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In Situ Quenching and Post-Polymerization Modification of Telechelic Polyisobutylene

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IN SITU QUENCHING AND POST-POLYMERIZATION MODIFICATION OF TELECHELIC POLYISOBUTYLENE

by

Todd Raymond Hartlage

Abstract of a Dissertation
Submitted to the Graduate School
of The University of Southern Mississippi
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ABSTRACT

IN SITU QUENCHING AND POST-POLYMERIZATION MODIFICATION OF TELECHELIC POLYISOBUTYLENE

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Polyisobutylene (PIB) is a saturated hydrocarbon elastomer that can only be produced by cationic polymerization. The water-initiated, chain transfer controlled synthesis conducted on an industrial scale produces monofunctional PIB with mixed olefin end groups. Living cationic techniques produce mono- and di-functional telechelic PIB. *In situ* quenching is the process of adding functional molecules to the polymerization reactor after all monomer is consumed. These quencher species bond to the chain ends, installing their latent functionality onto the polymer chain. To date, all quenchers utilized have been soft π-nucleophiles.

In the first project, free thiols, both aromatic and aliphatic, are shown to be effective quenchers of living PIB. These soft nucleophiles lack π electrons, but are sufficiently nucleophilic to directly attack a carbocation in an S_N1 reaction and form sulfide bonds with the polymer chain. By utilizing functional thiols, functional PIBs can be produced directly from the polymerization reactor, with no post-polymerization modification.

The second project utilized an established alkoxybenzene quencher, 3-bromopropoxy benzene, to produce bromine-terminated PIB. This material was then reacted with several functionalized carboxylates to displace the terminal bromine unit and produce PIBs with acrylate, methacrylate, and hydroxyl end groups.

The fourth chapter used two approaches to generate hydroxyl-terminated PIB. The first used an *in situ* quenching/deblocking sequence with living PIB to produce phenol-terminated PIB. The second used *exo*-olefin PIB in a radical thiol-ene reaction with 2-mercaptoethanol to produce aliphatic hydroxyl-terminated PIB. These functional PIBs are reacted with acid halides to produce telechelic PIB-based macromers and macroinitiators for radical copolymerizations.

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DEDICATION

To my wife, SarahBeth Hartlage, M.D. Without her unwavering support, none of this would have been possible.

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CHAPTER I

INTRODUCTION

Historical Development

Polyisobutylene (PIB) is the product of chain polymerization of isobutylene (IB), an olefinic hydrocarbon. PIB can only be produced by cationic polymerization. Pure PIB, when below a molecular weight of approximately 100,000 g mol^{-1}, is a perpetually tacky, clear and colorless viscous liquid or semi-solid; above that value, PIB forms a solid elastomeric species.[1] In industrial literature, the term polybutenes generally refers to polymers of less than 10,000 g mol^{-1} produced from raw C4 streams which contain ~15-30% isobutylene, with the balance being other olefins and alkanes such as butane and *n*-butene. Such materials are used as adhesives, caulking, or vibration dampeners.[1,2] Polymers produced by the cationic polymerization of pure isobutylene are rightly termed polyisobutylenes, regardless of molecular weight;[1] although polybutenes is often used in place of polyisobutylenes in the older literature. Synthesis and chemical modification of polyisobutylene is the focus of this dissertation.

Isobutylene was first acquired via distillation from animal fat by Michael Faraday in 1825.[1] The first isobutylene oligomers, produced at room temperature and catalyzed by BF_3, were reported by Butlerov and Gorianov in 1873.[3] However, true PIB polymers were unknown until German scientists Otto and Müller-Cunradi, working at IG Farbenindustrie AG (dissolved by the Allies in 1951, now BASF), were issued a patent for producing high molecular weight PIB at temperatures below -10 ºC with boron trifluoride (BF_3).[4] The highest molecular weights were achieved at -100 ºC using BF_3 dissolved in liquid ethylene.[5] Otto was brought to the Standard Oil Development Company (now Exxon) facility in Lindon, New Jersey in 1933 as a result of an agreement

between IG Farben and Standard Oil. There, Otto worked with R.M. Thomas and W.J. Sparks to synthesize PIBs with MWs of nearly 3 x 10^6 g mol^{-1} using the isobutylene/ethylene/BF_3 system.[1,6] These saturated hydrocarbon polymers lacked the olefinic groups necessary for vulcanization, but were nonetheless commercialized under the names Oppanol® (IG Farben/BASF) and Vistanex® (Standard Oil/Exxon) to improve oxidation resistance in blends with natural rubber.[7,8]

Being incapable of vulcanization severely hindered the utility of those first commercial PIBs. However, in 1937, Thomas and Sparks copolymerized IB with butadiene using aluminum chloride ($AlCl_3$) in methyl chloride (MeCl) to create an elastomeric rubber.[1] They later substituted butadiene for isoprene to produce the first butyl rubber,[9] a vulcanizable material highly resistant to oxidation and ideally suited for making the inner tubes of tires.[1,7] While their butyl rubber patent was not granted until 1944, larger events caused butyl rubber to be rapidly commercialized, namely the conquest of the natural rubber plantations in British Malaya and the Dutch East Indies (now Malaysia and Indonesia, respectively) by Imperial Japan in the early phases of the Pacific War (December 1941-May 1942).[10] Under the direction of the Rubber Reserve Company, a consortium of rubber companies established by President Franklin D. Roosevelt for the purpose of finding synthetic alternatives to natural rubber supplies, butyl rubber plants were built in Baton Rouge, Louisiana and Baytown, Texas, with the Baton Rouge facility coming online in 1943.[1,11] Butyl rubber, designated GR-I (Government Rubber – Isobutylene, now abbreviated internationally as IIR) joined GR-5, a styrene-butadiene rubber also introduced to combat the rubber shortage, and proved instrumental in producing the materiel necessary to win the conflict.[8,12]

Modern polyisobutylenes, including butyl rubber copolymers, are produced from isobutylene purified from mixed C4 streams by absorption into sulfuric acid.[13,14] Industrially, BF_3 (with water as a cocatalyst) and $AlCl_3$ are the primary Lewis acids used to produce polyisobutylenes. Processes using $AlCl_3$ are run using methyl chloride as a diluent at temperatures as low as -100 ºC.[1,8,15] In butyl rubber synthesis, 1.5-4.5 vol. % isoprene is utilized in the reaction.[15] At these temperatures, polymerization occurs in less than a second. BF_3 processes utilize isobutane solvent at -10 ºC.[11]

As mentioned earlier, PIB can only be produced via cationic polymerization. This class of reactions has a long developmental lineage, beginning with Bishop R. Watson's treatment of turpentine with sulfuric acid in 1789[16] and Deville's polymerization of styrene with tin tetrachloride ($SnCl_4$) in 1839.[17] Whitmore first put forth the idea that the reaction of an olefin and a strong acid involved an electron deficient, sp^2-hybridized carbon atom then called a carbonium ion, later revised to carbenium ion based on work by Olah,[18] and now more commonly called a carbocation (C^+).[19] Such a reaction with isobutylene is shown in Figure 1.

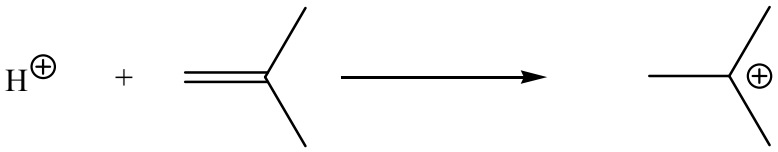


Figure 1. Addition of a proton to isobutylene.

However, this general scheme using a simple strong acid such as HCl does not produce high molecular weight polymers. The chloride anion is too nucleophilic toward a carbocation and rapidly bonds (collapses) to form the alkyl halide. The Lewis acids mentioned previously, when reacted with a proton donor such as water or a hydrogen halide, produce sufficiently non-nucleophilic conjugate bases to allow for carbocation

propagation. The combination of a proton (or carbenium ion) donor and a Lewis acid is termed an initiator-coinitiator complex. Industrial systems generally utilize adventitious water as the proton donor, rather than a deliberately added initiator species, since the low concentration of water necessary for this purpose is readily attained using common drying techniques. However, if more rigorous purification is undertaken, some Lewis acids ($AlCl_3$, $AlBr_3$, and BCl_3) are known to self-ionize and generate initiating acid species.[11,20] Thus, unless deliberately sought, initiation is not explicitly controlled with these systems. An example of the water-initiated process, used with BF_3 catalyzed systems is shown in Figure 2.

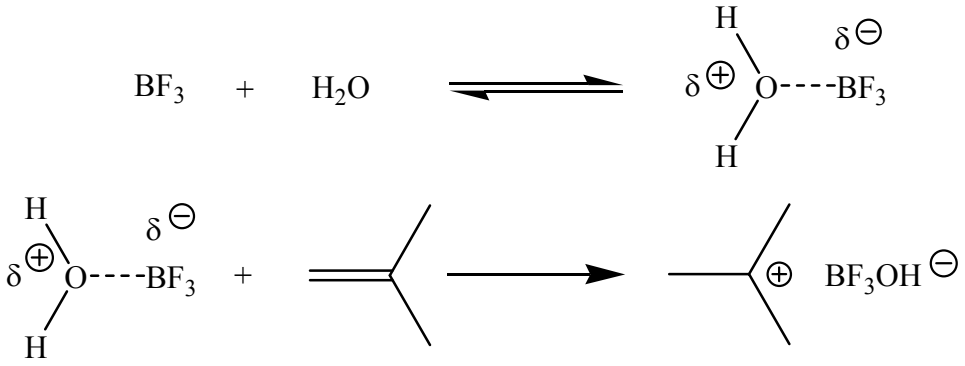


Figure 2. Initiation by an H_2O-BF_3 initiator-coinitiator complex.

Industrial methods, though highly cost effective, are chain-transfer dominated processes that do not produce polymers with either well-controlled polydispersities or quantitative end-group control. Figure 3 illustrates the bimolecular chain transfer to monomer common in $AlCl_3$ catalyzed systems.

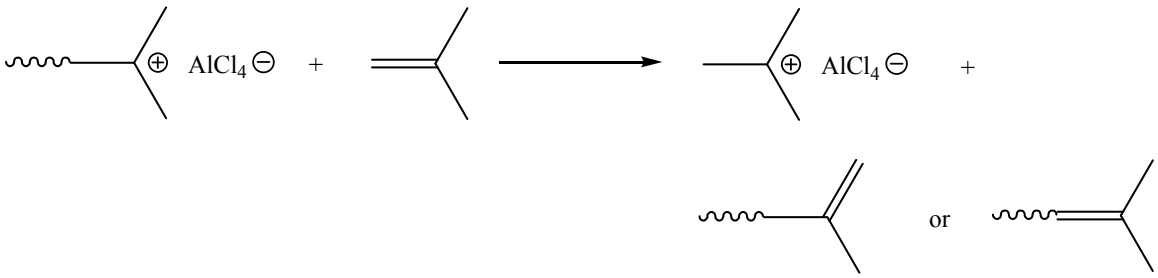


Figure 3. Bimolecular chain transfer in $AlCl_3$-catalyzed isobutylene polymerizations.

As shown in the figure, chain-transfer produces polymer molecules initiated by a proton, and thus, when transfer is the dominant chain forming reaction, the resulting polymer molecules are inherently monofunctional. To enable expansion of polyisobutylene-based polymers into other markets, for example thermoplastic elastomers, and to provide more precise control over molecular weight and polydispersity, it was necessary to gain control over the initiation process and to find conditions under which transfer reactions could be controlled or avoided. Synthetic developments over the last 40 years have largely accomplished these goals, allowing polyisobutylene to expand beyond commodity polymer applications into specialty applications such as block copolymers and end-functional (telechelic) polymers. This revolution was enabled through understanding and control of the polymerization mechanism.

Living Polymerizations

Living polymerizations are defined as chain polymerizations that proceed in the absence of chain transfer and chain termination reactions. Since their discovery, living polymerizations have led to an explosion of research and development in polymer chemistry. In an ideal living system, there would be no instance of either termination or chain transfer during propagation; the propagating centers would remain active indefinitely, and as long as monomer was provided, the chains would grow proportionally. However, this ideal condition is generally thought to be theoretical only,

since even in the most rigorous systems, side reactions occur at some very low (but still nonzero) rate, that prevent chains from retaining their capacity for growth indefinitely.

Despite the lack of a truly ideal system, practical living polymerizations have been realized in the laboratory for many systems, including anionic, cationic, and radical. These systems lack detectable chain transfer or termination processes, even though one or both may be occurring on a negligible level. With these previously uncontrolled chain-breaking processes under control, high levels of control over the molecular weight (MW) and polydispersity indices (PDI) can now be achieved, producing well defined, replicable synthetic polymer products that approach the uniformity of biologically-produced natural polymers (DNA, RNA, proteins, etc.).

Living systems without chain transfer processes also require a suitably fast initiation process to insure that every initiating species "sees" an equivalent molar concentration of monomer and thus has equal opportunity for propagation. Thus, the number of propagating chains is equal to the amount of initiator added and degree of polymerization rises in direct proportion to monomer conversion.

Anionic polymerizations were the first realm of polymer study to encounter living or nearly living systems. Ziegler first identified a system in 1928 while studying polybutadiene synthesis with metallic sodium initiator. Introduction of additional monomeric butadiene to a reactor containing polybutadienylsodium resulted in an increase in molecular weight.[21]

The widespread recognition of living polymerizations came about in 1956, due to the work of Szwarc and coworkers.[22] Their system consisted of styrene polymerization in tetrahydrofuran (THF), using a sodium-naphthalene initiating system. Qualitatively, they observed that the bright green catalyst system became red immediately upon

addition of styrene, which correlates to the color of styryl anions. This red color remained for days, unless air or moisture was permitted into the system, signifying the persistence of the active chain propagating species, even in the absence of monomer. When additional styrene and THF in the same ratio as the initial reaction formulation was introduced to the active polymer solution, an increase in solution viscosity was observed, at the same polymer concentration, indicating an increase in molecular weight; specifically, the living polymer ends readily added monomer to increase the molecular weight of the existing chains without generating any new chains via chain transfer to monomer. Szwarc's group then extended this system by adding isoprene to the living polystyrene chains, producing well defined block copolymers.[22,23] Others have expanded and extended this work, producing narrow distribution (PDI <1.1), high MW polystyrenes (M_n > 100,000 g mol^{-1}).[24,25] Sequential monomer addition, as pioneered by Szwarc, continues to be the method of choice for well-defined block copolymers via anionic polymerization, but monomer selection is largely limited to styrene and dienes such as butadiene and isoprene.

Prior to the work of Szwarc et al., in 1950, the three mechanisms for chain polymerization had been elucidated by Walling, Briggs, Cummings, and Mayo, when they analyzed copolymerizations of methyl methacrylate using three types of initiators: radical (benzoyl peroxide), cationic (tin tetrachloride, $SnCl_4$), and anionic (metallic sodium and potassium, Na and K, respectively).[26] Thus, while the primary mechanisms of action for all three chain polymerizations were known, and despite progress in living anionic polymerization, living cationic polymerization trailed behind. This was due not to lack of effort, but to the structural differences between carbocations and carbanions. Carbanions possess a full valence shell of eight electrons; whereas carbocations only

possess six. This imparts greater stability to carbanions relative to carbocations, and since stability has an inverse relationship to reactivity, carbocations are more prone to chain-breaking side reactions. Suppressing these side reactions would be necessary before carbocationic polymerization could join the ranks of living polymerizations.

Living Cationic Polymerization

To achieve living carbocationic polymerization (note: older literature will often refer to this process as quasiliving carbocationic polymerization; however the prefix "quasi" was recently dropped by the carbocationic research community), three main issues had to be addressed. These were: (1) controlled initiation, (2) suppressed chain transfer, and (3) reversible termination.[27]

Controlled initiation utilizes a deliberately added species capable of initiating polymerization. This species, either a small molecule or a polymer, satisfies the valence at the head of the growing polymer chain and determines the number of polymer chains produced. If the initiating species possesses two initiating sites, it can be used to produce bidirectional growth, leading to difunctional (telechelic) polymers.[27] Kennedy first explored this by adding tBuCl to isobutylene polymerizations catalyzed by $EtAlCl_2$; he observed extremely rapid reactions that replaced the original initiation by protogens like adventitious water.[28] This technique was refined to produce the first telechelic polyisobutylenes through the development of "inifers" (shorthand for *ini*tiator-trans*fer* agents) like dicumyl chloride, which possessed two ionizeable halogens, allowing for chain growth from both sides of the molecule. When used with BCl_3 in MeCl at low temperatures (-80 to -50°C) and relatively high inifer concentrations, the resulting systems were characterized by negligible chain transfer to monomer.[29,30] These early systems suffered from drawbacks, such as polymer precipitation above MWs of about

4000 g mol^{-1} (the solubility limit of PIB in MeCl), and relatively broad MW distributions as a result of chain transfer to the inifer. However, this research resulted in the development of numerous initiating species using different ionizing groups, such as halogen,[31] acetate,[32,33] ethers,[34] and esters.[35] Additionally, substantial work has been done to developed dual-functional initiators that contain a cationic polymerization moiety and another functional group inert towards cationic polymerization but allowing for later chemistry. These initiators include groups like acetate,[36] POSS,[37] and ATRP initiators.[38,39] Lactone-[40] and epoxide-[41,42] containing initiators ring-open upon initiation to produce ester and hydroxyl moieties.

To address the second obstacle of living cationic polymerization, chain transfer mechanisms that the highly reactive carbocation can undergo must be repressed. Bimolecular chain transfer to monomer was shown in Figure 3 for an isobutylene system catalyzed by $AlCl_3$. Unimolecular chain transfer usually occurs in the form of β-proton elimination, shown in Figure 4 for the same system.

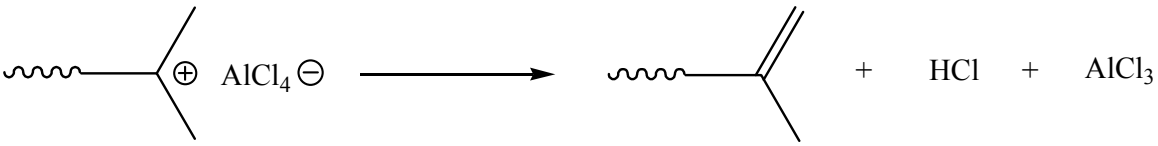


Figure 4. Unimolecular chain transfer in $AlCl_3$-catalyzed isobutylene polymerizations.

In cationic polymerization, the carbocation is usually paired with the counterion, so unimolecular chain transfer simply transfers a proton to the counterion, producing the original initiator-coinitiator complex, which rapidly reacts with monomer to begin a new chain. Since this process is zero-order in monomer, it is kinetically distinct from bimolecular chain transfer, even though the net result of the two processes is the same.

Given the high reactivity of the carbocation species, it consequently has a very short lifespan within a conventional reaction medium. Mentioned earlier, in industrial polymerizations, the propagating species exists for a second or less, before chain transfer/termination occurs. In contrast, active carbanions can last for days, years, or even decades (about 80 years for polystyrenyl anions dissolved in hydrocarbons) in the absence of oxygen and water. As a result, declarations regarding the unattainability of living carbocationic polymerizations were made as recently as 1975.[43]

However, cationic polymerization need not only progress through carbocations; oxonium ions are also capable of polymerization (e.g. cationic ring opening polymerizations of cyclic ethers and acetals). The first living cationic polymerization was performed in 1965, using THF monomer and $Ph_3C^+SbCl_6^-$ as initiator.[44] In 1974, Higashimura and Kishiro discovered a bimodal distribution in the molecular weights of polystyrene initiated by acetyl perchlorate in methylene chloride at 0 ºC.[45,46] They found that the weight fraction of the higher MW peak was increased by increasing the solvent polarity but decreased when either additional catalyst or a common salt was added. Differing propagating species within the reaction were thought to be responsible for the two peaks: a free ion or "loose" ion pair produced the higher MW peak and a contact ion pair producing the lower MW peak. These findings meshed well with the speculated structures of ions in solution proposed by Winstein and shown in Figure 5 for cationic polymerization.[47]

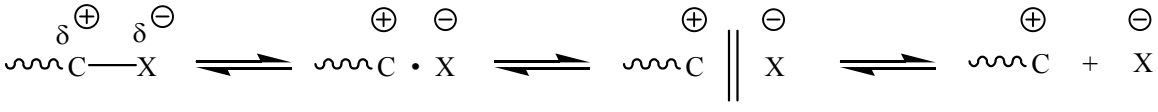


Figure 5. Winstein spectrum of ionicities for propagating cations.

By 1975, Higashimura had successfully produced a living cationic polymerization of p-methoxystyrene in CCl_4 using molecular iodine as the initiator. This system exhibited a linear increase of MW with conversion and would continue to increase in MW if fresh monomer was added to a previously exhausted reactor. Repeating the experiment in the more polar methylene chloride produced a nonliving system with broad PDIs. By adding a common ion salt, polymerizations in CH_2Cl_2 resembled those performed in CCl_4, with PDI = 1.3.[48-50] Using these systems, block copolymers with IBVE were successfully created using sequential monomer addition. This particular example was similar to Szwarc's early anionic work in that the red poly(p-methoxystyrene) cation solution became colorless upon addition of IBVE, wherein the propagating cation was no longer a chromophore.[50]

These early researchers had found that the key to a living carbocationic polymerization was establishment of the dormant/active equilibrium. This process was originally developed under the umbrella term "quasiliving," as the strict definition of a living polymerization is one in which all of the chains are capable of propagating at all times and only practically applicable in certain anionic systems. In quasiliving systems, reversible chain transfer and/or termination may occur. In a dormant/active equilibrium, most polymer chains are nonpropagating (dormant), while propagation is carried out by a much smaller fraction of active chains. The average number of monomer units added during a typical active period is known as the run number (RN).[51] The key for low PDI and controlled MW is a reversible equilibrium that turns active chains dormant and dormant chains active. Thus, most chains will experience short periods of propagation (low RN) followed by long inactive periods. This can be accomplished by withholding monomer ("monomer starvation"), such that the monomer concentration is kept low, but

constantly replenished. By utilizing readily reionizing systems of a Lewis acid (BCl_3, $AlCl_3$, or $TiCl_4$) initiated by cumyl chloride or adventitious H_2O, Kennedy and coworkers produced polymers of α-methylstyrene[52] and isobutylene.[53] Highly reactive IBVE was also polymerized by monomer starvation, using p-dicumyl chloride/$AgSbF_6$.[54] Monomer starvation methods effectively made unimolecular chain transfer reversible, although did not eliminate it entirely.

The second method for establishing quasiliving conditions was by tailoring the nucleophilicity of the counterion. This was discovered by Higashimura when refining the I_2/*p*-methoxystyrene system discussed previously. To correct for slow initiation, HI was added to the system, with I_2 as a coinitiator.[55] This, combined with work on the highly reactive N-vinylcarbazole,[56] produced the idea that a well-chosen nucleophile/carbocation pair could suppress termination and chain transfer. The more stable the carbocation, the more nucleophilic the counterion had to be, in order to make for an effective deactivation of the chains and produce an excess of dormant species. However, if the counterion were too nucleophilic, then a situation akin to Figure 1 could occur, wherein reionization is too slow and propagation is unevenly distributed amongst all the initiated chains.

The third approach to achieving quasiliving cationic polymerization is to add an external molecule that effects some change in the dormant/active equilibrium, particularly for less reactive monomers like isobutylene. Common ion salt precursors, based on ammonium ($nBu_4N^+Y^-$) or phosphonium ($nBu_4P^+Y^-$) cations, contain a nucleophilic anion ($Y^- = Br^-, Cl^-, I^-, CH_3CO_2^-$) that combines with the Lewis acid catalyst to produce complex anions that are identical to those associated with the growing carbocations. The introduction of such salts converted normally uncontrolled

polymerizations of IBVE/HCl with a strong Lewis acid cocatalyst, $SnCl_4$, into well controlled polymers with $M_w/M_n \sim 1.1$.[57] Through simple mass action, the salt suppressed the generation of free ions (Figure 6), which shifted the propagating species to the left side of the Winstein spectrum (Figure 5), resulting in more uniform propagation across all initiated chains.

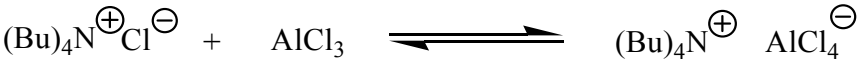


Figure 6. Generation of common ions using tertbutylammonium bromide.

It should be noted that the suppression of free ions has much less effect on cationic polymerizations than anionic. In anionic polymerization, free ions are 10^3 or 10^4 times more reactive than ion pairs, but only 5-50 times as reactive in cationic polymerizations. This is purely due to counterion size. Anionic counterions are typically small alkali metal atoms (Li^+, Na^+), while cationic counterions are much larger (ex. $Ti_2Cl_9^-$, $AlCl_4^-$, $AgSbF_6^-$) and cannot closely approach the cation due to large ionic radii. As the Coulomb force between charges is proportional to $1/r^2$, the force difference between ion pairs and free ions falls off rapidly. While solvent separated pairs are considered in the Winstein spectrum, their existence has not been demonstrated.

Electron-donating (ED) Lewis bases are a second class of external additive that suppress free ions by forming a common ion. The initial discovery was made for otherwise uncontrolled IBVE polymerizations with $EtAlCl_2$, which were rendered living by the addition of EtOAc, with the resulting polymers having $M_w/M_n < 1.2$.[58] Further work identified other chemical classes as suitable EDs, namely cyclic ethers (e.g. THF, oxepane, 1,4-dioxane),[59,60] cyclic formals (e.g. 1,3-dioxane, 1,3-dioxolane),[60] pyridine,[61] DMF,[61] and pyridine derivatives like 2,6-dimethylpyridine (2,6-lutidine).[62] However, the

effect was not universal, as species like propylene oxide produced no polymer, while 1,3,5-trioxane produced uncontrolled, free-ion dominated, polymerizations.[60]

It was initially thought that EDs coordinated with and stabilized the cation; however Faust observed that 2,6-di-*tert*-butylpyridine produced well controlled polymerizations with low PDIs[63,64] despite being too sterically bulky to interact with propagating cations.[65,66] Indeed, at loading levels only slightly above that of the protic impurities (HA) in the system, primarily water, the desired control was achieved.[64] This suggested that the role of EDs was to trap undesirable protogens that could initiate polymerizations in the manner of Figure 2. Support for this was provide by Storey, who utilized EDs that formed colored complexes with $TiCl_4$, but only when added in excess to the protic impurity concentration.[67] Only those reactions in which [ED] > [HA] produced living polymers, while the colorless, [ED] < [HA] reactions were nonliving. The colored 1:1 complex formed by 2-ethylhexyl *p*-(dimethylamino)benzoate and $TiCl_4$ was also used to determine that the typical [HA] within a normal glovebox system used for cationic polymerization was 1.0-2.0 x 10^{-3} M.[68]

While EDs were found to remove protic impurities from the system, their primary importance was common ion generation, which filled the same mechanistic role as the added common ion salts.[69] Without added 2,4-dimethylpyridine, $TiCl_4$-catalyzed IB polymerizations produced bimodal GPC traces reminiscent of those seen by Higashimura in the 1970s, and attributed to the same source: polymer chains initiated by ion pairs and free ions. Reaction with water, seen in Figure 7, produced the common counterion, $Ti_2Cl_9^-$, which suppressed ion pair dissociation and produced a polymer with monomodal GPC traces.

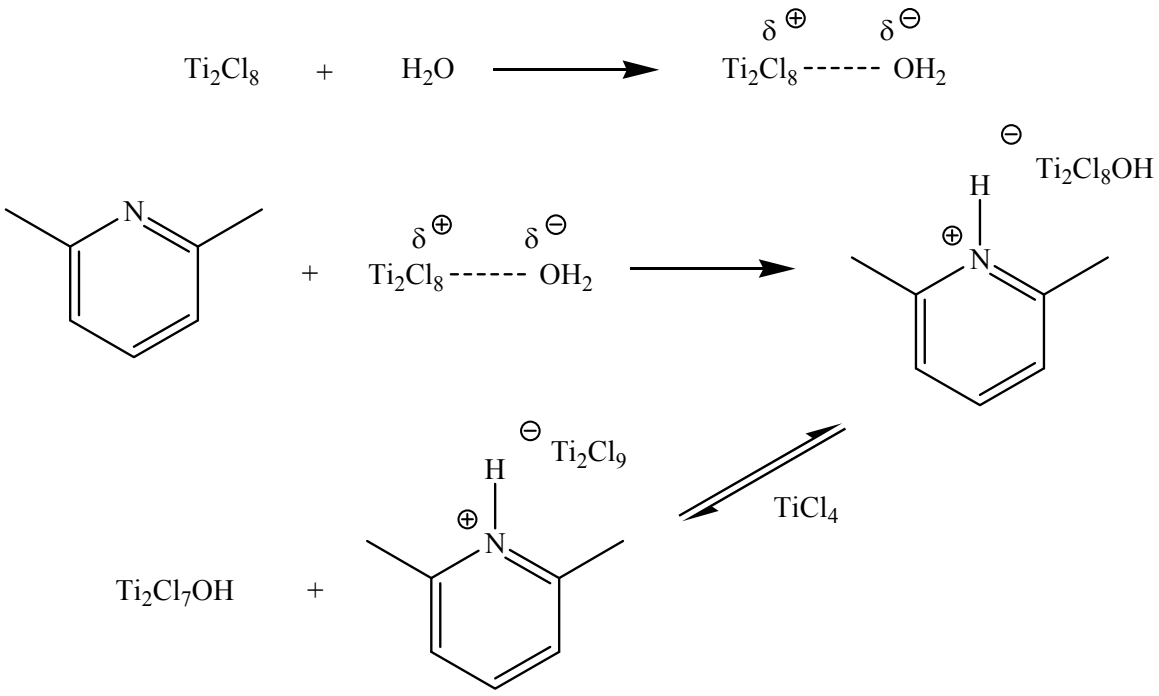


Figure 7. Mechanism of proton scavenging and common ion formation by Lewis base.

The three methods of creating a living cationic polymerization all rely on controlling the dormant/active equilibrium. Maintaining a large dormant:active chain ratio (typically 1 x 10^9:1, for $TiCl_4$-catalyzed IB polymerizations) requires not only the suppression of uncontrolled ionization, but the rapid return of an active chain towards dormancy, thus resulting in short cation lifetimes and low RN. The equilibrium must be highly dynamic, with rapid exchange between dormant and active states, such that each chain experiences an ionization and collapse before any other chain undergoes two such cycles. The appearance of longer lived cations results in higher PDIs. For some living $TiCl_4$/2,6-dimethylpyridine systems the calculated k_{-i} was 7.5 x 10^7 s^{-1} for isobutylene and 1.9 x 10^7 s^{-1} for styrene.[70] Under similar conditions, k_ps of 7 x 10^8 s^{-1} and 1.5 x 10^9 s^{-1} have been measured for isobutylene and styrene, respectively.[71] In contrast, apparent rate constants for ionization of 15 M^{-2} s^{-1} for isobutylene and 1.3 M^{-2} s^{-1} for styrene have been observed.

Clearly, deionization must be the favored process for living cationic systems, and in addition to the presence of EDs, other polymerization conditions, namely temperature and solvent polarity may be manipulated in order to shorten the active period and decrease the RN. Lower temperatures and more polar solvent systems encourage ionization and longer cation lifetimes. For example, styrene's RN in 60:40 (v:v) MCHex:Hex varies from 31 to 100 as the temperature is lowered from -59 ºC to -100 ºC.[70]

Polyisobutylene Functionalization

Most polyisobutylenes require post-polymerization modification in order to be a viable commercial product. Recall that the original PIB product, Oppanol®, was hampered at the time by its lack of backbone olefins for vulcanization. While PIB utility has greatly expanded beyond the rubber industry, without deliberate intervention, the number of functional groups available to bulk-production PIB is somewhat limited. Conventional industrial polymerizations using BF_3 catalysis produce two types of monofunctional olefin-terminated PIB, shown in Figure 8. $AlCl_3$-catalyzed species are more complex, and contain a sizeable amount of tri-substituted olefin and aliphatic end groups.[72]

A B

Figure 8. *Exo*-olefin (A) and *endo*-olefin (B) end groups of PIB.

Exo-olefin PIB is more useful synthetically than *endo*-olefin, due to higher reactivity, and PIB products with 70-90% *exo*-olefin end groups are typically marketed as

"highly reactive polyisobutylene."[73,74] Glissopal®, a low MW PIB made by BASF is used as the base material for fuel and lube additives, and has ~82% *exo*-olefin end groups. Glissopal® can be reacted with succinic anhydride to produce PIBSA (Figure 9), which is made into motor oil dispersants through further reactions of the anhydride.[75,76] Quantitative *exo*-olefin formation via the addition of external additives to the living polymerization has been achieved by the use of hindered bases (ex. 2,5-dimethylpyrrole),[77-80] (di)sulfides,[81,82] and alkoxysilanes/ethers.[83-85]

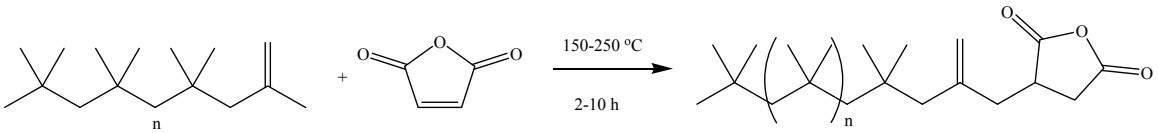


Figure 9. Synthesis of PIBSA from *exo*-olefin PIB and maleic anhydride.

The functional initiators discussed previously are one approach to functionalized PIB and some, such as silyl, have been patented.[86] Whether or not the initiator has additional functionality, PIBs produced by living processes possess *tert*-chloride chain ends, even upon addition of MeOH,[87] which is a standard method of terminating living PIB reactions on a laboratory scale.[72] *Tert*-chloride PIB can be converted into *exo*-olefin by dehydrochlorination, but reaction times are long (20 h).[88] *Exo*-olefin PIB has been the target of hydroboration-oxidation,[89] epoxidation,[90] sulfonation,[91] hydrobromination,[92] ozonolysis,[93,94] and other reactions.

End-capping a PIB chain during or immediately after polymerization is a second approach to installing alternate functionalities, provided that the nucleophile selected does not permanently complex with the Lewis acid, resulting in deactivation of one or both species. Generally, soft π-nucleophiles are effective with $TiCl_4$-catalyzed IB polymerizations. The use of non-polymerizing monomers, such as 1,1-diphenylethylene

and 1,1-ditolyletheylene, by Faust, resulted in single additions to PIB chains that remained in the active cationic state due to delocalization.[95,96] These long-lived cationic species were used as high-blocking-efficiency initiators of α-methylstyrene polymerizations.[97] Allyltrimethylsilane was found to add to a PIB chain end and then rearrange to produce an allyl end group, a useful synthetic handle for further transformations.[34,98] Other capping species include 1-butene, *cis*-2-butene and 1,3-butadiene.[99] Capping by 1,3-butadiene occurs via 1,4-addition followed by immediate ion-pair collapse, producing chloroallyl chain ends suitable for post-polymerization modification by nucleophilic substitution.[100,101]

Aromatic heterocycles are a second class of molecules capable of adding to living PIB chains. Furans, namely 2-methylfuran and 2-*tert*-butylfuran react with PIB carbocations to form stable allylic cations that can be used to initiate IBVE polymerization or couple two PIB chains.[102] *N*-methylpyrrole will quantitatively endcap IB chains in an isomeric mixture of 46% 2-PIB-*N*-methylpyrrole and 54% 3-PIB-*N*-methylpyrrole.[103] Thiophene-capped PIB has been converted into an anionic initiator using *n*-butyllithium and used to initiate *tert*-butyl methacrylate to form block copolymers.[104]

Effective alkylation of arenes has long been a goal of cationic polymerizations, with early examples of anisole-terminated[105] and phenol-terminated[106] chain ends. Use of triphenylaluminum as a co-catalyst and chain-terminating agent with 2,6-dichloro-2,6-dimethylheptane-initiated IB polymerizations produced increasing conversions of phenylation as the temperature decreased from -20 to -70 ºC;[107] although quantitative functionalization was not achieved ($f \sim 1.5$).[108] With a water-initiated/$TiCl_4$/IB system, 70-81% phenylation by triphenylamine was achieved using both post-polymerization

modification of *tert*-Cl/*exo*-olefin PIB and *in situ* addition to active polymerization reactions, though long reaction times were required (43 h) for the *in situ* approach.[109]

While *in situ* alkylation of arenes proved elusive, post-polymerization alkylation via Friedel-Crafts reaction with Lewis acids, Amberlyst 36, or trifluoromethanesulfonic acid was employed with *exo*-olefin PIB. Use of room temperature sulfuric acid catalysis in CH_2Cl_2 with anisole and phenol was successful in 60 h, but less activated benzenes were not.[110] Alkylation of *o*-alkyl anilines by Glissopal® with $AlCl_3$-catalysis occurred at 210 °C, but required 3 days for completion.[111]

Living cationic polymerizations have been used to produce suitable telechelic *exo*-olefin and *tert*-Cl PIB substrates for alkylation, with aromatic hydrocarbons (benzene, toluene, xylenes), phenol, and anisole successfully added with BF_3-etherate at 20-55 °C in CH_2Cl_2/toluene or hexane solutions. Higher temperatures however, favor depolymerization or degradation. This is also seen in $SnCl_4$-catalyzed phenol alkylations at -50-0 °C; although reaction times are more rapid, from 1-3 h.[112,113]

Storey et al. developed two classes of compounds capable of quantitative *in situ* end-functionalization of PIB under cationic polymerization conditions, rendering post-polymerizaton Friedel-Crafts alkylation unnecessary.[114,115] Furthermore, functionality can be preinstalled in these "quencher" molecules (i.e. those alkylated by PIB chains), facilitating the direct addition of moieties capable of further chemistries; however these groups must be compatible with polymerization conditions so as to not interfere with alkylation. Unprotected hydroxyls, for example, rapidly react with Lewis acid cocatalysts like $TiCl_4$, deactivating either the cocatalyst or the quencher.[34] Acyl groups form carbonyl-$TiCl_4$ complexes that reduce free $TiCl_4$ availability.[116]

Heterocyclic aromatics such as *N*-(2-*tert*-butoxyethyl)pyrrole produced 95% alkylation in 60/40 (v/v) hexane/MeCl at in -60 °C in 25-30 minutes.[117] Addition of 5 equivalents $EtAlCl_2$ and 2 equivalents H_2SO_4, and warming to room temperature, quantitatively removed the *tert*-butyl protecting groups to produce hydroxyl-terminated PIB. Refluxing this mixed-acid solution for 3 h at 69 °C resulted in alkylation of the remaining *exo*-olefin PIB as well as rearrangement of the mixed C2 and C3 isomers to produce 98% C3 alkylated isomers. The resulting quantitative hydroxyl-terminated PIB showed unimpeded reactivity with carboxylic acids and isocyanates. Another functional pyrrole, 1-(3-bromopropyl)pyrrole was used as a quencher molecule to produce primary-bromide terminated PIB. Bromide displacement with azide, followed by copper-catalyzed click chemistry with propargyl 2-(1-dodecylsulfanylthiocarbonylsulfanyl)-2-methylpropionate produced a PIB-based RAFT macroinitiator, which effectively produced narrow distribution PIB-b-PNIPAM copolymers (PDI = 1.02-1.08) with self-assembling and temperature-responsive properties.[118]

Morgan and Storey introduced alkoxybenzenes as effective *in situ* quenchers.[115,119,120] The quenching species and subsequent modifications are summarized in Figure 10. Several functionalities were installed directly onto the PIB chains, including primary halogen (Cl and Br), hydroxyl, and amine. By increasing the spacing between the reactive hydroxyl and amine moieties and the phenyl ring to four or more methylene units, direct functionalization was achieved. However, the hydroxyl and amine species required large excesses of $TiCl_4$ relative to chain ends (10.29x and 3.8x, respectively) and long reaction times (7-9 h) to compensate for complexation between the quencher and $TiCl_4$. In all cases, alkylation occurred exclusively at the *para* position and no instances of multiple alkylations were observed.

