2 provided 44 g (86%) of a colorless liquid. ^1H NMR ($CDCl_3$) δ (ppm) 1.36 (d, methyl, 6H), 4.57 (m, methine, 1H), 6.92 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.29 (t, aromatic, 2H). ^{13}C NMR δ 22.1 (methyl), 69.7 (methine), 115.9, 120.5, 129.5, 157.9 (aromatic).

Trimethyl(3-phenoxy-1-propynyl)silane. The alkyne moiety of phenyl propargyl ether was protected with trimethylsilane. Typically, 12.3 mL (95.5 mmol) of phenyl propargyl ether was dissolved in 50 mL of THF and chilled to -30 ^oC. To this solution

was added dropwise 66 mL (106 mmol) of methyl lithium as a 1.6 M solution in diethyl ether. After 15 min, 24 mL (189 mmol) of chlorotrimethylsilane was slowly charged to the reactor. After the initial exotherm, the reaction was allowed to warm and sit overnight at room temperature. The reaction mixture was filtered and concentrated on a rotary evaporator. Vacuum distillation from CaH_2 afforded 15.6 g (80 %) of colorless oil. ^{1}H NMR ($CDCl_3$) δ (ppm) 0.20 (s, methyl, 9H), 4.69 (s, methylene, 2H), 6.99 (d, aromatic, 2H), 7.02 (d, aromatic, 1H), 7.31 (t, aromatic, 2H); ^{13}C NMR δ -0.3 (C_6H_5-$CH_2C\equiv C$-Si(CH_3)$_3$), 56.7 (C_6H_5-$CH_2C\equiv C$-Si(CH_3)$_3$), 92.6 (C_6H_5-$CH_2C\equiv C$-Si(CH_3)$_3$), 100.1 (C_6H_5-$CH_2C\equiv C$-Si(CH_3)$_3$), 114.9, 121.4, 129.4 (C_6H_5-$CH_2C\equiv C$-Si(CH_3)$_3$).

4-Phenoxy-1-butanol. 4-Phenoxy-1-butanol was synthesized by $LiAlH_4$ reduction of 4-phenoxybutyric acid. Typically, 50 g (277 mmol) of 4-phenoxybutyric acid in 100 mL of THF was added dropwise to 10.5 g (277 mmol) of $LiAlH_4$ in 150 mL of THF at room temperature under N_2. After the initial exotherm, controlled by refluxing THF, the reaction sat overnight at room temperature. An aqueous solution of hydrochloric acid (0.1 M) was added to release the product, which was then extracted into diethyl ether and washed with deionized water until neutral. The organic layer was dried with Na_2SO_4, and the solvent was removed under vacuum. Vacuum distillation from CaH_2 afforded 33 g (72%) of colorless oil. ^{1}H NMR ($CDCl_3$) δ (ppm) 1.73 (m, methylene, 2H), 1.86 (m, methylene, 2H), 3.68 (t, -CH_2OH, 2H), 3.98 (t, -CH_2-OC_6H_5, t), 6.88 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.27 (t, aromatic, 2H); ^{13}C NMR δ 25.8, 29.5 (methylene), 62.4 (-CH_2OH), 67.7 (-CH_2-OC_6H_5), 114.5, 120.5, 129.4, 159.0 (aromatic).

6-Phenoxyhexylamine. 6-Phenoxyhexylamine was synthesized by reaction of phenolate with excess 1,6-dibromohexane, followed by displacement of bromide with

azide and reduction of azide. Typically, 19.3 g (205 mmol) of phenol and 8.6 g (215 mmol) of NaOH were combined in 200 mL of DMF, and the reaction flask was heated to 80 ^{o}C. After 10 min, 100 g (410 mmol) of 1,6-dibromohexane was charged to the reaction. After 1 h, the reaction mixture was cooled, and the product was extracted into diethyl ether and washed with deionized water. Fractional vacuum distillation from CaH_2 provided 25.1 g (48%) of (6-bromohexoxy)benzene as a colorless oil. ^{1}H NMR ($CDCl_3$) δ (ppm) 1.5 (m, methylene, 4H), 1.8 (m, methylene, 2H), 1.9 (m, methylene, 2H), 3.41 (t, -C*H*$_2$Br, 2H), 3.95 (t, -C*H*$_2$-OC_6H_5, t), 6.88 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.27 (t, aromatic, 2H); ^{13}C NMR δ 25.3, 28.0, 29.1, 32.7 (methylene), 33.9 (-*C*H_2Br), 67.6 (-*C*H_2-OC_6H_5), 114.5, 120.5, 129.4, 159.0 (aromatic). In conversion of bromide to azide, 25.1 g (97.6 mmol) of (6-bromohexoxy)benzene and 19 g (293 mmol) of sodium azide were placed in 100 mL of DMF, and the mixture was heated to 90 ^{o}C and allowed to react for 3 h. The product was washed with H_2O, dried over Na_2SO_4, and the residual solvents were removed under vacuum to yield 17.7 g (83%) of (6-azidohexoxy)benzene (219.28 g/mol). ^{1}H NMR ($CDCl_3$) δ (ppm) 1.5 (m, methylene, 4H), 1.64 (m, methylene, 2H), 1.8 (m, methylene, 2H), 3.28 (t, -C*H*$_2$$N_3$, 2H), 3.96 (t, -C*H*$_2$-$OC_6H_5$, t), 6.88 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.27 (t, aromatic, 2H); ^{13}C NMR δ 25.7, 26.5, 28.8, 29.2 (methylene), 51.4 (-*C*$H_2$$N_3$), 67.6 (-*C*$H_2$-$OC_6H_5$), 114.5, 120.5, 129.4, 159.0 (aromatic). In the reduction of the azide,[250] 17.7 g (80.7 mmol) of (6-azidohexoxy)benzene and 8.6 g (161 mmol) of ammonium chloride were placed into 100 mL of ethyl acetate at room temperature. While vigorously stirring, 7.9 g (121 mmol) of zinc dust was slowly added, and the exotherm was controlled by refluxing ethyl acetate. After 15 min, the reaction mixture was washed with NH_4OH and then deionized water.

Removal of the solvent under vacuum, followed by vacuum distillation from CaH_2 provided 14.3 g (92%) of colorless oil. ^{1}H NMR ($CDCl_3$) δ (ppm) 1.45 (m, methylene, 6H), 1.77 (m, methylene, 2H), 2.67 (t, -C*H*$_2$NH$_2$, 2H), 3.93 (t, -C*H*$_2$-OC$_6$H$_5$, t), 6.88 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.27 (t, aromatic, 2H); ^{13}C NMR δ 26.0, 26.7, 29.3, 33.7 (methylene), 42.1 (-*C*H$_2$NH$_2$), 67.7 (-*C*H$_2$-OC$_6$H$_5$), 114.5, 120.5, 129.4, 159.0 (aromatic).

6-Phenoxy-1-hexanol and 8-Phenoxy-1-octanol. The longer chain phenoxyalkanols were synthesized by reaction of phenolate with haloalkanols. For synthesis of 6-phenoxy-1-hexanol, 18.9 g (0.201 mol) of phenol and 18.3 g (0.457 mol) of NaOH were combined in 100 mL of DMF and heated to 80 ^{o}C. To the heated solution was charged 25 g (0.183 mol) of 6-chloro-1-hexanol. After 3 h, the reaction mixture was neutralized with HCl, and the product was extracted into diethyl ether and washed with deionized water. Vacuum distillation provided 34.8 g (78%) of a crystalline solid. ^{1}H NMR ($CDCl_3$) δ (ppm) 1.47 (m, methylene, 4H), 1.61 (m, methylene, 2H), 1.80 (m, methylene, 2H), 3.65 (t, -C*H*$_2$OH, 2H), 3.96 (t, -C*H*$_2$-OC$_6$H$_5$, t), 6.88 (d, aromatic, 2H), 6.95 (d, aromatic, 1H), 7.27 (t, aromatic, 2H); ^{13}C NMR δ 25.6, 25.9, 29.3, 32.7 (methylene), 62.9 (-*C*H$_2$OH), 67.7 (-*C*H$_2$-OC$_6$H$_5$), 114.5, 120.5, 129.4, 159.0 (aromatic). A similar reaction with 8-chloro-1-octanol yielded 8-phenoxyoctanol.

Instrumentation

Nuclear magnetic resonance (NMR) spectra were obtained using a 300 MHz Varian Mercury^{plus} NMR spectrometer. Standard ^{1}H and ^{13}C pulse sequences were used. Composite pulse decoupling was used to remove proton coupling in ^{13}C spectra. All ^{1}H chemical shifts were referenced to TMS (0 ppm), and all ^{13}C shifts were referenced to the

residual $CDCl_3$ solvent resonance (77.0 ppm). Samples were prepared by dissolving the polymer in $CDCl_3$ (20-50 mg/mL) and charging this solution to a 5 mm NMR tube.

Number average molecular weights ($\overline{M}_n$) and polydispersities (PDI = $\overline{M}_w/\overline{M}_n$) were determined with a gel-permeation chromatography (GPC) system consisting of a Waters Alliance 2695 separations module, an on-line multi-angle laser light scattering (MALLS) detector fitted with a gallium arsenide laser (power: 20 mW) operating at 658 nm (miniDAWN TREOS, Wyatt Technology Inc.), an interferometric refractometer (Optilab rEX, Wyatt Technology Inc.) operating at 35°C and 685 nm, and two PLgel (Polymer Laboratories Inc.) mixed E columns (pore size range 50-10^3 Å, 3 μm bead size). Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were *ca.* 15-20 mg of polymer/mL of THF, and the injection volume was 100 μL. The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology Inc.), and absolute molecular weights were determined by MALLS using a *dn/dc* calculated from the refractive index detector response and assuming 100% mass recovery from the columns.

Real-time ATR-FTIR monitoring of isobutylene polymerizations was performed using a ReactIR 4000 (Mettler-Toledo) integrated with a N_2 atmosphere glove box (MBraun Labmaster 130).[211] Isobutylene conversion during polymerization was determined by monitoring the area, above a two-point baseline, of the absorbance centered at 887 cm^{-1}, associated with the $=CH_2$ wag of isobutylene.

Polymerization, Quenching and Post-Polymerization Reactions

Polymerization and quenching reactions were performed within a N_2-atmosphere glovebox equipped with cryostated heptane bath. Total reaction volumes of 100-200 mL,

typically a 40/60 (v/v) hexane/methylchloride mixture, were contained in 250 mL round bottom flasks equipped with an overhead stirrer, thermocouple, and ReactIR probe. $TiCl_4$ catalyzed polymerizations of isobutylene at -70 ^oC in the presence of 2,6-lutidine (0.05 M) were initiated from either TMPCl or *t*-Bu-*m*-DCC at concentrations of 0.025-0.05 M. Isobutylene charges were chosen to target molecular weights of 2000-5000 g/mol. The $TiCl_4$ polymerization catalyst, typically around 0.015 M, resulted in polymerization times from 20-90 min, depending on the initiator and its concentration. At full monomer conversion, the alkoxybenzene quenchers were charged to the reaction, typically at 2.5-4 equiv per chain end. Additional $TiCl_4$ (1-6 equiv per chain end) was added to catalyze the alkylations reactions, resulting in overall $TiCl_4$ concentrations near 0.1 M. For alkoxybenzenes such as 4-phenoxy-1-butanol and 6-phenoxyhexylamine the $TiCl_4$ concentrations were augmented to account for complexation of the hydroxyl and amine moieties, respectively. Alkylations were allowed to proceed from 1-4 h in most cases; however, highly complexing alkoxybenzenes having hydroxyl and amine groups on the tether required 7-9 h for complete capping of the chain ends. With anisole and isopropoxybenzene an additional deblocking step was required before destruction of the catalyst to obtain phenolic PIB. For anisole, cleavage of the terminal methyl ether involved charging the reactor with an excess (6 equiv per chain end) of BBr_3 and allowing the reaction to warm at room temperature for 22 h. For isopropoxybenzene, additional $TiCl_4$ (2 equiv per chain end) and H_2SO_4 (0.3 mL) were charged to the reactor, and the reactor contents were allowed to warm at room temperature for 5.5 h under N_2. Finally, the catalysts were destroyed by addition of excess methanol, and the PIBs were isolated by precipitation from hexane into methanol. Table 5-1 shows the molecular

weights of the end-capped PIBs and further derivatives, as well as the conditions during the polymerization and alkylation reactions.

The primary chloride functional PIB obtained via quenching with (2-chloroethoxy)benzene was converted to a vinyl ether by dehydrochlorination with potassium *tert*-butoxide. Typically, 15 mL of heptane was used to dissolve 1.6 g of monofunctional primary chloride PIB (2.9×10^3 g/mol), and to this mixture was added an equal volume of DMF and 0.62 g (10 eq per chain end) of potassium *tert*-butoxide. The two phase reaction mixture was heated to reflux, where it became monophasic, and the reaction was conducted at reflux for 1 h. The reaction mixture was cooled, whereupon a biphasic mixture re-formed, and the heptane and DMF layers were separated. The heptane layer was washed with deionized water, dried over $MgSO_4$ and filtered, and finally the solvent was removed under vacuum.

The primary bromide functional PIB obtained via quenching with (3-bromopropoxy)benzene was converted to an azide functionality by reaction with NaN_3. Typically,10 g of difunctional primary bromide PIB (3.1×10^3 g/mol) was dissolved in 100 mL of a 50/50 (v/v) mixture of heptane and DMF. To this biphasic mixture was added 4.33 g (66.6 mmol) of sodium azide. The mixture was heated to 90 ^oC, upon which it became monophasic, and allowed to react for 2.5 h. After cooling and phase separation, the heptane layer was washed with deionized water; the polymer was precipitated into methanol, and the residual solvent was removed under vacuum.

Hydrogenation of the azide functional PIB provided primary amine functionality. Typically, 1.5 g of difunctional primary azide-terminated PIB was dissolved in 15 mL of hexane. To this solution was added 0.04 g of Pd on activated carbon. The solution was

pressurized with 50 psig of H_2 for 6 h on a Parr shaker-type hydrogenation apparatus. After the catalyst settled, the supernatant was passed through a 0.2 μm pore diameter PTFE filter, and the solvent was removed under vacuum.

