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Synthesis of *exo*-Olefin Terminated Polyisobutylene by Sulfide/Base Quenching of Living Polyisobutylene

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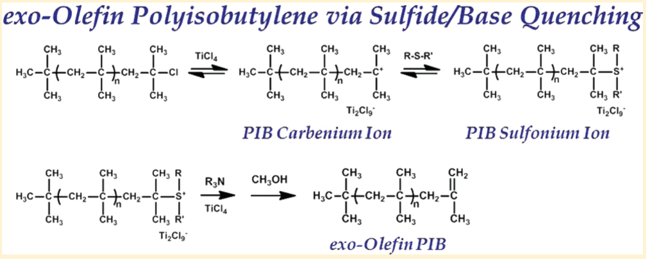
Supporting Information



ABSTRACT: *exo*-Olefin (methyl vinylidene)-terminated polyisobutylene (PIB) was synthesized in one pot by quenching $TiCl_4$-catalyzed living PIB with a dialkyl (or) diaryl sulfide at −60 to −40 °C, followed by addition of a base (*e.g.*, triethylamine), followed by warming of the reaction mixture to −20 to −10 °C and final termination with methanol. The initiator was 2-chloro-2,4,4-trimethylpentane (TMPCl); the solvent system was 60/40 hexane/methyl chloride, and 2,6-lutidine was used as a nucleophilic additive during polymerization. ^1H NMR spectroscopy was used characterize end-group composition of the product PIBs. Increasing yield of *exo*-olefin end groups was observed in the approximate order of increasing bulkiness of the substituent on the sulfide, *i.e.*, *tert*-butyl (100%) > isopropyl (98%) > phenyl (70%) > *n*-alkyl (39−55%). With diisopropyl sulfide (DIPS), optimized yield of *exo*-olefin (98%) required stoichiometric excess of DIPS relative to chain ends (CE), e.g., [DIPS]/[CE] = 4, addition of a base, and warming of the reaction prior to addition of methanol. With di-*tert*-butyl sulfide (D*t*BS), optimized yield was obtained with lesser stoichiometric excess, e.g., [D*t*BS]/[CE] = 1.5, with or without addition of a base, and with or without warming of the reaction prior to methanol termination. D*t*BS yielded 100% *exo*-olefin end groups under concentrated conditions, e.g., [CE] = 0.1 M, and 98% *exo*-olefin when the reaction was up-scaled to produce 0.8 kg of PIB. The method was successfully adapted to the synthesis of *telechelic* (difunctional) *exo*-olefin terminated PIB with quantitative functionality (100%).

INTRODUCTION

Low molecular weight olefin-terminated polyisobutylene (PIB) is of great commercial and scientific interest.[1] PIB-succinic anhydride (PIBSA),[2] a notable commercial intermediate critical toward the synthesis of dispersants for lubricating oils, is formed by the thermal ene reaction of maleic anhydride with low molecular weight *exo*-olefin (methyl vinylidene)-terminated PIB.[3,4] Commercial PIBs used in this process are formed in a chain transfer-dominated polymerization process and possess a single unsaturated terminus comprising mixed olefinic isomers, with the desired *exo*-olefin isomer occurring on 70−90% of the chains in BF_3-catalyzed polymerizations.[5] By its nature, the commercial process cannot be used to produce difunctional (*telechelic*) olefin-terminated PIB.

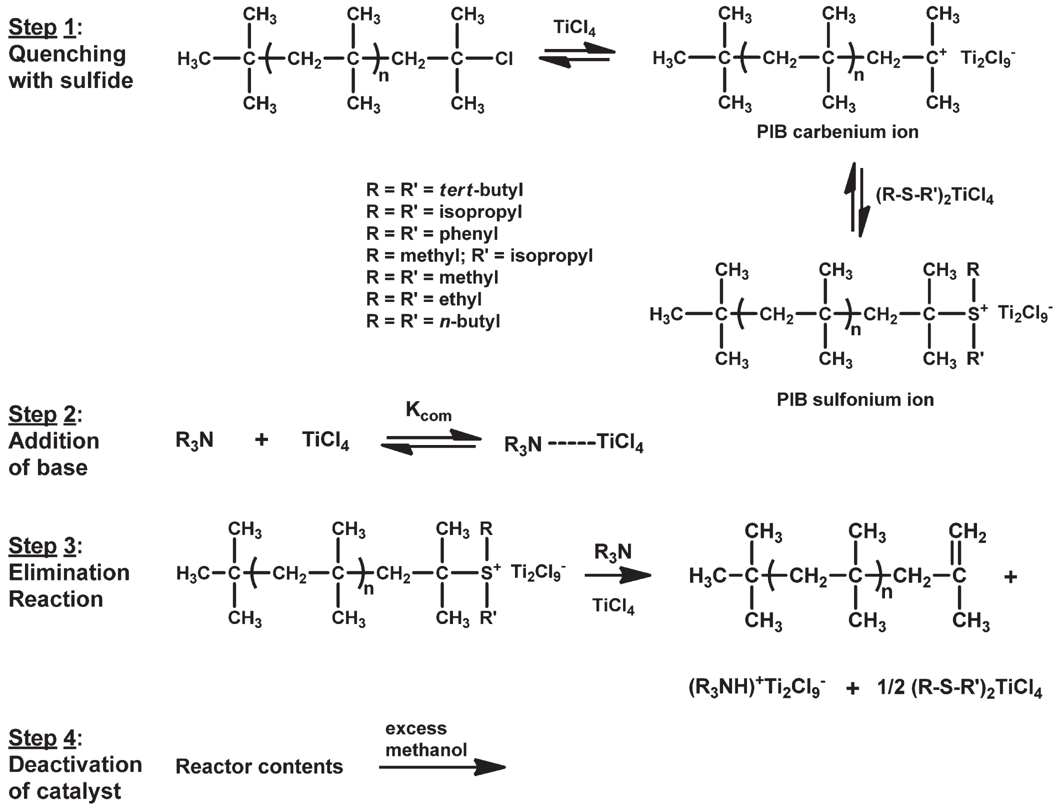
A number of methods have been reported, which enable the synthesis of both monofunctional and difunctional PIBs with near-quantitative *exo*-olefin functionality. In an oft-quoted paper, Kennedy et al. introduced a method that was to become the standard route to di- and polyfunctional olefin-terminated PIB for many years.[6] Theirs was a two-step method, wherein *tert*-chloride-terminated PIB was first synthesized via the inifer method,[7] and then regiospecific dehydrochlorination of the chain ends was carried out by reaction with a strong base, such as potassium *tert*-butoxide[6] or alkali ethoxides[8] in refluxing THF for 20−24 h. However, it was later shown that this process does not produce exclusively *exo*-olefin chain ends, but also leads to 5−8% *endo*-olefin.[9]

