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ELECTROPHILIC CLEAVAGE AND FUNCTIONALIZATION OF POLYISOBUTYLENES BEARING UNSATURATIONS IN THE BACKBONE AND SYNTHESIS OF POLYMERS FOR THIS PROCESS

by

Christopher Garrett Campbell

A Dissertation
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December 2017

ELECTROPHILIC CLEAVAGE AND FUNCTIONALIZATION OF POLYISOBUTYLENES BEARING UNSATURATIONS IN THE BACKBONE AND SYNTHESIS OF POLYMERS FOR THIS PROCESS

by Christopher Garrett Campbell

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ABSTRACT

ELECTROPHILIC CLEAVAGE AND FUNCTIONALIZATION OF POLYISOBUTYLENES BEARING UNSATURATIONS IN THE BACKBONE AND SYNTHESIS OF POLYMERS FOR THIS PROCESS

by Christopher Garrett Campbell

December 2017

Polyisobutylene is a polymer of high commercial and academic interest due to its low cost of synthesis, high gas barrier properties, and high chemical and oxidative stability. Polyisobutylene (PIB) can only be synthesized by the cationic polymerization of isobutylene (IB). Commercial processes are currently only capable of producing monofunctional PIB or copolymers thereof. The living cationic polymerization of isobutylene is capable of producing difunctional telechelic PIB, but at the expense of difficultly or expensively synthesized initiators. Thus there exists a need for new synthetic routes for multifunctional PIBs, which can be adopted on a commercial scale.

In the first project, we demonstrated a new reaction, which is a subset of the Friedel-Crafts alkylation reaction, in which the alkylating carbocation undergoes a cleavage reaction prior to reaction with the aromatic substrate. This reaction was discovered by the observation that when a PIB containing a large amount of coupled fraction was subjected to a mixture of protic and Lewis acids (HCl/$TiCl_4$) in the presence of an alkoxybenzene compound, the coupled fraction was quantitatively converted to its constituent monofunctional chains, which became functionalized by the alkoxybenzene.

In the second project, a commercial polymer, poly(isobutylene-*co*-isoprene) (butyl rubber) was used as a substrate upon which the aforementioned electrophilic

cleavage and functionalization reaction was performed. The goal of this project was to degrade a high molecular weight, main-chain olefin-containing copolymer of isobutylene into low molecular weight difunctional telechelic polyisobutylenes. This general process, though not necessarily proceeding by the aforementioned novel chemical reaction, has been described in the literature as “constructive degradation.” Though we were unable to synthesize truly telechelic polyisobutylenes by this method, we were able to demonstrate this method as a viable route to low molecular weight multifunctional PIBs.

In the third project, we attempted to synthesize a random copolymer, previously reported by Kennedy et al., of isobutylene and 2,4-dimethyl-1,3-pentadiene (DMPD). The interest in this copolymer was based on its structural similarity to the coupled PIB mentioned in the first project. However, we found that these two monomers are not well suited to the creation of random copolymers due to a large difference in reactivity ratios. The project presented in this chapter was then redirected toward the structural characterization of the products of attempted copolymerization and of the homo-polymerization of DMPD.

In the fourth project, we investigated the copolymer of isobutylene and β-pinene as a substrate for the aforementioned cleavage/functionalization reaction. We were able to synthesize high molecular weight copolymers of these two monomers via slurry polymerization catalyzed by either $TiCl_4$ or ethylaluminum dichloride (EADC), and though the degradation and functionalization kinetics were much slower than for butyl rubber, we did observe a drastic decrease in molecular weight accompanied by functionalization of the polymer, thus proving this chemistry is applicable to copolymers of isobutylene other than butyl rubber.

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DEDICATION

I would like to dedicate this work to my family.

To Randy, Donna, Hannah, and Lannah Campbell:

Thank you for your support these past years. I do not know where life will take me, but I know I will always be able to turn to you in times of need.

To my Grandparents, Aunts, Uncles, Cousins, and In-Laws:

You are the wide reaching solid bedrock that has supported me during my time at USM. I could wish for no better family than y'all.

To my Wife, Shayna:

Thank you for you love and support these past six years. You have been an endless well of comfort and adventure; without you, none of this would have been possible. I cannot wait to see what the future has in store for us. Our next chapter awaits, and I yearn to write it with you.

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CHAPTER I - INTRODUCTION TO POLYISOBUTYLENE

Polyisobutylene (PIB) is the fully saturated polymer of isobutylene (IB) and can only be synthesized via cationic polymerization. It is of commercial interest due to its thermal and oxidative stability, biological[1] and chemical[2] inertness, low gas permeability,[3] and low monomer cost. It is these properties that have made PIB an ideal material for use in the areas of fuel and lube additives,[4] biomaterials,[5] adhesives,[6] and automobile and truck tires.[7]

Early History of Polyisobutylene

Polyisobutylene was first reported in 1873 when it was found that when IB, a gaseous olefinic hydrocarbon, was treated with the Lewis acid BF_3, a high viscosity non-boiling liquid was produced.[8] In 1940, M. Otto and M. Muller-Cunradi of IG Farbenindustrie AG (now BASF) improved upon this process, reporting the production of solid polymer from isobutylene catalyzed by BF_3 at temperatures below -10°C.[9] The low temperature of this reaction served to reduce chain-transfer to monomer allowing for the production of PIB in the range of 3×10^5 g/mol at a temperature of -100°C. The resulting polymers lacked the olefinic groups present in natural rubber resulting in improved oxidation resistance. However, due to the lack of these unsaturations, the material could not be converted to a thermoset material via sulfur vulcanization. Around 1944, driven by an effort to produce PIB bearing cross-linkable unsaturations, Robert M. Thomas and William J. Sparks reported the copolymerization of IB and butadiene catalyzed by aluminum trichloride ($AlCl_3$) with methyl chloride (MeCl) as a solvent.[10] Later, butadiene was replaced with isoprene in this process, and the resulting copolymer was termed “butyl rubber”. Like natural rubber, butyl rubber was capable of being crosslinked by sulfur vulcanization, but because the presence of isoprene in the copolymer was only on the order of 1-3 mol%, it retained the oxidative and chemical stability of PIB.

Though this material was an improvement on the commercial products of the time, there developed a desire in academia to understand the fundamentals of cationic polymerization. Around the 1960s, other chain-growth polymerization chemistries were capable of producing well defined materials with low molecular weight distributions (MWD) and controlled molecular weights; properties which were not available by cationic polymerization at that time.[11] Driven by this desire, Kennedy and coworkers reported the conditions for the "quasiliving" polymerization of isobutylene capable of producing PIB with those characteristics.[12] These initial materials were monofunctional in nature meaning only one chain end was capable of bearing a functional chemical handle. Later, the production of difunctional telechelic PIBs, those bearing useful functionality at both chain ends, was realized by replacing the monofunctional initiator with a difunctional one such as p-dicumyl chloride.[13] These difunctional PIBs were of great academic interest due their utility in the production of variously complex block copolymer structures.[14] However, although PIB offers excellent chemical, thermal, and oxidative stability as well as better gas barrier properties than all other commodity elastomers in the same Tg range, the synthesis of the requisite difunctional initiators has proven commercially unfavorable relegating difunctional PIB nearly solely to laboratory use. The one notable exception to this is its use as a centerblock in the triblock copolymer poly(styrene-b-isobutylene-b-styrene)(SIBS) which has been used as a drug-eluting coating for the Taxus™ heart stent.[15]

In the present work, we will discuss a new method for the production of di- and multi-functional telechelic PIB via a process whereby a high molecular weight copolymer is degraded to produce difunctional telechelic oligomers. Relevant to this work are the current methods of producing high molecular weight copolymers of isobutylene, difunctional polyisobutylenes via living polymerization and in-situ quenching, and difunctional polyisobutylenes via non-conventional routes.

Production of Isobutylene Copolymers

As previously mentioned, commercial copolymers of isobutylene, the most notable of which is butyl rubber, are produced via the aluminum chloride or alkylaluminum chloride catalyzed polymerization of a comonomer mixture consisting predominantly of isobutylene but also containing a low concentration of a second cationically active monomer. The purpose of the comonomer is to provide sites for sulfur vulcanization of the copolymer. These copolymerizations are carried out in a polar solvent, such as methyl chloride, for two reasons. The first reason is that a polar environment promotes ionization of the growing chain ends resulting in rapid polymerization kinetics.[16] The second reason is that as the non-polar polymer is formed, it becomes insoluble in the polar solvent and precipitates from solution resulting in a decrease in viscosity as compared to a solution process. Additionally, these reactions are performed at very low temperatures, typically near the freezing point of the solvent (-97°C for methyl chloride), to decrease the occurrence of side reactions, notably chain transfer to monomer. Thus, under these conditions molecular weights greater than 100,000 g/mol can be achieved.[10]

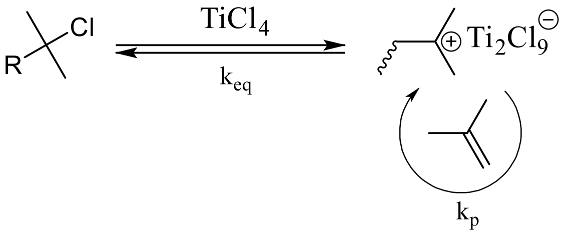
As mentioned previously, Thomas and Sparks initially investigated butadiene[10] as a comonomer to produce PIBs which were crosslinkable by sulfur vulcanization. However, butadiene's reactivity towards cationic polymerization is much lower than that of IB, and the resulting copolymer contains much less butadiene than the monomer feed.[17] This is presumably due to the unstable nature of the cation formed from butadiene, which exists in resonance between a secondary and primary carbon. In contrast, the comonomer isoprene is much more reactive as the carbocation formed from addition of the monomer exists in resonance between a tertiary and a primary carbon. Although isoprene was still found to be slightly less reactive than isobutylene, it nevertheless proved capable of yielding copolymers with adequate incorporation (up to 3 mol%) of unsaturated comonomer at reasonable monomer feed ratios.

Another comonomer of interest to this work is β-pinene (BP). The copolymerization of IB and BP, first patented by Emil Ott[18] and later investigated and further patented by Kennedy *et al.,*[19] displays an interesting trend concerning the reactivities of the two monomers. As reported by Kenned *et al.*, at a reaction temperature of -50°C, the reactivity ratio of β-pinene (r_{BP}) is much higher than that of isobutylene (r_{IB}) (r_{BP}=3, r_{IB}=0.27). However, as the reaction temperature is decreased, the difference between the two reactivity ratios decreases until at approximately -110°C an azeotropic copolymerization, i.e. one in which the polymer makeup matches the monomer feed, is observed for all monomer ratios in the feed (r_{BP}=r_{IB}=1). This azeotropic condition was verified by NMR as minimal amounts of BP-BP dyads were observed under the claimed azeotropic conditions for low BP concentrations.

Other monomers, particularly styrenics, have also been used as comonomers with IB.[20] The most interesting of these is p-methyl styrene. The copolymer of IB and p-methyl styrene and its brominated analogs (EXXPRO™ produced by ExxonMobil) are still capable of being crosslinked by sulfur vulcanization despite the lack of main-chain unsaturation present in the material. However as the polymerization products of these monomers do not contain a main-chain unsaturation or other cationogen, they are largely irrelevant to the rest of this work.

Living Cationic Polymerizations: Current Mechanistic Theory

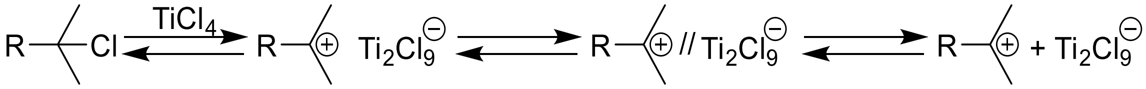
Currently, the most well reported living polymerizations of IB involve a tert-chloride functional initiator, $TiCl_4$ catalysis, and a mild hindered base, such as 2,6-lutidine, which serves as an electron pair donor.[21] The mechanism of this polymerization, presented in scheme 1, involves an activation/de-activation equilibrium which serves to mediate the carbocation concentration.



Scheme 1. Mechanism of $TiCl_4$ catalyzed IB polymerization.

In the first ionization event, R=initiator residue. For all subsequent ionization events, R=PIB

One important aspect of this mechanism is what is known as the "run number", or the average number of monomer units added during an ionization event. Typically, this number is around 4.7 at -70°C for an IB concentration of 0.5 M in a 60/40 methylcyclohexane/methyl chloride solvent system,[22] and although it is expected that the run number would increase with increasing monomer concentration, no studies have been performed proving this. Thus, for target molecular weights which would constitute multiple run numbers, low MWDs can be obtained.



Scheme 2. Winstein spectrum illustrating the complex equilibrium present during ionization of tertiary chlorides.

Steps in the Winstein spectrum from left to right: tertiary chloride, contact ion pair, solvent separated ion pair, free ion pair.

The role of the electron pair donor (EPD) and the nature if its interaction with the growing carbocation is a topic of much study.[23] During ionization of the chain end, the resulting ion is in equilibrium between three different states as shown in Scheme 2.[24] This complex equilibrium is known as the Winstein spectrum. It is generally accepted that electron pair donors, in combination with minor amounts of protic impurity form a salt with the Lewis acid (LA), some fraction of which exists as dissociated free ions (H-EPD$^+$ + LA-Cl$^-$). In forming free LA-Cl$^-$ counterions, the formation of free chain end carbocations (far right on the Winstein Spectrum) is suppressed via La Chatelier's principle such that no chain ends exist as a free carbocation. This lowers the MWD of the resulting material by lowering the run number; i.e. when the polymerization is mediated by an electron pair donor, no ionization events occur which would have a drastically higher run number.

Living Cationic Polymerizations: The History

As previously mentioned, the state of cationic polymerization prior to the 1980s lagged behind other chain polymerization techniques such as Ziegler-Natta and anionic polymerizations, which were capable of excellent structural control. A similar degree of control was first reported for cationic polymerizations in 1982 when a linear plot of molecular weight vs. monomer conversion was reported for polymerization of α-methyl styrene initiated by H_2O/BCl_3 at molecular weights above 150,000 g/mol.[25] This was achieved via incremental addition of the monomer to the polymerization, and it was noted that the addition rate of the monomer was very crucial to the “livingness” of the system. If the monomer was added too quickly, high monomer concentration would result in enhanced transfer to monomer. Conversely, if monomer was added too slowly, chain transfer via indane formation (an intramolecular cyclization reaction) would no longer be negligible.

In the mid 1980s, Kennedy *et al*. reported similar living behavior up to approximately 10,000 g/mol for the polymerization of isobutylene using a cumyl acetate/BCl_3 initiation system.[26] Soon after this first living polymerization, difunctional initiators such as 1,3-dicumyl acetate were employed to synthesize linear difunctional telechelic PIB with controlled molecular weights around 6,000 g/mol.[13] Originally, it was hypothesized that the acetate functional initiator formed a complex with BCl_3 and a monomer insertion mechanism, similar to that of Zeigler-Natta polymerizations, was responsible for the controlled molecular weights. However in 1990, a revised mechanism was proposed.[13] Instead of an insertion mechanism dominating the reaction, the tert-acetate functionality was converted to a tert-chloride in the first step of the reaction. The acetate salt of the Lewis acid catalyst formed from this reaction acted as an electron pair donor which served to mediate the polymerization as previously discussed, inhibiting chain transfer reactions. It was later discovered that when other electron pair donors, such as N,N-dimethylacetamide;[27] 2,4-dimethyl pyridine;[28] and 2,6-di-tert-butyl pyridine;[29] were added to polymerizations initiated by tert-chloride functional initiators, living polymerization behavior was observed. In fact, polymerizations initiated by tert-chloride functional initiators in the presence of such electron donors and a suitable Lewis acid, usually $TiCl_4$, exhibit the same or better livingness as afforded by acetate functional initiators,[23] and these latter initiator/electron pair donor systems are the most commonly reported systems in the current literature exhibiting living polymerization behavior at molecular weights up to 50,000 g/mol for monofunctional PIBs.[30]

Difunctional PIB via Living Polymerization

Since these first living IB polymerizations much research has been done regarding initiator design. Of the highest interest in this field are initiators which yield PIB with functionality of 2 or greater. These multi-functional PIBs are of high interest due to their utility in the synthesis of a variety of interesting polymer architectures. Kennedy *et al.* have published extensively on the topic of PIB based polyurethanes as a replacement for similar polyether based materials.[31] Similarly, Storey *et al.* have reported the synthesis of PIB based polyamides which are comparable to commercial polyether based polyamides (PEBAX produced by Arkema).[32] The interest in PIB as a new soft-block in these materials is due to its increased oxidative and biological stability as compared to these polyethers.

Additionally, many interesting PIB-based architectures have been reported whose synthetic routes involve difunctional telechelic PIB. One example of such research, reported by Ivan *et al*., is the formation amphiphilic conetworks (APCNs) produced by the copolymerization of di-acrylate functional PIB with a protected hydrophilic acrylate.[33] Similar APCNs based on elastomers other than PIB have found use in the areas of biomaterials, most notably in the area of extended wear contact lenses.[34]

Currently, the most frequently used initiator for the production of difunctional PIB is 5-tert-butyl-1,3-di(1-chloro-1-methylethyl)benzene (5-tert-butyl-1,3-di cumylchloride) (BDCC) and its various analogs.[35] The bulky tert-butyl group at C5 of this initiator prevents backbiting by electrophilic aromatic substitution after one IB addition,[36] so-called indane formation, which has been reported for 1,4-dicumyl initiators.[13] This makes BDCC the most tolerant difunctional initiator capable of producing difunctional PIB over a wide range of reaction temperatures and solvent polarities. However, the synthesis of this initiator involves a Grignard reaction requiring a 4-fold molar quantity of methylmagnesium bromide. Thus, as previously stated this initiator is largely relegated to laboratory use.

Difunctional aliphatic initiators have also been studied. 2,5-Dimethyl-2,5-dimethoxy-hexane and its acetoxy derivative have been reportedly used for the synthesis of low molecular weight telechelic PIB, but the products exhibited uncontrolled molecular weights and broad MWD.[37] Additionally, unpublished results by the Storey Research Group indicate that the 2,5-dimethyl-2,5-dihalogen hexane structure, the chloride analog of which is extremely inexpensive to produce, affords poor initiation efficiency in isobutylene polymerization when catalyzed by $TiCl_4$ in the presence of 2,6-lutidine. A similar initiator, 2,4,4,6-tetramethyl-2,6-dichloro heptane, was reported by Puskas *et al*. as an initiator capable of producing difunctional PIB. However, low initiator efficiency was observed, and the synthetic pathway for this initiator was far more costly than that of 2,5-dimethyl-2,5-dichloro hexane.[38]

A different approach toward the living synthesis of difunctional telechelic PIB involves the use of mono-functional initiators bearing residual functionality that are capable of producing asymmetric chain-end functionalities. These initiators are also potentially capable of producing symmetric difunctional telechelics by employing chain-coupling chemistries which will be discussed later. Lange *et al*. (BASF) have recently patented one such initiator, (4-chloro,2,2,4-trimethylpentylacetate),[39] that bears an acetoxy functionality on the non-initiating side of the initiator and hence yields a protected hydroxyl functional group on the α-end of the PIB chain. However, the initiator efficiency of this compound is only 46% at a target molecular weight of approximately 2400 g/mol as calculated based on data reported in that patent. Two interesting examples of similar initiators are found in two articles by Storey *et al*.[40] These initiators are similar to the one patented by Lange *et al.* except that the blocked hydroxyl group (ester function) has been extended from the remainder of the molecule either by one or three additional carbon atoms. By increasing the intramolecular distance between the ester functionality and the cationic polymerization initiating site, these initiators, especially the one extended by three carbon atoms, exhibited 100% initiation efficiency even at low target molecular weights, indicating rapid initiation. However, these initiators, especially the latter, are prohibitively expensive to produce, precluding their commercial favorability.

Epoxide functional initiators have been reported by Puskas *et* al.[41] In polymerizations using these initiators, the epoxide ring is opened by the Lewis acid to form a carbocation, which serves as the initiating site for polymerization, and an oxytitanium chloride group, which does not participate in the reaction. At the end of these polymerizations, when the catalyst is destroyed by addition of excess methanol, the oxytitanium chloride salt decomposes to produce a hydroxyl functionality, thus an asymmetric difunctional telechelic PIB is formed. However, these initiators exhibit low initiator efficiency due to competing cationic ring opening polymerization of the epoxide functionality.[41d] Additionally, the resulting polyether bears structural similarity to ether quenchers, which have been reported by Storey *et al.* to induce elimination at the living PIB chain ends to produce exo-olefin functionalities.[42] This is undesirable as exo-olefin chain ends may add to growing chain ends in a chain-coupling reaction that will be covered in depth in the next chapter. This coupling reaction, however, is likely exacerbated by conducting these polymerizations at low monomer concentrations, so polymerizations initiated by these compounds are usually terminated at low monomer conversions.

Chain-end Functionalization of Living Di-functional PIB via Quenching

The result of the living polymerization of isobutylene is a tert-chloride functional PIB. As this is not a particularly useful functional group, these chain ends must be converted to a more useful functionality. This is done either as a post-polymerization modification reaction or as an in-situ quenching reaction. Regarding post-polymerization modification of PIB chain ends, the most useful of these reactions involves the treatment of the tert-chloride PIB with a strong hindered base, such as potassium tert-butoxide, to produce exo-olefin functionality.[43] This technology, however, was rendered obsolete when it was discovered that hindered amine bases, when added to the polymerization along with additional Lewis-acid catalyst at complete monomer conversion, were capable of quantitatively converting the tert-chloride chain ends to exo-olefin functionality, negating the need for post-polymerization reactions.[44] This strategy of adding a reagent at the end of the polymerization to functionalize the chain end in-situ has been termed quenching in the literature, and although hindered amine quenching is not the first example of this approach, it serves to demonstrate its benefit compared to post-polymerization functionalization.

The quenchers which have been reported in the literature can be separated into three classes: β-proton abstractors, non-homo-polymerizable monomers, and Friedel-Crafts substrates. The hindered amine quenchers mentioned earlier were probably the first examples of β-proton abstractors.[44] However, this technology was shortly rendered nearly obsolete when it was discovered that sterically hindered ethers and sulfides are capable of performing the same reaction much more efficiently without complexing with free Lewis acid catalyst.[42(a,b),45]

The second classification of quenchers, non-homo-polymerizable monomers, can be further separated into two sub-groups. The first sub-group includes allyl- and methallyl-trimethylsilane and is characterized by an addition of the PIB chain-end to the olefin group of the quencher, followed by β-cleavage to release chlorotrimethylsilane and form an olefin at the chain end.[46] The second sub-group includes monomers that will add to a PIB chain end, but due to poor cation stability or stearic hindrance, are incapable of adding more than one unit. Butadiene is a good example of the former. When used to quench a living IB polymerization, it will add to the chain end but immediately becomes de-activated (collapse with the counterion); re-ionization of the new chain end is slowed by orders of magnitude.[47] This effectively terminates the polymerization and imparts allylic chloride functionality to the chain end. Quenching with 1,1-diphenylethylene results in a very stable di-phenyl cation which is too sterically hindered to add another unit of the 1,1-diphenylethylene.[48] However, this chain-end can be used to initiate the radical polymerization of acrylates to form block copolymers.

The third class of quenchers, Friedel-Crafts substrates, relates to compounds capable of reacting with the living PIB chain end via Friedel-Crafts alkylation. Furans were the first of this class used for the quenching of PIB chain ends.[49] The most notable technological advancement afforded by this technology is the quantitative coupling of PIB chains using di-furan compounds. This technology along with the use of functional initiators provides an alternate route for the synthesis of difunctional PIB.[50] The second family of compounds, N-alkylpyrroles, behave similarly to furan, but, due to the functional utility of the amine group as compared to the ether of furan, allowed for more precise tailoring of the functional terminus of the polymer chain.[51] For instance, Storey *et al*. reported the use of a pyrrole bearing a protected hydroxyl functionality, which quantitatively added to the living PIB chain end.[52] The protecting group was then removed via room temperature work-up of the polymer with excess Lewis acid to produce hydroxyl functional PIB in a two-step one-pot reaction. Additionally haloalkyl pyrroles have been used to impart the very useful primary halogen functionality to the chain end in a one-step reaction requiring no special work-up.[53] The third family of compounds in this class, alkoxybenzenes, were discovered by Storey *et al.* and have been used extensively in the literature due to their synthetic utility and inexpensive synthesis.[54] Particularly, 3-bromopropoxybenzene has proved quite useful as the primary bromide functionality imparted serves as a synthetic intermediate from which hydroxyl or amine functionality can be produced.[55] These compounds add to the PIB chain-end in a manner which more closely resembles the classic Friedel-Crafts alkylation reaction, yet are capable of participating in this reaction at cryogenic temperatures due to the stabilizing effect of the ether functionality on the carbocation formed during alkylation. Regarding this point, it should be noted that, in contrast to furan and potentially pyrrole quenchers,[49] after addition of the chain end to the aromatic ring, these compounds readily release HCl as a byproduct of the addition. The importance of this fact will be remarked upon in the next chapter.

Difunctional PIB by Non-Conventional Methods

In addition to the production of difunctional telechelic PIB via living polymerization, there exist a few non-conventional methods for the production of these materials. One notable route toward these materials is found in a patent issued in 1972 where it is claimed that when IB is contacted with 5A molecular sieves, a nearly telechelic olefin-functional PIB is formed.[56] The mechanism by which this occurs is not well defined, but it was suggested that it involves hydride extraction from IB. Additionally, these reactions were incredibly slow and inefficient, and the polymers formed were not truly telechelic since the claimed average functionality was approximately 1.8.

Another interesting approach to telechelic difunctional polymers, which does not require a difunctional initiator, is via a process dubbed “constructive degradation” by J. R. Ebdon in 1994.[57] In this process, a high molecular weight polymer is subjected to a cleavage reaction which serves to degrade its molecular weight while functionalizing the chain ends of the newly formed oligomers. Typically, the high molecular weight polymer is a copolymer containing a small amount (<3 mol%) of comonomer whose repeat unit imparts a main-chain functionality that can be chemically targeted for such a cleavage reaction. As it pertains to this work, there are two examples in the literature where a high molecular weight isobutylene-based copolymer was successfully converted to low molecular weight difunctional telechelic oligomers. In the first example, ozonolysis was used to cleave the main-chain unsaturation of butyl rubber resulting in the quantitative synthesis of α-ketone, ω-aldehyde telechelic PIB.[58] Though this reaction does not require a difunctional initiator, it has not seen use in a commercial application due to the lack of synthetic utility of the ketone/aldehyde chain ends as well as the fact that the copolymer must be purified prior to the ozonolysis reaction. Similarly, Chasmawala *et al.* have reported the cross-metathesis reaction of poly(isobutylene-co-butadiene) with unsaturated compounds bearing a latent functionality.[59] This process, though elegant, bears the same draw-backs of the ozonolysis reaction and additionally requires expensive catalysts and reagents for the formation of any synthetically useful functionality.

Related to this general approach of constructive degradation, Kennedy *et al.* have reported that the molecular weights of butyl and halo-butyl rubbers are drastically decreased in the presence of a combination of Lewis and Bronstead acids.[60] In the referenced article, a mechanism for this decrease in molecular weight is proposed, which involves protonation of the main-chain unsaturation followed by a β cleavage event that yields two new chain ends, one of which bears olefin functionality and the other of which bears tert-chloride functionality. It has been noted elsewhere that this reaction may be useful for the production of olefin-functional telechelics,[61] but it should be further noted that prior to the current work, no publications or patents exist which have reduced this reaction to the practice of producing a useful telechelic material. One potential reason for this failure is chain-end rearrangements catalyzed by Lewis acids in the absence of monomer or other carbocation-trapping agents, i.e. the quenchers discussed previously. Thus, although mixed Lewis/Bronstead acids serve to catalyze a cleavage reaction that targets the unsaturation of butyl rubber, the newly formed chain ends become rearranged precluding their utility for further chemical modification

References

1. a.) Kennedy, J.P. From Thermoplastic Elastomers to Designed Biomaterials. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43* (14), 2951−2963.

   b.) Mishra, Abhinay; Seethamraju, Kasyap; Delaney, Joseph; Willoughby, Patrick; Faust, Rudolf. Long-Term In Vitro Hydrolytic Stability of Thermoplastic Polyurethanes. *J. Biomed. Mat. Res., Part A* **2015**, 103(12), 3798-3806.

2. Heine, Jennifer; Rodehorst, Uta; Badillo, Juan Pablo; Winter, Martin; Bieker, Peter. Chemical Stability Investigations of Polyisobutylene as New Binder for Application in Lithium Air-Batteries. *Electrochimica Acta* **2015**, 155, 110-115.

3. Boyd, R. H.; Pant, P. V. K. *Macromolecules* **1991**, 24, 6325-6331

4. a.) Colucci, William Jay; Shanahan, Charles S.; Nuckols, Michel; Gauthier, Alice Diane; Loper, John T. Isomerization of Polyisobutylene and its Use for Preparing Detergent Additives. US 20170158785, **2017**.

   b.) Rath, Hans Peter; Lange, Arno; Hanefeld, Phillip; Mach, Helmut. Oil-Soluble Deposit Inhibitors - Detergents (Fuel Additives) DE 102008037662, **2009**.

   c.) Hueffer, Stephan; Schwab, Peter; Schuermann, Gregor; Rath, Hans Peter; Mach, Helmut; Schauss, Eckard. Fuel Emulsifiers Based on Maleated Low- and High-Molecular-Weight Polyisobutylene Derivatives. WO 2002094889, **2002**.

   d.) Storey, Robson F.; Stokes, Casey D.; Harrison, James J.; Martinez-Castro, Nemesio. Amine-Terminated Telechelic Polymers, Their Preparation, and Use in Lubricating Oils. WO 2010117619, **2010**.

5. a.) Delaney, Joseph T., Jr.; Gurung, Niraj; Willoughby, Patrick; Wulfman, David R.; Adenusi, Adegbola O.; Aremu, Adeniyi O. Polyisobutylene-Polyurethanes

and Medical Devices Containing the Same. WO 2017106774, **2017.**

b.) Toth, Kalman; Nugay, Nihan; Kennedy, Joseph P. Polyisobutylene-Based Polyurethanes: VII. Structure/Property Investigations for Medical Applications. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, 54(4), 532-543.

6. Nasrollahzadeh, M.; Ganji, F.; Taghizadeh, S. M.; Vasheghani-Farahani, E. "D-Optimal Experimental Design" Analysis in Preparing Optimal Polyisobutylene Based Pressure Sensitive Adhesives. *Int. J. Adhes. Adhes.* **2017**, 78, 28-37.

7. a.) Naik, Shreyas; Efimov, Konstantin; Jeromin, Dieter; Mueller, Matthias-Stephan. Rubber Composition for the Inner Layer or the Hose of Pneumatic Vehicle Tires and Pneumatic Vehicle Tires. EP 3196049, **2017**.

   b.) Lightbown, I. E.; Verde, L. S.; Brown, J. R., Jr. Performance of Butyl Inner Tubes. Influence on Tire Life. *Ind. Eng. Chem.* **1947**, 39, 141-6.

8. A. Butlerow, W. Goriainov, Annal. *Chem. Pharm.* **1873**, 169, 146-149

9. Thomas, R. M.; Sparks, W. J.; Frolich, Per K.; Otto, M.; Mueller-Cunradi, M. Preparation and structure of high-molecular-weight polybutenes. *J. Am. Chem. Soc.* **1940**, 62, 276-80.

10. Sparks, William J.; Thomas, Robert M. Rubber substitute. US 2363703, **1944**.

11. Kennedy, J. P. *J. Polym. Sci. A Polym. Chem.* **1999**, 37, 2285-2293

12. Faust, R.; Kennedy, J. P. *J. Polym. Sci. A Polym. Chem.* **1986**, 25, 1847-1864

13. Faust, R.; Nagy, A.; Kennedy, J. P. Living Carbocationic Polymerization. V. Linear Telechelic Polyisobutylenes by Bifunctional Initiators. *J. Macromol. Sci., Chem.* **1987**, A24(6), 595-609.

14. a.) Storey, Robson F.; Scheuer, Adam D.; Achord, Brandon C. Poly(Acrylate-B-Styrene-B-Isobutylene-B-Styrene-B-Acrylate) Block Copolymers via Carbocationic and Atom Transfer Radical Polymerizations. *J. Macromol. Sci., Pure Appl. Chem.* **2006**, 43(10), 1493-1512.

    b.) Binder, Wolfgang H.; Machl, Doris. Poly(Ether Ketone)-Polyisobutylene Block Copolymers: Synthesis and Phase Behavior. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, 43(1), 188-202.

15. Pinchuk, Leonard; Wilson, Gregory J.; Barry, James J.; Schoephoerster, Richard T.; Parel, Jean-Marie; Kennedy, Joseph P. Medical Applications of Poly(Styrene-Block-Isobutylene-Block-Styrene) ("SIBS"). *Biomaterials* **2008**, 29(4), 448-460.

16. Matyjaszewski, Krzysztof; Lin, Chih-Hwa; Bon, Angelique; Xiang, Jason S. Salt and Solvent Effects in "Living" Carbocationic Polymerization. *Macromol. Symp.* **1994**, 85, 65-78.

17. Kennedy, Joseph P.; Canter, Nathan H. Fundamental Studies in Cationic Polymerization. V. Aspects of the Copolymerization of Isobutene with Butadiene and Isoprene. *Ann. N.Y. Acad. Sci.* **1969**, 155(2), 419-30.

18. Ott, Emil. Terpene Resins. US 2373706, **1945**.

19. a.) Kennedy, Joseph P.; Chou, Tom. Poly(isobutylene-co-β-pinene): a new sulfur vulcanizable, ozone resistant elastomer by cationic isomerization copolymerizstion. I. Synthesis and reactivity studies. *Adv. Polym. Sci.* **1976**, 21, 1-30.

    b.) Kennedy, Joseph P.; Chou, Tom M. Isobutylene/beta-pinene copolymers. US 3923759, **1975**.

20. a.) Hull, Diana L.; Kennedy, Joseph P. Synthesis, Characterization, and Crosslinking of Novel Stars Comprising Eight Poly(Isobutylene-Azeotropic-Styrene) Copolymer Arms with Allyl or Hydroxyl Termini. I. Living Azeotropic Copolymerization of Isobutylene and Styrene. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, 39(9), 1515-1524.

b.) Lubnin, Alexander V.; Orszagh, Istvan; Kennedy, Joseph P. The Microstructure of Poly(Isobutylene-Co-P-Methylstyrene) by NMR Spectroscopy. *J. Macromol. Sci., Pure Appl. Chem.* **1995**, A32(11), 1809-30.

21. Deodhar, Tejal J.; Keszler, Balazs L.; Kennedy, Joseph P. Quantitative Preparation of Allyl Telechelic Polyisobutylene Under Reflux Conditions. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, 55(10), 1784-1789.

22. Storey, Robson F.; Thomas, Quinn A. Quasi-Living Cationic Polymerization of Styrene and Isobutylene: Measurement of Run Number and Calculation of Apparent Rate Constant of Ionization by TiCl4. *Macromolecules* **2003**, 36(14), 5065-5071.

23. Kaszas, G.; Puskas, J. E.; Chen, C. C.; Kennedy, Joseph P. Electron Pair Donors in Carbocationic Polymerization. 2. Mechanism of Living Carbocationic Polymerizations and the Role of In Situ and External Electron Pair Donors. *Macromolecules* **1990**, 23(17), 3909-15.

24. Pernecker, Tibor; Kennedy, Joseph P. Living Carbocationic Polymerization. XLVI. Living Isobutylene Polymerization Induced by the Common Ion Effect. *Polym. Bull.* **1991**, 26(3), 305-12.

25. R. Faust; A. Fehérvári; J. P. Kennedy. Quasiliving Carbocationic Polymerization. II. The Discovery: the α-Methylstyrene System J. Macromol. Sci. Chem. **1982**, A18(9), 1209.

26. Faust, R.; Kennedy, J. P. Living carbocationic polymerization. IV. Living Polymerization of Isobutylene. *J. Polym. Sci., Part A: Polym. Chem.* **1987**, 25(7), 1847-69.

27. Kaszas, Gabor; Puskas, Judit E.; Chen, C. Charles; Kennedy, Joseph P. Electron Pair Donors in Carbocationic Polymerization. I. Introduction into the Synthesis of Narrow Molecular-Weight-Distribution Poly(Isobutylenes). *J. Macromol. Sci., Chem.* **1989**, A26(8), 1099-14.

28. Storey, Robson F.; Maggio, Thomas L. Real-Time Monitoring of Carbocationic Polymerization of Isobutylene Via ATR-FTIR Spectroscopy: the Tert-Bu-M-DCC /DMP/BCl3 System. *Macromolecules* **2000**, 33(3), 681-688.

29. Gyor, Miklos; Fodor, Zsolt; Wang, Hsien-Chang; Faust, Rudolf. Polyisobutylene-Based Thermoplastic Elastomers. I. Synthesis and Characterization of Polystyrene-Polyisobutylene-Polystyrene Triblock Copolymers. *J. Macromol. Sci., Pure Appl. Chem.* **1994**, A31(12), 2055-65.

30. Fodor, Zsolt; Bae, Young Cheol; Faust, Rudolf. Temperature Effects on the Living Cationic Polymerization of Isobutylene: Determination of Spontaneous Chain-Transfer Constants in the Presence of Terminative Chain Transfer. *Macromolecules* **1998**, 31(14), 4439-4446.

31. a.) Nugay, Nihan; Toth, Kalman; Kekec, Nur Cicek; Nugay, Turgut; Kennedy, Joseph P. Polyisobutylene-Based Polyurethanes X: PU Nanocomposites with S-

Containing Soft Segments. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, 54(17), 2760-2765.

b.) Toth, Kalman; Nugay, Nihan; Kennedy, Joseph P. Polyisobutylene-Based Polyurethanes: VII. Structure/Property Investigations for Medical Applications. *J. Polym. Sci., Part A: Polym. Chem.* **2016**, 54(4), 532-543.

c.) Kang, Jungmee; Erdodi, Gabor; Kennedy, Joseph P.; Yilgor, Emel; Yilgor, Iskender. PIB-Based Polyurethanes. IV. The Morphology of Polyurethanes Containing Soft Co-Segments. *J. Polym. Sci., Part A: Polym. Chem.* **2009**, 47(22), 6180-6190.

32. Kucera, Lauren R.; Brei, Mark R.; Storey, Robson F. Synthesis and Characterization of Polyisobutylene-b-Polyamide Multi-Block Copolymer Thermoplastic Elastomers. *Polymer* **2013**, 54(15), 3796-3805.

33. a.)Pasztor, Szabolcs; Ivan, Bela; Kali, Gergely. Extreme Difference of Polarities in a Single Material: Poly(Acrylic Acid)-Based Amphiphilic Conetworks with Polyisobutylene Cross-Linker. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, 55(11), 1818-1821.

b.) Kali, Gergely; Ivan, Bela. Poly(methacrylic acid)-l-Polyisobutylene Amphiphilic Conetworks by Using an Ethoxyethyl-Protected Comonomer: Synthesis, Protecting Group Removal in the Cross-Linked State, and Characterization. *Macromol. Chem. Phys.* **2015**, 216(6), 605-613.

34. Erdodi, Gabor; Kennedy, Joseph P. Amphiphilic Conetworks: Definition, Synthesis, Applications. *Prog. Polym. Sci.* **2006**, 31, 1–18.

35. a.) Nielsen, Lars V.; Nielsen, Rasmus R.; Gao, Bo; Kops, Jorgen; Ivan, Bela. Synthesis of Isobutenyl-Telechelic Polyisobutylene by Functionalization with Isobutenyltrimethylsilane. *Polymer* **1997**, 38(10), 2529-2534.

    b.) Yang, Bin; Parada, Corey M.; Storey, Robson F. Synthesis, Characterization, and Photopolymerization of Polyisobutylene Phenol (Meth)acrylate Macromers. *Macromolecules* **2016**, 49(17), 6173-6185.

    c.) Roche, Conor P.; Brei, Mark R.; Yang, Bin; Storey, Robson F. Direct Chain End Functionalization of Living Polyisobutylene Using Phenoxyalkyl (Meth)acrylates. *ACS Macro Letters* **2014**, 3(12), 1230-1234.

36. Santos, R.; Kennedy, J.P.; Walters, M. *Polym. Bull.* **1984**, *11*, 261-267.

37. Walch, E.; Gaymans, R. J. Synthesis of Low-Molecular-Weight Telechelic Polyisobutylene. *Polymer* **1993**, 34(2), 412-17.

38. Castano, Marcela; Becker, Matthew L.; Puskas, Judit E. New Method for the Synthesis of Fully Aliphatic Telechelic Α,Ω-Dihydroxy-Polyisobutylene. *Polym. Chem.* **2014**, 5, 5436-5442

39. Lange, Arno; Kiefer, Matthias; kleiner, Matthias; Csihony, Szilard; Posselt, Dietmar. Method for Continuous Production of Bifunctional Polyisobutenes Using Lewis Acid Catalyst and Capping Agents in Solvent. WO2014056845, **2014**.

40. a.) Zhu, Yaling; Storey, Robson F. Effect of Structure on Cationic Initiation Efficiency of a Carbocatonic/ATRP Dual Initiator. *Macromolecules* **2012**, 45(3), 1217-1221.

    b.) Zhu, Yaling; Storey, Robson F. New Dual Initiators to Combine Quasi-living

Carbocationic Polymerization and Atom Transfer Radical Polymerization. *Macromolecules* **2010**, 43(17), 7048-7055.

41. a.) Alvarez Albarran, Alejandra; Silantyeva, Elena; Seo, Kwang Su; Puskas, Judit E. Synthesis of Functionalized Polyisobutylenes Using the Propylene Epoxide/Ticl4 Initiating System. *Polym. Chem.* **2014**, 5(16), 4710-4714.

    b.) Sen, Mustafa Y.; Puskas, Judit E.; Dabney, David E.; Wesdemiotis, Chrys; Absalon, Christelle. Precision Synthesis and Characterization of Thymine-Functionalized Polyisobutylene. *J. Polym. Sci., Part A: Polym. Chem.* **2010**, 48(16), 3501-3506.

    c.) Soytas, Serap Hayat; Lim, Goy Teck; Puskas, Judit E. Synthesis of POSS-Functionalized Polyisobutylene via Direct Initiation. *Macromol. Rapid Commun.* **2009**, 30(24), 2112-2115.

    d.) Soytas, Serap Hayat; Puskas, Judit E.; Kulbaba, Kevin. Real-Time FTIR Monitoring of the Mechanism of Initiation of Isobutylene Polymerizations by Epoxide/Lewis Acid Systems. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, 46(11), 3611-3618.

42. a.) Ummadisetty, Subramanyam; Storey, Robson F. Quantitative Synthesis of exo-Olefin-Terminated Polyisobutylene: Ether Quenching and Evaluation of Various Quenching Methods. *Macromolecules* **2013**, 46(6), 2049-2059.

    b.) Ummadisetty, Subramanyam; Morgan, David L.; Stokes, Casey D.; Harrison, J. J.; Campbell, Christopher G.; Storey, Robson F. In Situ Quenching Methods Toward exo-Olefin-Terminated Polyisobutylene. *Macromol. Symp.* **2013**, 323(1), 6-17.

c.) Storey, Robson F.; Kemp, Lisa K. Preparation of Exo-Olefin Terminated Polyolefins via Quenching with Alkoxysilanes or Ethers. US 20090318624, **2009.**

43. Kennedy, J. P.; Chang, V. S. C.; Smith, R. A.; Iván, B. *Polym. Bull.* **1979**, 1, 575–580

44. Simison, Kelby L.; Stokes, Casey D.; Harrison, James J.; Storey, Robson F. End-Quenching of Quasiliving Carbocationic Isobutylene Polymerization with Hindered Bases: Quantitative Formation of exo-Olefin-Terminated Polyisobutylene. *Macromolecules* **2006**, 39(7), 2481-2487.

45. Ummadisetty, Subramanyam; Morgan, David L.; Stokes, Casey D.; Storey, Robson F. Synthesis of exo-Olefin Terminated Polyisobutylene by Sulfide/Base Quenching of Living Polyisobutylene. *Macromolecules* **2011**, 44(20), 7901-7910.

46. a.) Nielsen, Lars V.; Nielsen, Rasmus R.; Gao, Bo; Kops, Jorgen; Ivan, Bela. Synthesis of Isobutenyl-Telechelic Polyisobutylene by Functionalization with Isobutenyltrimethylsilane. *Polymer* **1997**, 38(10), 2529-2534.

b.) Ivan, Bela; Kennedy, Joseph P. Living Carbocationic Polymerization. XX. Synthesis of Allyl-Telechelic Polyisobutylenes by One-Pot Polymerization-Functionalization. *Polym. Mater. Sci. Eng.* **1988**, 58, 869-72.

47. Ojha, Umaprasana; Rajkhowa, Ritimoni; Agnihotra, Shrikant Rao; Faust, Rudolf. A New General Methodology for the Syntheses of End-Functional Polyisobutylenes by Nucleophilic Substitution Reactions. *Macromolecules* **2008**, 41(11), 3832-3841.

48. Feng, Dingsong; Higashihara, Tomoya; Faust, Rudolf. Facile Synthesis of Diphenylethylene End-Functional Polyisobutylene and its Applications for the

Synthesis of Block Copolymers Containing Poly(Methacrylate)s. *Polymer* **2008**, 49(2), 386-393.