The primary bromide functional PIB obtained via quenching with (3-bromopropoxy)benzene was converted to primary hydroxyl by displacement with benzoate, followed by hydrolysis. Typically, 2.5 g of difunctional primary bromide PIB (3.5×10^3 g/mol) was dissolved in 25 mL of heptane. This solution was added to 1.83 g (8 equiv per chain end) of potassium benzoate in 25 mL of DMF. The two phase system was heated to reflux, where it became monophasic, and the reaction was conducted at reflux for 4 h. After cooling, the heptane layer was separated from the DMF layer and subsequently contacted with 2.2 g of NaOH in 25 mL of DMF. The reaction was again heated to reflux for 12 h. After cooling and phase separation, the heptane layer was washed with deionized water and dried over Na_2SO_4 and the solvent was removed under vacuum.

The trimethylsilyl protecting group on PIB capped with trimethyl(3-phenoxy-1-propynyl)silane was removed with TBAF. Typically, 0.4 g of trimethyl(3-phenoxy-1-propynyl)silane capped PIB (2.5×10^3 g/mol) was contacted with 10 mL of 1 M TBAF solution for 3 h at room temperature. The polymer solution was washed with deionized water, dried with $MgSO_4$ and filtered, and the solvent was removed under vacuum.

Results and Discussion

Anisole

Direct addition of anisole to a $TiCl_4$-catalyzed isobutylene polymerization at

-70 ^{o}C in a 40/60 (v/v) hexane/methyl chloride solvent system resulted in alkylation of anisole and quantitative end-capping of the polyisobutylene chain. Exclusively monoalkylation, *para* to the alkoxy moiety, was observed. This is consistent with previous reports of $TiCl_4$-catalyzed Friedel-Crafts alkylation of arenes with *tert*-butyl and *tert*-amyl chlorides, which suggested that only *para* substitution products are possible.[251] As shown by the ^{1}H NMR spectrum in Figure 5-1 A, resonances at 1.69 and 1.96 ppm due to the ultimate *gem*-dimethyl and methylene unit of *tert*-chloride PIB were absent, and a new resonance appeared at 1.79 ppm due to the ultimate PIB methylene unit adjacent to anisole, as well as resonances at 6.82, 7.27, and 3.79 ppm, due to the alkylated anisole. Integration of the anisole moiety resonances in comparison with the aromatic initiator resonance at 7.17 ppm indicated quantitative capping of the chain ends. Further evidence of anisole alkylation is shown by the ^{13}C NMR spectrum in Figure 5-2 A. Resonances at 71.9 and 35.2 ppm, representing the ultimate quaternary *gem*-dimethyl carbons of *tert*-chloride PIB, respectively, were not present after the alkylation reaction and were replaced by a new set of resonances in the aromatic region and a resonance at 55.15 ppm due to the anisole methyl carbon.

The anisole end group by itself is not particularly useful; but demethylation via cleavage of the terminal ether would provide phenolic PIB, a product of significant importance. Ether cleavage is often performed under strongly acidic conditions; however, methyl ethers are relatively difficult to cleave.[220] Under conditions for quasiliving isobutylene polymerization and quenching, i.e. with $TiCl_4$ present at -70 ^{o}C, no cleavage of the terminal ether was observed. To achieve quantitative ether cleavage to phenolic end groups required addition of excess BBr_3 and 22 h at room temperature.

Figure 5-1 C shows a ^{1}H NMR spectrum of phenolic PIB obtained from the BBr_3 assisted demethylation of anisole capped PIB. The resonance at 3.79 ppm due to the terminal methyl group was replaced by new a resonance at 4.57 ppm with 1/3 the intensity, due to the phenolic proton. Demethylation was also evidenced in the ^{13}C NMR spectrum of Figure 5-2 C by a disappearance of the methyl resonance at 55.15 ppm and an upfield shift of the resonance due to the aromatic carbon adjacent to oxygen from 157.1 to 152.9 ppm. The GPC chromatograms of Figure 5-3 A indicated no coupling during the alkylation/quenching reaction and no significant polymer degradation during BBr_3 assisted deblocking.

Isopropoxybenzene

The *in situ* demethylation of anisole-capped PIB to create phenolic end groups required harsh conditions, i.e. addition of BBr_3, due to the strength of the methyl ether bond. More facile ether cleavage would be possible with bulkier alkyl groups; hence, isopropoxybenzene was alkylated by quasiliving polyisobutylene under conditions similar to those used with anisole. Other alkyl groups could also be used to protect phenol, provided they are stable under the alkylation reaction conditions.

A ^{1}H NMR spectrum of the isopropoxybenzene-capped PIB is shown in Figure 5-1 B. Resonances due to the alkylated isopropoxybenzene ring appear at 6.79 and 7.23 ppm, and a resonance for the methine proton of the isopropyl moiety appears at 4.51 ppm. Evidence of isopropoxybenzene alkylation is also observed in the ^{13}C NMR spectrum of Figure 5-2 B by the appearance of resonances in both the aromatic region and at 22.2 and 69.7 ppm due to the terminal isopropyl moiety.

Attempted cleavage of the terminal isopropyl ether with excess $TiCl_4$ at room temperature for 30-48 h resulted in near quantitative (91%) phenol functionality. However, subsequent experiments with the addition of excess BBr_3 or BCl_3 quantitatively cleaved the ether in less than 3 h while warming from -70 ^{o}C. The simplest approach for rapid cleavage of the isopropyl ether was the addition of protic acid, namely H_2SO_4. With $TiCl_4$ and H_2SO_4 present in the reactor, less than 5 h was required to obtain quantitative phenol functional PIB. The NMR spectra of phenolic PIB obtained by H_2SO_4-assisted deblocking of isopropoxybenzene-capped PIB were identical to those in Figures 5-1 C and 5-2 C. Again, GPC chromatograms of Figure 5-3 B indicated no chain coupling and no polymer degradations during polymerization, quenching and deblocking.

2,6-Di-tert-butylphenol

Addition of phenol and various ring-alkylated phenols, such as 2-*tert*-butyl phenol, to $TiCl_4$-catalyzed isobutylene polymerizations did not yield alkylated chain ends. Only with the highly hindered phenol, 2,6-di-*tert*-butylphenol, did alkylation proceed at -70 ^{o}C in the 60/40 (v/v) methyl chloride/hexane solvent system. Mono-alkylation occurred in the *para*-position; however, de-*tert*-butylation from the *ortho* position was also observed. De-*tert*-butylation on arenes is known to occur in the presence of Lewis acids,[252] and under appropriate conditions, selective *ortho*-de-*tert*-butylation of substituted phenols has been demonstrated.[253] As shown by the ^{1}H NMR spectrum in Figure 5-4, 37% of the chain ends were de-*tert*-butylated in about 1 h, and this amount increased over time; 44% at 5 h and 57% at 7 h. GPC traces shown in Figure 5-3 C indicated the absence of chain coupling.

Allyl Phenyl Ether

Quenching with an alkoxybenzene bearing a terminal olefin would represent a potential means of obtaining PIBs with an α-olefin terminus. Unfortunately, alkylation of the simplest alkoxybenzene having an α-olefin functionality, allyl phenyl ether, was accompanied by simultaneous Claisen rearrangement and ether cleavage. Narasaka *et al.*[254] reported on the usefulness of $TiCl_4$ in catalyzing the [3,3]-sigmatropic concerted pericylic rearrangement of allyl aryl ethers and found that hydrochloric acid generated during the reaction often resulted in concomitant hydrochlorination of the newly formed *o*-allylphenol. As shown in Figure 5-5, simultaneous Claisen rearrangement and hydrochlorination were observed in addition to ether cleavage to provide chain ends capped with 2-(2-chloropropyl)phenol and phenol functionality. The GPC traces shown in Figure 5-3 D indicate that the α-olefin was unreactive towards polymerization or chain coupling. Higher α-olefin homologs were not investigated, because olefin functionality can more easily be obtained via dehydrohalogenation of a primary halide functional PIB obtained by *in situ* alkylation of ω-halo-alkoxybenzene.

(2-Chloroethoxy)benzene

Primary halide functional polyisobutylene was easily obtainable by quenching quasiliving polyisobutylene with (ω-haloalkoxy)benzenes having various tether lengths. For example, direct addition of 3 equiv per chain end of (2-chloroethoxy)benzene to a $TiCl_4$-catalyzed isobutylene polymerization at -70 ^{o}C in a 40/60 (v/v) hexane/methyl chloride solvent system resulted in alkylation of (2-chloroethoxy)benzene, as shown by the ^{1}H NMR spectrum in Figure 5-6 A. A resonance for the ultimate PIB methylene unit adjacent to (2-chloroethoxy)benzene appeared at 1.79 ppm, along with resonances at 3.79 (triplet), 4.21 (triplet), 6.83 (doublet) and 7.27 ppm (doublet), due to the alkylated (2-

chloroethoxy)benzene. Evidence of (2-chloroethoxy)benzene alkylation is also given by the ^{13}C NMR spectrum of Figure 5-7 A. Resonances at 71.9 and 35.2 ppm, representing the ultimate quaternary *gem*-dimethyl carbons of *tert*-chloride PIB, respectively, were not present after the alkylation reaction. A new set of resonances appeared in both the aromatic region and at 41.8 and 68.0 ppm due methylene carbons of the (2-chloroethoxy)benzene moieties.

Primary halide endgroups offer a wealth of opportunity for facile nucleophilic substitution reactions useful in conversion to other functionalities.[181] With a two carbon tether between the halide and oxygen, an easy transformation to a reactive macromonomer can be achieved by dehydrohalogenation. The primary chloride functional PIB was converted to a vinyl ether macromer by reaction with excess potassium *tert*-butoxide in a refluxing mixture of 50/50 (v/v) heptane/DMF. Under the conditions used, dehydrochlorination was complete in less than 1 h. As shown in the ^{1}H NMR spectrum in Figure 5-6 B, the resonances at 3.79 and 4.21 ppm due the (2-chloroethoxy)benzene methylene units are replaced by three doublet-of-doublets centered at 4.37, 4.72, and 6.63 ppm due the terminal vinyl ether. The ^{13}C NMR spectrum of Figure 5-7 B indicates formation of the vinyl ether by the appearance of resonances at 94.3 and 148.6 ppm. The GPC traces in Figure 5-8 A show that no chain coupling occurred during the alkylation reaction, and no changes in molecular the weight distribution were observed after dehydrochlorination to the PIB-vinyl ether macromer.

(3-Bromopropoxy)benzene

A primary bromide end group offers even easier transformation to other functionalities via nucleophilic substitution. Quantitative end-capping with (3-

bromopropoxy)benzene was attained by directly charging an excess (2.5 equiv per chain end) of the quencher to $TiCl_4$-catalyzed quasiliving polyisobutylene in 40/60 (v/v) hexane/methyl chloride at -70 ^oC. A greater (or lesser) excess of quencher can be used, resulting in shorter (or longer) quenching times. Figure 5-9 A shows a ^1H NMR spectrum of the resulting difunctional polyisobutylene bearing primary bromide end groups. Alkylation of (3-bromopropoxy)benzene by PIB is evident from the disappearance of the resonances at 1.68 and 1.96 ppm due to the *gem*-dimethyl and methylene protons of the ultimate repeat unit in *tert*-chloride PIB. Mono-alkylation occurs exclusively *para* to the alkoxy moiety, and a new resonance for the ultimate PIB methylene unit appears at 1.79 ppm, as well as resonances at 3.60 (triplet), 2.3 (quintet), 4.07 (triplet), 6.83 (doublet) and 7.27 ppm (doublet), due to the alkylated 3-bromopropoxybenzene moiety. Integration of the resonances due to the terminal 3-bromopropoxyphenyl moieties in comparison with the aromatic initiator resonance at 7.17 ppm indicates quantitative capping and production of difunctional, telechelic primary bromide PIB.

To further illustrate the utility of end capping polyisobutylene with (3-bromopropoxy)benzene, we have demonstrated the facile conversion of the primary bromide terminus to azide, and subsequently, primary amine. Sodium azide was found to rapidly displace the terminal bromide when reacted with the polymer in 50/50 (v/v) heptane/DMF under reflux. Figure 5-9 B shows a ^1H NMR spectrum of the resulting polymer, where evidence of quantitative conversion to azide is represented in an upfield shift in the resonances due to the tether methylene units, notably 3.6 to 3.51 ppm and 2.3 to 2.04 ppm. The terminal primary azide was readily converted to primary amine via

hydrogenation in the presence of Pd on activated carbon. Figure 5-9 C shows a ^{1}H NMR spectrum of the resulting telechelic primary amine PIB; quantitative reduction of the azide is evidenced by an upfield shift in the resonances due to the tether methylene units, 3.51 to 2.91 ppm and 2.04 to 1.92 ppm. Saturation of the aromatic initiator and quencher residues in the polymer did not occur during reduction of the azide. Presence of primary amine at the chain end was further confirmed by addition of excess phenyl isocyanate to the amine telechelic PIB in $CDCl_3$-*d* at room temperature. The amine rapidly and quantitatively reacted to form a urea, and as shown in Figure 5-9 D, the terminal methylene resonance shifted from 2.91 to 3.44 ppm, and the signal was split into a quartet due to coupling with the adjacent urea proton.

An additional endgroup of interest was primary hydroxyl. Figures 5-10 A and 5-11 A show ^{1}H and ^{13}C NMR spectra, respectively, of primary bromide telechelic PIB obtained by directly charging an excess (2.5 equiv per chain end) of (3-bromopropoxy)benzene to a $TiCl_4$-catalyzed quasiliving polyisobutylene in 40/60 (v/v) hexane/methyl chloride at -70 ^{o}C. After alkylation, the ^{13}C NMR spectrum exhibited new resonances in the aromatic region and at 30.1, 32.5 and 65.2 ppm due to methylene carbons of the (3-bromopropoxy)benzene moiety.

Conversion to primary hydroxyl was achieved by displacement of bromide with excess sodium benzoate and subsequent hydrolysis of the newly formed ester linkage.[103] The conversion was done in two steps in a solvent mixture of 50/50 (v/v) heptane/DMF, which are immiscible at room temperature but become monophasic upon heating above 70 ^{o}C. The thermorphic behavior of this solvent system allows for polar reactants to be mixed and reacted with polyisobutylene at high temperatures, while allowing facile

purification of the polymer upon cooling due to its high phase selectivity for heptane.[255] Sodium benzoate and the primary bromide terminated polymer were refluxed in 50/50 (v/v) DMF/heptane for 4 h. After cooling and phase separation, the benzyl ester terminated polymer was isolated in the heptane layer. The ^{1}H NMR spectrum in Figure 5-10 B shows the presence of the phenyl ester by multiplets at 7.43, 7.55 and 8.04 ppm, and the resonance for the terminal tether methylene unit has shifted downfield from 3.60 to 4.52 ppm due the electron withdrawing ester linkage. The PIB in heptane was then mixed with an equal volume of DMF containing sodium hydroxide and heated to reflux for 12 h. After cooling and phase separation, the primary hydroxyl terminated polymer was isolated in the heptane layer. Figure 5-10 C shows a ^{1}H NMR spectrum of the purified PIB in which the resonance for the methylene unit adjacent to the terminal hydroxyl appears at 3.87 ppm. Primary hydroxyl functionality is also evidenced in the ^{13}C NMR spectrum of Figure 5-11 B by the resonance at 60.9 ppm representing the carbon adjacent to the hydroxyl. The GPC traces of Figure 5-8 B indicated no changes in molecular weight during nucleophilic displacement of the bromide or hydrolysis of the ester.