Kennedy and co-workers[10,11] also reported the first *in situ* synthesis of olefin-terminated PIB, by addition of allyltrimethylsilane to a living carbocationic polymerization of isobutylene (IB). This functionalization chemistry eventually formed the basis for the commercial sealant, EPION, marketed by Kaneka.[12] In 1997, Nielsen and co-workers showed that difunctional *exo*-olefin PIB could be made in an analogous process using methallyltrimethylsilane.[13]

In 2005, Storey and co-workers reported a novel *in situ* quenching method yielding quantitative *exo*-olefin PIB through controlled elimination rather than addition. They showed that living PIB may be reacted with certain hindered bases, such as 2,5-dimethylpyrrole and 1,2,2,6,6-pentamethylpiperidine, to

Received: July 26, 2011
Revised: September 8, 2011
Published: September 21, 2011

Scheme 1. Formation and Decomposition of PIB Sulfonium Ion Salt



produce *exo*-olefin termini directly from the polymerization reaction.[14] The principle limitation of the method was reported to be formation of coupled PIB at high chain end concentrations. Subsequently, Storey and Kemp showed that similar results could be obtained by quenching living PIB with an alkoxysilane or alkyl ether.[15]

Recently, Storey et al. reported that organic sulfides were effective *in situ* quenchers for the production of *exo*-olefin PIB.[16] They showed that when a dialkyl or diaryl sulfide is added to a $TiCl_4$-catalyzed living polymerization of isobutylene, it immediately forms a complex with $TiCl_4$, and this complex reacts with the carbenium ions as they are formed (monomer consumption ceases), to yield the corresponding sulfonium ion (Scheme 1, step 1). The sulfonium ions thus obtained were shown to be stable at low temperatures ($T \leq 20$ °C), and their structures were characterized by NMR spectroscopy. Subsequent addition of a base, such as an amine or an alcohol (steps 2 and 3), followed by Lewis acid decomposition with methanol (step 4), was shown to cause decomposition of the adduct to form predominantly *exo*-olefin, but also minor amounts of other chain end products, depending on conditions, including *endo*-olefin, *tert*-chloride, methyl ether (from methanol termination), and coupled PIB.[17]

The various methods outlined above vary with regard to expense, ease of execution and how closely the product approaches the theoretical ideal of 100% *exo*-olefin end groups. In the present study, we have further investigated the sulfide quenching method discussed above, to achieve a better mechanistic understanding of the process and to develop reaction conditions yielding exclusively *exo*-olefin terminated PIB (mono and difunctional), particularly under conditions of high chain end concentration, which tend to promote coupling. The effect of sulfide structure, base, chain-end concentration, and termination temperature on the PIB end-group composition will be discussed.

■ EXPERIMENTAL SECTION

Materials. Hexane (anhydrous), 2,6-lutidine, titanium tetrachloride, methanol (anhydrous), chloroform-*d*, diisopropyl sulfide (DIPS), dimethyl sulfide, diethyl sulfide, di-*n*-butyl sulfide, diphenyl sulfide, isopropyl methyl sulfide, triethylamine, 2,5-dimethylpyrrole, 1,2,2,6,6-pentamethylpiperidine, and dichloromethane were used as received from Sigma-Aldrich. Di-*tert*-butyl sulfide (D*t*BS) was used as received from TCI America. Sodium carbonate and magnesium sulfate were used as received from Fisher Scientific. The source and purity of isobutylene (IB) and methyl chloride (MeCl) and the syntheses of 2-chloro-2,4,4-trimethylpentane (TMPCl) and 1,3-bis(2-chloro-1-methylethyl)-5-*tert*-butylbenzene (bDCC) have been reported.[18]

ATR-FTIR Spectroscopic Monitoring. Isobutylene consumption during polymerization was monitored using ATR-FTIR spectroscopy as previously described.[14]

Isobutylene Polymerization and Quenching. A representative polymerization and quenching reaction, performed within a N_2-atmosphere glovebox, was as follows. Hexane (60 mL) and methyl chloride (40 mL) were chilled to −60 °C and charged to a 300 mL round-bottom flask. To this mixture were added 0.665 g of TMPCl, 0.068 mL of 2,6-lutidine, and 14.2 mL of IB. After thermal equilibration to −60 °C, the polymerization was initiated by the addition of 0.84 mL of $TiCl_4$. After complete monomer conversion as determined by ATR-FTIR spectroscopic monitoring, 2.6 mL of diisopropyl sulfide was