49. Hadjikyriacou, Savvas; Faust, Rudolf. Cationic Macromolecular Design and Synthesis Using Furan Derivatives. *Macromolecules* **1999**, 32(20), 6393-6399.
50. Hadjikyriacou, Savvas; Faust, Rudolf. Living Coupling Reaction in Living Cationic Polymerization. 3. Coupling Reaction of Living Polyisobutylene Using Bis(furanyl) Derivatives. *Macromolecules* **2000**, 33(3), 730-733.
51. Storey, Robson F.; Stokes, Casey D.; Harrison, James J. N-Methylpyrrole-Terminated Polyisobutylene through End-Quenching of Quasiliving Carbocationic Polymerization. *Macromolecules* **2005**, 38(11), 4618-4624.
52. Morgan, David L.; Storey, Robson F. Primary Hydroxy-Terminated Polyisobutylene via End-Quenching with a Protected N-(ω-Hydroxyalkyl)pyrrole. *Macromolecules* **2010**, 43(3), 1329-1340.
53. Martinez-Castro, Nemesio; Morgan, David L.; Storey, Robson F. Primary Halide-Terminated Polyisobutylene: End-Quenching of Quasiliving Carbocationic Polymerization with N-(ω-Haloalkyl)pyrrole. *Macromolecules* **2009**, 42(14), 4963-4971.
54. Morgan, David L.; Martinez-Castro, Nemesio; Storey, Robson F. End-Quenching of TiCl4-Catalyzed Quasiliving Polyisobutylene with Alkoxybenzenes for Direct Chain End Functionalization. *Macromolecules* **2010**, 43(21), 8724-8740.
55. Morgan, David L.; Storey, Robson F. End-Quenching of QuasiLiving Isobutylene Polymerizations with Alkoxybenzene Compounds. *Macromolecules* **2009**, 42(18), 6844-6847.

56. Miller, Joseph A., Jr. Difunctional Polyisobutylene. U.S. **1972**, US 3634383 A 19720111

57. Ebdon, John R. Synthesis of New Telechelic Oligomers and Macromonomers by "Constructive Degradation". *Macromol. Symp.* **1994**, 84, 45-54.

58. Ho, K. W.; Guthmann, J. E. The Ozonolysis of Butyl and Halobutyl Elastomers. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, 27(7), 2435-55.

59. Chasmawala, M.; Chung, T. C. Telechelic Polyisobutylene: A Facile Synthesis via the Cross-Metathesis Reaction and Trialkylborane-Containing Olefins. *Macromolecules* **1995**, 28(5), 1333-9.

60. Kennedy, Joseph P.; Phillips, Robert R. Influence of Aluminum-Containing Lewis Acids on Polyisobutylene, Isobutylene-Isoprene Copolymers (Butyl Rubber), and Chlorinated Isobutylene-Isoprene Copolymer (Chlorobutyl). *J. Macromol. Sci., Chem.* **1970**, 4(8), 1759-84.

61. Yagci, Yusuf; Nuyken, Oskar; Graubner, Vera-Maria Edited by Mark, Herman F. Telechelic Polymers. *Encyclopedia of Polymer Science and Technology (4th Edition)* ***2*****014**, 13, 671-744.

CHAPTER II - DECOUPLING AND FUNCTIONALIZATION OF COUPLED POLYISOBUTYLENE VIA ALKOXYBENZENE QUENCHING

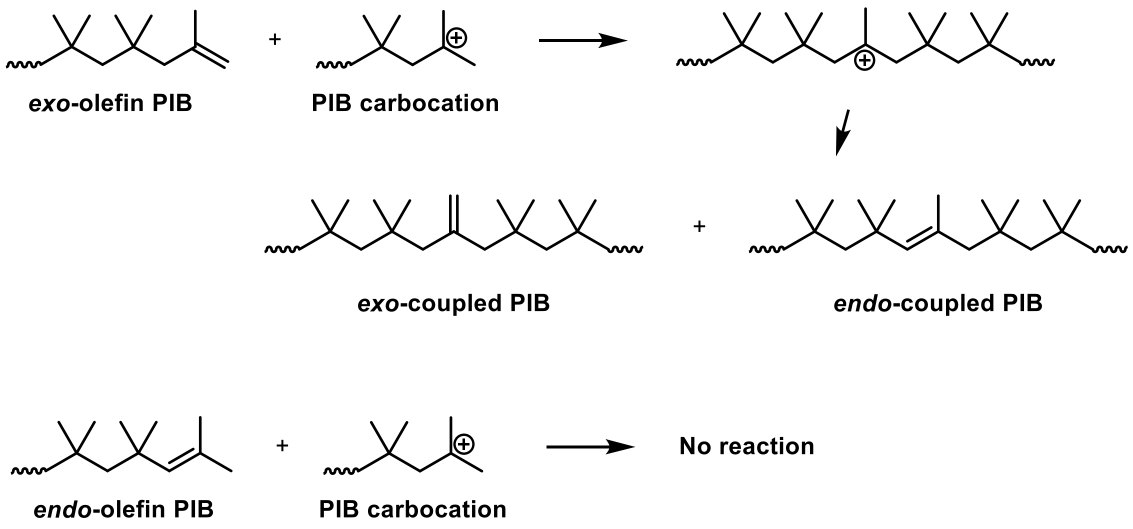
Introduction

Polyisobutylene (PIB) is a fully saturated hydrocarbon polymer with exceptional gas-barrier and energy damping properties, chemical, thermal, and oxidative stability, and biocompatibility.[1] For low molecular weight PIB, end-group functionalization is a critical consideration in the design of materials for specific applications. Olefin (methyl vinylidene and allyl), primary halogen (particularly bromide), primary hydroxyl, and phenol have emerged over the years as PIB terminal functional groups of primary importance. Other functional groups can usually be derived from one of these four. From a commercial point of view, the most important terminal group is *exo* olefin (methyl vinylidene) (structure shown Scheme 3).[2,3] Monofunctional PIBs possessing terminal olefins have been produced commercially for many years using chain-transfer-dominated cationic polymerization.[4] So-called “conventional” PIBs produced using $AlCl_3$ catalyst contain a complex mixture of terminal olefinic types, including high fractions of low reactivity tri- and tetrasubstituted olefins.[5,6,7,8] In contrast, high reactivity (HR) PIBs, produced using alcohol (or ether)/BF_3 catalyst complexes, possess a high fraction of *exo*-olefin end groups (typically 70-90%) and are favored because of their higher reactivity in subsequent functionalization reactions.[9] The dominant industrial use for terminally unsaturated PIB is reaction with maleic anhydride to form PIB-succinic anhydride (PIBSA). Subsequent reaction of PIBSA with a polyamine leads to various PIB-succinimides,[10] which are used as ashless dispersants for engine lubricating oils[11] and detergents/dispersants in fuel.[12] Recently, several groups have reported new processes toward HR PIB possessing potential advantages over current industrial practice such as higher polymerization temperatures, elimination of chlorinated solvents, and reduction of catalytic waste.[13]

Controlled and/or living carbocationic polymerization of isobutylene dramatically enhances the capability for synthesis of end-functional PIBs, particularly olefin. Difunctional (telechelic) and trifunctional PIBs carrying nearly exclusively *exo*-olefin end groups first became available via the "inifer" method of Kennedy et al.[14,15,16] More recently, living polymerization has enabled functionalization of PIB chain ends by the method of end quenching, in which a basic and/or nucleophilic compound is reacted directly with the living carbocationic chain ends to provide quantitative functionalization. For example, sterically hindered bases such as 2,5-dimethylpyrrole and 1,2,2,6,6-pentamethylpiperidine cause regiospecific elimination from the carbenium ion chain end to produce *exo* olefin.[3,17] Dialkyl ethers and alkoxy silanes, [18,19] and dialkyl sulfides and disulfides[20,21] react exhaustively with the growing chain ends to produce stable ononium adducts, which may then be decomposed to *exo* olefin. The non-polymerizing olefins, allyltrimethylsilane[22] and methallyltrimethylsilane,[23] undergo addition with the PIB carbenium ion, followed by β-scission and elimination of $(CH_3)_3Si^{\oplus}$, to yield allyl- or methallyl-terminated PIB.

End-quenching processes that lead to functional groups other than olefin have also been developed. Faust and coworkers have shown that 1,3-butadiene[24] will undergo a single addition to PIB carbenium ion followed by immediate collapse, resulting in haloallyl end functionality. Reactive aromatic substrates such as 2-substituted furans,[25] *N*-substituted pyrroles,[26] and alkoxybenzene compounds[27,28,29] react with PIB carbenium ion chain ends by Friedel-Crafts alkylation. As will be seen, end-quenching with alkoxybenzene compounds is especially relevant to the subject matter of this paper.

During any carbocationic polymerization of isobutylene and/or living carbocationic quenching process involving *exo*-olefin either as an intermediate or the final product, the situation may arise in which PIB carbenium ions and *exo*-olefin chain ends co-exist simultaneously in the polymerization reactor. Under this circumstance, carbenium ions can undergo addition to *exo*-olefin PIB to yield a coupled product (see Scheme 3), referred to as "coupled PIB," with a molecular weight approximately double that of the primary chains.[19,30 **Error! Bookmark not defined.**] Only *exo*-olefin PIB is susceptible to this side reaction; *endo*-olefin PIB is apparently too sterically hindered to react with PIB carbocation. Coupled product can be detected by ^{1}H NMR spectroscopy,[3 **Error! Bookmark not defined.**] and if the molecular weight distribution of the primary PIB chains is narrow, by GPC.[31,32,33] In the ^{1}H NMR spectrum, the two identical vinylidene protons of the *exo*-coupled PIB are observed at 4.82 ppm, and the single olefinic proton of the *endo*- coupled PIB is observed at 5.12 ppm.[30 **Error! Bookmark not defined.**] In GPC, coupled PIB is observed as a separate peak or shoulder at a lower elution volume relative to the main peak representing the primary PIB chains. To our knowledge, coupled PIB has always been observed as the elimination product (*exo* and *endo* isomers, as shown), apparently because collapse of the carbenium ion with the counterion to form the tetrahedral *tert*-chloride is too sterically demanding. The *exo*-coupled isomer is almost always the major isomer observed, and often there is no observable *endo*–coupled isomer.



Scheme 3. Formation of coupled polyisobutylene.

Formation of coupled PIB is especially likely under certain conditions and situations. It is especially common during end-quenching processes aimed at purposefully creating *exo* olefin PIB, but which are carried out under non-optimal conditions and/or at high chain end concentrations;[3,19] it is particularly promoted by non-bulky ethers such as di-*n*-butyl ether and diethyl ether.[19] **Error! Bookmark not defined.** Elimination and coupling have been observed in the presence of nucleophiles, electron donors, or proton traps that are not exhaustively complexed by Lewis acid.[32,33,34] Coupling is often observed when living polymerizations are initiated from compounds that contain functionalities that interact with the Lewis acid such as ethers and alcohols. For example, Puskas et al. have shown that epoxide initiators such as α-methylstyrene epoxide and 2,4,4-trimethylpentyl-1,2-epoxide are useful for placement of hydroxyl functionality onto the head group of living PIB.[35] According to the authors, however, a significant fraction of the initiator undergoes ring-opening polymerization to form polyether, which is expected to induce some degree of elimination and coupling. Indeed, Puskas et al.[36] reported "dimerization" of PIB chains initiated from cyclohexene epoxide initiators.

Experimental

The source and purity of purchased reagents, monomers, solvents, etc., are given in Appendix A. The syntheses of 4-phenoxy-1-butyl acrylate [37] and 2-chloro-2,4,4-trimethylpentane (TMPCl)[38] have been reported. Instrumentation and sample preparation for proton nuclear magnetic resonance (^{1}H NMR) spectroscopy and gel permeation chromatography (GPC) are given in Appendix A.

Isobutylene consumption during polymerization was monitored using ATR-FTIR spectroscopy. A ReactIR 45m FTIR instrument, in conjunction with fiber-optic conduit and DiComp™ probe (Mettler Toledo, Millersville, MD), was integrated with a N_2-atmosphere glovebox (MBraun Labmaster 30) to obtain real-time FTIR spectra and temperature profiles of isobutylene polymerizations. Reaction conversion was determined by monitoring the area, above a two-point baseline, of the absorbance centered at 887 cm^{-1}, associated with the $=CH_2$ wag of IB.

Preparation of Coupled PIB.

Several PIB samples were prepared so as to purposefully possess a significant fraction of coupled chains, as listed in Table 1.

Preparation of PIB1, PIB2, and PIB3.

PIB1, PIB2, and PIB3 were all prepared similarly. The procedure for synthesis of PIB3, which is representative, was as follows: Polymerization and quenching were carried out within a N_2-atmosphere glovebox equipped with cryostated heptane bath. Polymerization temperature was -60°C. A 250 mL 4-neck round-bottom flask, equipped with mechanical stirrer, thermocouple, and FTIR-ATR DiComp® probe (Mettler Toledo), was immersed into the bath and charged with hexane (60 mL, -60°C) and methyl chloride (40 mL, -60°C). To this mixture were added 2.25 g of TMPCl, 0.088 mL (81 mg) of 2,6-lutidine, and 48 mL (33 g) IB. After thermal equilibration of the solution to -60°C, polymerization was initiated by the addition of 0.90 mL (1.56 g) of $TiCl_4$ (neat and at room temperature). After complete monomer conversion as determined by ATR-FTIR spectroscopic monitoring, a pre-quench aliquot (2 mL) was removed from the reaction and precipitated into methanol. Then, 3.1 mL (2.4 g) di-*n*-butyl ether was charged to the reactor along with an additional

Table 1

PIB Samples Prepared to Purposefully Possess a Significant Coupled Fraction.

Sample	End-Group Composition Determined by ^{1}H NMR[a]						GPC	
	exo	*endo*	*tert*-Cl	Coupled		Other[b]	M_n (g/mol)	MWD
				exo	*endo*			
PIB1	50	2	6	38	4	-	2,250	1.35
PIB2	9	2	33	53	3	-	3,360	1.14
PIB3	11	2	40	41	6	0	2,840	1.15
Precursor PIB3	0	0	100	0	0	0	2,270	1.05
PIB4	40	trace	9	39	trace	12	4,880	1.16
PIB5	65	0	23	10	0	2	3,880	1.12
Precursor PIB4-5	0	0	100	0	0	0	3,230	1.08

[a] For PIB1 and PIB2, *exo* olefin, *endo* olefin, *tert*-chloride, and coupled PIB were assumed to represent 100% of the chain ends. For PIB3, PIB4, and PIB5, the fraction of each chain end type was calculated relative to the number of chain ends in the respective *tert*-Cl-functional PIB precursor prior to the quenching/coupling reaction.

[b] Thought to be a mixture of various structures resulting from carbocation rearrangement.

1.75 mL (3.03 g) of $TiCl_4$ (both neat and at room temperature). The di-*n*-butyl ether was allowed to react for 53 min. The reaction was terminated with 4 mL pre-chilled (-60°C) methanol. The mixture was allowed to warm to room temperature with evaporation of the methyl chloride, and the polymer was precipitated twice by addition to 200 mL methanol. The polymer was then dissolved in 50 mL hexane, and the resulting solution was washed with water (2x100 mL) and dried over magnesium sulfate ($MgSO_4$). The solution was filtered to remove magnesium sulfate, and the hexane was removed via rotary evaporation.

Preparation of PIB4 and PIB5

PIB4 and PIB5 were prepared similarly. The procedure for synthesis of PIB4, which is representative, was as follows: Into a 250 mL, one-neck round-bottom flask, equipped with magnetic stir bar, septum, and N_2 inlet needle, were charged monofunctional *tert*-chloride-terminated polyisobutylene (25.1 g, 3,230 g/mol, 7.8 mmol), hexane (75 mL), and methylene chloride (50 mL). After complete dissolution of the polymer at room temperature, the solution was chilled to -60°C by immersion of the flask into a thermostatted methanol bath. Once the reaction temperature had equilibrated, 2,6-lutidine (1.74 mL, 0.015 mol), 2,5-dimethylpyrrole (0.033 mL, 0.32 mmol), and $TiCl_4$ (5.5 ml, 0.50 mol) were injected into the reaction mixture, in that order, under continuous N_2 purge. After 47 min, the reaction was terminated by the addition of excess methanol, and the contents were allowed to warm to room temperature. The polymer was isolated by slow addition of the reaction mixture into excess methanol. The polymer was twice re-precipitated into methanol from hexane. The purified polymer was dissolved into hexane, and the solution was extracted three times with water to remove methanol, and then dried over magnesium sulfate. The solution was filtered to remove magnesium sulfate, and the hexane was removed via rotary evaporation.

Alkoxybenzene Quenching of Highly Coupled PIB

The coupled PIB samples of Table 1 were reacted with various alkoxybenzene compounds; the following procedure for the reaction of PIB4 with (3-bromopropoxy)benzene is representative: Into a 50 mL, one-neck round-bottom flask, equipped with magnetic stir bar, septum, and N_2 inlet needle, were charged PIB4 (1.17 g), hexane (7.5 mL), and methylene chloride (5 mL). After complete dissolution of the polymer at room temperature, the solution was chilled to -70°C by immersion of the flask into a thermostatted methanol bath. The decoupling/quenching reaction was initiated by the addition of water (3.4 uL), (3-bromopropoxy)benzene (0.11 mL), and $TiCl_4$ (0.15 mL), in that order, under continuous N_2 purge. Aliquots were taken at 1 h and 21 h, at which time the reaction was terminated by the addition of excess methanol, and the contents were allowed to warm to room temperature. The polymer was isolated by slow addition of the reaction mixture into excess methanol. The polymer was twice re-precipitated into methanol from hexane. The purified polymer was dissolved into hexane, and the solution was extracted three times with water to remove methanol, and then dried over magnesium sulfate. The solution was filtered to remove magnesium sulfate, and the hexane was removed via rotary evaporation.

PIB End-Group Quantitation by ^{1}H NMR Spectroscopy

The fractional molar amounts of *exo*-olefin, *endo*-olefin, *tert*-chloride, *exo*-coupled, and *endo*-coupled chain ends of PIB samples were quantified using ^{1}H NMR. A coupled PIB species was counted as two PIB chains, each bearing a “coupled PIB” end group. Two methods were used, depending on whether or not the *tert*-chloride precursor was available for the PIB under consideration. If the precursor was not available, only relative molar fractions could be calculated, i.e., the five species listed above were assumed to represent 100% of the chain ends. If the precursor was available for analysis, then the number of chain ends of each type was expressed as a fraction of the total amount of original *tert*-chloride chain ends. For coupled samples PIB1 and PIB2, no *tert*-chloride precursor was available. For these two samples, fractions of each type of chain end were obtained using equations such as that given below for determining the fraction of *exo* olefin (F_{exo}),

$$F_{exo} = \frac{A_{exo}}{A_{exo} + A_{endo} + A_{exo-coupled} + 2A_{endo-coupled} + A_{tert-Cl}/2} \tag{1}$$

where A_{exo} is the area of the upfield *exo*-olefinic proton at 4.64 ppm, A_{endo} is the area of the *endo*-olefinic proton at 5.15 ppm, and $A_{endo\text{-coupled}}$ is the area of the *endo*-olefinic proton of the coupled product at 5.12 ppm. The $A_{endo\text{-coupled}}$ term in eq 1 carries a coefficient of 2 because coupled product represents 2 original PIB chains.

$A_{exo\text{-coupled}}$ was calculated as follows:

$$A_{exo-coupled} = A_{4.75-5.0} - A_{exo} \tag{2}$$

where $A_{4.75\text{-}5.0}$ is the integrated area of the convoluted peaks from 4.75-5.0 ppm associated with the downfield *exo*-olefinic proton and the two identical olefinic protons of the *exo*-coupled product. The $A_{exo\text{-coupled}}$ term in eq 1 carries a net coefficient of 1 because coupled product represents 2 original PIB chains and $A_{exo\text{-coupled}}$ represents the contribution of two protons.

$A_{tert\text{-}Cl}$ was calculated as,

$$\mathrm{A}_{tert-Cl} = \mathrm{A}_{1.95-2.05} - 2\mathrm{A}_{exo} - 2\mathrm{A}_{exo-coupled} \tag{3}$$

where $\mathrm{A}_{1.95\text{-}2.05}$ is the integrated area of the convoluted peaks from 1.95 – 2.05 ppm associated with the ultimate methylene protons of *tert*-chloride, *exo*-olefin, and exo-coupled chain ends. It is important to note that including anything further upfield than 1.95 ppm in the integration of the *tert*-chloride peak risks including *endo*-coupled and rearranged chain ends. The $\mathrm{A}_{tert\text{-}\mathrm{Cl}}$ term in eq 1 is divided by 2 because this area represents the contribution of two protons.

After alkoxybenzene quenching/decoupling, chain ends bearing alkoxyphenyl moieties are produced, and these chain ends were quantified similarly. The fraction of (3-bromopropoxy)phenyl moieties (F_{3BPB}) was calculated using eq 4,

$$\mathrm{F}_{3BPB} = \frac{\mathrm{A}_{3BPB}/2}{\mathrm{A}_{exo} + \mathrm{A}_{endo} + \mathrm{A}_{exo-coupled} + 2\mathrm{A}_{endo-coupled} + \mathrm{A}_{tert-Cl}/2 + \mathrm{A}_{3BPB}/2} \tag{4}$$

where, A_{3BPB} is the average of the integrated areas of the $\mathrm{OCH_2}$ (triplet, 4.07 ppm) and $\mathrm{CH_2Br}$ (triplet, 3.60 ppm) protons of the propoxy tether. The fraction of methoxyphenyl moieties (F_{MB}) was calculated using eq 5,

$$\mathrm{F}_{MB} = \frac{\mathrm{A}_{MB}/3}{\mathrm{A}_{exo} + \mathrm{A}_{endo} + \mathrm{A}_{exo-coupled} + 2\mathrm{A}_{endo-coupled} + \mathrm{A}_{tert-Cl}/2 + \mathrm{A}_{MB}/3} \tag{5}$$

where, A_{MB} is the integrated area of the methoxy (singlet, 3.79 ppm) protons.

For coupled PIB samples PIB3, PIB4, and PIB5, a *tert*-chloride precursor was available, and therefore the number of chain ends of each type after coupling was expressed as a fraction of the total number of original *tert*-chloride chain ends. Thus, the fractions of *exo*-olefin, *endo*-olefin, *exo*-coupled, *endo*-coupled, and *tert*-chloride chain ends were calculated according to eq 6, 7, 8, 9, and 10, respectively,

$$\mathrm{F}_{exo} = \frac{\mathrm{A}_{exo}}{\mathrm{A}_{CH_3}} \times \frac{\mathrm{A}_{CH_3,pre}}{\mathrm{A}_{tert-Cl,pre}/2} \tag{6}$$

$$\mathrm{F}_{endo} = \frac{\mathrm{A}_{endo}}{\mathrm{A}_{CH_3}} \times \frac{\mathrm{A}_{CH_3,pre}}{\mathrm{A}_{tert-Cl,pre}/2} \tag{7}$$

$$\mathrm{F}_{exo-coupled} = \frac{\mathrm{A}_{exo-coupled}}{\mathrm{A}_{CH_3}} \times \frac{\mathrm{A}_{CH_3,pre}}{\mathrm{A}_{tert-Cl,pre}/2} \tag{8}$$

$$\mathrm{F}_{endo-coupled} = \frac{2\mathrm{A}_{endo-coupled}}{\mathrm{A}_{CH_3}} \times \frac{\mathrm{A}_{CH_3,pre}}{\mathrm{A}_{tert-Cl,pre}/2} \tag{9}$$

$$\mathrm{F}_{tert-Cl} = \frac{\mathrm{A}_{tert-Cl}}{\mathrm{A}_{CH_3}} \times \frac{\mathrm{A}_{CH_3,pre}}{\mathrm{A}_{tert-Cl,pre}} \tag{10}$$

where, A_{exo}, A_{endo}, $\mathrm{A}_{exo\text{-}coupled}$, $\mathrm{A}_{endo\text{-}coupled}$, and $\mathrm{A}_{tert\text{-}Cl}$ were obtained from the ^{1}H NMR spectrum of the coupled polymer and retain the same definitions as given above. A_{CH_3} and $\mathrm{A}_{CH_3,pre}$ are the peak intensities (integrated area from 1.05-1.20 ppm) of the PIB backbone methyl protons of the coupled polymer and the *tert*-chloride-functional precursor, respectively. $\mathrm{A}_{tert-Cl,pre}$ is the integrated area from 1.90-2.06 ppm representing the ultimate methylene protons nearest the *tert*-chloride end group of Precursor PIB3 and Precursor PIB4-5. Any remaining balance of chain ends was assigned to "other" and attributed to carbocation rearrangement.[39]

After alkoxybenzene quenching/decoupling, the fraction of (3-bromopropoxy)phenyl moieties was calculated using eq 11,

$$\mathrm{F}_{3BPB} = \frac{\mathrm{A}_{3BPB}}{\mathrm{A}_{CH_3}} \times \frac{\mathrm{A}_{CH_3,pre}}{\mathrm{A}_{tert-Cl,pre}} \tag{11}$$

and the fraction of methoxyphenyl moieties was calculated using eq 12,

$$\mathrm{F}_{MB} = \frac{\mathrm{A}_{MB}/3}{\mathrm{A}_{CH_3}} \times \frac{\mathrm{A}_{CH_3,pre}}{\mathrm{A}_{tert-Cl,pre}/2} \tag{12}$$

where, A_{3BPB} and A_{MB} were obtained from the ^{1}H NMR spectrum of the quenched/decoupled polymer and retain the same definitions as given above. The fraction of 4-acryloyloxybutoxyphenyl moieties was also calculated using eq 11, by replacing A_{3BPB} with $\mathrm{A}_{4\text{-}PBA}$, defined as the average of the integrated areas of the OCH_2 (triplet, 3.97 ppm) and CH_2OCO (triplet, 4.23 ppm) protons of the butoxy tether.

Quantitation of Coupled Fraction by Gel Permeation Chromatography

Mass fractions of coupled and non-coupled species within coupled PIB samples were determined by peak deconvolution of the GPC refractive index (RI) detector chromatogram of the coupled sample, assuming that the distributions (*i.e.* peak shapes) of the coupled and non-coupled fractions were asymmetrical (skewed) Gaussian distributions defined by eq 13:

$$\mathrm{RI} = \mathrm{RI}_{\max} \times e^{\frac{(t-t_{\max})^2}{-(2\sigma^2)}} \left[1 + erf\left(\frac{a(t-t_{\max})}{\sigma\sqrt{2}}\right)\right] \tag{13}$$

where $\mathrm{RI}_{\max}$ is the maximum refractive index (RI) value for the peak, $t_{\max}$ is the elution time (t) when $\mathrm{RI}_{\max}$ occurs, σ is a peak-width factor, and a is the skew factor. Then, the mass fractions of coupled and non-coupled PIB were calculated using eq 14 for the fractional mass of coupled PIB ($\mathrm{F}_{coupled}$),

$$\mathrm{F}_{coupled} = \frac{\sum_i \mathrm{RI}_{coupled_i}}{\sum_i \left(\mathrm{RI}_{coupled_i} + \mathrm{RI}_{non-coupled_i}\right)} \tag{14}$$

where $\mathrm{RI}_{coupled_i}$ and $\mathrm{RI}_{non-coupled_i}$ are the RI values for the coupled and non-coupled peaks, respectively, at elution time $t = i$. Assuming that the probability for coupling is independent of chain molecular weight within a polydisperse sample, the mass fractions determined in this way can be directly compared to the mole fractions determined by NMR. The deconvolution procedure is described in detail in Appendix A.

Results and Discussion

Synthesis of Coupled PIB

Table 1 lists PIB samples synthesized to purposefully possess significant coupled fractions. It should be recognized that most of these samples contain a gross fraction of coupled species, far in excess of the amount that would typically arise in the normal practice of living IB polymerization, in order to provide a clear and dramatic demonstration of decoupling during alkoxybenzene quenching. The downside to this approach is that the conditions used to achieve such high coupled fractions may cause some degree of chain end isomerization due to carbocationic rearrangement.[39] **Error! Bookmark not defined.** Rearranged chains should not easily undergo coupling, but in the event they do, the resulting coupled chain with isomerized structure may fail to decouple. Of the samples in Table 1, PIB5 with only 10% coupled chains comes closest to a typical sample that might arise in routine practice. As will be seen, this sample also displays near ideal behavior in the quenching/decoupling process.

PIB1, PIB2, and PIB3 were created using dialkyl ether quenching under non-optimal conditions. We have shown that bulky dialkyl ethers are extremely effective end-quenchers for converting living PIB quantitatively to *exo*-olefin chain ends, provided that the ether is supplied in sufficient excess to chain ends, typically ≥ 2[CE].[19] **Error! Bookmark not**

defined. At lower ether concentrations, however, significant coupling is observed. PIB1 was prepared by end-quenching of living PIB with diisopropyl ether at a concentration of 1.2[CE]. We also have shown that non-bulky ethers such as di-*n*-butyl ether (DBE) produce large fractions of coupled PIB even when used in excess, but especially when used at lower concentrations.[19] **Error! Bookmark not defined.** PIB2 and PIB3 were created by end-quenching of living PIB with [DBE] = 1.2[CE]. PIB1 and PIB2 were quenched directly from an isobutylene polymerization, without isolation of the *tert*-chloride-functional precursor polymer; PIB3 was also quenched directly from an isobutylene polymerization, but in this case a sample of the *tert*-chloride-functional precursor was obtained by removal of an aliquot from the reactor prior to addition of DBE.

PIB4 and PIB5 were created using 2,5-dimethylpyrrole quenching under non-optimal conditions. Both samples were prepared from a common *tert*-chloride-functional precursor (Precursor PIB4-5) by re-activating the latter with $TiCl_4$ and quenching with a deficient (0.04 and 0.20 eq per chain end, respectively) amount of 2,5-dimethylpyrrole.

Figure 1 depicts the ^{1}H NMR spectra of PIB5 (top), PIB4 (middle), and their common precursor, Precursor PIB4-5 (bottom). PIB4 is representative of the highly coupled samples of Table 1; PIB5 is more typical of the degree of coupling that might actually arise during a poorly living carbocationic polymerization or poorly designed quenching process. The spectrum of the precursor shows *tert*-chloride end groups only, indicated by the singlet at 1.96 ppm due to the ultimate methylene protons adjacent to chlorine. The spectrum of PIB4 shows three types of end groups present in significant amounts. *exo*-Coupled PIB is revealed by the prominent singlet at 4.82 ppm due to the two identical vinylidene protons of that structure, and the presence of *exo*-olefin PIB, in near-equal concentration, is shown by characteristic resonances at 4.64 and 4.85 ppm. A significant fraction of *tert*-chloride chain ends can also be observed in the spectrum, but no *endo*-coupled PIB or *endo*-olefin PIB are present, as indicated by the absence of characteristic signals at 5.12 and 5.15 ppm, respectively. Since the *tert*-chloride-functional precursor was available in this case, the absolute molar amounts of each type of chain end in PIB4 could be calculated relative to the total number of original *tert*-chloride chain ends. This method of analysis allows detection of chain-end degradation that may have occurred during the coupling reaction, typically revealed by an apparent loss of end groups in the ^{1}H NMR spectrum. Thus, the bottom spectrum showed that the ratio of isobutylene repeat units to *tert*-chloride chain ends was approximately 57.5:1 in Precursor PIB4-5. However, after the coupling reaction to produce PIB4, complete end group analysis using eqs 6-10 indicated 39% *exo*-coupled, 40% *exo*-olefin, and 9% *tert*-chloride chain ends, with perhaps trace amounts of *endo*-coupled and *endo*-olefin chain ends, for a total of only 88%. Thus after accounting for all of the chain ends visible by ^{1}H NMR, the ratio of isobutylene repeat units to chain ends was calculated to be only 57.5:0.88, indicating an apparent loss of approximately 12% of the chain ends. These chain ends still exist in the sample, but they have rearranged into a myriad of structures, no one of which is in sufficient concentration to yield a discernible ^{1}H NMR signal.[39] **Error! Bookmark not defined.** Among the coupled samples for which a *tert*-chloride precursor was available, PIB4 was the only one to show a significant loss of chain ends to rearrangement, but as will be seen, the presence of rearranged chains in sample PIB4 was irrelevant to the demonstration of decoupling by alkoxybenzene compounds.

The spectrum of PIB5 (Figure 1, top) indicates that *exo*-olefin and *tert*-chloride chain ends are the dominant chain end types, with a minor amount of *exo*-coupled chains. Using eqs 6-10, PIB5 was calculated to possess 65% *exo*-olefin, 23% *tert*-chloride, and 10% *exo*-coupled chain ends, thus accounting quantitatively for nearly all chain ends (minimal chain-end rearrangement).

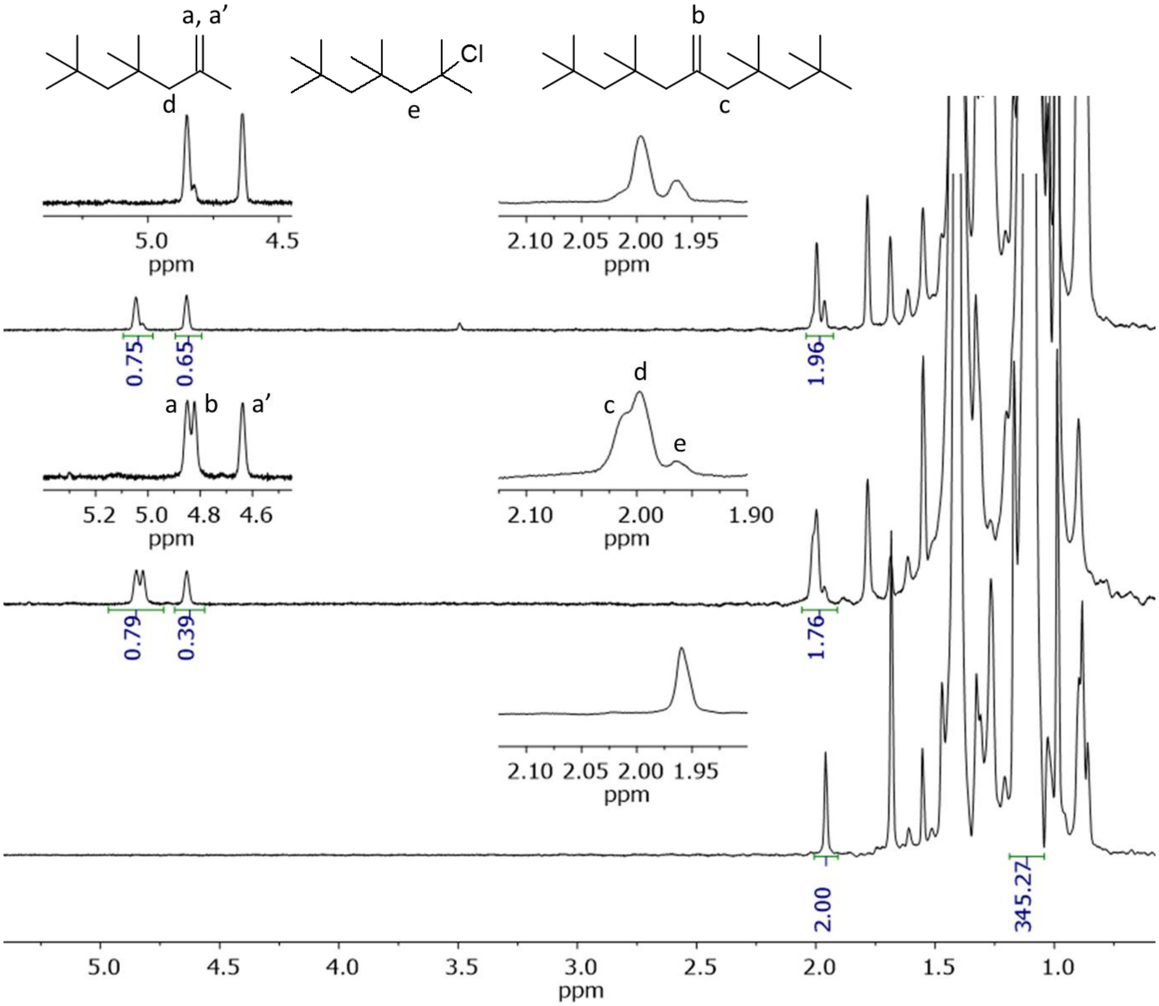


Figure 1 ^{1}H NMR spectra (300 MHz, $CDCl_3$, 23°C) of PIB5 (top), PIB4 (middle) and Precursor PIB4-5 (bottom).

Other methods for creating highly coupled PIB were explored, including simply reacting *tert*-chloride PIB with *exo*-olefin PIB in an approximately 1:1 ratio in the presence of excess 2,6-lutidine, and reacting *tert*-chloride PIB with ½ molar equivalents of methallyltrimethylsilane in the presence of excess 2,6-lutidine. Both of these

Table 2

Quenching/Decoupling Reactions Carried Out on Coupled PIB

Entry	PIB	Quenching Conditions						
		Q[a]	[CE] (M)	[Q] (M)	[$TiCl_4$] (M)	[Lut] (M)	[H_2O] (M)	Time (h)
1	PIB1	3-BPB	0.0092	0.058	0.051	-	-	5
2	PIB2	3-BPB	0.0087	0.057	0.046	-	-	5
3	PIB1	anisole	0.0092	0.059	0.049	-	-	5
4	PIB2	anisole	0.0087	0.057	0.047	-	-	5
5	PIB2	3-BPB	0.0084	0.055	0.070	0.024	-	12
6[d]	PIB3	3-BPB	0.014	0.057	0.047	-	-	19
7[d]	PIB3	3-BPB	0.014	0.057	0.053	-	0.0065	21
8a[d]	PIB4	3-BPB	0.025	0.050	0.098	-	0.015	0.25
8b[d]	PIB4	3-BPB	0.025	0.050	0.098	-	0.015	4
9[d]	PIB5	3-BPB	0.030	0.058	0.13	-	0.016	6
10a[d]	PIB4	3-BPB	0.013	0.024	0.049	-	0.0063	1
10b[d]	PIB4	3-BPB	0.013	0.024	0.049	-	0.0063	20
11[d,e]	PIB5	4-PBA	0.016	0.061	0.14			1
12[d]	PIB3	*N*-MePy	0.028	0.200	0.33	-	-	19
13[d]	PIB3	2-MeFu	0.018	0.118	0.14	-	-	18
14[d]	PIB4	ATMS	0.023	0.034	0.073	-	0.015	5.5
15[d]	PIB4	MATMS	0.026	0.037	0.072	-	0.014	4

Table 2 Continued

Quenched Product								
Chain-End Composition by ^{1}H NMR[b]						GPC		
exo olefin	*endo* olefin	coupled		*t*-Cl	Q	M_n (g/mol)	PDI	Coupled Fraction[c]
		exo	*endo*					
0	0	0	0	0	100	2,380	1.23	-
0	0	0	0	0	100	2,830	1.06	Trace
0	0	0	0	0	100	1,880	1.31	-
0	0	0	0	3	97	2,420	1.1	Trace
11	2	68	5	0	14	3,250	1.1	Large
0	0	0	0	0	100	2,350	1.06	Trace
0	0	0	0	0	100	2,610	1.06	Trace
0	0	15	12	20	47	4,460	1.14	Less
0	0	0	0	0	88	3,960	1.1	None
0	0	0	0	0	98	4,120	1.08	None
0	0	9	10	49	20	4,210	1.14	Less
0	0	0	0	4	83	3,980	1.08	None
0	0	0	0	0	99	3,940	1.08	None
11	2	41	6	0	40	2,960	1.29	Large
0	0	28	4	0	0	4,680	1.13	More
37	0	39	0	0	0	4,840	1.17	Large
48	0	37	8	0	0	4,960	1.19	Large

[a] Q = quencher; 3-BPB = (3-bromopropoxy)benzene; 4-PBA = 4-phenoxy-1-butyl acrylate; N-MePy = N-methylpyrrole; 2-MeFu = 2-methylfuran; ATMS = allyltrimethylsilane; MATMS = methallyltrimethylsilane.

[b] Balance is assumed to be rearranged products.

[c] Trace = barely visible by GPC, not visible by NMR; Large = Very visible by GPC; Less = Less coupled than starting material by GPC; More = More coupled than starting material by GPC

[d] GPC chromatograms before and after quenching/decoupling are shown in Chapter Two Appendix, Figures A2-2 –A2-11. 1H NMR spectra after reaction are shown along with the GPC chromatograms except for Entries 14 and 15.

[e] 40/60 (v/v) hexane/methylene chloride

approaches yielded PIB with a very high percentage of rearranged chain ends before coupling reached appreciable amounts (target: at least 25%).

Decoupling of Coupled PIB by Alkoxybenzene Quenchers

The coupled PIB samples of Table 1 were subjected to end-quenching with alkoxybenzene compounds under various conditions as listed in Table 2, Entries 1-11. Three different alkoxybenzenes were utilized to demonstrate scope of the method: anisole, which is representative of non-substituted alkyl phenyl ethers that can be cleaved to produce phenol-terminated PIB; (3-bromopropoxy)benzene, which yields primary bromide that can be converted to many other functional groups via nucleophilic substitution; and 4-phenoxybutyl acrylate, which allows for radical polymerization, but also represents ester-containing tethers that can be cleaved to yield primary hydroxyl end groups.

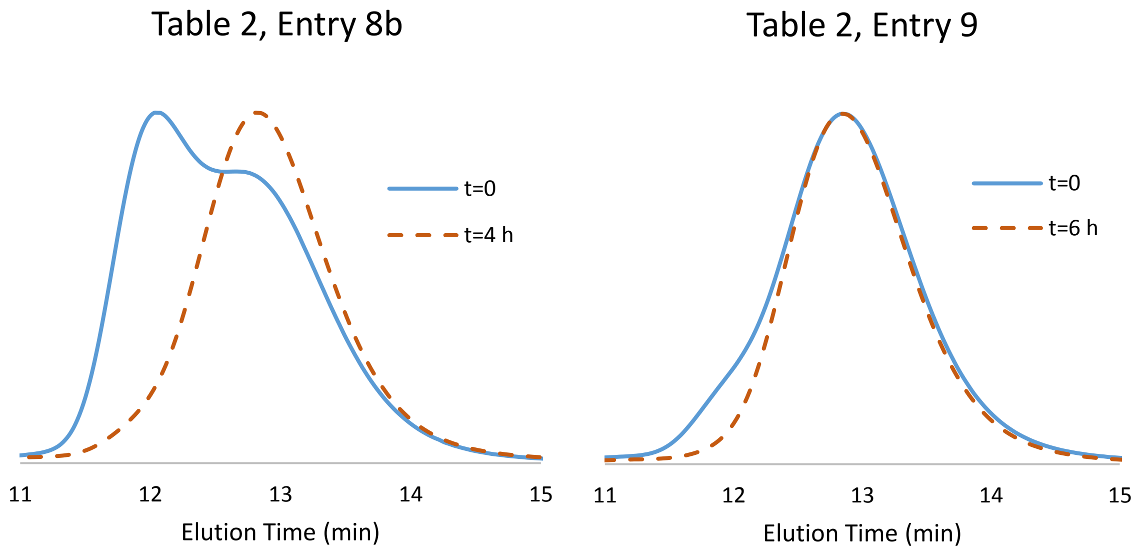


Figure 2 GPC chromatograms of PIB4 (left) and PIB5 (right) before and after quenching with (3-bromopropoxy)benzene at -70°C in 60/40 hexane/methylene chloride in the presence of $TiCl_4$.