3-Phenoxypropyldimethylchlorosilane

Functionalization PIB with Si-Cl and Si-H termini was first achieved by Kennedy *et al.*[44] via hydrosilylation of *exo*-olefin terminated PIB. Later, silicon functional initiators were developed,[115] and subsequent work has shown that silylchlorides can survive conditions of $TiCl_4$-catalyzed quasiliving isobutylene polymerization.[116,117,118] These approaches to silicon functional PIBs required either multiple steps or initiators that are not commercially available. With the alkoxybenzene quencher, 3-

phenoxypropyldimethylchlorosilane, silicon functional PIB was obtained in a single step. Figure 5-12 shows a ^{1}H NMR spectrum of silicon functionalized polyisobutylene obtained by direct addition of 3-phenoxypropyldimethylchlorosilane to $TiCl_4$-catalyzed quasiliving isobutylene polymerization in 60/40 (v/v) hexane/methyl chloride at -70 ^{o}C. As evidenced by the methyl resonance at 3.44 ppm, the highly reactive silyl chloride end groups were converted to silyl methoxy end groups after destroying the catalyst with excess methanol. The GPC traces shown in Figure 5-13 indicated that chain coupling did occurr. However, this was due to mutual reaction of the silyl end groups during work-up, rather than di-alkylation of the 3-phenoxypropyldimethylchlorosilane.

Trimethyl(3-phenoxy-1-propynyl)silane

There has been recent interest in alkyne terminated PIB for use in Huisgen 1,3-dipolar cycloaddition ("click") reactions that provide a facile route for synthesis of block copolymers[256,257] and cyclic PIBs.[258] Alkyne functionality on an alkoxybenzene presents difficulty due the activity of the triple bond in polymerization. When phenyl propargyl ether was added directly to a $TiCl_4$-catalyzed quasiliving isobutylene polymerization, a significant amount of chain coupling occurred. To prevent coupling, a trimethylsilyl blocking group was added, which was sufficient to prevent carbocation addition across the triple bond. As indicated by the resonance at 0.17 ppm in the ^{1}H NMR spectrum of Figure 5-14 A, the trimethyl silyl group stayed largely intact after termination of the polymerization. Upon treatment with TBAF, the alkyne proton triplet at 2.49 ppm became evident in the ^{1}H NMR spectrum of Figure 5-14 B. The GPC traces in Figure 5-13 B indicate no chain coupling during polymerization, quenching and deblocking.

Phenoxyalkanol and Phenoxyalkylamine

Direct addition of molecules with unprotected hydroxyl groups to reaction media containing strong Lewis acids such as $TiCl_4$ generally leads to decomposition of the Lewis acid and cessation of catalyst activity. Thus, most reports indicate that when a $TiCl_4$-catalyzed quasiliving isobutylene polymerization is charged with a hard nucleophile such as hydroxyl, *tert*-chloride chain ends are returned;[214] however, the use of low concentrations of unprotected hydroxyl groups on initiators[128] and capping agents[184] have been reported, but with complications. To alleviate these problems the hydroxyl group has been protected and unmasked only after the $TiCl_4$ catalyst has performed its service.[259] Rather than seek a suitable blocking group for a phenoxyalkanol, our approach involved direct addition of an unmodified phenoxyalkanol to the quasiliving PIB. The rationale for such an approach was that the site of alkylation, i.e. the phenyl ring, could be spatially separated from the functionality of interest, i.e. the hydroxyl. If the level of $TiCl_4$ in the reaction was sufficient to overcome the titanates formed *in situ*, then the alkylation could be successfully carried out, albeit with a higher demand for $TiCl_4$.

Our initial attempts with the simplest phenoxyalkanol having a two carbon tether, 2-phenoxyethanol, proved unsuccessful. With tether lengths of two and three carbons interaction with $TiCl_4$ was detrimental to the desired alkylation; however, phenoxyalkanols with carbon tethers of four or greater were alkylated by $TiCl_4$-catalyzed quasiliving polyisobutylene. Figure 5-15 illustrates the effect of the $TiCl_4$ concentration during alkylation of 4-phenoxybutanol. The alkylation reaction proceeds rapidly at first and then slows, with higher levels of $TiCl_4$ providing higher capping efficiencies at a

given reaction time. Analysis of the data in Figures 5-15 A and 5-15 B shows that the disappearance of *tert*-chloride functionality is more rapid than the appearance of hydroxyl functionality, particularly at high [$TiCl_4$]. This indicates accumulation of a slowly reacting intermediate, which we propose to be isomerized chain ends resulting from carbenium ion rearrangement.[260] When the ratio of $TiCl_4$ to 4-phenoxybutanol was 2.5 or higher, over 60% of the chain ends were capped within 30 min; however, 30-40% of the chain ends had also become rearranged. Despite the loss of *tert*-chloride functionality, alkylation slowly continued, and the hydroxyl functionality increased over time as shown in Figure 5-15 B. In this latter stage of reaction, we propose that alkylation occurs through isomerized structures that arise from $TiCl_4$-catalyzed rearrangement. Longer tether lengths were investigated to determine the effect of increased separation between the titanate and the site of alkylation. As shown in Figure 5-16, increasing the tether length to six and eight carbons did provide increased hydroxyl functionality for a given reaction time. However, the phenoxyalkanols with longer tethers were marginally better since the same result could be achieved with 4-phenoxybutanol using a longer reaction time or more $TiCl_4$.

To achieve near quantitative hydroxyl functionality via direct quenching, the alkylation of 4-phenoxybutanol was allowed to proceed for 8 h in the presence of a large excess of $TiCl_4$ as described in Figure 5-17. The terminal methylene unit adjacent to the hydroxyl end group was observed at 3.72 ppm in the ^1H NMR spectrum of Figure 5-17 A and the resonance at 62.6 ppm in the ^{13}C NMR spectrum of Figure 5-18 A. The GPC traces in Figure 5-19 A indicate that no coupling or degradation occurred during the 8 h alkylation reaction.

Arguably the more difficult direct functionalization via alkoxybenzene quenching would be with primary amine. Addition of amines to $TiCl_4$-catalyzed quasiliving PIB is often accompanied by proton extraction from the chain end.[151] To prevent proton abstraction, the amine must either be extremely hindered so as to prevent approach to the carbenium ion chain end or sufficiently unhindered so its basicity is mitigated through quantitative complexation with $TiCl_4$. When the completely unhindered amine, 6-phenoxyhexylamine was charged to a quasiliving isobutylene polymerization with excess $TiCl_4$ as described in Figure 5-17 B, alkylation proceeded much like that of 4-phenoxybutanol, and over 65% of the chains were capped within the first 20 min. The rate of alkylation then slowed significantly, likely due to the formation of $Ti_2Cl_9^-$ counterions that inhibit chain end ionization. After 9 h, near quantitative primary amine functionality was obtained. The ^{1}H NMR spectrum of Figure 5-17 B shows a triplet at 2.70 ppm characteristic of the terminal methylene unit adjacent to the amine, and the ^{13}C NMR spectrum of Figure 5-18 B shows a resonance at 42.1 ppm, also characteristic of the terminal methylene unit adjacent to the amine. In both the ^{13}C and ^{1}H NMR spectra there is no evidence of olefin formation.

Alkylation Kinetics

Figure 5-20 shows second-order kinetic plots for the alkylation of several alkoxybenzenes by $TiCl_4$-catalyzed quasiliving polyisobutylene at -70 ^{o}C in 40/60 (v/v) hexane/methyl chloride. From the plots it is evident that the rate of alkylation is heavily dependent on the identity of the alkyloxy tether. The fastest rate of alkylation was observed for butyl phenyl ether, and under the conditions described in Figure 5-20, near quantitative capping of the chain ends could be achieved in approximately 10 min. For

anisole, (3-bromopropoxy)benzene and allyl phenyl ether, the rate of alkylation was more than 2.5 times slower than that of butyl phenyl ether. When electron withdrawing halides were closer to the phenyl ring, as with (2-bromoethoxy)benzene and (2-choroethoxy)benzene, the reactivity was further decreased by a factor of five. Though longer alkyl tethers help to minimize electronic and steric interference with the alkylation reactions, as well as promote solubility, they come at the expense of increased mass at the PIB chain end.

The rate of alkoxybenzene alkylation by $TiCl_4$-catalyzed quasiliving polyisobutylene may be expressed by the conversion (p) of the *tert*-chloride chain ends,

$$\frac{dp}{dt} = k_c K_{eq}[TiCl_4]^2[PIBCl]_0(1-p)(M-p) \quad (1)$$

where k_c is the rate constant for alkylation, $[PIBCl]_0$ is initial chain end concentration, $[TiCl_4]$ is the concentration of $TiCl_4$ available for participation in the ionization equilibrium, $M = [\text{alkoxybenzene}]_0/[PIBCl]_0$ is the ratio of the initial alkoxybenzene concentration to the initial chain end concentration, and K_{eq} is the ionization equilibrium constant. In integrated form:

$$\ln\left(\frac{(M-p)}{M(1-p)}\right) = k_c K_{eq}[TiCl_4]^2[PIBCl]_0(M-1)t \quad (2)$$

Figures 5-21 A and 5-21 B show data for anisole alkylation plotted as the time derivative of eq 2 and a function of M and $[TiCl_4] = [TiCl_4]_{nominal}$ - 2[2,6-lutidine], respectively. In eq 2, no account has been made for the complexation that occurs between the alkoxybenzene and $TiCl_4$, although such complexation invariably occurs. The effect of complexation is manifested in Figure 21 B by the initially faster increase in the apparent rate with higher anisole concentration (when [anisole] < $[TiCl_4]$) that changes to a slower

but still increasing rate at anisole concentrations higher than the effective $TiCl_4$ concentration (when [anisole] > [$TiCl_4$]). Figure 5-21 A, shows that the alkylation of anisole has a second-order dependence on the $TiCl_4$ concentration.

Figure 5-22 demonstrates that the rate of alkylation increases with decreasing temperature. The increased rate at lower temperatures was due to the negative activation energy associated with the $TiCl_4$-catalyzed ionization of the *tert*-chloride chain ends. Activation energies for the apparent rate constant k_cK_{eq} calculated from the slopes of the data in Figure 5-22, where -7.0 and -6.6 kcal/mol, for the hexane/methylchloride and toluene/dichloromethane solvent systems, respectively.

Alkylation with Olefinic PIB

For all of the $TiCl_4$-catalyzed isobutylene polymerizations and *in situ* alkylation reactions discussed to this point, the resulting PIBs invariably lacked any terminal unsaturations, even under conditions were olefin terminated PIB would likely be formed via β-proton expulsion or abstraction, i.e. above 40 ^oC.[261] Though it would not be surprising that a PIB olefin terminus serves as an alkylating agent, the observed result is significant in this context, because quantitative functionalization with the alkoxybenzenes is still attainable even under conditions were the polymerization is non-living and termination has occurred. To definitively illustrate alkylation via olefinic PIB, Glissopal® having 85% *exo*-olefin and 15% *endo*-olefin functionality was reacted with (3-bromopropoxy)benzene under conditions similar to those used in the quasiliving polymerization of isobutylene, i.e. $TiCl_4$ catalysis at -70 ^oC in 40/60 (v/v) hexane/methylchloride. As shown by the ^1H NMR spectra of Figure 5-23, both *endo*- and *exo*-olefin are rapidly hydrochlorinated in the presence of $TiCl_4$. Within the first 5

min of reaction, no *exo*-olefin remains and only 10% of chains exhibit *endo*-olefin termini. Within 3.5 h the Glissopal chain ends were quantitatively capped with (3-bromopropoxy)benzene as indicated by the disappearance resonances at 1.69 and 1.96 ppm due to the ultimate *gem*-dimethyl and methylene unit of *tert*-chloride PIB as well as the disappearance of the resonances at 1.78, 2.0, 4.64 and 4.84 ppm due to *exo*-olefin and 1.62, 1.66 and 5.15 ppm due to *endo*-olefin. The remaining resonances at 1.79, 2.30, 3.6, 4.07, 6.83 and 7.27 ppm were due to the (3-bromopropoxy)benzene capped chain ends. The GPC traces in Figure 5-8 C, shows no significant differences in the molecular weight distribution before an after the alkylation reaction; the molecular weight (polydispersity) before and after the alkylation reaction were 3.1×10^3 (1.35) and 3.3×10^3 g/mol (1.30), respectively. The reaction was preformed in the absence of a basic additive; however, in the presence of an additive such as 2,6-lutidine used to enhance "livingness" of the isobutylene polymerization, both hydrochlorination and subsequent alkylation by Glissopal® were greatly inhibited. Evidently hydrochlorination was aided by the presence of adventitious moisture or other protic impurities in the reaction system. When quenching a $TiCl_4$-catalyzed quasiliving polymerization with an alkoxybenzene, excess HCl is generated as the alkylation progresses, producing concentrations in far excess of the base additive for moderately high chain end concentrations, i.e. > 0.01 M.

Conclusion

In this study we have shown that direct addition of alkoxybenzenes to $TiCl_4$-catalyzed quasiliving isobutylene polymerization provides a versatile method for chain end functionalization. Alkylation of simple alkyl phenols such as anisole and isopropoxybenzene with subsequent *in situ* deprotection allowed synthesis of phenolic

PIB. The alkylation reactions were also tolerant of primary halide, silyl chloride, and protected alkyne functionality, allowing placement of these functionalities on the PIB chain end in a single step. Sufficiently long alkyl tethers made possible the alkylation of alkoxybenzenes bearing the functionalities that highly interacted with $TiCl_4$, namely primary hydroxyl and amine. The $TiCl_4$/alkoxybenzene combination at low temperature provided rapid alkylation mixed *endo*-/*exo*-olefin terminated PIB, and for example, facile functionalization of PIB with primary halide.