Table 1. Polyisobutylene End-Group Composition: Effect of [Diisopropyl Sulfide]/[Chain End][a]

			PIB end-group composition (mol %) determined using ^{1}H NMR				
entry	[DIPS]/ [CE]	[TEA]/[CE]	*exo*-olefin	*endo*-olefin	coupled	^{t}Cl	ether
1	1.2	1.2	90.0	1.8	8.2	0.0	0.0
2	2.0	1.2	93.5	0.9	5.6	0.0	0.0
3	3.0	1.2	97.0	2.0	1.0	0.0	0.0
4	4.0	1.2	98.0	2.0	0.0	0.0	0.0
5[b]	4.0	8.0	89.3	2.7	0.0	8.0	0.0

[a] Hexane =60 mL, methyl chloride =40 mL; initiator = TMPCl; IB = 1.5 M; [CE] ≅ [TMPCl] = 0.039 M; [2,6-lutidine] = 0.005 M; [$TiCl_4$]/[CE] = 4.0; polymerization and quenching temperature = −60°C; termination temperature (methanol) = −20 °C. [b] Termination by methanol omitted.

charged to the reactor along with an additional 1.12 mL of $TiCl_4$. The diisopropyl sulfide was allowed to react for 30 min. Then TEA (0.75 mL) was added to the reaction mixture and allowed to react for 30 min. The reaction was allowed to slowly warm (about 0.33 °C/min), and aliquots (1 mL) were withdrawn at −60, −50, −40, and −30 °C, each of which was immediately terminated with 1 mL of prechilled methanol. Finally, the remaining reaction mixture was terminated at −20 °C by addition of 4 mL of prechilled methanol. The methyl chloride was allowed to evaporate, and the polymer was precipitated by addition of 200 mL methanol. The polymer was dissolved in 50 mL of hexane, and the resulting solution was washed with water (2 × 100 mL) and dried over magnesium sulfate ($MgSO_4$). The hexane was removed by vacuum stripping to yield a transparent polymer. Yield =10 g. *exo*-Olefin end group = 98%. Molecular weight (M_n) = 2150 g/mol. Molecular weight distribution (MWD) = 1.02.

Polymer Characterization. Gel permeation chromatography was performed as previously described.[14] Molecular weight and molecular weight distribution data of polymer samples are shown in Supporting Information (Table A-G). Composition of the PIB end groups was quantified via ^{1}H NMR integration using a 300 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer, with sample concentrations of 3−5% (w/w) in $CDCl_3$. It was assumed that the five end group species, *exo*-olefin, *endo*-olefin, *tert*-chloride, methoxy, and coupled PIB, represent 100% of the quenched chain ends. The fractional molar amount of each type of chain end was obtained using equations such as that given below for determining the fraction of *exo*-olefin (F_{exo}),

$$F_{exo} = (A_{exo})/(A_{exo} + A_{endo} + A_{\mathrm{coupled}} + A_{tert\text{-}\mathrm{Cl}}/2 + A_{\mathrm{ether}}/3) \qquad (1)$$

where A_{exo} is the area of the upfield *exo*-olefinic resonance at 4.64 ppm, A_{endo} is the area of the single olefinic resonance at 5.15 ppm, and A_{ether} is the area of the methoxy resonance at 3.16 ppm. A_{coupled} was calculated as follows:

$$A_{\mathrm{coupled}} = (A_{5.0-4.75} - A_{exo}) \qquad (2)$$

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

$$A_{tert\text{-}\mathrm{Cl}} = (A_{1.95-2.05}) - 2A_{exo} - 2A_{\mathrm{coupled}} \qquad (3)$$

where $A_{1.95-2.04}$ 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 coupled chain ends.

■ RESULTS AND DISCUSSION

In our previous paper on this topic,[16] it was shown that *exo*-olefin PIB could be synthesized at −60 °C by end-quenching $TiCl_4$-catalyzed living PIB with a dialkyl sulfide to form the PIB sulfonium ion, and then decomposing the sulfonium ion with a base to bring about elimination. The effect of sulfide structure was not examined in detail, but evidence was presented to suggest that a bulkier sulfide, such as diisopropyl sulfide (DIPS), gave a higher yield of the desired *exo*-olefin end groups than a small sulfide such as dimethyl sulfide, which tended to also yield a significant amount of *endo*-olefin. The effect of the identity of the base was examined in greater detail, using the PIB-diisopropyl sulfonium ion as a common precursor. The yield of *exo*-olefin was generally in the 85−90% range regardless of the identity of the base (ethanol, 2-propanol, *n*-butylamine, triethylamine), and this yield of *exo*-olefin was generally the same as that obtained by simple destruction of the Lewis acid with excess methanol. The exception was the case of the very hindered 2,6-di-*tert*-butylpyridine, which yielded 97% *exo*-olefin, 2% *endo*-olefin, and 1% *tert*-chloride end groups. The effect of temperature was not examined.