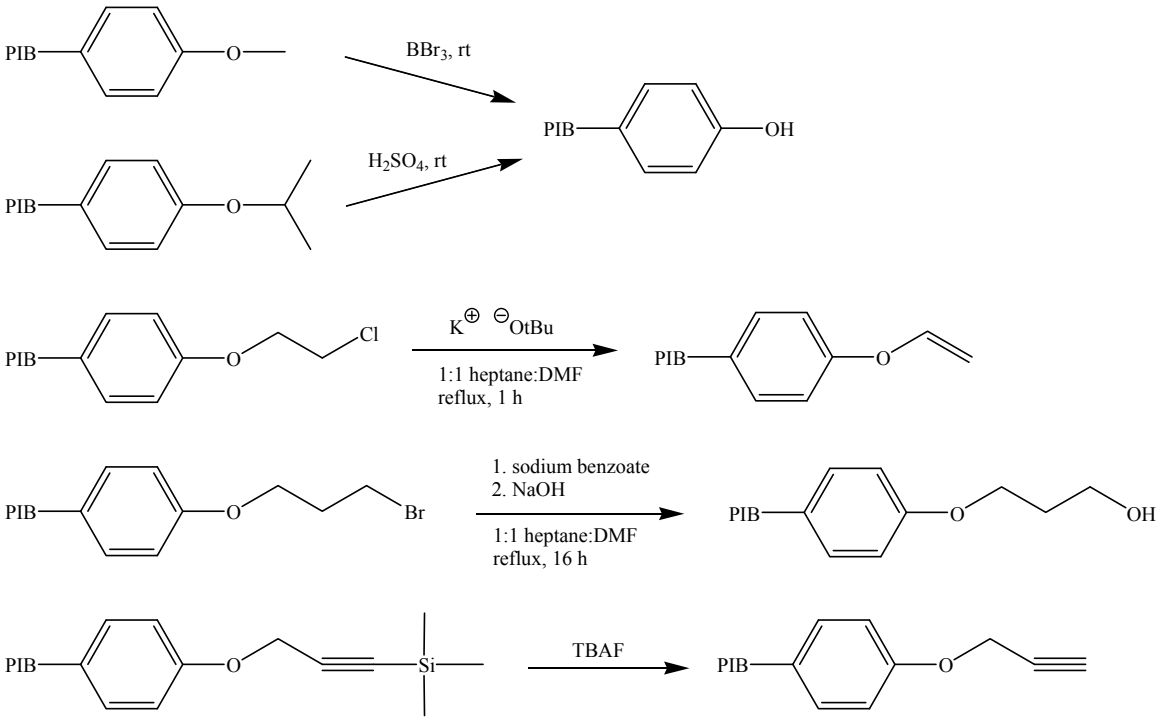


Figure 10. Alkoxybenzene terminated PIBs via *in situ* quenching and subsequent modification.

Derivitization of these alkoxybenzene quenchers, whether in the polymerization medium or post-polymerization offers huge opportunities for the exploration of PIB-based chemistries not readily accessed through other methodologies. The goal of this dissertation is to explore both these quenchers themselves as well as those post-polymerization modifications to expand the library of polyisobutylene-based materials.

CHAPTER II

IN SITU QUENCHING OF LIVING POLYISOBUTYLENE WITH THIOLS

Introduction

Polyisobutylene is an important industrial polymer only producible by cationic polymerization. The most commonly available form of PIB contains a single olefin terminus in high yield, between 70 and 90%, utilizing protic initiation and BF_3 catalysis.[73,74] Modifying the olefin end group is necessary to utilize PIB in chemistries that are not compatible with cationic polymerization conditions. Numerous post-polymerization modifications have been developed using *exo*-olefin PIB, including anti-Markovnikov hydrobromination,[92] hydroboration-oxidation,[89] and epoxidation.[90] Friedel-Crafts alkylations of arenes,[121] phenol,[122] anisole,[123] and aniline[111] have been performed using typical Lewis acid catalysis (e.g. $AlCl_3$, BF_3, BF_3-etherate) on both commercial samples and PIB produced using controlled living polymerizations, which can produce quantitative *tert*-Cl or *exo*-olefin termini.[81,84] *Exo*-olefin PIB has also been used as a substrate for the radical thiol-ene reaction. This technique offers the advantages of "click" chemistry, producing high yields with a high tolerance for other functional groups capable of numerous subsequent chemistries.[124] While high yields (>90%) have been achieved using commercial feedstocks, approximately 20% of the polymer chains are left unreacted in even the best (90% *exo*-olefin) PIBs,[125] necessitating chromatographic techniques such as liquid chromatography[126,127] or Soxhlet extraction[125] to remove the unreacted polymers. Using telechelic mono- and difunctional *exo*-olefin PIBs, Magenau et al. quantitatively produced primary chloride, carboxylic acid, hydroxyl, and amine-terminated PIBs using the corresponding functional thiols.[128]

The previous discussion has focused on post-polymerization modifications. Controlled living techniques allow for *in situ* functionalization of PIB chains, and these methods typically involve the use of functional initiators and/or reaction of the polymer chain end with a suitable nucleophile. Cationic initiators containing cyclic lactone[30] or epoxide[129] groups produce ester and hydroxyl groups, respectively, when ring-opened by $TiCl_4$. These species produce only a single functionality, with the chain terminus being *tert*-Cl in the absence of further modification.

Successful addition of a nucleophile to the polymerization medium requires careful selection to avoid interaction with the Lewis acid catalyst, which can eliminate the reactivity of one or both species. Most species studied have been soft π-nucleophiles, such as aromatic heterocycles (furans,[102] thiophene[104]) and non-homopolymerizeable monomers such as 1,1-diphenylethylene,[95,96] 1,3-butadiene, which produces chloroallyl chain ends via 1,4-addition, and allyltrimethylsilane, which rearranges upon addition to form allyl-terminated PIB. Telechelic mono- and di-functional *exo*-olefin PIB has been produced by *in situ* addition of (di)sulfides,[82,130] alkoxysilanes,[83] ethers,[84] and hindered nitrogen bases such as 2,5-dimethylpyrrole.[77,78,80] In the case of (di)sulfide and ether quenchers, the quencher first caps the chain end with a (di)sulfonium or oxonium cation that is stable under cationic polymerization conditions until an added base (such as methanol or triethylamine) causes β-hydride elimination to form the *exo*-olefin. For some disulfide species, treatment with base cleaves the disulfide bond instead, producing a thioether terminus. For example, PIB chain ends capped with di-p-tolyl disulfide form 85% thioether and 15% *exo*-olefin when treated with triethylamine at -60 °C in 60/40 (v/v) hexane/methyl chloride.

Alkoxybenzenes have emerged as a remarkably useful and effective quencher of $TiCl_4$-catalyzed living polyisobutylene. Morgan and Storey utilized alkoxybenzenes to install numerous functionalities, such a primary halide, alkyne, phenol, alcohol, and amine.[115] Direct alkylation of phenol is not possible due to strong interaction of the phenol hydroxyl moiety with $TiCl_4$; however protection with a methyl or isopropyl group followed by *in situ* deprotection using $BBr_3/TiCl_4$ or $H_2SO_4/TiCl_4$, respectively, produced quantitative phenol functionality. Direct alkylation by phenoxyalkanols was only possible if the free hydroxyl group was separated from the phenoxy group by four methylene units, and even then required substantial amounts of $TiCl_4$ (>10x relative to chain end concentration and long reaction times relative to other alkoxybenzene quenchers.[115]

Thiols exhibit a number of interesting properties, as they are extremely nucleophilic and considerably more acidic than their alcohol counterparts; the pKa of thiophenol is 6 while phenol is 10, for example. Both the radical and nucleophilic (Michael addition) thiol-ene reactions produce the anti-Markovnikov addition product. The electrophilic pathway, producing Markovnikov addition, is also possible in some cases. Bezumnova and Rozhkova alkylated a series of olefins with 2-mercaptobenzothiazole using BF_3-OEt_2 catalysis;[131] while Cottman produced a number of antioxidant species by traditional Friedel-Crafts alkylations of 4-mercaptophenols using 2-20 carbon alkylating species at or above room temperature (typically 40-100 ºC). It was noted that the sulfide-forming alkylation of the thiol group occurred preferentially relative to aromatic ring alkylation, but the latter reaction was also observed, particularly with secondary or tertiary alkylating groups.[132] BF_3-OEt_2 catalysis has also been used to catalyze the addition of 2-mercaptoethanol and 4-mercaptophenol to both 2,4,4-trimethyl-

2-pentene (TMP) and monofunctional commercial *exo*-olefin PIB samples at room temperature in methylene chloride.[126] However, this chemistry has, to our knowledge, not yet been applied to living polyisobutylene systems. In this work, we explore the direct quenching of living PIB with thiols.

Experimental

Materials

Thiophenol (97%), 4-methylbenzenethiol (98%), 4-methoxybenzenethiol (98%), 2-phenoxyethanethiol, 1-butanethiol (99+%), 2-propanethiol (≥97%), 2-methyl-2-propanethiol (99%), benzyl mercaptan (99%), 3-chloro-1-propanethiol (98%), titanium tetrachloride ($TiCl_4$) (99.9%), hexane (anhydrous, 95%), methanol (anhydrous, 99.8%), chloroform-d ($CDCl_3$) (99.8% atom D), and dichloromethane-d_2 (CD_2Cl_2) (99.96% atom D) were purchased from Sigma-Aldrich and used as received. Anhydrous magnesium sulfate ($MgSO_4$) was purchased from Fisher Scientific and used as received. 2-Mercaptoethanol (≥99%) was purchased from Sigma-Aldrich and dried over $MgSO_4$, then filtered before use. Methyl chloride (Alexander Chemical Corp.) (99.9+%) and isobutylene (BOC gases) (99%) were dried by flowing the gases through $CaSO_4$/molecular sieves/$CaCl_2$ packed columns and condensing within a N_2-atmosphere glovebox right before use. Cationic initiators 2-chloro-2,4,4-trimethylpentane (TMPCl) and1,3-bis-(1-chloro-1-methylethyl)-5-*tert*-butylbenzene (bDCC) were synthesized as previously described.[115]

Instrumentation

^1H and ^{13}C NMR spectra were collected using a 300 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer. Chemical shifts for both ^1H and ^{13}C were referenced to the $CDCl_3$ solvent reference (7.26 and 77.0 ppm, respectively).

Gel permeation chromatography (GPC) was used to measure all number average molecular weights (M_n) and polydispersities (PDI = M_w/M_n). The GPC system and analysis methods have been previously described.[115]

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed using a Bruker Microflex LRF MALDI-TOF mass spectrometer equipped with a nitrogen laser (337 nm) possessing a 60 Hz repetition rate and a 50 μJ energy output. PIB samples were prepared using the dried-droplet method. A 20 mg/mL matrix (dithranol) solution, a 10 mg/mL cationizing agent (silver trifluoroacetate, AgTFA) solution, and a 10 mg/mL polymer solution, all in THF, were mixed in a volumetric ratio of matrix:sample:cationizing agent = 10:10:1, and then a 0.5 μL aliquot was applied to a MALDI sample target for analysis. All spectra were obtained in the positive ion mode utilizing the reflector mode micro-channel plate detector and are the sum of 900-1000 shots. Molecular weights of the polymer end groups were determined by linear regression using the known molecular weight of the initiator residue (bDCC) and cationizing agent cation (Ag+).

Determination of End-group Composition

End-group compositions for small molecule species were determined by ^{1}H NMR under the assumption that five end group species constitute 100% of the chain ends: thiol quenched (sulfide formation), *tert*-chloride, *exo*-olefin, *endo*-olefin, and coupled. The fractional molar amount of each end group species was found using equations akin to Equation 1, derived from the work of Ummadisetty et al., for determining the fraction of thiol-quenched end groups ($F_{quenched}$),[130]

$$F_{quenched} = (A_{sulfide} / 2) / (A_{sulfide} / 2 + A_{exo} + A_{endo} + A_{coupled} + A_{tert\text{-}Cl} / 2)$$

Equation 1. Chain end functionality of sulfide-quenched species.

where $A_{sulfide}$ is the area of the terminal methylene protons of the chain end, the location of which varies slightly depending on the thiol used. For thiophenol, the terminal methylene appears at 1.70 ppm. A_{exo} is the area of the upfield *exo*-olefin peak at 4.64 ppm, A_{endo} is the area of the olefin resonance at 5.15 ppm, and $A_{coupled}$ is calculated by:

$$A_{coupled} = (A_{5.0\text{-}4.75} - A_{exo})$$

Equation 2. Area of integration for the ^{1}H NMR resonance of coupled species.

where $A_{5.0\text{-}4.75}$ refers to the integrated area of the convoluted peaks from 4.75 to 5.0 ppm attributed to the two equivalent protons of the coupled species and the downfield *exo*-olefin proton. Although two protons are represented by the coupled peak, two molecules combine to produce the peak, so the $A_{coupled}$ term has a net coefficient of one. For TMPCl, $A_{tert\text{-}Cl}$ is the area of the peak at 1.88 ppm, while for PIB $A_{tert\text{-}Cl}$ was determined by Equation 3:

$$A_{tert\text{-}Cl} = (A_{1.95\text{-}2.05}) - 2A_{exo} - 2A_{coupled}$$

Equation 3. Area of integration for the ^{1}H NMR resonance of *tert*-chloride terminated species.

in which $A_{1.95\text{-}2.05}$ is the integrated area of the convoluted peaks associated with the terminal methylene protons from 1.95-2.05 ppm of *tert*-chloride, *exo*-olefin, and coupled end groups.

Model Reactions with TMPCl

A representative reaction between TMPCl and a thiol was as follows (Table 1, Entry 5). All reactions were prepared and performed within a N_2-atmosphere glovebox. To a scintillation vial were added 10 mL CH_2Cl_2, 0.20 mL TMPCl ([CE] = 0.10 M), and 0.15 mL thiophenol ([SH]/[CE] = 1.25). The vial was capped and placed in a -70°C heptane bath. The bath level was maintained such that the reaction solution was fully

submerged but the vial's cap was above the liquid level to prevent contamination by heptane. The vial was chilled in the bath for 30 min, then 0.65 mL $TiCl_4$ ([$TiCl_4$]/[CE] = 5), neat and at room temperature, was added to the vial. After 2 h, 2 mL MeOH was added to deactivate the catalyst. The reaction contents were transferred to a separatory funnel and extracted 3x with 3 mL increments of 1 M aqueous NaOH, followed by 1x extraction with 3 mL deionized H_2O. The organic layer was separated, dried with $MgSO_4$, and filtered through a cotton plug, and the methylene chloride was evaporated with a stream of N_2.

Synthesis of Masterbatch Polyisobutylene

An unquenched difunctional masterbatch PIB was produced using the following procedure within a N_2-atmosphere glovebox. A 250 mL, 4-neck round bottom flask, equipped with an overhead stirrer, ReactIR probe, and RTD, was cooled to -70 ºC in a cryostated heptane bath. To the flask were added 1.72 g bDCC, 97 mL hexane, 65 mL MeCl, 0.12 mL 2,6-lutidine, and 41 mL IB. Polymerization was initiated by the addition of 0.47 mL $TiCl_4$, neat and at room temperature. Upon full monomer conversion (>98%, as determined by ReactIR), the reaction was terminated by the addition of neat methanol. The reactor was removed from the glovebox and allowed to warm to room temperature. Hexane was added, and the polymer solution was extracted with, and then precipitated into, methanol. The methanol was decanted, and the polymer was redissolved in hexane. The resulting solution was extracted with deionized water, dried over $MgSO_4$, and filtered, and finally the hexane was stripped to isolate the PIB product.

Quenching of Masterbatch Polyisobutylene with Thiols

The general sequence for the *in situ* quenching of masterbatch PIB by thiols was as follows. All reactions were performed within a N_2-atmosphere glovebox using a

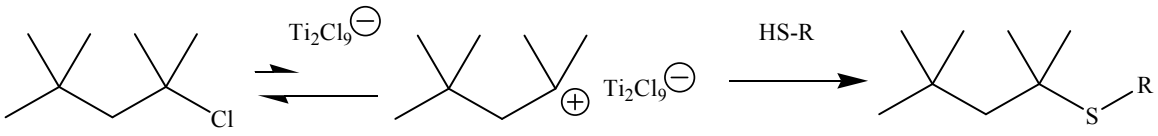
cryostated heptane bath cooled to -70 ºC. To a 100 mL, 3-neck round bottom flask equipped with an overhead stirrer and RTD were added 5 g masterbatch PIB (0.044 meq, M_n = 4000, PDI = 1.33), 20 mL hexane, 30 mL MeCl, thiol (1.73-1.93x [CE]), and $TiCl_4$ (5.95x [CE]). Reaction progress was monitored by ^{1}H NMR analysis of aliquots taken from the reactor and precipitated in MeOH. After completion of the reaction, MeOH was added to the reactor, and the reactor was allowed to warm to room temperature overnight. Polymer purification was carried out using the same procedure that was used for the masterbatch PIB.

Results and Discussion

Model Reactions with TMPCl

The impetus for this research came from an attempt to produce thiophenol-terminated PIB directly from *in situ* quenching of living PIB with thiophenol, using procedures analogous to alkoxybenzene-type quenching. However, the expected Friedel-Crafts alkylation product was not observed; nor were *exo*-olefin or *tert*-chloride end groups observed, which would indicate elimination, as in sulfide quenching, or preferential reaction of thiophenol with the $TiCl_4$ catalyst, respectively. Instead, two sets of aromatic resonances were observed in the ^{1}H NMR spectrum, with an integration ratio of 2:3, suggesting no reaction at the aromatic ring. Furthermore, under thiol Michael addition conditions, the polymer product was completely unreactive with propargyl acrylate, which has been previously demonstrated to react readily with thiol-terminated PIB produced by the reaction of thiourea and 3-bromopropoxybenzene-terminated PIB.[133] It was then hypothesized that the quenching reaction was proceeding via a S_N1 substitution reaction, involving nucleophilic attack of the thiol moiety at the PIB tertiary carbocation. To simplify the system and determine if this was indeed the dominant

reaction, a series of model studies was undertaken using the monofunctional cationic initiator 2-chloro-2,4,4-trimethylpentane (TMPCl), with the general reaction scheme shown in Scheme 1. The reference ^{1}H and ^{13}C NMR spectra for TMPCl are shown in Figure 11.



Scheme 1. Reaction of TMPCl and a thiol with $TiCl_4$ catalysis.

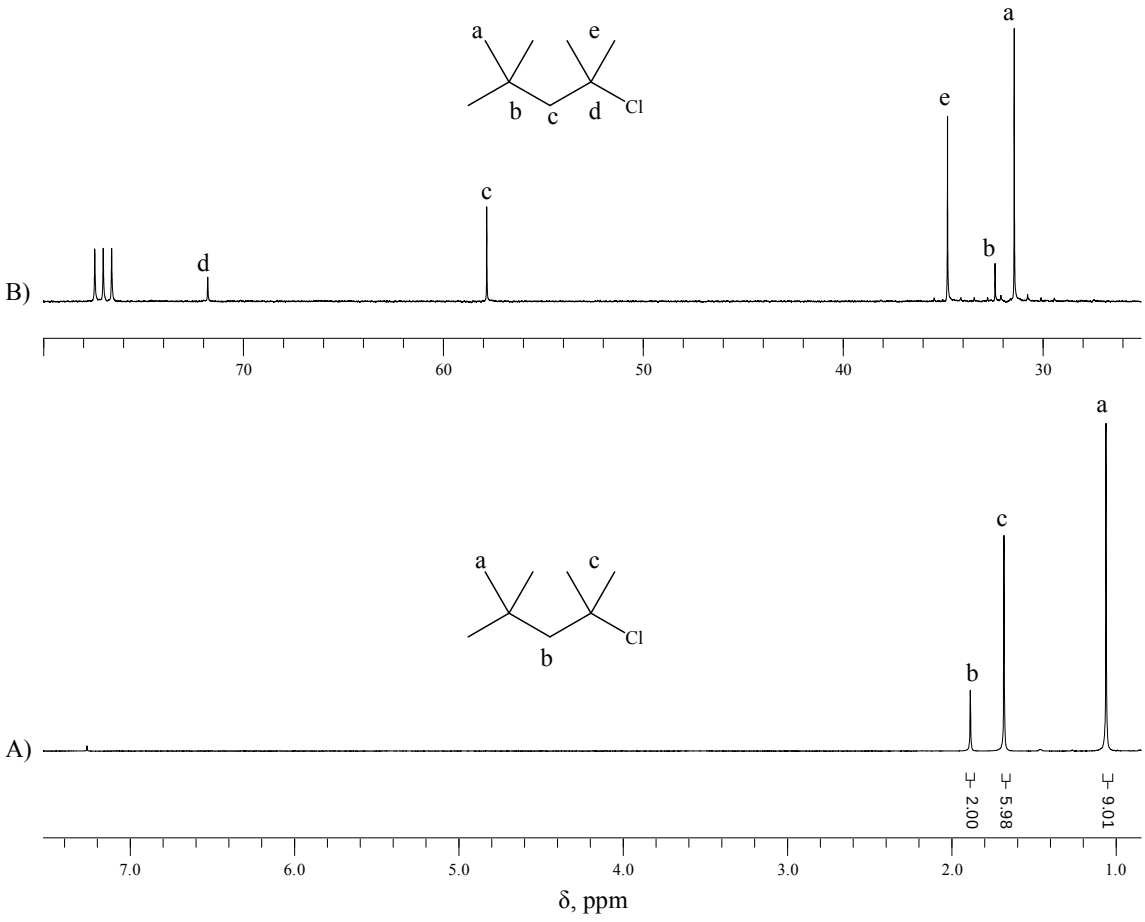


Figure 11. ^{1}H NMR (lower, A) and ^{13}C NMR (upper, B) spectra of 2-chloro-2,4,4-trimethylpentane

The initial studies with TMPCl were performed in pure methylene chloride at -70 °C using a series of *para*-substituted aromatic thiols, HS-C_6H_4-R (R = H, CH_3, OCH_3),

catalyzed by $TiCl_4$. Both [Thiol]:[TMPCl] and [$TiCl_4$]:[TMPCl] were varied, using a fixed 2 h reaction time. The results are summarized in Table 1 and the ^1H and ^{13}C NMR of the product sulfides appear in Figures 12 and 13, respectively.

Table 1

Effect of [Thiol] and [$TiCl_4$] on the Reaction Between TMPCl and Thiophenols

				Product Distribution by ^1H NMR (mol %)				
Entry	R	[SH]/ [CE]	[$TiCl_4$] / [CE]	Sulfide	*tert*-Cl	*exo*-olefin	*endo*-olefin	coupled
1	H	2.00	0.25	62.1	37.6	0.4	0.0	0.0
2	H	4.00	0.25	61.4	38.2	0.0	0.0	0.0
3	H	6.00	0.25	48.1	52.0	0.0	0.0	0.0
5	H	1.25	5.00	99.0	1.0	0.0	0.0	0.0
6	H	2.00	5.00	98.5	1.5	0.0	0.0	0.0
7	H	2.00	10.00	99.0	1.0	0.0	0.0	0.0
8	H[a]	4.00	10.00	99.0	1.0	0.0	0.0	0.0
9	CH_3	2.00	0.25	36.7	63.3	0.0	0.0	0.0
10	CH_3	4.00	0.25	44.0	56.0	0.0	0.0	0.0
11	CH_3	6.00	0.25	41.5	58.5	0.0	0.0	0.0
13	CH_3	1.25	5.00	98.5	1.5	0.0	0.0	0.0
14	CH_3	2.00	5.00	99.0	1.0	0.0	0.0	0.0
15	CH_3	2.00	10.00	99.0	1.0	0.0	0.0	0.0
16	CH_3[a]	4.00	10.00	99.0	1.0	0.0	0.0	0.0
18	OCH_3	1.25	5.00	100.0	0.0	0.0	0.0	0.0
19	OCH_3	2.00	5.00	99.0	1.0	0.0	0.0	0.0

Note. Reaction conditions: methylene chloride = 10 mL; TMPCl = 0.20 mL ([TMPCl] = 0.11 M); Temperature = -70°C, reaction time = 2 h. Reactions terminated by addition of 2 mL methanol. [a]Reactions terminated by addition of 4 mL methanol.

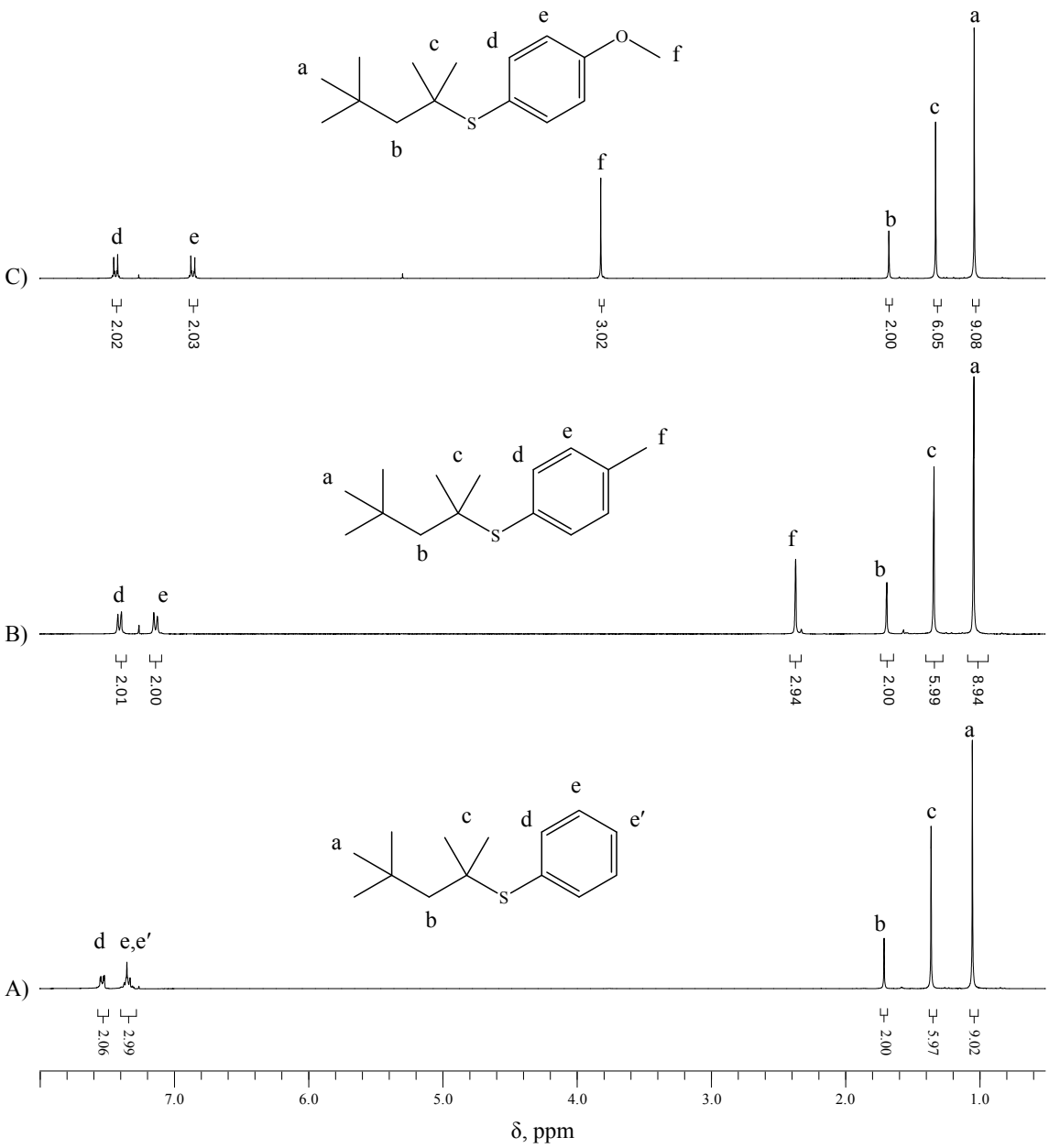


Figure 12. ^{1}H NMR spectra of A) (1,1,3,3-tetramethylbutylsulfanyl)benzene, B) 1-methyl-4-(1,1,3,3-tetramethylbutylsulfanyl)benzene, and C) 1-methyl-4-(1,1,3,3-tetramethylbutylsulfanyl)benzene, produced from $TiCl_4$-catalyzed reaction of TMPCl and thiophenol, 4-methylbenzenethiol, and 4-methoxybenzenethiol, respectively.

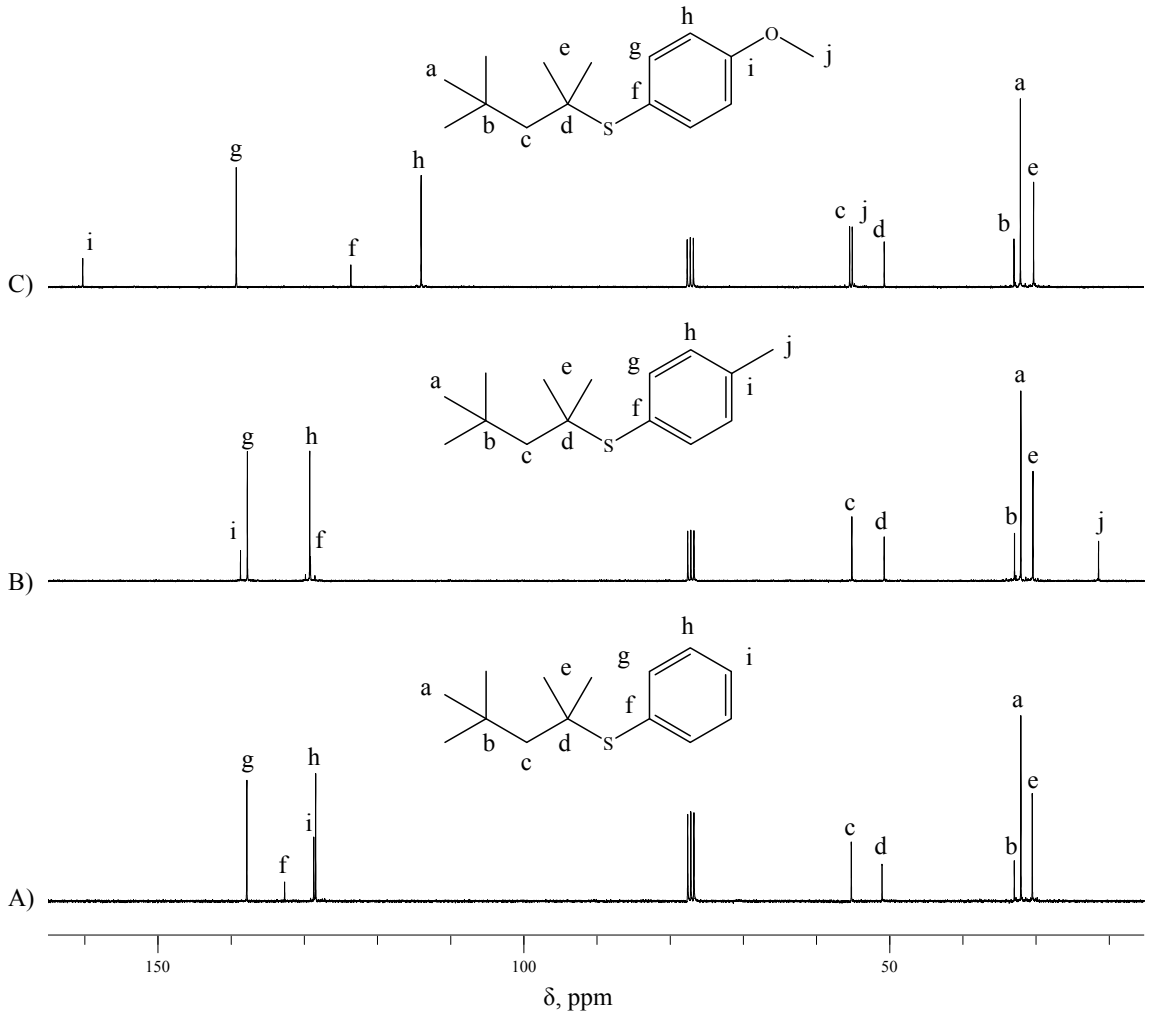


Figure 13. ^{13}C NMR spectra of A) (1,1,3,3-tetramethylbutylsulfanyl)benzene, B) 1-methyl-4-(1,1,3,3-tetramethylbutylsulfanyl)benzene, and C) 1-methoxy-4-(1,1,3,3-tetramethylbutylsulfanyl)benzene, produced from $TiCl_4$-catalyzed reaction of TMPCl and thiophenol, 4-methylbenzenethiol, and 4-methoxybenzenethiol, respectively.

In only one instance (Table 1, Entry 1) was any detectable olefin product formed during the $TiCl_4$-catalyzed reaction of TMPCl and *para*-substituted thiophenols; it is noteworthy that this occurred with the least nucleophilic thiol at its lowest concentration, conditions most favorable to the E1 mechanism. The ^1H NMR spectra of Figure 12 (Table 1, Entries 5, 14, and 18) show the disappearance of the methylene, at 1.88 ppm, and methyl groups, at 1.68 ppm, associated with the *tert*-Cl functional group. After reaction with thiophenol, the methylene peaks appear at 1.70 ppm and the methyls shift to

1.35 ppm. Furthermore, the single aromatic region of thiophenol becomes two distinct multiplets at 7.53 and 7.35 ppm, with an integration ratio of 2:3, indicating reaction through the thiol moiety and not alkylation, which would result in the loss of a proton and appearance of a pair of doublets of equal intensity, characteristic of *para*-substituted benzene. Additionally, no free thiol peak is present, which would be expected at 3.40 ppm. For 4-methylbenzenethiol, the sulfide methylene (1.68 ppm), sulfide methyls (1.33 ppm), and aromatic methyl (2.36 ppm) all appear, while the aromatic region is a pair of doublets at 7.40 and 7.14 ppm. With 4-methoxybenzenethiol, the sulfide methylene (1.67), sulfide methyls (1.32 ppm), and methoxy methyl (3.82 ppm) appear, along with the aromatic doublets at 7.43 and 6.86 ppm. In all cases, the *tert*-butyl protons show minimal movement, shifting from 1.05 ppm for TMPCl to 1.03-1.04 for the sulfides. The most notable shifts in the ^{13}C NMR spectra are the *tert*-Cl quaternary carbon (71.8 ppm) and methyl carbons (34.7 ppm) of TMPCl, which move to 50 and 30 ppm in the sulfide products.

When the concentration of $TiCl_4$ was low relative to both TMPCl and thiol (Table 1, Entries 1-3 and 9-11), the reactions were not completed in 2 h, but essentially only starting material and product were present at any time. Presumably, these reactions would go to completion if left for longer periods. Furthermore, while the extent of complexation between the thiol group and $TiCl_4$ has not yet been investigated, these same entries (where $[TiCl_4] < [SH]$) suggest that if complexation does occur to a significant extent, it does not prevent ionization. Conversely, when $TiCl_4$ is in excess to thiol ($[TiCl_4] > [SH]$), the thiol retains the ability to attack the carbocation and form a sulfide bond. No alkylation of the aromatic ring was observed in any instance.

Emboldened by these results, a battery of other thiols was reacted with TMPCl under conditions of excess $TiCl_4$ ([$TiCl_4$]:[TMPCl] = 5:1), with a low thiol excess ([Thiol]:[CE] = 1.25:1). The results are summarized in Table 2.

Table 2

Model Reactions of TMPCl with Various Thiols

		Product Distribution by ^{1}H NMR (mol %)				
Entry	Thiol	Sulfide	*tert*-Cl	*exo*-olefin	*endo*-olefin	coupled
1	thiophenol	99.0	1.0	0.0	0.0	0.0
2	4-methylbenzenethiol	98.5	1.5	0.0	0.0	0.0
3	4-methoxybenzenethiol	100.0	0.0	0.0	0.0	0.0
4	benzyl mercaptan	97.1	2.9	0.0	0.0	0.0
5	2-phenoxyethanethiol	99.5	0.5	0.0	0.0	0.0
6	3-chloro-1-propanethiol	100.0	0.0	0.0	0.0	0.0
7	2-mercaptoethanol	100.0	0.0	0.0	0.0	0.0
8	1-butanethiol	99.0	1.0	0.0	0.0	0.0
9	2-propanethiol	90.3	9.7	0.0	0.0	0.0
10	2-methyl-2-propanethiol	0.0	100.0	0.0	0.0	0.0
11	3-mercaptopropionic acid	99.5	0.5	0.0	0.0	0.0

Note. Reaction conditions: methylene chloride = 10 mL; TMPCl = 0.20 mL ([TMPCl] = 0.11 M); $TiCl_4$ = 0.65 mL ([$TiCl_4$]/[CE] = 5); [Thiol]/[CE] = 1.25. Temperature = -70°C, reaction time = 2 h. Reactions terminated by addition of 2 mL methanol.

In no case was any olefin or coupled species observed. Upon addition of $TiCl_4$, the clear and colorless solutions became a clear yellow color for all aliphatic thiols and dark red/black for the aromatic thiols. The reaction with benzyl mercaptan produced a substantial amount of white/yellow precipitate, which persisted throughout the reaction and was dissolved upon MeOH addition. If this was a thiol-$TiCl_4$ complex, it did not inhibit sulfide formation, as 97.1% sulfide formation was achieved in the 2 h reaction window. For most other reactions, the color either completely or largely disappeared upon MeOH addition.