Figure 2 shows GPC chromatograms of representative quenching reactions from Table 2: PIB4 (left) and PIB 5 (right) before and after quenching with (3-bromopropoxy)benzene at -70°C in 60/40 hexane/methylene chloride in the presence of $TiCl_4$. In each case, the before chromatogram is bimodal, clearly showing the non-coupled and coupled fractions. The after chromatogram is monomodal, and its peak

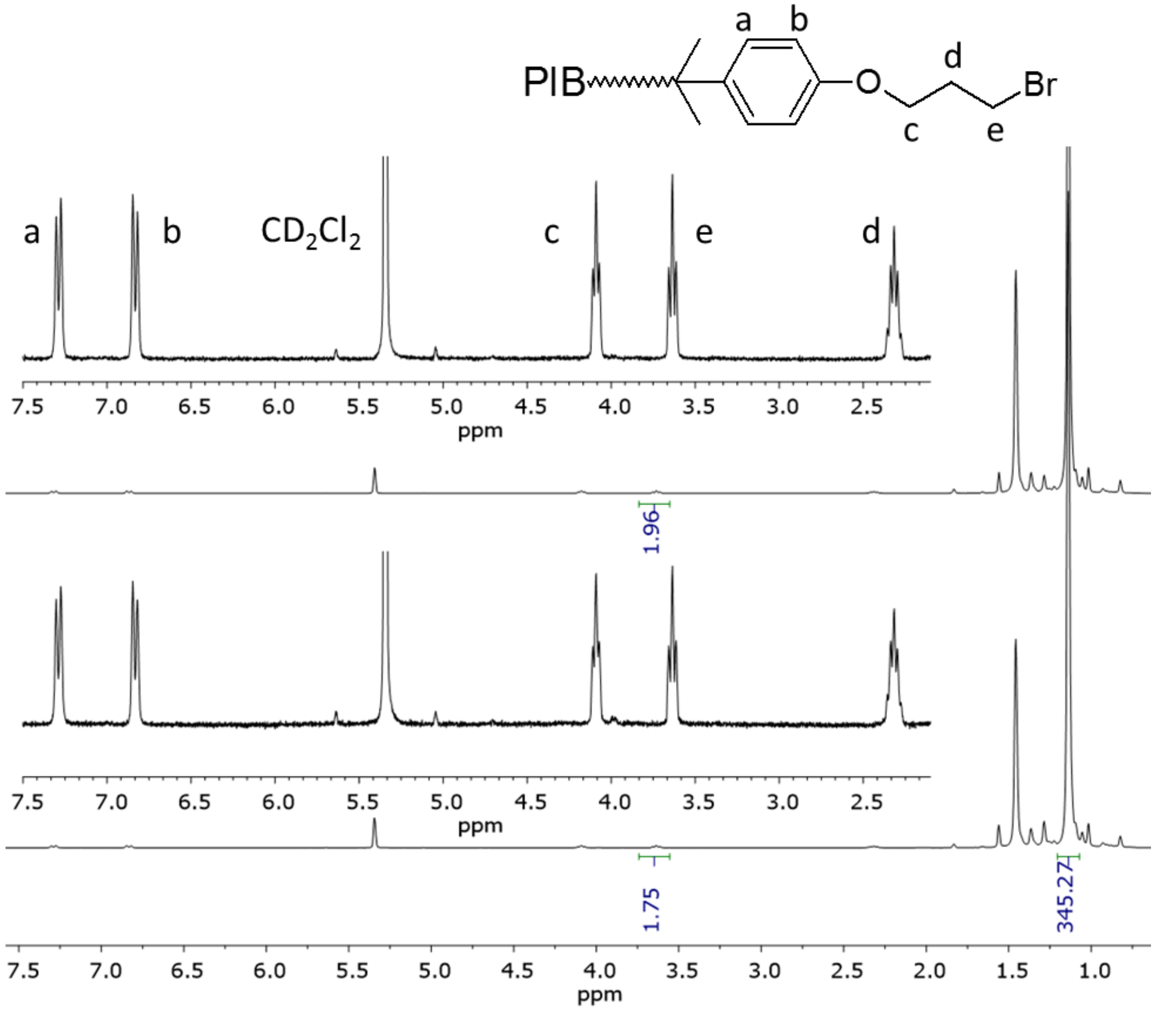


Figure 3 ^{1}*H NMR spectra (300 MHz,* CD_2Cl_2*, 23°C) of fully decoupled PIB4 (bottom) and PIB5 (top) after quenching with (3-bromopropoxy)benzene at -70°C in 60/40 hexane/methylene chloride in the presence of* $TiCl_4$ *(PIB4 reaction is Entry 8b and PIB5 reaction is Entry 9, in Table 2). The only end group type visible is (3-bromopropoxy)phenyl.*

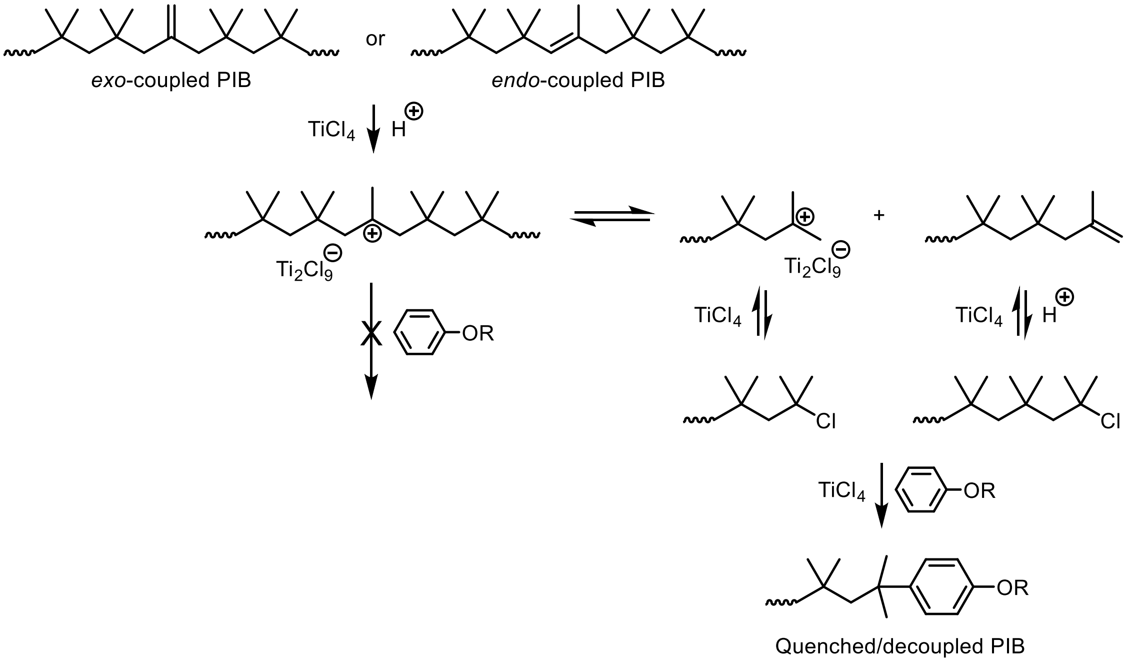
position corresponds to the non-coupled shoulder of the before chromatogram, indicating that the quenched sample has been completely decoupled.

The ^{1}H NMR spectra of PIB4 and PIB5 after decoupling/quenching are shown in Figure 3. The only chain end type visible in the spectra is (3-bromopropoxy)phenyl resulting from reaction of the chain ends with the alkoxybenzene quencher. These chain ends are indicated by the characteristic triplet at 3.60 ppm (e) due to the methylene protons adjacent to bromide and the companion triplet at 4.07 ppm (c) due to the methylene protons adjacent to oxygen.

GPC chromatograms and ^{1}H NMR spectra for alkoxybenzene quenching/decoupling reactions in entries 6-11, Table 2, are shown in Appendix A, Figures A3–A8, respectively.

Mechanism of Decoupling

The proposed mechanism of decoupling during alkoxybenzene quenching is shown in Scheme 4. The first step involves protonation of either the *exo*-coupled or *endo*-coupled structure to provide the main-chain carbenium ion shown. In some of the alkoxybenzene quenching reactions in Table 2, a small amount of external proton source (H_2O) was added to accelerate this initial step; however, an external proton source is not necessary if adventitious protic sources and/or some fraction of *tert*-chloride chain ends are present. For example, Entries 1-3, 6, and 11 represent experiments in which decoupling/functionalization reached completion in the absence of any added proton source. The second step of the mechanism is decomposition of the main-chain carbenium ion. This species is too sterically hindered to alkylate the alkoxybenzene compound; instead, it preferentially undergoes β-scission to form two fragments, a terminal PIB carbenium ion and an *exo*-olefin chain end. An analogous β-scission reaction has been reported by Kennedy and Phillips[40] for butyl rubber in the presence of strong Lewis acids such as ethylaluminum dichloride. Although not shown in Scheme 4, the carbenium ion fragment may alkylate the alkoxybenzene quencher immediately. More likely, however, it will reversibly collapse with the counterion to become part of the general pool of dormant *tert*-chloride chain ends. The *exo*-olefin fragment is converted to a PIB carbenium ion by protonation. It may then either alkylate the quencher (not shown) or reversibly collapse. Over the course of successive ionization/deactivation cycles, all of the *tert*-chloride and terminal olefinic chain ends ultimately undergo alkoxybenzene quenching via Friedel-Crafts alkylation.



Scheme 4. Proposed mechanism for quenching/decoupling of coupled PIB.

Analysis of an aliquot removed from a quenching reaction carried out on PIB4 (Entry 10a, Table 2) at an intermediate time of 1 h supports the mechanism presented in

Scheme 4. Figure 4 (upper) shows the GPC chromatogram of this aliquot. Analysis of the GPC chromatogram by peak deconvolution showed that the coupled fraction had been reduced to 20.8%, from 39% originally. For reference, Figure A7 in Appendix A shows initial (PIB4 prior to reaction) and final (Entry 10b, Table 2, 20 h reaction time) GPC chromatograms for this reaction. The 20 h chromatogram indicates that essentially all coupled species had been cleaved by this time. The ^{1}H NMR spectrum of the 1 h aliquot (Figure 4, lower) revealed 9% *exo*-coupled, 10% *endo*-coupled, 20% alkoxybenzene quenched, and 49% *tert*-chloride chain ends, but no *exo*- and no *endo*-olefin chain ends. The sum of these fractions equals the fraction of non-rearranged chain ends detected in PIB4 originally. Thus, at an intermediate reaction time, while the coupled fraction has decreased greatly, and the *exo*-olefin fraction has disappeared, the *tert*-chloride fraction has greatly increased from 9% to almost half of all chain ends. These results are in harmony with the mechanism of Scheme 4 and indicate that the presence of a significant concentration of external protic source causes rapid conversion of the original *exo*-olefin end groups to *tert*-chloride, and that β-scission and alkylation proceed in concert but relatively more slowly. Interestingly, the 1 h aliquot contains *endo*-coupled PIB; whereas this species was not present in PIB4. This indicates acid-catalyzed isomerization of the *exo*-coupled double bond that proceeds at a higher rate than β-scission. The ^{1}H NMR spectrum of the final product after 24 h reaction time (Figure A7, Appendix A) shows that all visible (i.e., non-rearranged) chain ends were functionalized with (3-

bromopropoxy)phenyl groups, and the resulting product is indistinguishable from a product obtained from quenching a living isobutylene polymerization with an alkoxybenzene quencher.

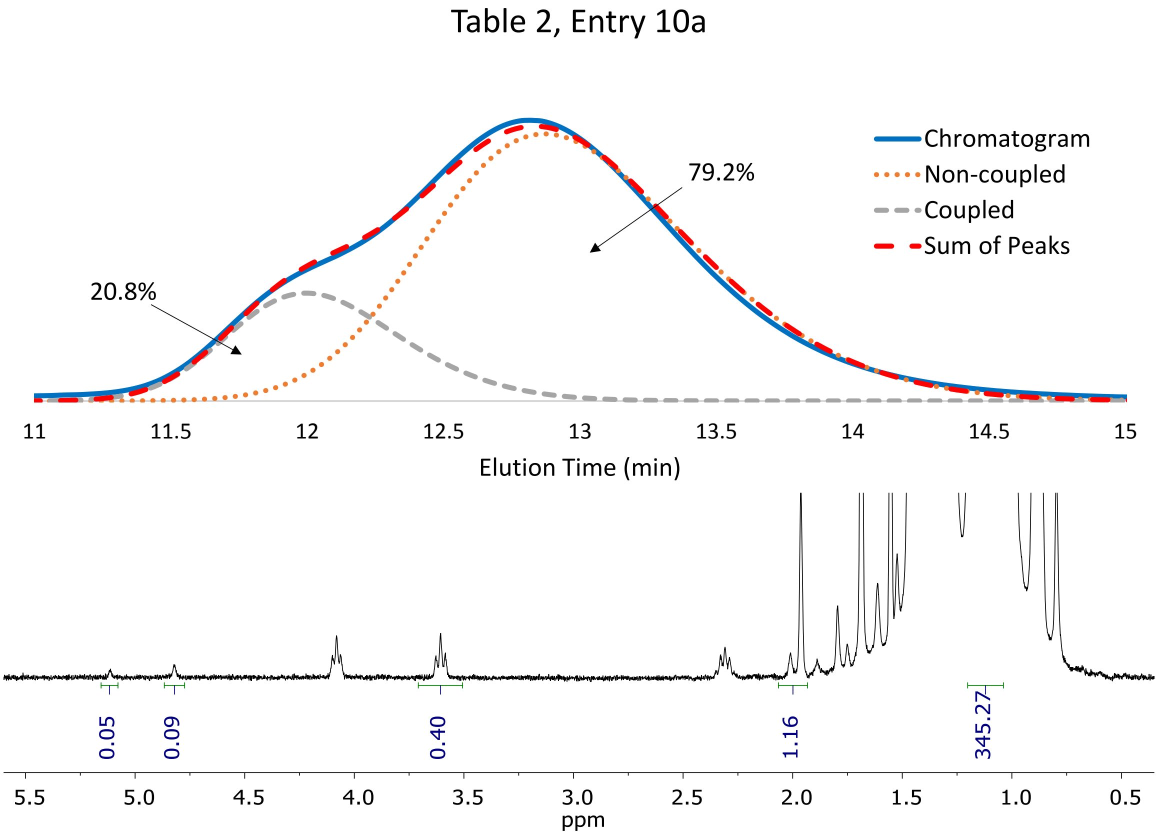


Figure 4 Reaction aliquot (at 1 h) of PIB4 during quenching/decoupling with (3-bromopropoxy)benzene (Entry 10a, Table 2). GPC chromatogram with coupled and non-coupled components obtained by peak fitting (upper), and ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 23°C).

A control experiment (Entry 5, Table 2) was performed in the presence of a proton trap to further validate the mechanism of Scheme 4. PIB2 was quenched with 3BPB under conditions similar to those used for Entry 2, Table 2, except that 2,6-lutidine was added to the reaction at approximately 3 equivalents per chain end. Additional $TiCl_4$ in the amount of one equivalent per equivalent of lutidine was also added to maintain the same concentration of free Lewis acid that was used in Entry 2. These conditions were designed to prevent protonation of coupled PIB and hence to suppress decoupling by β-scission. The data in Table 2 indeed show that no decoupling occurred; in fact the fraction of coupled chains increased. PIB2 initially contained 33.5% *tert*-chloride chain ends, which are capable of ionization by the Lewis acid to form PIB carbenium ion. Some of these carbenium ions underwent alkylation to produce the 14.2% of (3-bromopropoxy)phenyl chain ends observed, and some apparently reacted with *exo*-olefin chain ends to produce additional coupled product.

Attempted decoupling of couplied PIB using other quenchers

According to the mechanism presented in Scheme 4, the alkoxybenzene quencher plays no role in the forward β-scission reaction. Assuming that this reaction is reversible, the alkoxybenzene quencher does serve to drive the forward process by trapping the product carbenium ions and thereby preventing reversal. This interpretation, however, suggests that any quenching molecule capable of trapping carbenium ions might serve the same purpose. We therefore examined several other types of quenchers to test this hypothesis, including *N*-methylpyrrole, 2-methylfuran, allyltrimethylsilane (ATMS), and methallyltrimethylsilane (MATMS). The results of these experiments are presented in Table 2, Entries 12-15.

N-Methylpyrrole and 2-methylfuran are Friedel-Crafts substrates similar to alkoxybenzene compounds, although considerably more reactive, and we thus had a reasonable expectation that they might be effective quenching/decoupling agents for coupled PIB. Although protic acid (water) was routinely used to increase the rate of quenching/decoupling with alkoxybenzene compounds, when used with either *N*-methylpyrrole or 2-methylfuran, it caused rapid production of a precipitate, assumed to be the protonated quencher, and the experiment typically resulted in an increase in the fraction of coupled PIB. Although furans and pyrroles are not generally considered strong bases, they are readily protonated (usually at C2) by strong acids such as $HCl \cdot Ti_2Cl_8$. Thus, an insoluble salt is formed, and protons are removed from the system. This suppresses β-scission, and the system is driven toward more coupled PIB as *tert*-chloride chain ends ionize and react with *exo*-olefin. We therefore omitted all purposefully added protic compounds in further experiments and relied only on adventitious moisture. A representative experiment involving *N*-methylpyrrole, reacted with PIB3 in this case, is recorded as Entry 12 in Table 2. ^{1}H NMR analysis of the product revealed that only the original *tert*-chloride chain ends of PIB3 were able to alkylate *N*-methylpyrrole (Figure A9, bottom, Appendix A); no reaction occurred with any olefinic chain end. GPC (Figure A9, top, Appendix A) confirmed that no decoupling occurred. Friedel-Crafts alkylation reactions involving an olefin typically require only catalytic protic acid since a proton is released upon re-aromatization of the intermediate addition product. This mechanism is apparently inoperable in this case, and one of two possible alternative processes seems likely. Either the non-aromatic intermediate does not immediately release a proton to re-aromatize, or the proton is immediately released, but then quickly protonates unreacted *N*-methylpyrrole. The latter process would increase the stoichiometric amount of *N*-methylpyrrole required for complete reaction. It has been reported by Stokes *et al.* that approximately one equivalent of *N*-methylpyrrole is sufficient to quantitatively quench a living polymerization of isobutylene;[26c] therefore, we hypothesize that addition of PIB carbenium ion to *N*-methypyrrole creates a stable non-aromatic intermediate, which persists until the Lewis acid is destroyed by the addition of methanol. Hadjikyriacou and

Faust observed the same phenomenon when *tert*-chloride PIB was reacted with 2-alkylfuran.[25] **Error! Bookmark not defined.**

Attempted quenching/decoupling with 2-methylfuran produced different results, which were difficult to interpret (representative experiment recorded as Entry 13 in Table 2). The ^{1}H NMR spectrum of the product (Figure A10, bottom, Appendix A) suggested that some decoupling had occurred (from 47 to 32%), but the remaining 32% coupled PIB (28% *exo*-coupled, 4% *endo*-coupled PIB) were the only type of chain ends that could positively be assigned. No *exo*- or *endo*-olefin, no *tert*-chloride, and no 2-methylfuran chain ends were observed. To further confuse these results GPC of the final product actually indicated an increase in coupling (Figure A10, top, Appendix A). This suggests formation of a new coupled species, which we were unable to identify in the ^{1}H NMR spectrum.

ATMS and MATMS are similar quenchers that undergo addition to PIB carbenium ion, followed by β-scission and elimination of $(CH_3)_3Si^{\oplus}$. Thus, unlike a Friedel-Crafts-type quencher, these compounds do not eliminate a proton after addition, and therefore provide no means of converting olefinic chain ends to carbenium ions. Consequently, an external protic acid (water) was used for experiments with these quenchers, and PIB4 was chosen as a representative coupled PIB (Entries 14-15, Table 2). For both of these experiments, no reaction of PIB4 was observed (see Figures A11 and A12, Appendix A). We hypothesize that in each case, the quencher was decomposed in the strong acidic medium to produce propylene (or isobutylene) and $(CH_3)_3SiCl$.

Conclusions

We have demonstrated that alkoxybenzene compounds can serve to decouple coupled PIB in the presence of $TiCl_4$ and yield a functionalized product. We have further shown that alkoxybenzene compounds are fairly unique in this regard, possessing a moderately high reactivity toward carbon-centered electrophiles and little to no tendency to sequester the protons necessary for conversion of the various olefinic chain ends to carbenium ions. We believe that the decoupling/quenching process is applicable to alkoxybenzenes generally, provided the alkoxybenzene does not contain functional groups that interact strongly with the Lewis acid or otherwise enter into side reactions. This decoupling/quenching process can facilitate the use of non-ideal initiators or comonomers, which, though they may bear a desired functionality, yield a coupled fraction in the final product. Furthermore, it may serve as a means of "correcting" faulty PIB syntheses. For instance, if a large-scale synthesis of *exo*-olefin-terminated PIB using, say, ether quenching[19 **Error! Bookmark not defined.**] were to be carried out under non-ideal conditions, the product would most likely contain a significant quantity of coupled PIB. Using alkoxybenzene quenching, this faulty PIB could be repurposed and reused.

Finally, as we will report in subsequent papers, this chemistry can be used to synthesize difunctional telechelic and multifunctional PIBs through a process termed constructive degradation. As we have shown, the reported reaction yields two functionalized chain-ends from a coupled species. Thus, by carrying out this chemistry on PIB-based copolymers that possess main-chain functionalities capable of yielding hindered cations, we are capable of synthesizing telechelic and/or multifunctional polymers without the use of controlled/living polymerization from a difunctional or polyfunctional initiator

References

1. Kennedy, J.P. From Thermoplastic Elastomers to Designed Biomaterials. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43* (14), 2951−2963.
2. Kennedy, J.P.; Iván, B. *Designed Polymers by Carbocationic Macromolecular Engineering: Theory and Practice*; Hanser: Munich, Germany, **1991**; 173-177.
3. Simison, K.L.; Stokes, C.D.; Harrison, J.J.; Storey, R.F. End-Quenching of Quasiliving Carbocationic Isobutylene Polymerization with Hindered Bases: Quantitative Formation of *exo*-Olefin-Terminated Polyisobutylene. *Macromolecules* **2006**, *39* (7), 2481-2487.
4. Schriesheim, A.; Kirshenbaum, I. Industrial Friedel-Crafts Chemistry – Past and Future. *CHEMTECH.* **1978**, 310-314.
5. Puskas, I.; Banas, E.M.; Nerheim, A.G. The Nature of the Double Bond in Low Molecular Weight Polyisobutylenes and "Polybutene" Copolymers. *J. Polym. Sci., Polym. Symp.* **1976**, *56* (1), 191-202.
6. Harrison, J.J.; Young, D.C.; Mayne, C.L. 2D-INADEQUATE Structural Assignment of Polybutene Oligomers. *J. Org. Chem.* **1997**, *62* (3), 693-699.
7. Günther, W.; Maenz, K.; Stadermann, D. Structural Investigations on Low-Molecular-Weight Polyisobutenes. *Angew. Makromol. Chem.* **1996**, *234* (1), 71-90.
8. Argo, C.; Gillam, S.M.; Orsini, F. Identification of Olefin End Groups in Commercial Polybutene Oligomers. *Polym. Bull.* **2000**, *44* (1), 71-78.
9. Mach, H.; Rath, P. Highly Reactive Polyisobutene as a Component of a New Generation of Lubricant and Fuel Additives. *Lubr. Sci.* **1999**, *11* (2), 175-185.

10. Anderson, R.G.; Stuart, F.A.; Drummond, A.Y. N-Dialkylaminoalkyl Alkenyl Succinimides. U.S. Patent 3,018,291, Jan. 23, 1962.

11. Harrison, J.J.; Mijares, C.M.; Cheng, M.T.; Hudson, J. Negative Ion Electrospray Ionization Mass Spectrum of Polyisobutenylsuccinic Anhydride: Implications for Isobutylene Polymerization Mechanism. *Macromolecules* **2002**, *35* (7), 2494-2500.

12. Alemán-Vázquez, L.O.; Villagómez-Ibarra, J.R. Polyisobutenylsuccinimides as Detergents and Dispersants in Fuel: Infrared Spectroscopy Application. *Fuel* **2001**, *80* (7), 965-968.

13. (a) Kostjuk, S.V.; Yeong, H.Y.; Voit, B. Cationic Polymerization of Isobutylene at Room Temperature. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51* (3), 471-486.

(b) Vasilenko, I.V.; Frolov, A.N.; Kostjuk, S.V. Cationic Polymerization of Isobutylene Using $AlCl_3OBu_2$ as a Coinitiator: Synthesis of Highly Reactive Polyisobutylene. *Macromolecules* **2010**, *43* (13), 5503-5507.

(c) Liu, Q.; Wu, Y.-X.; Zhang, Y.; Yan, P.-F.; Xu, R.-W. A Cost-Effective Process for Highly Reactive Polyisobutylenes via Cationic Polymerization Coinitiated by $AlCl_3$. *Polymer* **2010**, *51* (25), 5960-5969.

(d) Liu, Q.; Wu, Y.; Yan, P.; Zhang, Y.; Xu, R. Polyisobutylene with High *exo*-Olefin Content via β-H Elimination in the Cationic Polymerization of Isobutylene with $H_2O/FeCl_3$/Dialkyl Ether Initiating System. *Macromolecules* **2011**, *44* (7), 1866-1875.

(e) Vasilenko, I.V.; Shiman, D.I.; Kostjuk, S.V. Highly Reactive Polyisobutylenes via $AlCl_3OBu_2$-Coinitiated Cationic Polymerization of Isobutylene: Effect of Solvent Polarity, Temperature, and Initiator. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50* (4), 750-758.

(f) Dimitrov, P.; Emert, J.; Faust, R. Polymerization of Isobutylene by $AlCl_3$/Ether Complexes in Nonpolar Solvent. *Macromolecules* **2012**, *45* (8), 3318-3325.

(g) Kumar, R.; Dimitrov, P.; Bartelson, K.J.; Emert, J.; Faust, R. Polymerization of Isobutylene by $GaCl_3$ or $FeCl_3$/Ether Complexes in Nonpolar Solvents. *Macromolecules* **2012**, *45* (21), 8598-8603.

(h) Radhakrishnan, N.; Hijazi, A.K.; Komber, H.; Voit, B.; Zschoche, S.; Kühn, F.E.; Nuyken, O.; Walter, M.; Hanefeld, P. Synthesis of Highly Reactive Polyisobutylenes Using Solvent-Ligated Manganese(II) Complexes as Catalysts. *J. Polym. Sci., Part A: Polym. Chem.* **2007**, *45* (23), 5636-5648.

14. Kennedy, J.P.; Chang, V.S.C.; Smith, R.A.; Iván, B. New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers). V. Synthesis of α-*tert*-Butyl-ω-isopropenylpolyisobutylene and α, ω-Di(isopropenyl)polyisobutylene. *Polym. Bull.* **1979**, *1* (8), 575-580.

15. Kennedy, J.P.; Smith, R.A. New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Ini*tiator-Trans*fer* Agents (Inifers). II. Synthesis and Characterization of α,ω-Di(*tert*-chloro)polyisobutylenes. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18* (5), 1523-1537.

16. Kennedy, J.P.; Ross, L.R.; Lackey, J.E.; Nuyken, O. New Telechelic Polymers and Sequential Copolymers by Polyfunctional *Ini*tiator-Trans*fer* Agents (Inifers). 10.

Three-Arm Star Telechelic Polyisobutylenes Carrying Chlorine, Olefin or Primary Alcohol Endgroups. *Polym. Bull.* **1981**, *4* (1-2), 67-74.

17. Morgan, D.L.; Harrison, J.J.; Stokes, C.D.; Storey, R.F. Kinetics and Mechanism of End-Quenching of Quasiliving Polyisobutylene with Sterically Hindered Bases. *Macromolecules* **2011**, *44* (8), 2438-2443.

18. Storey, R.F.; Kemp, L.K. Preparation of Exo-Olefin Terminated Polyolefins via Quenching with Alkoxysilanes or Ethers. U.S. Patent 8,063,154, November 22, 2011.

19. Ummadisetty, S.; Storey, R.F. Quantitative Synthesis of exo-Olefin-Terminated Polyisobutylene: Ether Quenching and Evaluation of Various Quenching Methods. *Macromolecules* **2013**, *46*(6), 2049-2059.

20. Morgan. D.L.; Stokes, C.D.; Meierhoefer, M.A.; Storey, R.F. Sulfonium Ion Adducts from Quasiliving Polyisobutylene and Mono- or Disulfides. *Macromolecules* **2009**, *42* (7), 2344-2352.

21. (a) Stokes, C.D. Production of Vinylidene-Terminated and Sulfide-Terminated Telechelic Polyolefins via Quenching with Disulfides. U.S. Patent 8,133,954, March 13, 2012.

    (b) Stokes, C.D. Production of Vinylidene-Terminated and Sulfide-Terminated Telechelic Polyolefins via Quenching with Disulfides. U.S. Patent 8,383,760, Feb. 26, 2013.

22. Ivan, B.; Kennedy, J. P. Living Carbocationic Polymerization. XXX. One-Pot Synthesis of Allyl-Terminated Linear and Tri-Arm Star Polyisobutylenes, and

Epoxy- and Hydroxy-Telechelics Therefrom. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28* (1), 89–104.

23. (a) Roth, M.; Mayr, H. A Novel Method for the Determination of Propagation Rate Constants: Carbocationic Oligomerization of Isobutylene. *Macromolecules* **1996**, *29* (19), 6104–6109.

(b) Nielsen, L. V.; Nielsen, R. R.; Gao, B.; Kops, J.; Ivan, B. *Polymer* **1997**, *38* (10), 2529–2534.

24. (a) De, P.; Faust, R. Relative Reactivity of C4 Olefins toward the Polyisobutylene Cation. *Macromolecules* **2006**, *39* (20), 6861–6870.

(b) De, P.; Faust, R. Carbocationic Polymerization of Isobutylene Using Methylaluminum Bromide Coinitiators: Synthesis of Bromoallyl Functional Polyisobutylene. *Macromolecules* **2006**, *39* (22), 7527-7533.

25. Hadjikyriacou, S.; Faust, R. Cationic Macromolecular Design and Synthesis Using Furan Derivatives. *Macromolecules* **1999**, *32* (20), 6393-6399.

26. (a) Martinez-Castro, N.; Morgan, D.L.; Storey, R.F. Primary Halide-Terminated Polyisobutylene: End-Quenching of Quasiliving Carbocationic Polymerization with *N*-(ω-Haloalkyl)pyrrole. *Macromolecules* **2009**, *42* (14), 4963-4971.

(b) Morgan, D.L.; Storey, R.F. Primary Hydroxy-Terminated Polyisobutylene via End-Quenching with a Protected *N*-(ω-Hydroxyalkyl)pyrrole. *Macromolecules* **2010**, *43* (3), 1329–1340.

(c) Stokes, C.D., Storey, R.F., Harrison, J.J. Living and Quasiliving Cationic Telechelic Polymers Quenched by N-Substituted Pyrrole and Methods for Their Preparation. U.S. Patent 6,969,744, Nov. 29, 2005.

(d) Stokes, C.D., Storey, R.F., Harrison, J.J. Process for Preparing Terminally Functionalized Living and Quasiliving Cationic Telechelic Polymers. U.S. Patent 7,576,161, Aug. 18, 2009.

(e) Storey, R.F.; Morgan, D.L. In Situ Formation of Hydroxy Chain End Functionalized Polyolefins. U.S. Patent 8,394,898, Mar. 12, 2013.

(f) Storey, R.F.; Stokes, C.D.; Harrison, J.J.; Martinez-Castro, N. Amine-Terminated Telechelic Polymers and Precursors Thereto and Methods for Their Preparation. U.S. Patent 8,552,122, Oct. 8, 2013.

27. Morgan, D.L.; Storey, R.F. End-Quenching of Quasi-Living Isobutylene Polymerizations with Alkoxybenzene Compounds. *Macromolecules* **2009**, *42* (18), 6844–6847.

28. Morgan, D.L.; Martinez-Castro, N.; Storey, R.F. End-Quenching of $TiCl_4$-Catalyzed Quasiliving Polyisobutylene with Alkoxybenzenes for Direct Chain End Functionalization. *Macromolecules* **2010**, *43* (21), 8724-8740.

29. (a) Storey, R.F.; Morgan, D.L. Functionalization of Polyolefins with Phenoxy Derivatives. U.S. Patent No. 8,344,073, January 1, 2013.

    (b) Storey, R.F.; Morgan, D.L. Vinyl Ether End-Functionalized Polyolefins. U.S. Patent 8,592,527, Nov. 26, 2013.

30. Kemp, L.K.; Poelma, J.E.; Cooper, T.R.; Storey, R.F. Structural Confirmation of *Exo*-Olefin-Coupled Polyisobutylene *via* Model Compound Synthesis and Characterization. *JMS – Part A: Pure Appl. Chem.* **2008**, *45* (2), 137-143.

31. Storey, R.F.; Curry, C.L.; Hendry, L.K. Mechanistic Role of Lewis Bases and Other Additives in Quasiliving Carbocationic Polymerization of Isobutylene. *Macromolecules* **2001**, *34* (16), 5416-5432.

32. Held, D.; Iván, B.; Müller, A.H.E.; de Jong, F.; Gaarfland, T. Stability of Propagating Species in Living Cationic Polymerization of Isobutylene. *ACS Symp. Ser.* **1997**, *665*, Chap. 6, pp. 63-74.

33. Bae, Y.C.; Faust, R. The Role of Pyridine Derivatives in Living Carbocationic Polymerization: Lewis base or Nucleophile? *Macromol. Symp.* **1998**, *132* (1), 11-23.

34. Bae, Y.C.; Faust, R. β-Proton Elimination by Free Bases in the Living Carbocationic Polymerization of Isobutylene. *Macromolecules* **1997**, *30* (23), 7341-7344.

35. Puskas, J.E.; Brister, L.B.; Michel, A.J.; Lanzendörfer, M.G.; Jamieson, D.; Pattern, W.G. Novel Substituted Epoxide Initiators for the Carbocationic Polymerization of Isobutylene. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38* (3), 444-452.

36. Soytaş, S.H.; Lim, G.T.; Puskas, J.E. Synthesis of POSS-Functionalized Polyisobutylene via Direct Initiation. *Macromol. Rapid. Comm.* **2009**, *30* (24), 2112-2115.

37. Roche, C.P.; Brei, M.R.; Yang, B.; Storey, R.F. Direct Chain End Functionalization of Living Polyisobutylene Using Phenoxyalkyl (Meth)acrylates. *ACS Macro Lett.* **2014**, *3*, 1230-1234.

38. Morgan, D.L.; Storey, R.F. Primary Hydroxy-Terminated Polyisobutylene via End-Quenching with a Protected *N*-(ω-Hydroxyalkyl)pyrrole. *Macromolecules* **2010**, *43* (3), 1329-1340.

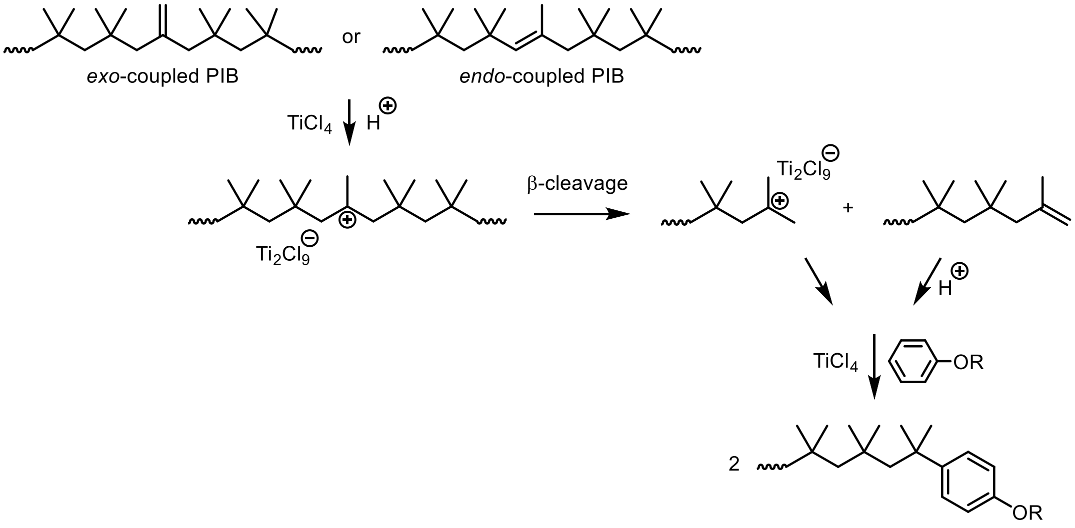
39. Storey, R.F.; Curry, C.L.; Brister, L.B. Carbocation Rearrangement in Controlled/Living Isobutylene Polymerization. *Macromolecules* **1998**, *31* (4), 1058-1063.

40. Kennedy, J.P.; Phillips, R.R. The Influence of Aluminum-Containing Lewis Acids on Polyisobutylene, Isobutylene-lsoprene Copolymers (Butyl Rubber), and Chlorinated Isobutylene-lsoprene Copolymer (Chlorobutyl). *J. Macromol. Sci.-Chem.* **1970**, *A4* (8), 1759-1784.

CHAPTER III – FUNCTIONAL POLYISOBUTYLENES VIA ELECTROPHILIC CLEAVAGE/ALKYLATION

Introduction

During living carbocationic polymerization of isobutylene (IB), marginal polymerization conditions may lead to the formation of "coupled" polyisobutylene (PIB), caused by addition of PIB carbocation to PIB *exo* olefin.[1] We recently reported [2] that coupling of PIB is quantitatively reversed by end-quenching of the living chains with an alkoxybenzene, and that the regenerated chain ends possess the desired alkoxybenzene functionality (Scheme 5). This reaction represents a novel variation of Friedel-Crafts alkylation chemistry in which a bulky carbenium ion, which is sterically incapable of alkylation, undergoes β-cleavage to yield two smaller fragments that readily undergo alkylation. In our previous report[2] **Error! Bookmark not defined.** we noted that high molecular weight PIB-based copolymers, possessing bulky, main-chain unsaturations similar to those found in coupled PIB, might be subjected to this novel cleavage/alkylation chemistry to produce difunctional

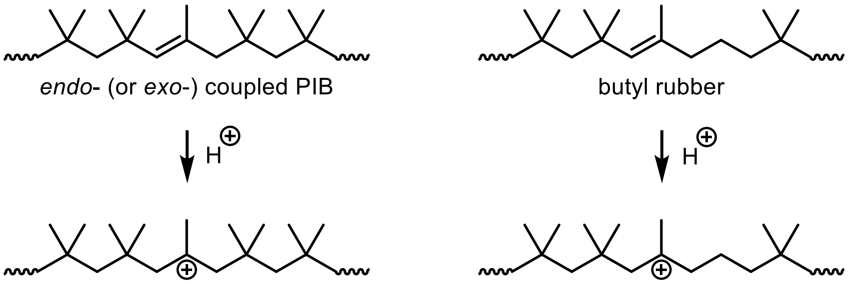


Scheme 5. Quenching/decoupling of coupled PIB (adapted from reference 2).

telechelic or polyfunctional PIB chains without need for expensive or difficultly-synthesized polyfunctional initiators.[3] Furthermore, because the cleavage/alkylation reaction requires the same catalyst, i.e., a Lewis acid, which is used during cationic polymerization of the starting copolymer, this process could theoretically be performed in the same vessel subsequent to copolymerization.

The general synthetic strategy, whereby a high molecular weight copolymer is cleaved such that the resulting oligomers bear reactive groups at their chain ends, is known and has been described in the literature as constructive degradation.[4] The most common approach has been ozonolysis of main-chain double bonds, introduced into a polymer by copolymerization of a diene[5] or monosubstituted acetylene,[6] and with regard to the former approach, one of the most common substrates has been poly(isobutylene-*co*-isoprene) (butyl rubber).[7] The action of ozone on butyl rubber typically yields oligomeric PIBs possessing a broad mixture of methyl ketone, aldehyde, and carboxylic acid end groups, and hence this process is of marginal usefulness for the synthesis of well-defined telechelic prepolymers; however it has been reported that such a mixture can be reduced to hydroxyl using $LiAlH_4$.[7a] Metathesis degradation of polymers containing main-chain double bonds has also been reported as a means of synthesizing telechelic prepolymers.[5b,8]

Herein, we have chosen butyl rubber as an initial PIB-based copolymer upon which to apply the newly discovered cleavage/alkylation chemistry involving alkoxybenzenes. It should be noted that the main-chain unsaturations of butyl rubber are similar to but less bulky than those found in coupled PIB (Scheme 6). They are thus predicted to yield a less sterically hindered carbenium ion upon protonation, resulting in a lower impetus for cleavage. However, because of its ready commercial availability, butyl rubber was a convenient and obvious platform upon which to base these initial investigations.



Scheme 6. Comparison of unsaturations, and resulting carbenium ions after protonation, in coupled PIB and butyl rubber.

Experimental

Materials

Butyl rubber (EXXON™ Butyl 365) was obtained from ExxonMobil Corporation, and determined by GPC/MALLS to have a number average molecular weight (M_n) of 1.91 x 10^5 g/mol and polydispersity index (PDI) of 1.66. The mole fraction of isoprene (IP) comonomer units in the copolymer, F_{IP}, was determined to be 0.0230 (IB units/IP units ≅ 42.5) from ^{1}H NMR data (Figure A1, Appendix B) using eq 1,

$$F_{IP} = \frac{A_{5.05}}{A_{1.11}/6 + A_{5.05}} \cong 0.0230 \tag{1}$$

where, $A_{1.11}$ is the integrated area of the singlet from 1.20-1.05 ppm representing the six methyl protons of the isobutylene (IB) repeats units, and $A_{5.05}$ is the integrated area of the triplet from 5.12-4.98 ppm representing the single olefinic proton of the IP repeat units. This measurement also allowed calculation of the IP equivalent weight of the butyl rubber, EW_{IP}, according to eq 2,

$$EW_{IP} = n_{IB}M_{IB} + M_{IP} \cong 2.45\ \text{x}10^3\ \text{(g/mol)} \tag{2}$$

where M_{IB} and M_{IP} are the molecular weights of the IB repeat unit (56.1 g/mol) and the IP repeat unit (68.1 g/mol), respectively, and n_{IB} is the IB/IP repeat unit molar ratio in the copolymer (≅42.5), which is also the average IB homopolymer sequence length assuming isolated IP units.

$TiCl_4$ (99.9%), $AlCl_3$ (99.9%), (3-bromopropoxy)benzene (BPB, 96%), and deuterated chloroform ($CDCl_3$, 99.8+%, .03v/v% TMS) were purchased from Sigma Aldrich and used as received. Sulfuric acid, hexane (*n*-hexane 95+%, extra pure), methylene chloride (99.9%), and methanol (ACS grade, 99.9%) were purchased form Fisher Scientific and used as received.

Instrumentation

Proton nuclear magnetic resonance (^1H NMR) spectra were obtained using a 300 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer. Standard ^1H pulse sequences were used with a relaxation delay of 5 s, and all ^1H chemical shifts were referenced to TMS (0 ppm). Samples were prepared by dissolving the polymer in $CDCl_3$ (20-50 mg/mL) and charging this solution to a 5 mm NMR tube.

Number average molecular weights (M_n) and polydispersities (PDI = M_w/M_n) were determined using a gel-permeation chromatography (GPC) system consisting of a Waters Alliance 2695 separations module, an on-line multi-angle laser light scattering (MALLS) detector fitted with a gallium arsenide laser (power: 20 mW) operating at 658 nm (miniDAWN TREOS, Wyatt Technology Inc.), an interferometric refractometer (refractive index detector) (T-rEX, Wyatt Technology Inc.) operating at 35°C and 685 nm, and two PLgel (Polymer Laboratories Inc.) mixed D columns (pore size range 50-10^3 Å, 3 μm bead size). Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were *ca.* 5-6 mg of polymer/mL of THF, and the injection volume was 100 μL. The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology Inc.), and absolute molecular weights were determined by MALLS using a *dn/dc* calculated from the refractive index detector response and assuming 100% mass recovery from the columns.

Constructive Degradation of Butyl Rubber

A representative procedure for cleavage/alkylation of butyl rubber was as follows: Butyl rubber (2 g) and *n*-hexane (30 mL) were charged to a one-neck round bottom flask equipped with a magnetic stir bar, and the mixture was stirred overnight at room temperature to dissolve the copolymer. The resulting solution was diluted with methylene chloride (20 mL) and with continuous stirring equilibrated to -70ºC by immersing the flask into a chilled methanol bath for 30 min. Then, (3-bromopropoxy)benzene (1.5 mL, 2.05 g, 9.52 mmol), concentrated sulfuric acid (0.05 mL, 0.092 g, 0.938 mmol), and $TiCl_4$ (2 mL, 3.4 g, 18.2 mmol) were added in that order, neat and at room temperature, and the reaction mixture was stirred at -70˚C for 24 h. Excess methanol was then added to the flask to terminate the reaction. The resulting solution was warmed to room temperature and then precipitated into methanol. The precipitate was collected by re-dissolution in fresh hexane, and the resulting solution was re-precipitated into excess methanol. The precipitate was collected by re-dissolution in fresh hexane, and the resulting solution was washed twice with deionized water, dried over $MgSO_4$, and then vacuum stripped to yield the isolated polymer.

For reactions involving $AlCl_3$, it was likewise the last component added and was added as a neat, room-temperature powder into the stirred, temperature-equilibrated reaction mixture.

Rather than dissolving the butyl rubber in hexane overnight and subsequently diluting with methylene chloride, similar results were obtained by dissolving the butyl rubber in the mixed solvent system over the course of approximately 1-1.5 hours.

Since solvents and reaction components such as alkoxybenzene, Lewis acid, etc. were measured volumetrically at room temperature, the molar concentrations of reaction components in Table 3 were calculated using a total reaction volume corrected for thermal expansion, as outlined in Appendix B.

Determination of Functional Equivalent Weight

Functional equivalent weight (EW_Q) of constructively degraded polymers with respect to alkoxybenzene quencher (Q) residues was calculated from ^{1}H NMR data using eq 3,

$$\mathrm{EW_Q} = \frac{\mathrm{IB}}{\mathrm{Q}}\left[\mathrm{M_{IB}} + \frac{\mathrm{M_{IP}}}{\mathrm{n_{IB}}}\right] + \mathrm{M_Q} \tag{3}$$

where M_Q is the molecular weight of the quencher (Q) (for BPB, M_Q = 215.1 g/mol) and IB/Q is the mole ratio of IB units to Q units in the product. The latter ratio was calculated using eq 4,

$$\frac{\mathrm{IB}}{\mathrm{Q}} = \frac{A_{1.11}/6}{A_{3.61}/2} \tag{4}$$

where $A_{3.61}$ is the integrated area of the peak from 3.70-3.50 ppm representative of the -CH_2-Br protons of the quencher residue. Number average functionality, F_n, of the constructively degraded polymers was calculated by dividing the number average molecular weight of the polymer as determined by GPC by its EW_Q as determined by NMR spectroscopy. Other characteristics of the degraded polymers, such as the extent of cleavage of IP units, X_C, and the extent of quenching (alkylation) of newly-formed chain ends, X_{EQ}, may by calculated as described in Appendix B (eqs AB-2-AB-6).