The results outlined above suggested that reaction of the base with the PIB sulfonium ion (Scheme 1, step 3) was not effective at −60 °C either because the base preferentially attacked the Lewis acid instead (the alcohols, *n*-butylamine) or was too extensively complexed with the Lewis acid (triethylamine). The effectiveness of di-*tert*-butylpyridine, which can neither attack nor form a complex with $TiCl_4$, supported this conclusion. In the present work, we initially reasoned that any common tertiary amine, *e.g.*, triethylamine (TEA), could be rendered effective if the temperature of the reaction were raised such that the complexation equilibrium in step 2 was shifted toward free amine. This would produce an effective concentration of free amine and yield a reasonable rate for step 3. We initially examined this strategy using DIPS as the quencher and TEA as the base. The highest reasonable temperature for the reaction in a cosolvent system containing 40 vol % MeCl was determined to be −20 °C. As will be shown, this strategy was reasonably successful in the case of DIPS; however, for less hindered or more hindered sulfides, higher free base concentration proved to be moot, since sulfonium ion decomposition predominantly followed different pathways.

Effect of Sulfide/Chain End Molar Ratio. PIB sulfonium ions (with $Ti_2Cl_9^-$ counterions) are stable below about 20 °C and in equilibrium with PIB *tert*-chloride and PIB carbenium ion (Scheme 1, step 1).[16] Although formation of PIB-diisopropyl sulfonium cation is quantitative at −60 °C using a 1:1 molar ratio of diisopropyl sulfide to *tert*-chloride, increasing temperature

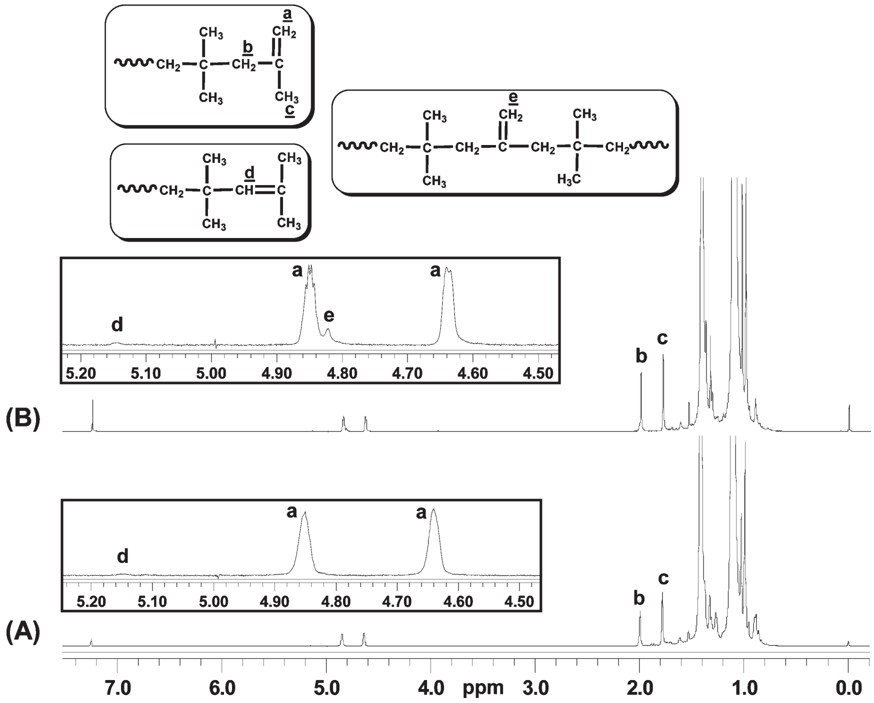


Figure 1. ^{1}H NMR spectra of olefin-terminated PIBs: (A) [DIPS]/[CE] = 4.0 (Table 1, entry 4), and (B) [DIPS]/[CE] = 1.2 (Table 1, entry 1). Reactions were warmed to −20 °C before termination by excess methanol.

favors reversal back to PIB *tert*-chloride via the intermediacy of the carbenium ion, *i.e.*, E1 elimination of R−S−R′, followed by collapse with the counterion.[16] The backward reaction is also favored by increasing bulkiness of the groups attached to sulfur.[16] To ensure that the reaction did not fail at −20 °C due to this reversal, four experiments were performed in which the molar ratio of diisopropyl sulfide to chain ends, [DIPS]/[CE], was varied from 1.2−4 (entries 1−4, Table 1). Polymerization and quenching with DIPS were performed at −60 °C. TEA, at a molar ratio of 1.2 to chain ends, was then added and allowed to equilibrate at −60 °C for 30 min. The reactor was then allowed to slowly warm, and the reaction was terminated with excess methanol when the temperature had reached −20 °C. Table 1 shows the experimental conditions and the end-group composition of the resulting PIBs.

The results indicate that the percentage of *exo*-olefin end groups increases, and the percentage of coupled PIB decreases to zero, with increasing excess of diisopropyl sulfide. The balance of the end groups is *endo*-olefin, which remains nearly constant at about 2%. The formation of near-quantitative (98.0%) *exo*-olefin-terminated PIB (Entry 4, Table 1) is observed at [DIPS]/[CE] = 4.0. Coupled product is produced when PIB−sulfonium salt spontaneously reverses back into the *tert*-chloride/carbenium ion equilibrium, and the carbenium ion adds to *exo*-olefin PIB. Warming the reaction is necessary to provide free base for the elimination reaction, but higher temperatures cause reversal of the sulfonium ion back to *tert*-chloride PIB. To prevent coupling, elimination must reach completion without the occurrence of significant reversal. At lower [DIPS]/[CE] ratios this apparently fails to happen, and some fraction of the chains reverse to *tert*-chloride. This provides a source of carbenium ion via the ionization equilibrium, and coupling results. At the highest [DIPS]/[CE] ratio, the reverse reaction is sufficiently retarded so that the concentration of PIB *tert*-chloride remains essentially zero.