The use of 2-phenoxyethanol provided a unique opportunity to compare the reactivity of the Friedel-Craft alkylation of an alkoxybenzene to the nucleophilic attack by a thiol on the tertiary carbocation (Table 2, Entry 5). The result was exclusively sulfide formation. The ^{1}H NMR spectrum of the reaction product is shown in Figure 3.4.

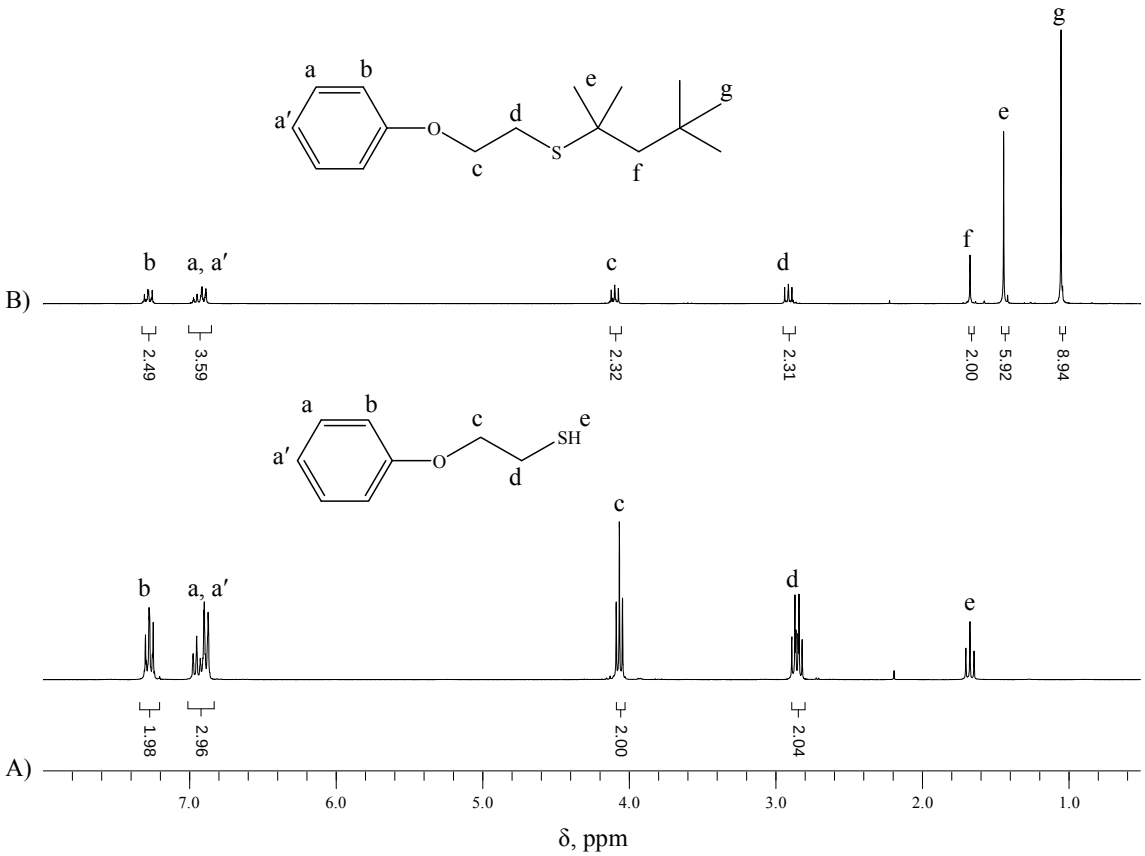


Figure 14. ^{1}H NMR spectra of A) 2-phenoxyethanethiol and B) [2-(1,1,3,3-tetramethylbutylsulfanyl)ethoxy]benzene produced by the $TiCl_4$-catalyzed reaction of TMPCl and 2-phenoxyethanethiol. Elevated integration values are due to residual 2-phenoxyethanethiol.

While some residual 2-phenoxyethanethiol is present, the ratio of *meta*/*para* to *ortho* phenyl group protons is 1.44, close to the ideal value of 1.5, indicating that the *para*-position has not been alkylated. Furthermore, no thiol protons are evident, and the methylene unit adjacent to the thiol group at 2.84 ppm is a quartet (overlapping doublet

of triplets) in 2-phenoxyethane thiol, but becomes a triplet at 2.90 ppm after reaction with TMPCl, indicating sulfide formation. The ^{13}C NMR spectra of 2-phenoxyethanethiol and [2-(1,1,3,3-tetramethylbutylsulfanyl)ethoxy]benzene are shown in Figure 3.5.

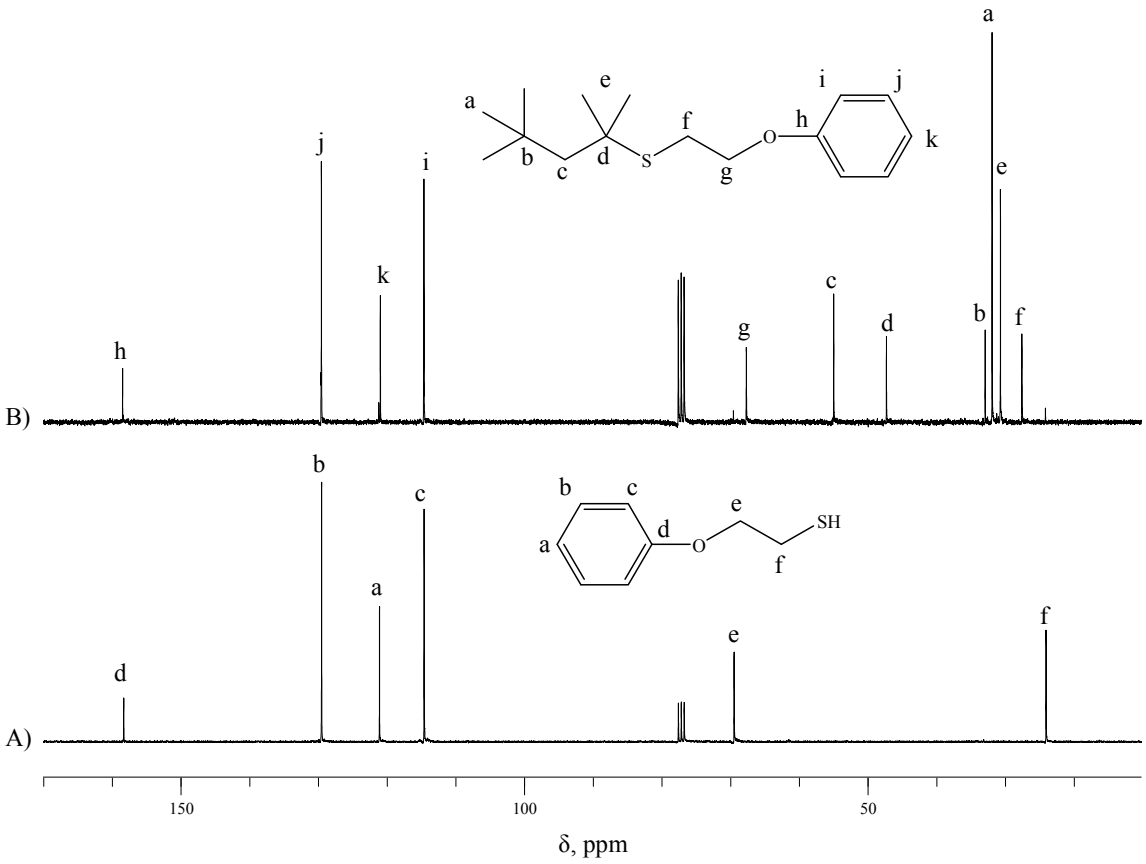


Figure 15. ^{13}C NMR spectra of A) 2-phenoxyethanethiol and B) [2-(1,1,3,3-tetramethylbutylsulfanyl)ethoxy]benzene produced by the $TiCl_4$-catalyzed reaction of TMPCl and 2-phenoxyethanethiol. Minor peaks due to residual 2-phenoxyethanethiol are present in spectrum B.

The tether protons of the thiol have shifted from 69.3 and 23.8 ppm to 67.5 ppm and 27.4 ppm, respectively, in the resulting sulfide. Additionally, the overall structure of the sulfide aromatic region is unchanged from that of the thiol. If alkylation of the phenyl ring had occurred, the alkylated phenyl carbon would be expected to shift to approximately 145 ppm, but clearly it does not move from its original location of approximately 121 ppm.[115]

A series of reactions between TMPCl and several increasingly bulky thiols provided insight into steric limitations. The methyl groups of TMPCl provide necessary carbocation stability but are nonetheless bulky units that impede the approach of large substituents. 2-Methyl-2-propanethiol is an equally bulky tertiary thiol that cannot easily approach the carbocation, and no reaction was observed within the 2 h time window. Interestingly, no elimination was observed in the isolated reaction product. In contrast, the primary thiol 1-propanethiol encountered no steric resistance, readily reaching near quantitative conversion under the same conditions (Figure 3.6). The secondary thiol, 2-propanethiol, was somewhat hindered sterically, reaching about 90% conversion; although the full effect of steric bulk between 1° and 2° thiols was moderated by the reaction conditions, which were highly favorable towards the rate limiting carbocation formation step.

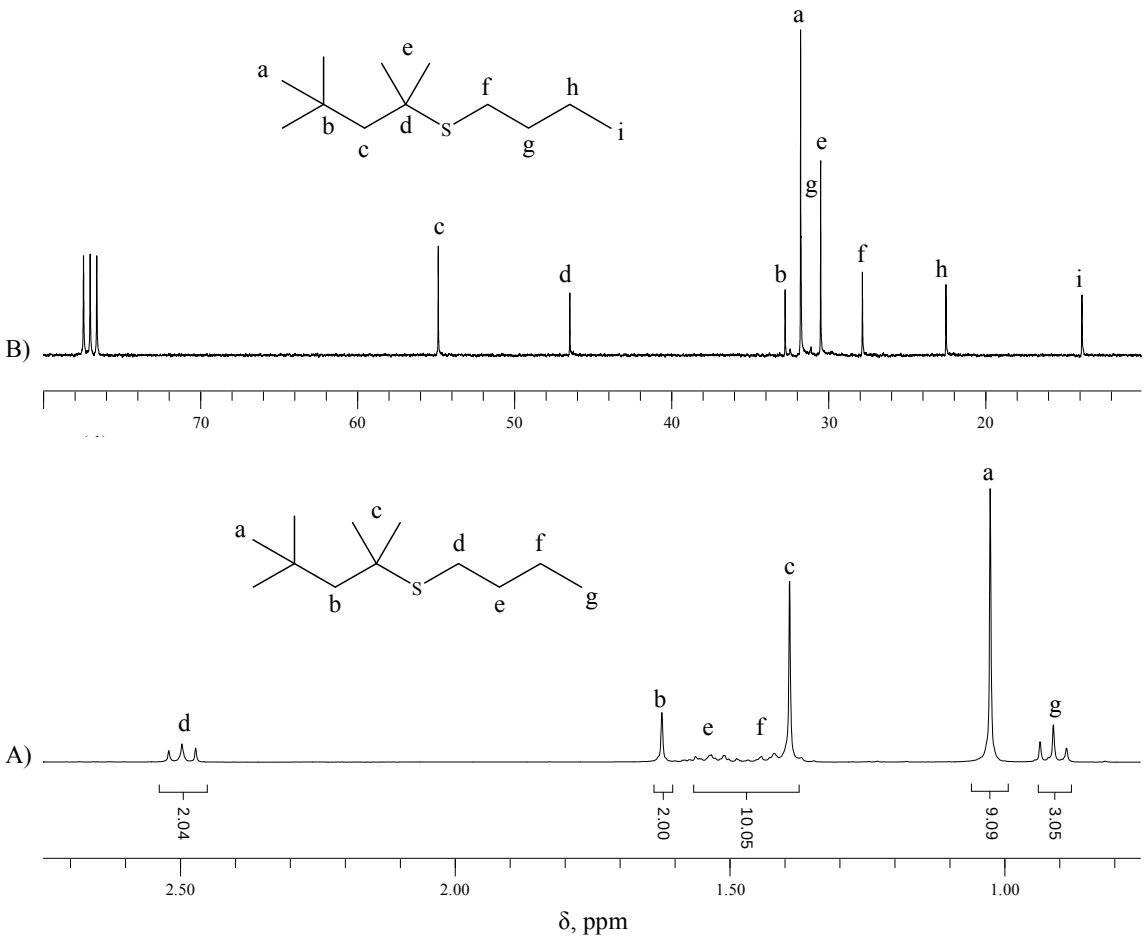


Figure 16. A) ^{1}H NMR, and B) ^{13}C NMR spectra of 2-butylsulfanyl-2,4,4-trimethylpentane produced from $TiCl_4$-catalyzed reaction of TMPCl and 1-butanethiol

The use of functional thiols to make functionalized PIBs would greatly expand the utility of the thiol substitution mechanism. To this end, several species were successfully reacted with TMPCl. Alkyl chloride was added through the use of 3-chloro-1-propanethiol, shown in Figure 17. The methylene tethers of the alkyl chloride unit appear at 3.64 ppm (triplet), 2.65 ppm (triplet), and 2.01 ppm (multiplet). The methyl groups adjacent to the sulfide linkage appear as a singlet at 1.40 ppm, and the methylene and *tert*-butyl units of the TMP residue are observed at 1.63 and 1.03 ppm, respectively.

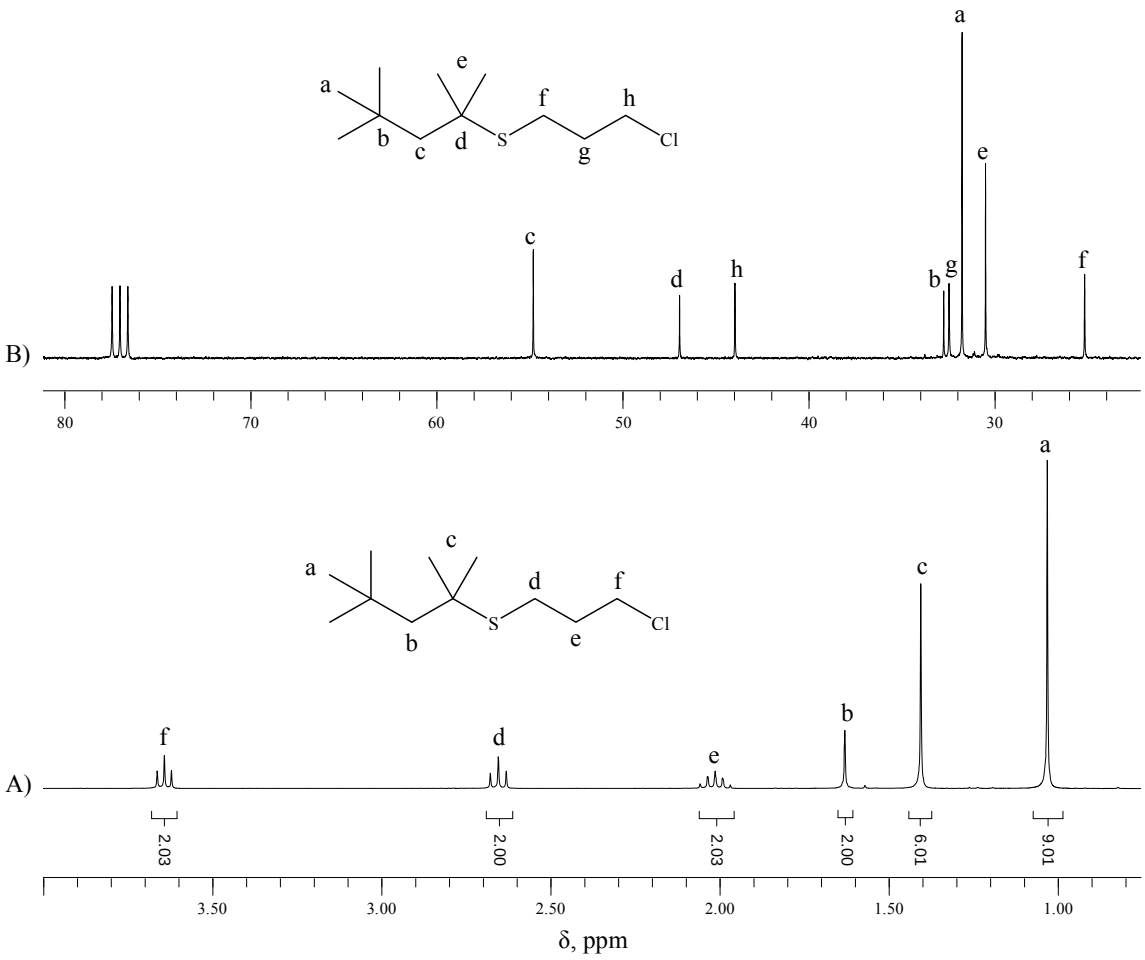


Figure 17. A) ^{1}H NMR, and B) ^{13}C NMR spectra of 2-(3-chloropropylsulfanyl)-2,4,4-trimethylpentane produced from $TiCl_4$-catalyzed reaction of TMPCl and 3-chloro-1-propanethiol.

In the ^{13}C spectrum, the alkyl chloride methylene units appear at 43.9 ppm, 32.4 ppm, and 25.1 ppm. While highly effective in the reaction with TMPCl, 3-chloro-1-propanethiol may not be the most economical method for introduction of primary chloride, due to the high cost of the molecule.

Direct *in situ* synthesis of hydroxyl-terminated polyisobutylene has long been an important synthetic goal. Unfortunately, hydroxyl moieties rapidly form strong complexes with $TiCl_4$, requiring either protecting groups that must be removed subsequent to quenching,[115,117] or large excesses of $TiCl_4$ relative to the chain end to

achieve quantitative conversion.[115] 2-Mercaptoethanol is a hydroxyl-functional thiol commonly used in biochemistry to cleave disulfide bonds and is an inexpensive multifunctional species that is less malodorous than many other thiols. The reaction with TMPCl under the conditions described in Table 2 (Entry 7) achieved full conversion to the Markovnikov sulfide product, shown in Figure 18. In the ^{1}H spectrum, two sets of peaks corresponding to the methylene units of the 2-mercaptoethanol residue appear as triplets at 3.59 ppm and 2.85 ppm, with the hydroxyl proton appearing at 2.73 ppm. In the ^{13}C spectrum, the 2-mercaptoethanol-originating methylene units appear at 43.4 and 30.5 ppm. In contrast, the anti-Markovnikov product would contain a chiral tertiary carbon, which would render the adjacent methylene protons diastereomeric, resulting in 8 sets of peaks in the ^{1}H NMR spectrum compared to 6 for the Markovnikov product.

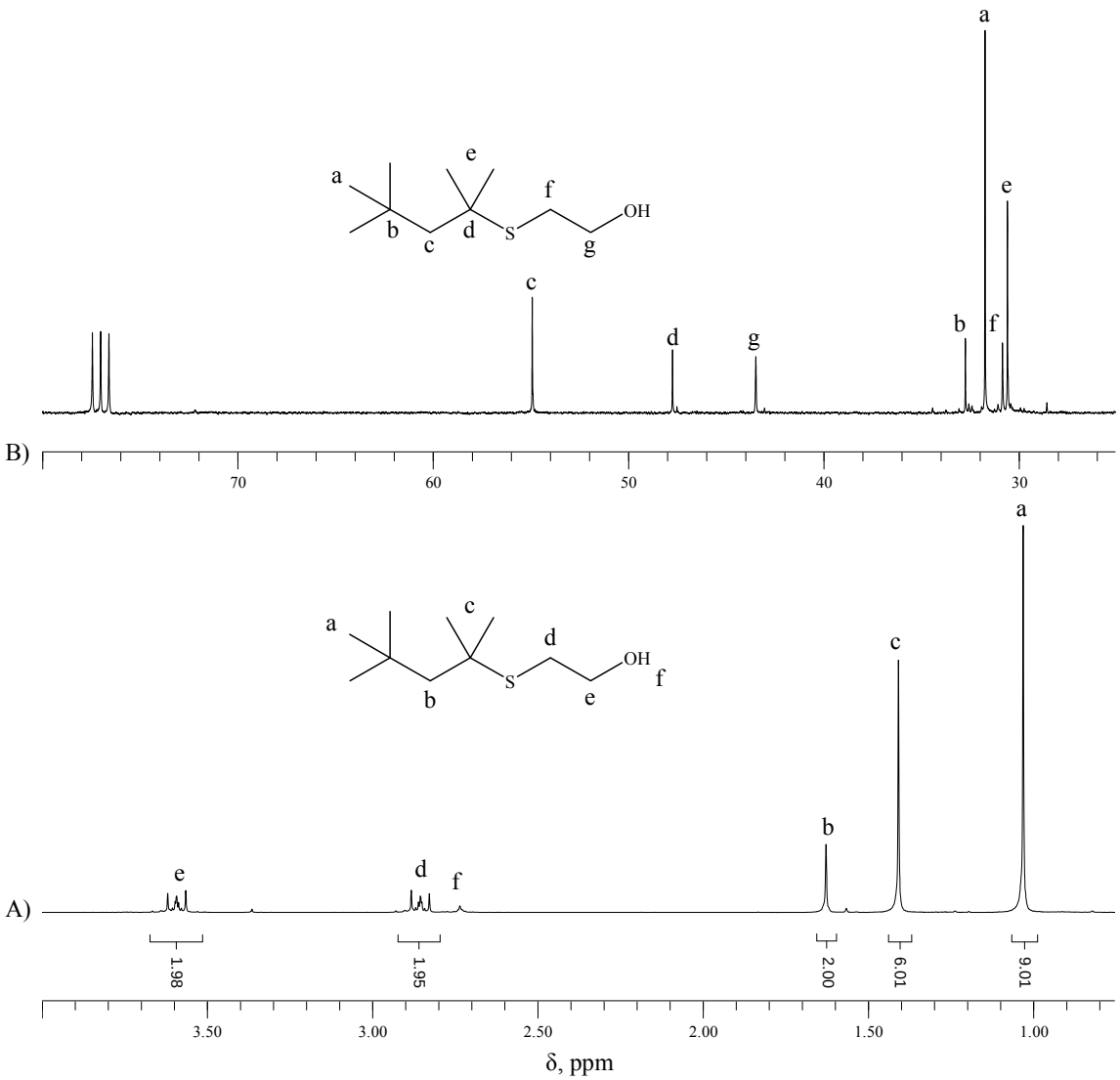


Figure 18. A) ^{1}H NMR, and B) ^{13}C NMR spectra of 2-(1,1,3,3-tetramethyl-butylsulfanyl)ethanol produced from $TiCl_4$-catalyzed reaction of TMPCl and 2-mercaptoethanol.

Gorski et al. described two complications of the S_N1 reaction between TMP and 2-mercaptoethanol.[126] First, the formation of side products as a result of sulfur oxidation limited the product yield to 10-15%. Second, a greater than stoichiometric equivalent of BF_3-OEt_2 was required for the reaction to proceed; whereas a non-hydroxyl-containing thiol, i.e. 1-ocytlthiol, proceeded with only 5 mol% catalyst. In this work, no sulfur oxidation was observed in any $TiCl_4$-catalyzed reactions between TMPCl and

2-mercaptoethanol, with isolated product yields as high as 95% being achieved. The aforementioned requirement of a stoichiometric excess of catalyst was expected, given the known tendency of hydroxyls to complex with Lewis acids. To examine the extent of catalyst consumption by the hydroxyl group of 2-mercaptoethanol, a series of reactions was run in which the [$TiCl_4$]:[2-mercaptoethanol] ratio was varied while maintaining a fixed [2-mercaptoethanol]:[TMPCl] ratio of 1.25 in pure methylene chloride at -70 °C. Reactions were allowed to proceed for 2 h, and then the $TiCl_4$ was deactivated by the addition of 2 mL neat MeOH. The results are shown in Table 3.

Table 3

Reaction of TMPCl and 2-Mercaptoethanol with Varying [$TiCl_4$]

		Product Distribution by ^{1}H NMR (mol %)				
Entry	[$TiCl_4$]/[Thiol]	Sulfide	*tert*-Cl	*exo*-olefin	*endo*-olefin	coupled
1	4.0	100.0	0.0	0.0	0.0	0.0
2	1.6	93.9	6.1	0.0	0.0	0.0
3	1.2	87.7	12.3	0.0	0.0	0.0
4	1.0	82.6	17.4	0.0	0.0	0.0
5	0.8	78.7	21.3	0.0	0.0	0.0
6	0.5	11.4	82.5	5.3	0.9	0.0

Note. Reaction conditions: methylene chloride = 10 mL; TMPCl = 0.20 mL ([TMPCl] = 0.11 M); 2-mercaptoethanol = 0.10 mL ([Thiol]/[CE] = 1.25). Temperature = -70°C, reaction time = 2 h. Reactions terminated by addition of 2 mL methanol.

Interestingly, under these conditions, addition proceeds even when the stoichiometric amount of $TiCl_4$ is less than or equal to the amount of 2-mercaptoethanol, conditions in which the reaction would not be expected to proceed at all. Catalyst complexation with the hydroxyl moiety is occurring, as evidenced by the decreasing conversions in the fixed reaction time as [$TiCl_4$] decreases, but complexation is not

enough to fully inhibit the reaction. Only at the lowest level, 0.5:1 [$TiCl_4$]:[Thiol] is the addition reaction sufficiently slowed to permit competitive elimination reactions.

The final functionality tested with TMPCl was carboxylic acid, in the form of 3-mercaptopropionic acid, under the conditions stated in Table 2. The reaction proceeded via addition as expected, but upon terminating the reaction with MeOH, it was found that the carboxylic acid moiety had reacted with methanol to form the methyl ester. The ^{1}H and ^{13}C NMR spectra of the methyl ester product are shown in Figure 19. In the ^{1}H NMR spectrum, the methylene units of the 3-mercaptopropionate unit appear as triplets at 2.75 and 2.54 ppm, with the methyl unit of the ester appearing as a singlet at 3.67 ppm. In the ^{13}C spectrum, the methylene carbons resonate at 34.4 and 23.1 ppm, the carbonyl carbon at 172.5 ppm, and the methyl carbon at 51.7 ppm. A second attempt at this reaction utilizing 1 M aqueous NaOH deactivated the $TiCl_4$ without esterifying the carboxylic acid terminus.

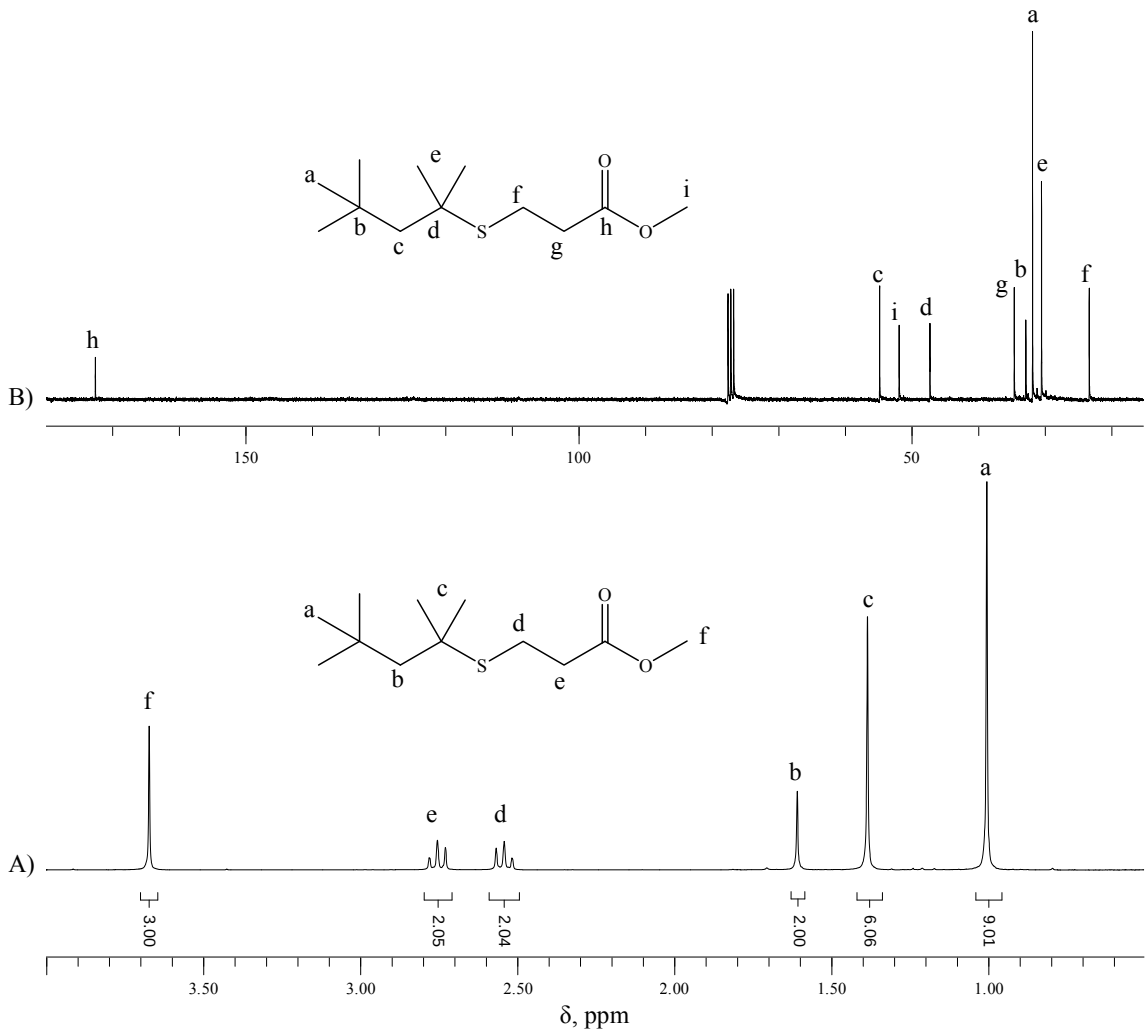


Figure 19. A) ^{1}H NMR, and B) ^{13}C NMR spectra of 3-(1,1,3,3-tetramethyl-butylsulfanyl)propionic acid methyl ester produced from $TiCl_4$-catalyzed reaction of TMPCl and 3-mercaptopropionic acid.

In situ Quenching of Masterbatch PIB with Thiols

The previously synthesized difunctional masterbatch PIB was returned to living cationic polymerization conditions to examine the quenching ability of free thiols onto PIB chain ends. Under polymerization conditions, the solvent medium is substantially less polar than for the small molecule TMPCl reactions in order to sufficiently dissolve the PIB and depress the ionization rate, as too much chain end ionization can result in chain end rearrangements or coupling. Indeed, the masterbatch PIB was itself not ideal,

containing 73% *tert*-Cl termini, 17% *exo*-olefin termini, and 10% *endo*-olefin termini. However, this proved beneficial as it allowed for the simultaneous observation of thiol quenching behavior in the presence of all commonly observed termini in living PIB synthesis. Morgan et al. observed that alkoxybenzene quenchers are alkylated by Glissopal® and in living polymerizations that are less than ideal, olefin termini are ultimately alkylated as well. The generation of HCl by the alkoxybenzene alkylation readily hydrochlorinates both *exo*- and *endo*-olefin chain ends, converting them into *tert*-Cl chain ends, which then reenter the sequence of ionization and alkylation.[115] With thiol quenching, that mechanism was again shown, wherein the large fractions of olefin termini were essentially eliminated by the end of the reaction. Figure 20 shows the reaction product after 5 h quenching with thiophenol. Olefin and *tert*-Cl peaks are absent, and peaks due to the aromatic thiophenol now appear, split into 2 multiplets with an integration ratio of 2:3, indicating no alkylation of the phenyl ring. Thus reaction proceeded via the thiol unit only, to form a sulfide linkage. Other reactions using 4-methoxybenzenethiol and 3-chloro-1-propanethiol likewise demonstrated the near total conversion of the chain ends to sulfide linkages (Figure 21). In the ^{1}H NMR spectrum of 4-methoxybenzenethiol-quenched PIB, the aromatic region consists of two sets of doublets of equal integration value at 7.44 and 6.85 ppm and a large singlet at 3.81 ppm corresponding the methoxy methyl group. For 3-chloro-1-propanethiol-quenched PIB, the methylene tether protons appear at 3.65 ppm, 2.66 ppm, and 2.02 ppm.

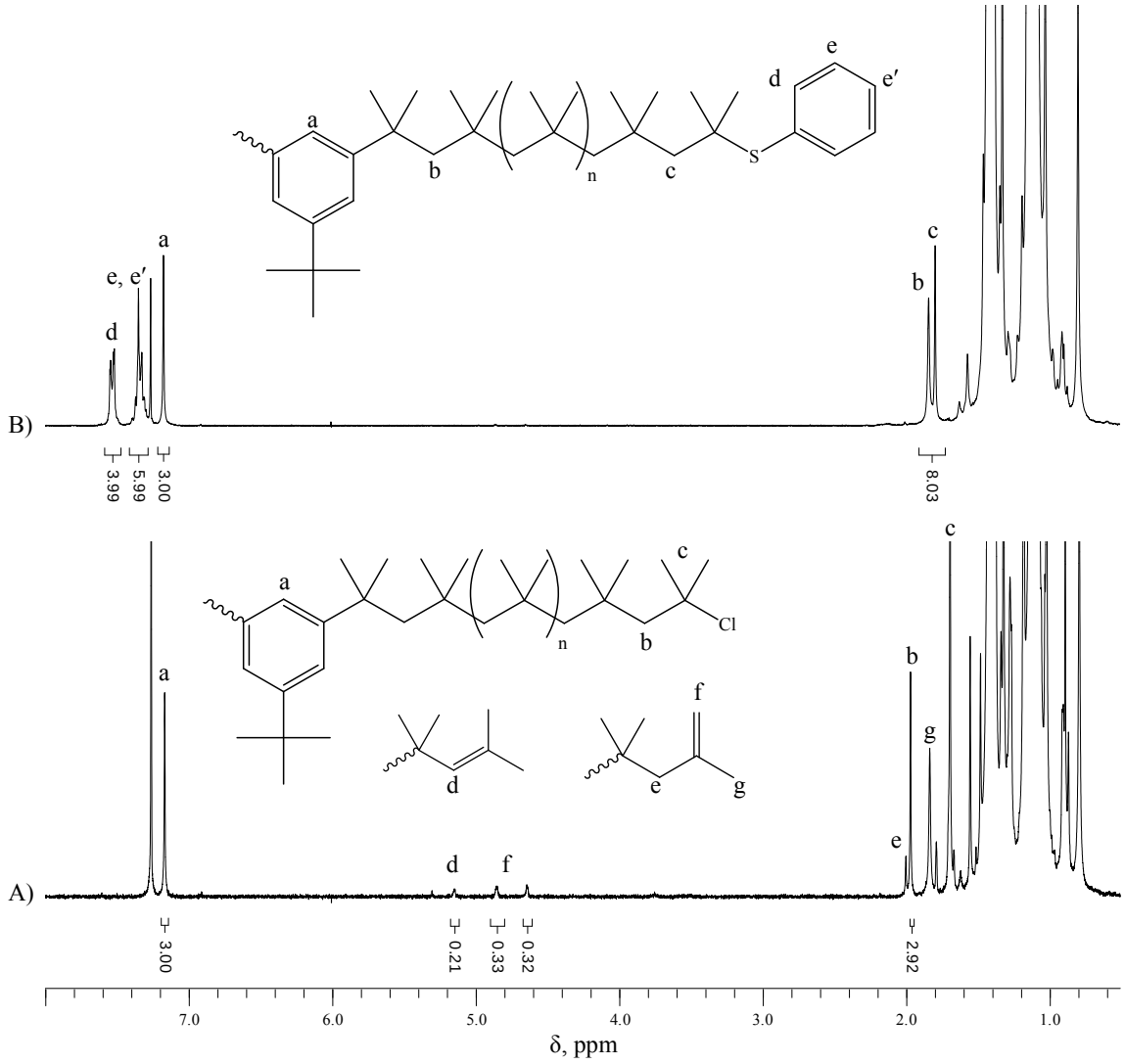


Figure 20. ^{1}H NMR spectra of A) masterbatch difunctional PIB containing a mixture of *tert*-Cl, *exo*-, and *endo*-olefin termini, and B) *α,ω*-PIB-benzenesulfide produced by $TiCl_4$-catalyzed quenching of masterbatch difunctional-PIB.

In the ^{13}C spectrum (Figure 22, B), the methylene tether carbons appear at 47.2 ppm, 43.9 ppm, and 25.2 ppm. In the ^{13}C spectrum of thiophenol-quenched PIB (Figure 22, A), the aromatic carbons are readily visible at 137.8 ppm, 132.7 ppm, 128.6 ppm, and 128.3 ppm.

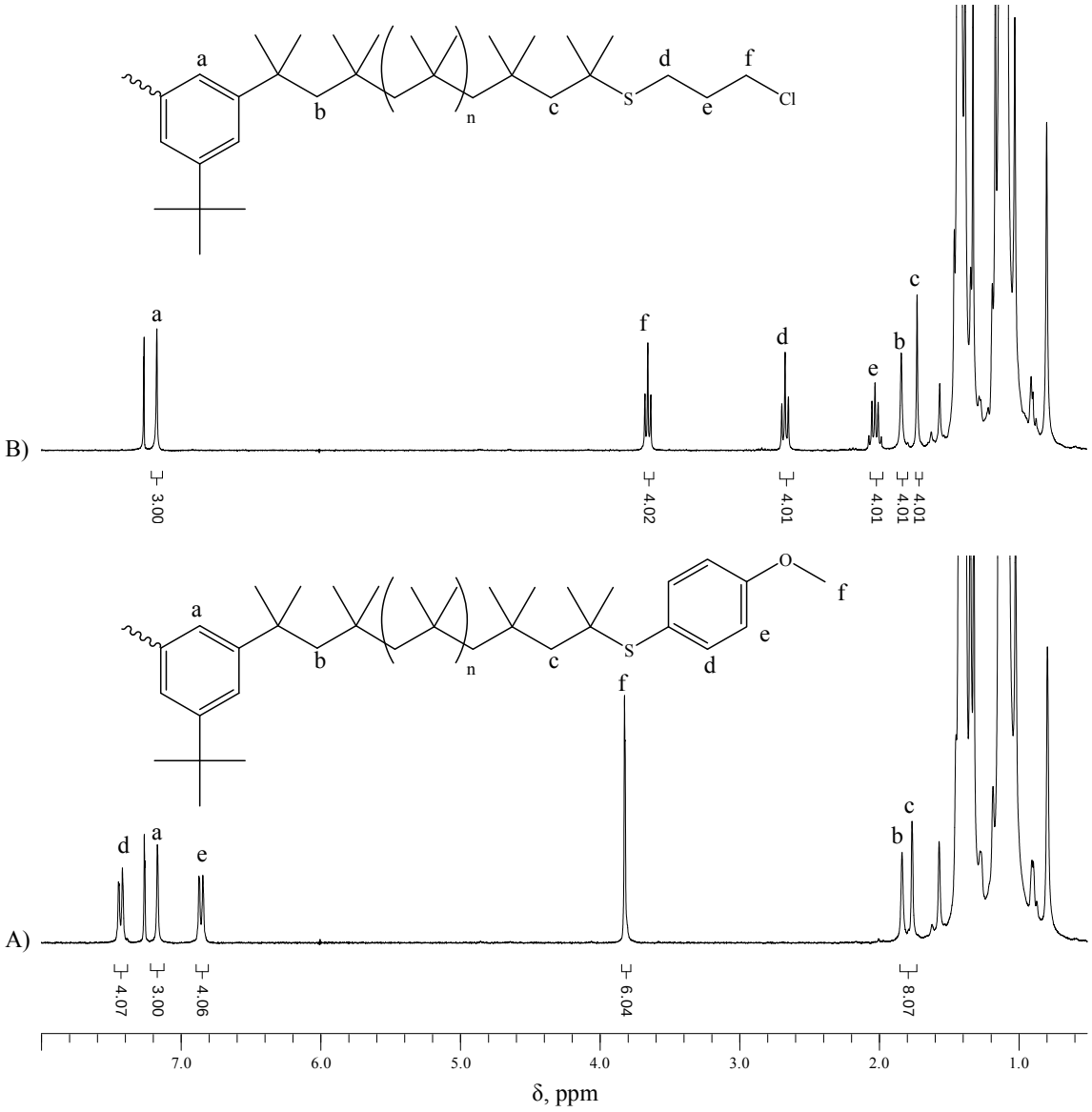


Figure 21. ^{1}H NMR spectra of A) *α,ω*-PIB-4-methoxybenzenesulfide and B) *α,ω*-PIB-3-chloropropylsulfide, produced from $TiCl_4$-catalyzed in situ quenching of masterbatch difunctional-PIB with 4-methoxybenzenethiol and 3-chloro-1-propanethiol, respectively.