Table 5-1. Conditions for quasiliving isobutylene polymerizations and alkylation (quenching) reactions

quencher	nominal component concentrations (mol/L) [a] initiator	IB	$TiCl_4$ pzn.	quencher	$TiCl_4$ quench	reaction time (h) pzn.	quench	$\overline{M}_n$ x 10^{-3} (PDI)[f]
anisole	0.025[b]	1.14	0.016	0.125	0.066	0.36	3.63	2.9 (1.14), 3.1 (1.10), 3.2 (1.08)[g]
isopropoxybenzene	0.025[b]	1.12	0.015	0.125	0.115	0.36	2.05	3.4 (1.05), 3.4 (1.04), 3.5 (1.03)[g]
2,6-di-*tert*-butylphenol	0.025[c]	0.75	0.017	0.100	0.167	0.71	1.06	2.0 (1.34), 2.2 (1.09)
allyl phenyl ether	0.050[c]	1.75	0.015	0.150	0.100	0.56	2.16	2.7 (1.34), 2.9 (1.31)
(2-chloroethoxy)benzene	0.040[c]	1.59	0.012	0.100	0.092	1.42	3.42	3.0 (1.21), 2.9 (1.23), 3.0 (1.22)[h]
(3-bromopropoxy)benzene	0.050[b]	2.08	0.012[e]	0.250	0.112	1.58	3.42	3.1 (1.13), 3.5 (1.04), 3.5 (1.12)[i]
3-phenoxypropyldimethylchlorosilane [d]	0.010[b]	0.76	0.100	0.060	0.100	0.33	1.50	4.9 (1.01), 5.6 (1.05)
Trimethyl(3-phenoxy-1-propynyl)silane	0.025[c]	0.75	0.017	0.100	0.167	0.68	5.35	2.2 (1.19), 2.5 (1.18), 2.5 (1.16)[j]
4-phenoxybutanol	0.024[b]	1.05	0.014	0.144	0.494	0.40	7.70	2.9 (1.07), 3.2 (1.05)
6-phenoxyhexylamine	0.025[b]	1.09	0.015	0.125	0.190	0.48	9.00	3.1 (1.07)

[a]polymerization and alkylation reactions at -70 ^{o}C in 40/60 (v/v) hexane/methyl chloride, [b]initiated from bDCC, [c]TMPCl, [d]60/40 (v/v) hexane/methylchloride, [e]added in two equal portions to control exotherm, [f]molecular weight prior to alkylation, after alkylation, and after further modification (see Experimental) to [g]phenolic, [h]vinyl ether, [i]hydroxyl, and [j]alkynyl functional PIB

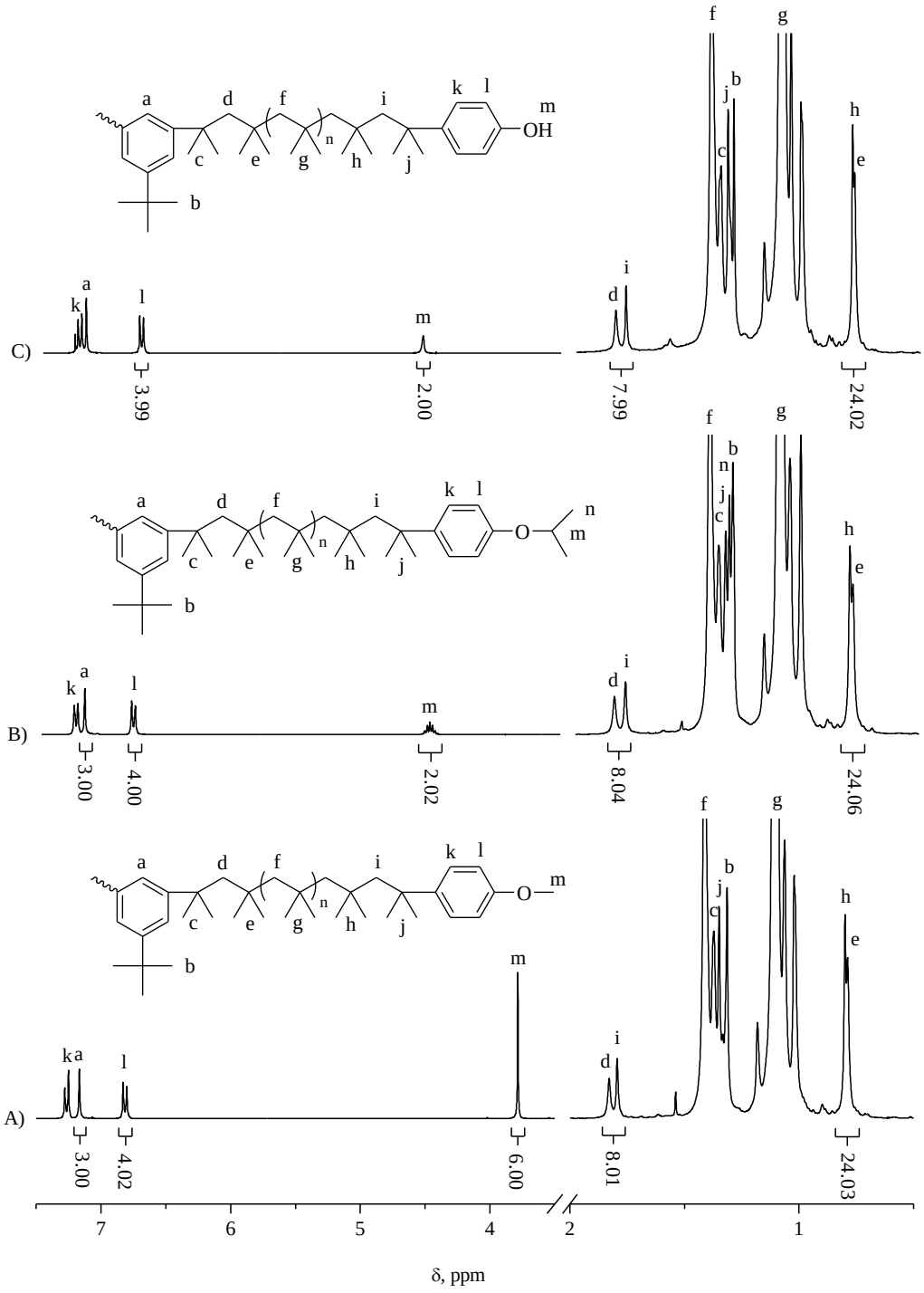

Figure 5-1. ^{1}H NMR (300 MHz, $CDCl_3$, 22 ^{o}C) spectra of A) A) α,ω-*bis*[4-methoxyphenyl]polyisobutylene and B) α,ω-*bis*[4-isopropoxyphenyl]polyisobutylene obtained by direct addition of anisole and isopropoxybenzene, respectively, to $TiCl_4$-catalyzed quasiliving isobutylene polymerizations; and C) α,ω-*bis*[4-hydroxyphenyl]polyisobutylene obtained by *in situ* de-methylation or de-isopropylation.

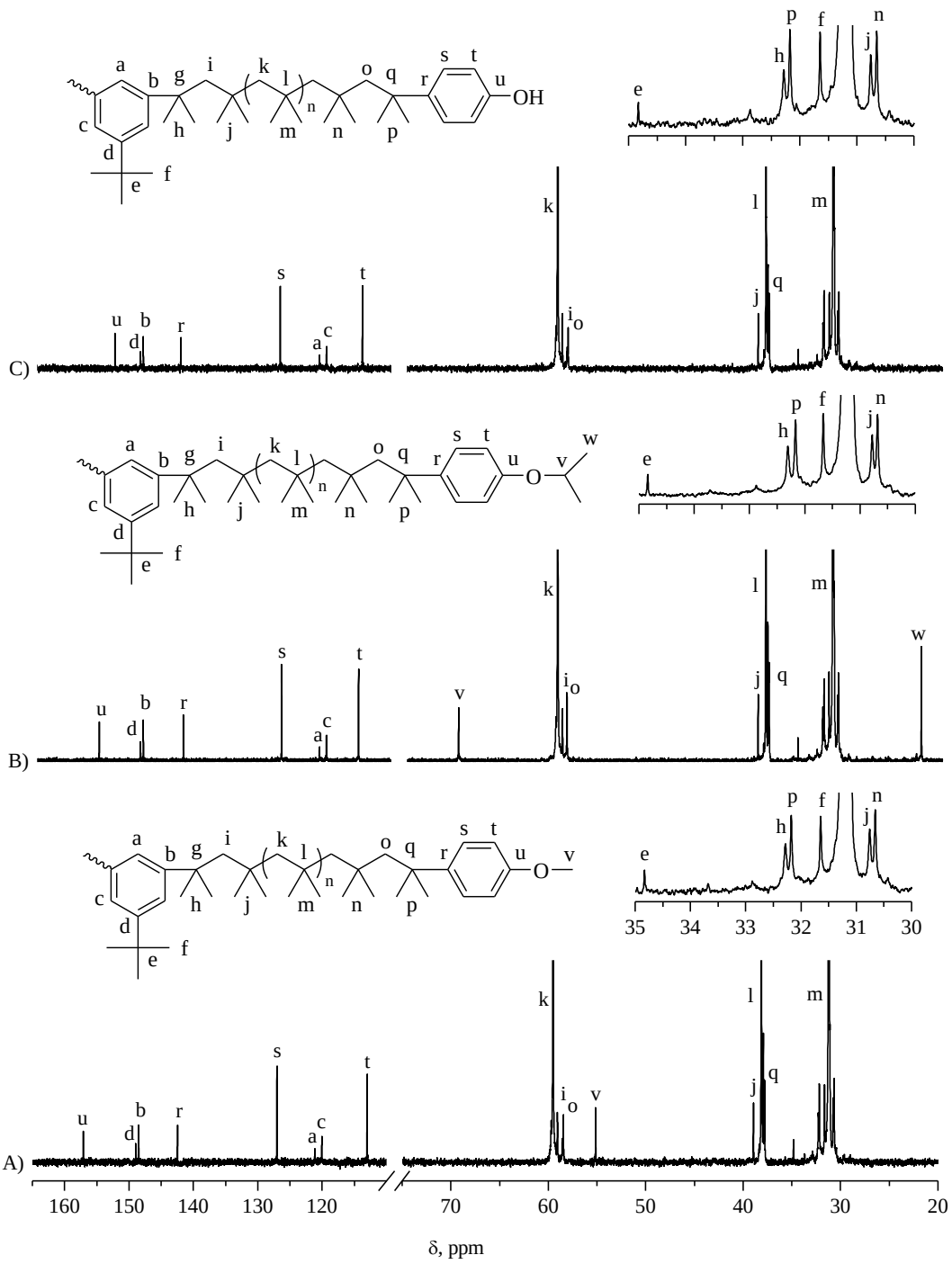

Figure 5-2. ^{13}C NMR (75 MHz, $CDCl_3$, 22 ^oC) spectra of A) A) α,ω-*bis*[4-methoxyphenyl]polyisobutylene and B) α,ω-*bis*[4-isopropoxyphenyl]polyisobutylene obtained by direct addition of anisole and isopropoxybenzene, respectively, to $TiCl_4$-catalyzed quasiliving isobutylene polymerizations; and C) α,ω-*bis*[4-hydroxyphenyl]polyisobutylene obtained by *in situ* de-methylation or de-isopropylation.

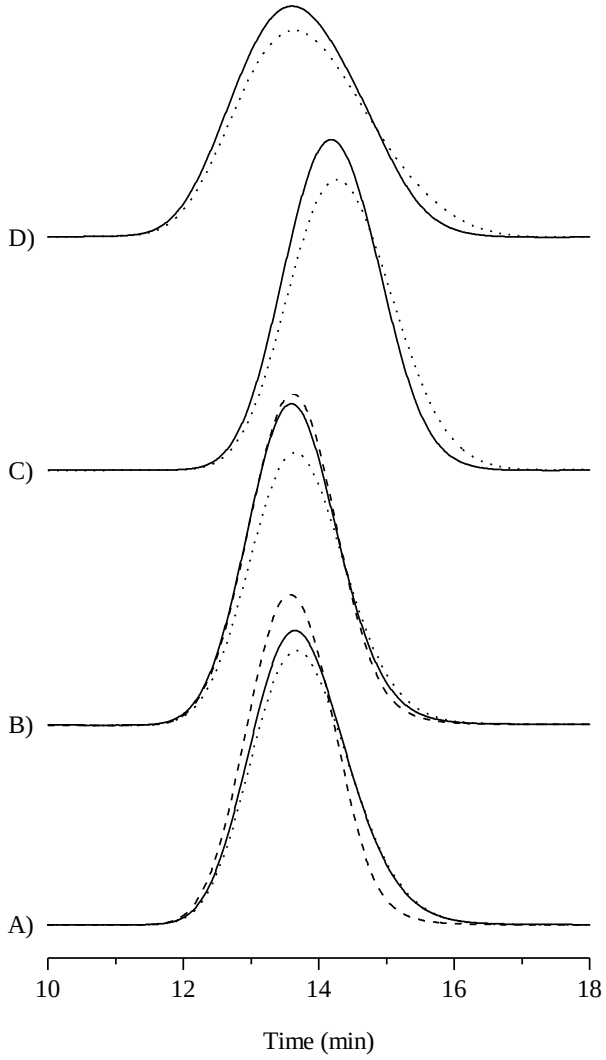

Figure 5-3. GPC differential refractive index traces PIB before quenching (⋯) $TiCl_4$-catalyzed quasiliving isobutylene polymerizations A) anisole, B) isopropoxybenzene, C) 2,6-di-*tert*-butylphenol and D) allyl phenyl ether; after quenching (——) and after deblocking (---) to provide phenolic PIB (A and B only).