To provide direct evidence that free TEA is indeed causing elimination at the PIB−diisopropyl sulfonium cation, an additional experiment was run and reported in Table 1 (entry 5). Entry 5 is similar to entry 4 except that the TEA concentration was dramatically increased to 8 times [CE], which happened also to be 2 times [$TiCl_4$], and termination by methanol was omitted. Thus, after addition of TEA, the reaction was allowed to warm to −20 °C; however, instead of termination with methanol in the usual way, an aliquot was removed within the drybox, hexane and methyl chloride were evaporated using a stream of dry nitrogen and replaced by $CDCl_3$, and the resulting solution was directly analyzed for end group composition by ^{1}H NMR. The aim of such a high TEA concentration was to ensure complexation of all excess $TiCl_4$ in the reaction. Therefore, if free base were not causing elimination, one would reasonably expect that as temperature was increased, the sulfonium ion/carbenium ion/*tert*-chloride equilibrium (step 1, Scheme 1) would shift in favor of *tert*-chloride PIB, and this shift would be irreversible due to complexation of the released $TiCl_4$ by TEA. The result would be observation of predominantly *tert*-chloride chain ends. However, this was not the case. Entry 5, Table 1 shows 89% *exo*-olefin and only 8% *tert*-chloride chain ends. We therefore conclude that free TEA caused elimination at the PIB-diisopropyl sulfonium cation.

Parts A and B of Figure 1 show ^{1}H NMR spectra of olefin-terminated PIBs made at [DIPS]/[CE] = 4.0 and 1.2 and [TEA]/[CE] = 1.2. The resonances observed at 4.64, 4.85, and 5.15 ppm are due to protons of *exo* and *endo*-olefin-terminated PIB. The proton resonance at 4.82 ppm is due to coupled PIB.[16,17]

Effect of Termination Temperature. The data in Table 1 (entries 1−4) pertain to the final polymers obtained from reaction mixtures that were reacted with TEA for 30 min at −60 °C, slowly warmed to −20 °C, and then terminated with methanol. However, during the warming period, aliquots (1 mL)

Table 2. Polyisobutylene End-Group Composition: Effect of Temperature[a]

				PIB end-group composition (mol %) determined using ^{1}H NMR				
entry	solvent	polym. and quench temp (°C)	term temp (°C)	*exo*-olefin	*endo*-olefin	coupled	^{t}Cl	ether
1	Hex/CH_3Cl (60/40, v/v)	−60	−20	98.0	2.0	0.0	0.0	0.0
			−30	98.0	2.0	0.0	0.0	0.0
			−40	90.5	1.8	1.8	2.3	3.6
			−50	79.8	3.2	0.8	4.0	12.2
			−60	75.3	3.8	1.5	6.4	13.0
2	Hex/CH_2Cl_2 (60/40, v/v)	−40	0	98.0	1.0	1.0	0.0	0.0
			−10	98.0	1.0	1.0	0.0	0.0
			−20	97.1	1.9	1.0	0.0	0.0
			−30	96.0	1.9	1.9	0.0	0.2
			−40	87.7	2.6	0.9	3.5	5.3

[a] Sulfide = diisopropyl sulfide; initiator = TMPCl; [CE] ≅ [TMPCl] = 0.039 M; [IB] = 1.5 M; [2,6-lutidine] = 0.005M; [DIPS]/[CE] = [$TiCl_4$]/[CE] = 4.0; [TEA]/[CE] = 1.2.

Table 3. Polyisobutylene End-Group Composition: Effect of Base[a]

		PIB end-group composition (mol %) determined using ^{1}H NMR				
entry	base	*exo*-olefin	*endo*-olefin	coupled	^{t}Cl	ether
1	TEA	98.0	2.0	0.0	0.0	0.0
2	2,6-Lut	98.0	1.0	1.0	0.0	0.0
3	2,5-DMP	99.0	1.0	0.0	0.0	0.0
4	---	79.3	12.7	1.6	5.1	1.3

[a] Hexane =60 mL, methyl chloride =40 mL; sulfide = diisopropyl sulfide; initiator = TMPCl; IB = 1.5 M; [CE] ≅ [TMPCl] = 0.039 M; [2,6-lutidine] = 0.005M; [DIPS]/[CE] = [$TiCl_4$]/[CE] = 4.0; [base]/[CE] = 1.2; polymerization and quenching temperature = −60 °C; termination temperature = −20 °C.

were taken at temperatures of −60, −50, −40, and −30 °C and terminated with 1 mL of methanol. End-group analysis of these aliquots, shown in Table 2, entry 1 for [DIPS]/[CE] = 4.0, illustrate the positive effect of warming the reaction prior to termination. Percentage of *exo*-olefin end groups systematically increased from 75.3 to 98.0% as the termination temperature increased from −60 to −20 °C. We theorize that the principal effect of elevated temperature is to shift the TEA-$TiCl_4$ complexation equilibrium back toward higher concentrations of free TEA, thereby promoting regiospecific elimination at the PIB sulfonium cation (Scheme 1, Step 3). Most of the gain in *exo*-olefin end groups came from elimination of ether (methoxy) and *tert*-chloride end groups (13.0 and 6.4 mol % of the total at −60 °C, respectively). These substitution products are characteristically obtained when intact PIB sulfonium ions are decomposed with methanol at −60 °C.[16]

We also performed a similar quenching experiment in hexane/methylene chloride (60/40, v/v) (Table 2, Entry 2), which, due to the higher boiling point of the halogenated cosolvent, allowed the entire process, particularly termination, to be carried out at higher temperatures,. Polymerization, sulfide quenching, and TEA addition were conducted at −40 °C, and termination of aliquots (1 mL) was carried out at −40, −30, −20, −10, and 0 °C. The results of this experiment were almost identical to the one carried out in hexane/methyl chloride, at an equivalent termination temperature. The mole percentage of *exo*-olefin increased from 87.7 to 98.0% with increasing termination temperature from −40 to −10 °C; further increase of the termination temperature to 0 °C had no effect on the end group composition.