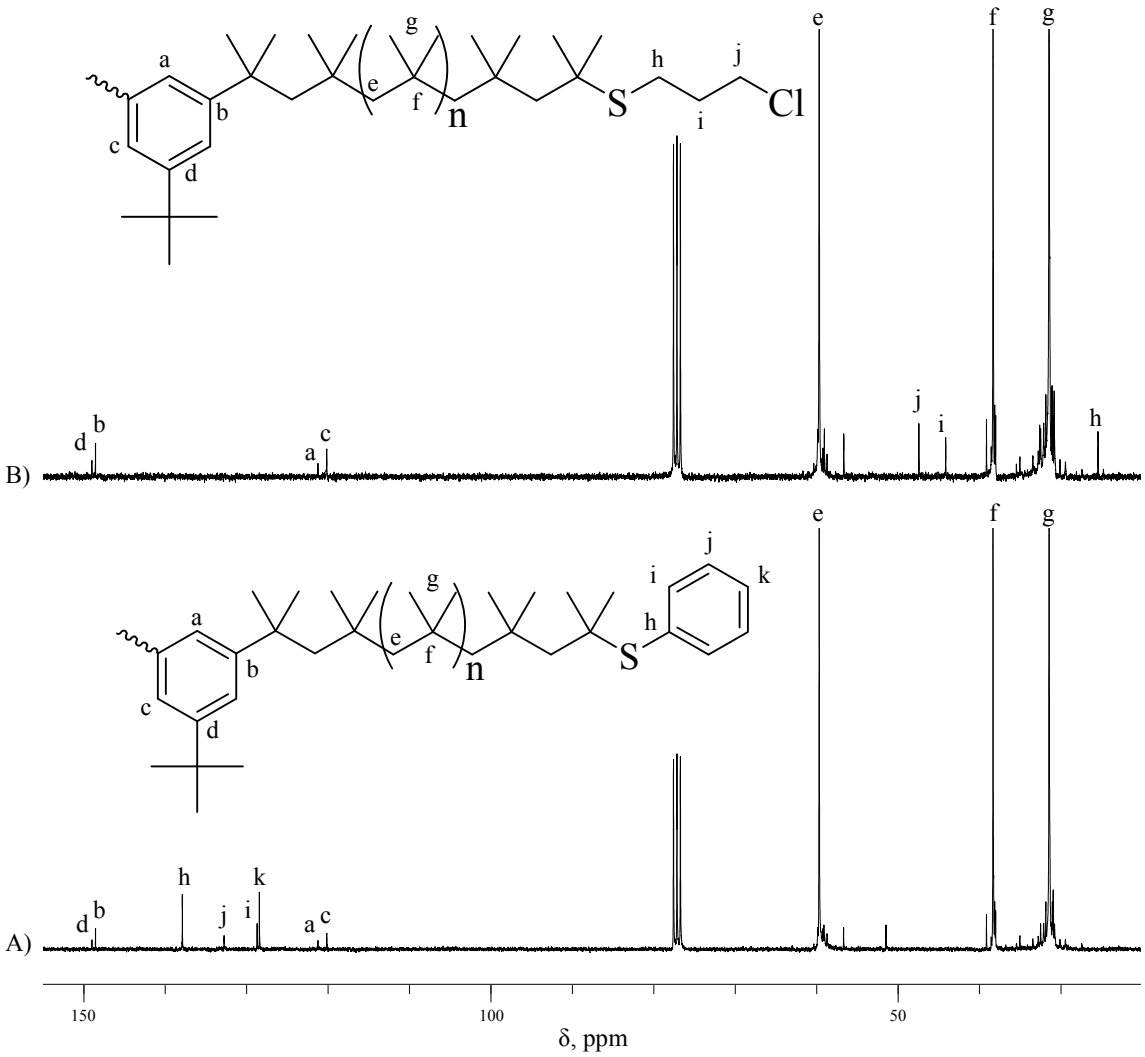


Figure 22. ^{13}C NMR spectra of A) *α,ω*-PIB-benzenesulfide and B) *α,ω*-PIB-3-chloropropylsulfide, produced from $TiCl_4$-catalyzed in situ quenching of masterbatch difunctional-PIB with thiophenol and 3-chloro-1-propanethiol, respectively.

GPC analysis of the masterbatch PIB showed no coupling or polymer degradation due to thiol addition. The RI GPC traces for the starting masterbatch PIB and the three thiol quenched samples are shown in Figure 23 and the numerical GPC data in Table 4.

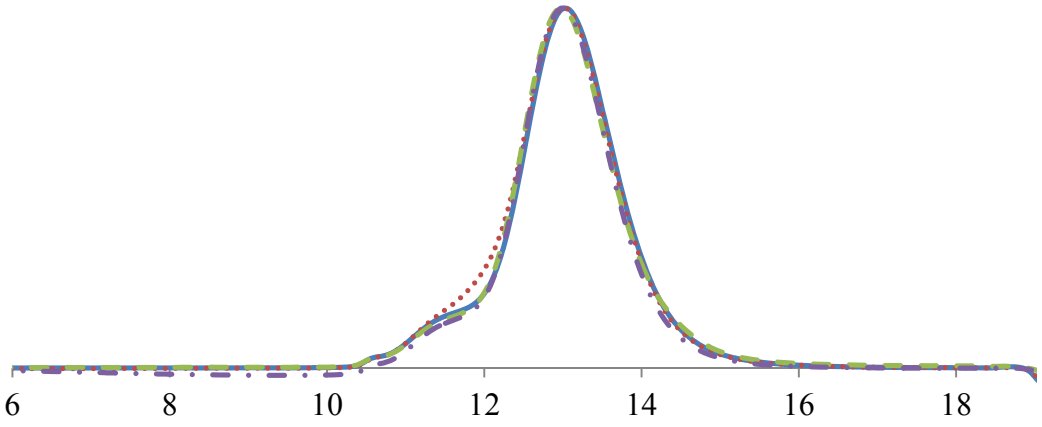


Figure 23. GPC RI traces of *α,ω*-PIB-^{t}Cl (solid), *α,ω*-PIB-benzenesulfide (dotted), *α,ω*-PIB-4-methoxybenzenesulfide (dashed), and *α,ω*-PIB-3-chloropropylsulfide (dot dash)

Table 4

GPC Results for Masterbatch and Thiol-Quenched Polyisobutylenes

Entry	Quencher	M_n (g/mol)	PDI
1	masterbatch	4000	1.33
2	thiophenol	4300	1.28
3	4-methoxybenzenethiol	4100	1.31
4	3-chloro-1-propanethiol	4200	1.29

MALDI-TOF-MS analysis was performed on the thiol-quenched PIB species to confirm the presence of the thiol end-groups. The individual MALDI-TOF spectra are shown in Figures 24-26. All were produced with AgTFA cationizing agent and show a backbone repeat structure with ~56 Da differences between the individual peaks. Linear regression was used to calculate the end group MWs, and the data are shown in Table 5. MW_{Theo} was calculated using Equation 4:

$$MW_{Theo} = 2*EG + I + C$$

Equation 4. Calculation of Theoretical Molecular Weights

where, EG is MW of the thiol quencher minus a single proton lost during quenching, I is the MW of the initiator residue, and C is the molecular weight of the cationizing agent cation, silver.

Table 5

MALDI-TOF-MS Regression Analysis for Thiol-quenched Polyisobutylenes

End-Group	End-Group MW (g/mol)	MW_{Theo} (g/mol)	MW_{Exp} (g/mol)	Difference (g/mol)
thiophenol	109.17	434.71	436.64	1.93
4-methoxybenzenethiol	139.20	494.76	492.82	1.94
3-chloro-1-propanethiol	103.55	495.89	493.31	2.58

In the case of the 3-chloro-1-propanethiol quencher, a reaction occurred between the silver cation and the chlorine atom. Assuming that a single chlorine atom was fragmented from the chain and its mass replaced by a silver atom provides the best agreement between MW_{Theo} and MW_{Exp} for that sample.

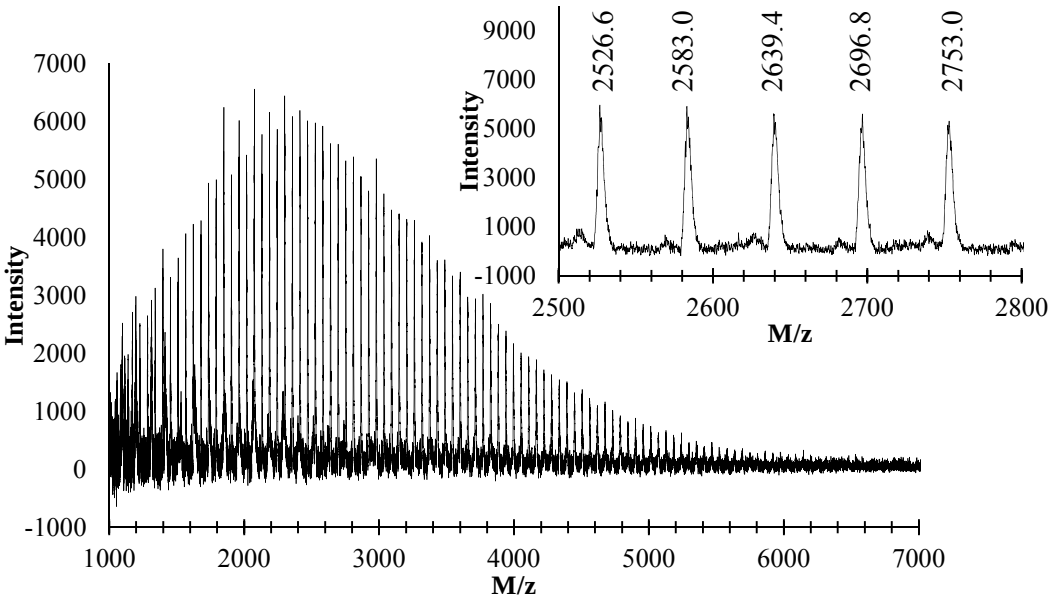


Figure 24. MALDI-TOF-MS spectrum of α,ω-PIB-benzenesulfide.

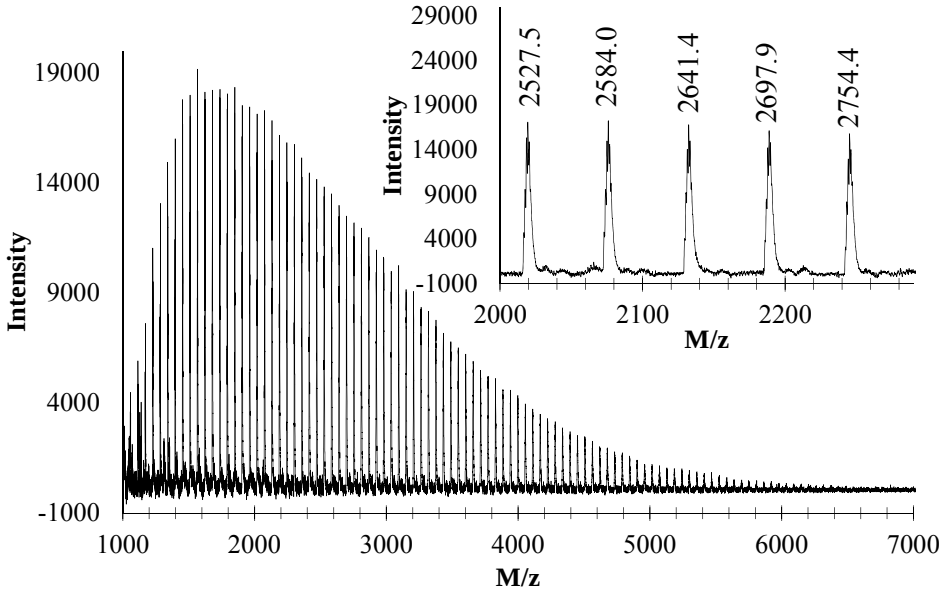


Figure 25. MALDI-TOF-MS spectrum of α,ω-PIB-4-methoxybenzenesulfide.

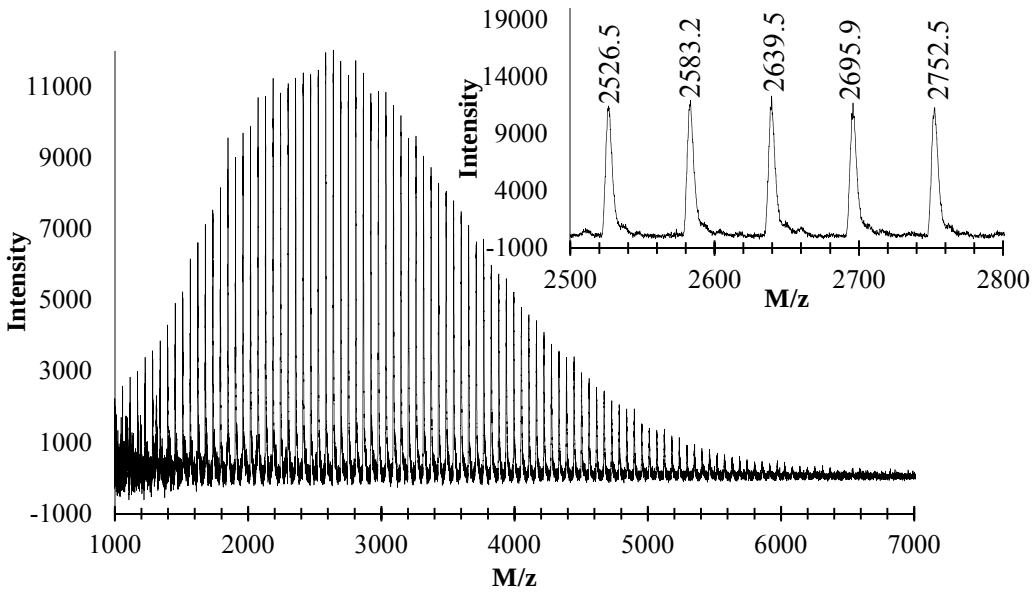


Figure 26. MALDI-TOF-MS spectrum of α,ω-PIB-3-chloropropylsulfide.

Conclusions

The direct addition of a free thiol to a tertiary carbocation has been observed using $TiCl_4$ catalysis for both TMPCl and pre-formed masterbatch PIB. For TMPCl, at -70 ºC in pure methylene chloride, thiols with varied structures were observed to form sulfide in quantitative or nearly quantitative amounts in 2 h. Thiol quenching of PIB was performed under living polymerization conditions of 40/60 (v/v) hexane/MeCl and near quantitative alkylation was observed of both *tert*-Cl and olefin terminated PIB chains. Further study of the *in situ* synthesis and thiol quenching of the living cationic polymerization of polyisobutylene is underway.

CHAPTER III

SYNTHESIS OF TELECHELIC POLYISOBUTYLENE PREPOLYMERS BY CARBOXYLATE SUBSTITUTION

Introduction

Polyisobutylene (PIB) is a saturated hydrocarbon elastomer with unique properties, including gas impermeability, thermal and oxidative stability, and high mechanical damping, which lead to its use in a number of important and diverse applications. Some of these applications, particularly those in the fuel and lubricating oil area, require PIB grades with reactive terminal functionality to allow further derivatization. Commercial PIBs produced via BF_3-catalysis, such as Glissopal®, contain approximately 70-90% *exo*-olefin termini, but the chain transfer-dominated polymerization process inherently produces only monofunctional polymers.[73,74] Living cationic polymerization techniques produce telechelic mono- and di-functional PIBs with excellent molecular weight control and narrow (<1.2) polydispersities.[27] Unless an external quenching compound is employed, the PIB chain ends in living polymerization are exclusively *tert*-chloride.[134]

Addition of a suitable, external quenching compound to living PIB enables the facile synthesis of functional PIBs within the polymerization reactor. Several classes of quenchers have been developed to produce various functionalities at the chain ends. Hindered bases, such as 2,6-dimethylpyridine and 1,2,2,6,6-pentamethylpiperidine, cause elimination at the carbenium ion to form exclusively *exo*-olefin.[77,78] Other classes of quenchers operate through addition to the carbenium ion. Sulfides, such as di-*tert*-butyl sulfide, and ethers, such as diisopropyl ether, add to the carbenium ions as they are

formed to generate stable sulfonium[81] or oxonium[84] cations at 100% of the chain ends that, upon decomposition by a base or methanol, produce solely *exo*-olefin termini.

To produce functional PIBs other than *exo*-olefin, a popular method is to use a quencher in which the functional group of interest is tethered to another functional group, such as an activated aromatic ring, that is capable of addition to the carbenium ion. Numerous functionalities have been introduced in this manner, including hydroxyl,[117] amine, and alkyne.[115] In terms of synthetic variety, primary halogen termini, particularly bromine, represent a very versatile functional group. Several classes of functional quenchers have been developed that lead to primary halogen-terminated PIB, including 1,3-butadiene[99] and alkoxybenzenes, such as 3-bromopropoxybenzene.[119,120] PIBs with primary bromine-termini have been shown to be highly effective as substrates for S_N2 reactions for installation of numerous functionalities, such as vinyl ether,[101] thiol,[133] hydroxyl,[115] and amine.[135]

Acrylate and methacrylate-terminated PIBs offer the potential for synthesis of PIB networks with high hydrolytic and oxidative resistance, as well as excellent mechanical damping. (Meth)acrylate-PIBs have been synthesized via both acid halide reaction with hydroxyl-terminated PIB and by substitution of bromoallyl-terminated PIB produced using 1,3-butadiene quenching.[101] However, 1,3-butadiene produces allyl chloride end groups unless an entirely brominated Lewis acid catalyst system is utilized.[136] Due to the complexity of the latter remedy, and since chloride does not perform nearly as well as bromide in typical S_N2 reactions, bromide functionalities must be added in a separate halogen exchange reaction using LiBr.[100] (3-Bromopropoxy)benzene provides primary bromine functionality without special catalysts or post-polymerization modification. In

this work, carboxylate-type nucleophiles have been utilized to displace bromine termini to produce (meth)acrylate and tetrahydroxy-functional PIBs.

Experimental

Materials

Titanium tetrachloride ($TiCl_4$) (99.9%), hexane (anhydrous, 95%), (3-bromopropoxy)benzene (96%), (2-bromoethoxy)benzene (98%), 2,6-lutidine (≥99%), *N*,*N*-dimethylformamide (DMF) (≥99.9%), methanol (anhydrous, 99.8%), tetrabutylammonium bromide (≥99.0%), hydroquinone monomethyl ether (MEHQ, ≥98.0%), acrylic acid (99%), and 2,2-bis(hydroxymethyl)butyric acid (98%) were purchased and used as received from Sigma-Aldrich. Methacrylic acid (99.5%) was purchased from Acros Organics and used as received. Heptane (98.3%, HPLC grade) and potassium hydroxide (ACS grade) were purchased from Fisher Scientific and used as received. THF (HPLC grade) was purchased from Fisher Scientific and distilled over CaH_2 prior to use. Methyl chloride (CH_3Cl, Alexander Chemical Corp, 99.95%), and isobutylene (BOC Gases, 99.5%) were dried by flowing the gaseous reagents through packed columns of $CaSO_4$/4 Å molecular sieves and $CaSO_4$, respectively, and condensed in a N_2-atmosphere glovebox immediately prior to use. Cationic initiators 2-chloro-2,4,4-trimethylpentane (TMPCl) and 1,3-bis-(1-chloro-1-methylethyl)-5-*tert*-butylbenzene (bDCC) and phenoxy bromide terminated polyisobutylenes were synthesized as previously described.[115]

Instrumentation

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) was performed using a Bruker Microflex LRF MALDI-TOF mass spectrometer equipped with a nitrogen laser (337 nm) possessing a 60 Hz repetition rate

and a 50 μJ energy output. PIB homopolymer samples were prepared using the dried-droplet method. For PIB homopolymer, a 20 mg/mL matrix (dithranol) solution, a 10 mg/mL cationizing agent (silver trifluoroacetate or sodium trifluoroacetate) (AgTFA or NaTFA) solution, and a 10 mg/mL polymer solution, all in THF, were mixed in a volumetric ratio of matrix:sample:cationizing agent = 10:10:1, and then a 0.5 μL aliquot was applied to a MALDI sample target for analysis. All spectra were obtained in the positive ion mode utilizing the reflector mode micro-channel plate detector and are the sum of 900-1000 shots. Molecular weights of the polymer end groups were determined by linear regression using the known molecular weight of the initiator residue (1,3-diisopropyl-5-tertbutylbenzene) and cationizing agent cation (Ag+ or Na+).

Gel permeation chromatography (GPC) was used to measure all number average molecular weights (M_n) and polydispersities (PDI = M_w/M_n) using a system composed of a Waters Alliance 2695 separations module, an online laser light scattering (MALLS) detector equipped with a 20 mW gallium arsenide laser operating at 658 nm (miniDAWN TREOS, Wyatt Technology Corp.) and an interferometric refractometer operating at 658 nm and 35 °C (Optilab rEX, Wyatt Technology Corp.). Separation was provided by two PLgel mixed-E columns (Polymer Laboratories Inc.) with 3 μm beads, connected in series, operating at 35°C, using freshly distilled THF as the mobile phase at a rate of 1.0 mL/min. Sample solutions (~5-12 mg of polymer/mL of THF) were filtered through 0.2 μm PTFE filters prior to analysis, with a 100 μL injection volume. Data were recorded using ASTRA V software (Wyatt Technology Corp.). Absolute molecular weights were calculated from MALLS data using either a known dn/dc value[114] or a dn/dc value calculated from the refractometer response assuming 100% mass recovery from the columns.

NMR was performed using a 300 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer. Samples were analyzed in 5 mm o.d. tubes with ^{1}H and ^{13}C chemical shifts referenced to the $CDCl_3$ solvent resonance (7.26 ppm and 77.0 ppm, respectively).

Synthesis of Acrylate-terminated Polyisobutylene

In a vial, 1.60 g PIB-$(Br)_2$ (5000 MW, PDI = 1.18) was dissolved in 7.5 mL heptane. Into a 100 mL, 2-neck round-bottom flask, were charged 0.171 g monomethylether hydroquinone (MEHQ), 0.089 g KOH, 0.433 g TBAB, 7.5 mL heptane, 15 mL DMF, and 0.11 mL acrylic acid. The reactor was fitted with a condenser and N_2 purge, and then immersed into a 105 °C oil bath. After the reactor had equilibrated for15 min in the bath, the PIB/heptane solution was rapidly injected into the reactor. After 1.5 h reaction, the reactor was removed from the bath and cooled for 25 min under N_2 purge. The reactor contents were then transferred to a separatory funnel and allowed to cool to rt. The DMF layer was then drained, and the heptane layer was extracted 4x with 5 mL increments of deionized H_2O. The organic layer was then dried over $MgSO_4$ and filtered, and the solvent was stripped to yield the final PIB-$(acrylate)_2$.

Synthesis of Methacrylate-terminated Polyisobutylene

In a vial, 1.602 g PIB-$(Br)_2$ (5000 MW, PDI = 1.18) was dissolved in 7.5 mL heptane. Into a 100 mL, 2-neck round-bottom flask were charged 0.158 g MEHQ, 0.094 g KOH, 0.405 g TBAB, 7.5 mL heptane, and 15 mL DMF. The reactor was fitted with a condenser and Ar purge, and then placed into a 105 ºC oil bath. After 15 min of equilibration in the bath, 0.13 mL methacrylic acid was injected into the reactor, followed by the PIB/heptane solution. After 2.3 h reaction, the reactor was removed from the bath and cooled for 15 min under Ar purge. Reactor contents were transferred to a separatory funnel and cooled to room temperature. The DMF layer was drained, and the heptane

layer was extracted 4x with 5 mL increments of deionized H_2O. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was stripped to yield the final PIB-(methacrylate)$_2$.

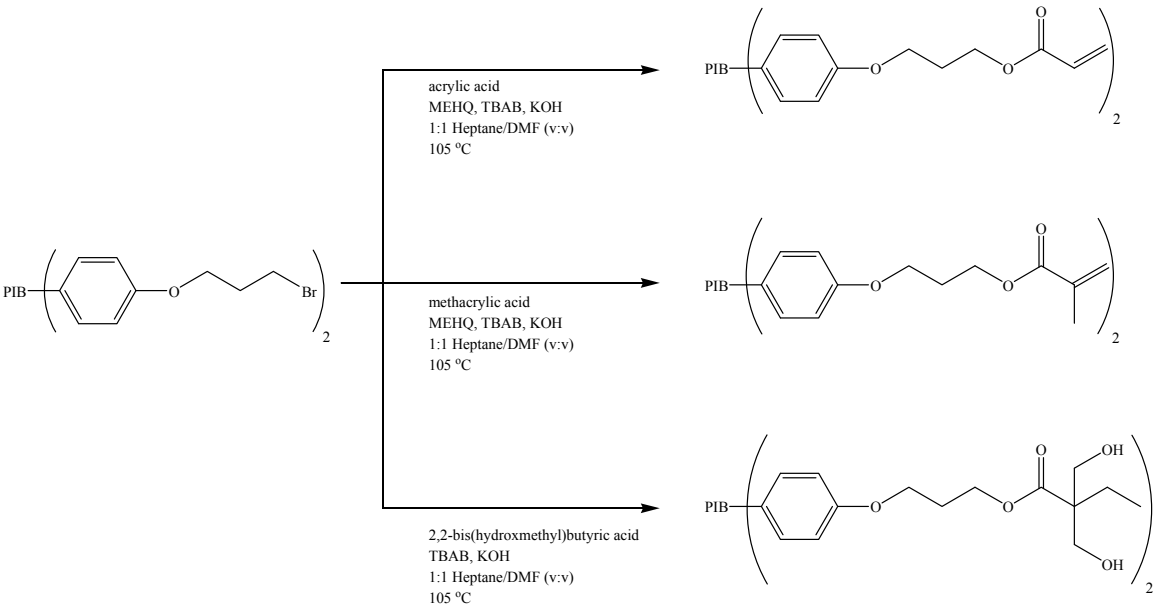
Synthesis of Tetrahydroxy-functional Polyisobutylene

In a vial, 1.603 g PIB-$(Br)_2$ (5000 MW, PDI = 1.18) was dissolved in 7.5 mL heptane. Into a 100 mL, 2-neck round-bottom flask, were charged 0.089 g KOH, 0.102 g TBAB, 0.232 g 2,2-bis(hydroxymethyl)butyric acid, 7.5 mL heptane, and 15 mL DMF. The PIB/heptane solution was added to the reactor, which was fitted with a N_2 purge and condenser. The reactor contents were then refluxed at 105 °C for 3 h. The reactor was removed from the bath and cooled for 15 min under N_2 purge, and then the contents were transferred to a separatory funnel and allowed to cool to room temperature. The DMF layer was drained, and the heptane layer was extracted 4x with 5 mL increments of MeOH. The polymer product was precipitated in MeOH and redissolved in hexane, and the hexane was stripped to reveal the final PIB-$(OH)_4$.

Results and Discussion

Primary bromide is a sufficiently effective leaving group that it undergoes S_N2 reactions quite readily even with relatively weak nucleophiles such as carboxylate. The general reaction scheme used for PIB-Br displacement reactions is shown in Scheme 2. A practical difficulty is that the highly hydrophobic polyisobutylene is most readily dissolved in nonpolar (alkanes) or, at best, mildly polar solvents (alkyl halides, THF), while carboxylates are highly hydrophilic and require polar solvents. When synthesizing acrylate-PIB from allyl-bromide-terminated PIB, Faust utilized refluxing THF as a medium-polarity solvent to bridge the gap between sodium acrylate and PIB.[101] However, this compromise required the use of large excesses (29x and 32x, respectively)

of sodium acrylate and the phase transfer catalyst, tetrabutylammonium bromide, relative to the chain end concentration ([CE],) to achieve full conversion in 6 h. Conversely, this research utilized a heptane/DMF cosolvent system, usually in a 50/50 (v/v) ratio, which has been utilized successfully in the S_N2 reactions of α,ω-PIB-Br.[115,133] These cosolvents, while immiscible at room temperature, become monophasic above ~70 ºC, thereby allowing the nonpolar PIB and polar carboxylate to intimately mix during reaction, which is conducted at heptane reflux temperatures (98-99 ºC). These cosolvents also offer significant advantages during reaction work-up. After the reaction is complete, cooling the reactor to room temperature causes the solvents to once again separate. The denser DMF layer contains the alkali bromide by-product, excess carboxylate, and catalyst, which are thus separated from the PIB product by simply draining away the lower layer using a separatory funnel. The upper PIB/heptane solution is then easily extracted with water or MeOH to produce a pure polymer product. To achieve reproducible reaction temperatures, the relationship between internal reactor temperature and external oil bath temperature was determined and used to create the calibration curve shown in Figure 27.



Scheme 2. Synthesis of PIB-(acrylate)$_2$, PIB-(methacrylate)$_2$, and PIB-(OH)$_4$.

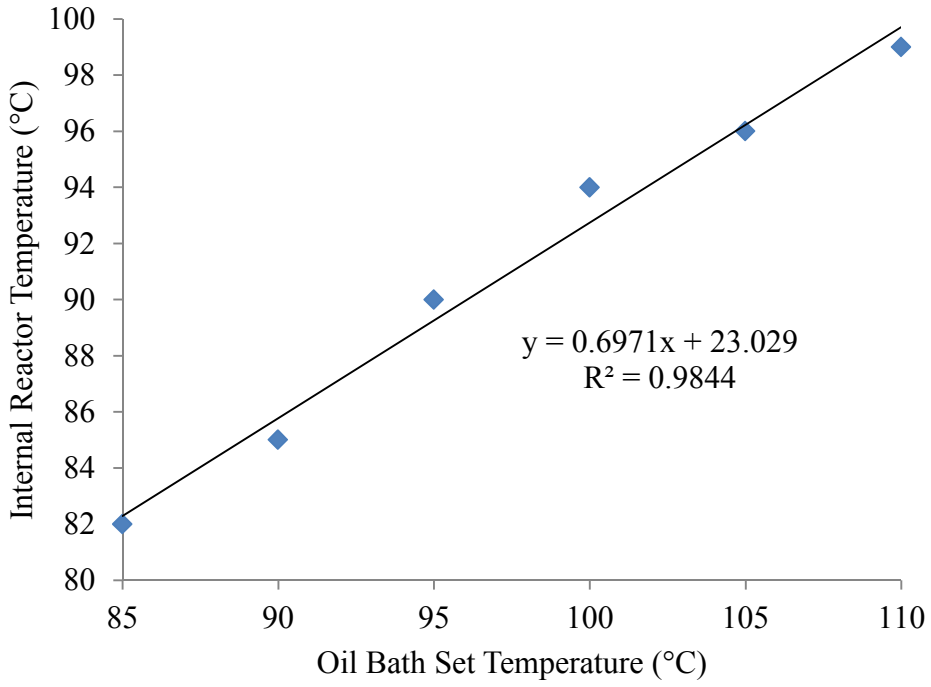


Figure 27. Internal reactor temperature as a function of the oil bath set point.

Initial reactions to produce a monofunctional PIB-acrylate with a 3000 MW PIB-Br did not utilize any phase transfer catalyst, but several test reactions revealed a significant rate increase when even slight (0.5/1 [TBAB]/[CE]) amounts were utilized.

After having thus established the benefit of using a phase transfer catalyst, the conversion of PIB-Br to PIB-acrylate was examined used a fixed ratio of 0.5/1 TBAB/CE and varying the potassium acrylate (KA)/CE ratio from 1.5-2.5/1. As seen in Figure 28, the conversion vs. time plots for different [KA] were essentially the same, indicating that the reaction was insensitive to [KA] and suggesting that a phase boundary, not visible to the naked eye, remained between the supposedly miscible solvents. Thus, in the presence of a less than stoichiometric amount of TBAB, the majority of the reaction was being caused by acrylate species that were being shuttled into the hydrophobic PIB/heptane by TBAB cations.

A kinetic study of the effect of [TBAB] on rate of PIB-acrylate production was then undertaken using 3000 MW monofunctional PIB. Additionally, the heptane content of the solvent mixture was varied from 40-70% by volume, to examine the effect of solvent polarity on reaction rate. The initial reaction rates are summarized in Table 6.

Table 6

Initial reaction rates of the PIB-Br/potassium acrylate reaction as a function of heptane:DMF ratio and [TBAB]/[CE] ratio

	Initial Reaction Rate (mol L^{-1} s^{-1}, $x10^5$) [TBAB]/[CE]				
Heptane/DMF	0	0.5	1	2	3
40/60	0.79	1.81	2.76	3.41	3.99
50/50	1.13	3.04	3.76	4.75	5.38
60/40	0.69	2.80	7.19	8.46	6.18
70/30	0.31	2.51	3.15	6.27	6.38

Note. [KA] = 0.05 M; [CE] = 0.02 M; [MEHQ] = 0.04 M

Some general observations can be made from the data in Table 7. In most cases, increasing [TBAB] increased the reaction rate in every solvent mixture, as expected if it

is transporting the bulk of the acrylate anion across the solvent phase boundary. However, when [TBAB] exceeded the potassium acrylate concentration ([KA]), i.e., when [TBAB]/[CE] > 2.5, further increases in [TBAB] did not cause a further increase in rate, which is expected, since the acrylate anions become saturated with TBAB cations. In the case of the 60/40 (v/v) heptane/DMF mixture, the rate actually decreased. Figure 29 shows conversion versus time plots for various [TBAB]/[CE] ratios in 50/50 heptane/DMF, at a fixed ratio of [KA]/[CE] = 2.5. The greatest increase in reaction rate occurred between the control reaction containing no TBAB and the one in which 0.5/1 [TBAB]/[CE] was used. Thus, from a material cost and efficiency standpoint, a small amount of TBAB is better than a larger amount, as larger amounts yield diminishing returns in the corresponding reaction yield, particularly as [TBAB]/[KA] approaches unity or greater.

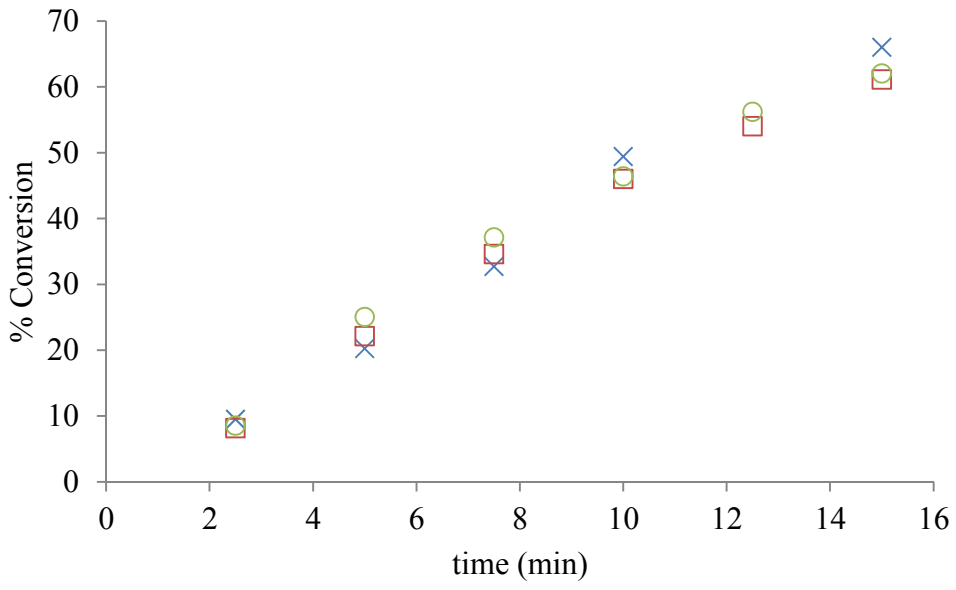


Figure 28. Conversion vs. time plots of PIB-Br/potassium acrylate reaction in 50:50 (v:v) heptane:DMF with [CE] = 0.02 M, [MEHQ] = 0.04 M, [TBAB]:[CE] = 0.5:1, and [KA]:[CE] of 1.5:1 (○), 2:1 (□), and 2.5:1 (x).