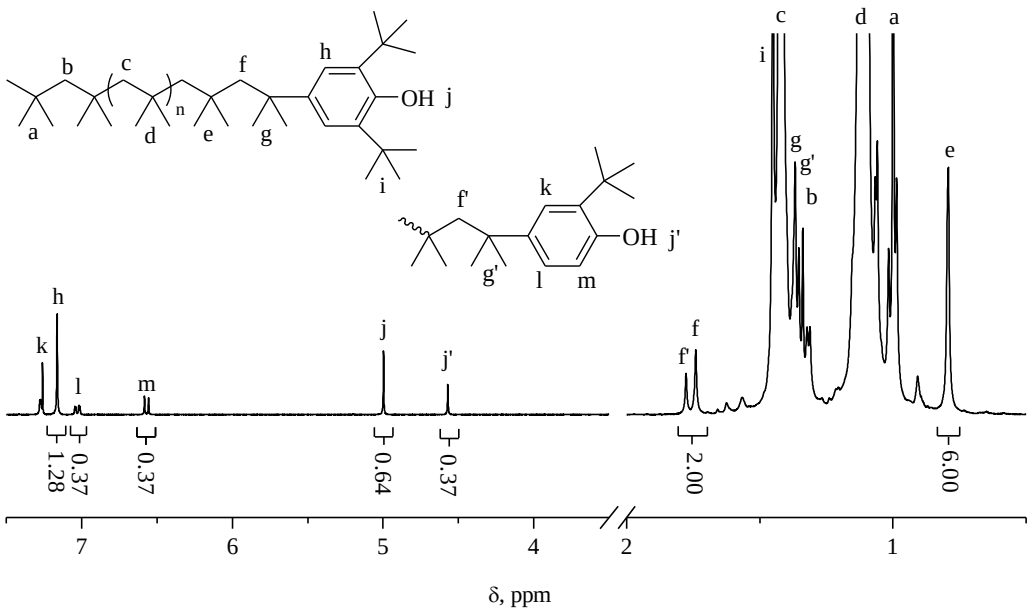

Figure 5-4. ^{1}H NMR (300 MHz, $CDCl_3$, 22 ^{o}C) spectrum of 2,6-di-*tert*-butyl-4-polyisobutylphenol and 2-*tert*-butyl-4-polyisobutylphenol obtained by direct addition of 2,6-di-*tert*-butylphenol to a $TiCl_4$-catalyzed quasiliving isobutylene polymerization.

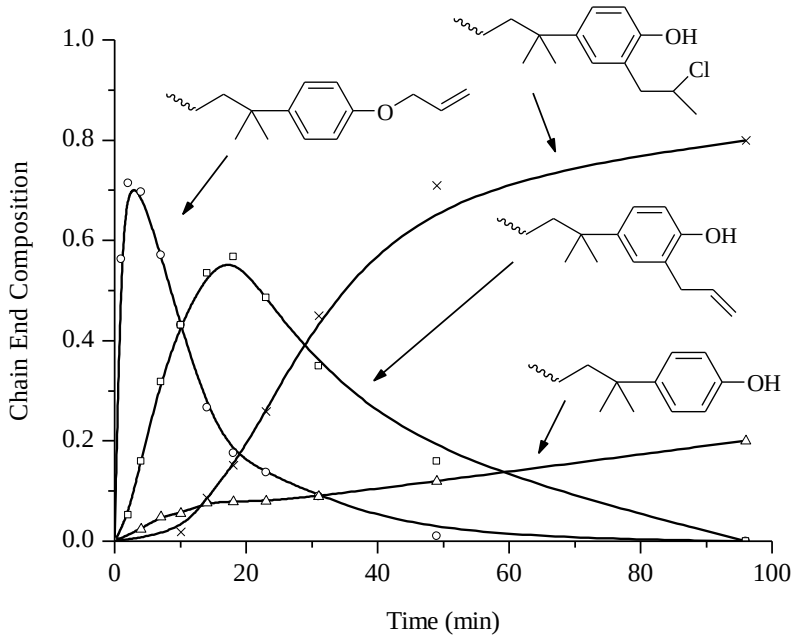

Figure 5-5. PIB chain-end composition after direct addition of allyl phenyl ether to a $TiCl_4$-catalyzed isobutylene polymerization. Alkylation of allyl phenyl ether (○) is accompanied by Claisen rearrangement to form 2-allylphenol end groups (□) and ether cleavage to form phenol end groups (△). The allyl functionality is also hydrochlorinated to provide 2-(2-chloropropyl)phenol end groups (×).

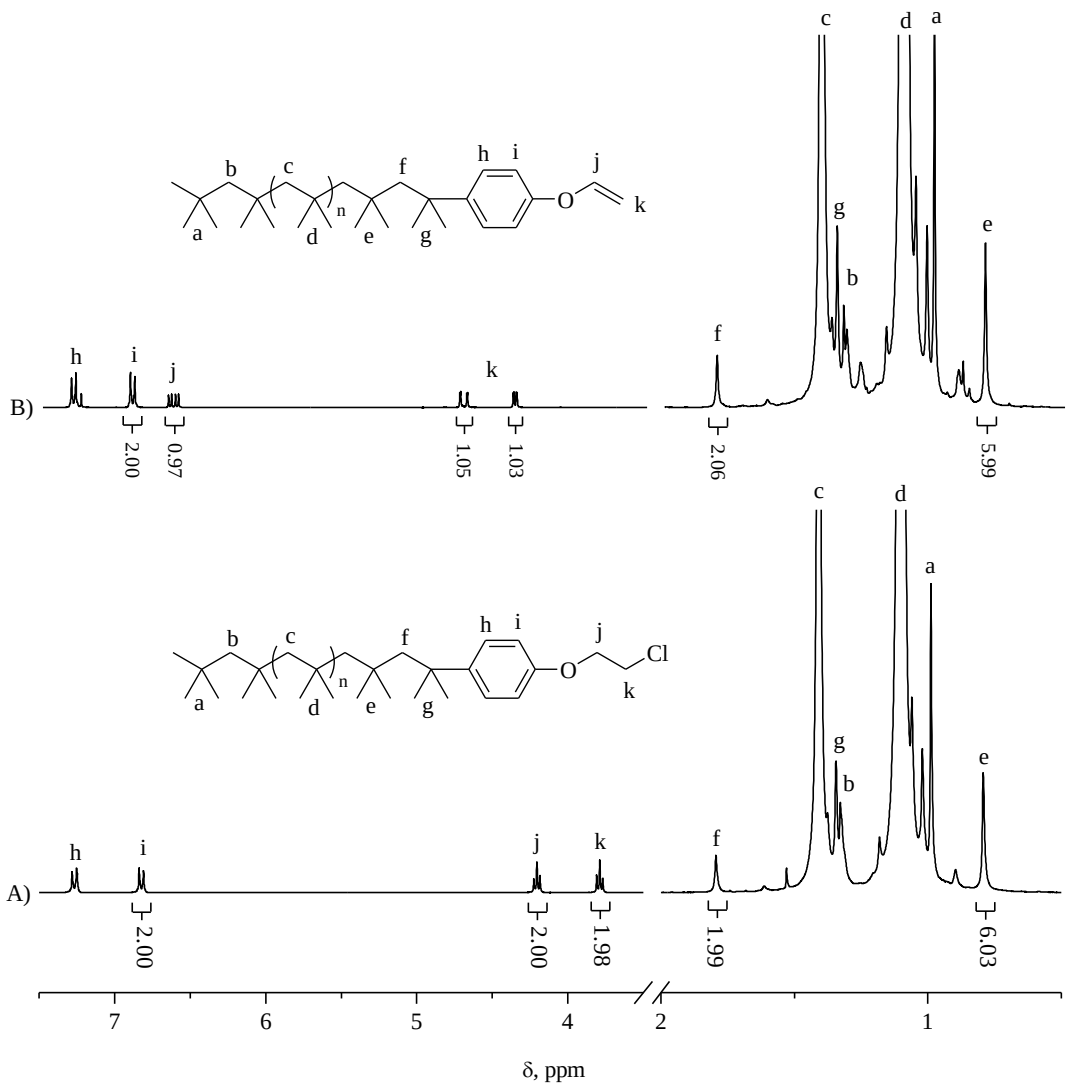

Figure 5-6. ^{1}H NMR (300 MHz, $CDCl_3$, 22 ^{o}C) spectra of A) 1-(2-chloroethoxy)-4-polyisobutylbenzene and B) 1-vinyloxy-4-polyisobutylbenzene obtained by direct addition of 2-chloroethoxybenzene to $TiCl_4$-catalyzed quasiliving isobutylene polymerization and subsequent post-polymerization dehydrochlorination of the primary halide terminus.

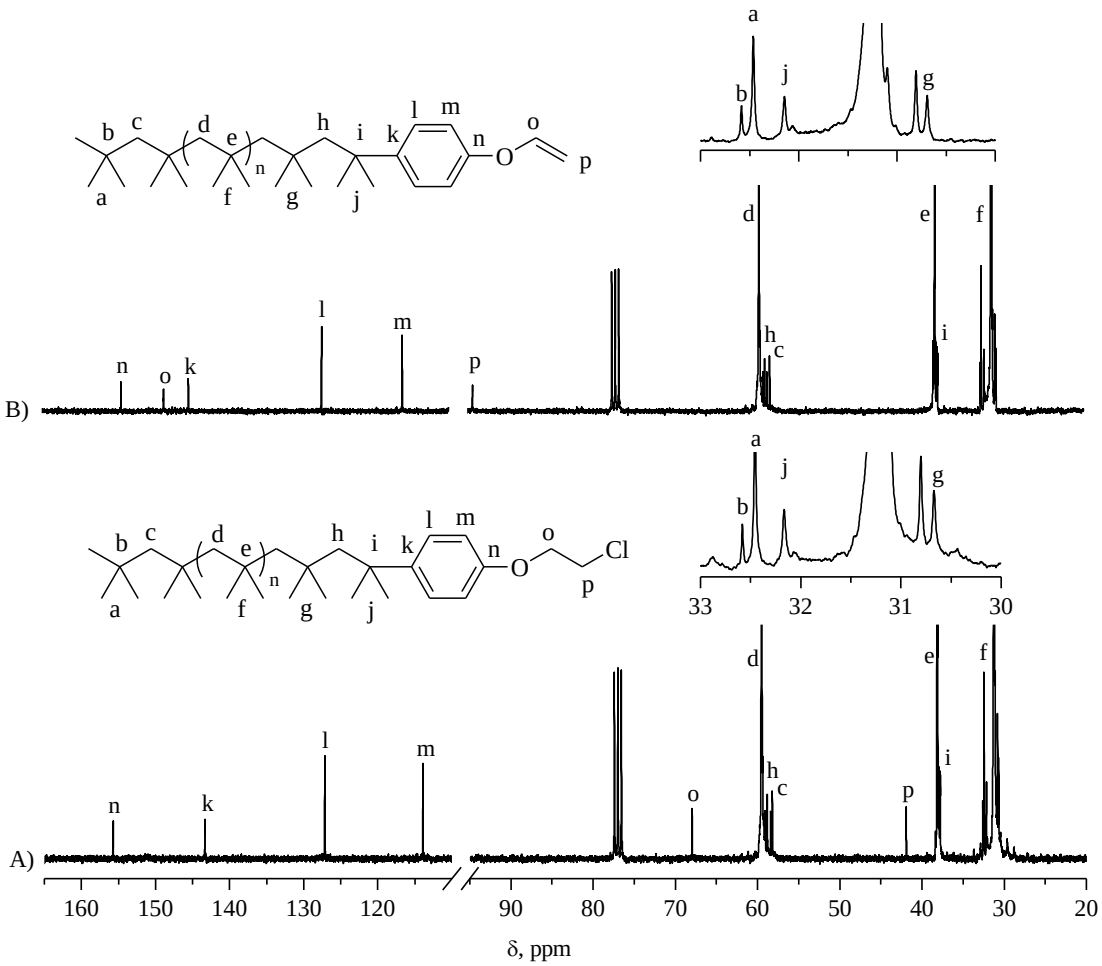

Figure 5-7. ^{13}C NMR (75 MHz, $CDCl_3$, 22 ^{o}C) spectra of A) 1-(2-chloroethoxy)-4-polyisobutylbenzene and B) 1-vinyloxy-4-polyisobutylbenzene obtained by direct addition of 2-chloroethoxybenzene to $TiCl_4$-catalyzed quasiliving isobutylene polymerization and subsequent post-polymerization dehydrochlorination of the primary halide terminus.

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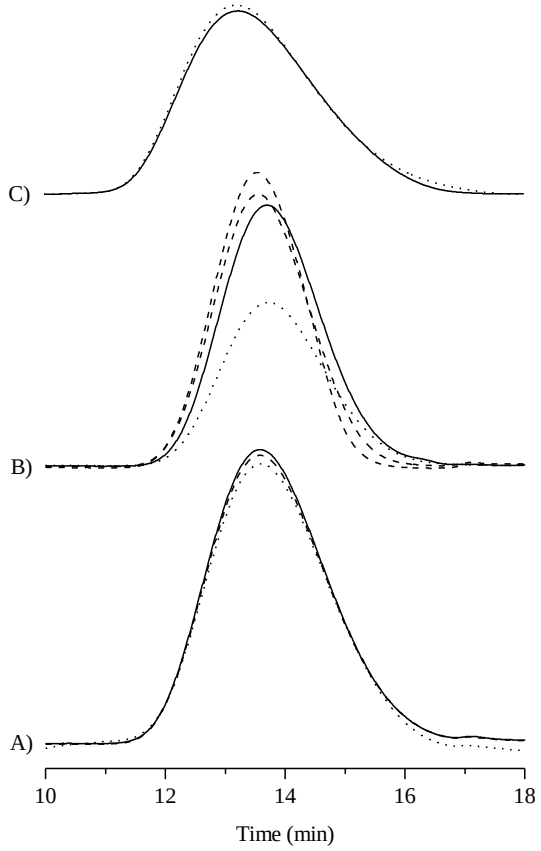

Figure 5-8. GPC differential refractive index traces of PIB before quenching (·····) a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with A) (2-chloroethoxy)benzene and B) (3-bromopropoxy)benzene; after quenching (——) and after conversion of the primary halide to vinyl ether (A only) and hydroxyl via benzoate hydrolysis (B only) (---). C) Glissopal® was also used to alkylate (3-bromopropoxy)benzene under conditions for $TiCl_4$-catalyzed quasiliving isobutylene polymerization.