Effect of Base. Table 3 shows PIB end group compositions resulting from reaction of different bases, *i.e.*, TEA, 2,6-lutidine (2,6-Lut), and 2,5-dimethylpyrrole (2,5-DMP) with PIB-diisopropyl sulfonium cation at −60 °C, followed by termination with methanol at −20 °C. Also included in the table is a control experiment in which the base was omitted (entry 4). The results show that the presence of a base is critical to production of high *exo*-olefin content, but the identity of the base is not. The same result, approximately 98% *exo*-olefin terminated PIB, was obtained with each base. However, in the absence of a base, only 79.3% of chains possessed the desired *exo*-olefin end groups, with the balance composed primarily of *endo*-olefin and *tert*-chloride (Table 3, entry 4). This clearly indicates that the base is essential to obtaining quantitative and regiospecific elimination at the PIB-diisopropyl sulfonium cation. Using 2,5-DMP, 99.0% *exo*-olefin terminated PIB was obtained (Table 3, Entry 3). In this case, the species that abstracts a proton from the PIB sulfonium ion is actually the η^5-2,5-dimethylpyrrolyltitanium trichloride complex, as recently reported by Storey and co-workers.[19]

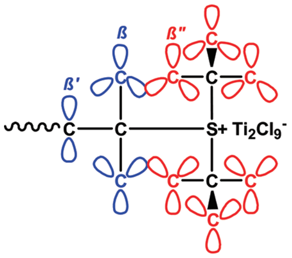
Effect of Sulfide Structure. In this series of experiments, we investigated PIB end-group composition as a function of structure of the sulfide quencher with R = R′ = *tert*-butyl, isopropyl, phenyl, methyl, ethyl, and *n*-butyl, and in one case an asymmetrical sulfide, with R = methyl, R′ = isopropyl (Scheme 1). Table 4 lists the reaction conditions and results. In general, increasing yield of *exo*-olefin end groups was observed in the approximate order of increasing bulkiness of the substituent on the sulfide, *i.e.*, *tert*-butyl > isopropyl > phenyl > *n*-alkyl. Among the *n*-alkyls, an obvious trend was the tendency toward higher proportions of

Table 4. Polyisobutylene End-Group Composition: Effect of Sulfide Structure[a]

		PIB end-group composition (mol %) determined using ^{1}H NMR				
entry	sulfide	*exo*-olefin	*endo*-olefin	coupled	^{t}Cl	ether
1	di-*tert*-butyl sulfide	100.0	0.0	0.0	0.0	0.0
2	diisopropyl sulfide	98.0	2.0	0.0	0.0	0.0
3	diphenyl sulfide	70.0	20.0	10.0	0.0	0.0
4	methyl isopropyl sulfide	55.0	7.1	2.7	18.6	16.6
5	dimethyl sulfide	55.0	13.2	1.6	12.6	17.6
6	diethyl sulfide	51.3	7.7	3.6	20.8	16.6
7	di-*n*-butyl sulfide	39.0	9.5	4.0	40.0	7.5

[a] Hexane = 60 mL, methyl chloride = 40 mL; initiator = TMPCl; IB = 1.5 M; [CE] ≅ [TMPCl] = 0.039 M; [2,6-lutidine] = 0.005 M; [sulfide]/[CE] = [$TiCl_4$]/[CE] = 4.0, [TEA]/[CE] = 1.2; polymerization and quenching temperature = −60 °C, termination temperature = −20 °C.

Scheme 2. Steric Interactions in PIB−Di-*tert*-butyl Sulfonium Cation



tert-chloride end groups as the length of the alkyl group increased from methyl to ethyl to *n*-butyl. The single asymmetric sulfide, isopropyl methyl sulfide, behaved nearly indistinguishably from the symmetrically substituted di-*n*-alkyl sulfides.

The most noteworthy finding of this study was the extraordinary effectiveness of di-*tert*-butyl sulfide, which yielded 100% *exo*-olefin-terminated PIB (Table 4, entry 1) with no other detectable end groups within the sensitivity limitation of 300 MHz ^{1}H NMR. More remarkably still, aliquots removed from the reaction at −60, −50, −40 °C, etc., during the warming process after addition of the base (Supporting Information, Table H) showed that 100% *exo*-olefin was obtained at the initial quenching temperature of −60 °C. Thus, a rise in temperature to produce a higher concentration of base is unnecessary with di-*tert*-butyl sulfide. A more detailed discussion of the scope of di-*tert*-butyl sulfide quenching is presented in later sections.

The effect on end-group composition of the different substituents on sulfur can be related to both steric and inductive effects.