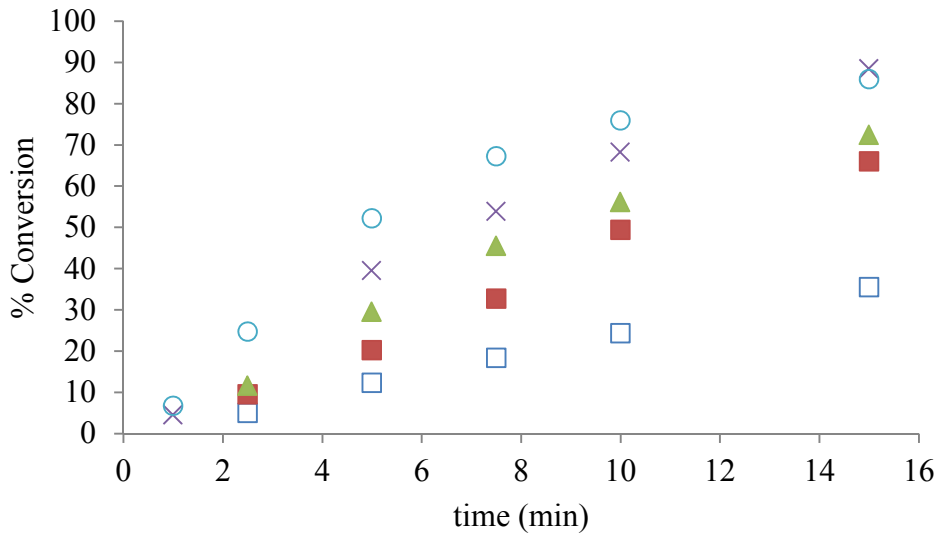


Figure 29. Conversion vs. time plots of PIB-Br/potassium acrylate reaction in 50:50 (v:v) heptane:DMF with [CE] = 0.02 M, [MEHQ] = 0.04 M, [KA]:[CE] = 2.5:1, and [TBAB]:[CE] of 0:1 (□, control), 0.5:1 (■), 1.5:1 (Δ), 2:1 (x), and 3:1 (○).

Potassium hydroxide was used exclusively as the base to generate carboxylate anions from the parent carboxylic acid. This selection was made largely as a result of an early kinetic experiment that was conducted in which sodium and potassium were compared in the absence of TBAB. The resulting second-order kinetic plot of acrylate termini formation versus time is shown in Figure 30. The potassium counterion yielded a significantly higher reaction rate than sodium, producing complete reaction in approximately 1 h, while the sodium reaction was incomplete after 8 h. This was attributed to greater solubility of KOH in DMF relative to NaOH, although KOH did not fully dissolve in DMF until the reaction was heated. Furthermore, the polar aprotic nature of DMF makes it an excellent solvent for cations, separating ion pairs, and resulting in acrylate anions with greater charge density and thus greater nucleophilicity for the substitution reaction. As a larger atom, potassium is more readily solubilized by DMF than sodium. It is possible that the differential advantage of potassium over sodium may be diminished in the presence of TBAB.

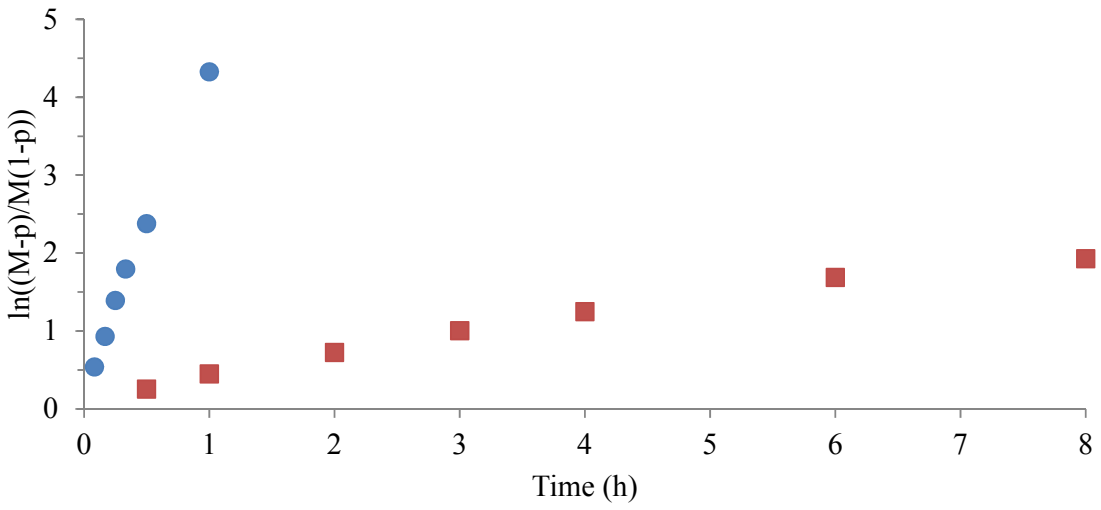


Figure 30. Second order kinetic plot of the reaction of PIB-$(Br)_2$ with KOH (●) and NaOH (■) with [CE] = 0.02 M, [KA] = 0.05 M, [MOH] = 0.05 M, [HQ] = 2.06 mM, [TBAB] = 0.02 M in 50:50 (v:v) heptane:DMF at 105 °C.

Faust et al. utilized pre-made sodium (meth)acrylates,[101] which has the potential advantage of generating no water, which could possibly interfere in the reaction as a competitive nucleophile. In the present research, the generation of potassium carboxylate *in situ* was found to be facile, and the water thus generated did not adversely affect the bromide substitution reaction (i.e. no hydroxyl termini were observed on the product PIBs). This was attributed in part to the biphasic nature of the reaction. The generated water molecules were expected to remain in the DMF phase, and therefore undergo negligible interaction with the PIB chain ends in the heptane phase.

The final factor in successful installation of (meth)acrylate termini was suppression of radical side reactions involving the (meth)acrylate groups, causing loss of acrylate functionality. Without any added radical inhibitor, full conversion of the bromide termini to acrylate termini could be achieved, but only 60-70% of the expected integration values of the acrylate protons was found via ^{1}H NMR. Addition of

hydroquinone suppressed this side reaction, allowing for quantitative integration values of the acrylate protons. However the polymer product resulting from hydroquinone-inhibited reactions was a cloudy, light brown material. Replacing hydroquinone with hydroquinone monomethyl ether produced a clear, colorless polymer product. Representative ^{1}H and ^{13}C NMR spectra of α,ω-PIB-acrylate are shown in Figure 31 and 32, respectively. The acrylate protons appear as three sets of peaks at 6.43 ppm, 6.14 ppm, and 5.83 ppm. The terminal methylene unit shifts from 3.61 ppm in PIB-$(Br)_2$ to 4.38 ppm in PIB-$(acrylate)_2$. The other tether protons shift from 4.09 and 2.32 ppm to 4.06 and 2.17 ppm, respectively. The ^{13}C NMR spectrum shows the acrylate carbons at 130.7 ppm and 128.5 ppm and the carbonyl carbon at 166.1 ppm.

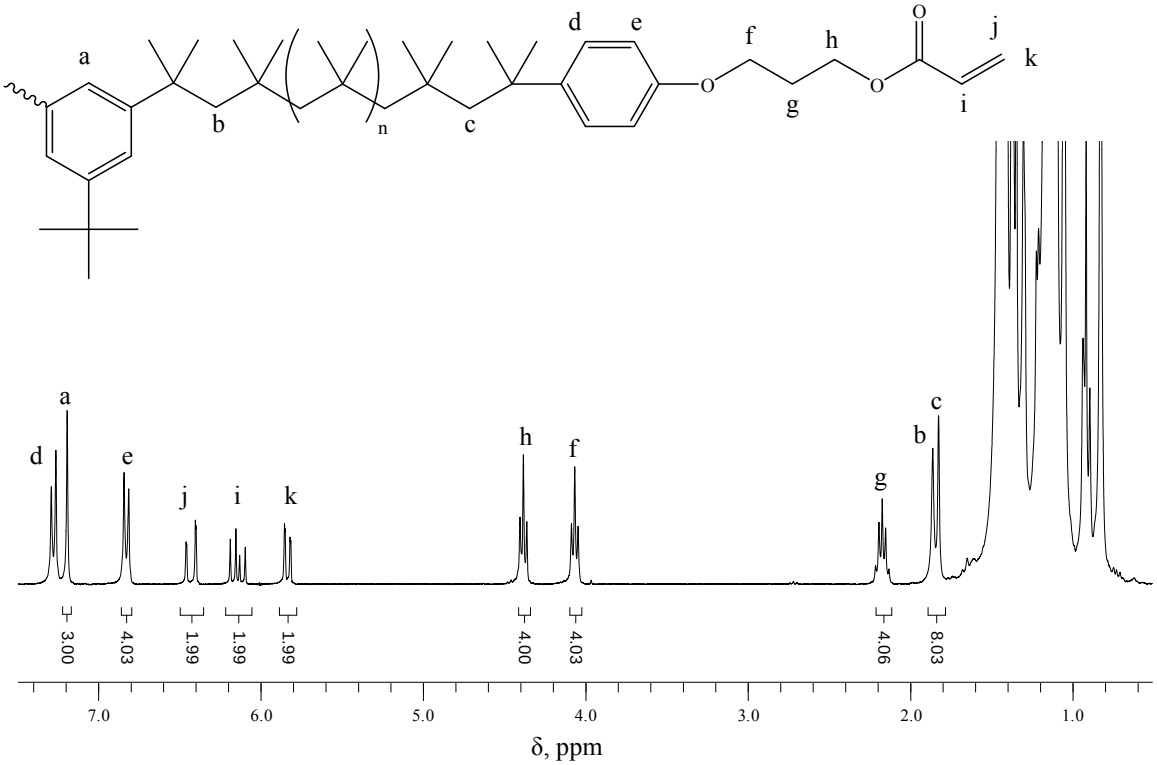


Figure 31. ^{1}H NMR spectrum of PIB-$(acrylate)_2$.

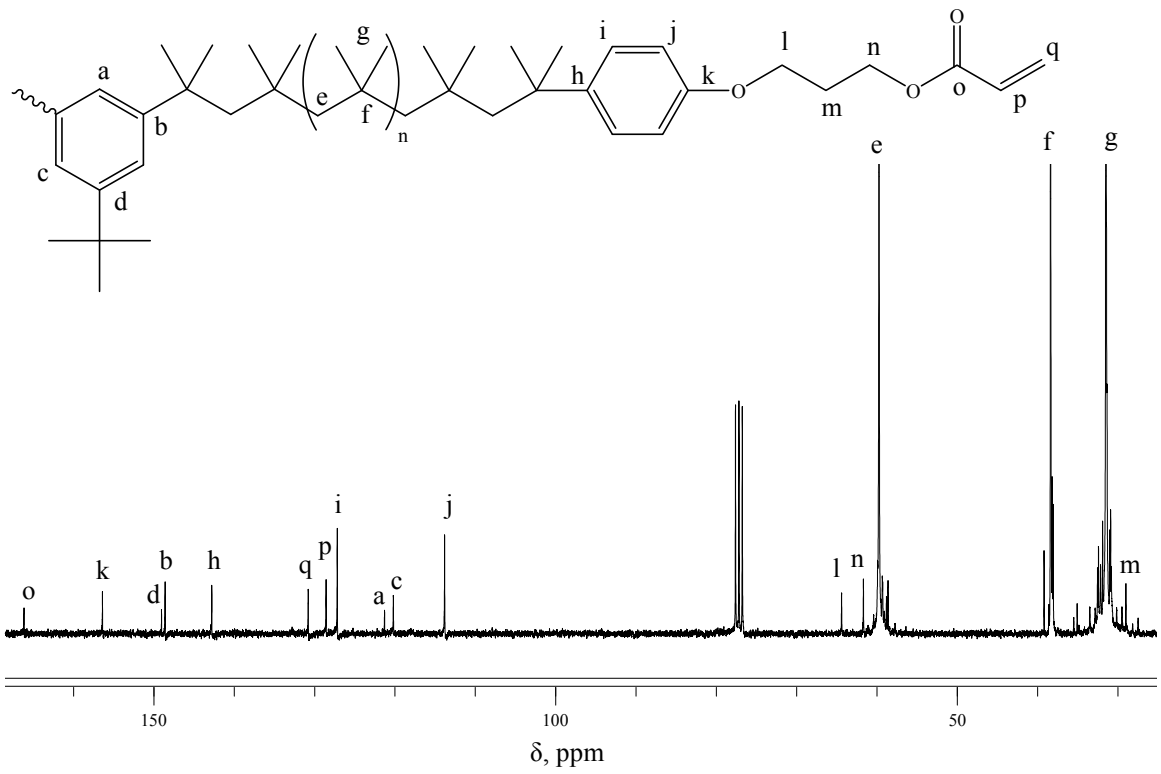


Figure 32. ^{13}C NMR spectrum of PIB-(acrylate)$_2$.

α,ω-PIB-methacrylate was synthesized via the same procedure as α,ω-PIB-acrylate. A kinetic comparison of methacrylate versus acrylate is shown in Figure 33. The slightly higher reaction rate for potassium methacrylate can be attributed to the additional methyl group, which contributes additional electron density to the carboxylate group and makes the molecule more nonpolar, increasing its solubility in the heptane/PIB phase relative to acrylate.

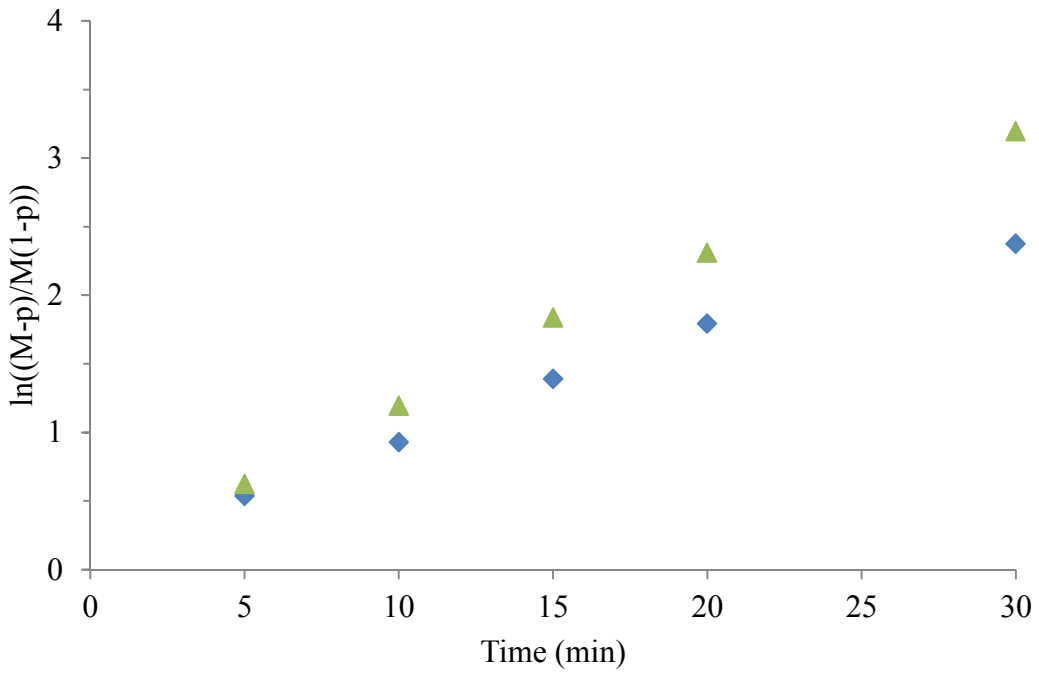


Figure 33. Second-order kinetic plot of PIB-(methacrylate)$_2$ (▲) and PIB-(acrylate)$_2$ (♦) synthesis from α,ω-PIB-Br. Conditions used: α,ω-PIB-Br (0.01 M, [CE] = 0.02 M), K(M)A/CE = 2.5/1, [hydroquinone] = 2.06 mM, [TBAB] = 0.02 M, 1/1 (v/v) heptane/DMF.

The ^{1}H and ^{13}C NMR spectra of α,ω-PIB-methacrylate are shown in Figures 34 and 35, respectively. The methacrylate olefinic protons appear at 6.12 ppm and 5.57 ppm. The methylene tether protons resonate at 4.35 ppm, 4.06 ppm, and 2.16 ppm. The methacrylate olefinic carbon peaks appear at 136.3 ppm and 125.4 ppm. The carbonyl carbon and methacrylate methyl carbon resonate at 167.3 and 18.4 ppm, respectively.

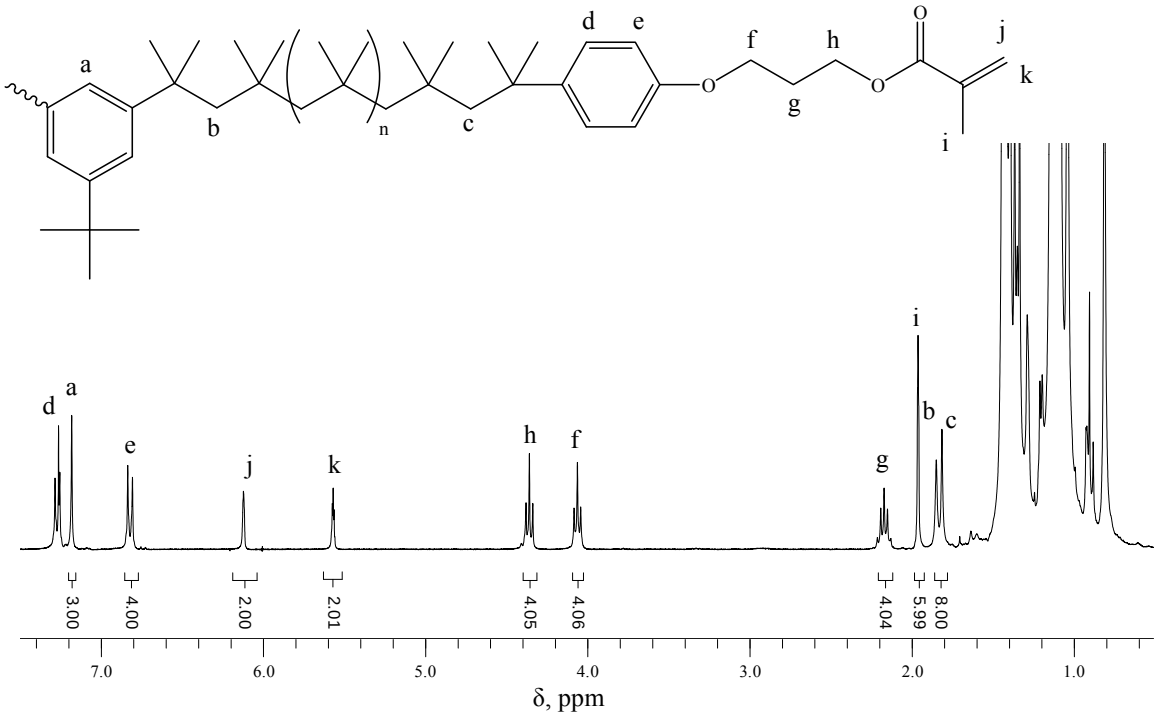


Figure 34. ^{1}H NMR spectrum of PIB-(methacrylate)$_2$.

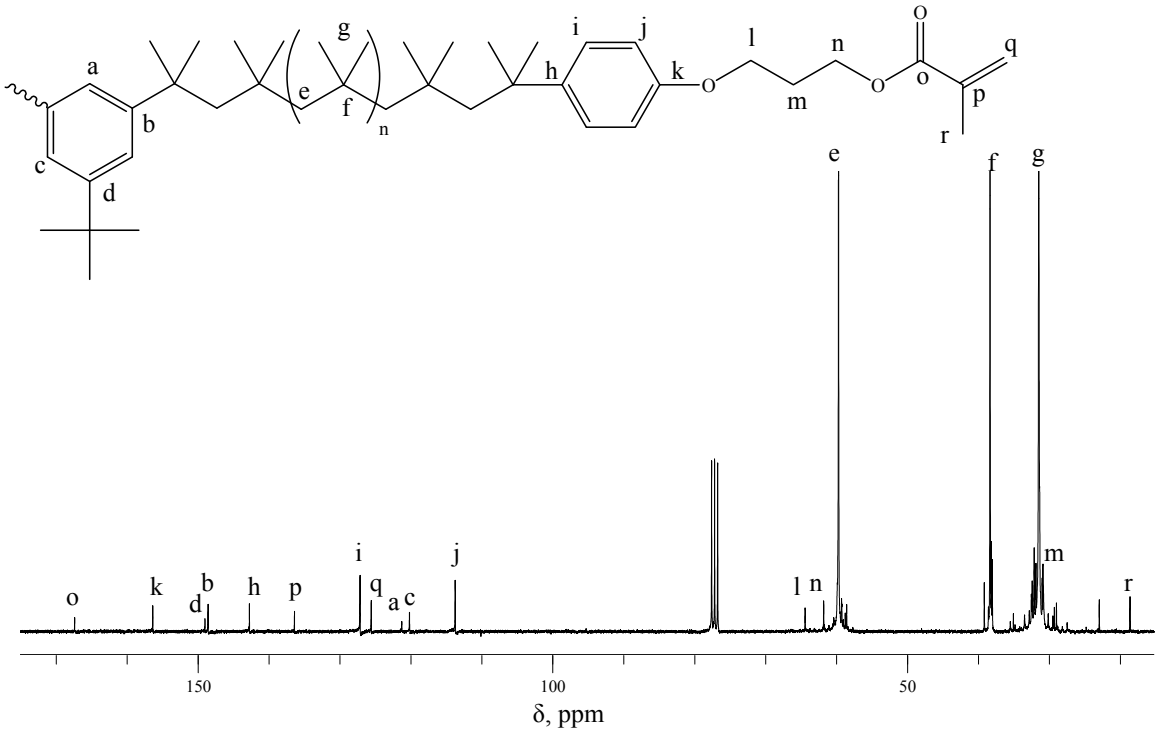


Figure 35. ^{13}C NMR spectrum of PIB-(methacrylate)$_2$.

α,ω-PIB-Br has been converted to *α,ω*-PIB-OH via a two-step sequence utilizing sodium benzoate to displace the bromine, followed by ester hydrolysis. Conversion to a tetra-hydroxy functional PIB would allow for dendritic structures or crosslinked networks. Tetra-hydroxy functional PIBs have been produced using thiol-terminated PIB and sequential thiol-ene/thiol-yne reactions,[133] but simple bromine displacement by 2,2-bis(hydroxymethyl)butyric acid offers similar functionality in a single synthetic step. The reaction utilized similar conditions to the (meth)acrylate reactions, but did not require any radical inhibitor. The ^{1}H NMR spectrum of *α,ω*-PIB-$(OH)_2$ is shown in Figure 36. In $CDCl_3$, the methylene protons of the hydroxymethyl moieties are split into two sets of doublets at 4.02 ppm and 3.73 ppm, one set of which overlaps the methylene protons of the propoxy tether unit at 4.06 ppm. The other propoxy methylene units appear at 4.40 ppm and 2.15 ppm. The methylene unit of the ethyl moiety appears at 1.61 ppm, while its adjacent methyl protons are buried beneath the PIB backbone proton resonances. The terminal hydroxyl protons appear at 2.85 ppm.

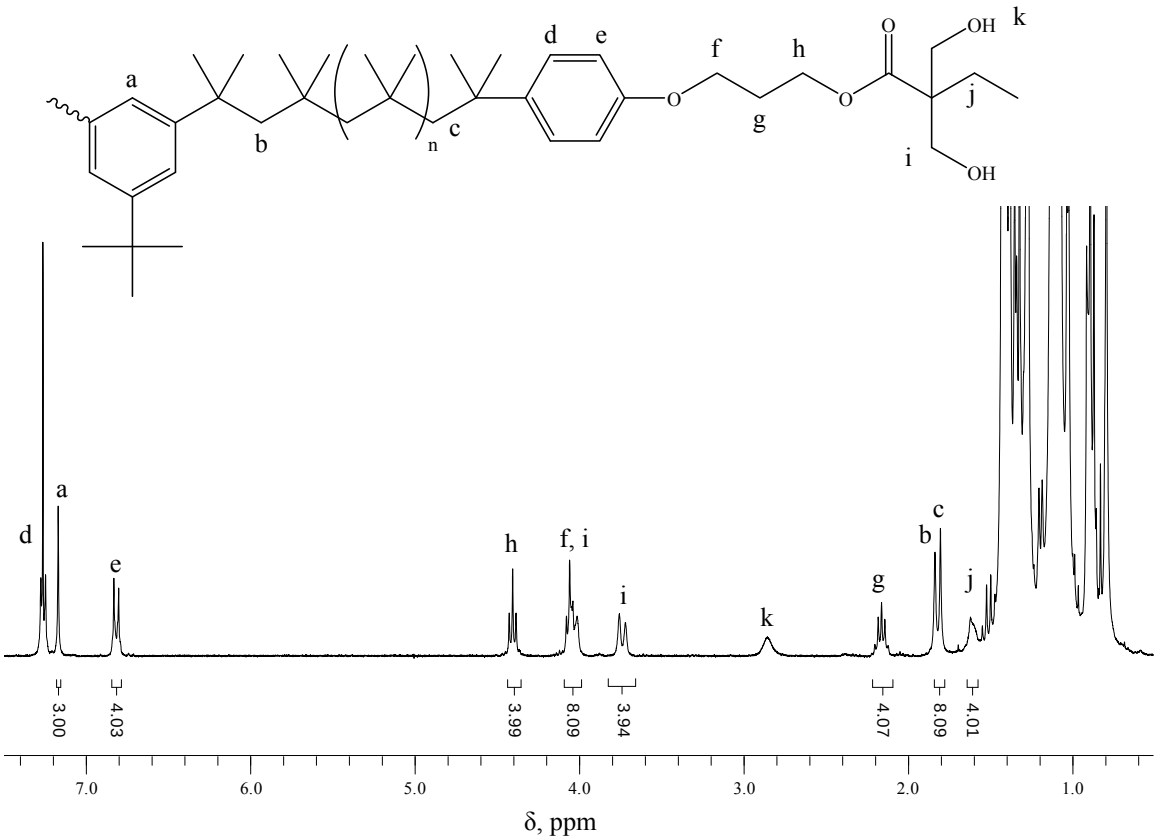


Figure 36. ^{1}H NMR of PIB-$(OH)_4$.

In the ^{13}C spectrum, shown in Figure 37, the carbonyl carbon resonates at 175.2 ppm, the hydroxymethyl carbons appear at 62.2 ppm, and the central quaternary carbon is observed at 53.0 ppm. The ethyl moiety carbons appear at 24.7 ppm and 8.7 ppm. End group peak assignments for both the ^{1}H and ^{13}C NMR of *α,ω*-PIB-$(OH)_2$ were aided by 2-D HSQC NMR shown in Figure 39.

The GPC RI traces of the starting PIB-$(Br)_2$ (M_n = 5000 g/mol, PDI = 1.18) and product PIB-$(acrylate)_2$ (M_n = 5080 g/mol, PDI = 1.17) are shown in Figure 40. GPC RI traces of PIB-$(methacrylate)_2$ (M_n = 5160 g/mol, PDI = 1.15) and PIB-$(OH)_4$ (M_n = 5300 g/mol, PDI = 1.14) relative to the starting PIB-$(Br)_2$ are shown in Figure 41. No coupling or degradation was observed during the substitution reactions.

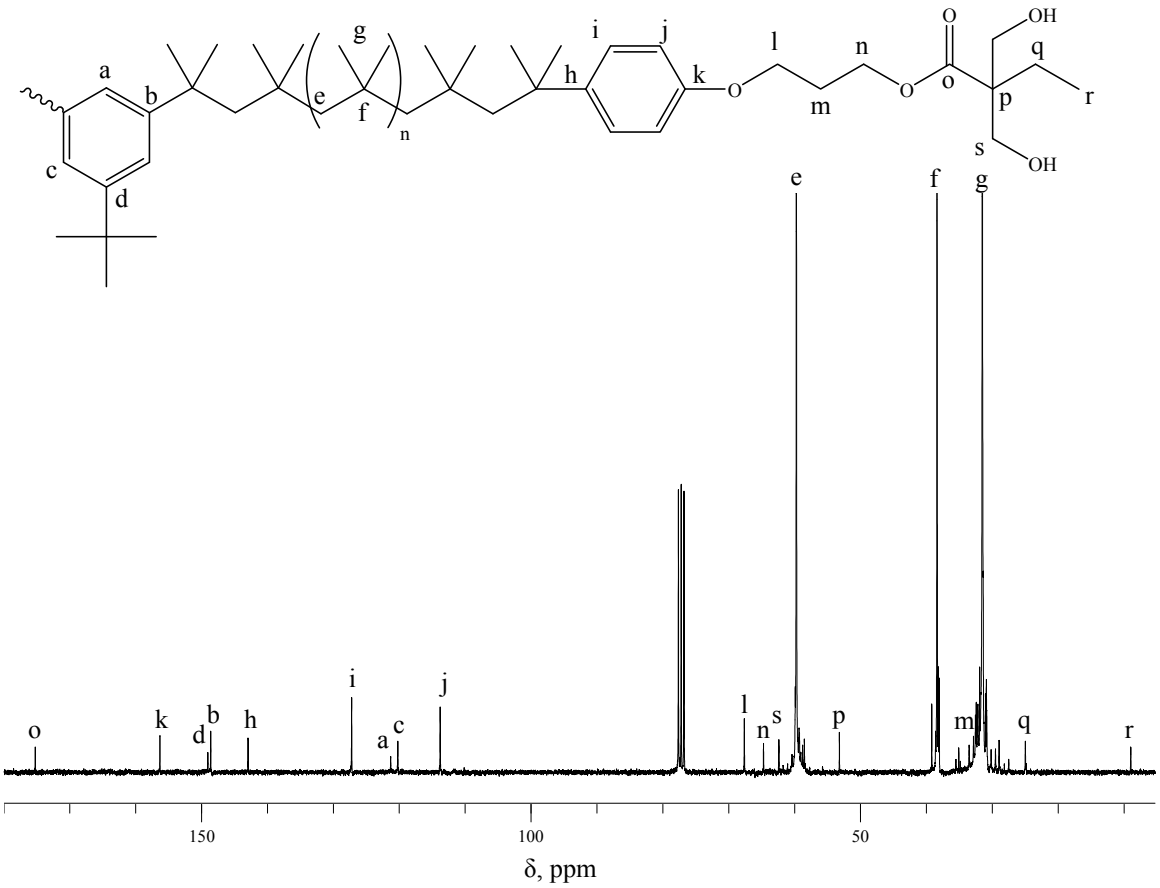


Figure 37. ^{13}C NMR spectrum of PIB-(OH)$_4$.

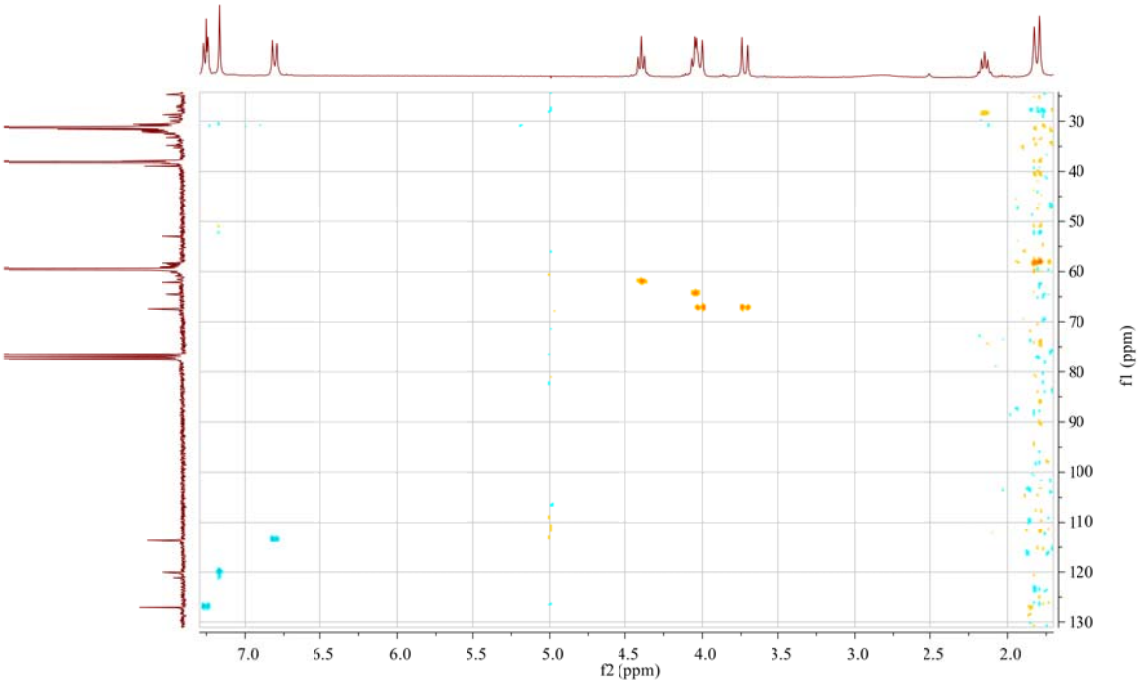


Figure 38. HSQC spectrum of the end-group region of PIB-$(OH)_4$.

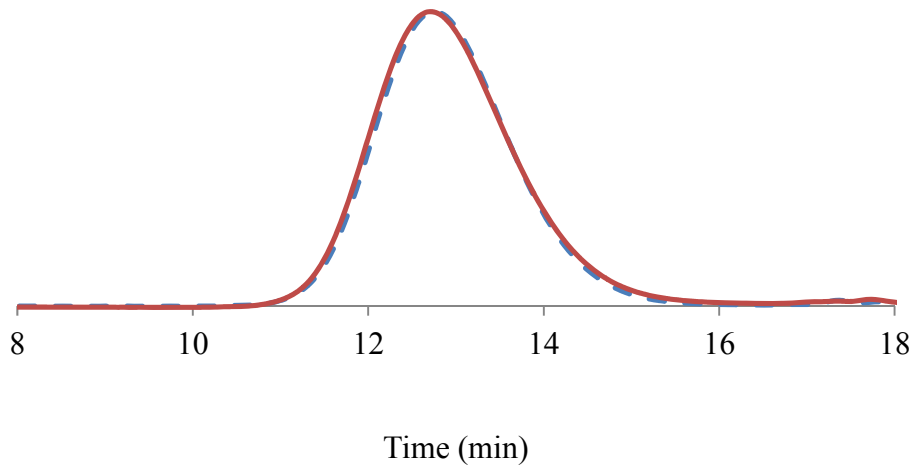


Figure 39. RI GPC traces of PIB-$(Br)_2$ (solid) and PIB-$(acrylate)_2$ (dashed).

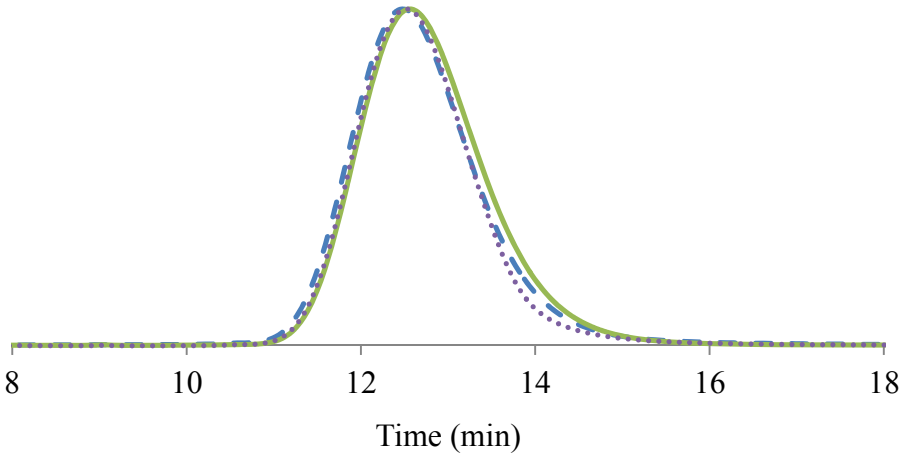


Figure 40. RI GPC traces of PIB-$(Br)_2$ (solid), PIB-$(methacrylate)_2$ (dashed), and PIB-$(OH)_4$ (dotted).

MALDI-TOF analysis was performed on each functional PIB sample. The results are summarized in Table 7. A sample MALDI-TOF mass spectrum of PIB-$(acrylate)_2$ is shown in Figure 42, with the inset clearly showing the spacing between the individual peaks very close to that of the IB repeat unit at 56 Da.

Table 7

MALDI-TOF-MS End-group Analysis for Functional PIBs

End-Group	End-Group MW (g/mol)	Cation	MW_{Theo} (g/mol)	MW_{Exp} (g/mol)	Difference (g/mol)
acrylate	205.23	Na	626.83	623.68	3.15
methacrylate	219.26	Ag	654.89	654.75	0.14
2,2-bis(hydroxymethyl)butyrate	281.33	Ag	779.02	782.98	3.96

A plot of M/z vs. degree of polymerization is shown in Figure 41 for PIB-$(acrylate)_2$, which is representative. The slope obtained by linear regression represents the MW of the polymer repeat units, and the intercept is the MW of the residue species, defined as $MW_{residue} = 2*MW_{Endgroup} + MW_{Initiator}$ and is equivalent to MW_{Exp} shown in Table 7.

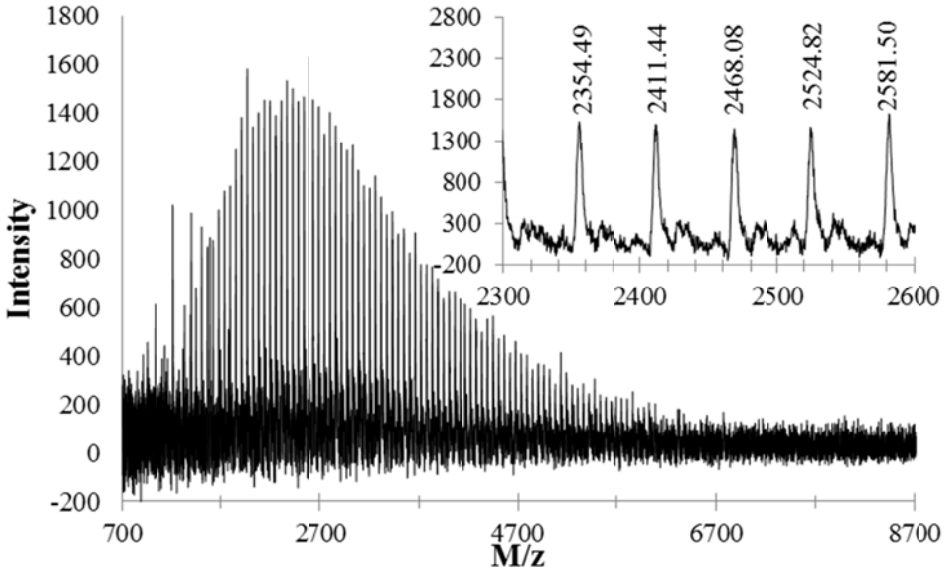


Figure 41. MALDI-TOF mass spectrum of PIB-(acrylate)$_2$ illustrating the individual repeat units of the polymer structure.