Results and Discussion

Table 3 lists the results of experiments carried out using a typical alkoxybenzene, (3-bromopropoxy)benzene (BPB), and catalyzed by a mixture of Lewis and Bronstead acids. In each case the product of constructive degradation was characterized with regard to number average molecular weight (GPC/MALLS) and number of IB repeat units per quencher residue, i.e., the IB/Q ratio (^{1}H NMR).

When butyl rubber was reacted with an alkoxybenzene, two phenomena were observed to occur. The first, and most obvious, was a significant reduction in the molecular weight of the copolymer as listed in Table 3 and shown in the GPC chromatograms in Figure . This was expected, and similar degradation of molecular weight in the presence of Lewis acid catalysts has been reported by Kennedy *et al.* in the absence of an alkoxybenzene.[9] However, the severity of the molecular weight decrease observed here was much greater than that reported by Kennedy *et al.*, even when accounting for the lower isoprene content in the starting material employed by those authors. The second phenomenon is functionalization of the polymer by the alkoxybenzene as shown by the ^{1}H NMR spectra in Figure 6. Quantitative conversion of IP repeat units and incorporation of the alkoxybenzene quencher moiety was revealed by

Table 3

Constructive Degradation of Butyl Rubber by Alkylation of an Alkoxybenzene[a]

Entry	Temp. (°C)	Time (h)	[$TiCl_4$] (mol/L)	[$AlCl_3$] (mmol/L)	[H_2SO_4] (mmol/L)	[H_2O] (mmol/L)	[BPB][b] (mol/L)	[IP][c] (mmol/L)	M_n[d] (g/mol)	F_n[e]	IB/Q
1	-70	24	0.37	-	19	-	0.19	17	10,800	3.99	43.2
2	-70	24	0.37	-	19	-	0.10	18	7,900	2.91	43.4
3	-40	24	0.36	-	18	-	0.18	16	4,900	2.45	31.0
4	-70	7.7	0.37	-	-	56	0.056	25	10,700	3.89	43.9
5	-70	20	0.37	-	-	56	0.056	25	7,740	3.13	39.2
6	-40	2	-	50	-	9.2	0.18	24	6,400	1.58	66.3
7	-40	18.8	-	50	-	9.2	0.18	24	5,380	2.38	35.4
8	-10	2	-	44	-	3.7	0.19	16	4,950	2.18	35.7

[a] EXXON□ Butyl 365 with Mn = 1.91 x105 g/mol, PDI = 1.61, 2.30 mol% isoprene units; 60/40 (v/v) hexane/methylene chloride.

[b] BPB = (3-bromopropoxy)benzene. c IP = isoprene. d number average molecular weight of constructively degraded product. e number average functionality of constructively degraded product with respect to BPB quencher units.

the disappearance of the olefinic peak at 5.1 ppm in the starting material and the appearance of the alkyl tether peaks characteristic of BPB at 4.1 and 3.6 ppm in the final product. The IB/Q ratio, listed in Table 3, was determined by quantitative comparison of the characteristic peaks of the methyl groups of the IB repeats units with that of BPB (eq 4). This value was then converted into a functional equivalent weight (EWQ) or molar mass per quencher residue using eq 3. Dividing the number average molecular weight of the degraded product, determined by GPC, by its EWQ yielded the number average functionality, (Fn), or average number of quencher residues per chain. As shown in Table 3, the value of Fn was always greater than 2, which informed our mechanistic view of this process.

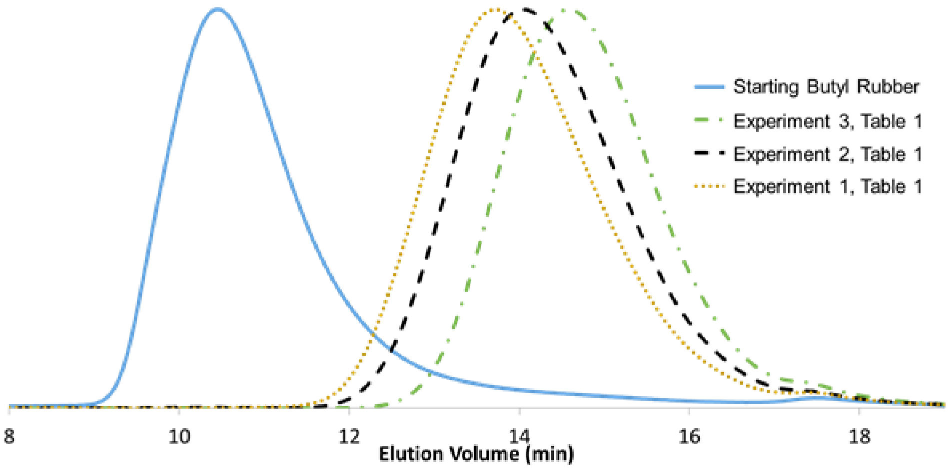


Figure 5 GPC chromatograms of starting butyl rubber and constructively degraded products of selected experiments in Table 3.

Based on our experience with decoupling of coupled PIB,[2] **Error! Bookmark not defined.** we initially entertained the possibility that every isoprene unit might be cleaved prior to functionalization, yielding difunctional oligomers ($F_n = 2$) with M_n equal to the isoprene equivalent weight of the starting butyl rubber plus the molecular weight of two quencher

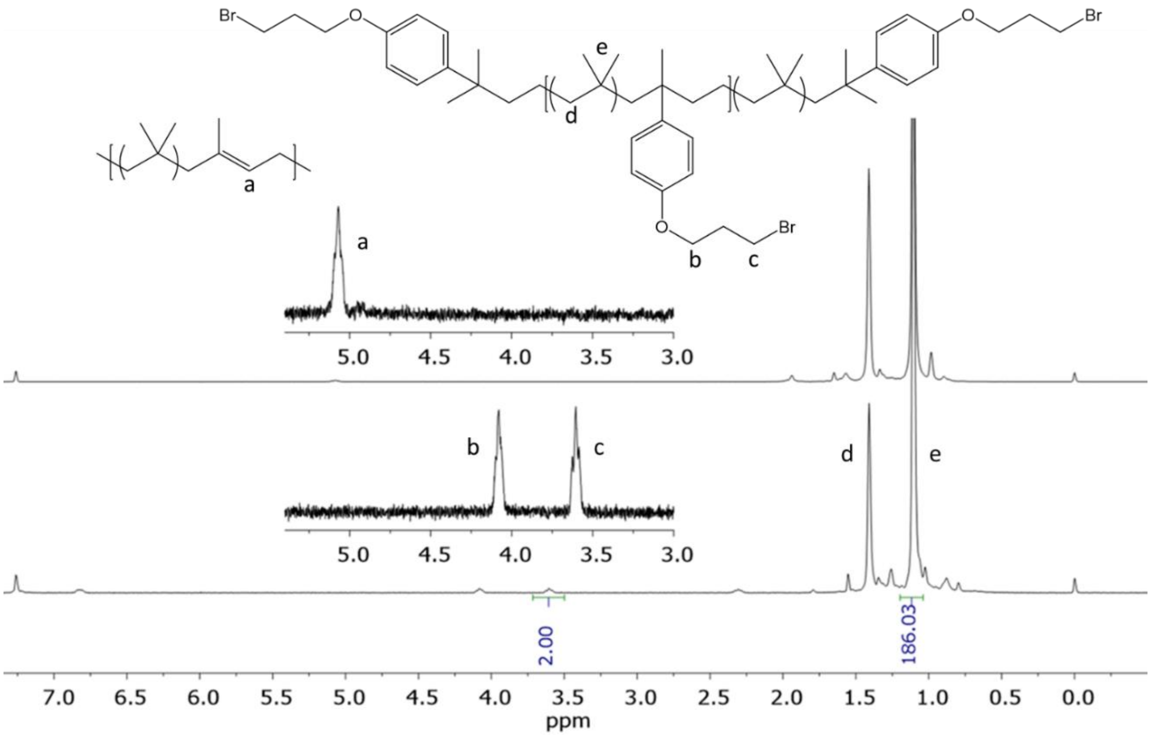
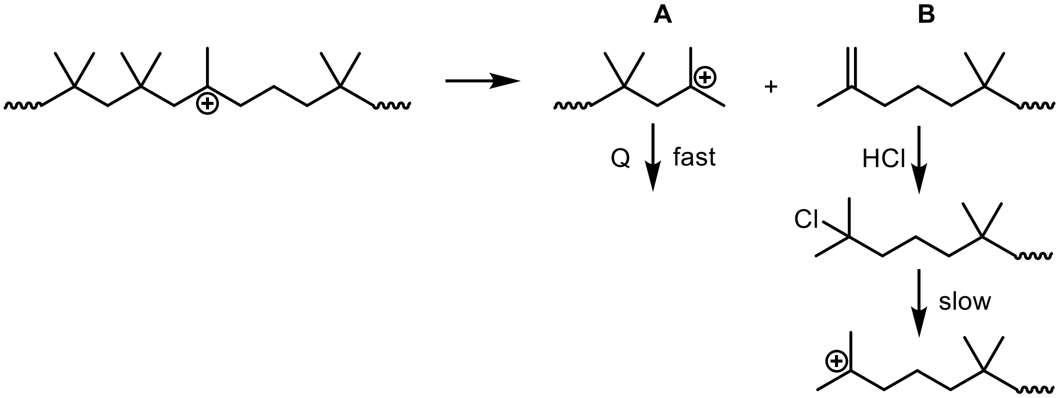


Figure 6 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 23°C) of the starting butyl rubber (Top) and Table 3, Entry 3 (Bottom).

molecules. Since our products possessed M_ns significantly greater than EW_{IP} and a functionality greater than 2 in all cases, we concluded that the cation resulting from protonation of the IP unit of butyl rubber is sufficiently sterically unhindered to allow attack by the alkoxybenzene, and functionalization often occurs without an accompanying cleavage event for that unit. We termed this process backbone quenching. Thus, the overall constructive degradation process may be viewed as a competition between the cleavage reaction and backbone quenching. As the rate of cleavage increases relative to the rate of backbone quenching, the molecular weight and functionality of the final product should decrease. Therefore, one way to drive the reaction toward lower molecular weights would be to decrease the rate of backbone quenching by decreasing the amount of BPB present in the reaction. Indeed, as shown in Figure 5 for two reactions carried out at -70°C

(Entries 1 and 2, Table 3), when the amount of quencher was decreased, the molecular weight of the final product also decreased. Furthermore, when the reaction temperature was increased to -40°C (compare Entries 1 and 3, Table 3), the relative rate of cleavage increased compared to backbone quenching resulting in lower molecular weight; indeed, the -40°C product possessed $M_n \cong 2 \times EW_{IP}$, indicating cleavage of about half of the IP units ($X_C = 0.56$, eqs AB-3-AB-4, Appendix B). Based on the observed effect of temperature, we concluded that the activation energy for cleavage is higher than that for backbone quenching.

Another interesting observation was the effect of temperature on the IB:Q ratio of the product. As shown in Table 3, for most experiments carried out at -70°C the IB:Q ratio of the product was approximately equal to n_{IB}, the IB:IP ratio of the starting butyl rubber, ≅ 42.5. This indicated that almost exactly one quencher molecule was added per IP unit and would be the expected result if all IP units underwent backbone quenching; however, if upon cleavage of an isoprene unit both newly-formed chain ends were functionalized by the quencher, the IB:Q ratio would necessarily decrease. Since this was typically not observed at -70°C, and ^{1}H NMR revealed that all of the polymers of Table 3 (except Entry 6) had undergone complete consumption of IP unsaturations, we hypothesized that one of the two newly-formed chain ends is slower to react with the alkoxybenzene. As shown in Scheme 7, this is reasonable due to the expected lower backstrain[10] in fragment **B** which is missing the *gem*-dimethyl substituents on the β carbon. This would result in a decreased rate of formation of the carbenium ion from fragment **B**. When the reaction was performed at -40°C, not only did the molecular weight of the product decrease, but so also did the



Scheme 7. Cleavage of protonated isoprene repeat unit yielding asymmetric fragments **A** and **B**

IB:Q ratio. This result indicates increased alkylation by the less back-strained chain-end; in this instance we estimate that approximately two-thirds of the type-**B** chain ends were alkylated by the quencher (X_{EQ} = 0.83, eq AB-3-AB-5 Appendix B). We recognize that an alternate explanation for the failure of the IB/Q ratio to fall below n_{IB} is the failure of some backbone sites to alkylate the quencher. Given that the original IP unsaturation is no longer present, such a scenario would imply some consumptive pathway for these unsaturations other than quenching. One such possibility is carbocation rearrangement. However, carbocation rearrangements at the PIB chain end have never been observed in $TiCl_4$ catalyzed alkoxybenzene quenching reactions, for quenchers that are non-interactive with the Lewis acid; therefore we have assumed that carbocation rearrangements do not significantly effect the $TiCl_4$-catalyzed reaction. Besides, it would seem highly unlikely that the number of backbone sites lost to rearrangement would exactly offset the number of **B**-type chain ends that were successfully quenched.

It is known that Friedel-Crafts alkylation is reversible, especially for bulky alkylating agents.[11] This suggested that backbone quenching might be reversible, and consequently the extent of cleavage might increase with reaction time. Entries 4 and 5 of Table 3 show that this is indeed the case. These two entries represent aliquots removed at 7.7 h and 20 h from the same reaction. At 7.7 h, molecular weight of the product remained relatively high, about 10,700 g/mol, but ^{1}H NMR showed that all backbone unsaturations had been consumed and the IB/Q ratio had fallen approximately to 42.5. This suggested that essentially all uncleaved IP units had by this time undergone backbone quenching. In contrast, after 20 h the molecular weight of the product had been reduced to 7,740 g/mol, and the IB/Q ratio had fallen to 39.2. Reversibility of backbone alkylation is the only plausible explanation for the additional cleavage reactions that occurred between 7.7 and 20 h.

Two further points regarding Entries 4 and 5 are noteworthy. For this reaction, water rather than sulfuric acid was used as the proton source, demonstrating that a strong protic acid is not required for successful constructive degradation. Secondly, it may be noted that after 20 h (Entry 5) the IB/Q ratio had fallen below 42.5 by an experimentally significant amount, even though the reaction temperature was -70°C. We hypothesize that this was due to the higher protic acid concentration used in this case.

$AlCl_3$ Catalyzed Reactions

Although $TiCl_4$ provides excellent control over the cleavage/alkylation reaction, with low rate of undesired side-reactions, such as carbocation rearrangement, it must be used in relatively high concentrations to achieve adequate overall rate of cleavage/alkylation. Moreover, the concentration of Ti_2Cl_8 dimer, which is the species active in ionization, is governed by an equilibrium that is exothermic in the forward direction, and therefore its concentration decreases with increasing temperature.[12] We expect this to partially or possibly completely offset any rate increases for the overall cleavage/alkylation process that might be achieved by increases in temperature.

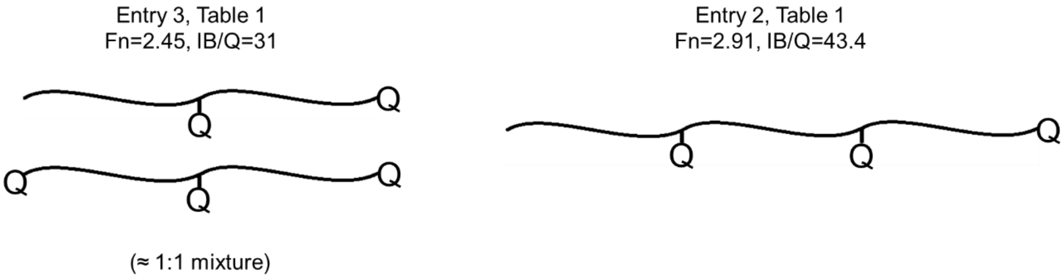
For the reasons outlined above, we examined $AlCl_3$ as an alternative Lewis acid. Entries 6 and 7 of Table 3 represent aliquots removed at 2 h and 18.8 h from the same reaction conducted at -40°C. At 2 h, the reaction was clearly not complete with IB/Q significantly greater than the IB/IP molar ratio ($\cong$ 42.5) and isoprene backbone unsaturations still visible by ^1H NMR. However, at 18.8 h (Entry 7) the reaction product compared favorably to that of Entry 3, also conducted at -40°C but with $TiCl_4$. Similar results were obtained from the two reactions in terms of M_n, F_n, and IB/Q, yet for Entry 7 the reaction time was significantly shorter and the $AlCl_3$ concentration was 7 times lower than the $TiCl_4$ concentration used in Entry 3.

We next examined the effect of higher reaction temperature on the $AlCl_3$-catalyzed system. Entry 8 shows data for reaction conducted at -10°C. Reaction rate was significantly faster at the higher temperature. After only 2 h, no isoprene unsaturations were detected by ^1H NMR; M_n was reduced to approximately two times EW_{IP} ($X_C = 0.56$, i.e., about half of the IP units had been cleaved), and the IB/Q ratio was reduced to 35.7. For a given extent of degradation, the ideal IB/Q ratio, i.e., which would be obtained for quantitative quenching of all chain ends as well as quantitative backbone quenching of all non-cleaved IP units, may be calculated using eq AB-6 in Appendix B. In the case of Entry 8, $(IB/Q)_{ideal}$ is 27.5. This value is lower than the observed value reported in Table 3, which indicates failure to alkylate some chain ends and/or failure to backbone alkylate all uncleaved IP units. If indeed some backbone sites failed to alkylate, this would indicate some other consumptive pathway for these sites, *e.g.*, carbocation rearrangement, since this sample displayed no residual IP unsaturations by ^{1}H NMR. It has been shown that when quenching isobutylene polymerizations with alkoxybenzenes using $AlCl_3$ at temperatures of -25°C and higher, chain end rearrangements can occur under non-optimal conditions[13]. The same may be true for the carbocations produced by protonation of IP units along the backbone of butyl rubber. Thus we feel that carbocation rearrangements, of chain end or backbone carbocations or both, are more likely to contribute to higher-than-ideal IB/Q ratios in $AlCl_3$ compared to $TiCl_4$ systems.

Entries 6-8 illustrate the practical advantage of $AlCl_3$ as it pertains to the potential commercial adoption of this method. However, since $AlCl_3$ is prone to allowing chain-end rearrangements, it is not likely that the use of this catalyst, in an unmodified state, would result in well controlled/defined PIBs. However, several groups have demonstrated that the activity of $AlCl_3$ can be finely tuned by the addition of nucleophiles, such as dialkyl ethers.[14] Such complexes and less active Lewis acids such as ethylaluminum dichloride and BF_3 will be studied in future.

Conclusion

In summary, we have reported a new synthetic route toward low molecular weight multifunctional polyisobutylenes. Under conditions designed to promote backbone cleavage, the products produced from commercial butyl rubber are functional oligomers with the approximate average structures shown in Scheme 8. We have demonstrated that the alkoxybenzene quencher molecule, Q, may be pre-fitted with primary bromide,[15] which may be converted to many other useful groups.[16] We fully expect that other



Scheme 8. Approximate average structures of functional oligomers produced by constructive degradation of butyl rubber.

Q = quencher residue.

alkoxybenzenes will show similar effectiveness including phenoxyalkyl (meth)acrylates,[17] and simple alkyl phenyl ethers, such as isopropoxybenzene, which yield phenol functionality by simple heating.[15,18] **Error! Bookmark not defined.** These functional oligomers are convenient starting materials for the synthesis of graft copolymers,[19] lubricating oil additives,[20] amphiphilic conetworks,[21] and photocurable coatings, sealants, and adhesives.[18,22] **Error! Bookmark not defined.** The process described herein has a number of advantages compared to alternate routes toward functional oligomers. Notably it does not require the synthesis and use of a multifunctional initiator. Compared to other constructive degradation techniques such as ozonolysis, it yields functional groups of a uniform nature. The catalyst required for the process is of the same family as that required for the synthesis of the starting copolymer, potentially allowing the development of a one-pot, "monomers-to-telechelic-polymers" process. Though perfectly difunctional telechelic polymers have not been obtained from butyl rubber, isobutylene copolymers derived from alternative comonomers such as 2,4-dimethyl-1,3-pentadiene[23] or β-pinene are predicted to yield products closer to difunctional telechelic oligomers. In future publications, we will discuss the effect of Lewis acid identity and concentration, quencher identity and concentration, temperature, and solvent polarity on the kinetics of this reaction and the structure of the product. Furthermore, this process will be applied to other copolymers of isobutylene to attempt to produce truly difunctional telechelic polymers.

References

1. (a) Kemp, L.K.; Poelma, J.E.; Cooper, T.R.; Storey, R.F. Structural Confirmation of *Exo*-Olefin-Coupled Polyisobutylene *via* Model Compound Synthesis and Characterization. *J. Macromol. Sci., Part A: Pure Appl. Chem.* **2008**, *45*(2), 137-143.

   (b) Ummadisetty, S.; Storey, R.F. Quantitative Synthesis of *Exo*-Olefin-Terminated Polyisobutylene: Ether Quenching and Evaluation of Various Quenching Methods. *Macromolecules* **2013**, *46*(6), 2049-2059.

   (c) Held, D.; Iván, B.; Müller, A.H.E.; de Jong, F.; Gaarfland, T. Stability of Propagating Species in Living Cationic Polymerization of Isobutylene. *ACS Symp. Ser.* **1997**, *665*, Chap. 6, pp. 63-74.

   (d) Nielsen, L.V.; Nielsen, R.R.; Gao, B.; Kops, J.; Iván, B. Synthesis of Isobutenyl-Telechelic Polyisobutylene by Functionalization with Isobutenyltrimethylsilane. *Polymer* **1997**, *38*(10), 2529-2534.

   (e) Bae, Y.C.; Faust, R. The Role of Pyridine Derivatives in Living Carbocationic Polymerization: Lewis Base or Nucleophile? *Macromol. Symp.* **1998**, *132*, 11-23.

   (f) Bae, Y.C.; Faust, R. β-Proton Elimination by Free Bases in the Living Carbocationic Polymerization of Isobutylene. *Macromolecules* **1997**, *30*(23), 7341-7344.

2. Campbell, C.G.; Ummadisetty, S.; Storey, R.F. Decoupling and Functionalization of Coupled Polyisobutylene via Alkoxybenzene Quenching. *Macromolecules* **2016**, *49*(20), 7642-7652.

3. (a) Wang, B.; Mishra, M.K.; Kennedy, J.P. Living Carbocationic Polymerization XII. Telechelic Polyisobutylenes by a Sterically Hindered Bifunctional Initiator. *Polym. Bull.* **1987**, *17*, 205-211.

(b) Wang, B.; Mishra, M.K.; Kennedy, J.P. Living Carbocationic Polymerization XIII. Telechelic Polyisobutylenes by the Linear Bifunctional Aliphatic Initiator System: $CH_3OC(CH_3)_2CH_2C(CH_3)_2CH_2C(CH_3)_2OCH_3/BCl_3$. *Polym. Bull.* **1987**, *17*, 213-219.

(c) Mishra, M.K.; Wang, B.; Kennedy, J.P. Living Carbocationic Polymerization IX. Three-Arm Star Telechelic Polyisobutylenes by $C_6H_3(C(CH_3)_2OCH_3)_3/BCl_3$ Complexes. *Polym. Bull.* **1987**, *17*, 307-314.

(d) Huang, K.J.; Zsuga, M.; Kennedy, J.P. Living Carbocationic Polymerization XIX. Synthesis of Four-Arm Star Polyisobutylenes Capped by *t*-Chloride and Isopropylidene Groups. *Polym. Bull.* **1988**, *19*, 43-50.

(e) Jacob, S.; Majoros, I.; Kennedy, J.P. New Stars: Eight Polyisobutylene Arms Emanating from a Calixarene Core. *Macromolecules* **1996**, *29*(27), 8631-8641. (f) Puskas, J.E.; Pattern, W.; Wetmore, P.M.; Krukonis, V. Synthesis and Characterization of Novel Multiarm-Star Polyisobutylene-Polystyrene Thermoplastic Elastomers. *Rubb. Chem. Tech.* **1999**, *72*(4), 559-568.

4. (a) Ebdon, J.R. Synthesis of New Telechelic Oligomers and Macromonomers by "Constructive Degradation". *Macromol. Symp.* **1994**, *84*, 45-54.

(b) Ebdon, J.R.; Flint, N.J.; Rimmer, S. Degradative Routes to Telechelic Oligomers and Macromonomers. *Macromol. Rep.* **1995**, *A32*, 603-611.

5. (a) Ebdon, J.R.; Rimmer, S. A One-Pot Method for the Preparation of Latices of Telechelic Oligomers, by Ozonolysis of Latices of Polymers Containing Main-Chain Unsaturation. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*(15), 3255-3262.

(b) Reyx, D.; Campistron, I. Controlled Degradation in Tailor-Made Macromolecules Elaboration. Controlled Chain-Cleavages of Polydienes by Oxidation and by Metathesis. *Die Angew. Makromol. Chem.* **1997**, *247*, 197-211.

(c) Baldwin, F.P. Novel Mastic Compositions and Process of Producing Same. U.S Patent 3,392,154, July 9, 1968.

(d) Dix, L.R.; Ebdon, J.R.; Hodge, P. Synthesis of Telechelic Methyl Methacrylate and Styrene Oligomers with Fluorophenyl Ketone End Groups by the Ozonolysis of Copolymers Containing 4-Fluorophenyl Butadiene Units. *Polymer* **1993**, *34*(2), 406-411.

6. Ebdon, J.R.; Flint, N.J. Preparation of α-Phenyl Ketone-, ω-Carboxylate-Ended Telechelic Methyl Methacrylate Oligomers by the Ozonolysis of Regioregular Methyl Methacrylate-Phenylacetylene Copolymers. *Macromolecules* **1994**, *27*(23), 6704-6707.

7. (a) Macias, A.; Rubio, B. Preparation and Crosslinking of Low-Molecular-Weight Polyisobutylenes with Reactive Terminal Groups. I. Preparation and Characterization. *Revista de Plasticos Modernos* **1978**, *35*(263), 604-611, 623.

(b) Weider, R.; Köhler, B.; Ebert, W.; Scholl, T.; Horn, K. Block Copolycarbonates with Polyisobutylene-α-Haloketocarboxylic Acid Blocks. U.S. Patent No. 5,717,027, Feb. 10, 1998.

(c) Ho, K.W.; Guthmann, J.E. The Ozonolysis of Butyl and Halobutyl Elastomers. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*(7), 2435–2455.

8. Chasmawala, M.; Chung, T.C. Telechelic Polyisobutylene: A Facile Synthesis via the Cross-Metathesis Reaction and Trialkylborane-Containing Olefins. *Macromolecules* **1995**, *28*(5), 1333-1339.

9. Kennedy, J.P.; Phillips, R.R. The Influence of Aluminum-Containing Lewis Acids on Polyisobutylene, Isobutylene-Isoprene Copolymers (Butyl Rubber), and Chlorinated Isobutylene-Isoprene Copolymer (Chlorobutyl). *J. Macromol. Sci.-Chem.* **1970**, *A4*(8), 1759-1784.

10. (a) Brown, H.C. A New Steric Effect in Organic Chemistry. *Science* **1946**, *103*, 385-387.

    (b) Brown, H.C.; Fletcher, R.S. Chemical Effects of Steric Strains. I. The Effect of Structure upon the Hydrolysis of Tertiary Aliphatic Chlorides. *J. Am. Chem. Soc.* **1949**, *71*, 1845-1854.

    (c) Brown, H.C.; Berneis, H.L. Steric Strains as a Factor in the Solvolytic Reactions of Neopentyldimethyl and Dineopentylmethylcarbinyl Chlorides. *J. Am. Chem. Soc.* **1953**, *75*(1), 10-14.

11. (a) Saleh, S.A.; Tashtoush, H.L. De-*tert*-Butylation of Substituted Arenes. *Tetrahedron* **1998**, *54*(47), 14157-14177.

    (b) Frost, J.R.; Cheong, C.B.; Donohoe, T.J. Iridium-Catalyzed C4-Alkylation of 2,6-Di-*tert*-butylphenol by Using Hydrogen-Borrowing Catalysis. *Synthesis* **2016**, *48*, A-G.

(c) Hales, N.J.; Heaney, H.; Hollinshead, J.H.; Sharma, R.P. Rearrangement Reactions of Bicyclic Systems. Part V. Acid-Catalysed Rearrangements of 1,4-Dihydro-1,5,8-trimethoxy-1,4-ethenonaphthalene and the Remarkable Effect of Aromatic Methoxy-Groups on the Course of the Reaction. *Tetrahedron* **1995**, *51*(27), 7403-7410.

(d) Bacci, J.P.; Kearney, A.M.; Van Vranken, D.L. Efficient Two-Step Synthesis of 9-Aryl-6-hydroxy-3*H*-xanthen-3-one Fluorophores. *J. Org. Chem.* **2005**, *70*(22), 9051-9053.

12. (a) Webb, S.P.; Gordon, M.S. Intermolecular Self-Interactions of the Titanium Tetrahalides TiX_4 (X = F, Cl, Br). *J. Am. Chem. Soc.* **1999**, *121*(11), 2552-2560.

(b) Schlaad, H.; Kwon, Y.; Sipos, L.; Faust, R.; Charleux, B. Determination of Propagation Rate Constants in Carbocationic Polymerization of Olefins. 1. Isobutylene. *Macromolecules* **2000**, *33*(22), 8225-8232.

(c) Smith, Q.A.; Storey, R.F. Quasiliving Cationic Polymerization of Styrene and Isobutylene: Run Number and Apparent Rate Constant of Ionization by $TiCl_4$ and Energies of Activation of Elementary Reactions. *Macromolecules* **2005**, *38*(12), 4938-4988.

13. Yang, B.; Storey, R.F. End-Quenching of *tert*-Chloride-Terminated Polyisobutylene with Alkoxybenzenes: Comparison of $AlCl_3$ and $TiCl_4$ Catalysts. *Polymer Chemistry*, **2015**, 6, 3764-3774.

14. (a) Vasilenko, I.V.; Frolov, A.N.; Kostjuk, S.V. Cationic Polymerization of Isobutylene Using $AlCl_3OBu_2$ as a Coinitiator: Synthesis of Highly Reactive Polyisobutylene. *Macromolecules* **2010**, *43* (13), 5503-5507.

(b) Liu, Q.; Wu, Y.-X.; Zhang, Y.; Yan, P.-F.; Xu, R.-W. A Cost-Effective Process for Highly Reactive Polyisobutylenes via Cationic Polymerization Coinitiated by $AlCl_3$. *Polymer* **2010**, *51* (25), 5960-5969.

(c) Vasilenko, I.V.; Shiman, D.I.; Kostjuk, S.V. Highly Reactive Polyisobutylenes via $AlCl_3OBu_2$-Coinitiated Cationic Polymerization of Isobutylene: Effect of Solvent Polarity, Temperature, and Initiator. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50* (4), 750-758.

(d) Dimitrov, P.; Emert, J.; Faust, R. Polymerization of Isobutylene by $AlCl_3$/Ether Complexes in Nonpolar Solvent. *Macromolecules* **2012**, *45* (8), 3318-3325.

15. Morgan, D.L.; Martinez-Castro, N.; Storey, R.F. End-Quenching of $TiCl_4$-Catalyzed Quasiliving Polyisobutylene with Alkoxybenzenes for Direct Chain End Functionalization. *Macromolecules*, **2010**, *43*(21), 8724–8740.

16. Ojha, U.; Rajkhowa, R.; Agnihotra, R.; Faust, R. A New General Methodology for the Syntheses of End-Functional Polyisobutylenes by Nucleophilic Substitution Reactions. *Macromolecules* **2008**, *41*(11), 3832-3841

17. Roche, C.P.; Brei, M.R.; Yang, B.; Storey, R.F. Direct Chain End Functionalization of Living Polyisobutylene Using Phenoxyalkyl (Meth)acrylates. *ACS Macro Lett.* **2014**, *3*(12), 1230-1234.

18. Yang, B.; Parada, C.M.; Storey, R.F. Synthesis, Characterization, and Photopolymerization of Polyisobutylene Phenol (Meth)acrylate Macromers. *Macromolecules* **2016**, *49*(17), 6173-6185.

19. Kennedy, J.P.; Hiza, M. Macromers by Carbocationic Polymerization. IV. Synthesis and Characterization of Polyisobutenyl Methacrylate Macromer and Its

Homopolymerization and Copolymerization with Methyl Methacrylate. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 1033-1044.

20. Kolp, C.; Gieselman, M.D.; Eveland, R.A.; Pike, P.; Pudelski, J.; Covitch, M.J.; Friend, C. Diene-Containing Polymer-Based Dispersants Used as Viscosity Modifiers in Fuels and Engine Oil Lubricants. PCT Int. Appl., WO 2005087821 A2, Sept. 22, 2005.

21. (a) Kali, G.; Vavra, S.; László, K.; Iván, B. Thermally Responsive Amphiphilic Conetworks and Gels Based on Poly(N-isopropylacrylamide) and Polyisobutylene. *Macromolecules* **2013**, *46*(13), 5337-5344.

    (b) Erdodi, G.; Kennedy, J.P. Amphiphilic Conetworks: Definition, Synthesis, Applications. *Prog. Polym. Sci.* **2006**, *31*(1), 1-18.

    (c) Puskas, J.E.; Chen, Y.; Dahman, Y.; Padavan, D. Polyisobutylene-Based Biomaterials. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*(13), 3091-3109.

22. (a) Tripathy, R.; Crivello, J.V.; Faust, R. Photoinitiated Polymerization of Acrylate, Methacrylate, and Vinyl Ether End-Functional Polyisobutylene Macromonomers. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*(2), 305-317.

    (b) Tripathy, R.; Ojha, U.; Faust, R. Syntheses and Characterization of Polyisobutylene Macromonomers with Methacrylate, Acrylate, Glycidyl Ether, or Vinyl Ether End-Functionality. *Macromolecules* **2009**, *42*(12), 3958-3964.

23. Kaszas, G.; Puskas, J.E.; Kennedy, J.P. Carbocationic Copolymerization in the Presence of Electron Pair Donors. 2. Copolymerization of Isobutylene and Isoprene or 2,4-Dimethyl-1,3-pentadiene with Titanium Tetrachloride-Based Initiating

Systems Yielding in Situ Electron Pair Donors. *Macromolecules* **1992**, *25*(6), 1775-1779.

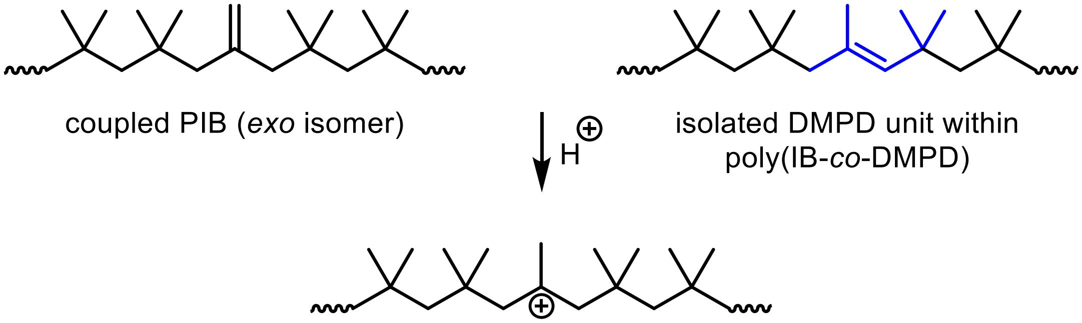
CHAPTER IV – CARBOCATIONIC COPOLYMERIZATION OF ISOBUTYLENE AND 2,4-DIMETHYL-1,3-PENTADIENE

Introduction

Difunctional telechelic polyisobutylene (PIB) is a material of great academic and commercial interest, due to its utility as a saturated hydrocarbon soft segment within various elastomeric materials, to which it imparts excellent barrier properties, chemical and oxidative stability, biocompatibility, and low cost of the constituent monomer.[1] However, the current most feasible means of its production is via the living polymerization of isobutylene (IB) initiated by a difunctional initiator.[2] The most common of these difunctional initiators is 5-*tert*-butyl-1,3-di(1-chloro-1-methylethyl)benzene (5-*tert*-butyl-1,3-dicumyl chloride) or the corresponding methoxide derivative,[3,4,5,6,7] which is produced by a multi-step synthesis, one step of which requires a four-fold molar equivalent of Grignard reagent. Because of its complicated and expensive synthesis, this initiator has been very rarely used for other than research purposes. A notable exception is its use in the synthesis of poly(styrene-*b*-isobutylene-*b*-styrene) (SIBS), which has been used commercially as a bio-inert coating on medical devices.[8] Other difunctional initiators have been reported, but each has its shortcomings. 1,4-Di(1-chloro-1-methylethyl)benzene (1,4-dicumyl chloride) tends to result in a loss of initiating sites due to cyclization after addition of one isobutylene (IB) unit, resulting in an indanyl moiety and PIBs with functionality less than two.[9] Epoxide-functional initiators such as 2-methyl-2-phenyloxirane are of interest since they essentially yield difunctional PIB by virtue of generating a hydroxyl group at the α chain end.[10] However, these polymerizations must be prematurely terminated due to side reactions at high conversions, and the initiator efficiency tends to be low due to homopolymerization of the epoxide.[11]

We have recently reported that when coupled PIB[12,13] is subjected to a mixed Lewis/Bronstead acid catalyst system in the presence of an alkoxybenzene, the coupling reaction is quantitatively reversed to form the two original PIB chains, which then become end-functionalized through Friedel-Crafts alkylation of the alkoxybenzene.[14] Building upon this, we reported that a similar reaction may be applied to the copolymer of isobutylene and isoprene (butyl rubber), which is a readily available copolymer bearing sterically hindered main-chain unsaturations similar, but not identical, to that of coupled PIB.[15] When high molecular weight butyl rubber is subjected to the same conditions reported for the cleavage and functionalization of coupled PIB, the result is a lower molecular weight PIB with a functionality always greater than two. This process of degrading a high molecular weight copolymer in a manner which functionalizes the chain-ends of the newly formed oligomers has been termed “constructive degradation,” and under optimal conditions, the material resulting from constructive degradation would exhibit a functionality of two. The higher functionalities reported by Storey *et al.* for the simultaneous cleavage/alkylation of butyl rubber were attributed to a phenomenon we termed “backbone quenching,” which occurs when the first formed carbocation in the backbone of the butyl rubber alkylates the alkoxybenzene without an accompanying cleavage event. However, this behavior was never observed to occur when the alkylating substrate was coupled PIB. This difference was attributed to the less sterically hindered cation present in butyl rubber which allows attack of the alkoxybenzene.

With this in mind, we set out to synthesize PIB-based copolymers possessing main-chain unsaturations more hindered than those of butyl rubber. We became particularly interested in the diene comonomer, 2,4-dimethyl-1,3-pentadiene (DMPD), which has been reported by Kennedy *et al.*[16] to undergo simultaneous copolymerization with IB in a living manner, to produce random copolymers. As shown in Scheme 9, protonation of an isolated DMPD unit would form a main-chain carbocation that is structurally identical to the carbocation formed from the protonation of coupled PIB. Thus, this copolymer would be an ideal substrate which, when subjected to the conditions reported by Storey *et al.* would result in nearly perfectly difunctional telechelic PIBs. Further review of the relevant literature, however, suggested that this copolymerization may not be as easily carried out as reported.



Scheme 9. Comparison of Coupled PIB (left) and an isolated DMPD unit of a hypothetical random copolymer of IB and DMPD (right).

Protonation of either of these species give the same intermediate which is capable of β cleavage.

Prior to the copolymerization work of Kennedy *et al.*, it was reported that DMPD readily cyclodimerizes in acidic environments, a side reaction that could significantly interfere with its ability to undergo cationic polymerization in a controlled/living fashion.[17,18] Furthermore, in a patent that issued prior to their work on IB-DMPD simultaneous copolymerization, Kennedy *et al.* disclosed the sequential block copolymerization of IB with various diene comonomers.[19] Example 4 of that patent involved formation of a living, difunctional PIB centerblock using the dicumyl ether/$TiCl_4$ initiating system at -80°C in 60/40 (v/v) hexane/methyl chloride, followed by sequential addition of DMPD. Loss of olefinic groups in the final polymer was reported and attributed to cyclization of the poly(DMPD) block. Formation of a "pentablock structure" was also observed by GPC, which according to the inventors, resulted from chain coupling. Finally, the molecular weight of the poly(DMPD) blocks was much lower than would be expected based on the reported charge ratios. All of the observations suggested that DMPD is a very reactive monomer in cationic polymerization, with a tendency toward side reactions.

Notwithstanding the disclosures in the aforementioned patent, when similar conditions were employed by these same inventor/authors to conduct IB/DMPD simultaneous copolymerizations, the copolymerizations were described as living and neither coupling nor cyclization involving DMPD were reported, even at a slightly higher temperature of -60°C.[16] **Error! Bookmark not defined.** The authors reported copolymer composition as a function of time for a simultaneous copolymerization carried out using a comonomer feed ratio of 97/3 (IB/DMPD). Their data are plotted as a pseudo-first-order kinetic plot in Figure A1 in Appendix C. Initially (up to 0.5 h) the fraction of DMPD incorporated into the copolymer (9.1 mol%) was higher than its fraction in the comonomer feed (3.0 mol%). However, beyond 0.5 h, the relative consumption of the two monomers was the same at a constant feed composition of about 1.5 mol% DMPD, i.e., the slopes of the two first-order plots are almost equal, indicating an azeotropic copolymerization. This suggests that the reactivity ratios, r_{IB} and r_{DMPD} are both much much greater than 1, and furthermore, that r_{DMPD} is much greater than r_{IB}. Such a drastic difference in reactivity ratios predicts that the synthesis of random poly(IB-*co*-DMPD) copolymers would be difficult.[20] Copolymerizations of IB and conjugated polyenes other than isoprene or DMPD have also been reported in the literature, and some of these tend to be of a very blocky nature, depending on structure. This is particularly true when the conjugated polyene contains more than one trisubstituted alkene. For instance, Puskas *et al.* have reported that alloocimene can be copolymerized with IB, but the resulting polymers are diblock or triblock copolymers, which function as thermoplastic elastomers.[21] Thus, it became apparent that if the copolymer of DMPD and IB were to be studied as a substrate for simultaneous cleavage/alkylation, more information related to the copolymerization of these two monomers was required. In this report, we will discuss our findings related to this copolymerization as well as the homopolymerization of 2,4-dimethyl-1,3-pentadiene.

Experimental

Materials

Mesityl oxide (99% mixture of alpha (93%) and beta (7%) isomers), $TiCl_4$ (99.9%), ethylaluminum dichloride (EADC), 2,6-lutidine (99%), and hexane (Anhydrous, 95%) were purchased from Sigma-Aldrich and used as received. Methyl chloride (CP grade, 99.5%) and isobutylene (CP grade, 99%) were purchased from Southern Gas and Supply and distilled prior to use. The synthesis of coupled PIB containing an <u>*endo*</u>-coupled fraction has been previously reported;[14] **Error! Bookmark not defined.** the coupled PIB used herein is the same as PIB 3 in the cited work. 2-Chloro-2,4,4-trimethylpentane (TMPCl) was prepared according to a published procedure.[3] **Error! Bookmark not defined.**

Instrumentation

Proton and carbon nuclear magnetic resonance (^1H NMR, ^{13}C NMR) spectra were obtained using either a 300 MHz Varian Mercury^{plus} (VNMR 6.1C) or a 600 MHz Bruker

Avance (TopSpin 3.5) NMR spectrometer. Standard ^{1}H pulse sequences were used with a collection period of 2 s and pre-scan delay of 3 s, and all ^{1}H chemical shifts were referenced to TMS (0 ppm). Standard ^{13}C pulse sequences were used with a pre-scan delay of 1 s and all ^{13}C chemical shifts were referenced to residual $CHCl_3$ (77.0 ppm). Samples were prepared by dissolving the polymer in $CDCl_3$ (20-50 mg/mL) and charging this solution to a 5 mm NMR tube.

Heteronuclear single-quantum correlation (HSQC) spectra were acquired on a Bruker Avance NMR spectrometer operating at a frequency of 600.13 MHz for proton and using a standard 5mm BBFO probe. Samples were dissolved in $CDCl_3$ and transferred into 5mm NMR tubes. The acquisition parameters were as follows: The recycle delay was 2.0 s, the ^{1}H 90° pulse width was 11.7 μs, the ^{1}H spectral width was 11.0 ppm, the ^{13}C spectral width was 165 ppm, and the acquisition time was 155 ms. The number of t_1 increments was 256 with 96 scans per increment. TPPI phase cycling was used to obtain phase sensitive data. An additional 7936 t_1 points were added via linear prediction, whereas t_2 was zero-filled to 4096 total points. Both t_1 and t_2 were apodized using a square sine filter prior to Fourier transformation. Baselines were corrected using the ablative algorithm as implemented in the Mestrec Labs MNova software.