(i). Steric Effect. Increasing steric bulk on sulfur, specifically branching at the carbon bonded directly to sulfur, increases steric strain in the PIB sulfonium cation due to compressive interactions between the R, R′ groups and the *gem*-dimethyl and methylene groups of the final isobutylene repeat unit. Since attack by the base (E2 elimination) relieves steric strain, the rate of elimination and the degree of regiospecificity toward *exo*-olefin (Hofmann-type elimination) increases for bulkier R, R′, culminating in 100% *exo*-olefin for R = R′ = *tert*-butyl. This is illustrated in Scheme 2, which is a diagram of the PIB−di-*tert*-butyl sulfonium salt. In Scheme 2, β, β′, and β″ are protons of the *gem*-dimethyl and methylene groups of the final IB repeat unit and methyl groups of the *tert*-butyl groups on the sulfonium cation, respectively. In the PIB−di-*tert*-butyl sulfonium cation, the interaction between the β and β″ hydrogens is large compared to the analogous interactions in the PIB−diphenyl sulfonium cation and especially the PIB-dimethyl/diethyl/dibutyl sulfonium cations, which can adopt preferred conformations that relieve these interactions. PIB−di-*tert*-butyl sulfonium cation, and to a slightly lesser extent, PIB−diisopropyl sulfonium cation, has a tendency to release steric strain by E2 elimination at a β hydrogen, which represents the most open site for attack by the base.

The product distribution observed for the di-*n*-alkyl sulfides suggests that very little, if any, elimination occurred by reaction with the base. Methyl ether end groups are formed by reaction of PIB sulfonium ion with methanol during termination of the reaction. Significant fractions of methyl ether groups indicate the presence of significant unreacted PIB sulfonium ion at the point of methanol introduction. Additional evidence indicating that PIB-di-*n*-alkyl sulfonium ions largely fail to react with the base is the fact that end group composition is largely constant for aliquots removed from the reactions of Table 4 at −60, −50, −40 °C, etc., during the warming process after addition of the base (Supporting Information, Table H). Greater stability, and hence lower reactivity of PIB-di-*n*-alkyl sulfonium ions is consistent with lower steric strain at the sulfonium ion center due to reduced interaction between β and β″ hydrogens. In addition, as the length of the *n*-alkyl chain increases from methyl to ethyl to *n*-butyl, the sulfonium ion becomes sterically inaccessible to the base, and to a certain extent, methanol. Thus, termination is accompanied by significant spontaneous decomposition (collapse) of the PIB-S(RR′)$^+$$Ti_2Cl_9^-$ ion pair, as methanol preferentially attacks the Lewis acid. This process characteristically returns *tert*-chloride chain ends, and this result is dramatically in evidence in the data of Table 4, as the length of the *n*-alkyl substituent increases (entries 5−7).

The stability of the unstrained PIB−di-*n*-alkyl sulfonium cations, and their resulting inertness even toward free TEA base was dramatically demonstrated in a set of two experiments carried out using PIB−dimethyl sulfonium cation, which was chosen because it presents the least steric hindrance to attack by TEA. A reaction carried out with dimethyl sulfide under the same conditions as entry 1, Table 1, yielded essentially the same end group composition at any temperature from −60 to −20 °C whether TEA was present in the reactor or not (Supporting Information, Table I). This shows that no E2 elimination occurs at the PIB−di-*n*-alkyl sulfonium cations, even in the presence of significant concentrations of free TEA at higher temperatures, *e.g.*, −30 and −20 °C.

(ii). Inductive Effect. The data in Table 4 show that some fraction of *endo*-olefin-terminated PIB was obtained in all cases except for di-*tert*-butyl sulfide. Diphenyl sulfide produced considerably

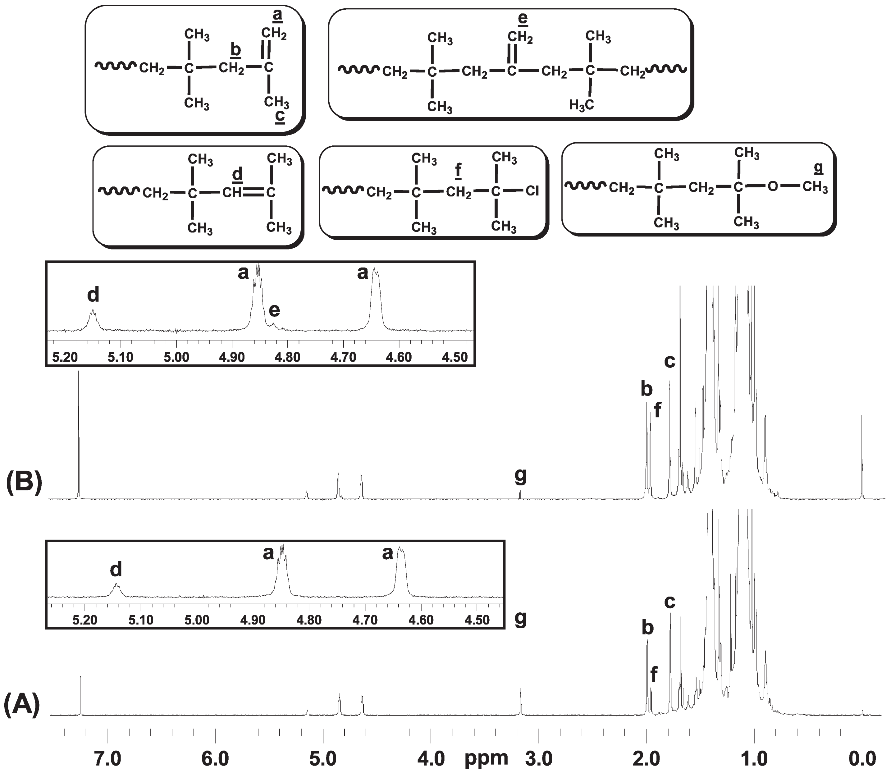


Figure 2. ^{1}H NMR spectra of living PIB quenched with: (A) dimethyl sulfide (Table 4, entry 5), and (B) di-*n*-butyl sulfide (Table 4, entry 7). Reactions were warmed to −20 °C before termination by excess methanol.