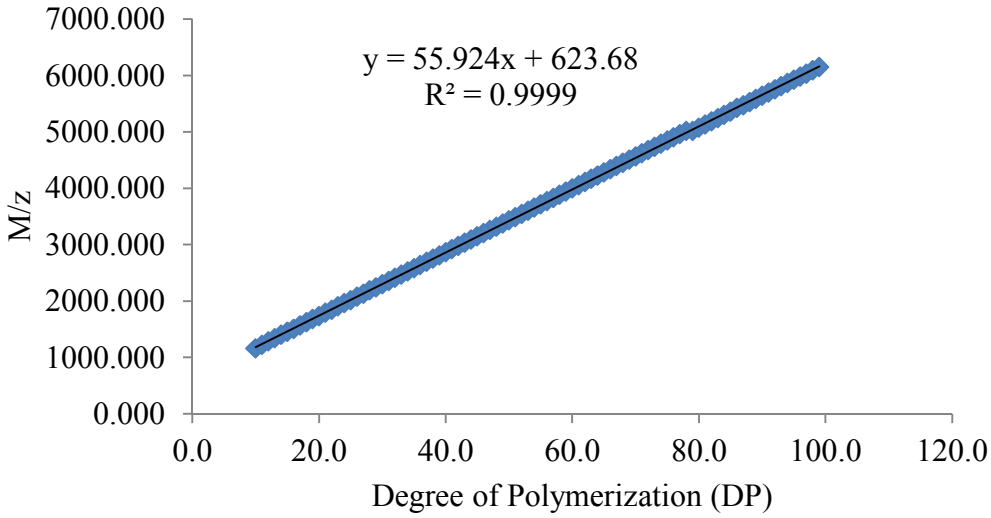


Figure 42. Linear regression of MALDI data of PIB-(acrylate)$_2$.

One interesting negative result was an attempt to produce thiol-terminated PIB using 3-mercaptopropionic acid. The carboxylic acid moiety has a pK_a of around 4-4.5, while the typical aliphatic thiol pK_a is around 10. While the majority of the bromine was indeed displaced by the carboxylic acid moiety, the highly nucleophilic sulfur atom

displaced approximately 35% of the bromine termini, producing a highly coupled polymer product, the RI trace of which is shown in Figure 44.

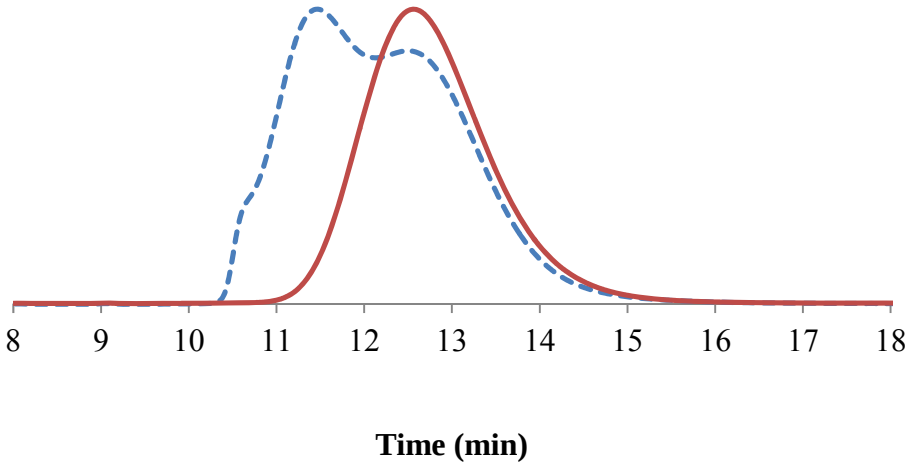


Figure 43. Refractive index GPC trace of PIB-$(Br)_2$ before (solid) and after (dashed) reaction with 3-mercaptopropionic acid. Coupling through the thiol group to form sulfide linked PIB is evident.

Conclusions

PIB-$(acrylate)_2$, PIB-$(methacrylate)_2$, and PIB-$(OH)_4$ were synthesized by the carboxylate S_N2 displacement of primary bromide termini from PIB-$(Br)_2$. The solvent system of 50/50 (v/v) heptane/DMF allowed for facile reactions as the two dissimilar solvents become relatively miscible at the reaction temperature, then phase separate at room temperature, simplifying polymer clean-up and isolation. Potassium hydroxide was used to generate the carboxylates from the parent carboxylic acid. The phase transfer catalyst, tetrabutylammonium bromide, greatly increased reaction rate when used at less than stoichiometric amounts relative to carboxylate, but produced progressively diminishing rate increases as its concentration approached that of carboxylate. During substitution reactions involved acrylate or methacrylate anions, the radical inhibitor

monomethylether hydroquinone suppressed radical side reactions while producing a clear, colorless polymer product.

CHAPTER IV

DERIVATIZATION OF PHENOL- AND HYDROXYL-TERMINATED POLYISOBUTYLENES

Introduction

Polyisobutylene is a saturated hydrocarbon elastomer with growing commercial utility,[137] which is obtainable only through the cationic polymerization of isobutylene. Commercial processes for cationic polymerization of isobutylene typically produce a mixture of several characteristic end-terminal functionalities, the most desirable being *exo*-olefin. However, substantial work has been done on both *in situ* and post-polymerization modification of PIB chain ends, both those produced by traditional commercial processes, which are inherently monofunctional, and those based on living PIB polymerizations, which can produce mono-, di-, or tri-functional PIB depending on the initiator structure. Numerous functional groups have since been installed on PIB, including primary halogen,[115] acrylate,[101,138] thiol,[133] amine,[92,111,139] and hydroxyl.[92,117,140]

Particular emphasis on the synthesis of hydroxyl-terminated polyisobutylene, both aromatic (PIB-phenol) and aliphatic, has been undertaken due to the high synthetic versatility of this functional group. Kennedy first produced difunctional hydroxyl-terminated PIB from telechelic *tert*-Cl PIB produced by the inifer process via a two-step post-polymerization sequence: dehydrochlorination to *exo*-olefin PIB, following by hydroboration-oxidation.[88] Other post-polymerization approaches utilized displacement of a primary halogen[92] and a thiol-ene reaction between *exo*-olefin PIB and a hydroxyl-functional thiol.[128] Phenol-terminated PIB has been synthesized directly via Friedel-Crafts alkylation of phenol by either *exo*-olefin or *tert*-chloride PIB.[122,127,141]

In situ approaches to hydroxyl-functional PIB follow two routes: functional initiators and nucleophilic quenchers. With regard to the former, Puskas and coworkers utilized α-methylstyrene epoxide and 1,2-epoxy-2,4,4-trimethylpentane, an epoxy derivative of 2,4,4-trimethyl-1-pentene (precursor to the common PIB initiator, TMPCl), which would epoxy-ring open with $TiCl_4$ or BCl_3 catalysis and initiate polymerization, producing PIB with one hydroxyl-terminus and one *tert*-chloride terminus.[42,129,142] Nucleophilic quenchers can be added to the polymerization reactor once all monomer is consumed, provided that the interaction between the quencher and the Lewis acid is not sufficient to deactivate one or the other. Unprotected hydroxyl groups and phenol will rapidly interact with typical polymerization catalysts, such as $TiCl_4$, and are generally not suited for direct addition. Protected heterocyclic aromatics, such as *N*-(ω-*tert*-butoxyalkyl)pyrrole,[117] and alkoxybenzenes,[115] such as isopropoxybenzene and anisole, are readily alkylated by PIB chains, and the protecting groups may be removed in situ by charging additional Lewis acid ($TiCl_4$, $EtAlCl_2$, BBr_3) and H_2SO_4, and warming the reaction. Storey et al. have recently shown that unprotected phenoxyalkanols with tether lengths of four or more could be quantitatively alkylated by PIB chains, but required long reaction times and large (10x) excesses of $TiCl_4$.[115]

In situ methods producing quantitative telechelic *exo*-olefin PIB, such as hindered bases,[77-80] (di)sulfides,[82,130] and ethers,[84] allow for facile direct synthesis of prepolymers for modification by thiol-ene reaction. Radical thiol-ene click reactions are extremely tolerant of functional groups such as hydroxyl, and make for an interesting alternate pathway to functional PIBs.[128]

Once produced, hydroxyl- and phenol-terminated PIBs have been further modified with additional chemistries. Kennedy reacted phenol-terminated PIB with

epichlorohydrin to produce telechelic glycidyl ether-terminated PIBs that were then reacted with a tetrafunctional amine to form flexible films.[122] Telechelic hydroxyl-terminated PIB has been further derivatized to produce (meth)acrylate,[138,143,144] and isocyanate-terminated PIB,[145,146] and has been used to initiate ring opening polymerization of ε-caprolactone[147] and L-lactide.[148,149]

In this work, we expand on the library of functional telechelic PIBs suitable as platforms for block copolymer or network synthesis, particular those utilizing radical polymerizations.

Experimental

Materials

Titanium tetrachloride ($TiCl_4$) (99.9%), hexane (anhydrous, 95%), 2,6-lutidine (≥99%), *N*,*N*-dimethylformamide (DMF) (≥99.9%), methanol (anhydrous, 99.8%), diisopropyl ether (anhydrous, 99%), 2-mercaptoethanol (≥99.9%), chloroform (99.9+%, ACS), acryloyl chloride (≥97%), 2,2-dimethoxy-2-phenylacetophenone (99%), and 2-bromopropionyl bromide (97%) were purchased from Sigma-Aldrich and used as received. Methacryloyl chloride (95%) and chloroform-*d* (99.8 atom% D) were purchased from Acros Organics and used as received. 2-Bromoisobutyryl bromide (>98%) was purchased from TCI America and used as received. THF was purchased from Fisher Scientific and distilled over CaH_2 prior to use. Isopropoxybenzene (97%) was purchased from Oakwood Chemical and used as received. Difunctional cationic polymerization initiator 1,3-bis-(1-chloro-1-methylethyl)-5-*tert*-butylbenzene (bDCC), [119] α,ω-bis(4-hydroxyphenyl)polyisobutylene (α,ω-PIB-phenol, M_n = 5200 g/mol, PDI = 1.18),[115] and α,ω-(methylvinylidenemethyl)polyisobutylene (α,ω-PIB-*exo*, M_n = 3600, PDI = 1.11)[84] were synthesized as previously described.

Instrumentation

Gel permeation chromatography (GPC) was used to measure all number average molecular weights (M_n) and polydispersities (PDI = M_w/M_n) using a system composed of a Waters Alliance 2695 separations module, an online laser light scattering (MALLS) detector equipped with a 20 mW gallium arsenide laser operating at 658 nm (miniDAWN TREOS, Wyatt Technology Corp.) and an interferometric refractometer operating at 658 nm and 35 °C (Optilab rEX, Wyatt Technology Corp.). Separation was provided by two PLgel mixed-E columns (Polymer Laboratories Inc.) with 3 μm beads, connected in series, operating at 35°C, using freshly distilled THF as the mobile phase at a rate of 1.0 mL/min. Sample solutions (~5-12 mg of polymer/mL of THF) were filtered through 0.2 μm PTFE filters prior to analysis, with a 100 μL injection volume. Data were recorded using ASTRA V software (Wyatt Technology Corp.). Absolute molecular weights were calculated from MALLS data using either a known d*n*/d*c* value[114] or a d*n*/d*c* value calculated from the refractometer response assuming 100% mass recovery from the columns.

NMR was performed using a 300 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer. Samples were analyzed in 5 mm o.d. tubes with ^{1}H and ^{13}C chemical shifts referenced to the $CDCl_3$ solvent resonance (7.26 ppm and 77.0 ppm, respectively).

Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed using a Bruker Microflex LRF MALDI-TOF mass spectrometer equipped with a nitrogen laser (337 nm) possessing a 60 Hz repetition rate and a 50 μJ energy output. PIB homopolymer samples were prepared using the dried-droplet method. For PIB homopolymer, a 20 mg/mL matrix (dithranol) solution, a 10 mg/mL cationizing agent (silver trifluoroacetate or sodium trifluoroacetate) (AgTFA or

NaTFA) solution, and a 10 mg/mL polymer solution, all in THF, were mixed in a volumetric ratio of matrix:sample:cationizing agent = 10:10:1, and then a 0.5 μL aliquot was applied to a MALDI sample target for analysis. All spectra were obtained in the positive ion mode utilizing the reflector mode micro-channel plate detector and are the sum of 900-1000 shots. Molecular weights of the polymer end groups were determined by linear regression using the known molecular weight of the initiator residue (1,3-diisopropyl-5-*tert*-butylbenzene) and cationizing agent cation (Ag+ or Na+).

Synthesis of α,ω-(4-acryloylphenyl)polyisobutylene (α,ω-PIB-acrylate)

To a scintillation vial were added 1.00 g α,ω-PIB-phenol (M_n = 5200 g/mol, 0.38 meq) and 10 mL freshly distilled THF. To the stirring solution were added triethylamine (0.080 mL, 0.57 mmol) and acryloyl chloride (0.047 mL, 0.57 mmol). Upon addition of acryloyl chloride, the clear colorless solution immediately became cloudy white. After 1 h reaction at rt, the THF was removed, and the polymer was dissolved in hexane, filtered through a cotton plug, and precipitated into stirred MeOH. The MeOH was decanted, and residual MeOH was removed with an N_2 stream. The polymer was redissolved in hexane, and the hexane was stripped under vacuum to yield the final α,ω-PIB-acrylate.

Synthesis of α,ω-(4-methacryloylphenyl)polyisobutylene (α,ω-PIB-methacrylate)

To a scintillation vial were added 1.00 g α,ω-PIB-phenol (M_n = 5200 g/mol, 0.38 meq) and 10 mL freshly distilled THF. To the stirring solution were added triethylamine (0.080 mL, 0.57 mmol) and methacryloyl chloride (0.056 mL, 0.57 mmol). Upon addition of methacryloyl chloride, the clear colorless solution slowly became cloudy white, becoming more opaque as the reaction progressed. After 1 h reaction at rt, the THF was removed, and the polymer was dissolved in hexane, filtered through a cotton plug, and precipitated into stirred MeOH. The MeOH was decanted, and residual MeOH

was removed with an N_2 stream. The polymer was redissolved in hexane, and the hexane was stripped under vacuum to yield the final α,ω-PIB-methacrylate.

Synthesis of α,ω-[4-(2-bromopropionyloxy)phenyl]polyisobutylene

(α,ω-PIB-bromopropionate)

To a scintillation vial were added 1.00 g α,ω-PIB-phenol (M_n = 5200 g/mol, 0.38 meq) and 10 mL freshly distilled THF. To the stirring solution were added triethylamine (0.080 mL, 0.57 mmol) and 2-bromopropionyl bromide (0.08 mL, 0.77 mmol). Upon addition of 2-bromopropionyl bromide, the clear colorless solution immediately became cloudy yellow. After 2 h reaction at rt, the THF was removed, and the polymer was dissolved in hexane, filtered through a cotton plug, and precipitated into stirred MeOH. The MeOH was decanted, and residual MeOH was removed with an N_2 stream. The polymer was redissolved in hexane, and the hexane was stripped under vacuum to yield the final α,ω-PIB-bromopropionate.

Synthesis of α,ω-[4-(2-bromo-2-methylpropionyloxy)phenyl]polyisobutylene

(α,ω-PIB-bromoisobutyrate)

To a scintillation vial were added 1.00 g α,ω-PIB-phenol (M_n = 5200 g/mol, 0.38 meq) and 10 mL freshly distilled THF. To the stirring solution were added triethylamine (0.080 mL, 0.57 mmol) and 2-bromoisobutyryl bromide (0.10 mL, 0.77 mmol). Upon addition of 2-bromoisobutyryl bromide, the clear colorless solution immediately became cloudy white. After 2 h reaction at rt, the THF was removed, and the polymer was dissolved in hexane, filtered through a cotton plug, and precipitated into stirred MeOH. The MeOH was decanted, and residual MeOH was removed with an N_2 stream. The polymer was dissolved in hexane, and the hexane was stripped under vacuum to yield the final *α,ω*-PIB-bromoisobutyrate.

Synthesis of 2-hydroxyethylsulfanyl-terminated polyisobutylene (α,ω-PIB-S-OH)

To a dry one-neck 50 mL round-bottom flask equipped with a magnetic stir bar were added 0.105 g 2,2-dimethoxy-2-phenylacetophenone (0.41 mmol, 1.5 wt%), 6.00 g α,ω-PIB-*exo* (4000 g/mol, 3.0 meq) dissolved in 25 mL $CHCl_3$, and 0.85 mL 2-mercaptoethanol (12 mmol). The reactor was cooled in an ice bath for 20 min, and then placed under a UV lamp for 10 min at 0 °C. The solvent was removed by rotary evaporation, the polymer was dissolved in hexane, extracted 3x with MeOH, and then precipitated into stirred MeOH. The MeOH was decanted, and residual MeOH was removed with a N_2 stream. The polymer was redissolved in hexane, and the hexane was stripped under vacuum to yield the final α,ω-PIB-OH.

Synthesis of α,ω-(2-acryloyloxyethylsulfanyl-2-methylpropane-1,3-diyl)polyisobutylene (α,ω-PIB-S-acrylate)

To a scintillation vial were added 1.009 g *α,ω*-PIB-OH (M_n = 3900, 0.52 meq) and 6 mL THF. After the PIB was fully dissolved, 0.214 mL TEA (1.54 mmol, 3x [CE]), and 0.086 mL acryloyl chloride (1.54 mmol, 3x [CE]) were added to the stirred PIB solution at rt. The reaction mixture immediately became cloudy white upon addition of acryloyl chloride. After 1 h reaction, the solvent was stripped, and the polymer was redissolved in hexane. The reactor contents were filtered through a cotton plug, and precipitated into stirred MeOH. The MeOH was decanted, and residual MeOH was removed with an N_2 stream. The polymer was redissolved in hexane, and the hexane was stripped to provide the final *α,ω*-PIB-S-acrylate.

Synthesis of α,ω-(2-methacryloyloxyethylsulfanyl-2-methylpropane-1,3-diyl)polyisobutylene (α,ω-PIB-S-methacrylate)

To a scintillation vial were added 1.005 g *α,ω*-PIB-OH (M_n = 3900, 0.52 meq), and 6 mL THF. After the PIB was fully dissolved, 0.21 mL TEA (1.54 mmol, 3x [CE]) and 0.15 mL methacryloyl chloride (1.54 mmol, 3x [CE]) were added to the stirred PIB solution at rt. After 1 h reaction, the solvent was stripped, and the polymer was dissolved in hexane. The hexane solution was filtered through a cotton plug, and the polymer was precipitated into stirred MeOH. The MeOH was decanted, and residual MeOH was removed with an N2 stream. The polymer was redissolved in hexane, and the hexane was stripped to provide the final *α,ω*-PIB-S-methacrylate.

Synthesis of α,ω-(2-bromopropionyloxyethylsulfanyl-2-methylpropane-1,3-diyl)polyisobutylene (α,ω-PIB-S-bromopropionate)

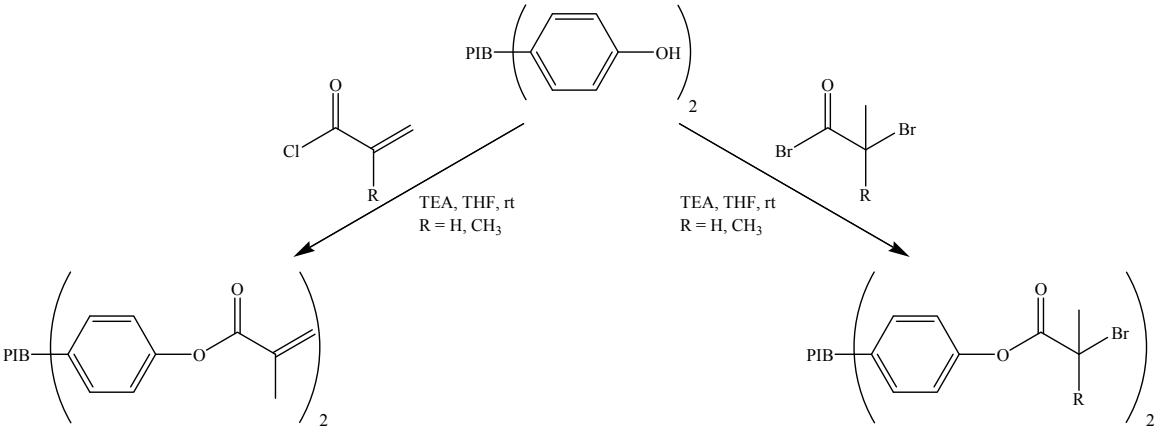
To a scintillation vial were added 1.009 g *α,ω*-PIB-OH (M_n = 3900, 0.52 meq) and 6 mL THF. After the PIB was fully dissolved, 0.107 mL TEA (0.77 mmol, 1.5x [CE]), and 0.11 mL 2-bromopropionyl bromide (1.03 mmol, 2x [CE]) were added to the stirred PIB solution at rt. The reaction mixture turned cloudy white immediately upon addition of 2-brompropionyl bromide, and then slowly developed a yellow color as the reaction progressed. After 2 h reaction, the solvent was stripped, and the polymer was redissolved in hexane. The reactor contents were filtered through a cotton plug and precipitated into stirred MeOH. The MeOH was decanted, and residual MeOH was removed with an N_2 stream. The polymer was redissolved in hexane, and the hexane was stripped to provide the final *α,ω*-PIB-S-bromopropionate.

Synthesis of α,ω-(2-bromo-2-methylpropionyloxyethylsulfanyl-2-methylpropane-1,3-diyl)polyisobutylene (α,ω-PIB-S-bromoisobutyrate)

To a scintillation vial were added 1.015 g *α,ω*-PIB-OH (M_n = 3900, 0.52 meq) and 6 mL THF. After the PIB was fully dissolved, 0.107 mL TEA (0.77 mmol, 1.5x

[CE]), and 0.13 mL 2-bromoisobutyryl bromide (1.03 mmol, 2x [CE]) were added to the stirred PIB solution at rt. Upon addition of 2-bromoisobutyryl bromide, the reaction mixture immediately became cloudy white. After 2 h reaction, the solvent was stripped, and the polymer was redissolved in hexane. The reactor contents were filtered through a cotton plug and precipitated into stirred MeOH. The MeOH was decanted, and residual MeOH was removed with an N_2 stream. The polymer was redissolved in hexane, and the hexane was stripped to provide the final *α,ω*-PIB-S-bromoisobutyrate.

Results and Discussion



Scheme 3. Synthesis of *α,ω*-PIB-based macromers and macroinitiators from *α,ω*-PIB-phenol

α,ω-PIB-phenol-based Systems

Phenol-terminated polyisobutylenes offer an excellent platform for further modification or as a macromer for block copolymer synthesis. Acid halide chemistry is an extremely efficient method for rapid installation of desired functionality on a laboratory scale; although the cost of acid halides and their acidic reaction byproducts do not lend themselves toward large commercial processes. Several different post-polymerization reaction schemes have been used in the past to produce phenol-terminated PIB,[106,110,122] but this project utilized the recently reported[115] *in situ* quenching of living

polyisobutylene with isopropoxybenzene to quantitatively install isopropoxybenzene functionality. The isopropoxy group is readily cleaved *in situ* by the addition of H_2SO_4 and additional $TiCl_4$, followed by warming the reaction to room temperature. The general reaction scheme utilizing *α,ω*-PIB-phenol to synthesize *α,ω*-PIB-based macromers and macroinitiators is shown in Scheme 3. The ^{1}H NMR spectrum of a representative starting *α,ω*-PIB-phenol is shown in Figure 44. The phenolic proton is readily apparent at 4.5 ppm, and the doublets due to the phenolic ring protons are located at 7.22 ppm and 6.74 ppm.

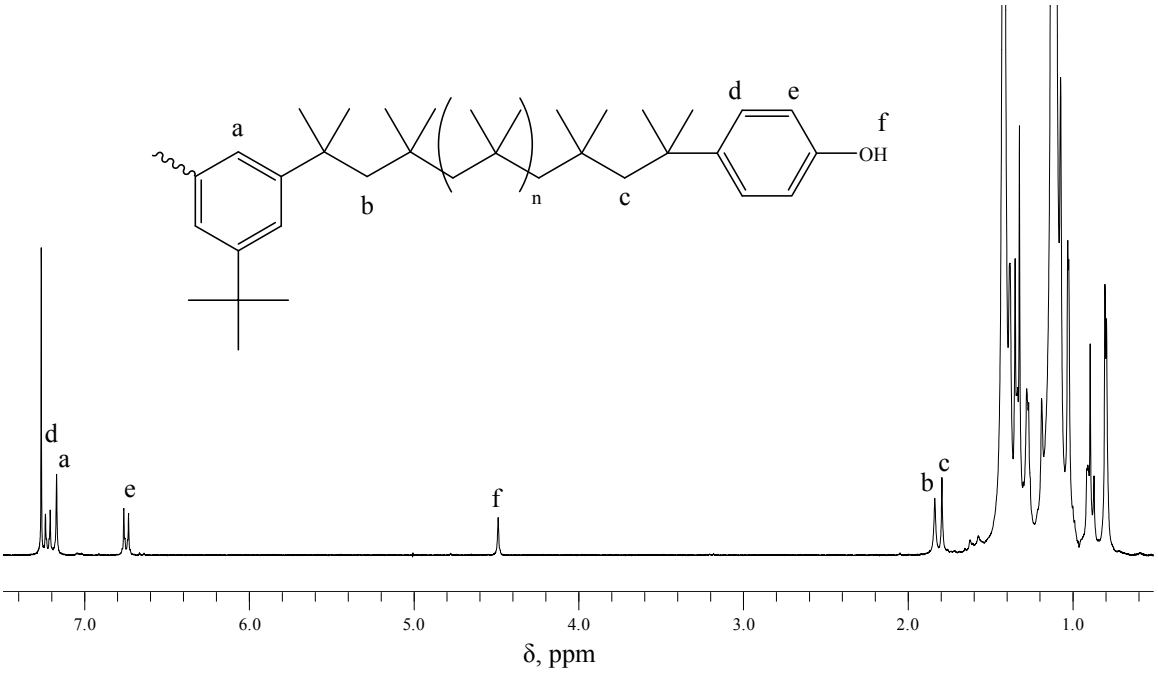


Figure 44. ^{1}H NMR spectrum of *α,ω*-PIB-phenol obtained by quenching of living polyisobutylene with isopropoxybenzene, followed by *in situ*, acid-catalyzed de-blocking of the isopropoxy group.

Reacting *α,ω*-PIB-phenol with (meth)acryloyl chloride produces a telechelic species readily capable of undergoing radical copolymerization. Maenz and Stadermann produced comb-like polymers by copolymerizing monofunctional methacryl-terminated PIBs with MMA and MA.[150] The methacryl-terminated PIBs were themselves produced

by the reaction between phenol-terminated PIB and methacryloyl chloride. However, by utilizing commercial PIBs to produce PIB-phenol, a purification step was required to remove unreactive PIB chains from the functionalized species.[127] By utilizing telechelic PIBs, network formation is possible, with opportunities for use as adhesives or films.

The reaction with (meth)acryloyl chloride was rapid and efficient in THF at rt, with quantitative conversion to the desired (meth)acrylate product. ^{1}H NMR spectra of the (meth)acrylate products are shown in Figure 45. The phenolic proton at 4.5 ppm has been eliminated and replaced by the three acrylate peaks in (A) at 6.61 ppm, 6.32 ppm, and 6.00 ppm, and the two methacrylate protons in (B) at 6.35 ppm and 5.74 ppm. The methyl group of the methacrylate moiety is also visible in (B) at 2.06 ppm.

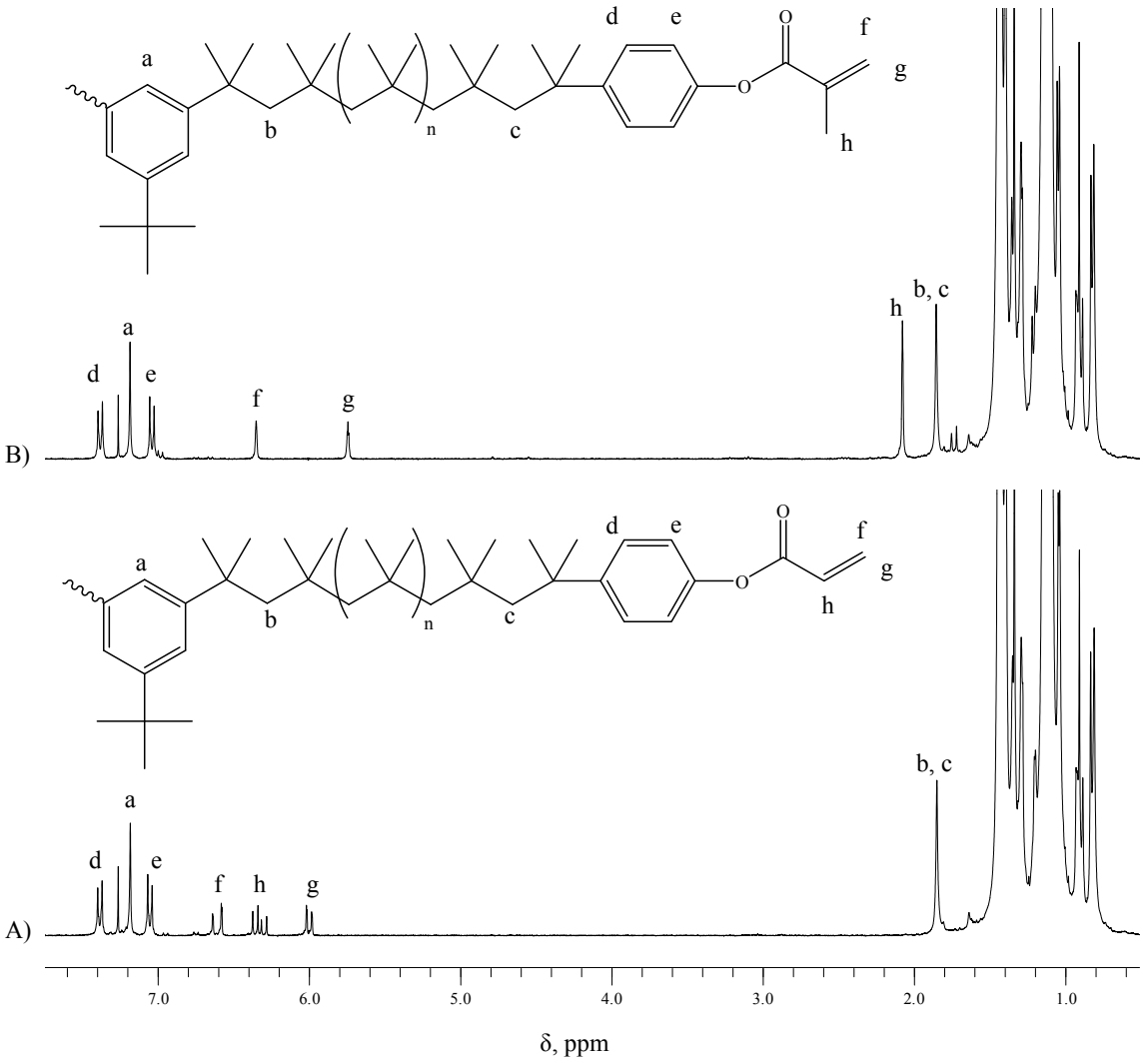


Figure 45. ^{1}H NMR spectra of A) *α,ω*-PIB-acrylate from the reaction of acryloyl chloride and α,ω-PIB-phenol and B) *α,ω*-PIB-methacrylate from the reaction of methacryloyl chloride and *α,ω*-PIB-phenol.

In the ^{13}C NMR spectrum of *α,ω*-PIB-acrylate, Figure 46, the carbonyl carbon appears at 164.6 ppm, along with the acrylate carbons at 132.2 ppm and 128.1 ppm. Similarly, in the ^{13}C NMR spectrum of *α,ω*-PIB-methacrylate, Figure 47, the carbonyl carbon is at 165.9 ppm, and the methacrylate olefinic carbons are at 136.0 ppm and 126.9 ppm, along with the methyl carbon at 18.5 ppm.

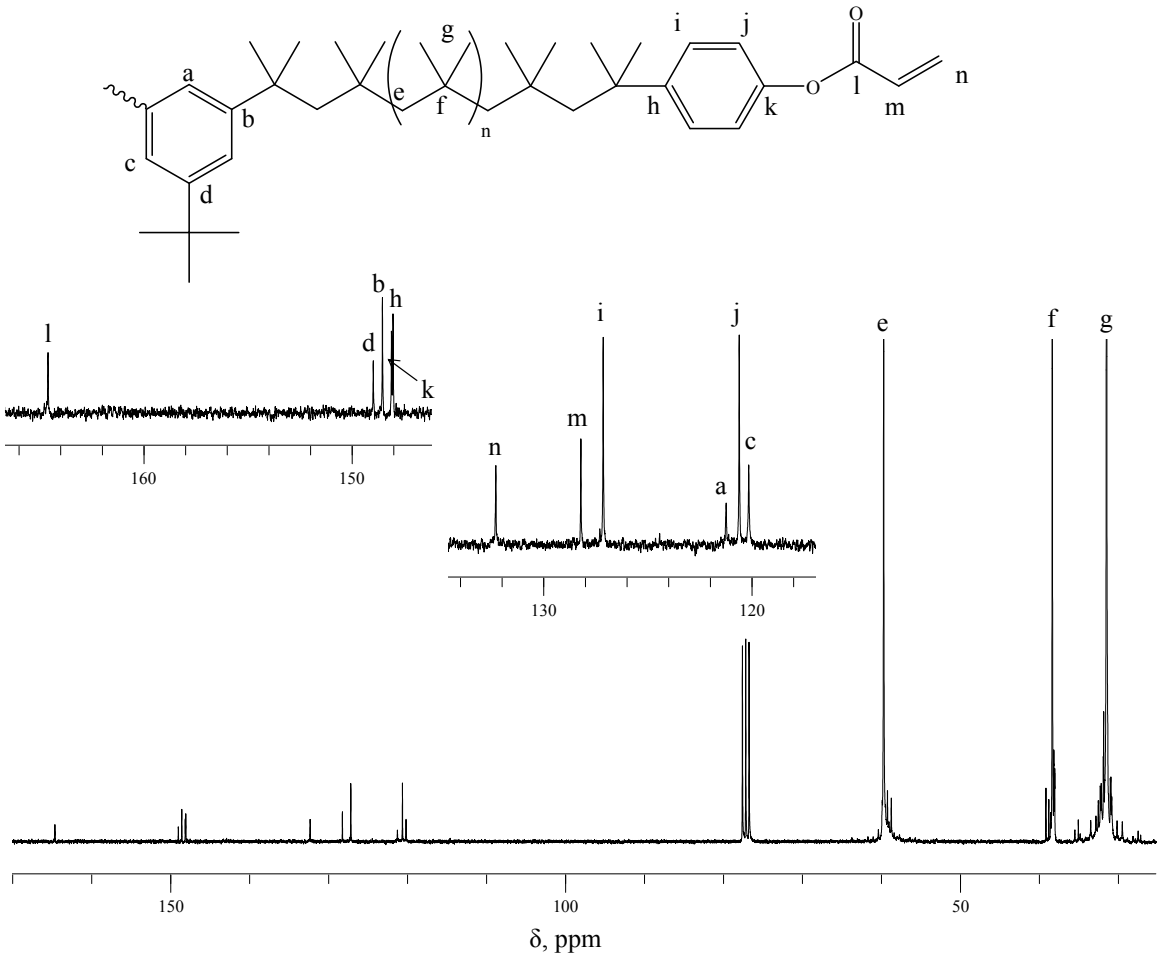


Figure 46. ^{13}C NMR spectrum of *α,ω*-PIB-acrylate from the reaction of acryloyl chloride and *α,ω*-PIB-phenol.

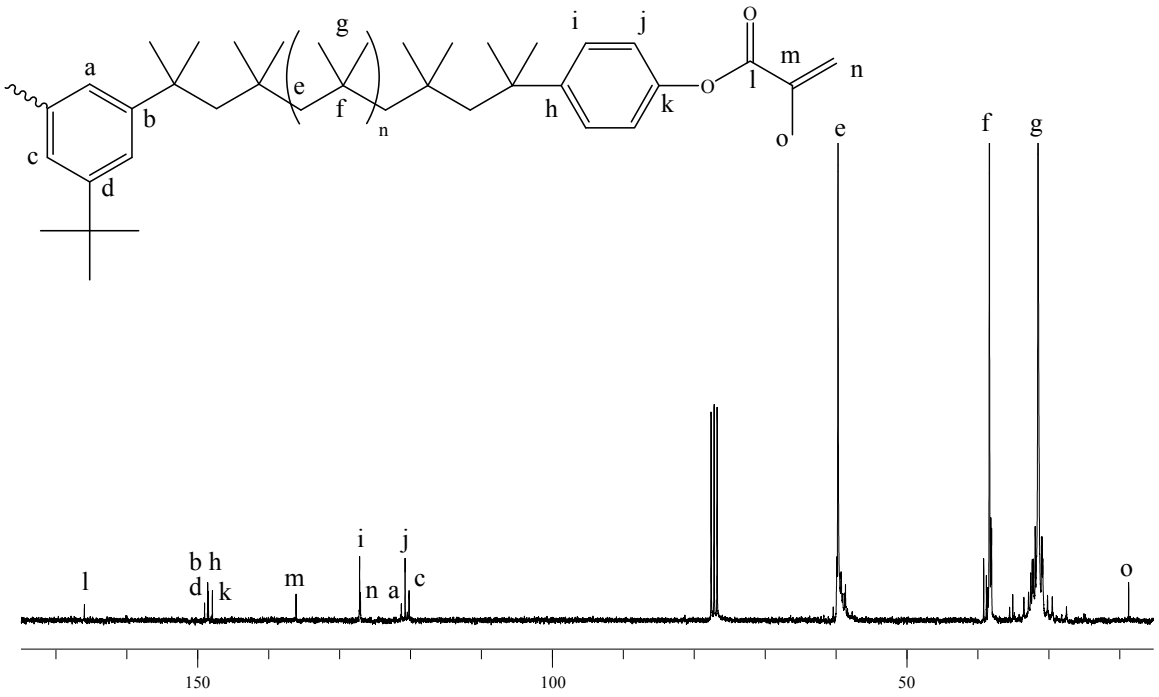


Figure 47. ^{13}C NMR spectrum of *α,ω*-PIB-methacrylate from the reaction of methacryloyl chloride and *α,ω*-PIB-phenol.

GPC traces of the (meth)acrylate-terminated PIBs, shown in Figure 48 indicate that no degradation or coupling of the PIB chains occurred, with *α,ω*-PIB-acrylate (M_n = 5800 g/mol, PDI = 1.22) and *α,ω*-PIB-methacrylate (M_n = 5400, PDI = 1.17) showing nearly identical RI traces to the starting *α,ω*-PIB-phenol.