Total Correlation Spectroscopy (TOCSY) spectra were acquired on a Bruker Avance spectrometer operating at a frequency of 600.13 MHz for proton and using a 5mm BBFO probe. Samples were dissolved in $CDCl_3$ and transferred into 5mm NMR tubes. The acquisition parameters were as follows: The recycle delay was 2.0s, the ^{1}H 90° pulse width was 11.7 μs, the ^{1}H spectral width in both dimensions was 11.0 ppm, and the acquisition time was 155 ms. The number of t_1 increments was 256 with 16 scans per increment. The mixing time was 100 ms. States-TPPI phase cycling was used to obtain phase sensitive data. An additional 3840 t_1 points were added via linear prediction, whereas t_2 was zero-filled to 4096 total points. A sine squared apodization was applied to both t_1 and t_2 prior to Fourier transformation. Baselines for both F1 and F2 were corrected using the ablative algorithm as implemented in the Mestrec Labs MNova software.

Number average molecular weights (M_n) and polydispersities (PDI = M_w/M_n) were determined using a gel-permeation chromatography (GPC) system consisting of a Waters Alliance 2695 separations module, an on-line multi-angle laser light scattering (MALLS) detector fitted with a gallium arsenide laser (power: 20 mW) operating at 658 nm (miniDAWN TREOS, Wyatt Technology Inc.), an interferometric refractometer (refractive index detector) (T-rEX, Wyatt Technology Inc.) operating at 35°C and 685 nm, and two PLgel (Polymer Laboratories Inc.) mixed D columns (pore size range 50-10^3 Å, 3 μm bead size). Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were *ca.* 5-6 mg of polymer/mL of THF, and the injection volume was 100 μL. The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology Inc.), and absolute molecular weights were determined by MALLS using a *dn/dc* calculated from the refractive index detector response and assuming 100% mass recovery from the columns.

Monomer Conversion by Real-time ATR-FTIR Spectroscopy

Real-time ATR-FTIR analysis was performed using a ReactIR 4000 (Mettler-Toledo) integrated with a N_2 atmosphere glove box.[22] DMPD conversion during homopolymerizations was determined by monitoring the area, above a two-point baseline, of the absorbance centered at 891 cm^{-1}, associated with the $=CH_2$ wag of DMPD. During

IB/DMPD copolymerizations, the $=CH_2$ wag vibrations of IB and DMPD were observed to be highly convoluted (IB centered at 887 cm^{-1}). Total (combined) comonomer conversion during copolymerizations was determined by monitoring the area of this combined peak, above a two-point baseline, assuming that the extinction coefficient of the two signals were equal.

Copolymer Composition by ^1H NMR Spectroscopy

The mole fractions of IB and DMPD monomer units, F_{IB} and F_{DMPD}, respectively, in IB/DMPD copolymers was determined by ^{1}H NMR spectroscopy using eqs 1 and 2,

$$F_{DMPD} = \frac{\mathrm{A}_{4.8-5.3}}{\mathrm{A}_{1.1}} \tag{1}$$

$$F_{IB} = 1 - F_{DMPD} \tag{2}$$

where, $\mathrm{A}_{4.8\text{-}5.3}$ is the area of the olefinic proton signals of DMPD units integrated from 4.8-5.3 ppm, and $\mathrm{A}_{1.1}$ is the area of the combined *gem* dimethyl proton signals of IB and DMPD units integrated from 0.96-1.22 ppm.

DMPD Conversion During Copolymerization by ^1H NMR Spectroscopy

DMPD conversion during copolymerization, i.e., the fraction of DMPD in the feed that had incorporated into the copolymer, p_{DMPD}, was determined by ^{1}H NMR spectroscopy using eq 3,

$$p_{\mathrm{DMPD}} = \frac{F_{\mathrm{DMPD}}}{f_{\mathrm{DMPD}}} \times p_{\mathrm{total}} \tag{3}$$

where, f_{DMPD} is the fraction of DMPD in the monomer feed and p_{total} is the total (combined) monomer conversion as detected by real-time ATR-FTIR spectroscopy.

Synthesis of 2,4-Dimethyl-1,3-pentadiene (DMPD)

DMPD was synthesized by Grignard reaction of mesityl oxide with methyl magnesium bromide, followed by reactive distillation. An example procedure was as follows: to a 1-L round bottom flask equipped with a magnetic stir-bar, addition funnel, and dry nitrogen inlet was added 360 mL of methylmagnesium bromide solution (3 molar in diethyl ether, 1.11 mol). The solution was cooled with stirring in an ice bath for 30 min. Then, mesityl oxide (100 ml, 0.874 mol) was charged to the addition funnel and then added dropwise to the reaction over a period of 2 h. The reaction was then allowed to warm to room temperature and left to stir overnight. Then, the reaction was poured over approximately 500 g of ice in a 2-L beaker, forming a white slurry that was stirred for one hour. The ethereal layer was collected, and the aqueous layer was washed 3 times with 100 mL diethyl ether. The organic layers were combined and then dried with magnesium sulfate, filtered, and then concentrated by rotary evaporation. The product, a viscous oil, was then vacuum distilled to yield 2,4-dimethyl-3-pentene-2-ol. Then, 20 mL DI water and one drop of sulfuric acid were added to the distillate contained in a 200 mL one-neck round bottom flask, and from this mixture was distilled a mixture of water and 2,4-dimethyl-1,3-pentadiene, which was dried with magnesium sulfate, filtered, and distilled over calcium hydride to yield 2,4-dimethyl-1,3-pentadiene (60 mL, 0.464 mol, 53% yield). A portion of this product was further purified by column chromatography on basic alumina (Brockman 1) with a pentane mobile phase and subsequent distillation over calcium hydride.

IB/DMPD Slurry Copolymerizations (Entries 1-3, Table 4)

In an attempt to synthesize high molecular weight polymers, IB and DMPD were copolymerized by slurry polymerization in MeCl as well as in Hex/MeCl mixtures. A representative procedure was as follows (Entry 1, Table 4): A 250 mL 3-neck round-bottom flask equipped with an overhead stirrer and ReactIR probe, was submerged in a -70°C heptane bath in an inert atmosphere glovebox. To this flask were added MeCl (90 mL), IB (30 mL, 0.373 mol), and DMPD (1.32 mL, 0.01 mol). Ethylaluminum dichloride (0.61 mg) was dissolved in approximately 5 mL MeCl. Upon dropwise addition of approximately 1 mL of this solution, polymerization was observed as indicated by turbidity of the solution. As determined by ReactIR, the conversion of monomer sharply increased, and then stalled. An additional 1 mL of the EADC solution was added dropwise, and the reaction continued as determined by monomer consumption detected by ReactIR. The polymer then began to precipitate out of solution onto the stirbar and IR probe, at which point, the reaction was terminated by the addition of chilled methanol.

IB/DMPD Solution Copolymerizations (Entries 4-5, Table 4)

To allow for the gathering of aliquots at intermediate conversions, IB and DMPD were copolymerized in 60/40 (v/v) Hex/MeCl, which provided homogeneous reaction conditions. A representative procedure was as follows (Entry 4, Table 4): A 250 mL 3-neck round-bottom flask equipped with an overhead stirrer and ReactIR probe was submerged in a -40°C heptane bath within an inert atmosphere glovebox. To this flask were added hexane (65.7 mL), MeCl (43.8 mL), TMPCl (0.05 mL, 0.003 mol), 2,6-lutidine (0.052 mL, 0.004 mol), IB (37.72 mL, 0.445 mol), and DMPD (1.35 g, 0.0141 mol). The reaction was stirred for 30 min to allow temperature equilibration, at which time the reaction was initiated by the addition of $TiCl_4$ (0.93 mL, 0.0085 mol, neat and at room temperature). Aliquots were taken intermittently to determine DMPD incorporation and molecular weight. Once monomer had been completely consumed, the reaction was terminated by addition of chilled MeOH. The aliquots were purified by methanol precipitation (2x). The final precipitate was dissolved in hexane, and the resulting solution was washed with deionized water (2x), dried over $MgSO_4$, filtered, concentrated under a stream of dry nitrogen gas, and vacuum dried.

DMPD Solution Homo-polymerizations (Entries 6-8, Table 4)

Solution homopolymerizations of DMPD were carried out using either a 60/40 Hex/MeCl mixed cosolvent system or hexane. A representative procedure was as follows (Entry 7, Table 4): A 100 mL 3-neck round-bottom flask equipped with an overhead stirrer and ReactIR probe was submerged in a -70°C heptane bath within an inert atmosphere glovebox. To this flask was added hexane (46.44 mL), TMPCl (0.02 mL, 0.0012 mol), 2,6-lutidine (0.017mL, 0.00015 mol), and DMPD (3.23 mL, 0.025 mol). The reaction was stirred for 30 min to allow temperature equilibration, at which time the reaction was initiated by the addition of $TiCl_4$ (0.02 mL, 1.824×10^{-4} mol, neat and at room temperature). As determined by ReactIR, the conversion of monomer sharply increased, and then stalled. During this stall, an aliquot was taken and precipitated into chilled methanol. Subsequent additions of $TiCl_4$ (0.01 mL, 9.12×10^{-4} mol) resulted in similar rapid consumption of monomer followed by a stall. In total, three additions of 0.01 mL $TiCl_4$ were performed after the initial addition of 0.02 mL $TiCl_4$, and aliquots were taken during the stall which accompanied each addition. After the third addition, the monomer was completely consumed. At this time, the reaction was terminated by addition of chilled MeOH. The aliquots and final reaction product were purified by methanol precipitation (2x). The final precipitate was dissolved in hexane, and the resulting solution was washed with deionized water (2x), dried over $MgSO_4$, filtered, concentrated under a stream of dry nitrogen gas, and vacuum dried.

DMPD Slurry Homo-polymerizations (Entries 9 and 10, Table 4)

Slurry homo-polymerizations of DMPD which were performed in an effort to produce polymers of high molecular weight. A representative procedure was as follows: A 50 mL round-bottom flask equipped with a magnetic stir-bar was submerged in a -70°C heptane bath within an inert atmosphere glovebox. To the flask were added DMPD (1.6 mL) and MeCl (23.4 mL). The flask was then stoppered, removed from the dry box, and transferred to an acetone bath which was cooled to -96°C by addition of liquid nitrogen directly to the bath. The contents of the flask were stirred for 30 min to allow for temperature equilibration, and then $TiCl_4$ (0.01 mL, neat and at room temperature) was added to the mixture. A polymer precipitate was observed immediately upon addition of the catalyst. After 5 min, the reaction was quenched by addition of excess methanol, and the flask was placed in a fume hood where solvents were allowed to evaporate overnight. The polymer was then dissolved in hexane and purified by methanol precipitation (2x). The final precipitate was dissolved in hexane, and the resulting solution was washed with deionized water (2x), dried over $MgSO_4$, filtered, concentrated under a stream of dry nitrogen gas, and vacuum dried.

Results and Discussion

Isobutylene/DMPD Slurry Copolymerizations

In the design of copolymers for cleavage/alkylation, the molecular weight of the starting copolymer should be as high as practically possible, to minimize the concentration of original copolymer end groups. Some of these end groups, for example, the α end of proton-initiated chains, are non-reactive with the quencher and thus remain non-functional end groups that depress the overall functionality of the system. With this in mind, we first attempted to synthesize random IB/DMPD copolymers via a chain transfer controlled, aluminum-catalyzed slurry process since similar conditions have been traditionally used for the production of high molecular weight IB copolymers.[23] In the slurry method a solvent is chosen in which the monomers are soluble, but the resulting polymer is not, resulting in a dispersed phase of the insoluble polymer in the solvent upon production of the polymer. An advantage of this method is low viscosity of the reaction solution regardless of the molecular weight of the product polymer.

Table 4, Entries 1-3, summarize our attempts to produce IB/DMPD copolymers by a slurry process. The initiator/catalyst system was moisture/ethylaluminum dichloride; the solvent was either pure MeCl or 34/66 Hex/MeCl (v/v), and the temperature was in the range -76 to -70 °C. Entry 2 represents an early, low-conversion aliquot of the experiment listed as Entry 3. The slurry process indeed proved capable of creating acceptably high molecular weights (> 200,000 g/mol) but only when the DMPD concentration was reduced to 1.5 mol% in the feed. However, contrary to our expectations based on the report by Kennedy *et al.*, we found that at moderate-to-high conversions, the incorporation of DMPD into the copolymer was less than its presence in the feed. For the experiment of Entry 2, for which we obtained an early aliquot, (Entry 2a in Table 4), we noticed a trend similar to that reported by Kennedy *et al.*, where at low conversions DMPD is present in the

Table 4

IB/DMPD Co- and IB Homo-polymerizations[a]

Entry	Temp	%DMPD in feed	%DMPD in Copolymer	Catalyst	Initiator	Solvent System	Total Conv.	Theo. M$_n$ (Da)	M$_n$ (Da)	MWD
1[b]	-70	3%	2.5	EADC	Moisture	MeCl	~50%		48,700	2.2
2a[b]	-76	3%	9.4	EADC	Moisture	MeCl	~18%		Low	Unknown
2[b]	-76	3%	0.7	EADC	Moisture	MeCl	~90%		111,000	1.8
3[b]	-75	1.5%	0.8	EADC	Moisture	Hex/MeCl 34/66	~45%		208,900	1.8
4a[c]	-40	3%	10.4	$TiCl_4$	TMPCl	Hex/MeCl 60/40	~10%	~11,378	6,400	1.2
4b[c]	-40	3%	1.6	$TiCl_4$	TMPCl	Hex/MeCl 60/40	55%	62,557	29,900	1.1
4[c]	-40	3%	1.1	$TiCl_4$	TMPCl	Hex/MeCl 60/40	100%	113,777	44,500	1.1
5a[c]	-60	3%	59.5	$TiCl_4$	TMPCl	Hex/MeCl 60/40	<10%	<10,475	1,800	1.9
5[c]	-60	3%	1.0	$TiCl_4$	TMPCl	Hex/MeCl 60/40	100%	104,758	67,500	1.1
6[c]	-70	100%	100	$TiCl_4$	TMPCl	Hex/MeCl 60/40	100%	28,331	3,800	1.5
7[c]	-70	100%	100	$TiCl_4$	TMPCl	Hexane	100%	28,331	7,000	1.6
8[c]	-70	100%	100	$TiCl_4$	TMPCl	Hexane	100%	28,331	6,100	1.7
9[d]	-96	100%	100	$TiCl_4$	Moisture	MeCl	Unknown		6,500	1.5
10[d]	-96	100%	100	EADC	Moisture	MeCl	Unknown		10,100	1.2

[a] Entry 2a is an early aliquot of the experiment of Entry 2. Entries 4a and 4b are early aliquots of the experiment of Entry 4. Entry 5a is an early aliquot of the experiment of Entry 5. Conversions given for examples 1-3 are approximate due to clumping of precipitated polymer on the ReactIR probe tip. [b] Copolymerization of IB and DMPD performed via the slurry process. [c] Living polymerizations. 2,6 lutidine added as proton trap (0.03 mol/L). [d] Homopolymerization of DMPD perfomed via the slurry process.

copolymer at a higher ratio than its presence in the feed. However, contrary to what was reported by Kennedy *et al.*, this trend did not continue throughout the polymerization, and the final product contained less DMPD than was present in the feed (Entry 2 in Table 4). At this point, it was decided that the method of polymerization would need to be altered so that intermediate aliquots could be taken and characterized to determine the presence of DMPD in the copolymer throughout the polymerization. To track monomer incorporation by taking aliquots, one must employ a solution-based polymerization. Thus, we shifted to $TiCl_4$-catalyzed living polymerization conditions (Entries 4-5 in Table 4)

Isobutylene/DMPD Solution Copolymerizations

Solution polymerization conditions allowed for the collection of intermediate aliquots and determination of kinetics of incorporation of DMPD. As shown in Figure 7, for the experiment of Entry 4, Table 4, the conversion of DMPD increased sharply at the beginning of the polymerization, then remained constant throught the remainder of the reaction. As we will discuss later, this rapid initial polymerization of DMPD represents

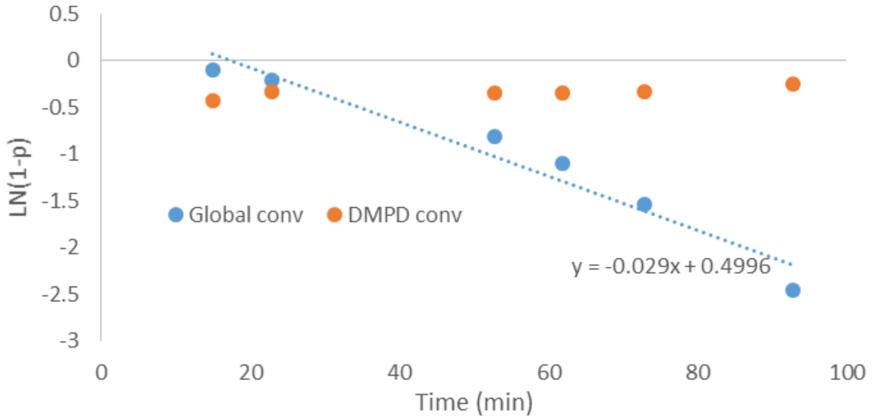


Figure 7 Pseudo-first order kinetic plot of the parent experiment of Entries 4-4b in Table 4.

The deviation from linearity and non-zero intercept of the global conversion data is presumably due to a slight temperature increase during the beginning of the reaction.

the formation of a polyDMPD block, which apparently crosses over to IB upon exhaustion of DMPD. The initial rapid polymerization of DMPD is accompanied by side reactions, the most likely of which is cyclization, which irreversibly consume DMPD in a manner other than polymerization. This results in the observed low DMPD incorporation in the copolymer, relative to the comonomer feed, at higher total monomer conversions. Spectroscopic evidence for these side reactions was found when the methanol layer from the precipitation step of the purification process was concentrated to isolate any side-products from this reaction. These side-products, when characterized by NMR spectroscopy, were found to contain olefinic materials which are not present in the methanol wash of isobutylene homo-polymerizations. Though we observed these impurities, we did not characterize them further to determine their precise structure as doing so would be prohibitively complicated.

Solution and Slurry Homopolymerizations of DMPD

To provide a model for polyDMPD sequences within IB-DMPD copolymers and to aid in determining ^{1}H NMR peak assignments, we synthesized homopolymers of DMPD using both solution and slurry techniques. During the synthesis of these homopolymers, we observed that the polymerizations were too rapid to obtain meaningful kinetic data, even when the non-polar solvent hexane was used as the sole solvent. Furthermore, during these reactions, the monomer consumption was observed to consistently stall during incremental addition of $TiCl_4$, i.e., after a small amount of $TiCl_4$ was added dropwise, rapid but incomplete consumption of DMPD would occur. Subsequent dropwise additions of $TiCl_4$ caused the same behavior until, through this incremental addition of $TiCl_4$, all monomer was depleted. This behavior, specifically the fact that the monomer rapidly

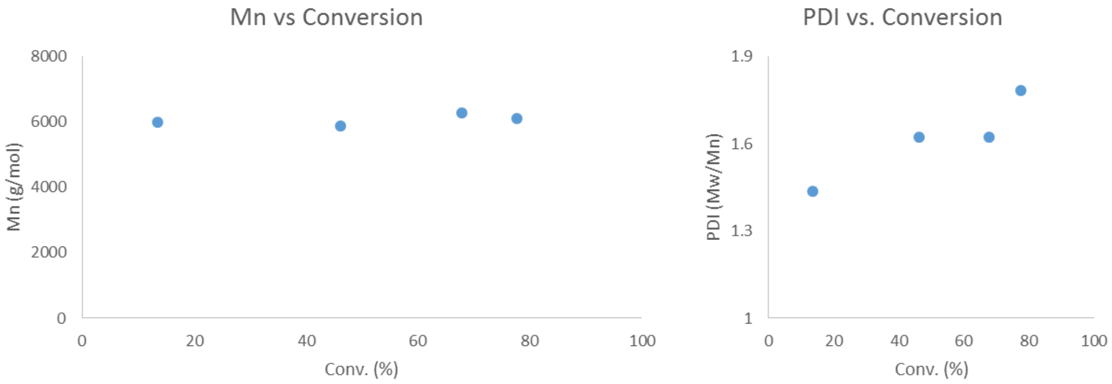


Figure 8 M_n vs. conversion (left) and PDI vs. conversion plots (right) for DMPD homo-polymerization, Entry 7, Table 4.

polymerized in hexane, served as our first indication that DMPD is far too reactive to successfully copolymerize with IB. Furthermore, monitoring of the molecular weight of the polymer throughout the reaction we find that the molecular weight increases immediately to approximately 6,000 g/mol and remains constant throughout the polymerization (Figure 8). This behavior is clear evidence that the polymerization is chain-transfer dominated under conditions whereby the polymerization of IB is living. However, the mode of chain-transfer appears to be complex in nature as evidenced by two characteristics: 1.) the stalling behavior mentioned previously and 2.) the ability of this polymerization to proceed to high monomer conversion and still yield a very low molecular weight polymer. The stalling behavior mentioned previously is indicative of transfer to counter-ion. During this process, HCl is produced which is sequestered by the proton trap to yield a salt of 2,6-Lutidine and $H^+Ti_2Cl_9^-$. Thus, for every molecule of HCl which is sequestered, two molecules of $TiCl_4$ are also sequestered. Because the Lewis acid was added dropwise, its concentration was kept low enough that this chain transfer event was capable of sequestering enough $TiCl_4$ to stop the polymerization before complete monomer conversion. However, for this reaction, the target Mn was approximately 28,000 g/mol, and the polymer which was produced exhibited a molecular weight of approximately 6,000. If we assume that the only operable transfer mechanism is transfer to counter-ion, even if every initiator did initiate polymerization, the reaction would stall at approximately 21% and not continue with additional $TiCl_4$, barring some mode of $TiCl_4$ catalyzed autopolymerization. This suggests that transfer to initiator is accompanied by transfer directly to monomer. This general behavior agrees with the results published by Kennedy *et* al. whereby the achieved molecular weight of polyDMPD was much lower than the target.[19] **Error! Bookmark not defined.**

Structural Characterization of Copolymers

Figure 9 shows the ^{1}H NMR spectrum of a representative IB/DMPD copolymer (Entry 4a, Table 4), including an expansion of the olefinic region of the spectrum. The olefinic region consists of a major resonance at 5.11 ppm, a minor resonance at 5.06 ppm, and a downfield shoulder to the major resonance at approximately 5.14 ppm. In their 1992 paper, Kennedy *et al.* described the major peak at 5.11 ppm as the “only” resonance in the

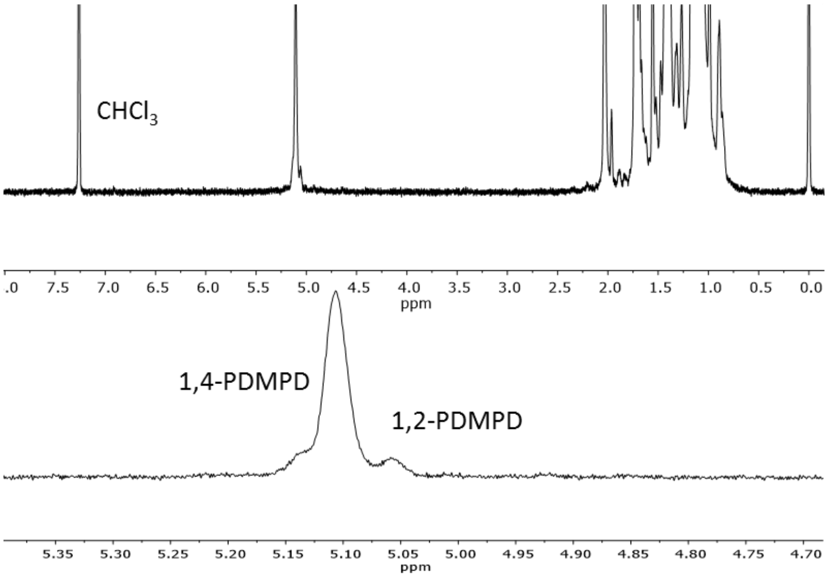
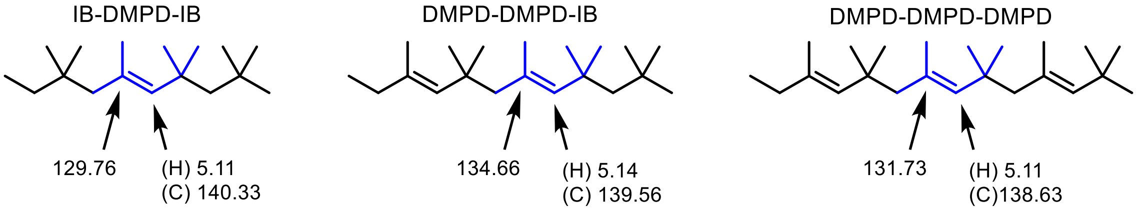


Figure 9 ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 23℃) of representative a IB/DMPD copolymer.

(Entry 4a, Table 4)(Top). Expansion of olefinic region (Bottom).

olefinic region and attributed it to DMPD units within the copolymer. They described their copolymers as random, suggesting that these DMPD units were isolated units, flanked on both sides by IB units. Initially, assignment of the major resonance at 5.11 ppm to isolated DMPD units seemed to be supported by the fact that this is the same chemical shift displayed by "endo-coupled PIB" [12,24] **Error! Bookmark not defined.** which possesses an identical structure to, and thus is a convenient model for, an IB-DMPD-IB sequence within an IB/DMPD copolymer (Scheme 10, left). However, as will be discussed later, this shift is coincident with the proton NMR chemical shift of the homopolymer of DMPD as well. Thus distinguishing between blocky and random IB/DMPD copolymers based solely on its olefinic signal in the proton NMR spectrum is not possible. Although the minor resonance at 5.06 ppm was visible in their published spectrum, it was not mentioned by Kennedy *et al.* As discussed in a later section, we have assigned the peak at 5.06 ppm to 1,2-addition of the DMPD monomer.



Scheme 10. Various possible DMPD-centered comonomer sequences in poly(IB-*co*-DMPD).

Figure 10 shows the ^{13}C NMR spectrum of a representative IB/DMPD copolymer, including an expansion of the olefinic region of the spectrum. The olefinic region consists of two pairs of signals representing two different olefin structures. The first pair at 138.63 and 131.72 ppm corresponds to the repeat unit of poly(DMPD) suggesting that the copolymers we produced contained a large fraction of DMPD homopolymer. The second pair at 139.56 and 134.66 ppm is unreported in the literature, and we have attributed these shifts to the DMPD-DMPD-IB triad illustrated in Scheme 10.

In the process of assigning the downfield shoulder at 5.14 ppm in the ^{1}H NMR spectrum of the copolymer, we noted that this chemical shift is very close to the reported chemical shift of *endo*-olefin PIB[25] and thus might be attributed to this chain end structure within the copolymer. However, the ^{13}C NMR spectrum did not contain the associated peak at 135.39 ppm.[26] Using HSQC NMR (Figure A2, Appendix C), we were able to determine that the proton resonance at 5.14 ppm was associated with a carbon resonance at 139.56 ppm. These shifts together do not correspond to any known PIB structure. We have tentatively assigned them to the olefinic methine group of the central DMPD unit within a DMPD-DMPD-IB sequence. Specifically, we propose that this unit represents the final DMPD unit of a polyDMPD block, which crosses over to IB upon depletion of DMPD monomer. This comonomer sequence is illustrated in Scheme 2, center, with chemical shift assignments, along with other comonomer sequences to be

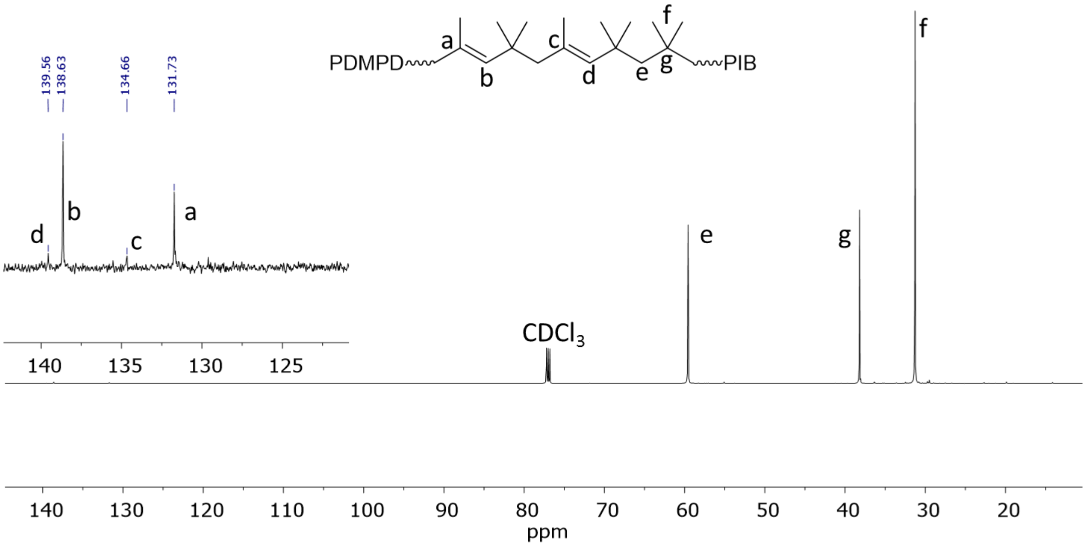


Figure 10 ^{13}C NMR spectrum of poly(IB-co-DMPD), Entry 4b, Table 4.

discussed below. Later, we will present additional evidence supporting the formation of such block copolymers during the copolymerization.

Structural Characterizaton of PolyDMPD

Comparing the ^{1}H NMR spectrum of PDMPD homopolymer to that of poly(IB-*co*-DMPD) revealed that the homopolymer exhibits the same main olefinic peak at 5.11 and also the minor peak at 5.06, but not the downfield shoulder at 5.14 ppm (Figure 11). This has a number of implications. The first, as stated in a previous section, is that reference to the chemical shift of *endo*-coupled PIB showed that the "randomness" of this copolymer cannot be determined based solely on the proton NMR spectrum of the product i.e. a truly random copolymer and a block copolymer of these two monomers would exhibit the same olefinic proton NMR shift at 5.11 ppm. However, comparison of the ^{13}C NMR spectrum of the IB-DMPD copolymers in Figure 10 to that of *endo*-coupled PIB in Figure A3 of Appendix C (we have previously reported the synthesis of this polymer[14] **Error! Bookmark not defined.**), indicates the absence of any structure in the copolymer of IB and DMPD that resembles *endo*-coupled PIB. This shows that IB-DMPD-IB sequences (Scheme 10, left) do not exist in the copolymer. In fact, when taking into account the NMR evidence, the rapid kinetics of DMPD homopolymerization, and the kinetics of DMPD incorporation during copolymerization, one can only conclude that during these attempted copolymerizations, DMPD does not randomly copolymerize with IB. Instead, some fraction of DMPD forms a block at the beginning of the reaction which is capable of initiating further polymerization of IB while the remainder is consumed by side-reactions preventing its incorporation into the polymer. Thus the vast majority of DMPD units within the copolymer exist as DMPD-DMPD-DMPD sequences (Scheme 10, right), which are identical to the DMPD homopolymer.

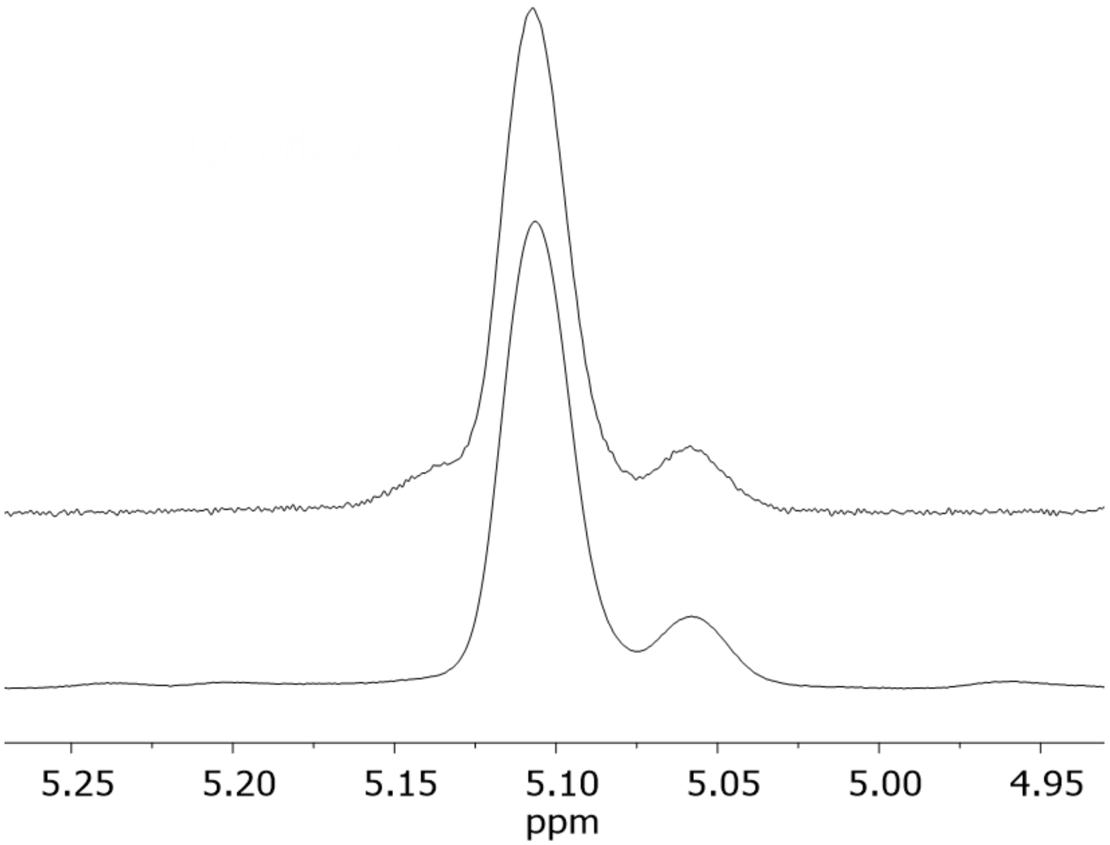


Figure 11 Olefinic region of the NMR spectra of the copolymer of IB and DMPD (entry 5) (top) and the homopolymer of DMPD (entry 13)(bottom).

The second implication relates to the minor peak at 5.06 ppm. The presence of this structure in the homopolymer of DMPD signifies that either polyDMPD chain ends or a secondary mode of DMPD addition is present in the IB/DMPD copolymers. If this minor structure were due to chain ends, then based on the intensity of the 5.06 ppm peak and assuming that it represents a single methine proton, the molecular weight of the copolymer could be no higher than 960 or 1920 g/mol, respectively, for mono-functional and di-functional chains. This is far lower than the molecular weight measured by GPC, which effectively eliminates polyDMPD chain ends as being responsible for this minor peak.

Similar calculations have been previously employed by White *et al.* to rule out alternative assignments of minor olefinic peaks in isobutylene copolymers.[27] The most likely alternative cause for this minor peak is a secondary mode of addition of DMPD during polymerization. Generally, when an olefin adds to a cationic chain end derived from a diene (especially isoprene), addition occurs almost always at C4, resulting in predominantly 1,4 enchainment of the diene; 1,2 enchainment is rarely observed. This is due to the relative stabilities of the 1,4 and the 1,2 addition products. In the case of DMPD, both 1,4 and 1,2 modes of addition result in a trisubstituted alkene, thus the product of either modes of addition are expected to have similar enthalpies of formation. However, we still expect and have found 1,4 addition to be the favored mode of addition due to stearic hindrance of the attack at the 2 position. Figure 12 shows a high resolution ^{1}H NMR spectrum of polyDMPD. A number of peaks are present in the aliphatic region that do not belong to the 1,4 addition product. Specifically, the set of peaks around 1.66 ppm and the single peak at 1.17 ppm integrate 6:1 and 3:1, respectively, relative to the minor peak at 5.06 ppm, which is consistent with our assignment of 1,2 addition. Further evidence for these assignments was provided by HSQC and TOCSY NMR spectra, presented in Figures A4 and A5 of Appendix C, respectively. Using these techniques, we were able to determine that these aliphatic peaks are methyl groups, and that only the set of peaks at 1.66 ppm correlate strongly to the peak at 5.06 ppm. The latter point is important as it rules out short-chain branching due to back-biting, as reported by White *et* al. for IB-isoprene copolymers,[27] **Error! Bookmark not defined.** as being the structure responsible for the shift at 5.06 ppm. If this type of branching were responsible for this shift, we would expect to find a methylene group that also correlates to this peak at 5.06 ppm. This is further illustrated and discussed in more detail in Appendix C (Figure A6).

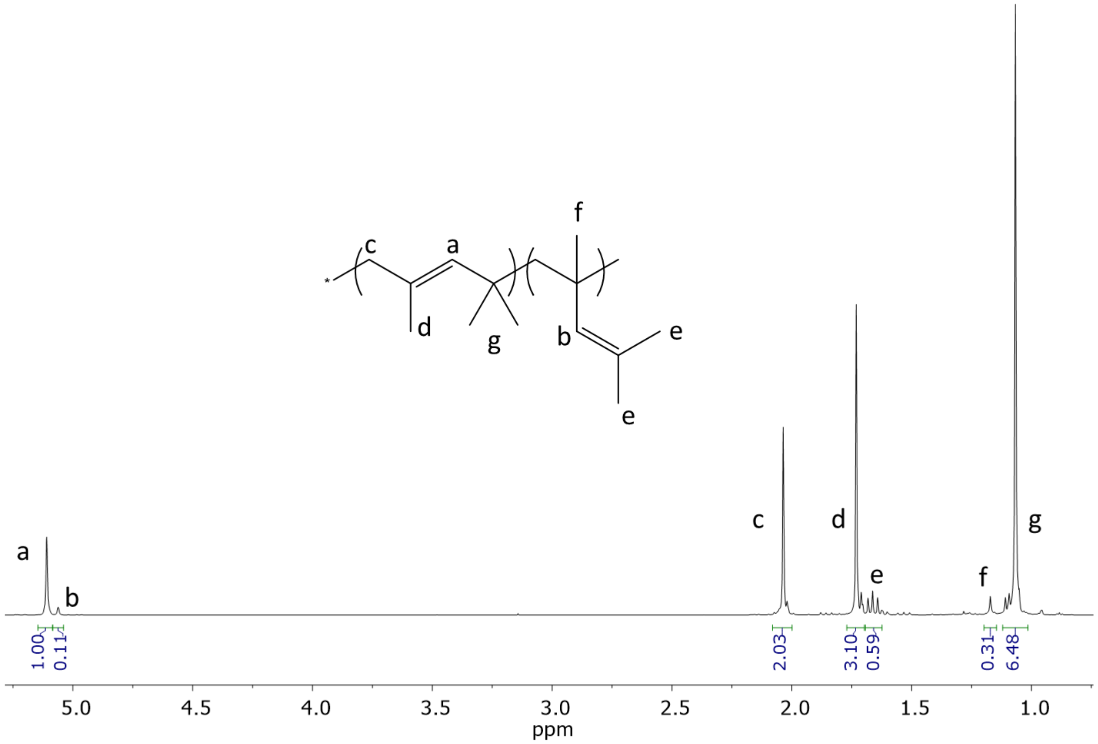


Figure 12 High resolution ^{1}H NMR spectrum (600 MHz, CDCl$_3$, 23℃) of poly(DMPD) (Entry 13, Table 4).

Conclusions

Previously we have reported a novel process for producing multifunctional PIB via simultaneous cleavage/alkylation of butyl rubber. Though we originally predicted that the copolymer of DMPD and IB would be an ideal substrate for the production of difunctional PIB utilizing this process, we were unable to synthesize a suitable copolymer. Kennedy *et al.* previously reported that copolymerization of these two monomers yields a random copolymer, yet in our attempts several issues arose which were not considered in that report. Firstly, DMPD does not add in solely a 1,4 fashion. Evidence for this has been presented, and we have shown that similar evidence was present in the report by Kennedy *et* al., but was probably missed by those authors due to the lower resolution NMR available at the time. High percentages of 1,2 addition mean that, even if random copolymers were achieved, the material would be incapable of producing difunctional polymers by the aforementioned process; the 1,2 mode of addition yields an unsaturation in the backbone of the polymer which would be likely to react with quencher without an accompanying cleavage event. Secondly, in our experience, the homo-polymerization of DMPD is not living under conditions suitable for living IB polymerization, and chain transfer is very apparent during these homo-polymerizations. In addition, we found evidence of olefin-containing impurities in the methanol wash from these copolymers, which is not present in IB homo-polymerizations and suggests that DMPD undergoes a cyclization reaction under these conditions as well. Thus it is likely that cross-transfer rates, which are generally higher than homo-transfer rates,[28] would drastically limit the maximum achievable molecular weight for a copolymer of these two monomers. Finally, DMPD is far too reactive a monomer to successfully randomly copolymerize with IB. As we have shown, during the copolymerization of DMPD and IB, nearly all of the DMPD is consumed during the beginning of the reaction and incorporation of DMPD is halted at low global monomer conversions. This is further evidenced in the ^{13}C NMR spectrum of these copolymers, where no isolated DMPD units were found.

References

1. Kennedy, J.P. From Thermoplastic Elastomers to Designed Biomaterials. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43*(14), 2951−2963.
2. (a) Walch, E.; Gaymans, R.J. Synthesis of Low-Molecular-Weight Telechelic Polyisobutylene. *Polymer* **1993**, *34*(2), 412-17.

   (b) Deodhar, Tejal J.; Keszler, Balazs L.; Kennedy, Joseph P. Quantitative Preparation of Allyl Telechelic Polyisobutylene Under Reflux Conditions. *J. Polym. Sci, Part A: Polym. Chem.* **2017**, 55(10), 1784-1789.
3. Morgan, D.L.; Storey, R.F. Primary Hydroxy-Terminated Polyisobutylene via End-Quenching with a Protected *N*-(ω-Hydroxyalkyl)pyrrole. *Macromolecules* **2010**, *43*(3), 1329-1340.
4. Kucera, L.R.; Brei, M.R.; Storey, R.F. Synthesis and Characterization of Polyisobutylene-*b*-Polyamide Multi-Block Copolymer Thermoplastic Elastomers. *Polymer* **2013**, *54*(15), 3796-3805.
5. Chang, Y.; Stokes, C.D.; Morgan, D.L. Manufacture of Copolymers of Polyaminopolyolefins and Polyanhydrides Useful as Viscosity Modifiers for Lubricant Oils and Fuel. *PCT Int. Appl.* WO 2014,085,047 A1, June 5, 2014.
6. Sipos, L.; Som, A.; Faust, R.; Richard, R.; Schwarz, M.; Ranade, S.; Boden, M.; Chan, K. Controlled Delivery of Paclitaxel from Stent Coatings Using Poly(hydroxystyrene-*b*-isobutylene-*b*-hydroxystyrene) and Its Acetylated Derivative. *Biomacromolecules* **2005**, *6*(5), 2570-2582.

7. Kennedy, J.; Nugay, T.; Nugay, N. Photochemical Preparation of Hydroxyl-Terminated Polyisobutylenes and Related Methods and Uses. *PCT Int. Appl.* WO 2014,138,001 A1, September 12 2014.
8. Pinchuk, L.; Wilson, G.J.; Barry, J.J.; Schoephoerster, R.T.; Parel, J.-M.; Kennedy, J.P. Medical Applications of Poly(styrene-*block*-isobutylene-*block*-styrene) ("SIBS"). *Biomaterials* **2008**, *29*(4), 448-460.
9. Chang, V.S.C.; Kennedy, J.P. New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers). 12. Synthesis of New Model Compounds for Cycloalkylation Studies and ^{13}C NMR Characterization of Polyisobutylene. *Polym. Bull.* **1981**, *4*(9), 513-520.
10. Puskas, J.E.; Soytas, S.H.; Lim, G.T. Novel Epoxide Initiators for the Carbocationic Polymerization of Isobutylene. *Macromol. Symp.* **2011**, *308*, 61-67.
11. Puskas, J.E.; Brister, L.B.; Michel, A.J.; Lanzendorfer, M.G.; Jamieson, D.; Pattern, W.G. Novel Substituted Epoxide Initiators for the Carbocationic Polymerization of Isobutylene. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*(3), 444-452.
12. Kemp, L.K.; Poelma, J.E.; Cooper, T.R.; Storey, R.F. Structural Confirmation of *Exo*-Olefin-Coupled Polyisobutylene via Model Compound Synthesis and Characterization. *JMS - Part A: Pure Appl. Chem.* **2008**, 45(2), 137-143.
13. Ummadisetty, S.; Storey, R.F. Quantitative Synthesis of *exo*-Olefin-Terminated Polyisobutylene: Ether Quenching and Evaluation of Various Quenching Methods. *Macromolecules* **2013**, *46*(6), 2049-2059.

14. Campbell, C.G.; Ummadisetty, S.; Storey, R.F. Decoupling and Functionalization of Coupled Polyisobutylene via Alkoxybenzene Quenching. *Macromolecules* **2016**, *49*(20), 7642-7652.

15. Campbell, C.G.; Storey, R.F. Functional Polyisobutylenes via Electrophilic Cleavage/Alkylation. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*(12), 1991-1997.

16. Kaszas, G.; Puskas, J.E.; Kennedy, J.P. Carbocationic Copolymerization in the Presence of Electron Pair Donors. 2. Copolymerization of Isobutylene and Isoprene or 2,4-Dimethyl-1,3-pentadiene with $TiCl_4$-Based Initiating Systems Yielding in Situ Electron Pair Donors. *Macromolecules* **1992**, *25*(6), 1775-1779.