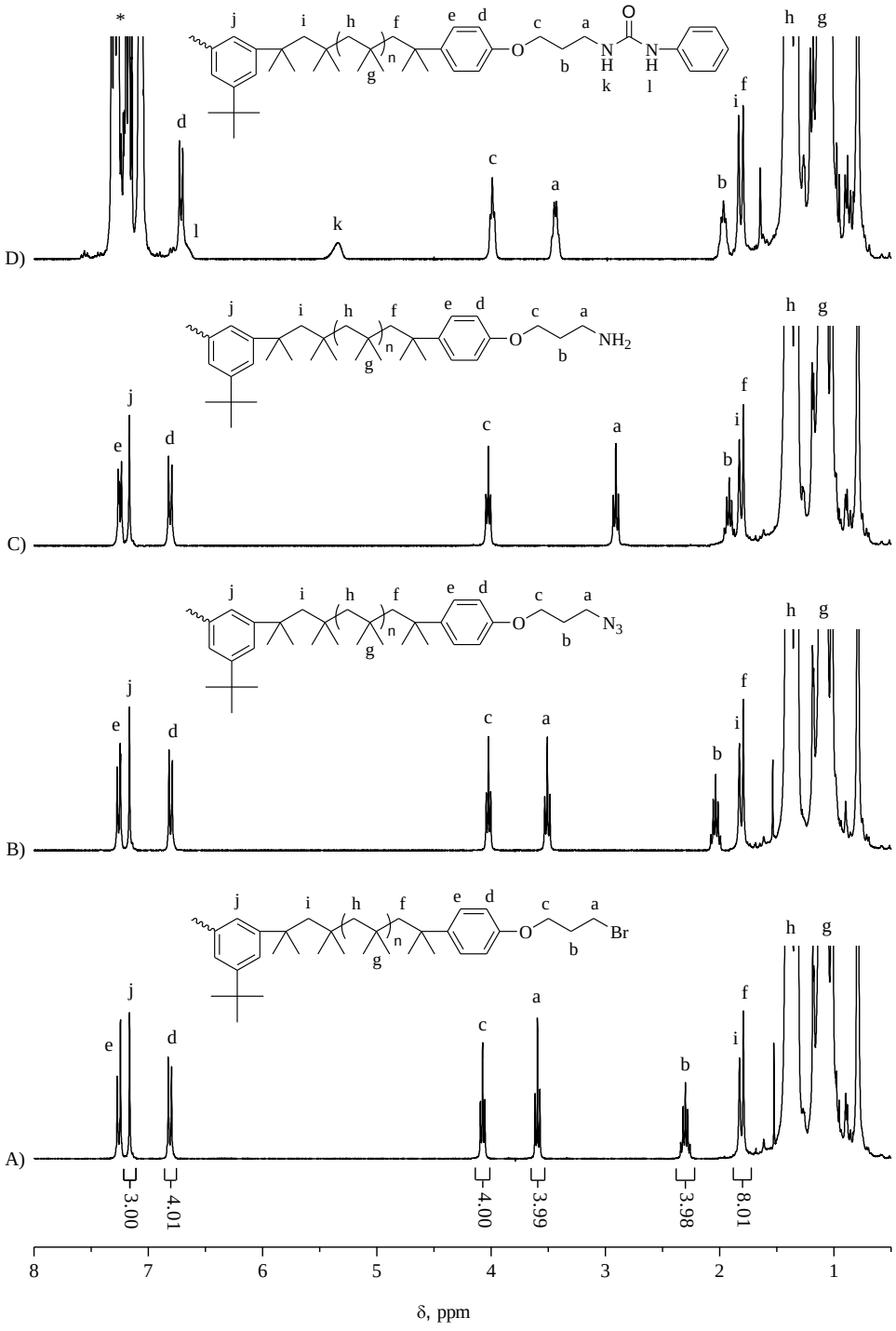

Figure 5-9. ^{1}H NMR (300 MHz, $CDCl_3$, 25 ^{o}C) spectra of A) α,ω-*bis*[4-(3-bromopropoxy)phenyl]polyisobutylene with peak integrations, B) α,ω-*bis*[4-(3-azidopropoxy)-phenyl]polyisobutylene, C) α,ω-*bis*[4-(3-aminopropoxy)phenyl]polyisobutylene and D) the reaction product of α,ω-*bis*[4-(3-aminopropoxy)phenyl]polyisobutylene and excess phenyl isocyanate (*).

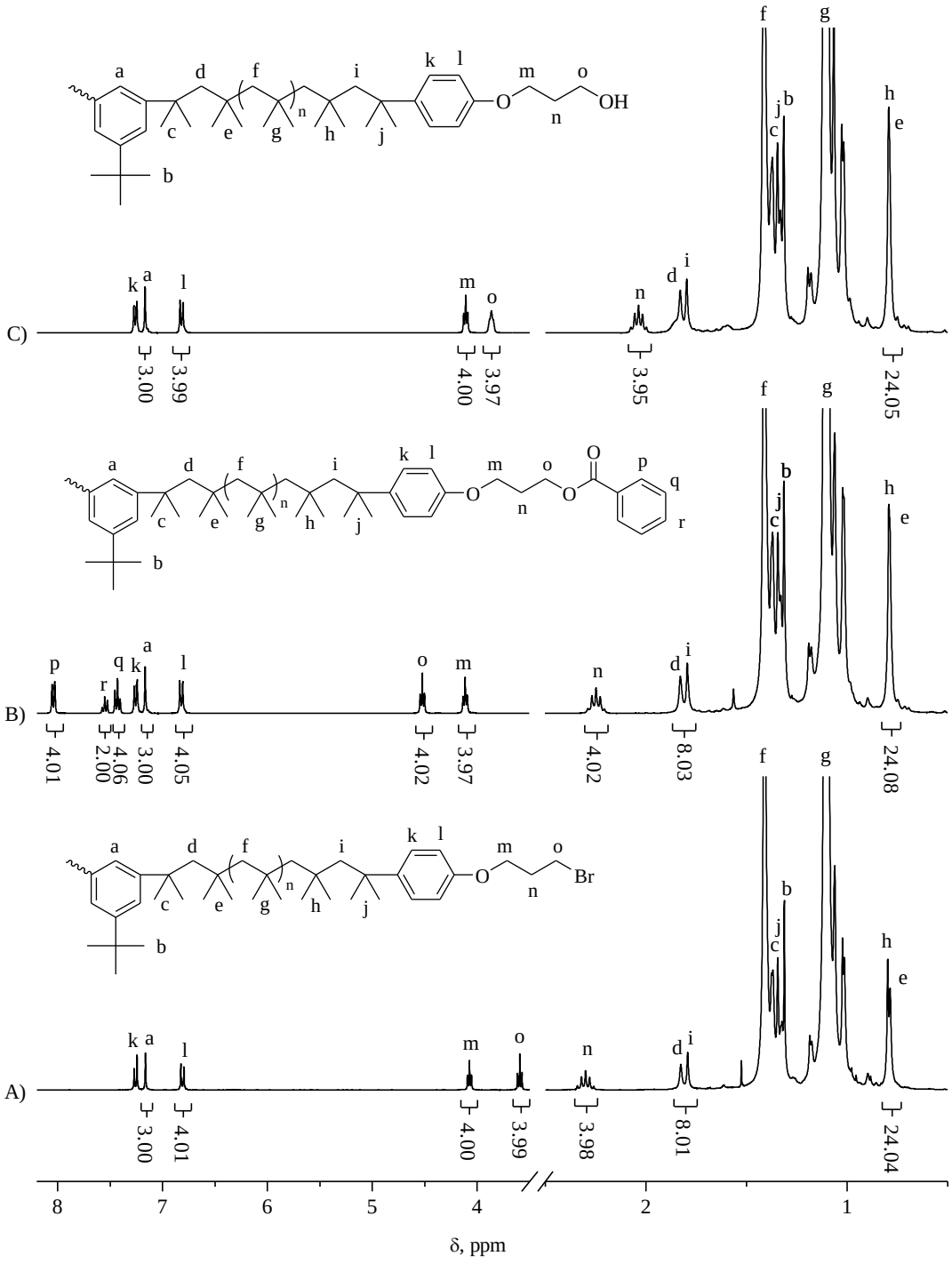

Figure 5-10. ^{1}H NMR (300 MHz, $CDCl_3$, 22 ^{o}C) spectra of A) α,ω-*bis*[4-(3-bromopropoxy)phenyl]polyisobutylene obtained by direct quenching of a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with (3-bromopropoxy)benzene, B) α,ω-*bis*[4-(3-benzoyloxypropoxy)phenyl]polyisobutylene obtained by displacement of the primary bromide with benzoate and C) α,ω-*bis*[4-(3-hydroxypropoxy)phenyl]polyisobutylene obtained by subsequent hydrolysis.

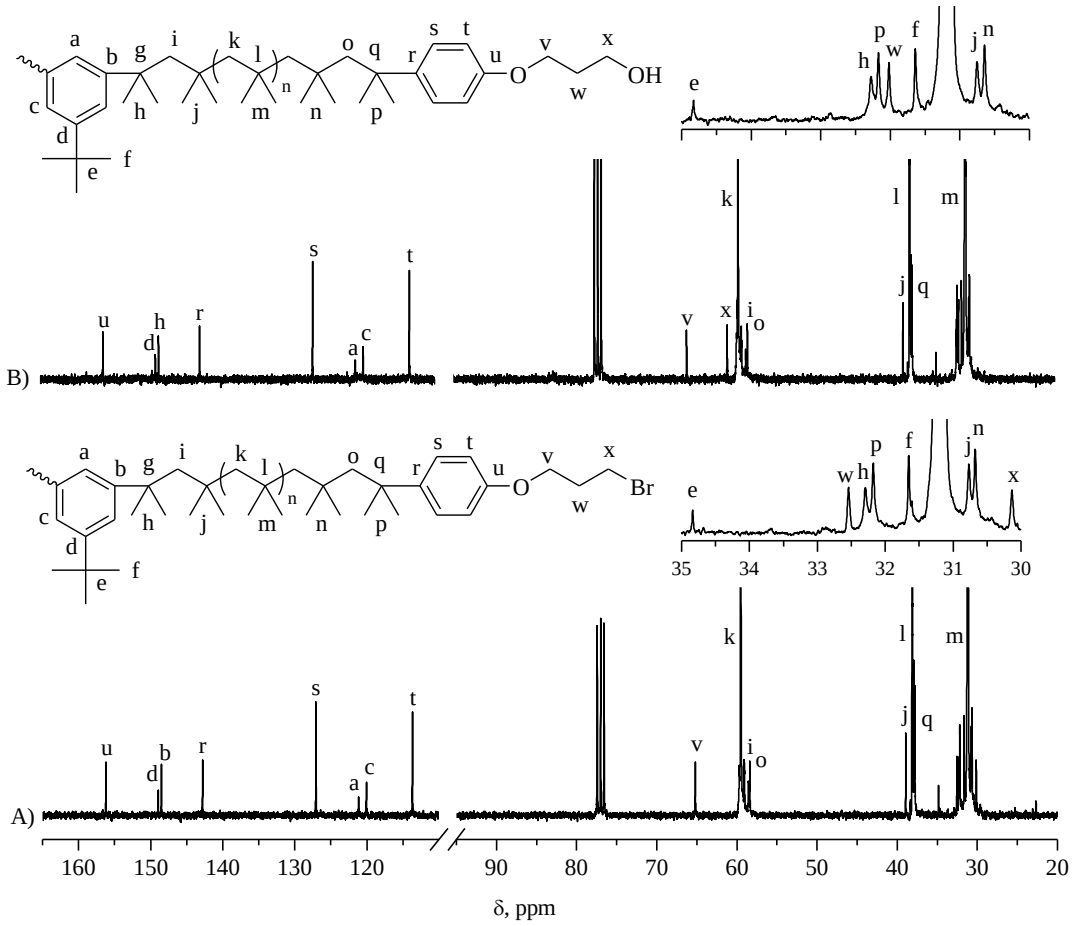

Figure 5-11. ^{13}C NMR (75 MHz, $CDCl_3$, 22 ^oC) spectra of A) α,ω-*bis*[4-(3-bromopropoxy)phenyl]polyisobutylene obtained by direct quenching of a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with (3-bromopropoxy)benzene and B) α,ω-*bis*[4-(3-hydroxypropoxy)phenyl]polyisobutylene obtained by displacement of the primary bromide by benzoate and subsequent hydrolysis.

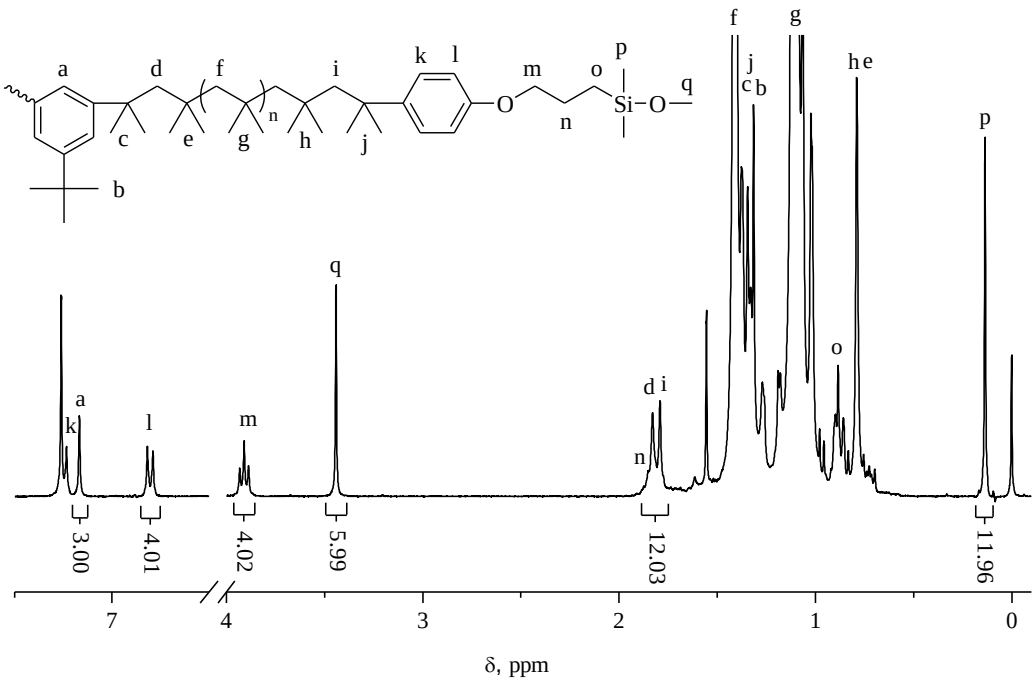

Figure 5-12. ^{1}H NMR (300 MHz, $CDCl_3$, 22 ^{o}C) spectrum of α,ω-*bis*[4-(3-(methoxydimethylsilyl)propoxy)phenyl]polyisobutylene obtained by direct quenching of a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with 3-phenoxypropyldimethylchlorosilane and subsequent reaction with methanol.