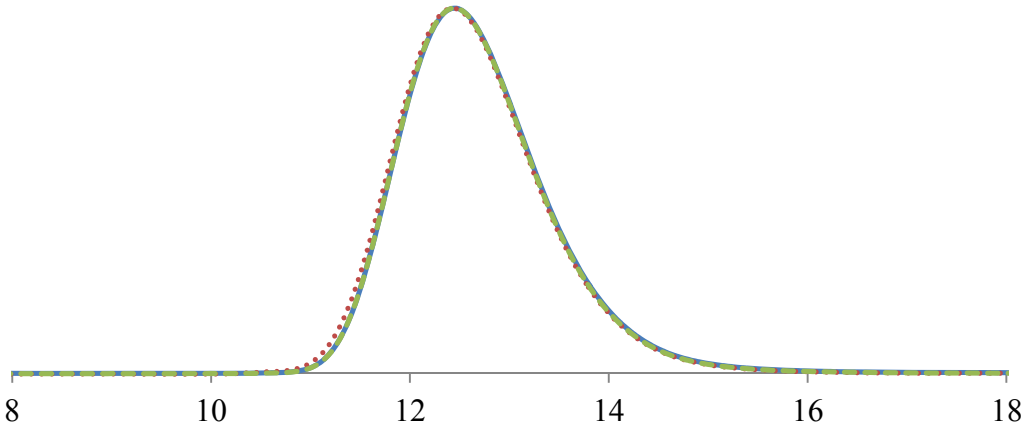


Figure 48. GPC RI traces of *α,ω*-PIB-phenol (solid), *α,ω*-PIB-acrylate (dotted), and *α,ω*-PIB-methacrylate (dashed).

MALDI-TOF MS analysis of *α,ω*-PIB-acrylate and *α,ω*-PIB-methacrylate is summarized in Table 8. Either cationizing agent, AgTFA or NaTFA, provided sufficient ionization of the PIB species; good agreement (<1% deviation) was observed between theoretical and experimental values for residual (end group) mass.

Table 8

MALDI-TOF-MS Analysis of End-groups for Derivatives of α,ω-PIB-phenol

End-Group	End-Group MW (g/mol)	Cation	MW_{Theo} (g/mol)	MW_{Exp} (g/mol)	Difference (g/mol)
acrylate	147.14	Ag	618.54	614.33	4.21
		Na	533.66	530.20	3.46
methacrylate	161.18	Ag	646.63	641.89	4.74
		Na	561.72	557.17	4.55
2-bromopropionate	228.07	Ag	780.40	775.15	5.25
		Na	695.40	690.79	4.61
2-bromoisobutyrate	242.09	Ag	808.45	809.63	1.18

Experimental values were determined by linear regression of a plot of degree of polymerization (DP) versus the mass to charge ratio (m/z, assumed to be 1). The slope of the plot is theoretically equivalent to the MW of the polymer repeat unit, 56.1 Da for PIB. The y-intercept of this plot is theoretically represented by Equation 5:

$$Y_{intercept} = 2\ EG + I + C$$

Equation 5. Value of $Y_{intercept}$ of MALDI-TOF MS regression Plot.

where EG is the MW of the polymer end group, multiplied by 2 because the PIB is difunctional, I is the MW of the initiator residue, and C is the MW of the cation of the cationizing agent, either Ag or Na. A representative example for *α,ω*-PIB-acrylate is shown in Figure 49. The value of 55.6 Da for the repeat unit is very close to the ideal value; the value of 614.33 Da for the end group residual is within 4 Da (0.6%) of the theoretical value of 618.54 ($C_{34}H_{38}O_4Ag$). The MALDI-TOF MS traces of *α,ω*-PIB-acrylate and *α,ω*-PIB-methacrylate with AgTFA are shown in Figures 50 and 51. The insets of these figures highlight several of the peaks with the measured peak molecular weights listed, confirming the separation of each peak by a single monomer unit.

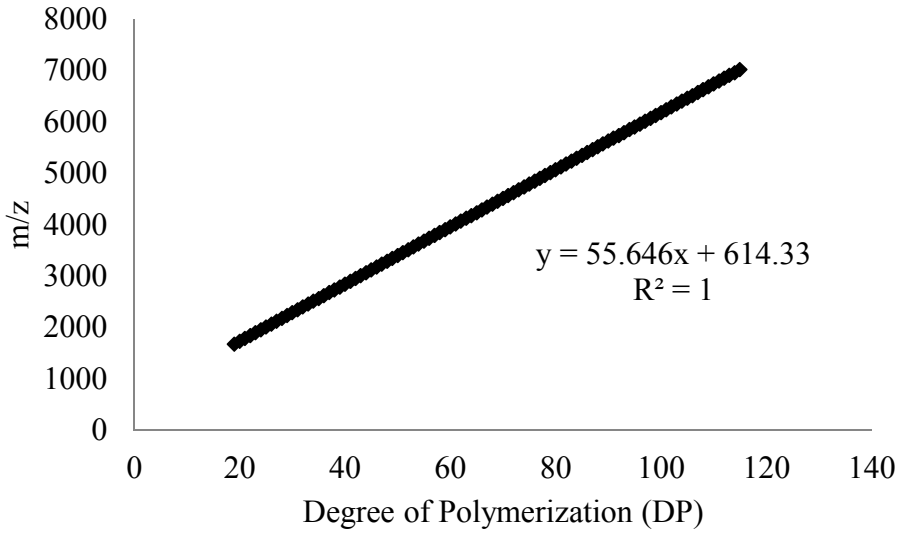


Figure 49. Linear regression of MALDI-TOF spectrum of α,ω-PIB-acrylate.

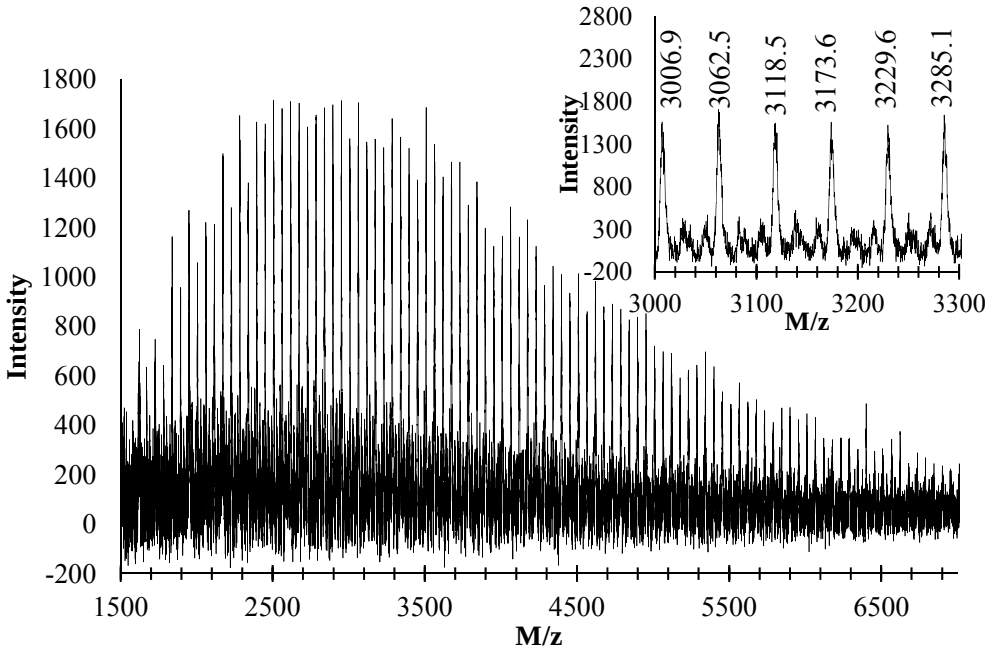


Figure 50. MALDI-TOF MS plot of *α,ω*-PIB-acrylate with AgTFA cationizing agent.

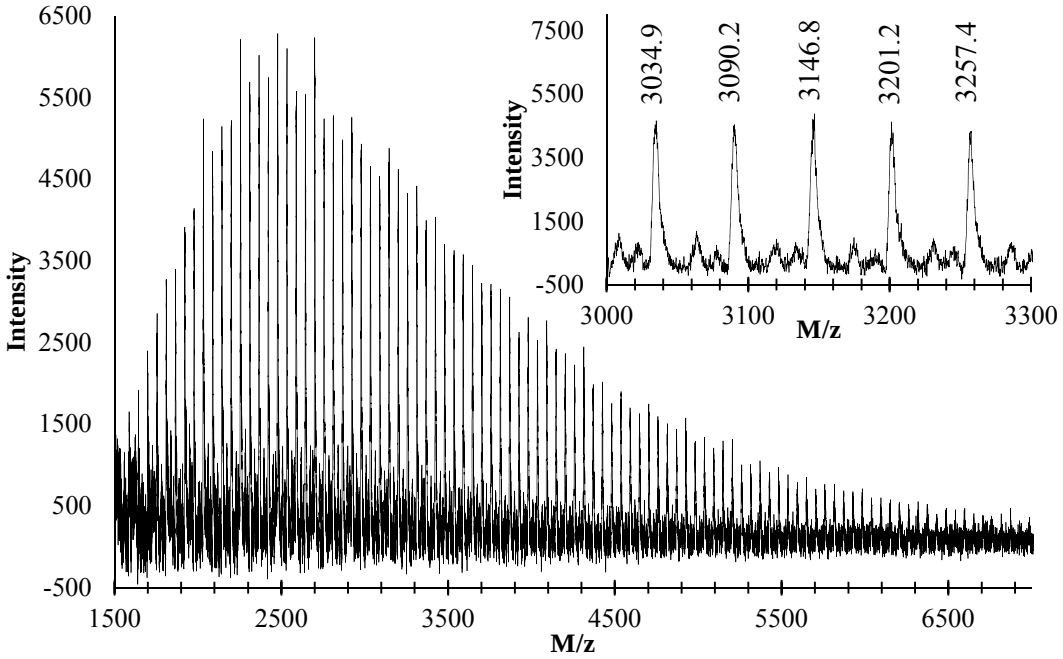


Figure 51. MALDI-TOF MS plot of *α,ω*-PIB-methacrylate with AgTFA cationizing agent.

PIB-based macromers have been utilized as radical initiating species for both RAFT and ATRP processes. Magenau and Storey developed PIB-based CTAs to produce PIB-*b*-*N*-isopropylacrylamide diblock copolymers.[118] Zhu and Storey produced linear diblock copolymers of PIB and methyl acrylate using an initiating species containing a cationic-initiating moiety and an ATRP moiety consisting of either 2-bromopropionate or 2-bromoisobutyrate.[151] Addition of an ATRP initiating moiety was also adapted to difunctional cationic initiators to produce miktoarm star polymers.[38] Both approaches produced a single ATRP block per individual copolymer unit. A PIB-based macromer containing two ATRP-initiating 2-bromoisobutyrate sites has been produced by the reaction of 2-bromoisobutyryl bromide with PIB containing a 2,2-bis(hydroxymethyl)propionate unit.[152] The efficiency of acid bromide chemistry is clearly shown by the mild reaction conditions (2 h at rt) needed to achieve high chain-end functionality. The ^{1}H NMR spectra of *α,ω*-PIB-bromopropionate and

α,ω-PIB-bromoisobutyrate are shown in Figure 52. The phenolic proton of *α,ω*-PIB-phenol is absent in both species. For *α,ω*-PIB-bromopropionate (A), the bromopropyl methine proton appears at 4.58 ppm, and is split into a quartet by the adjacent methyl group, which appears as a doublet at 1.95 ppm. For *α,ω*-PIB-bromoisobutyrate (B), the two equivalent methyl groups appear as a large singlet at 2.07 ppm. The ^{13}C NMR spectra for both species are shown in Figure 53. For *α,ω*-PIB-bromopropionate (A), the carbonyl carbon resonates at 169.8 ppm, the bromopropyl methine carbon at 58.5 ppm, and the bromopropyl methyl group at 21.5 ppm. For *α,ω*-PIB-bromoisobutyrate (B), the carbonyl carbon appears at 170.3 ppm, the bromoisobutyryl quaternary carbon at 55.4 ppm, and the bromoisobutyryl methyl carbons at 27.3 ppm.

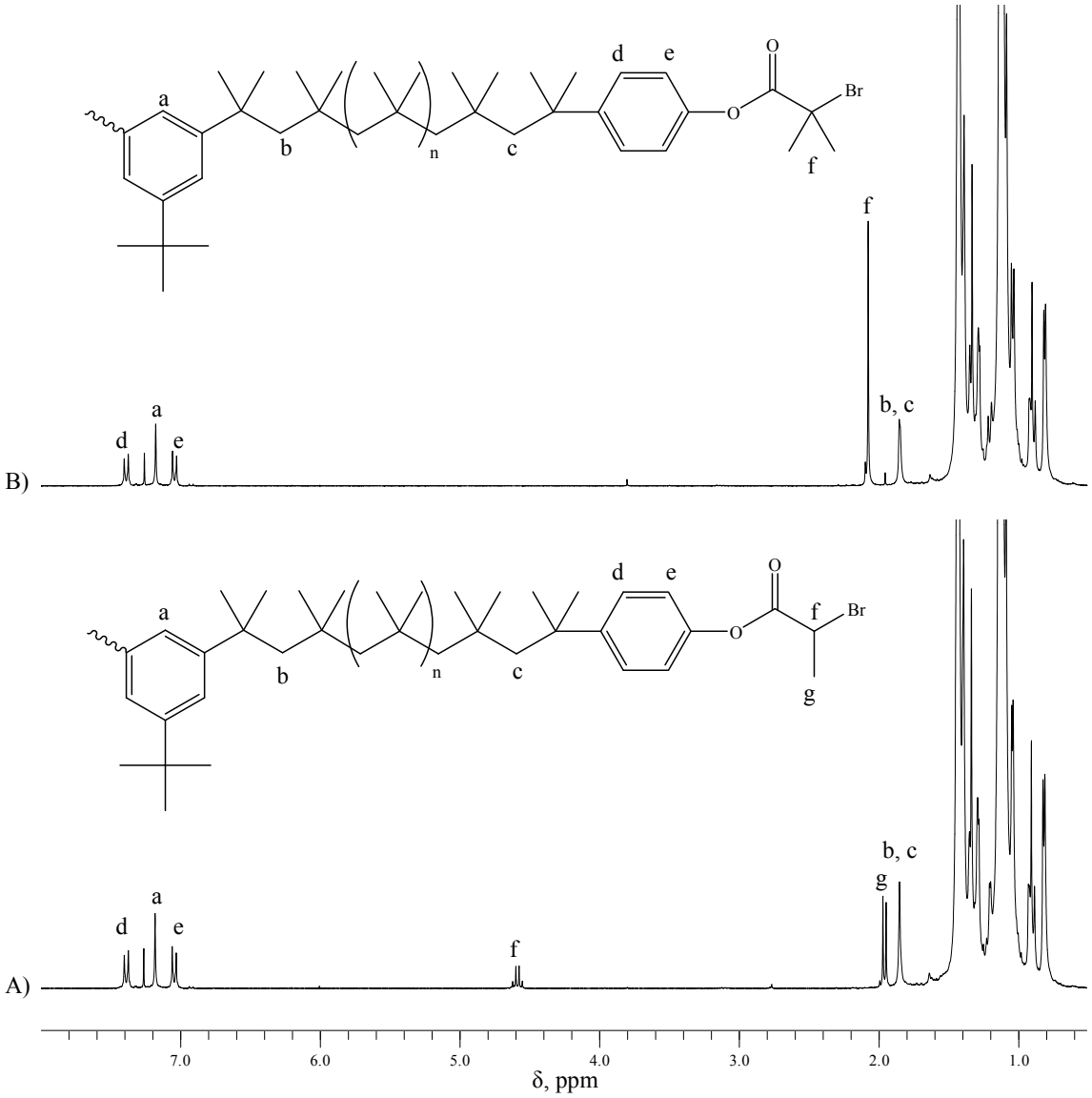


Figure 52. ^{1}H NMR spectra of A) *α,ω*-PIB-bromopropionate from the reaction of 2-bromopropionyl bromide and *α,ω*-PIB-phenol, and B) *α,ω*-PIB-bromoisobutyrate from the reaction of 2-bromoisobutyryl bromide and *α,ω*-PIB-phenol.

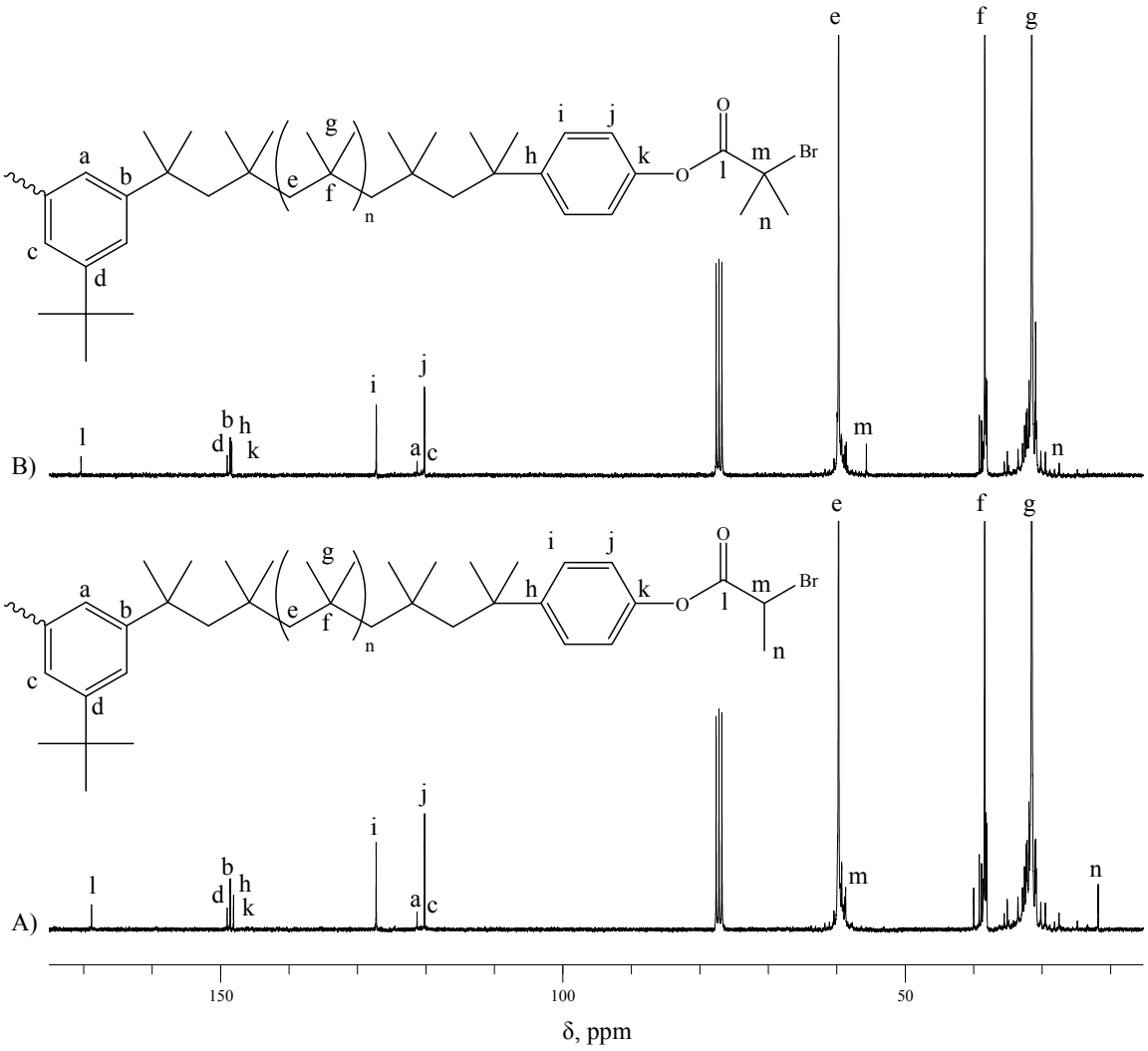


Figure 53. ^{13}C NMR spectra of A) *α,ω*-PIB-bromopropionate from the reaction of 2-bromopropionyl bromide and *α,ω*-PIB-phenol, and B) *α,ω*-PIB-bromoisobutyrate from the reaction of 2-bromoisobutyryl bromide and *α,ω*-PIB-phenol.

GPC RI traces for *α,ω*-PIB-bromopropionate (M_n = 5400 g/mol, PDI = 1.18) and *α,ω*-PIB-bromoisobutyrate (M_n = 5500 g/mol, PDI = 1.18) relative to the starting *α,ω*-PIB-phenol (M_n = 5200 g/mol, PDI = 1.18) are shown in Figure 54. No coupling or chain decomposition is evident, and the shapes of the traces are nearly identical.

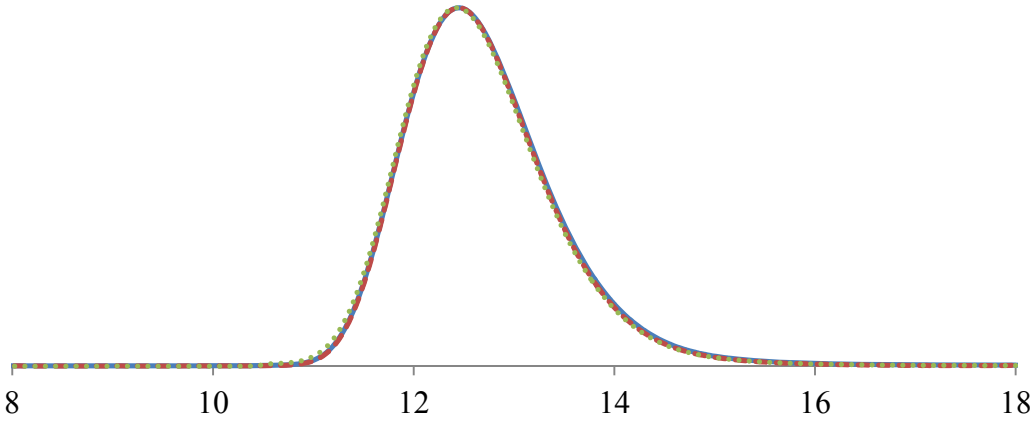


Figure 54. GPC RI traces of *α,ω*-PIB-phenol (solid), *α,ω*-PIB-bromopropionate (dashed), and *α,ω*-PIB-bromoisobutyrate (dotted).

MALDI-TOF MS data are shown in Table 8, calculated by the same linear regression method as the acrylate and methacrylate species already discussed. The MALDI-TOF MS plots are shown in Figure 55 for *α,ω*-PIB-bromopropionate and Figure 56 for *α,ω*-PIB-bromoisobutyrate. The insets to both plots indicate the difference between the individual peaks is very close to the ideal value of 56.1 Da.

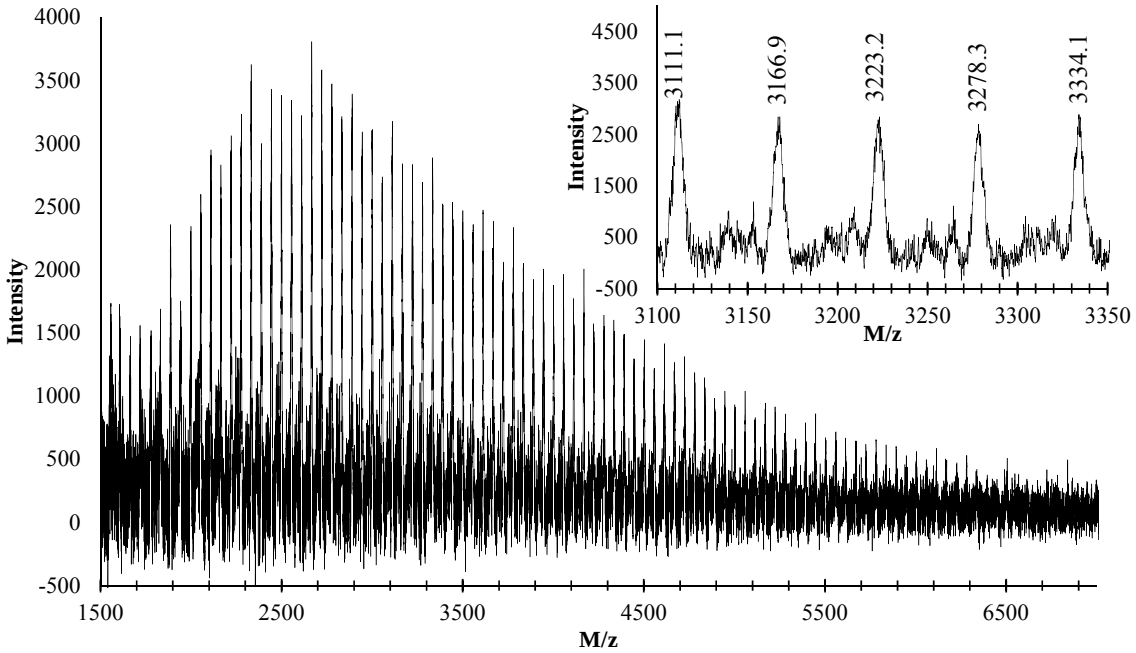


Figure 55. MALDI-TOF MS plot of α,ω-PIB-bromopropionate with AgTFA cationizing agent.

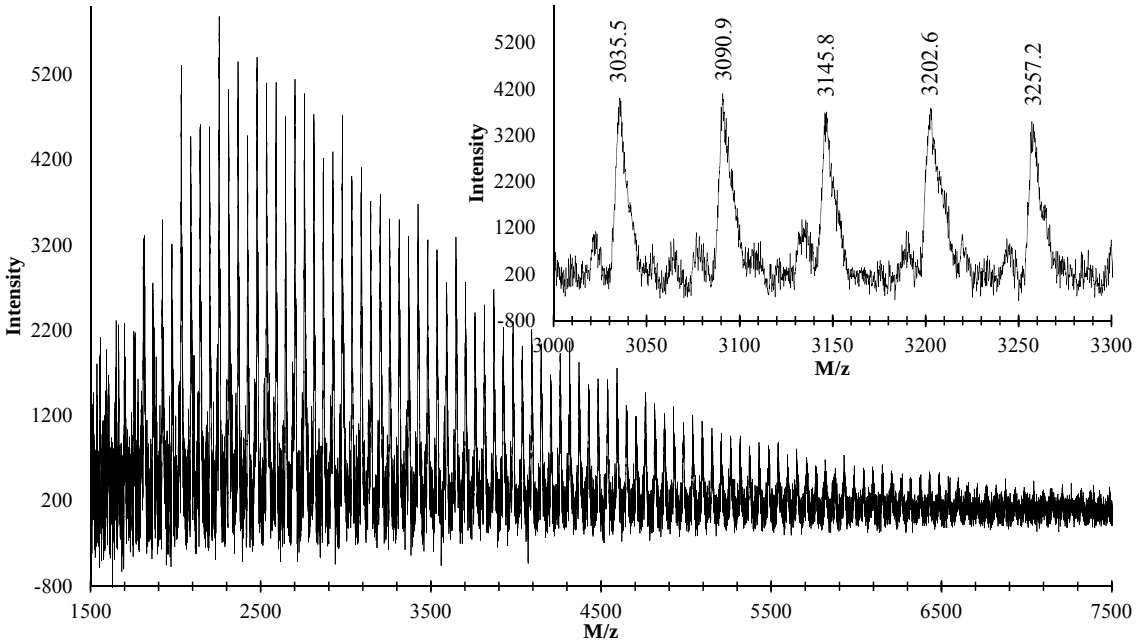


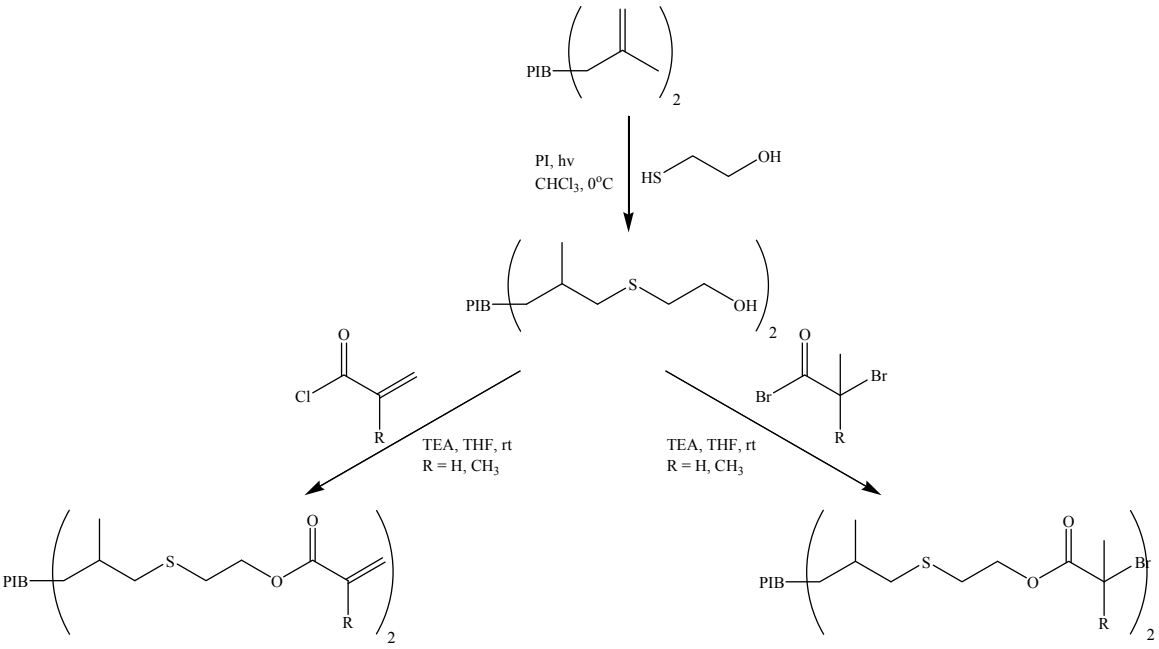
Figure 56. MALDI-TOF MS plot of α,ω-PIB-bromoisobutyrate with AgTFA cationizing agent.

α,ω-PIB-OH-based Systems

Thiol-ene reactions offer a convenient "click" chemistry approach to introducing functionality to PIB. Early efforts focused on commercially available monofunctional PIBs, but even those with the largest fraction of *exo*-olefin end groups retain a nonzero percentage of *endo*-olefin groups or other more complex structures which are ill-suited to radical thiol-ene reactions. This prevents quantitative functionalization and sometimes necessitates purification to remove the non-functional polymer chains.[125,126] Even with such limitations, 2-mercaptoethanol has been successfully added to commercial *exo*-olefin PIBs, and the products were further derivatized using methacryloyl chloride with *p*-toluenesulfonic acid catalysis.[126] With the development of quenchers to produce quantitative *exo*-olefin PIB, it became possible to utilize thiol-ene chemistry to quantitatively functionalize PIB without tedious polymer purification. Magenau et al. produced mono- and difunctional *exo*-olefin PIBs with near-quantitative functionality using the hindered base quencher 1,2,2,6,6-pentamethylpiperidine.[77] They then utilized radical thiol-ene reactions to attach thiols containing a variety of secondary functionalities, including hydroxyl (using 5-mercaptopentanol), carboxylic acid, and amine.[128] In this work, their technique has been adapted to install 2-mercaptoethanol onto the end of *exo*-olefin PIB using the radical initiator 2,2-dimethoxy-2-phenylacetophenone and chloroform solvent at 0 ºC (Scheme 4). The reaction is complete within 10 min with no residual *exo*-olefin peaks (4.62 and 4.84 ppm). The ^{1}H NMRs of both the starting *α,ω*-PIB-*exo* (A) and *α,ω*-PIB-OH (B) are shown in Figure 57. The *exo*-olefin peaks are eliminated in the product spectrum (B), and the anti-Markovnikov addition inherent to the radical thiol-ene mechanism results in a chiral methine carbon appearing at 1.74 ppm, splitting the adjacent methylene protons into a pair of diastereomers at 2.53 ppm and 2.35

ppm. The methylene protons from the mercaptoethanol moiety appear as a triplet at 2.72 ppm adjacent to the sulfide linkage and a doublet of triplets at 3.71 ppm adjacent to the hydroxyl moiety.

In the ^{13}C NMR spectra, shown in Figure 58, the olefinic carbons in the precursor spectrum (A) appear at 143.9 and 114.4 ppm, along with the terminal methyl carbon at 25.8 ppm. In the product spectrum (B), these resonances disappear and are replaced by the mercaptoethanol signals at 60.0 and 29.5 ppm. Additionally, the terminal methyl group shifts upfield to 22.6 ppm, and the methylene carbon bound to the sulfide linkage appears at 41.6 ppm.



Scheme 4. Synthesis of *α,ω*-PIB-based macromers and macroinitiators from *α,ω*-PIB-*exo*.

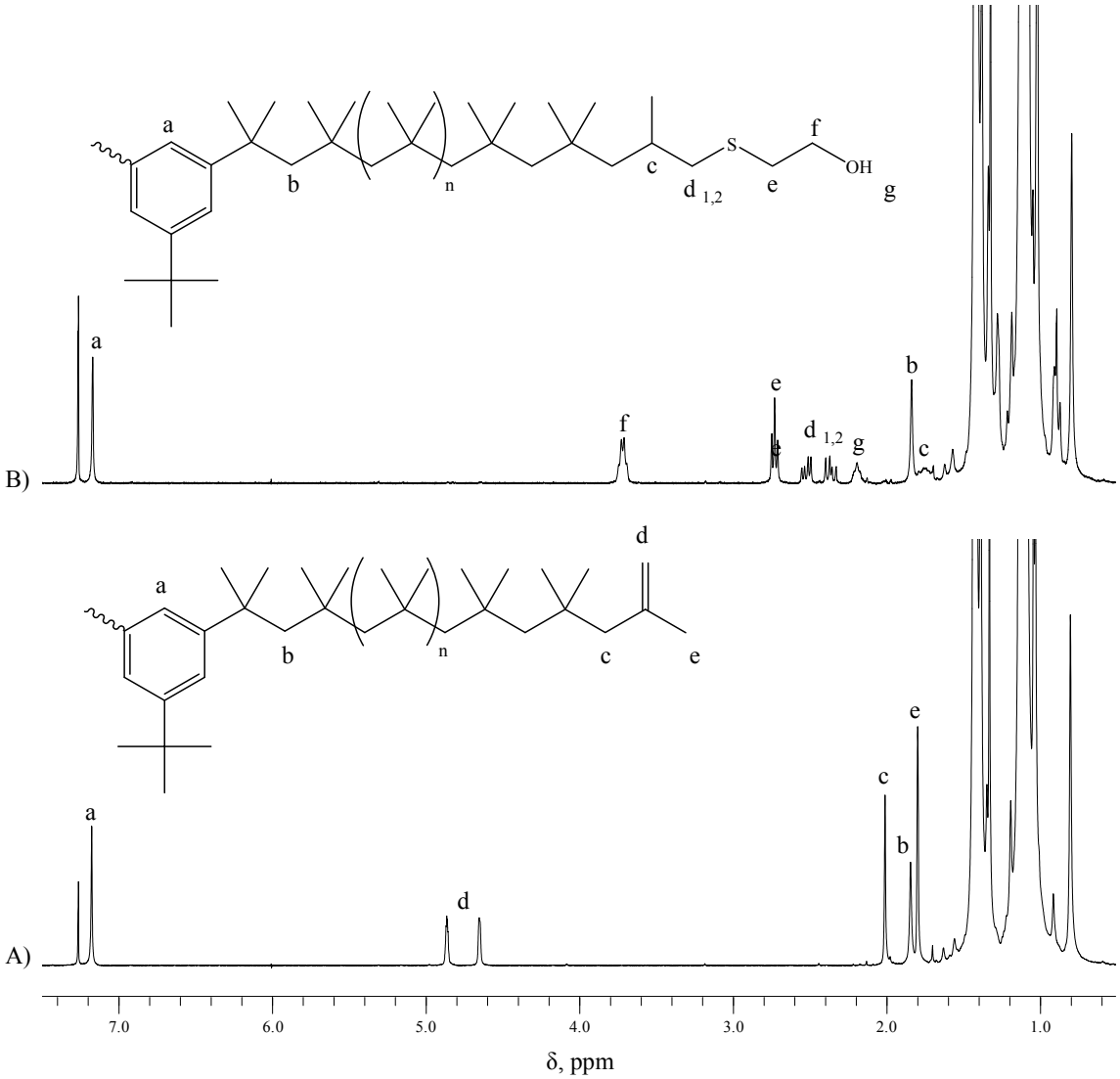


Figure 57. ^{1}H NMR spectra of A) *α,ω*-PIB-*exo* obtained from *in situ* quenching of living cationic polyisobutylene with diisopropyl ether followed by treatment with excess methanol, and B) *α,ω*-PIB-OH obtained from the radical thiol-ene reaction of *α,ω*-PIB-*exo* and 2-mercaptoethanol.