17. Ghosh, S.; Bauld, N.L. Hole-Catalyzed and Photoassisted Hole-Catalyzed Pericyclic Reactions on Zeolites. *J. Catal.* **1985**, 95(1), 300-304.

18. Gassman, P.G.; Singleton, D.A. Distinction between Aminium Cation Radical and Protic Acid Catalyzed “Diels-Alder” Reactions. *J. Am. Chem. Soc.* **1984**, *106*(25), 7993-7994.

19. Kaszas, G.; Puskas, J.E.; Kennedy, J.P. Thermoplastic Elastomers Having Isobutylene Block and Cycliclized Diene Blocks. U.S. Patent 4,910,261, March 20, 1990.

20. Kennedy, J.P.; Kelen, T.; Tüdös, F. Analysis of the Linear Methods for Determining Copolymerization Reactivity Ratios. II. A Critical Reexamination of Cationic Monomer Reactivity Ratios. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*(10), 2277-2289.

21. Puskas, J.E.; Gergely, A.L.; Kaszas G. Controlled/Living Carbocationic Copolymerization of Isobutylene with Alloocimene. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*(1), 29–33.

22. Storey, R.F.; Donnalley, A.B.; Maggio T.L. Real-Time Monitoring of Carbocationic Polymerization of Isobutylene Using in Situ FTIR-ATR Spectroscopy with Conduit and Diamond-Composite Sensor Technology. *Macromolecules* **1998**, *31*(5), 1523-1526.

23. Sparks, W.J.; Thomas, R.M. Rubber Substitute. U.S. Patent 2,363,703, November 28, 1944.

24. *Endo*-coupled PIB is the tri-substituted olefinic product created by addition of a PIB carbenium ion to *exo*-olefin (methyl vinylidene) PIB followed by elimination of a proton from either α-methylene group.

25. Si, J.; Kennedy, J.P. Analysis of ^{1}H-NMR Spectra of Various End-Functionalized Polyisobutylenes. *J. Polym. Sci., Part A: Polym. Chem.* **1994**, *32*(11), 2011-2021.

26. Harrison, J.J.; Young, D.C.; Mayne, C.L. 2D-INADEQUATE Structural Assignment of Polybutene Oligomers. *J. Org. Chem.* **1997**, *62*(3), 693-699.

27. White, J.L.; Shaffer, T.D.; Ruff, C.J.; Cross, J.P. Incorporation of Isoprene in Isobutylene/Isoprene Copolymers: NMR Identification of Branching in Butyl Rubber. *Macromolecules* **1995**, *28*(9), 3290-3300.

28. Kennedy, J.P.; Chou, T. Poly(isobutylene-*co*-*β*-pinene): A New Sulfur Vulcanizable, Ozone Resistant Elastomer by Cationic Isomerization Copolymerization. I. Synthesis and Reactivity Studies. *Adv. Polym. Sci.* **1976**, *21*, 1-30.

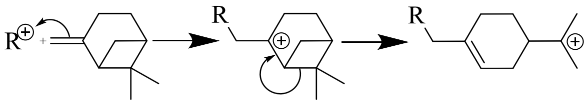
CHAPTER V – SIMULTANEOUS CLEAVAGE AND FUNCTIONALIZATION OF POLY(ISOBUTYLENE-CO-β-PINENE) IN THE PRESENCE OF (3-BROMOPROPOXY)BENZENE

Introduction

Polyisobutylene is a material with a wide range of commercial applications. Its favorable material properties include low glass transition temperature (T_g),[1] low permeability,[2] and the low cost of its constituent monomer. Commercially, this material is made via non-living chain transfer dominated cationic polymerization, which is capable of producing only monofunctional homo- and co-polymers.[3] Though there is significant demand for these monofunctional materials, there has been much interest in the development of di- and multi-functional PIB as a building block for the construction of crosslinked networks,[4,5] amphiphilic conetworks,[6,7] varyingly complex block copolymers,[8,9,10] and multi-functional amphiphilic soot dispersants.[11,12] The most direct route towards these multi-functional PIBs is the living cationic polymerization of isobutylene from either a multifunctional initator[13,14] or a monofunctional initiator bearing some desired residual functionality.[15,16] However, these initiators are either expensive to synthesize, exhibit low initiator efficiency, or require very specific reaction conditions to avoid side reactions. The most commonly reported difunctional initiator, 5-*tert*-butyl-1,3-di(1-chloro-1-methylethyl)benzene (Blocked DiCumyl Chloride, BDCC),[17] is highly efficient and very tolerant of changing reaction conditions, but it is expensive, requiring a 4-fold equivalence of methyl magnesium bromide for its synthesis, which effectively limits its use to laboratory preparations and high-value-added applications such as biomedical.[18] Epoxide functional initiators have been reported by Puskas *et* al.[19,20] They are both low cost and highly tolerant to changes in reaction condition but are inefficient due to their tendency to undergo competitive ring opening homopolymerization under living IB polymerization conditions.[21] The resulting polyether also bears ether functionalities which are similar to ether quenchers reported by Storey *et* al.,[22] and, though this has not been expressly reported, it is highly likely that these polyethers are capable of converting living chain ends to *exo*-olefin functionalities at high monomer conversions in a manner conducive to chain end coupling.[23] Thus polymerizations initiated by these compounds must be halted well before all monomer has been consumed to preserve the growing chain ends.

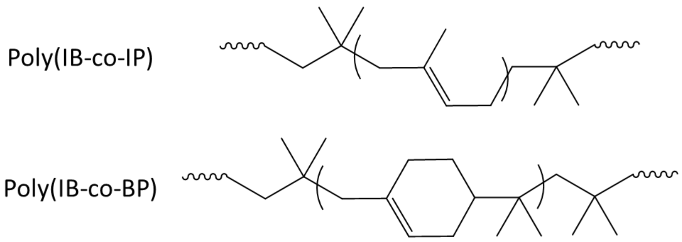
We have previously reported a novel method for the production of multifunctional low molecular weight PIB via the simultaneous electrophilic cleavage and functionalization of high molecular weight isobutylene copolymers bearing main-chain olefinic functionality, in the presence of a quenching agent consisting of an activated Friedel-Crafts substrate such as an alkoxybenzene.[24] This reaction is characterized by protonation of a hindered olefin to produce a hindered cation, which then undergoes β-cleavage to form two fragments, a new, less hindered cation and a less hindered olefin. The cation is then functionalized by the quenching agent, which releases the catalytic protic acid. Meanwhile the olefinic chain end may be protonated to form a cation, which reacts with the quenching agent in a similar manner. This reaction was first demonstrated in the decoupling and functionalization of coupled PIB, in which we observed quantitative cleavage of the internal olefin and subsequent quantitative functionalization of the resulting chain ends under conditions typically employed during alkoxybenzene quenching of living IB polymerizations.[25] Expanding upon this, we hypothesized that the copolymer of isobutylene and isoprene (butyl rubber) would be an ideal starting material which, when subjected to this process, would result in low molecular weight difunctional telechelic PIB oligomers. In practice, however, we were unable to achieve quantitative cleavage of the isoprene residues of the copolymer, and the resulting materials were of higher-than-anticipated molecular weight and possessed functionalities greater than two. Non-quantitative cleavage was attributed to the less sterically hindered nature of the isoprene unit of the copolymer, allowing for functionalization of the cation, which results from protonation of the double bond, without an accompanying cleavage event.

Our attention then shifted toward a different PIB-based copolymer, poly(isobutylene-*co*- 2,4-dimethyl-1,3pentadiene) (IB-co-DMPD), whose diene comonomer units are structurally identical to coupled PIB (*endo* isomer) and would thus be expected to undergo quantitative decoupling/functionalization. Though Kennedy *et al.* had reported the random copolymerization of IB and DMPD,[26] we concluded that their findings were in error and showed instead that DMPD is so much more reactive than IB, the products of copolymerization are essentially sequential block copolymers, and that a significant fraction of the DMPD is lost to side-reactions.[27] Thus our attention shifted to other comonomers which would yield main-chain unsaturations when copolymerized with IB.



Scheme 11. Initiation step of BP polymerization depicting the rearrangement characteristic of this reaction.

β-Pinene (BP) is a cationically active monomer whose polymerization proceeds via a ring-opening rearrangement, as depicted in Scheme 11.[28,29] Copolymerization of BP with IB has been reported.[30,31] The rearranged comonomer repeating unit bears an unsaturation that is similar to that of an IP-IB comonomer sequence in butyl rubber, but is more sterically hindered due to the ring structure (comparison between the two copolymers is shown in Scheme 12). The copolymerization of IB and BP, carried out via a slurry process, has been reported by Kennedy *et al.* but is characterized by an odd phenomenon.[30] **Error! Bookmark not defined.** At temperatures between -40 and -110°C the reactivity ratio of BP is greater than that of IB, and the product of these reactivity ratios is 1 ($r_{BP} > r_{IB}$, $r_{BP} \times r_{IB} = 1$). This results in an initial copolymer that is richer in BP than the feed. While lowering the temperature from -40°C it was observed that r_{BP} decreased while r_{IB} increased until, at -110°C the two reactivity ratios became equal at unity ($r_{BP} = r_{IB} = 1$) indicating an azeotropic polymerization where the composition of the copolymer matches the composition of the feed at all feed compositions. Recently, others have reported the azeotropic copolymerization of IB and BP at much higher temperatures.[31] **Error! Bookmark not defined.** However, in this latter report, the resulting copolymers were of very low molecular weight (<2000 g/mol), and it is unclear whether low molecular weights were intended or simply the result of extensive chain transfer.



Scheme 12. Structural comparison of poly(IB-co-IP) and poly(IB-co-BP). The residues of IB and BP in their respective copolymers are denoted by parenthesis.

Herein we report the synthesis and simultaneous cleavage/functionalization of copolymers of IB and BP. It should be noted that this chemistry is unique among known "constructive degradation" chemistries in being capable of degrading the molecular weight of this copolymer. Other chemistries, notably ozonolysis[32] and metathesis,[33] serve only to ring-open the BP residue with no accompanying molecular weight decrease.

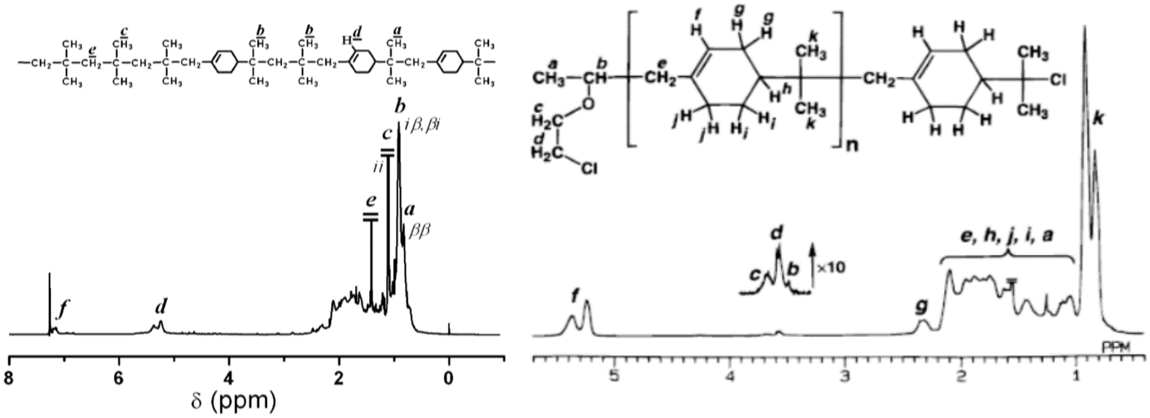


Figure 13 ^{1}H NMR spectra of poly(IB-co-BP)(left) and poly(BP)(right)

Images reproduced from references 31 (left) and 34 (right) with permission

Additionally, there remains a poorly addressed question in the literature regarding the mode of incorporation of BP during both homopolymerization and copolymerization. As shown in Figures 1 and 2, when β-pinene is polymerized via a cationic route, either as a copolymer (Figure 13, Left)[31] **Error! Bookmark not defined.** or as a homopolymer (Figure 13, Right),[34] the olefinic region displays two major peaks. Cataldo *et* al. have attempted to explain this complex NMR spectrum by referencing a ring opening event at the 5-position of β-pinene. However, their explanation leaves much to desired as they do not provide a mechanism for the formation of this structure.[35] Our findings regarding the effect of catalyst choice and solvent polarity during reaction on the complexity of the olefinic region of the ^{1}H NMR, as well as a more plausible explanation for this complex signal, will be presented in this chapter as well.

Experimental

Reagents

Hexane (anhydrous, 95% n-hexane), $MeCl_2$ (99.9%), and 1-butyl chloride (anhydrous, 99.9% pure) were purchased from Fisher Scientific Inc. and used as received. Methyl chloride (99.5%), and IB (99%), purchased from Southern Gas and Supply, and propane (99.5%), purchased from Gas Innovations, were dried by passing the gases through columns of CaSO4/molecular sieves/CaCl2 and condensed within a N2-atmosphere glovebox immediately prior to use. $AlCl_3$ (anhydrous, 99%), ethylaluminum dichloride (EADC) (97%), $TiCl_4$ (99.9% trace metals basis), and 2,6-lutidine (>99%) were purchased from Sigma Aldrich and used as received. β-Pinene (>99%) was purchased from Sigma Aldrich and distilled over calcium hydride prior to use.

Synthesized Polymers.

Poly(IB-*co*-BP) and polyBP were synthesized by cationic polymerization catalyzed by either $TiCl_4$ or EADC, carried out within an inert atmosphere glove-box at a temperature of either -70°C or -115°C. A representative $TiCl_4$-catalyzed polymerization was as follows (Entry 1, Table 5): To a 4-neck round-bottom flask equipped with a thermocouple and a mechanical stirrer in a pentane bath cooled to -70°C was added 1-butylchloride (111 mL), IB (35.57 mL), and β-Pinene (1.73 mL). The pentane bath was then cooled to -115°C and the reaction was allowed to stir until it too had reached -115°C. Meanwhile, a solution of $TiCl_4$ in butyl chloride was prepared by adding 0.3 mL $TiCl_4$ to 3 mL butyl chloride. This solution was then added to the polymerization flask very slowly while monitoring the temperature to avoid an uncontrollable exotherm. Immediately upon addition of this solution, a white precipitate was observed indicating that polymerization was taking place.

In all, only 1.4 mL of the $TiCl_4$ solution was added to the reaction over the course of 10 min. During this time, the reaction temperature fluctuated between -117° and -115°C the reaction was terminated by addition of excess methanol. The polymer was then dried to remove solvent and dissolved in hexane, precipitated twice in methanol, redissolved in hexane, and dried by rotary evaporation. Polymer yield was 5.63 g; mol% BP incorporated was 2.96%; M_n = 52,330 g/mol; PDI = 2.0.

An example of an EADC-catalyzed polymerization was as follows (Entry 3, Table 5): To a 4-neck round-bottom flask equipped with a thermocouple and a mechanical stirrer in a pentane bath cooled to -70°C was added 1-butylchloride (111 mL), IB (35.57 mL), and β-Pinene (1.73 mL). The pentane bath was then cooled to -115°C and the reaction was allowed to stir until it too had reached -115°C. Meanwhile, a solution of EADC in methylene chloride was prepared by adding 0.084 g EADC to 2 mL methylene chloride. This solution was then added to the polymerization flask very slowly while monitoring the temperature to avoid an uncontrollable exotherm. Immediately upon addition of this solution, a white precipitate was observed indicating that polymerization was taking place. After the entire solution had been added to the reaction, the reaction was terminated by addition of excess methanol. The polymer was then dried to remove solvent and dissolved in hexane, precipitated twice in methanol, redissolved in hexane, and dried by rotary evaporation. Polymer yield was 2.437 g; % BP incorporated was 2.38%; M_n = 217,400 g/mol; PDI = 1.5.

An example of a $TiCl_4$ catalyzed homo-polymerization of BP was as follows (Entry 5, Table 5): Polymerization of BP was carried out at -70°C within a N2-atmosphere glovebox equipped with cryostated heptane bath. A 250 mL 4-neck round-bottom flask, equipped with mechanical stirrer, thermocouple, and FTIR-ATR DiComp® probe (Mettler Toledo), was immersed into the bath and charged with hexane (74 mL, -70°C) and methyl chloride (49 mL, -70°C). To this mixture were added 0.06 g of TMPCl (4 x10^{-4} mol), 0.085 mL (80 mg, 7 x10^{-4} mol) of 2,6-lutidine, and 22.9 mL (20 g, 1.47 x10^{-1} mol) β-pinene. After thermal equilibration of the solution to -70°C, polymerization was initiated by the addition of 6.16 mL (10.72 g, 5.68 x10^{-2} mol) of $TiCl_4$ (neat and at room temperature). After complete monomer conversion as determined by ATR-FTIR spectroscopic monitoring, the reaction was terminated with excess pre-chilled (-70°C) methanol. The mixture was allowed to warm to room temperature with evaporation of the methyl chloride, and the polymer was precipitated twice from hexane by addition to 200 mL methanol. The polymer was then dissolved in 50 mL hexane, and the resulting solution was washed with water (2x100 mL) and dried over magnesium sulfate (MgSO4). The solution was filtered to remove magnesium sulfate, and the hexane was removed via rotary evaporation.

Simultaneous Cleavage/Functionalization.

Simultaneous cleavage/functionalization of poly(IB-*co*-BP) was carried out using a modification of a published method.[24] **Error! Bookmark not defined.** A representative procedure was as follows: Poly(IB-*co*-BP) (0.68 g), hexane (10.27 mL), and $MeCl_2$ (6.83 mL) were charged to a screw-top test tube equipped with a magnetic stir bar. The tube was tightly capped, and the mixture was stirred overnight at room temperature to dissolve the copolymer. The resulting solution was equilibrated to -40ºC by immersing the flask into a chilled methanol bath for 30 min. Then, (3-bromopropoxy)benzene (0.51 mL, 0.70 g, 3.26 mmol), H_2O (5 uL, 0.28 mmol), and $AlCl_3$ (0.25 g, 1.9 mmol) were added in that order, neat and at room temperature, and the reaction mixture was stirred at -40˚C for 21.5 h with an aliquot taken at 1.5 h. Excess methanol was then added to the test tube to terminate the reaction. The resulting solution was warmed to room temperature and then precipitated into methanol. The precipitate was collected by re-dissolution in fresh hexane, and the resulting solution was re-precipitated into excess methanol. The precipitate was collected by re-dissolution in fresh hexane, and the resulting solution was washed twice with deionized water, dried over $MgSO_4$, and then vacuum stripped to yield the isolated polymer.

Characterization.

Number average molecular weights (M_n) and polydispersities (PDI = M_w/M_n) were determined using a gel-permeation chromatography (GPC) system consisting of a Waters Alliance 2695 separations module, an on-line multi-angle laser light scattering (MALLS) detector fitted with a gallium arsenide laser (power: 20 mW) operating at 658 nm (miniDAWN TREOS, Wyatt Technology Inc.), an interferometric refractometer (refractive index detector) (T-rEX, Wyatt Technology Inc.) operating at 35°C and 685 nm, and two PLgel (Polymer Laboratories Inc.) mixed D columns (pore size range 50-10^3 Å, 3 μm bead size). Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were *ca.* 5-6 mg of polymer/mL of THF, and the injection volume was 100 μL. The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology Inc.), and absolute molecular weights were determined by MALLS using a *dn/dc* calculated from the refractive index detector response and assuming 100% mass recovery from the columns.

Proton nuclear magnetic resonance (^1H NMR) spectra were obtained using a 300 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer. Standard ^1H pulse sequences were used with a relaxation delay of 5 s, and all ^{1}H chemical shifts were referenced to TMS (0 ppm). Samples were prepared by dissolving the polymer in $CDCl_3$ (20-50 mg/mL) and charging this solution to a 5 mm NMR tube. NMR data were analyzed using MestReNova version 9.0.1-13254. The peaks from 5.5 to 5.1 ppm were deconvoluted using the peak fitting function of MestReNova. Assuming three signals, each due to the olefinic C-H of a rearranged BP structure, the fraction of each rearranged structure was quantified using equations such as eq 1, wherein $F_{5.36}$ is the fraction of BP units that causes the signal at 5.36 ppm and $A_{5.36}$, $A_{5.32}$, and $A_{5.24}$ are the areas of the deconvoluted peaks at 5.36, 5.32, and 5.24 ppm respectively.

$$F_{5.36} = A_{5.36} / (A_{5.36} + A_{5.32} + A_{5.24}) \qquad \text{Eq 1}$$

Results and Discussion

Polymer Synthesis and Characterization.

High molecular weight is a desired property for copolymers which will be subjected to simultaneous cleavage/functionalization because as the molecular weight of the parent copolymer increases, the inherent concentration of non-functionalizable chain ends decreases. Thus, for conditions whereby every cleavable site is cleaved prior to functionalization, as the molecular weight of the copolymer increases (while keeping the ratio of monomer and comonomer constant) the product produced by this process more closely resembles a perfectly difunctional oligomer. Non-functionalizable chain ends could be eliminated entirely by employing a living copolymerization initiated from a difunctional initiator or a mono-functional initiator with a functionalizable α end. In the reported "living" process[31] **Error! Bookmark not defined.** the molecular weights were too low to be useful for our application. Therefore, we adopted, with a few minor changes, the slurry process outlined by Kennedy *et al.*[30] **Error! Bookmark not defined.** as high molecular weight copolymers were reported by this process. We should note also that an ideal random copolymerization (r_1=r_2=1), or if possible one whereby the non-IB comonomer is less reactive than IB (similar to the copolymerization if IB and isoprene (IP)), was very much desired as such a process would yield a material with well distributed comonomer units and with a minimum of BP-BP dyads. This latter point is important as such a dyad is not expected to behave the same as an IB-BP dyad during the cleavage/functionalization reaction due to the low cation stability of the BP chain end. Even if these homo-dyads did behave similarly, the result would likely be the formation of a low molecular weight BP unit functionalized by alkoxybenzene quencher.

Table 5 describes the polymers produced in this work using the slurry process. According to the data, EADC yields a higher molecular weight polymer as compared to $TiCl_4$ under nearly identical conditions, while the molecular weight of the resulting polymer is nearly unaffected by solvent polarity. We had planned to modify the slurry process to achieve living polymerization conditions by adding a non-polar solvent and using a less active Lewis acid; however, we found that as the solvent polarity decreased, BP became relatively more reactive even at temperatures below -110°C resulting in polymers richer in BP than the feed. This effect may be observed by comparison of Entries 1 and 2 and Entries 3 and 4. Since solubility of the growing polymer chain,and homogeneity of the reaction medium in general, are necessary for living polymerization, the living process was abandoned in this work. It should be noted that although the copolymerization behavior induced by living conditions is negative for the relatively narrow pursuits of this study, we recognize that it is not necessarily negative with regard to the effect of living conditions on this comonomer pair, in general

Table 5

Isobutylene/β-pinene Co- and β-Pinene Homo-Polymers[a]

Entry	Sample	Solvent	Lewis Acid	Temp (˚C)	Yield (%)	M_n (g/mol)	MWD	BP (mol%)[c]		Intensity in ^{1}H NMR		
								Feed f_{BP}	**Copolym. F_{BP}**	**5.36 ppm**	**5.32 ppm**	**5.24 ppm**
1	Copolymer	BuCl	$TiCl_4$	-115	21.38	52,330	2.0	2.4	2.96	86.5	8.9	4.6
2	Copolymer	BuCl/C_3H_8 60/40	$TiCl_4$	-115	14.77	49,860	2.5	2.4	3.78	92.6	3.3	4.2
3	Copolymer	BuCl	EADC	-115	9.25	217,400	1.5	2.4	2.38	70.7	23.6	5.6
4	Copolymer	BuCl/C_3H_8 60/40	EADC	-115	26.09	193,900	1.4	2.4	4.27	81.5	10.6	7.9
5	PolyBP	Hex/MeCl 60/40	$TiCl_4$	-70	100	17,290	1.5	100	100	63.5	0.0	36.5

[a] Entries 1-4 represent copolymers of IB and BP produced via a slurry process.

[b] Entry 5 represents a homopolymer of BP which was synthesized via TiCl4-catalyzed cationic polymerization.

[c] fBP and FBP are the mole fractions of BP present in the feed and copolymer, respectively.

Table 6

Simultaneous Cleavage/Functionalization of Poly(IB-co- BP)[a]

Entry	Parent Polymer (Table 5)	Polymer Conc. (g/mL)	$AlCl_3$ conc. (M)	H_2O Conc. (M)	PPB Conc. (M)	Rxn. Time (h)	Mn (g/mol)	MWD	IB/BP Parent	IB/Q	Funct. eq. wt.	Functionality
1	1	0.0367	0.101	0.0149	0.175	1.5	13,310	1.36	32.5	87.9	5283.7	2.5
2	1	0.0367	0.101	0.0149	0.175	21.33	5,973	1.34	32.5	28.3	1936.2	3.1
3	2	0.0367	0.097	0.0147	0.175	1.5	12,070	1.69	25.5	85.9	5170.9	2.3
4	2	0.0367	0.097	0.0147	0.175	21.33	6,213	1.48	25.5	25.5	1783.0	3.5
5	3	0.0367	0.103	0.0161	0.175	1.5	16,620	1.41	41.0	94.6	5657.3	2.9
6	3	0.0367	0.103	0.0161	0.175	21.33	9,627	1.34	41.0	41.5	2675.6	3.6
7	4	0.0368	0.088	0.0163	0.175	1.5	14,450	1.39	22.4	81.0	4895.5	3.0
8	4	0.0368	0.088	0.0163	0.175	21.33	6,932	1.28	22.4	28.9	1972.1	3.5

[a]All reactions were conducted at -40□C in 60/40 (v/v) Hex/MeCl2.

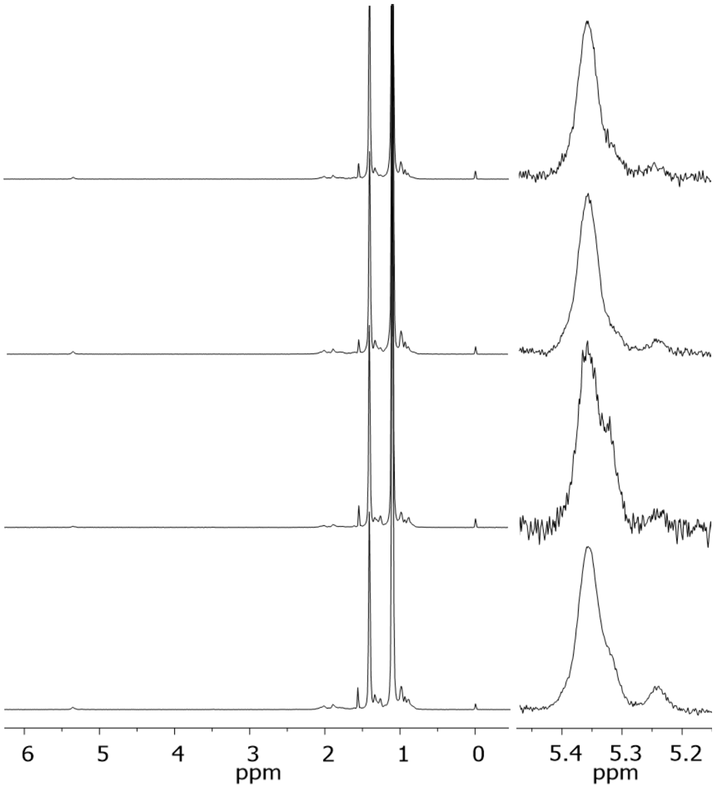


Figure 14 NMR spectra of the copolymers which we produced. These polymers are presented in Table 5 Entries 1 (Top) through 4 (Bottom).

Molecular weight and BP incorporation are not the only factors affected by catalyst choice and solvent polarity. As mentioned in the introduction and illustrated in Figure 14, the olefinic region of the ^{1}H NMR spectrum of these copolymers displays multiple signals; at 5.36, 5.32, and 5.24 ppm. Originally, we assumed that the olefinic signal of an IB-BP dyad would be different from a BP-BP dyad, resulting in two olefinic signals in the copolymer. To assess this assumption, we synthesized a homopolymer of BP via $TiCl_4$ catalyzed polymerization at -70°C. NMR characterization of this homopolymer, shown in Figure 15, revealed the two signals often reported in the literature.[34,35] **Error! Bookmark not defined.**,**Error! Bookmark not defined.** One of these signals was coincident with the main olefinic signal at 5.36 ppm, while the other signal was coincident with the minor signal at 5.24 ppm.

The immediate conclusion one might draw is that the peak at 5.32, which only occurs in the copolymer of IB and BP, is the result of IB-BP dyads, but this is unlikely. If such were the case, the copolymers that we synthesized would be very blocky and unlikely to degrade in the proper fashion; entire blocks of BP would be lost to the process and molecular weight would not appreciably decrease, an outcome which we did not observe as we will discuss later. Additionally, these copolymerizations were terminated at low total monomer conversions, and though some of the resulting materials contained more BP than the monomer feed, the difference was not enough to suggest that block copolymers were formed. A more likely conclusion is that the olefinic signals of IB-BP dyads and BP-BP dyads have nearly the same chemical shift (5.36 ppm) and cannot be resolved under our conditions. Operating under this assumption, the two remaining peaks at 5.32 and 5.24 ppm remain to be assigned.

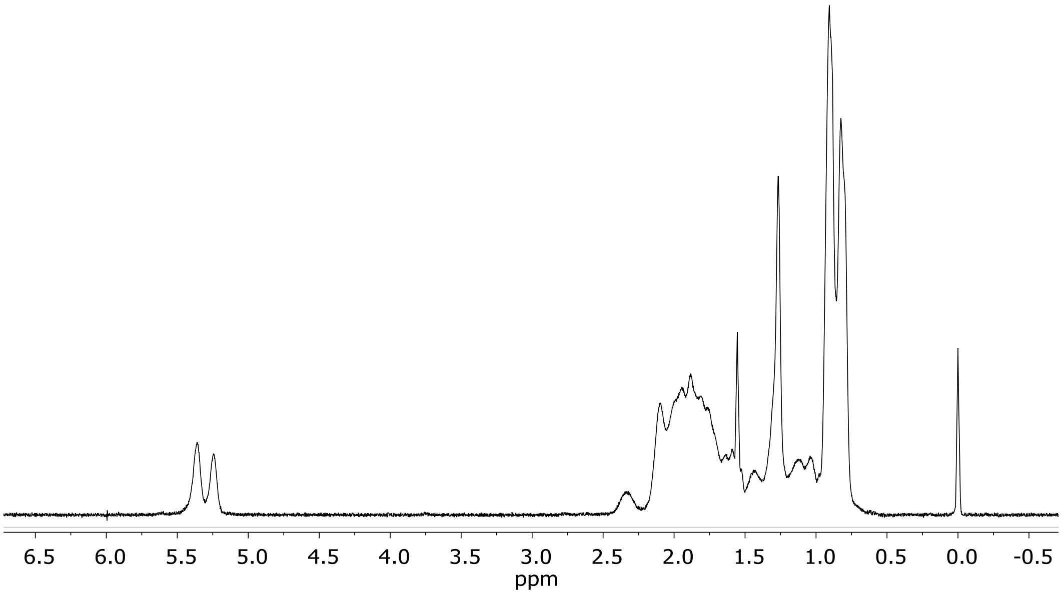
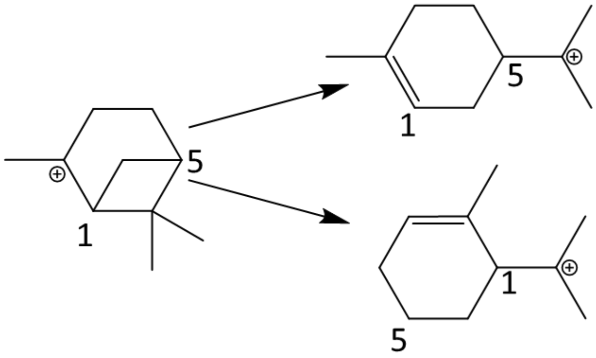


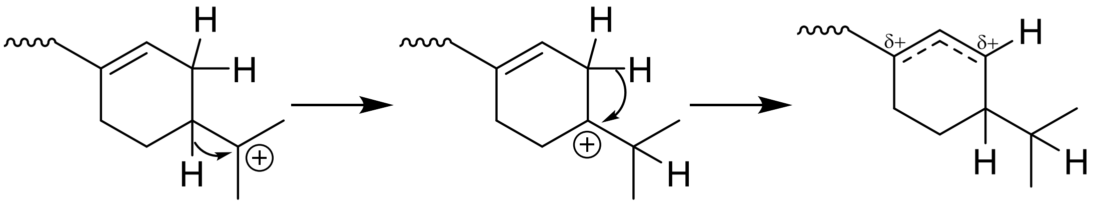
Figure 15 NMR spectrum of poly-BP (Table 5, Entry 5).

We will first discuss the 5.25 ppm signal, observed in both copolymers and homopolymers. Based on the observed intensities, this signal represents a major structure in homopolymers produced at relatively warmer temperature; for example, Entry 5 of Table 5 shows that it accounts for 36.5% of the olefinic units at -70°C. In spite of its prominence, several authors have presented NMR data showing this secondary peak but have remained silent with regard to its structural assignment.[30,31,34] **Error! Bookmark not defined.**Cataldo *et al.* have proposed an alternate ring-opened structure (Scheme 13) and attributed this structure to the signal at 5.24 ppm. [35,36] **Error! Bookmark not defined.** However, no mechanism for the formation of such a structure was presented in that article. White *et al*. have proposed a mechanism for the formation of short chain branches in butyl rubber, the resulting structure of which causes similar anomalous NMR signals, which involves an intramolecular back-biting reaction to form a methallylic carbocation.[37] This might explain these alternative peaks in the copolymer of IB and BP, but it cannot for the homopolymer of BP, as intramolecular backbiting would require an extremely strained intermediate. Furthermore, the intramolecular backbiting reaction occurs much less frequently in IB/IP copolymerizations than we observe for IB/BP copolymerizations despite the IB/BP polymerizations being carried out at lower temperatures.

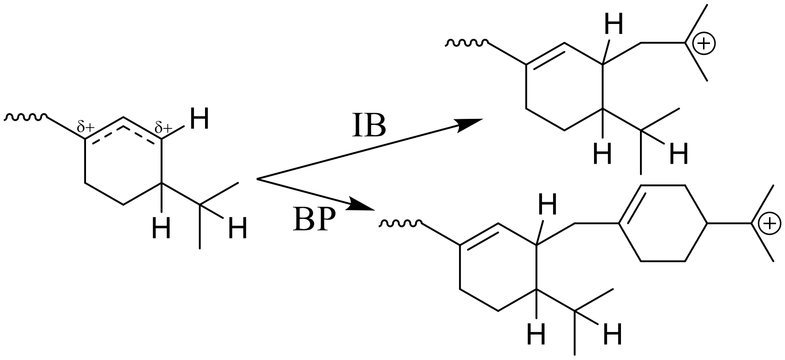


Scheme 13. Illustration of the structures resulting from the known ring-opening at the 1 position (top) and ring-opening at the 5 position (bottom) which was proposed by Cataldo *et al*.

Due to the lack of reasonable literature explanations, we have developed a new hypothesis regarding this secondary structure. It is known that Lewis acid catalyzed hydride and methide shifts can occur during IB polymerization under monomer starved conditions at long reaction times.[38,39] For these to occur though, a secondary carbocation intermediate must be formed which is energetically unfavorable, and thus PIB cation rearrangement is characterized by very slow kinetics; as reported by Storey *et al*. the ratio of k_p/k_{tr} was found to be $3*10^4$ M^{-1}. Much more rapid rearrangements have been observed when no high-energy intermediate is involved; for example, the rearrangement of 3-methyl-1-butene competes favorably with propagation at low temperatures.[40] We hypothesize that a sequence of hydride shifts occurs at the BP chain-end, illustrated in Scheme 14, which results in an energetically favored 1,3-dialkylallylic carbocation. This sequence is expected to occur relatively rapidly since it does not involve a high-energy



Scheme 14. Illustration of sequence of shifts which yield a methallylic chain end during polymerization of BP.



Scheme 15. Addition of the methallylic BP chain end to either IB (Top) or BP (Bottom) results in structures which would be expected to display different signals in ^1H NMR.

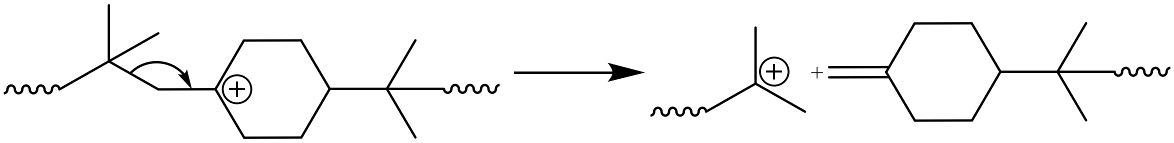
secondary carbocation intermediate. During BP homopolymerization, the allylic carbocation would add to BP to produce the structure shown in Scheme 15 (bottom). We propose that the olefinic proton of this rearranged repeat structure is responsible for the 5.24 ppm signal. During copolymerization, the BP-IB dyad structure, shown in Scheme 15 (top), is produced, and this olefin is assigned to the 5.32 ppm signal.

Having presented our hypothesis for the structural cause of the extra olefinic NMR signals, it is important to note the effect of solvent polarity and catalyst selection on the formation of these structures. Comparing examples 1 and 3 with examples 2 and 4 respectively, it is apparent that decreasing the solvent polarity results in fewer rearranged BP units. This is likely due to a decrease in the stability of the intermediate during the first hydride shift in the less polar solvent. Comparing examples 1 and 2 with examples 3 and 4 it is apparent that the use of $TiCl_4$ as a catalyst also results in fewer rearranged BP structures. This is likely due to the lower catalytic activity of $TiCl_4$ as compared to EADC which would again result in a decreased stability of the intermediate of the first hydride shift.

With regards to the simultaneous cleavage/functionalization of these polymers, the structure arising from the addition of the allylic cation to IB (Scheme 15, top) is not problematic as this structure would be expected to cleave at least as readily, upon protonation, as the structure resulting from normal addition. The addition of BP to this methallylic cation, however, results in a structure (Scheme 15, Bottom) whose behavior during this reaction is not easily predictable due to protonation of either unit resulting in a number of possible products as shown in Figure A1 of Appendix D.

Cleavage/Functionalization of Poly(IB-co-BP)

As we have reported previously, subjecting a PIB-based copolymer bearing hindered backbone unsaturations to conditions similar to those employed during alkoxybenzene quenching of living PIB results in a simultaneous reduction of molecular weight and functionalization of the polymer (Table 6). In the case of poly(IB-*co*-IP) (butyl rubber) we previously reported that, though we were unable to achieve functionalization of every chain-end resulting from the cleavage reaction, we were able to functionalize a majority of them as evidenced by the fact that the ratio of isobutylene units to quencher residue (IB/Q) of the product was lower than the ratio of isobutylene units to isoprene units (IB/IP) in the starting polymer. Furthermore, when butyl rubber was used as the substrate, the reactions were essentially complete after approximately 1 h reaction time.



Scheme 16. Cleavage of protonated BP repeat unit in the synthesized copolymers. This step yields a cationic isobutylenic chain end (left structure on product side) and an olefinic b-pinenic chain end (right structure on product side).

When subjecting poly(IB-*co*-BP) to similar reaction conditions, the rate of degradation was qualitatively observed to be much slower. After 1.5 h reaction time, some of the internal olefin from the starting material still remained as evidenced in the ^{1}H NMR spectrum of the product. Additionally, we saw that the reaction was not nearly complete at this time as the IB/Q ratios in the products were much greater than the IB/BP ratios in the parent copolymers. Furthermore in the aliquots taken at this time, a signal at 4.4 ppm was visible in the ^{1}H NMR spectrum, as shown in Figure 16. We have attributed this signal to the BP chain end formed from the cleavage reaction illustrated in Scheme 16.

Table 7

Comparison of Molecular Weights by GPC and NMR

Entry from Table 6	Mn (GPC)	Mn (NMR)
1	13310	13180
3	12070	10286
5	16620	16332
7	14450	9685

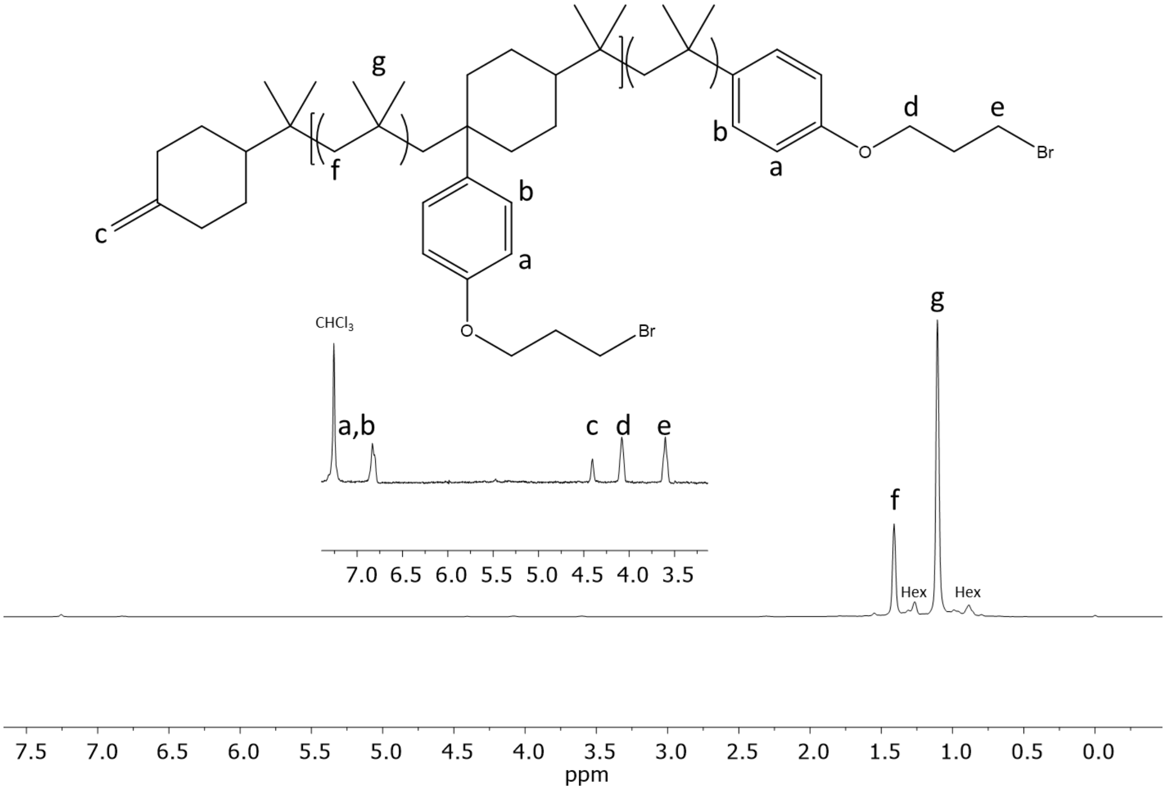


Figure 16 NMR spectrum of the product of cleavage/functionalization of poly(IB-co-BP).

This hypothesis is further supported in that, for three out of these four reactions at short reaction times, molecular weight determination by chain end analysis of the NMR spectrum agrees fairly well with the molecular weight determined by GPC (Table 7). This suggests that the formation of a tert-chloride from the BP residue is unfavorable and that SP_2 configuration about this carbon is preferred.

Allowing the reaction to proceed results in further decrease of both molecular weight and IB/Q of the resulting polymer. The value of IB/Q, however, does not decrease substantially below the IB/BP ratio of the parent materials. Additionally, the signal at 4.4 ppm begins to decrease as well indicating either functionalization or, less likely, rearrangement of the pinenic chain end. However, even after 21 hours reaction time, olefinic pinenic chain ends remain.

Conclusions

The simultaneous cleavage/functionalization of isobutylene copolymers remains of very high interest. During this work we were able to synthesize high molecular weight copolymers of IB and BP, the internal olefin of which was successfully targeted for this reaction. Additionally, we have attempted to address a question which remains in the literature regarding rearranged structures which appear during cationic polymerization of BP. Instead of a non-standard ring opening mechanism, we propose that the odd olefinic NMR signals are due to sequential hydride shifts that take place after the ring-opening step to form an energetically favorable methallylic cation. If this is indeed the case, addition of this cation seems to favor addition to BP as evidenced in NMR spectroscopy of the copolymers.

We were able to subject these polymers to the simultaneous cleavage/functionalization reaction resulting in a polymer of a much lower molecular weight but functionality greater than 2 suggesting that the backbone quenching reaction which we observed for butyl rubber also occurs for poly(IB-co-BP). Furthermore, the resulting polymers displayed IB/Q values which nearly matched the IB/BP ratios of their parent polymers. This has led us to conclude that one of the chain ends resulting from the cleavage reaction is not functionalized in the final product. Whether this chain end is an isobutylenic or pinenic chain-end has not been definitively proven, but all evidence thus far points toward rearrangement of PIB chain ends. Such rearrangements under conditions similar to the ones we have employed have been reported in the case of PIB chain ends and must not be ruled out unless evidence for its absence is presented. Furthermore, the disappearance of the olefinic signal of the pinenic chain end accompanied by no appearance of extra olefinic signals suggests that functionalization, as opposed to rearrangement, does occur on pinenic chain ends further suggesting that rearrangement of IB chain ends is the reason for incomplete functionalization.