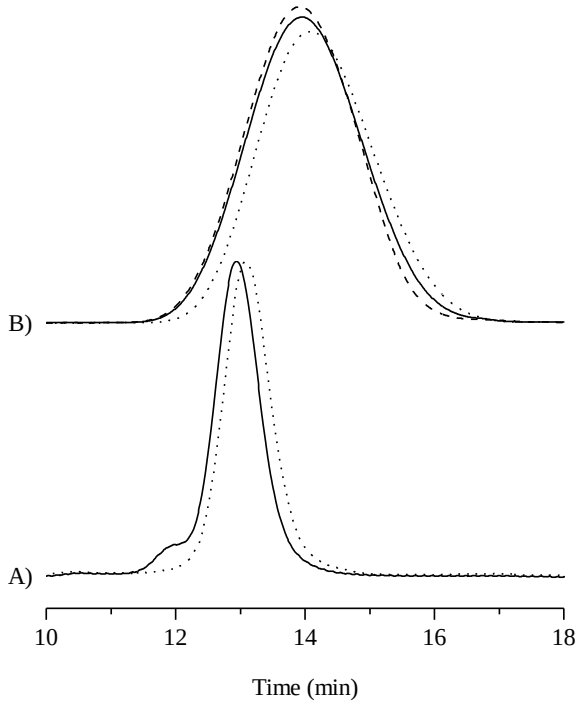

Figure 5-13. GPC differential refractive index traces of PIB before quenching (⋯⋯) a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with A) 3-phenoxypropyldimethylchlorosilane and B) trimethyl(3-phenoxy-1-propynyl)silane; after quenching (——) and after deprotection (---) of the alkyne moiety (B only).

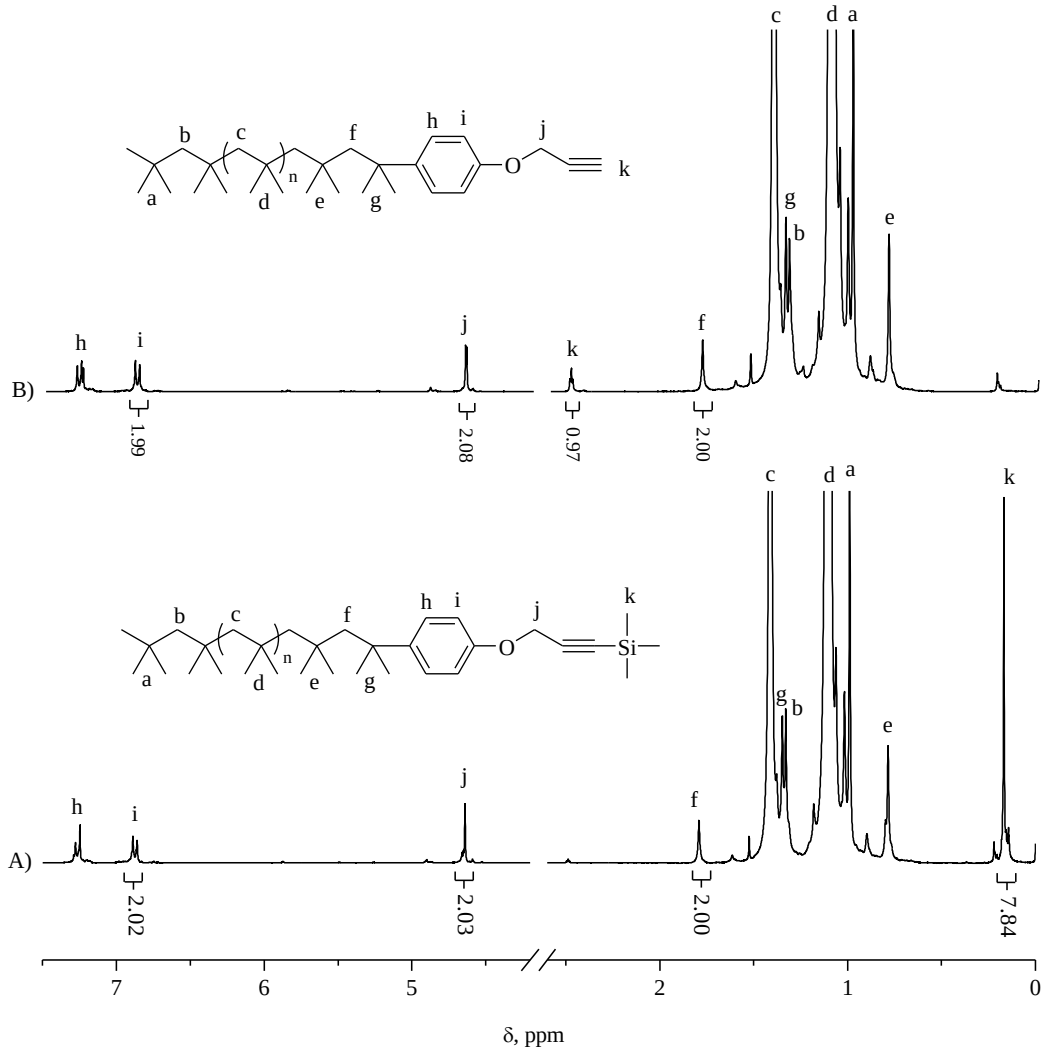

Figure 5-14. ^{1}H NMR (300 MHz, $CDCl_3$, 22 ^{o}C) spectra of A) 1-(3-trimethylsilyl-2-propynyloxy)-4-polyisobutylbenzene and B) 1-(propargyloxy)-4-polyisobutylbenzene obtained by direct addition of trimethyl(3-phenoxy-1-propynyl)silane to $TiCl_4$-catalyzed quasiliving isobutylene polymerization and subsequent post-polymerization removal of the trimethylsilyl blocking group.

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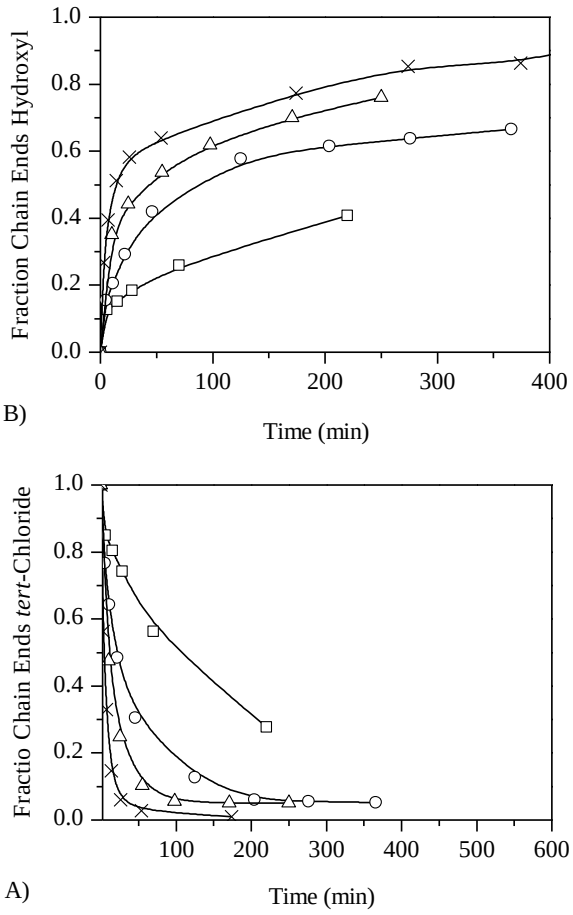

Figure 5-15. Fraction of chain ends bearing A) *tert*-chloride and B) hydroxyl functionality as function of time for various concentrations of $TiCl_4$ after direct addition of 4-phenoxybutanol to $TiCl_4$-catalyzed quasiliving isobutylene polymerizations. Polymerization/quench at -70°C in 40/60 (v/v) hexane/methylchloride, [2,6-lutidine] = 0.005 M, [*t*-Bu-*m*-DCC] = 0.025 M, [isobutylene] = 1.09 M, [$TiCl_4$] = 0.015 M (polymerization), [4-phenoxybutanol] = 0.125 M, and [$TiCl_4$] = 0.165 (□), 0.19 (○), 0.215 (△) and 0.315 M (×) during alkylation.

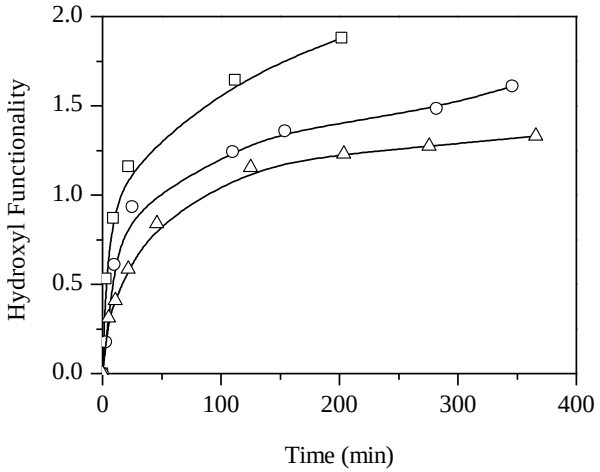

Figure 5-16. Number average hydroxyl functionality of quasiliving PIB quenched with 4-phenoxybutanol (△), 6-phenoxyhexanol (○) and 8-phenoxyoctanol (□). Polymerization/quench at -70^{o}C in 40/60 (v/v) hexane/methylchloride, [2,6-lutidine] = 0.005 M, [*t*-Bu-*m*-DCC] = 0.025 M, [isobutylene] = 1.1 M, [$TiCl_4$] = 0.015 M (polymerization), [quencher] = 0.125 M, and [$TiCl_4$] = 0.19 M during alkylation.

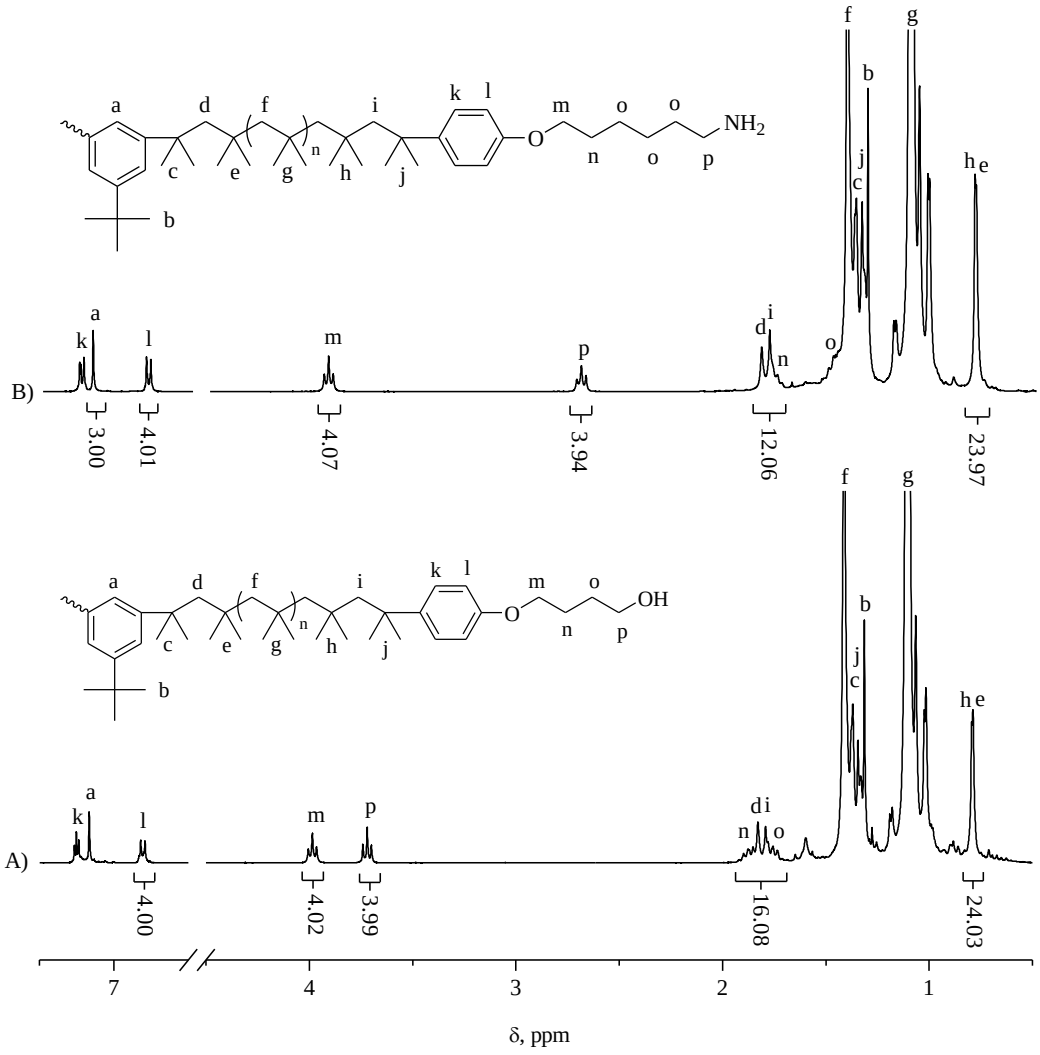

Figure 5-17. ^{1}H NMR (300 MHz, $CDCl_3$, 22 ^{o}C) spectra of A) α,ω-*bis*[4-(4-hydroxybutoxy)phenyl]polyisobutylene obtained by direct quenching of a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with 4-phenoxy-1-butanol and B) α,ω-*bis*[4-(6-aminohexoxy)phenyl]polyisobutylene obtained by quenching with 6-phenoxyhexylamine. Polymerization/quench at -70^{o}C in 40/60 (v/v) hexane/methylchloride, [2,6-lutidine] = 0.005 M, [$TiCl_4$] = 0.015 M (polymerization). A) [*t*-Bu-*m*-DCC] = 0.024 M, [IB] = 1.05 M, [4-phenoxy-1-butanol] = 0.144 M, and [$TiCl_4$] = 0.494 M (alkylation). B) [*t*-Bu-*m*-DCC] = 0.025 M, [IB] = 1.09 M, [6-phenoxyhexylamine] = 0.125 M, and [$TiCl_4$] = 0.19 M (alkylation).