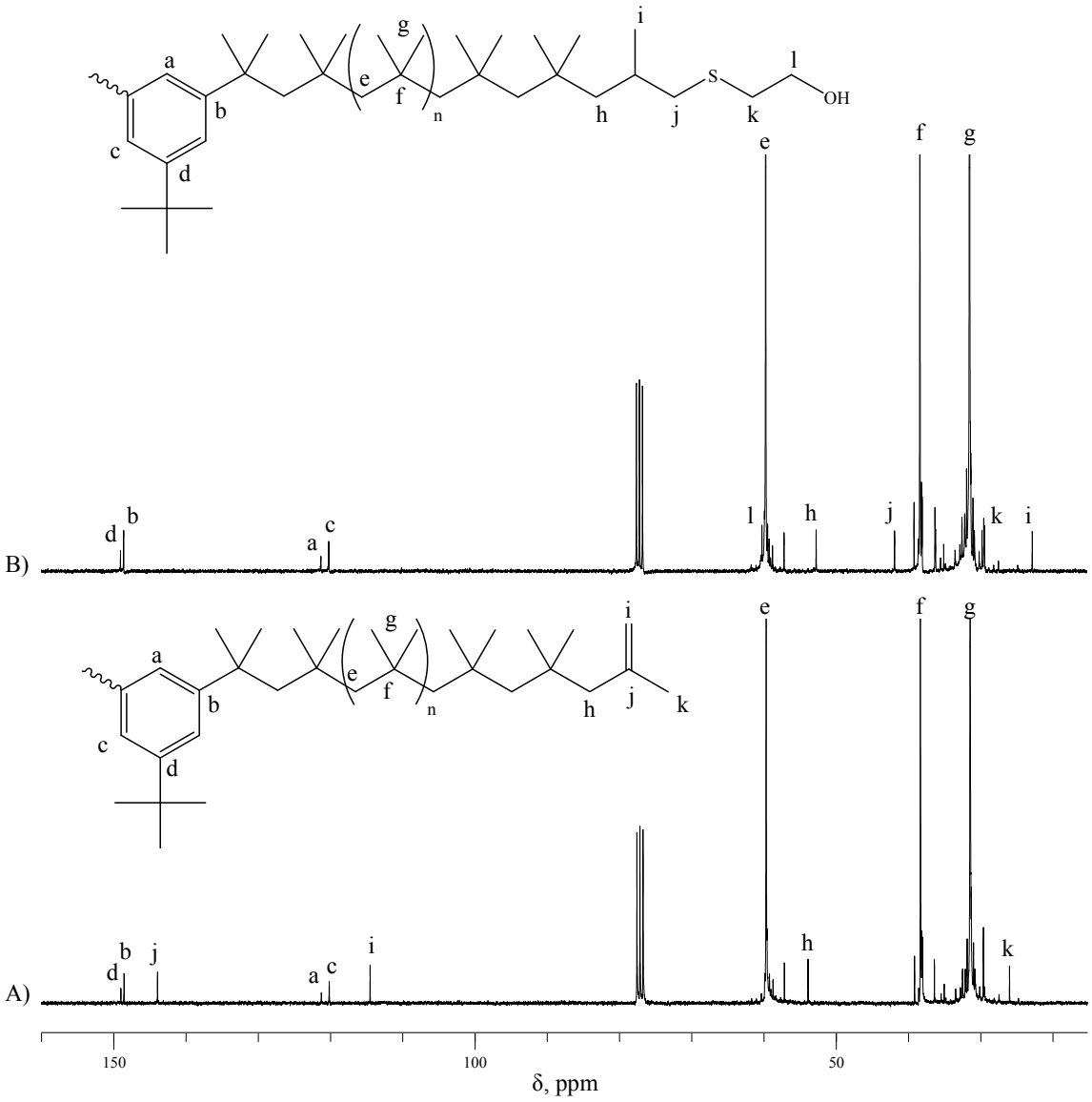


Figure 58. ^{13}C NMR spectra of A) *α,ω*-PIB-*exo* obtained from *in situ* quenching of living cationic polyisobutylene with diisopropyl ether followed by treatment with excess methanol, and B) *α,ω*-PIB-OH obtained from the radical thiol-ene reaction of *α,ω*-PIB-*exo* and 2-mercaptoethanol.

Refractive index GPC traces of *α,ω*-PIB-OH and *α,ω*-PIB-*exo* are shown in Figure 59 and indicate no degradation of the polymer backbone or coupling during the radical thiol-ene reaction, as expected. The MALDI-TOF MS plot of *α,ω*-PIB-OH, shown in Figure 60 indicates a regular repeating structure of 56.4 Da, and the MW_{Theo} and MW_{Exp} are in agreement, differing by 2.24 Da, as shown in Table 9.

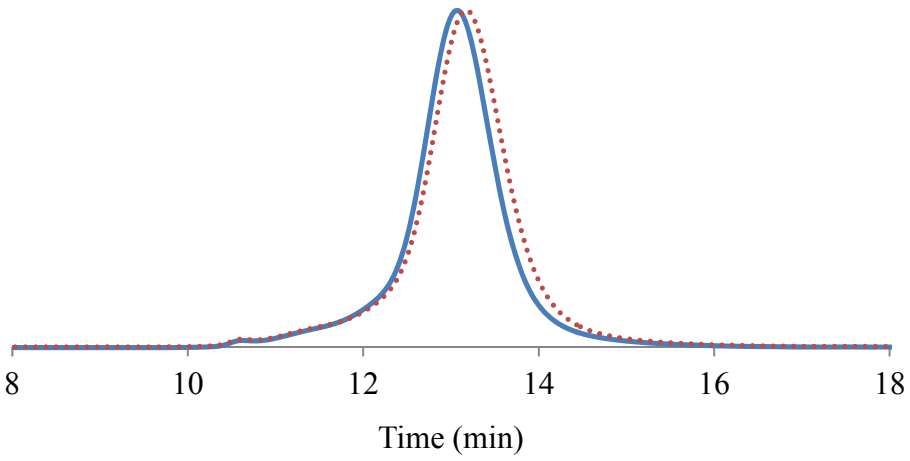


Figure 59. GPC RI traces of *α,ω*-PIB-OH (solid) produced from the thiol-ene reaction of *α,ω*-PIB-*exo* (dotted) and 2-mercaptoethanol.

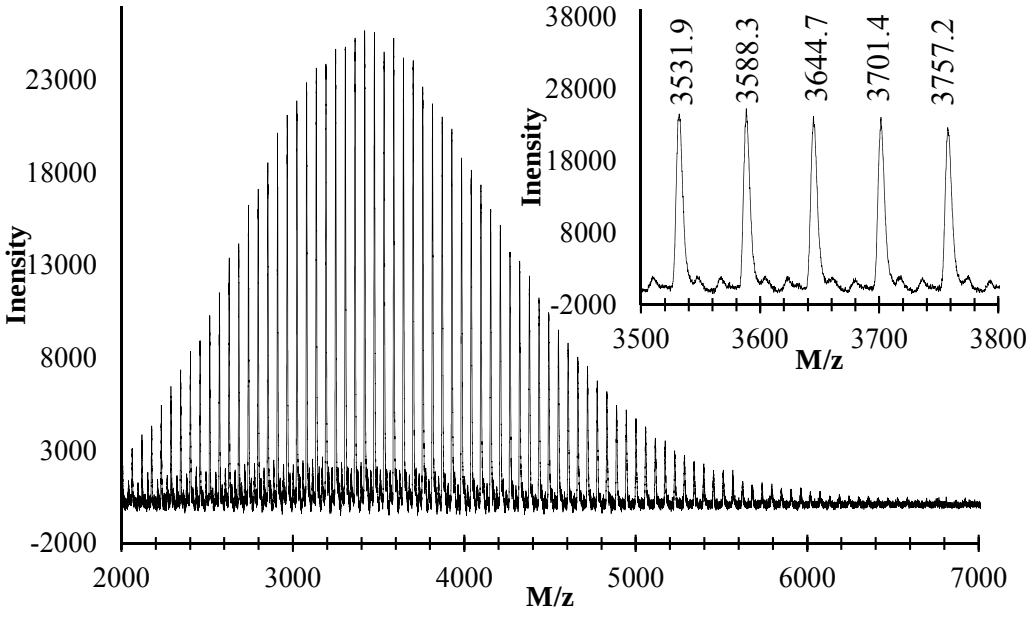


Figure 60. MALDI-TOF-MS spectrum of *α,ω*-PIB-OH with AgTFA cationizing agent.

Table 9

MALDI-TOF-MS End-group Analysis for α,ω-PIB-OH and Derivatives using AgTFA as Cationizing Agent

End-Group	End-Group MW (g/mol)	MW_{Theo} (g/mol)	MW_{Exp} (g/mol)	Difference (g/mol)
mercaptoethanol	77.13	478.49	480.73	2.24
acrylate	147.14	589.44	589.24	0.20
methacrylate	161.18	614.64	610.73	3.91
2-bromopropionate	228.07	720.864	729.19	8.33
2-bromoisobutyrate	242.09	668.36	673.59	5.23

Derivatization of *α,ω*-PIB-OH into macromers and macroinitiators followed the procedure outlined in Scheme 4. Regardless, high end-group functionalization was achieved for all species studied. Figure 61 shows the ^{1}H NMR spectra of *α,ω*-PIB-S-acrylate (A) and *α,ω*-PIB-S-methacrylate (B). In both spectra, the hydroxyl proton of the starting *α,ω*-PIB-OH at 2.18 ppm is absent. The methylene units of the mercaptoethanol moiety, which appear at 3.70 ppm and 2.72 ppm in the small-molecule reagent, are observed at 4.31 ppm and 2.77 ppm in *α,ω*-PIB-S-acrylate and 4.29 ppm and 2.77 ppm in *α,ω*-PIB-S-methacrylate. The acrylate protons of *α,ω*-PIB-S-acrylate appear at 6.44 ppm, 6.15 ppm, and 5.85 ppm. The methacrylate protons resonate at 6.12 ppm and 5.58 ppm in *α,ω*-PIB-S-methacrylate. In the ^{13}C spectrum of *α,ω*-PIB-S-acrylate (Figure 62, A), the acrylate olefinic carbons appear at 131.0 ppm and 128.3 ppm, and the carbonyl carbon appears at 165.9 ppm. The mercaptoethanol methylene carbons are observed at 36.0 ppm and 63.7 ppm compared to 29.5 and 60.0 ppm in the small-molecule reagent. For *α,ω*-PIB-S-methacrylate (B), the methacrylate olefinic carbons appear at 136.1 ppm and 125.8 ppm, with the carbonyl carbon at 167.1 ppm and the mercaptoethanol methylene carbons in nearly identical positions to those of *α,ω*-PIB-S-acrylate.

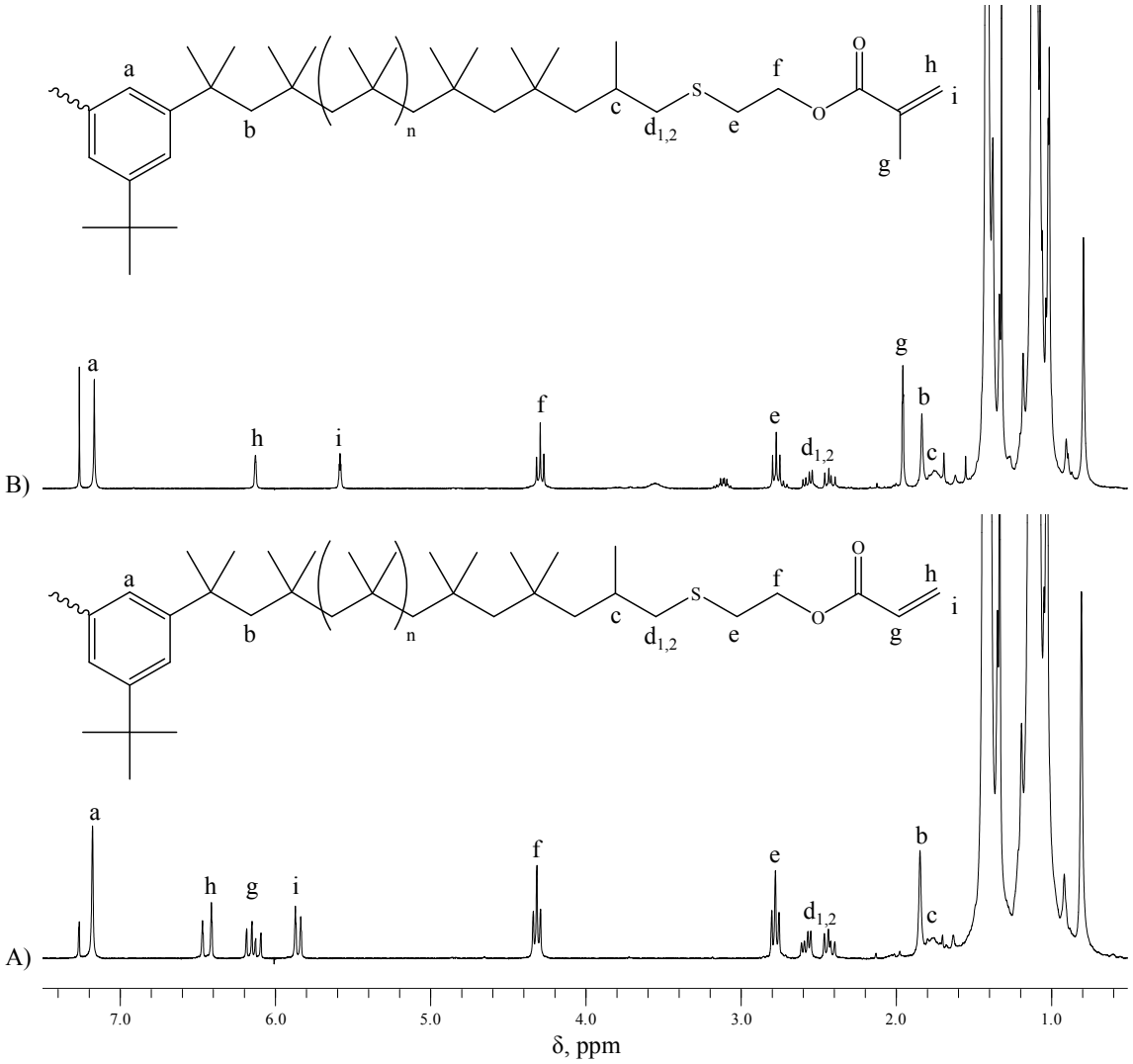


Figure 61. ^{1}H NMR spectra of A) *α,ω*-PIB-S-acrylate from the reaction of *α,ω*-PIB-OH and acryloyl chloride, and B) *α,ω*-PIB-S-methacrylate from the reaction of *α,ω*-PIB-OH and methacryloyl chloride.

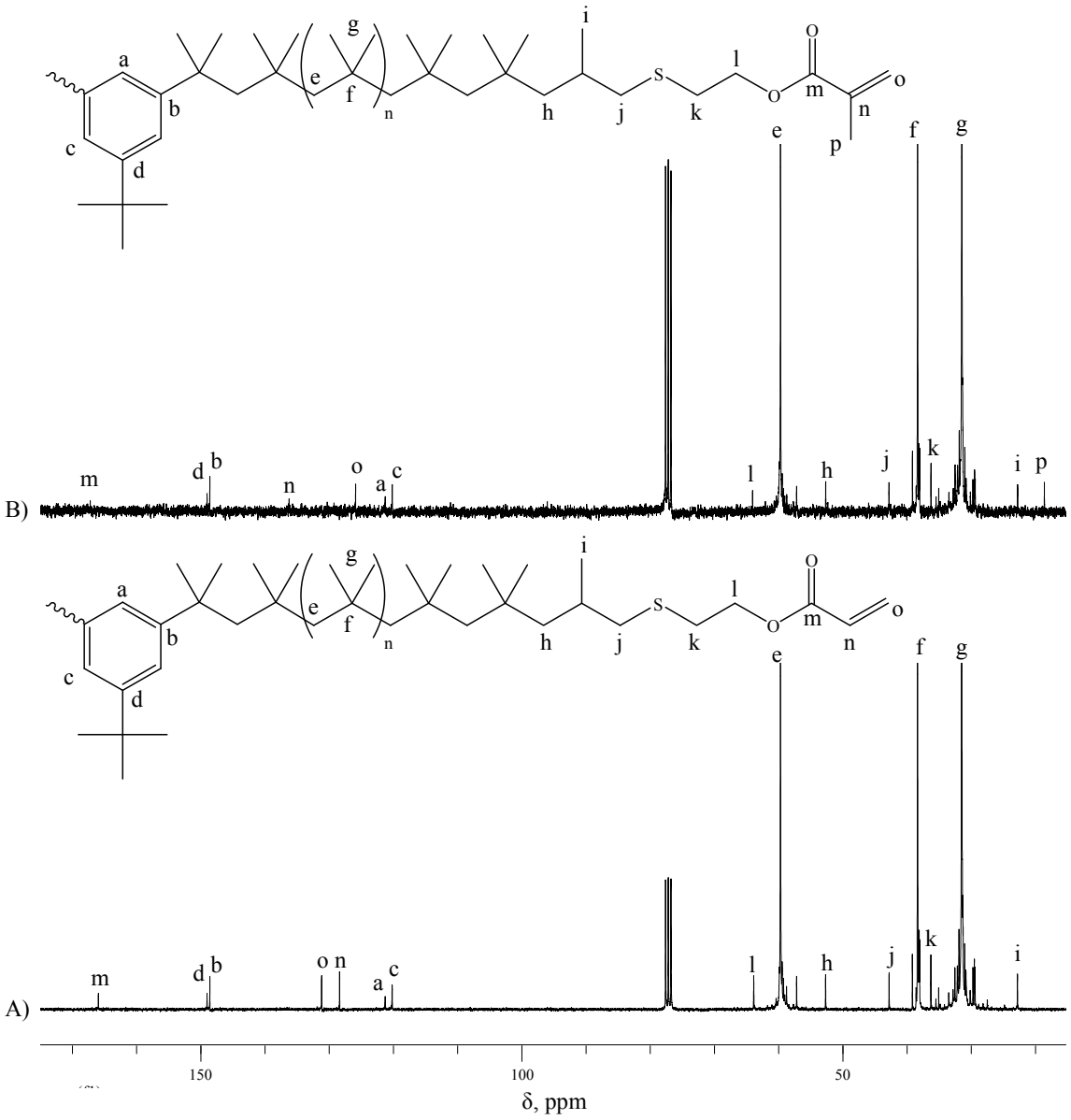


Figure 62. ^{13}C NMR spectra of A) *α,ω*-PIB-S-acrylate from the reaction of *α,ω*-PIB-OH and acryloyl chloride, and B) *α,ω*-PIB-S-methacrylate from the reaction of *α,ω*-PIB-OH and methacryloyl chloride.

Refractive index GPC traces for the *α,ω*-PIB-S-acrylate (M_n = 4200 g/mol, PDI = 1.12) and *α,ω*-PIB-S-methacrylate (M_n = 4200 g/mol, PDI = 1.13) show no evidence of coupling or radical homopolymerization of the (meth)acrylate end groups (Figure 63); although upon drying in a vacuum oven for several days at 50 ºC, one *α,ω*-PIB-S-methacrylate sample did undergo reaction, forming a clear, colorless rubbery

solid that proved insoluble in THF. No other sample dried in the same way reacted in this manner.

MALDI-TOF MS data for *α,ω*-PIB-S-(meth)acrylates are shown in Table 9. Good agreement was observed between MW_{Theo} and MW_{Exp} of the end-group residues, and the individual peaks in the spectra showed a regular spacing of around 56 Da.

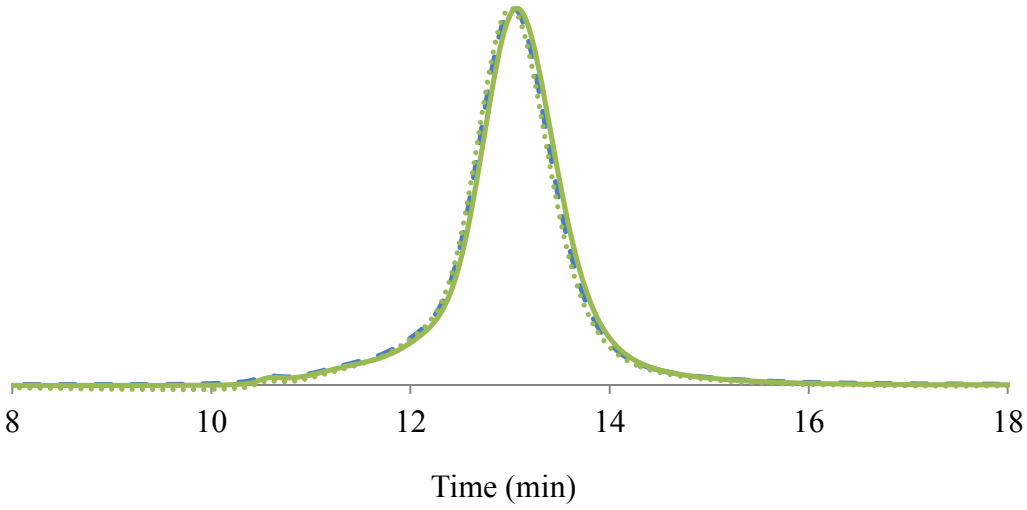


Figure 63. GPC RI traces of *α,ω*-PIB-OH (solid), *α,ω*-PIB-S-acrylate (dashed), and *α,ω*-PIB-methacrylate (dotted).

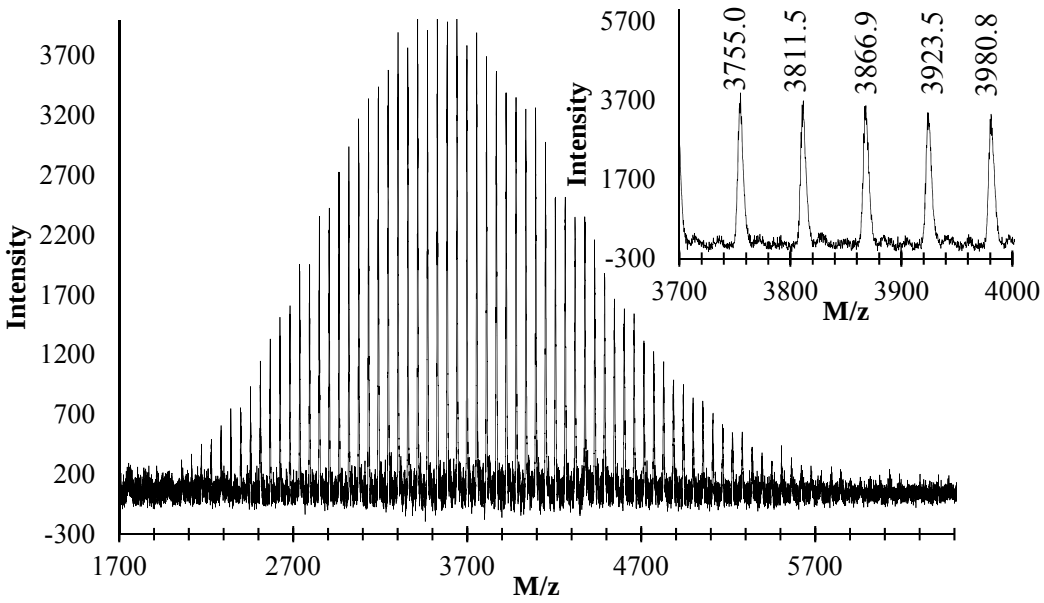


Figure 64. MALDI-TOF mass spectrum of *α,ω*-PIB-S-acrylate with AgTFA cationizing agent.

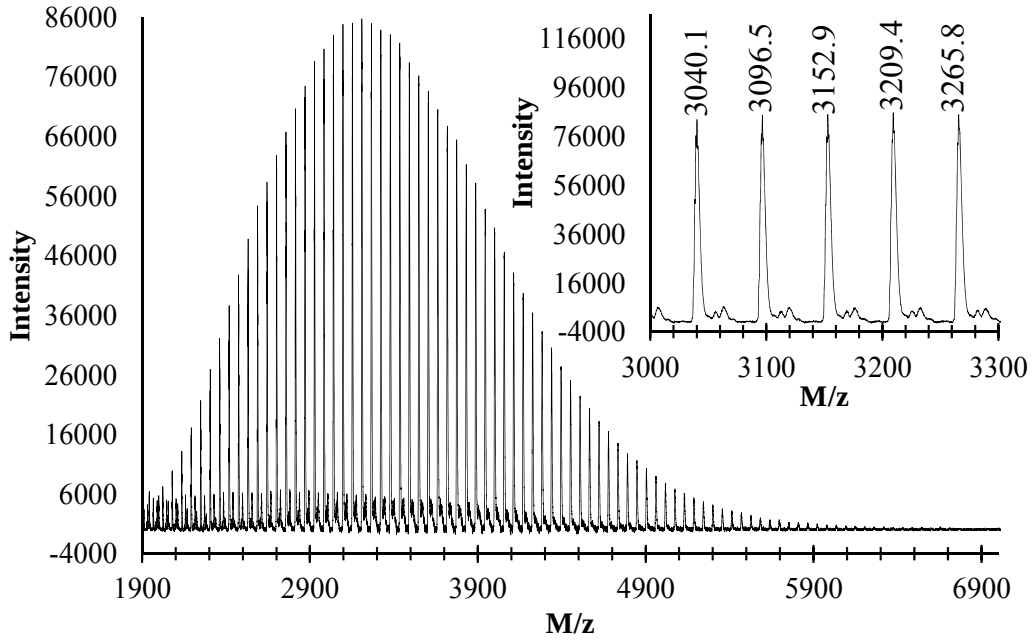


Figure 65. MALDI-TOF mass spectrum of *α,ω*-PIB-S-methacrylate with AgTFA cationizing agent.

α,ω-PIB-based macroinitiators were produced in accordance with Scheme 4 and the resulting ^{1}H NMR spectra are shown in Figure 66. Hydroxyl groups that would result

from residual α,ω-PIB-OH are absent in both spectra, and the mercaptoethanol methylene tether protons appear at 2.76 ppm and 4.31 ppm. In the spectrum of α,ω-PIB-S-bromopropionate (A) the methine proton (c) appears as a quartet partially overlapping the tether protons at 4.37 ppm; while the terminal methyl group (h) appears as a doublet that is convoluted with the methylene protons of the first IB repeat unit at 1.84 ppm. For α,ω-PIB-S-bromoisobutyrate, the terminal methyl groups produce a large singlet at 1.95 ppm.

In the ^{13}C NMR spectrum of α,ω-PIB-S-bromopropionate, Figure 67 (A), the carbonyl carbon, terminal methine carbon, and terminal methyl carbon are visible at 170.0, 39.8, and 21.7 ppm, respectively. For α,ω-PIB-S-bromoisobutyrate (B), the carbonyl carbon appears at 171.4 ppm, the terminal quaternary carbon at 55.6 ppm, and the terminal methyl carbons at 29.5 ppm.

RI GPC traces (Figure 68) reveal no chain coupling or degradation of α,ω-PIB-S-bromopropionate (M_n = 4300, PDI = 1.14) and α,ω-PIB-S-bromoisobutyrate (M_n = 4533, PDI = 1.15). The MALDI-TOF mass spectrum of α,ω-PIB-S-bromoisobutyrate shows a regular spacing of 56.7 Da (Figure 69). The α,ω-PIB-S-bromopropionate mass spectrum contained a sodium ion impurity from the sample plate and is not shown. Interestingly, these bromine containing species do not ionize as well using NaTFA. With AgTFA, the bromine atoms react with the silver ions, forming darkened sample solutions prior to spotting onto the sample plate. Linear regression reveals good agreement between the MW_{Theo} and MW_{Exp} (Table 9), if the reaction between silver and bromine is accounted for (i.e. fragmentation of the bromine atoms from the chains). For α,ω-PIB-S-bromopropionate, assuming the loss of a single bromine atom per chain yields the regression result, while both bromine atoms are lost for α,ω-PIB-S-bromoisobutyrate.

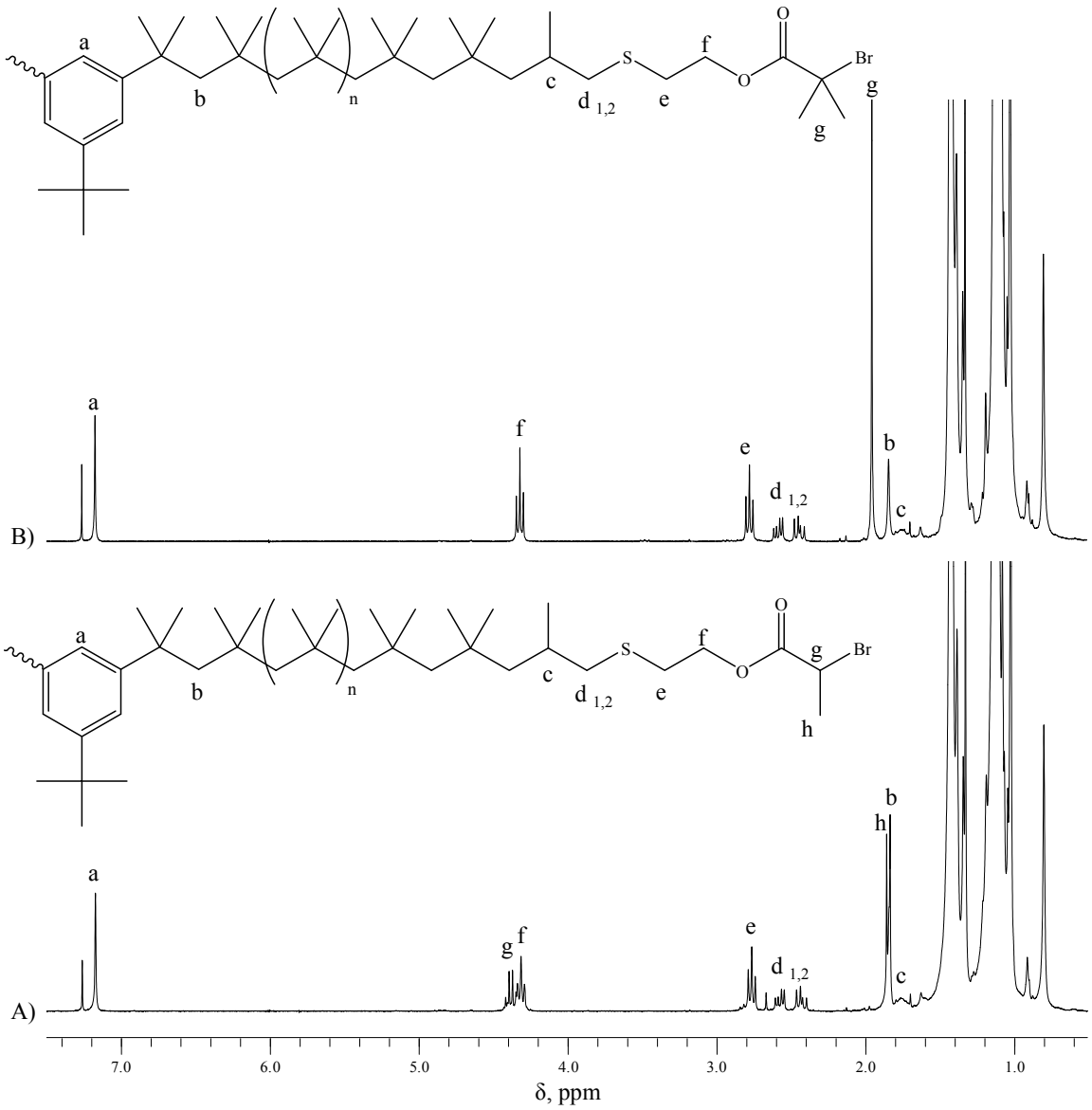


Figure 66. ^{1}H NMR spectra of A) *α,ω*-PIB-S-bromopropionate from the reaction of *α,ω*-PIB-OH and 2-bromopropionyl bromide, and B) *α,ω*-PIB-S-bromoisobutyrate from the reaction of *α,ω*-PIB-OH and 2-bromoisobutyryl bromide.

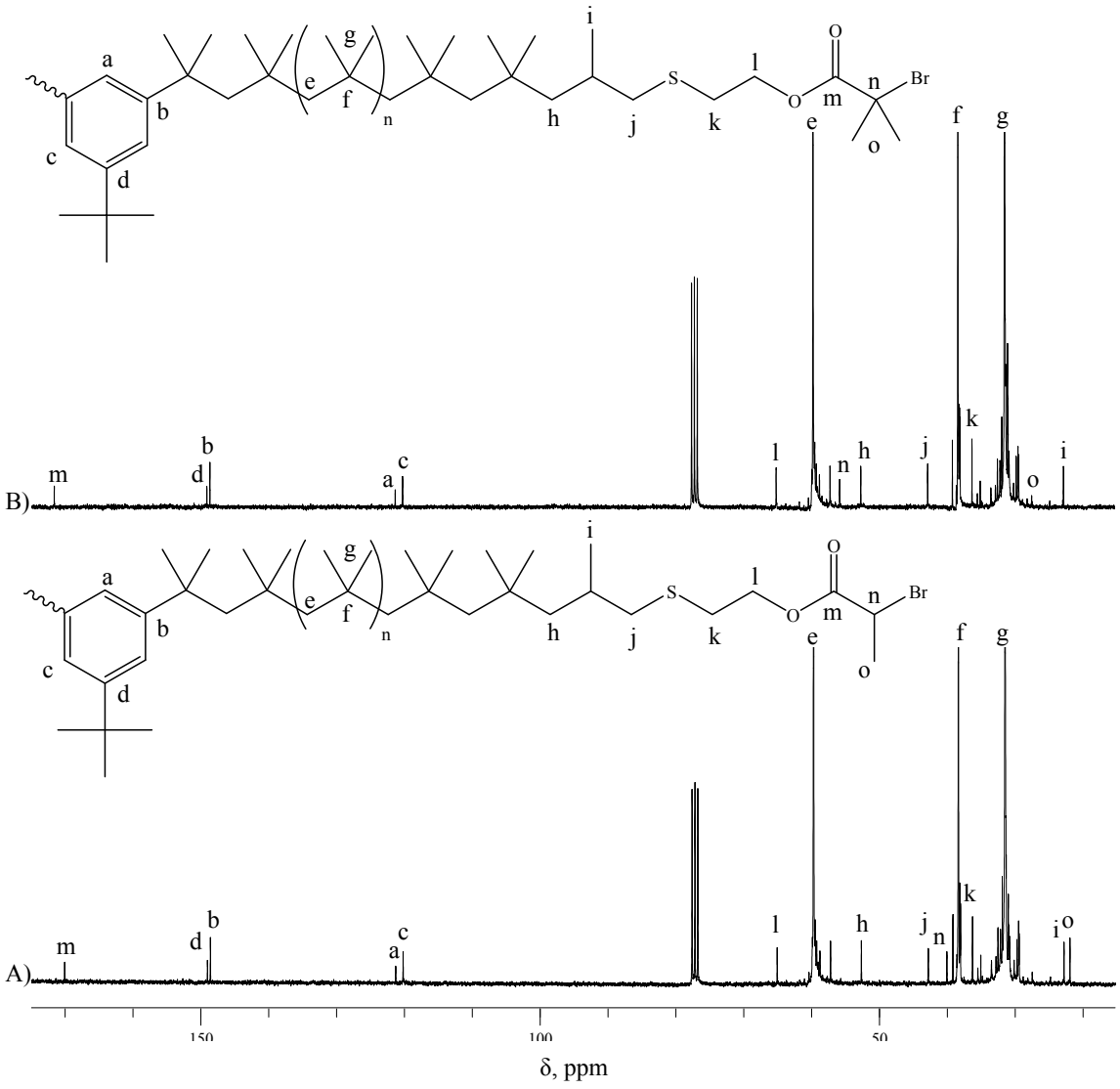


Figure 67. ^{13}C NMR spectra of A) *α,ω*-PIB-S-bromopropionate from the reaction of *α,ω*-PIB-OH and 2-bromopropionyl bromide, and B) *α,ω*-PIB-S-bromoisobutyrate from the reaction of *α,ω*-PIB-OH and 2-bromoisobutyryl bromide.

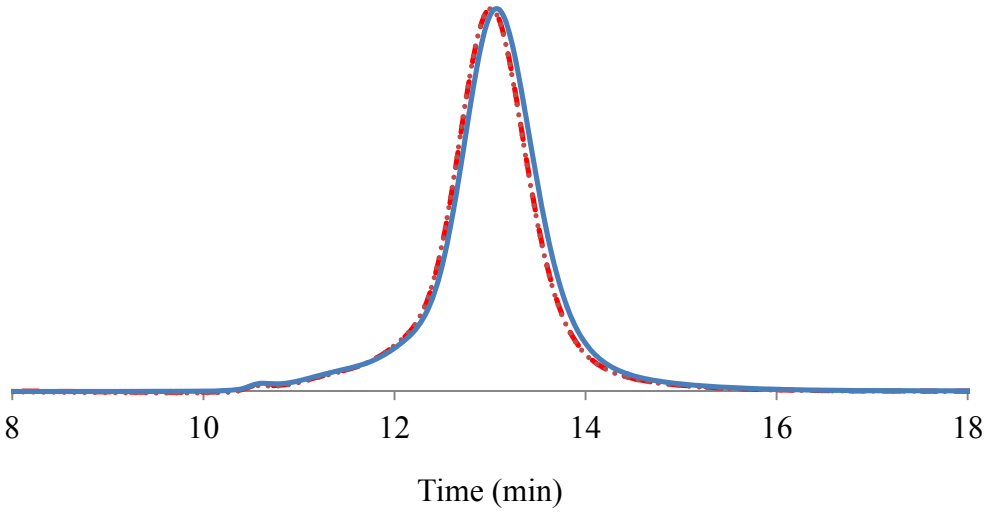


Figure 68. GPC RI traces of *α,ω*-PIB-OH (solid), *α,ω*-PIB-S-bromopropionate (dashed), and *α,ω*-PIB-bromoisobutyrate (dotted).

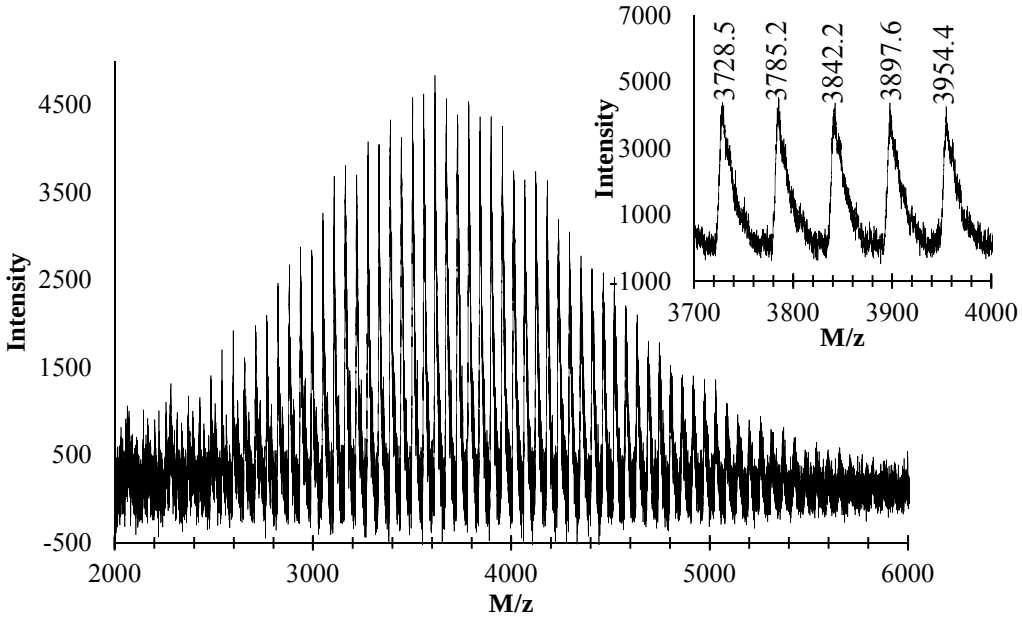


Figure 69. MALDI-TOF mass spectrum of *α,ω*-PIB-S-bromoisobutyrate with AgTFA cationizing agent.

Conclusions

α,ω-PIB-based macromers and macroinitiators capable of participating in or initiating radical polymerizations have been produced using telechelic polyisobutylenes produced via *in situ* quenching methods. Difunctional hydroxyl-PIBs, both aromatic and aliphatic, were produced and subsequently modified via facile acid halide reactions under mild conditions with TEA catalysis. Macromer PIBs containing (meth)acrylate termini, capable of radical copolymerization have been synthesized and characterized. PIB-based ATRP macroinitiators have been produced with bromopropionate and bromoisobutyrate termini.

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