References

1. Malhotra, S. L.; Minh, Ly; Blanchard, L.P. Thermal Decomposition and Glass Transition Temperature of Poly(isobutylene). *J. Macromol. Sci-Chem.*, **1982** A18(3), 455-475.

2. Pauly, S. Permeability and diffusion data J. Brandrup, E.H. Immergut, E.A. Grulke (Eds.), *Polymer Handbook*, Wiley, New York **1999**, 543-569

3. Rath, Hans Peter. Basf Aktiengesellschaft, assignee. Patent US5962604 A. **5 Oct. 1999**.

4. Tripathy, Ranjan; Crivello, James V.; Faust, Rudolf. Photoinitiated Polymerization of Acrylate, Methacrylate, and Vinyl Ether End-Functional Polyisobutylene Macromonomers. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, 51(2), 305-317.

5. Yang, Bin; Parada, Corey M.; Storey, Robson F. Synthesis, Characterization, and Photopolymerization of Polyisobutylene Phenol (Meth)acrylate Macromers. *Macromolecules* **2016**, 49(17), 6173-6185.

6. Kali, Gergely; Ivan, Bela. Poly(methacrylic acid)-l-Polyisobutylene Amphiphilic Conetworks by Using an Ethoxyethyl-Protected Comonomer: Synthesis, Protecting Group Removal in the Cross-Linked State, and Characterization. *Macromol. Chem. Phys.* **2015**, 216(6), 605-613.

7. Karunakaran, Radhakrishnan; Kennedy, Joseph P. Novel Amphiphilic Conetworks by Synthesis and Crosslinking of Allyl-Telechelic Block Copolymers. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, 46(12), 4254-4257.

8. Storey, Robson F.; Scheuer, Adam D.; Achord, Brandon C. Poly(Acrylate-B-Styrene-B-Isobutylene-B-Styrene-B-Acrylate) Block Copolymers via

Carbocationic and Atom Transfer Radical Polymerizations. *J. Macromol. Sci., Pure Appl. Chem.* **2006**, 43(10), 1493-1512.

9. Knauer, Katrina M.; Zhu, Yaling; Storey, Robson F.; Morgan, Sarah E. Phase Separation and Permeability in Polyisobutylene-Based Miktoarm Star Polymers. *J. Polym. Sci., Part B: Polym. Phys.* **2016**, 54(9), 916-925.

10. Zhang, Longhe; Kucera, Lauren R.; Ummadisetty, Subramanyam; Nykaza, Jacob R.; Elabd, Yossef A.; Storey, Robson F.; Cavicchi, Kevin A.; Weiss, R. A. Supramolecular Multiblock Polystyrene-Polyisobutylene Copolymers via Ionic Interactions. *Macromolecules* **2014**, 47(13), 4387-4396.

11. Chang, Young; Stokes, Casey D.; Morgan, David L. Manufacture of Copolymers of Polyaminopolyolefins and Polyanhydrides Useful as Viscosity Modifiers for Lubricant Oils and Fuel. PCT Int. Appl. **2014**, WO 2014085047 A1 20140605.

12. Kolp, Christopher; Gieselman, Matthew D.; Eveland, Renee A.; Pike, Philip; Pudelski, John K.; Covitch, Michael J.; Friend, Christopher. Dispersant Viscosity Modifiers Based on Diene-Containing Polymers. US7750089 B2. **2010**

13. Walch, E.; Gaymans, R. J. Synthesis of Low-Molecular-Weight Telechelic Polyisobutylene. Polymer **1993**, 34(2), 412-17.

14. Storey, Robson, F.; Lee, Youngkwan. Living Carbocationic Polymerization of Isobutylene Using Blocked Dicumyl Chloride or Tricumyl Chloride/Titanium Tetrachloride/Pyridine Initiating System. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, A29(11), 1017-30.

15. Zhu, Yaling; Storey, Robson F. Effect of Structure on Cationic Initiation Efficiency of a Carbocatonic/ATRP Dual Initiator. *Macromolecules.* **2012**, 45(3), 1217-1221.

16. Lange, Arno; Kiefer, Matthias; Kleiner, Matthias; Csihony, Szilard; Posselt, Dietmar. Method for Continuous Production of Bifunctional Polyisobutenes Using Lewis Acid Catalyst and Capping Agents in Solvent. PCT Int. Appl. **2014**, WO 2014056845 A1

17. Gyor, Miklos; Wang, Hsien Chang; Faust, Rudolf. Living Carbocationic Polymerization of Isobutylene with Blocked Bifunctional Initiators in the Presence Of Di-Tert-Butylpyridine as a Proton Trap. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, A29(8), 639-53.

18. Price, Matthew J. Coronary Stenting: A Companion to Topol's Texbook of Interventional Cardiology. Philadelphia: Elsevier, **2014**. Print.

19. Alvarez Albarran, Alejandra; Silantyeva, Elena; Seo, Kwang Su; Puskas, Judit E. Synthesis of Functionalized Polyisobutylenes Using the Propylene Epoxide/$TiCl_4$ Initiating System. *Poly. Chem.* **2014**, 5(16), 4710-4714.

20. Soytas, Serap Hayat; Lim, Goy Teck; Puskas, Judit E. Synthesis of POSS-Functionalized Polyisobutylene via Direct Initiation. *Macromol. Rapid Commun.* **2009**, 30(24), 2112-2115.

21. Soytas, Serap Hayat; Puskas, Judit E.; Kulbaba, Kevin. Real-Time FTIR Monitoring of the Mechanism of Initiation of Isobutylene Polymerizations by Epoxide/Lewis Acid Systems. *J. Polym. Sci., Part A: Polym. Chem.* **2008**, 46(11), 3611-3618.

22. Ummadisetty, Subramanyam; Storey, Robson F. Quantitative Synthesis of exo-Olefin-Terminated Polyisobutylene: Ether Quenching and Evaluation of Various Quenching Methods. *Macromolecules* **2013**, 46(6), 2049-2059.

23. Kemp, Lisa K.; Poelma, Justin E.; Cooper, Timothy R.; Storey, Robson F. Structural Confirmation of Exo-Olefin-Coupled Polyisobutylene via Model Compound Synthesis and Characterization. *J. Macromol. Sci., Pure Appl. Chem.* **2008**, 45(2), 137-143.

24. Campbell, C. Garrett; Storey, Robson F. Functional Polyisobutylenes via Electrophilic Cleavage/Alkylation. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, 55(12), 1991-1997.

25. Campbell, C. Garrett; Ummadisetty, Subramanyam; Storey, Robson F. Decoupling and Functionalization of Coupled Polyisobutylene via Alkoxybenzene Quenching. *Macromolecules* **2016**, 49(20), 7642-7652.

26. Kaszas, Gabor; Puskas, Judit E.; Kennedy, J. P. Carbocationic Copolymerization in the Presence of Electron Pair Donors. 2. Copolymerization of Isobutylene And Isoprene or 2,4-Dimethyl-1,3-Pentadiene With Titanium Tetrachloride-Based Initiating Systems Yielding In-Situ Electron Pair Donors. *Macromolecules* **1992**, 25(6), 1775-9.

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28. Karasawa, Yukari; Kimura, Madoka; Kanazawa, Arihiro; Kanaoka, Shokyoku; Aoshima, Sadahito. New Initiating Systems for Cationic Polymerization of Plant-Derived Monomers: $GaCl_3$/Alkylbenzene-Induced Controlled Cationic Polymerization of Β-Pinene. *Polym. J.* **2015**, 47(2), 152-157.

29. Pietila, Heikki; Sivola, Arto; Sheffer, Howard. Cationic Polymerization of Β-Pinene, Styrene, and Α-Methylstyrene. *J. Polym. Sci., Part A: Polym. Chem*. **1970**, 8(3), 727-37.

30. Kennedy, Joseph P.; Chou, Tom. Poly(Isobutylene-co-B-Pinene): A New Sulfur Vulcanizable, Ozone Resistant Elastomer by Cationic Isomerization Copolymerizstion. I. Synthesis and Reactivity Studies. *Adv. Polym. Sci.* **1976**, 21, 1-30.

31. Li, An-Long; Zhang, Wei; Liang, Hui; Lu, Jiang. Living Cationic Random Copolymerization of β-Pinene and Isobutylene with 1-Phenylethyl Chloride/$TiCl_4$ /$Ti(OiPr)_4$/nBu_4NCl. Polymer **2004**, 45(19), 6533-6537.

32. Ebdon, J.R.; Flint, N.J.; Rimmer, S. Degradative Routes to Telechelic Oligomers and Macromonomers. *Macromol. Rep.* **1995**, A32, 603-611.

33. Chasmawala, M.; Chung, T.C. Telechelic Polyisobutylene: A Facile Synthesis via the Cross-Metathesis Reaction and Trialkylborane-Containing Olefins. *Macromolecules* **1995**, 28(5), 1333-1339.

34. Lu, Jiang; Kamigaito, Masami; Sawamoto, Mitsuo; Higashimura, Toshinobu; Deng, Yun-Xiang. Living Cationic Isomerization Polymerization of β-Pinene. 1. Initiation with HCl-2-Chloroethyl Vinyl Ether Adduct/$TiCl_3$(OiPr) in Conjunction with nBu_4NCl. *Macromolecules.* **1997**, 30(1), 22-26.

35. Cataldo, Franco; Angelini, Giancarlo; Capitani, Donatella; Gobbino, Marco; Ursini, Ornella; Forlini, Fabrizio. Determination of the Chemical Structure of Poly-β(-)-pinene by NMR Spectroscopy. *J. Macromol. Sci., Pure Appl. Chem.* **2008**, 45(10), 839-849.

36. The shift reported by Cataldo *et al.* was actually 5.29 ppm. This difference is likely due to the difference in NMR solvents. We used $CDCl_3$; whereas Cataldo *et al.* used $C_2D_2Cl_4$.

37. White, Jeffery L.; Shaffer, Tim D.; Ruff, Charles J.; Cross, John P. Incorporation of Isoprene in Isobutylene/Isoprene Copolymers: NMR Identification of Branching in Butyl Rubber. *Macromolecules.* **1995**, 28(9), 3290-300.

38. Robson F. Storey; Christopher L. Curry; L. Bryan Brister. Carbocation Rearrangement in Controlled/Living Isobutylene Polymerization. *Macromolecules*. **1998**, 31 (4), pp 1058–1063.

39. Dimitrov, P.; Emert, J.; Hua, J.; Keki, A.; Faust, R. Mechanism of Isomerization in the Cationic Polymerization of Isobutylene. *Macromolecules.* **2011**, *44* (7), 1831-1840.

40. Kennedy, J. P.; Thomas, R. M. Crystalline Poly(3-Methyl-1-Butene) Obtained by Cationic Polymerization. *Makromol. Chem.* **1962**, 53, 28-32.

APPENDIX A

Materials

Hexane (anhydrous, 95%), titanium tetrachloride ($TiCl_4$) (99.9%,), 2,6-lutidine (redistilled, 99.5%), 2,5-dimethylpyrrole (25DMP) (98%), diisopropyl ether (99%), di-*n*-butyl ether (99.3%), anisole (anhydrous, 99.7%), (3-bromopropoxy)benzene (96%), *N*-methylpyrrole (99%), 2-methylfuran (99%), tetrahydrofuran (THF) (anhydrous, 99.9%), calcium hydride (CaH_2) (95%), methanol (anhydrous, 99.8%), methylene chloride-d_2 (CD_2Cl_2) (99.8%), and chloroform-*d* ($CDCl_3$) were purchased from Sigma-Aldrich Co. and used as received. Anhydrous magnesium sulfate ($MgSO_4$), sodium carbonate, and magnesium sulfate was purchased and used as received from Fisher Scientific. Isobutylene (IB) (99%) and methyl chloride (99.5%) (both Gas and Supply Co., Hattiesburg, MS) were dried by passing the gaseous reagent through a column of $CaSO_4$/molecular sieves/$CaCl_2$ and condensing within a N_2-atmosphere glovebox immediately prior to use.

Instrumentation

Proton nuclear magnetic resonance (^1H NMR) spectra were obtained using a 300 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer. Standard ^1H pulse sequences were used, and all ^1H chemical shifts were referenced to TMS (0 ppm). Samples were prepared by dissolving the sample in $CDCl_3$ or CD_2Cl_2 (20-50 mg/mL) and charging this solution to a 5 mm NMR tube.

Number average molecular weights ($\overline{M}_n$) and polydispersities (PDI = $\overline{M}_w / \overline{M}_n$) were determined using a gel-permeation chromatography (GPC) system consisting of a Waters Alliance 2695 separations module, an on-line multi-angle laser light scattering (MALLS) detector fitted with a gallium arsenide laser (power: 20 mW) operating at 658 nm (miniDAWN TREOS, Wyatt Technology Inc.), an interferometric refractometer (refractive index detector) (T-rEX, Wyatt Technology Inc.) operating at 35°C and 685 nm, and two PLgel (Polymer Laboratories Inc.) mixed E columns (pore size range 50-10^3 Å, 3 μm bead size). Freshly distilled THF served as the mobile phase and was delivered at a flow rate of 1.0 mL/min. Sample concentrations were *ca.* 5-6 mg of polymer/mL of THF, and the injection volume was 100 μL. The detector signals were simultaneously recorded using ASTRA software (Wyatt Technology Inc.), and absolute molecular weights were determined by MALLS using a *dn/dc* calculated from the refractive index detector response and assuming 100% mass recovery from the columns.

Procedure for GPC Peak Deconvolution

Mass fractions of coupled and non-coupled species within coupled PIB samples were determined by peak deconvolution of the GPC differential refractive index (RI) chromatogram of the sample. The accuracy of this analysis was enhanced by defining the distribution (*i.e.* peak shape) of the non-coupled fraction to be the same as the *tert*-chloride PIB precursor from which the coupled PIB sample was derived. The only assumption necessary in this regard is that all precursor chains possess an equal likelihood to become coupled, regardless of size. This is a very good assumption for the *tert*-chloride precursors of this work, which all possess very low PDI.

The peak deconvolution procedure was as follows: In a first step, the baseline-corrected, normalized GPC RI data for the *tert*-Cl PIB precursor were exported to a Microsoft Excel spreadsheet, and the data were fitted to the equation for an asymmetric (skewed) Gaussian distribution,

$$\mathrm{RI} = \mathrm{RI}_{\max} \times e^{-\frac{(t-t_{\max})^2}{(2\sigma^2)}}\left[1 + erf\left(\frac{a(t-t_{\max})}{\sigma\sqrt{2}}\right)\right] \tag{1}$$

where $\mathrm{RI}_{\max}$ is the maximum refractive index (RI) value for the fitted peak, $t_{\max}$ is the elution time (t) when $\mathrm{RI}_{\max}$ occurs, σ is a peak-width factor, and a is the skew factor used in the Gauss error function (erf). Fitting was carried out using Excel's Solver Add-in. After inputting reasonable starting values for $\mathrm{RI}_{\max(nc)}$, $t_{\max(nc)}$, $\sigma_{(nc)}$, and $a_{(nc)}$, the best-fit values for these four parameters were determined iteratively by minimizing the summation of the squared differences between the calculated value of $\mathrm{RI}_{(nc)}$ from eq 1 and the height of the experimental RI chromatogram, at each distribution of the non- coupled fraction,

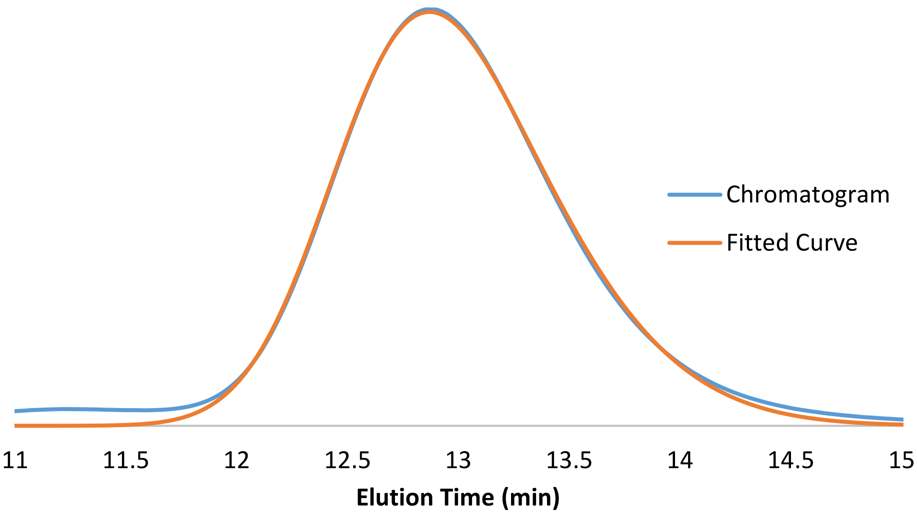


Figure A1. GPC RI chromatogram (blue) and fitted curve (orange) for Precursor PIB4-5.

which has been defined to be equal to the distribution of the *tert*-Cl precursor. Figure A1 shows the experimental RI chromatogram of Precursor PIB4-5 along with the fitted curve generated using the above procedure.

Having thus defined an asymmetric Gaussian distribution to describe the GPC RI chromatogram of the *tert*-Cl PIB precursor, in a second step we imported the GPC RI data for the coupled PIB into an Excel spreadsheet. The best-fit values of $\mathrm{RI}_{\max(\mathrm{nc})}$, $t_{\max(\mathrm{nc})}$, $\sigma_{(\mathrm{nc})}$, and $a_{(\mathrm{nc})}$, previously determined, were transferred to this same Excel sheet. A set of reasonable starting values for $\mathrm{RI}_{\max(\mathrm{c})}$, $t_{\max(\mathrm{c})}$, $\sigma_{(\mathrm{c})}$, and $a_{(\mathrm{c})}$ were inputted to be used for calculation of the coupled peak distribution, as signified by the subscript "(c)." Using the Excel Solver, the best-fit values for $\mathrm{RI}_{\max(\mathrm{c})}$, $t_{\max(\mathrm{c})}$, $\sigma_{(\mathrm{c})}$, and $a_{(\mathrm{c})}$ and $\mathrm{RI}_{\max(\mathrm{nc})}$ were iteratively determined by minimizing the summation of the squared differences between the sum of $\mathrm{RI}_{(\mathrm{nc})}$ and $\mathrm{RI}_{(\mathrm{c})}$ calculated from eq 13 and the height of the experimental RI chromatogram of the coupled PIB, at each elution time point. The previously determined, fitted values of $t_{\max(\mathrm{nc})}$, $\sigma_{(\mathrm{nc})}$, and $a_{(\mathrm{nc})}$ were held fixed during this process. The end result were fitted equations describing the distributions of the coupled and the uncoupled fraction of the sample. Figure A2 shows the experimental RI chromatogram of coupled sample PIB4, the fitted curves for the coupled and non-coupled distributions, and the sum of the two fitted distributions.

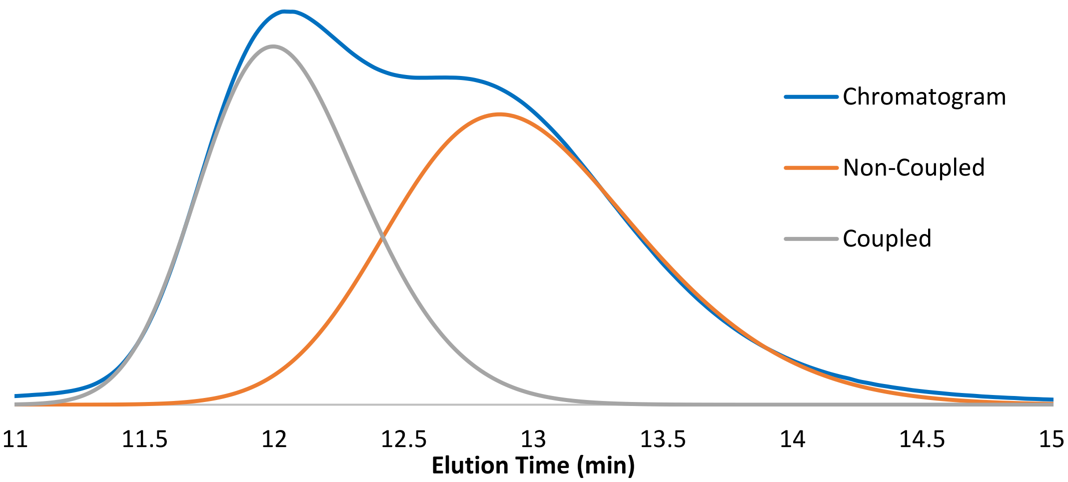


Figure A2. RI chromatogram of PIB4 (blue), fitted curves for coupled distribution (gray) and non-coupled distribution (orange), and the sum of the two fitted distributions (red).

In some cases, a coupled PIB sample was subjected to a partial decoupling reaction, such that the coupled fraction was reduced but not eliminated. In this situation, the second step above could be carried out to generate fitted equations describing the new proportions of coupled and uncoupled species. However, when the fraction of coupled species becomes very small, we found that greater accuracy could be obtained by holding constant the previously determined best-fit parameters, $t_{\max(nc)}$, $\sigma_{(nc)}$, and $a_{(nc)}$ and $t_{\max(c)}$, $\sigma_{(c)}$, and $a_{(c)}$, and using $RI_{\max(c)}$ and $RI_{\max(nc)}$ as the sole fitting parameters.

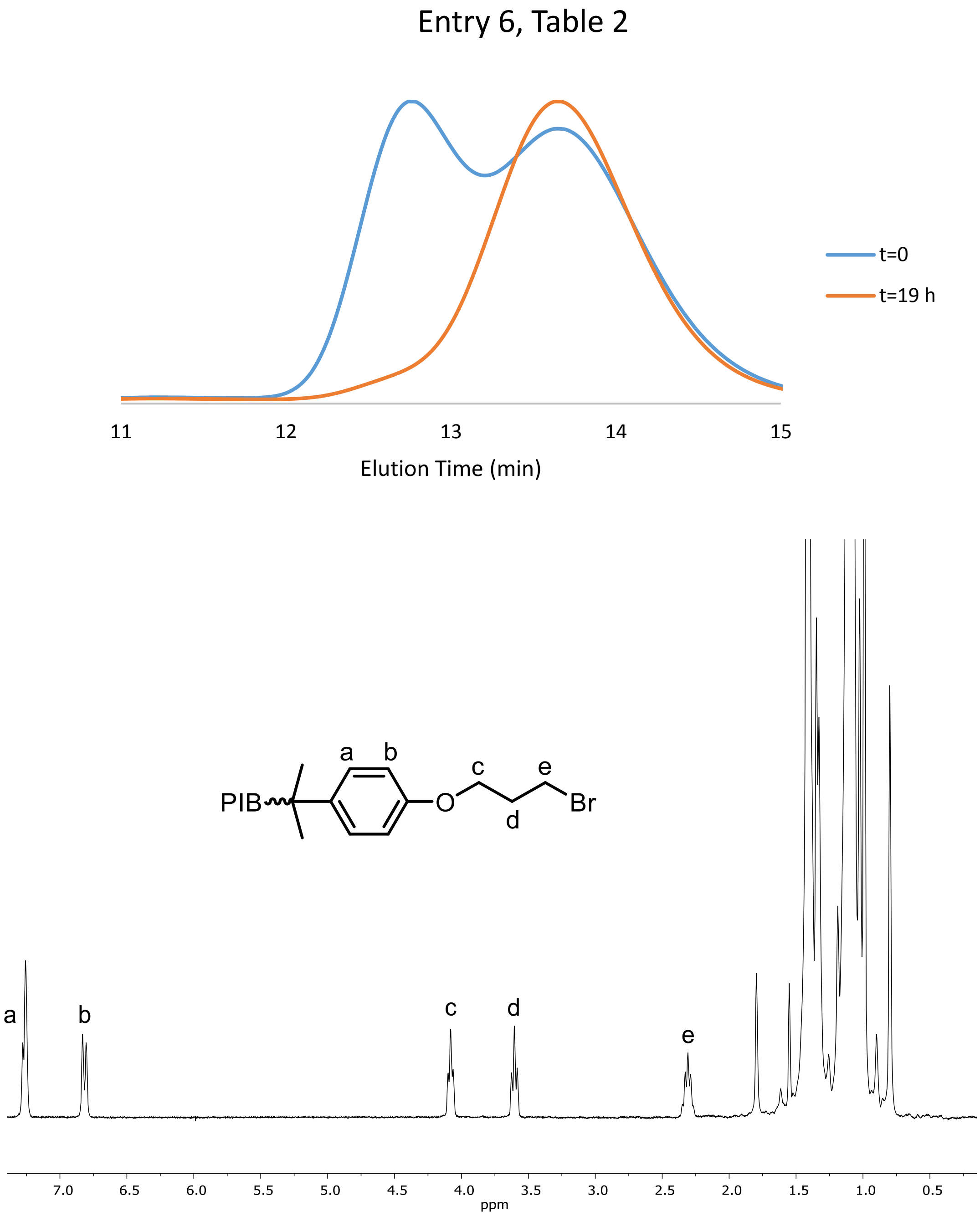


Figure A3. GPC chromatogram (top) and NMR spectrum (bottom) of Entry 6, Table 2: PIB3 quenched/decoupled by reaction with 3-BPB for 19 h with no added protic source.

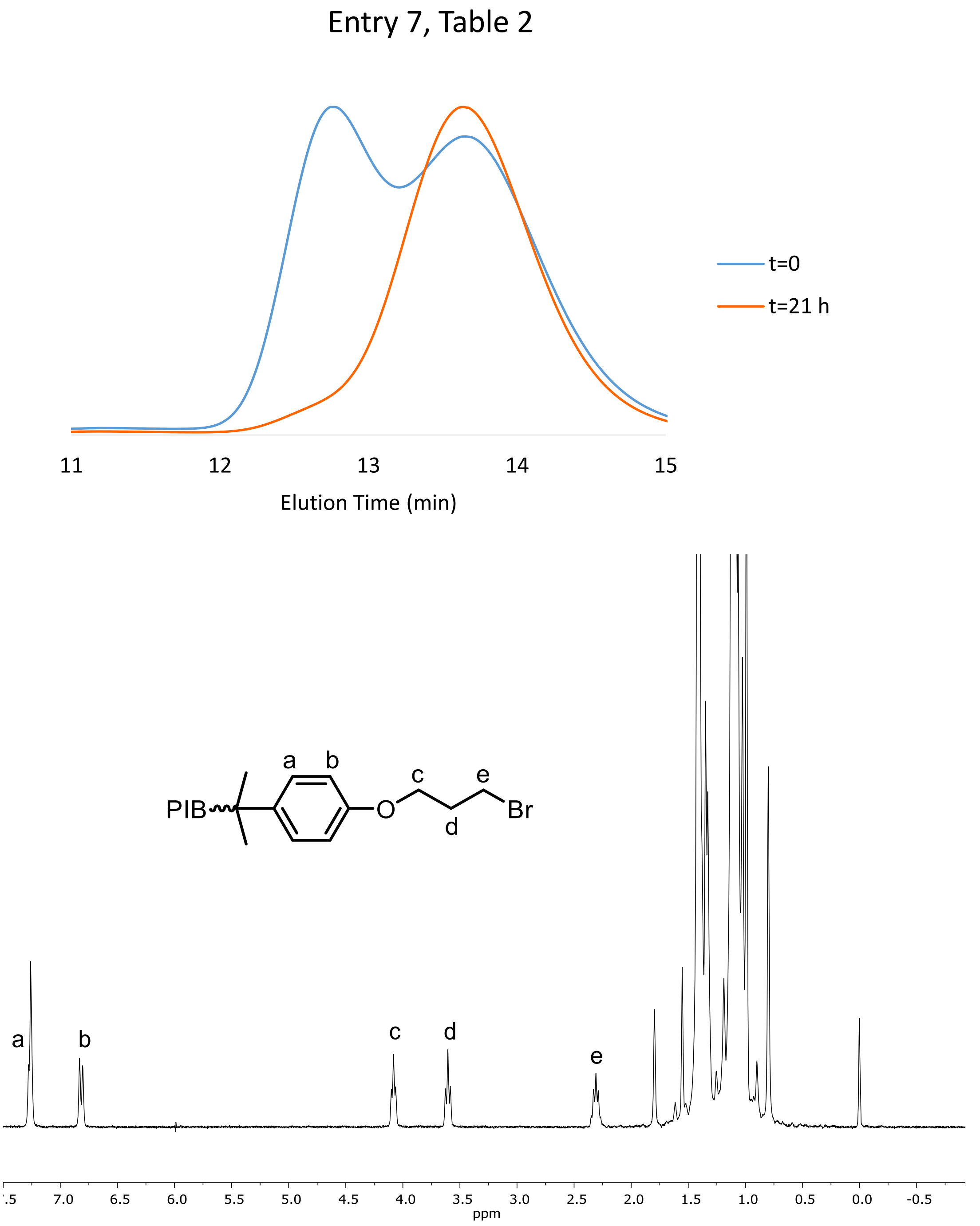


Figure A4. GPC chromatogram (top) and NMR spectrum (bottom) of Entry 7, Table 2: PIB3 quenched/decoupled by reaction with 3-BPB for 21 h with added protic source (6.5 mM H_2O).

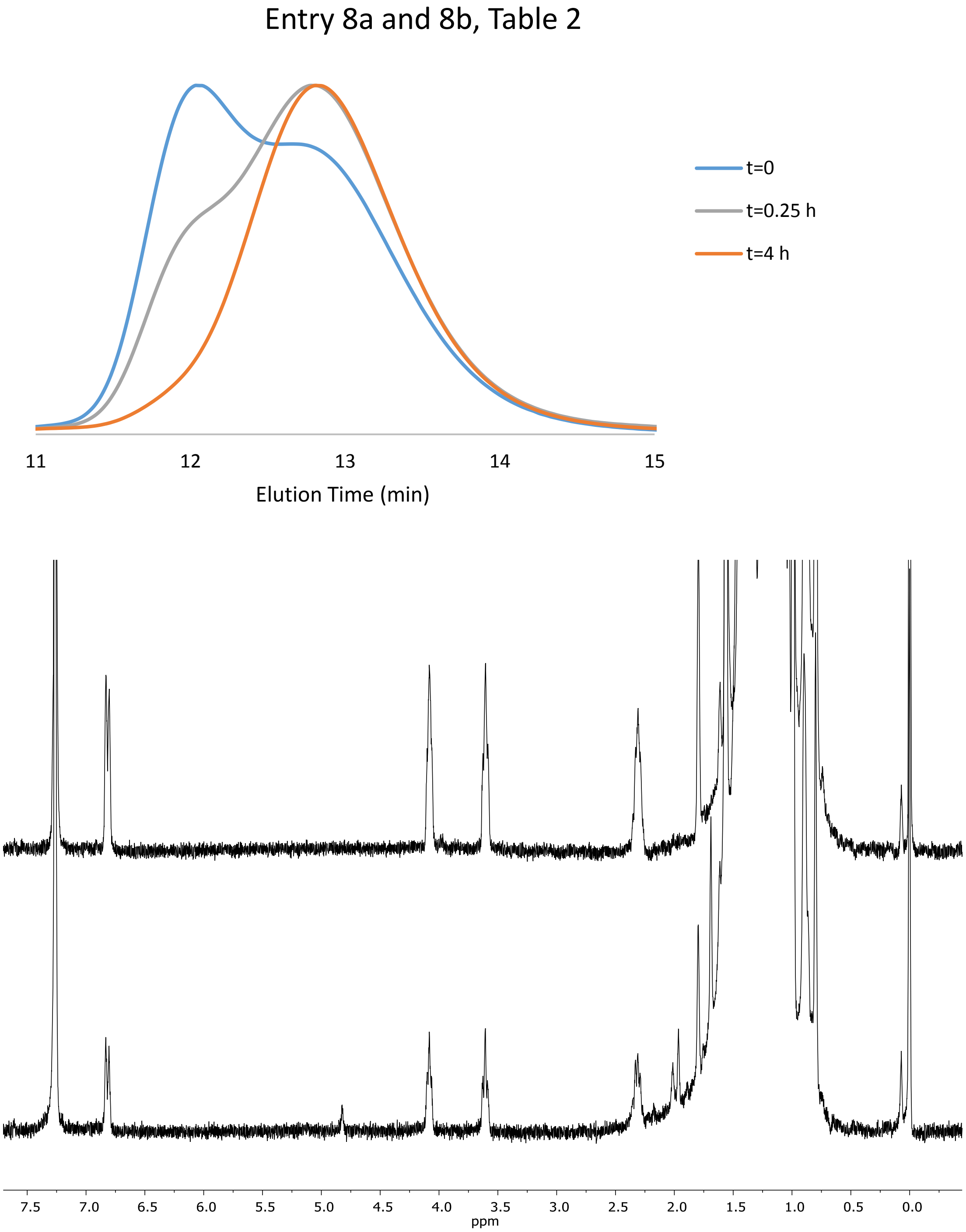


Figure A5. GPC chromatogram (top) and NMR spectrum (bottom) of Entries 8a (lower spectrum) and 8b (upper spectrum), Table 2: PIB4 quenched/decoupled by reaction with 3-BPB for 0.25 h and 4 h with added protic source (15 mM H_2O).

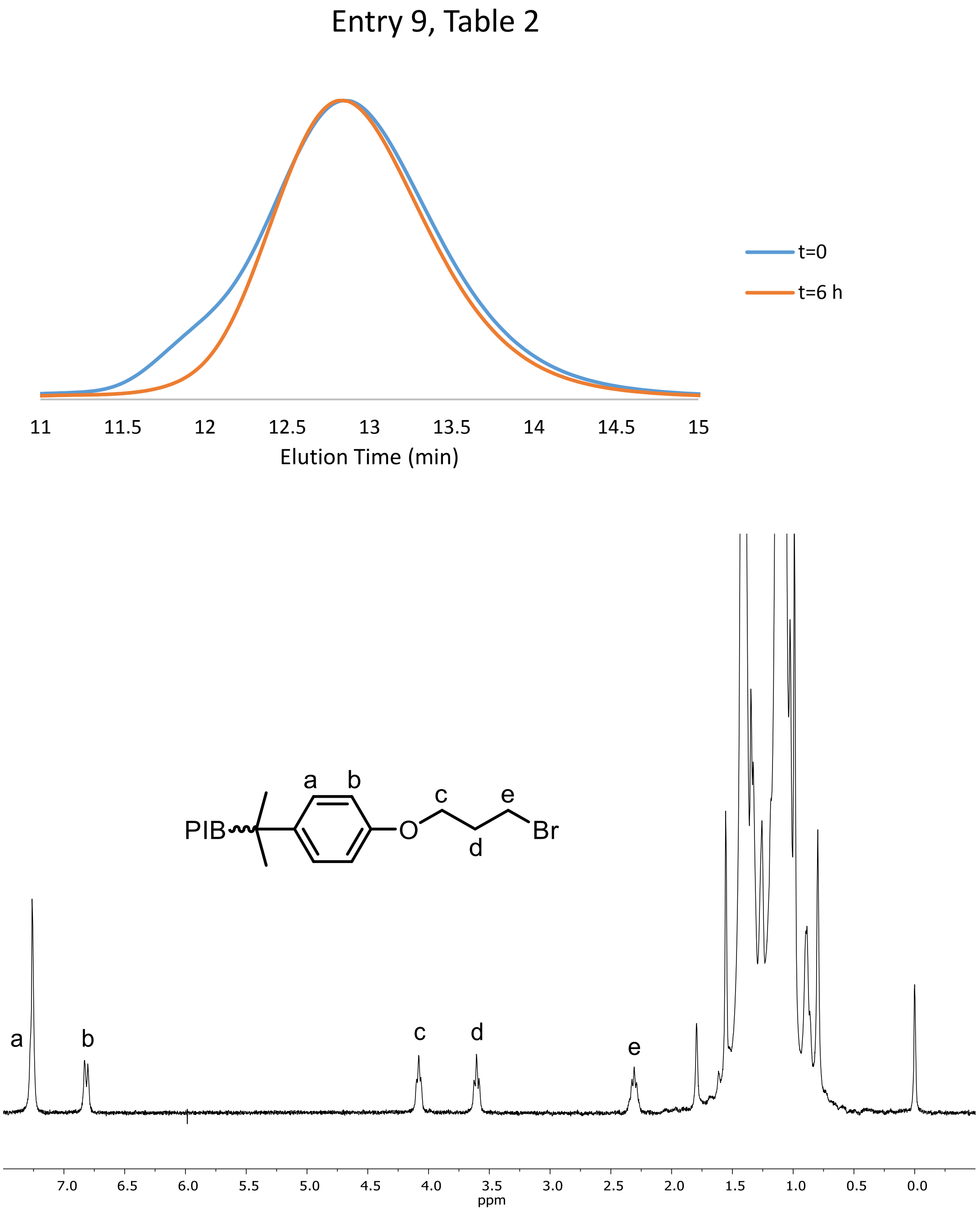


Figure A6. GPC chromatogram (top) and NMR spectrum (bottom) of Entry 9, Table 2: PIB5 quenched/decoupled by reaction with 3-BPB for 6 h with added protic source (16 mM H_2O).

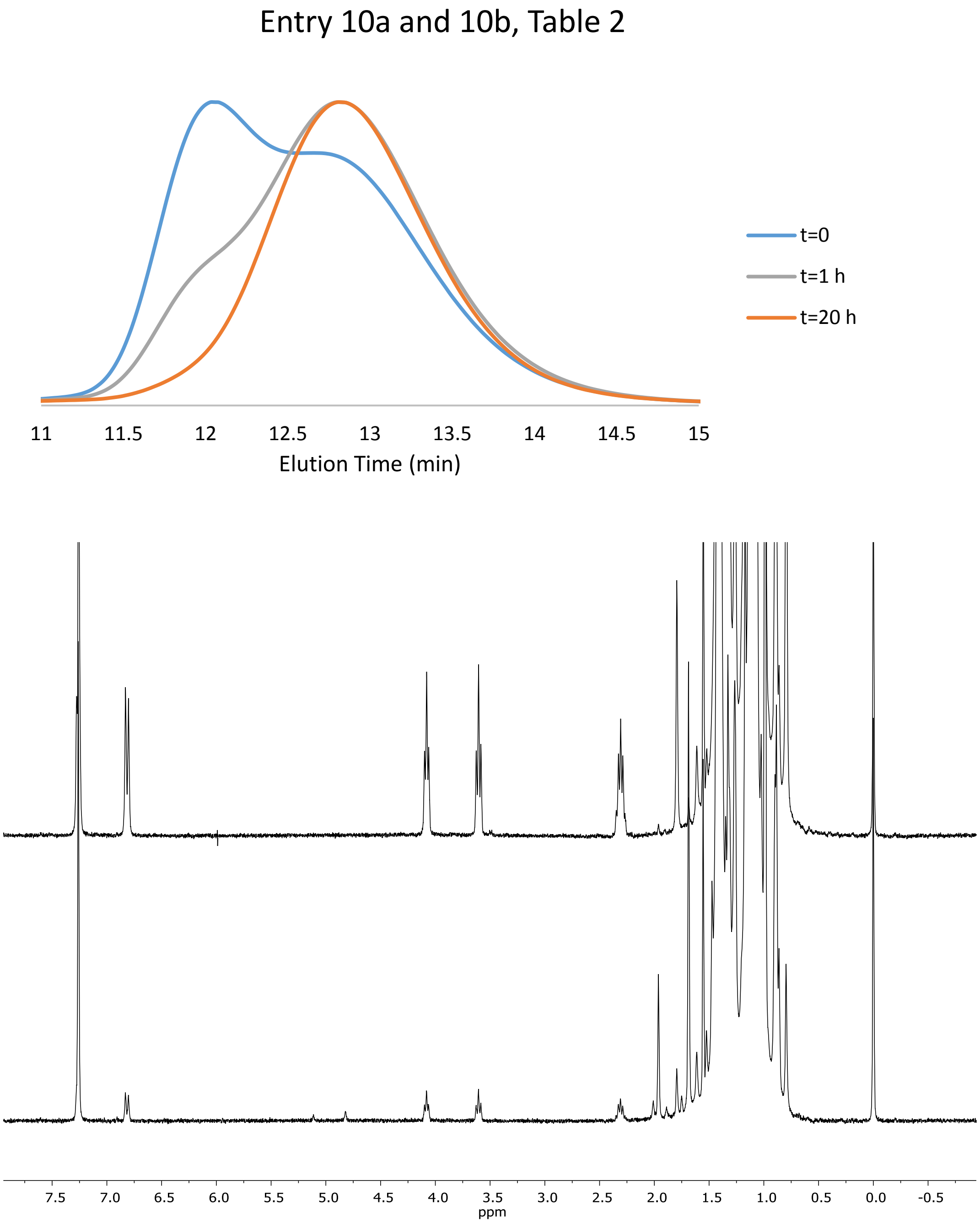


Figure A7. GPC chromatograms (top) and NMR spectra (bottom) of Entries 10a (lower spectrum) and 10b (upper spectrum), Table 2. PIB4 quenched/decoupled by reaction with 3-BPB for 1 h and 20 h with added protic source (6.3 mM H_2O).

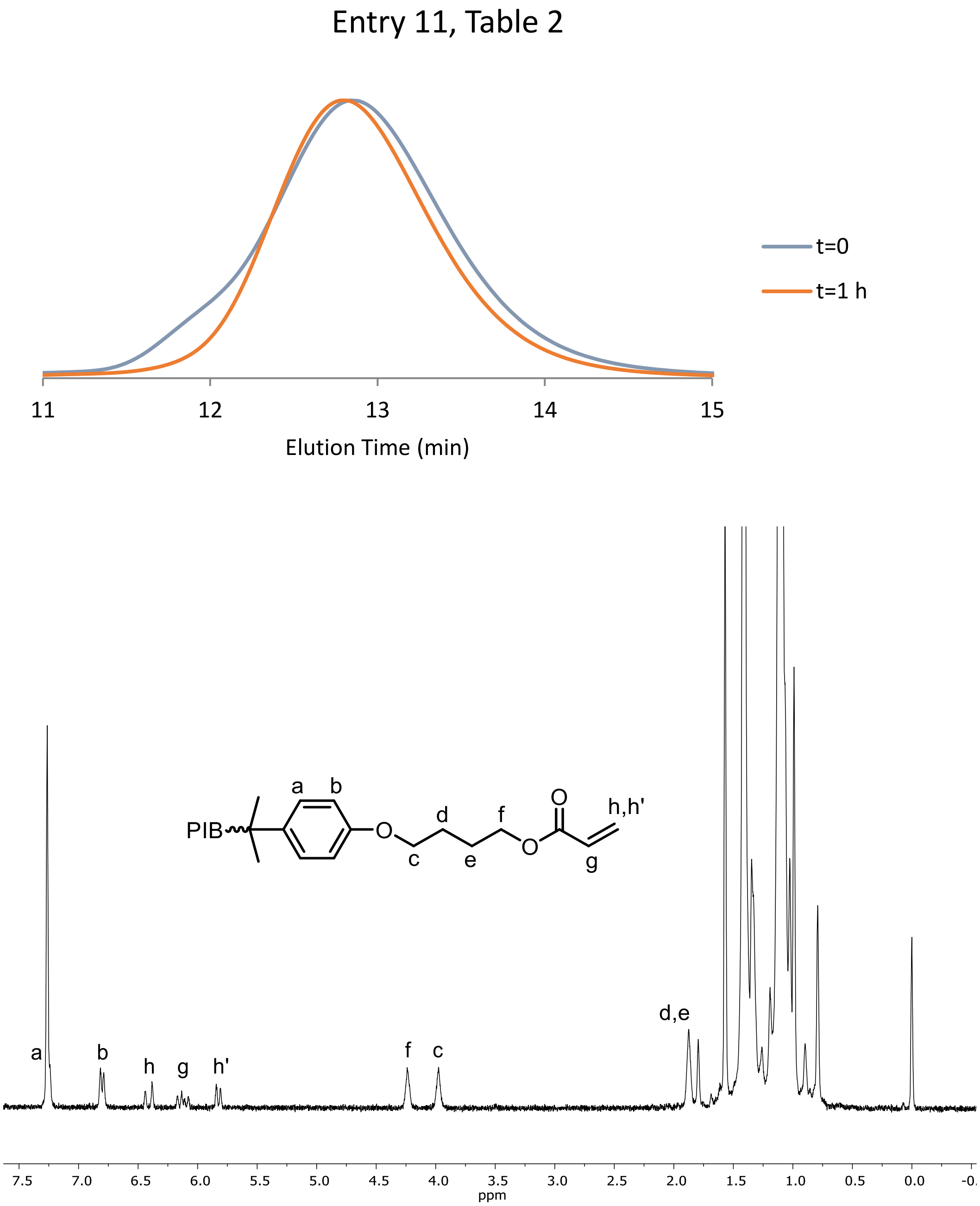


Figure A8. . GPC chromatogram (top) and NMR spectrum (bottom) of Entry 11, Table 2: PIB5 quenched by reaction with 4-PBA for 1h with no added protic source.