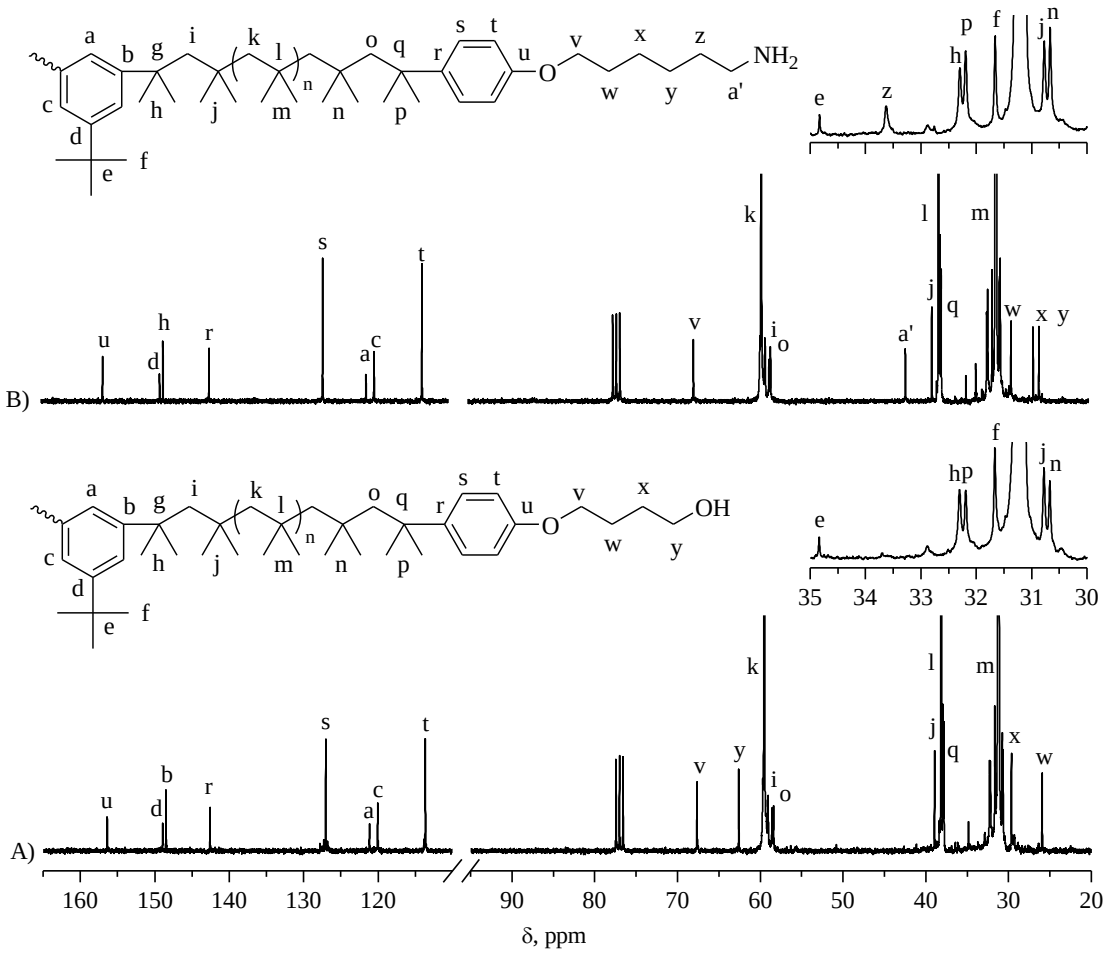

Figure 5-18. ^{13}C NMR (75 MHz, $CDCl_3$, 22 ^oC) spectra of A) α,ω-*bis*[4-(4-hydroxybutoxy)phenyl]polyisobutylene obtained by direct quenching of a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with 4-phenoxy-1-butanol and B) α,ω-*bis*[4-(6-aminohexoxy)phenyl]polyisobutylene obtained by quenching with 6-phenoxyhexylamine. See Figure 5-17 for reaction conditions.

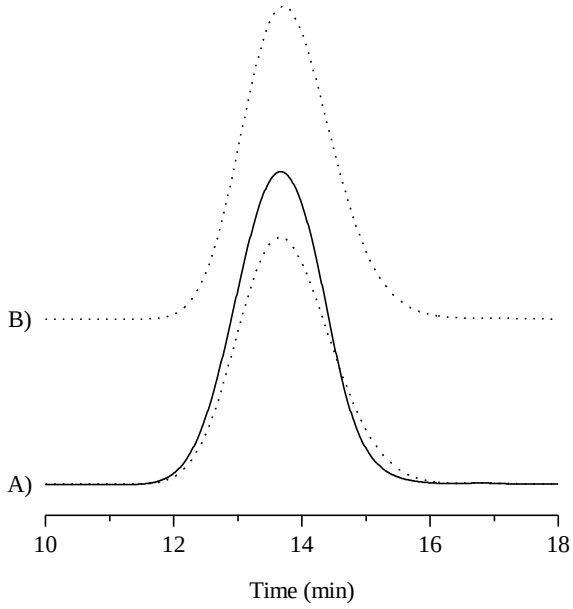

Figure 5-19. GPC differential refractive index traces of PIB before quenching (⋯⋯) a $TiCl_4$-catalyzed quasiliving isobutylene polymerization with A) 4-phenoxybutanol and B) 6-phenoxyhexanol; after quenching (—) (only A).

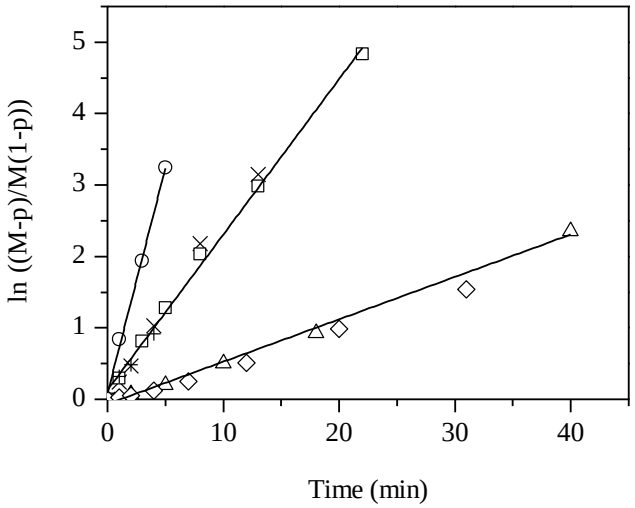

Figure 5-20. Second-order kinetic plots for $TiCl_4$-catalyzed alkylation of alkoxybenzenes by quasiliving PIB. Polymerization/quenching reactions at -70 ^{o}C in 40/60 (v/v) hexane/methylchloride, [2,6-lutidine] = 0.005 M, [TMPCl] = 0.05 M, [isobutylene] = 1.58 M, [$TiCl_4$] = 0.015 M (polymerization), [quencher] = 0.1 M and [$TiCl_4$] = 0.09 M during alkylation with butyl phenyl ether (○), (3-bromopropoxy)benzene (×), anisole (□), allyl phenyl ether (+), (2-bromoethoxy)benzene (△) and (2-chloroethoxy)benzene (◊).

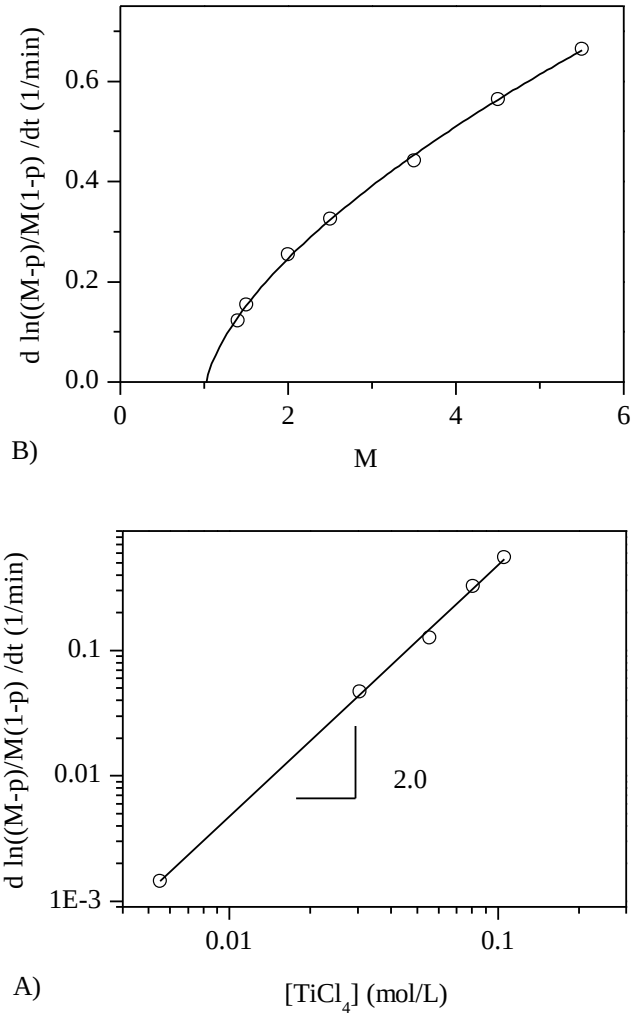

Figure 5-21. Plots of the second-order rate constant for $TiCl_4$-catalyzed alkylation of anisole by quasiliving PIB as a function of A) the $TiCl_4$ concentration and B) the anisole concentration as M = $[anisole]_0/[TMPCl]$. Polymerization/quench at -70 ^oC in 40/60 (v/v) hexane/methylchloride, [2,6-lutidine] = 0.005 M, [TMPCl] = 0.05 M, [isobutylene] = 1.58 M, $[TiCl_4]$ = 0.015 M (polymerization), [anisole] = 0.125 M (A only), and $[TiCl_4]$ = 0.09 M (alkylation B only).

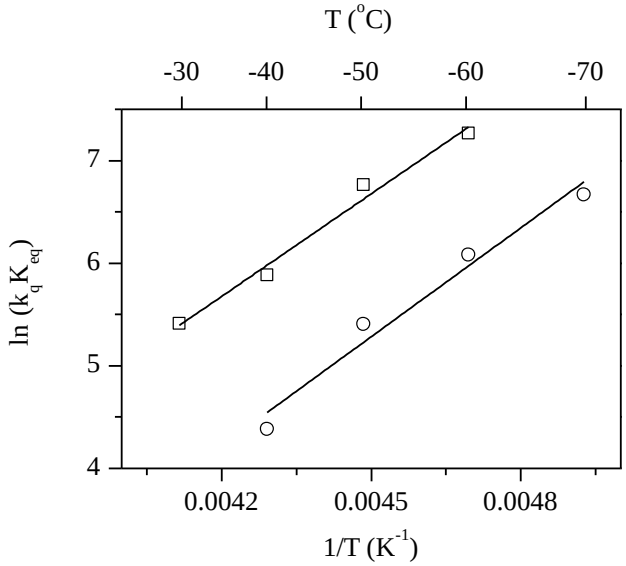

Figure 5-22. van't Hoff plots for $TiCl_4$-catalyzed alkylation of anisole by quasiliving PIB using a 40/60 (v/v) hexane/methylchloride (○) and 50/50 (v/v) toluene/methylene chloride (□) solvent systems. Polymerization/quench at -70 °C, [2,6-lutidine] = 0.005 M, [TMPCl] = 0.05 M, [isobutylene] = 1.58 M, [$TiCl_4$] = 0.015 M (polymerization), [anisole] = 0.1 M and [$TiCl_4$] = 0.09 M (alkylation).

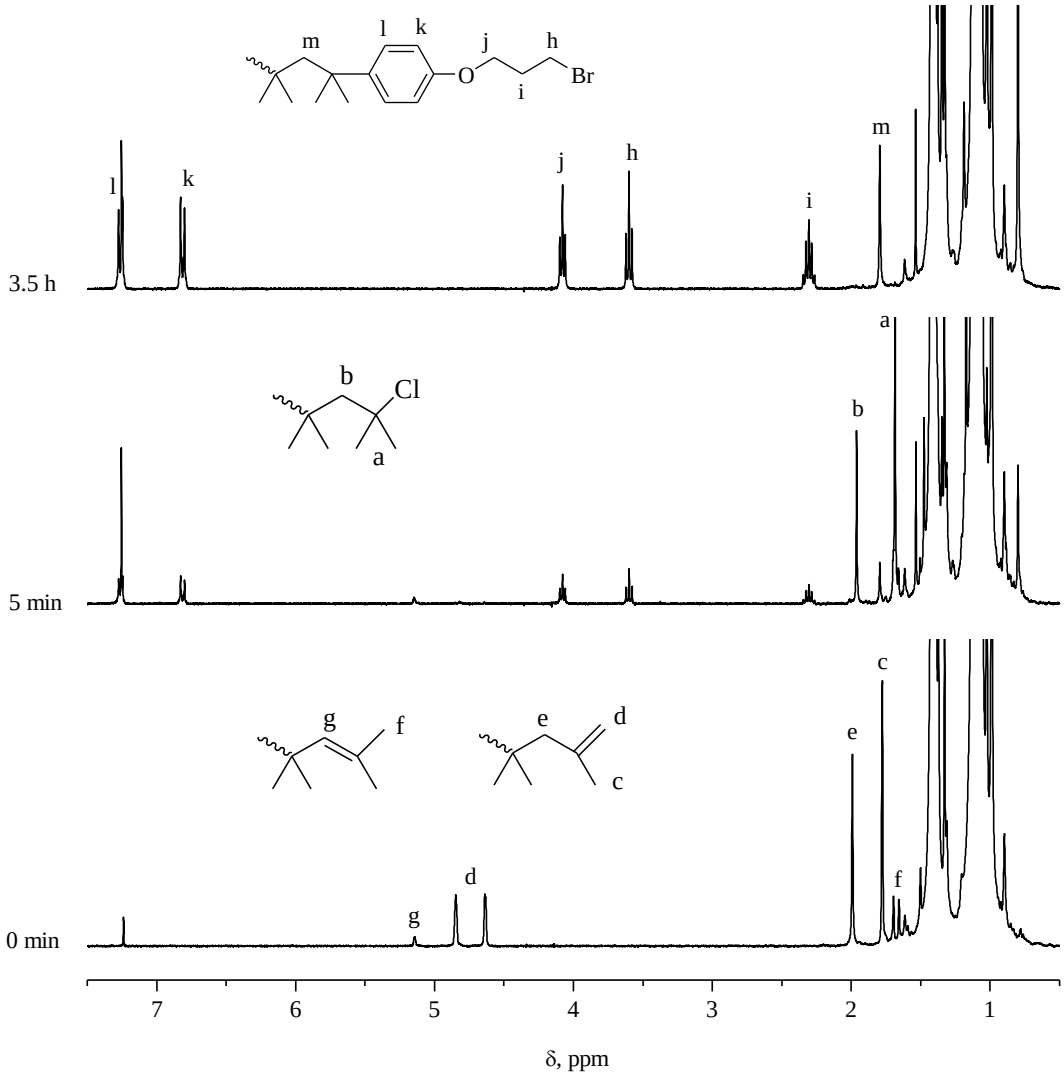

Figure 5-23. ^{1}H NMR (300 MHz, $CDCl_3$, 22 ^{o}C) spectra of Glissopal® as a function of time during the $TiCl_4$-catalyzed alkylation of (3-bromopropoxy)benzene. -70 ^{o}C in 40/60 (v/v) hexane/methyl chloride, [Glissopal] = 0.01 M, [(3-bromopropoxy)benzene] = 0.03 M, [$TiCl_4$] = 0.06 M.

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