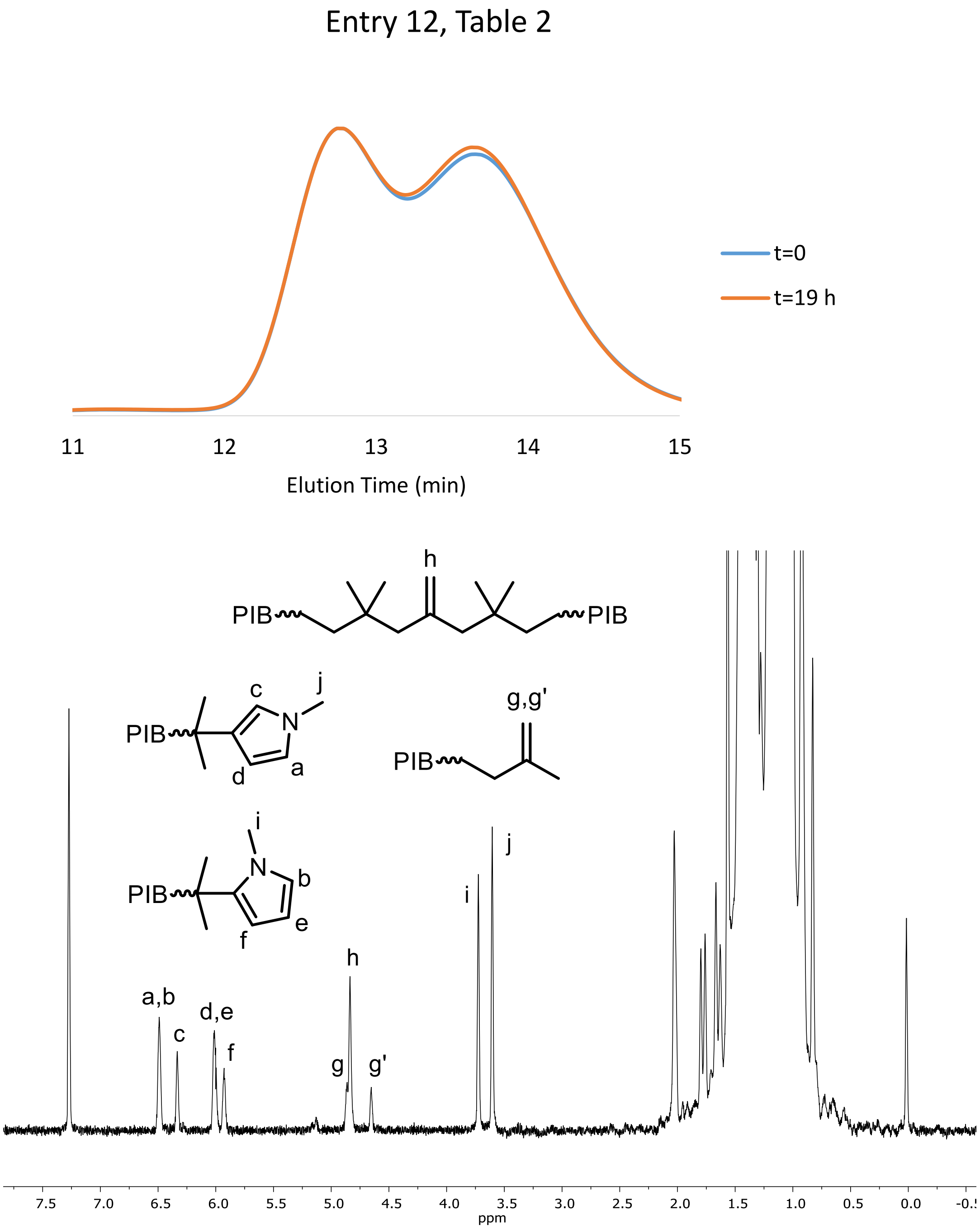


Figure A9. GPC chromatogram (top) and NMR spectrum (bottom) of Entry 12, Table 2: PIB3 quenched by reaction with *N*-MePy for 19 h with no added protic source.

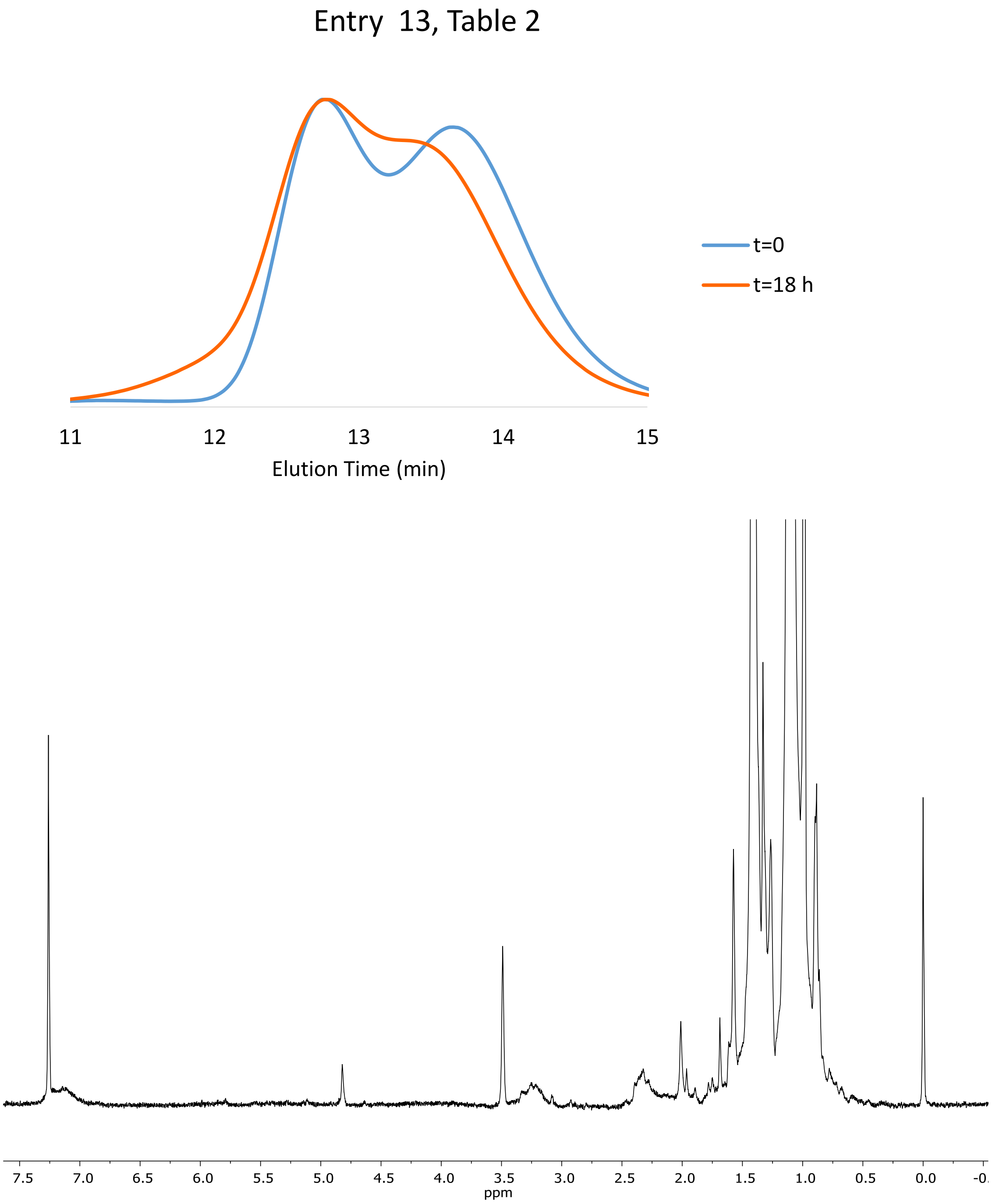


Figure A10. GPC chromatogram (top) and NMR spectrum (bottom) of Entry 13, Table 2: PIB3 quenched by reaction with 2-MeFu for 18 h with no added protic source.

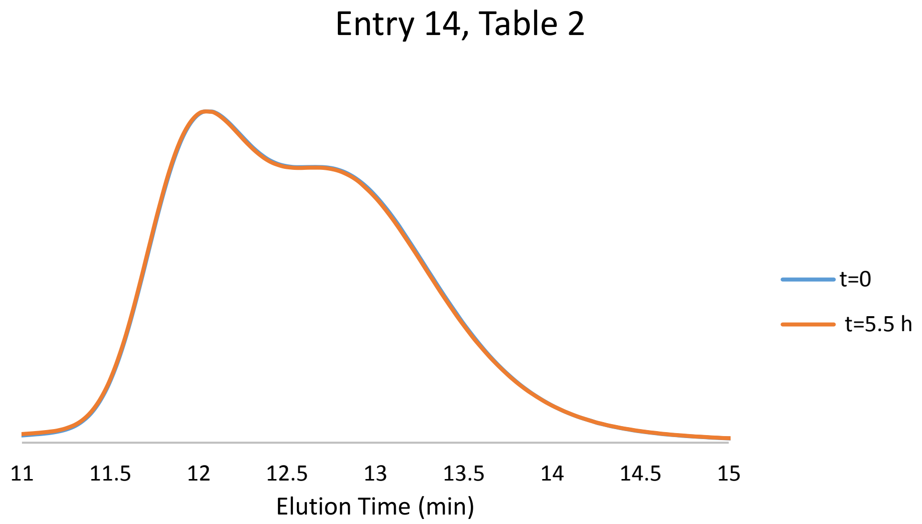


Figure A11. GPC chromatogram of Entry 14, Table 2. PIB4 quenched by reaction with ATMS for 5.5 h with added protic source (15 mM H_2O).

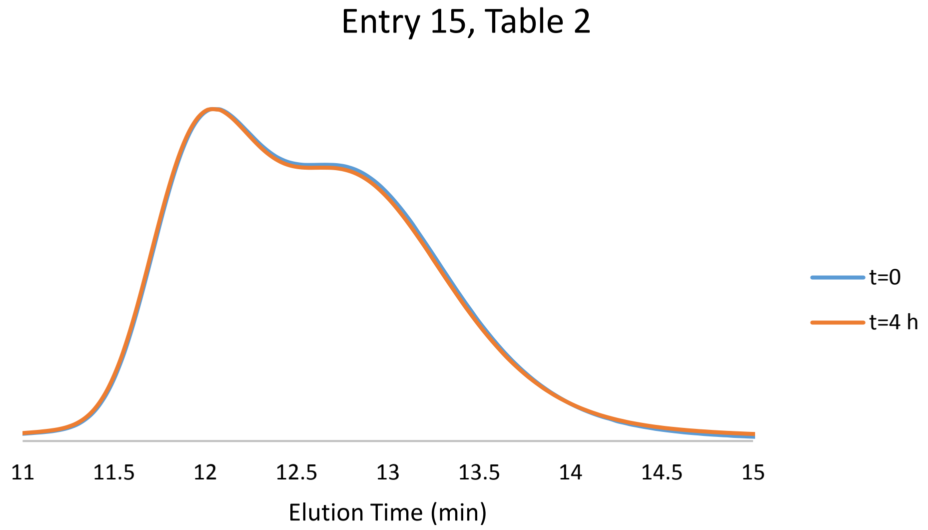


Figure A12. GPC chromatogram of Entry 15, Table 2. PIB3 quenched by reaction with MATMS for 4 h with added protic source (14 mM H_2O).

APPENDIX B
Correction of Reaction Volume for Thermal Expansion

Solvent volumes at reaction temperature were calculated according to equation AB-1, where V_f and V_i are the final and initial volumes of solvent respectively, and a, T_c, and m are solvent-specific thermal expansion parameters.[1] A solvent-composition-weighted thermal expansion parameter was then calculated and applied to the entire reaction volume. These calculated reaction volumes were used to determine concentration values in Table 2.

$$\frac{V_f}{V_i} = \exp\left[\int_i^f a(1 - T/T_c)^m \, dT\right] \qquad \text{(AB-1)}$$

Calculation of X_C, X_{EQ}, and Ideal IB/Q Ratio

The starting butyl rubber copolymer was treated as possessing an idealized structure consisting of IB homopolymer sequences separated by single IP units, and infinite molecular weight ($x \rightarrow \infty$) such that original end groups in the starting copolymer could be ignored:

$$\left[-\!\left(\mathrm{IB}\right)_{n_{IB}}\!-\!\!-\mathrm{IP}- \right]_x$$

From the measured mole fraction of IP units in the starting copolymer (F_{IP}), measured by ^{1}H NMR, the average IB homopolymer sequence length, n_{IB}, was calculated according to eq AB-2, assuming isolated IP units.

$$n_{IB} = \frac{1 - F_{IP}}{F_{IP}} \qquad \text{(AB-2)}$$

The IP equivalent weight, EW_{IP}, was calculated according to eq AB-3,

$$EW_{IP} = n_{IB}M_{IB} + M_{IP} \cong 2.45 \times 10^3 \text{ (g/mol)} \qquad \text{(AB-3)}$$

where M_{IB} and M_{IP} are the molecular weights of the IB repeat unit (56.1 g/mol) and the IP repeat unit (68.1 g/mol), respectively.

The polymer after degradation was treated as possessing an idealized structure consisting of N_S IB homopolymer sequences, $(N_S - 1)$ non-cleaved IP units, and one cleaved IP unit:

$$\mathrm{Y}\!\left[\!-\!\left(\mathrm{IB}\right)_{n_{IB}}\!-\!\mathrm{Z}\!-\!\right]_{N_S - 1}\!-\!\left(\mathrm{IB}\right)_{n_{IB}}\!-\!\mathrm{Y}$$

The unit Z is either an unreacted IP unit, a backbone-quenched IP unit, or an IP unit that has reacted via a pathway other than quenching (e.g. rearrangement). The unit Y is an end group created by cleavage of an IP unit and may or may not have reacted with a quencher (Q) (i.e., alkoxybenzene) molecule.

From the number average molecular weight (M_n) of the polymer after degradation, determined by GPC/MALLS, the average number of IB homopolymer segments per degraded polymer molecule, N_S, was calculated using eq AB-4,

$$N_S = \frac{M_n\left(1 - \dfrac{M_Q}{EW_Q}\right)}{EW_{IP}} \tag{AB-4}$$

From a consideration of the structure of the degraded polymer, it is apparent that the fraction of IP units cleaved, X_C, is reciprocally related to N_S:

$$X_C = \frac{1}{N_S} \tag{AB-4}$$

The IB/Q mole ratio of the degraded polymer, determined by ^{1}H NMR, has the following functional relationship,

$$\frac{IB}{Q} = \frac{N_S}{2X_{EQ}+N_S-1} n_{IB} \tag{AB-5}$$

where, X_{EQ} is the fraction of Y units that have successfully quenched. In the ideal case, when $X_{EQ} = 1$, we have:

$$\left(\frac{IB}{Q}\right)_{ideal} = \frac{N_S}{N_S+1} n_{IB} \tag{AB-6}$$

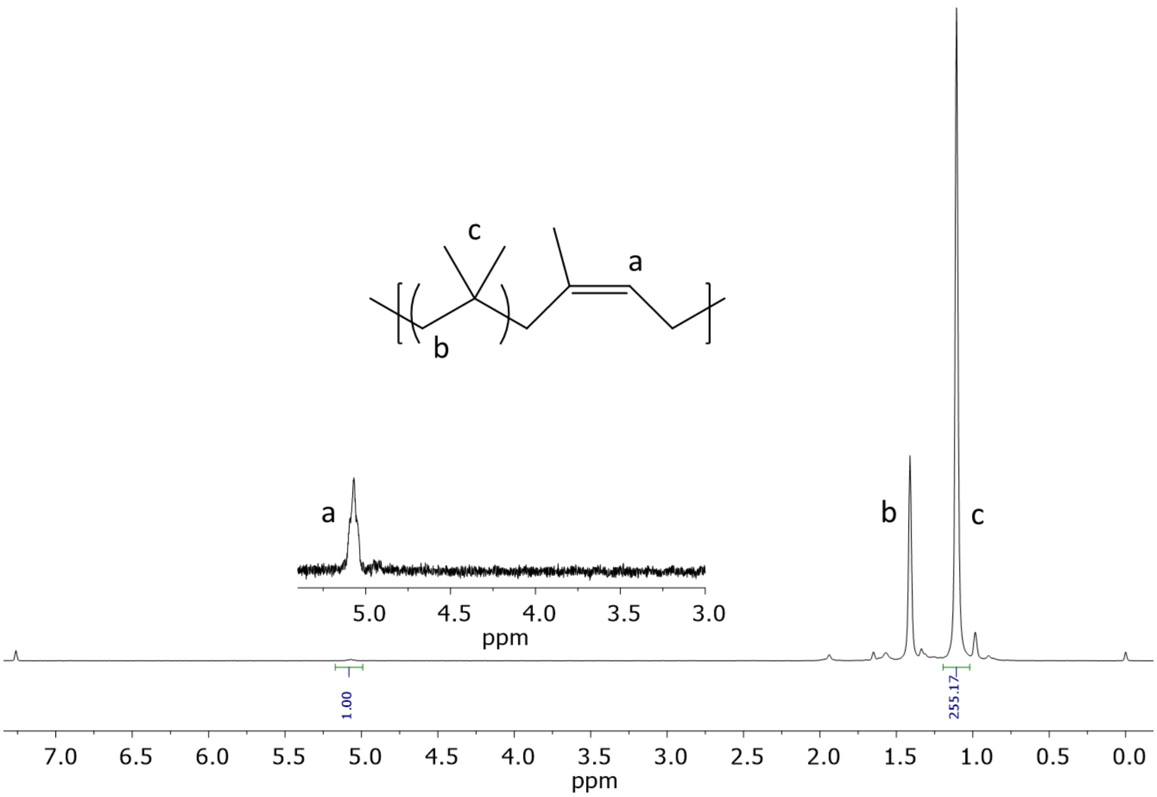


Figure A1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 23°C) of butyl rubber (EXXON™ Butyl 365) used in this work.

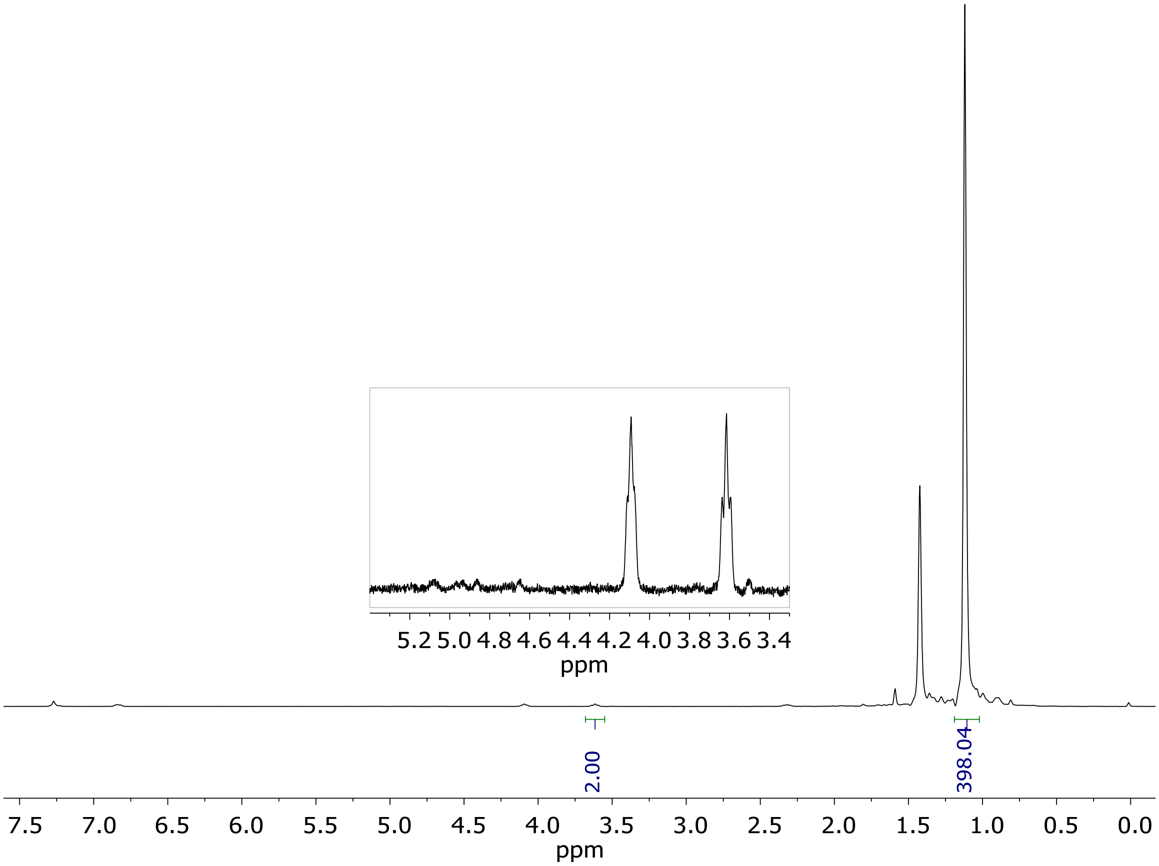


Figure A2. ^{1}H NMR spectrum (300 MHz, CDCl$_3$, 23°C) of the product of Entry 6 in Table 3.

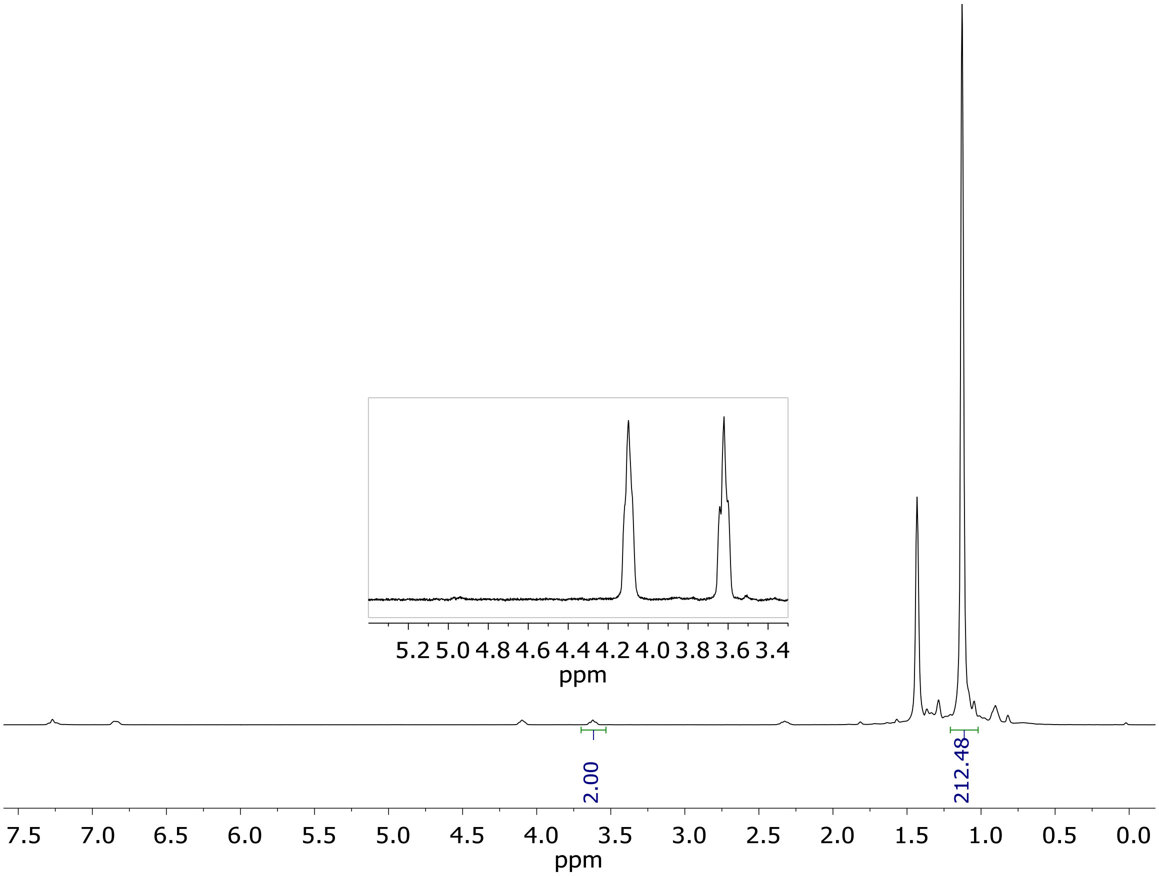


Figure A3. ^{1}H NMR spectrum (300 MHz, $CDCl_3$, 23°C) of the product of Entry 7 in Table 3.

References

1. Coker, A.K. Ludwig’s Applied Process Design for Chemical and Petrochemical Plants, Volume 2, 4th Edition. **2010**. 2(4) 757-792.

APPENDIX C

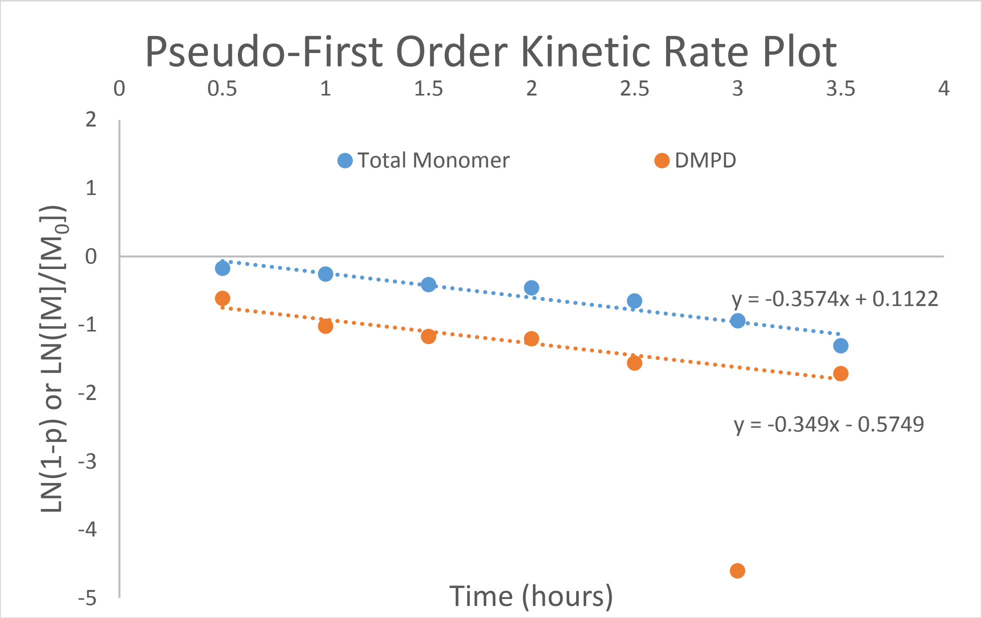


Figure A1. Pseudo-first-order kinetic plot of the data presented by Kennedy *et al.*[1]

The point in the DMPD series at 3 h should be ignored as it is likely the result of a typographical error in the original manuscript.

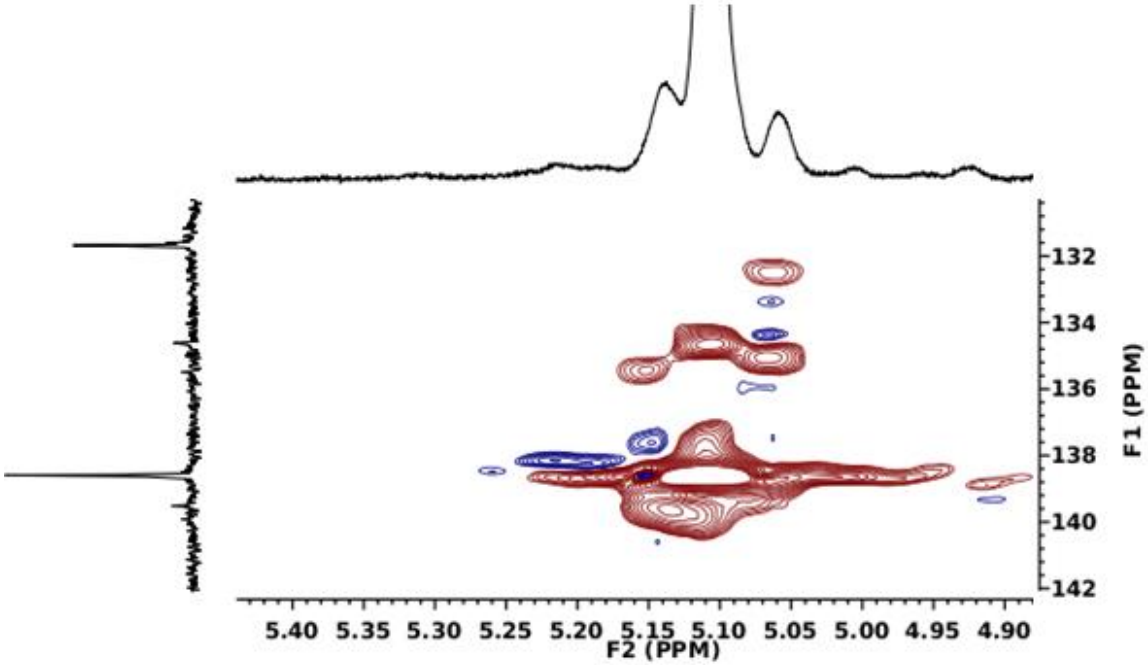


Figure A2. HSQC 2-D NMR spectrum of the olefinic region of a representative poly(IB-*co*-DMPD), Entry 4b, Table 2.

Figure A4-2 shows the expected correlation between the olefinic proton resonance at 5.11 ppm and the olefinic carbon resonance at 138.64 ppm. Furthermore, a correlation exists between the proton resonance at 5.14 ppm and a carbon at 139.56 ppm. We have assigned the proton at 5.14 ppm and the carbon at 139.56 ppm to the final DMPD unit of a homo-DMPD block prior to polymerization of IB initiated by polyDMPD.

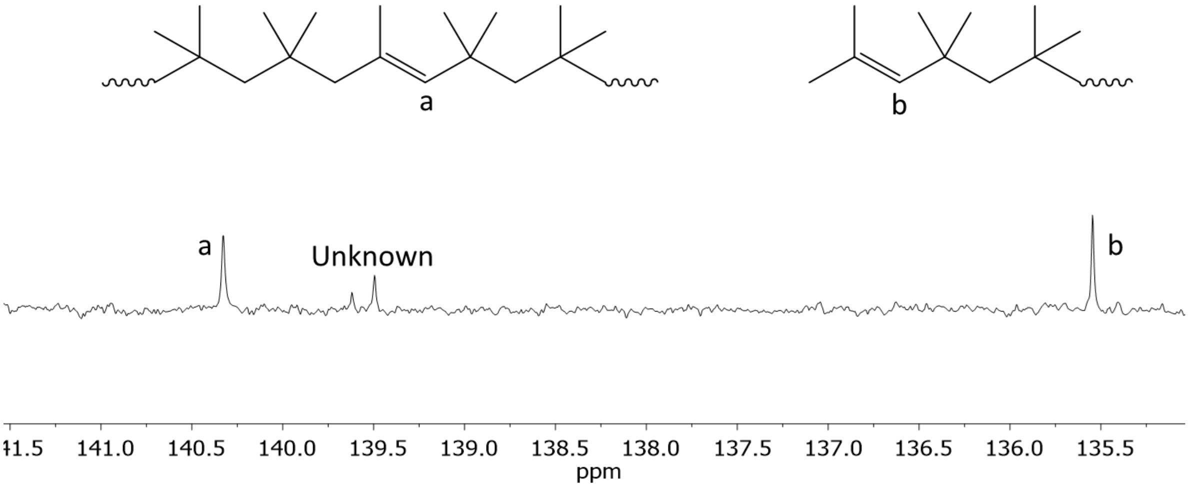


Figure A3. ^{13}C NMR spectrum (125 MHz, CDCl$_3$, 23°C) of a PIB sample containing *endo*-coupled PIB (140.33 ppm) and *endo*-olefin PIB structures (135.55 ppm).

The identity of the peaks near 139.5 are unknown, but likely belong to a number of possible rearranged species. The high amount of noise in the baseline is due to low population of these functionalities in the polymer.

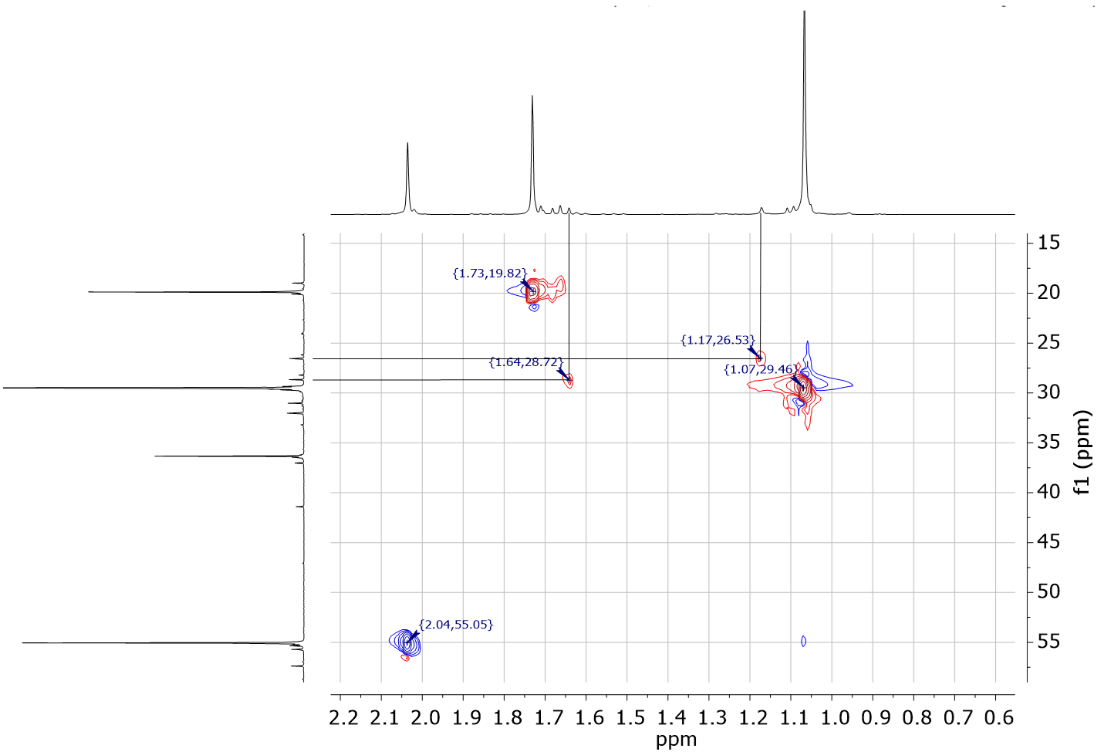


Figure A4. HSQC 2-D NMR spectrum of the aliphatic region of poly(DMPD).

Red indicates a positive correlation and means that the carbon is bonded to an odd number of protons, while blue represents a negative correlation and means that the carbon is bonded to an even number of protons. The carbon resonances at 26.53 ppm and 28.72 ppm represent carbons possessing an odd number of protons. As there is not a feasible mechanism for the formation of aliphatic methine groups in this polymer, we have assigned these resonances to methyl groups.)

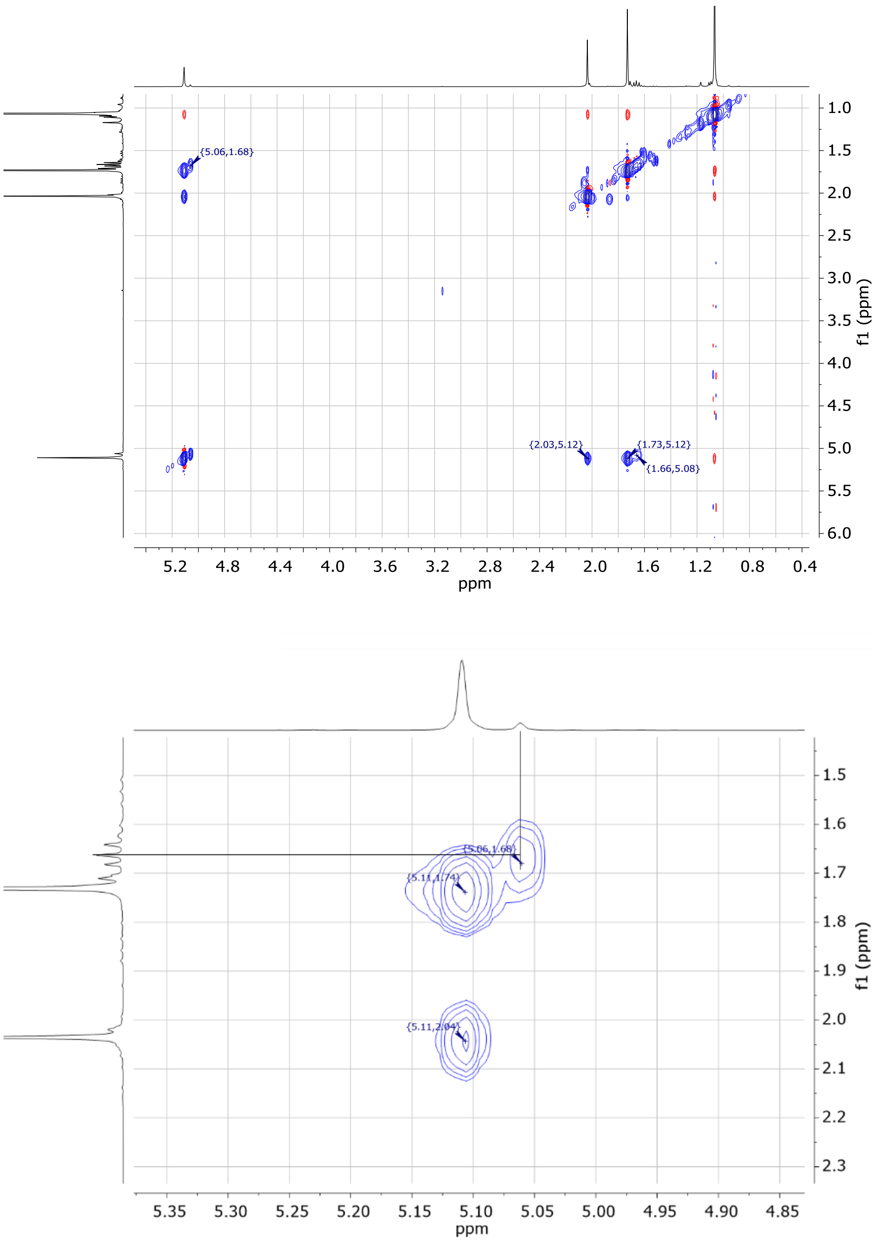


Figure A5. TOCSY 2-D NMR spectrum of poly(DMPD): (top) entire range, (bottom) aliphatic-olefinic correlations. The olefinic proton resonance at 5.06 ppm shows a positive correlation with the resonance at 1.68 ppm indicating that these two protons are within 3-4 bonds of each other.

The olefinic proton at 5.11 ppm (a) correlates to the methylene protons at 2.04 ppm (c) and the methyl protons at 1.74 ppm (d). The olefinic proton at 5.11 ppm (a) does not show a correlation with the gem dimethyl protons at 1.07 ppm (g), even though the number of bonds separating them (4) is the same as the number of bonds separating protons (a) and (c), as well as (a) and (d) (Figure A4-5a). This is due to the allylic splitting between proton (a) and protons (c) and (d), which is not present between proton (a) and proton (g).

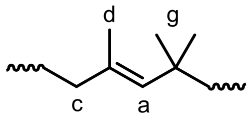
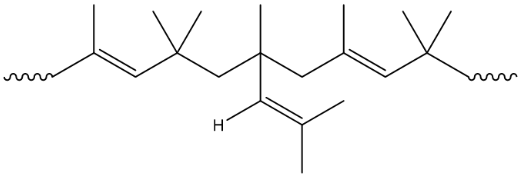


Figure A6. Illustration of the 1,4 repeat unit of polyDMPD with protons labels.

The resonance at 5.06 ppm only correlates to the resonances around 1.64 ppm, which have been shown to belong to methyl groups. The most reasonable explanation for this would be 1,2 addition of the monomer. When DMPD adds in a 1,2 fashion, only allylic methyl protons are present. In contrast, if an intramolecular methide shift were to occur resulting in a branch point, the resulting structure would contain both allylic methyl and allylic methylene structures and the olefinic proton would be expected to show a correlation in the TOCSY NMR spectrum to each of these structures in the same way as the 1,4 mode of addition behaves (Figure A4-5b).


1,2-addition

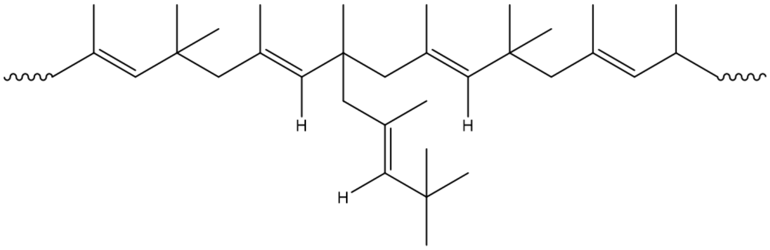

Potential intramolecular methide shift

Figure A7. Illustration of the structures resulting from 1,2 addition of DMPD (top) and branching due to intramolecular methide shift (bottom).

References

1. Kaszas, G.; Puskas, J.E.; Kennedy, J.P. Carbocationic Copolymerization in the Presence of Electron Pair Donors. 2. Copolymerization of Isobutylene and Isoprene or 2,4-Dimethyl-1,3-pentadiene with TiCl4-Based Initiating Systems Yielding in Situ Electron Pair Donors. *Macromolecules* **1992**, *25*(6), 1775-1779.

APPENDIX D

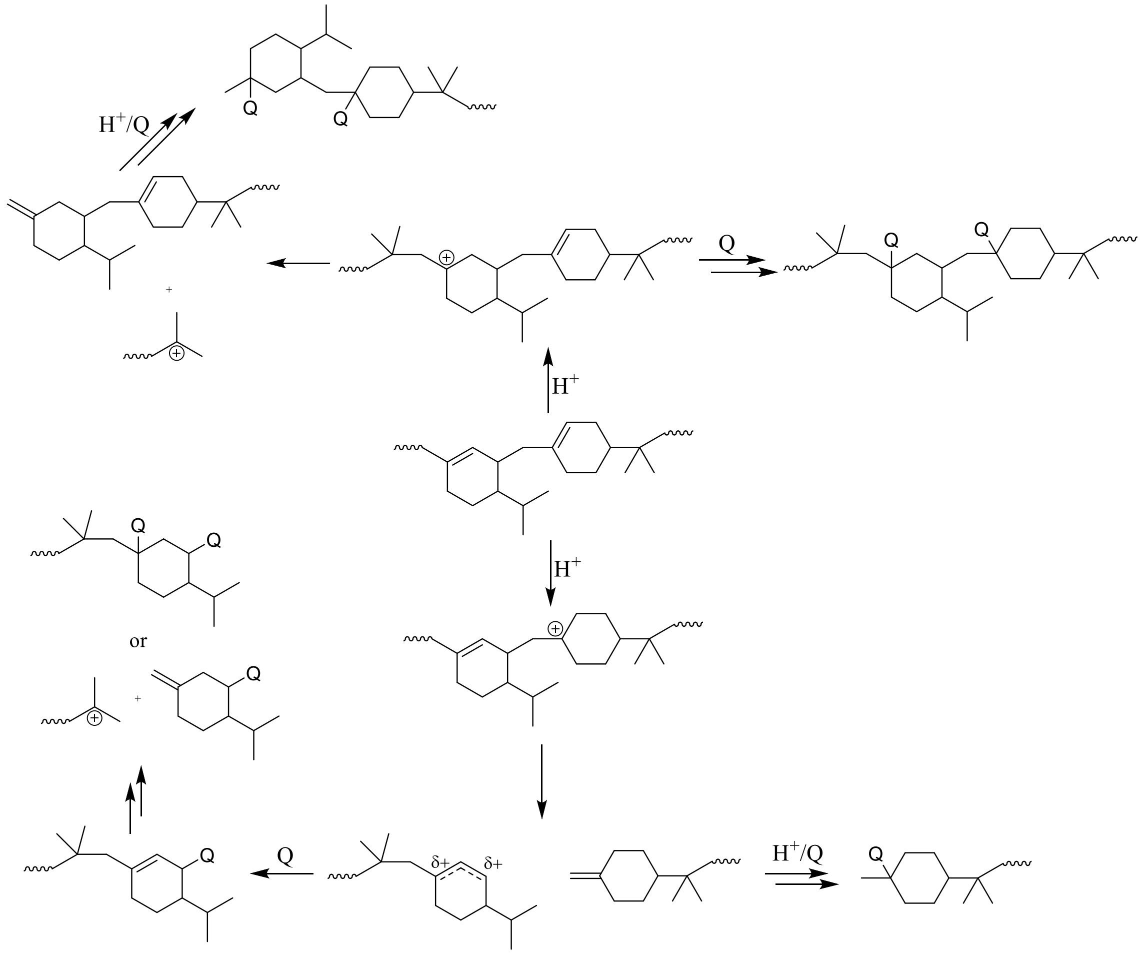


Figure A1. All possible mechanistic routes following protonation of the lower right structure of scheme 15.

If protonation follows the top path, cleavage between the two pinene units cannot occur. If protonation follows the bottom path, cleavage is likely to rapidly occur due to the enthalpic favorability of the methallylic carbocation. In this scheme the counter ion to all carbocations and protons is the anionic chloride of the Lewis acid (LA-Cl$^-$). Q=alkoxybenzene.