more *endo*-olefin terminated PIB (~20%) than any other sulfide, about twice as much on average as the di-*n*-alkyl sulfides. This could be a consequence of the known destabilization of cations by phenyl relative to methyl, which has been ascribed to the inductively electron withdrawing nature of phenyl.[20] Although phenyl is expected to stabilize the sulfonium cation by resonance delocalization, it has been suggested that the offsetting inductive effect is dominant. Destabilization by inductive electron withdrawal, without steric crowding, is expected to decrease regioselectivity of the E2 elimination reaction and lead to *endo*-olefin. The *n*-alkyl substituents, which are inductively donating (stabilizing) and do not impose destabilizing steric effects at the sulfonium cation center, all yielded approximately the same fraction of *endo*-olefin, which was about the same as obtained in the absence of a base (Table 3, entry 4). This suggests, again, that the progress of E2 elimination was low and the sulfonium cation was mostly intact at the time of termination of the reaction by addition of methanol.

Table 4 shows that low fractions of coupled product were produced with the *n*-alkyl substituted sulfides; whereas an unusually high proportion, ~10%, was obtained with diphenyl sulfide. The latter result is probably related to the high fraction of *endo*-olefin also produced by diphenyl sulfide. If the PIB-diphenyl sulfonium ion is particularly unstable, its equilibrium formation (Scheme 1, Step 1) may not be quantitative, particularly when the temperature is raised toward −20 °C.

Figure 2 shows ^{1}H NMR spectra of the final PIB product after quenching with (A) dimethyl sulfide/TEA and (B) di-*n*-butyl sulfide sulfide/TEA, followed by addition of methanol after warming to −20 °C.

Di-*tert*-butyl Sulfide. Experiments were conducted to further explore quenching reactions involving di-*tert*-butyl sulfide (Table 5). For each experiment, polymerization, quenching, and reaction with base (if performed) were carried out at −60 °C. Then an aliquot of the reaction was removed and terminated with methanol at −60 °C, and the balance of the reaction was warmed to −20 °C prior to methanol termination. Entries 1 and 2 are identical except that the base TEA was omitted from entry 2. The latter experiment resulted in 100% *exo*-olefin end groups irrespective of the methanol termination temperature (see ^{1}H NMR spectrum in Figure 3 of product terminated at −60 °C), demonstrating that addition of a base is unnecessary with D*t*BS quenching. Such was not the case for DIPS quenching (Table 3, entry 4) or for less-bulky sulfides such as dimethyl sulfide.[16] The mechanism by which elimination occurs in the absence of a base presents several possibilities. We considered whether the PIB sulfonium ion might decompose to *exo*-olefin spontaneously prior to methanol introduction, via an E1 elimination mechanism. But this is obviously not the route, because the first step of this reaction would be loss of D*t*BS and reversal back into the *tert*-chloride/carbenium ion equilibrium (reversal of step 1 of Scheme 1). This would yield *tert*-chloride-terminated PIB upon methanol termination. The absence of any *tert*-chloride PIB in the product strongly suggests that the PIB sulfonium ion is fully intact at the point of methanol termination. Next, we considered the possibility of spontaneous decomposition of the PIB-di-*tert*-butyl sulfonium cation by reaction with the counterion, induced by the loss of $TiCl_4$ from the system. However, this does not seem plausible, since this reaction invariably causes transfer of a chloride ion to the positive center (*i.e.*, collapse), to produce *tert*-chloride PIB. After careful consideration, we propose that the mechanism must be E2 elimination, with methanol serving as the base. We know this to be a significant reaction when PIB-dialkyl

Table 5. Polyisobutylene End-Group Composition from Di-*tert*-butyl Sulfide Quenching[a]

				PIB end-group composition (mol %) determined using ^{1}H NMR				
entry	base	[D*t*BS]/[CE]	term temp MeOH	*exo*-olefin	*endo*-olefin	coupled	^{t}Cl	ether
1	TEA	4.0	−60	100.0	0.0	0.0	0.0	0.0
			−20	100.0	0.0	0.0	0.0	0.0
2	---	4.0	−60	100.0	0.0	0.0	0.0	0.0
			−20	100.0	0.0	0.0	0.0	0.0
3	TEA	1.5	−60	100.0	0.0	0.0	0.0	0.0
			−20	100.0	0.0	0.0	0.0	0.0

[a] Hexane = 60 mL, methyl chloride = 40 mL; initiator = TMPCl; [IB] = 1.5 M; [CE] ≅ [TMPCl] = 0.039 M; [2,6-lutidine] = 0.005 M; $[TiCl_4]/[CE]$ = 4.0; [TEA]/[CE] = 1.2; polymerization and quenching temperature = −60 °C.

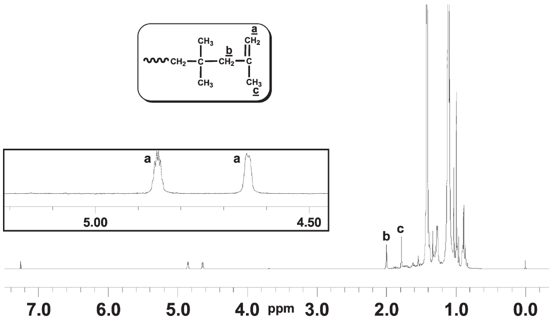


Figure 3. ^{1}H NMR spectrum of *exo*-olefin terminated PIB: [di-*tert*-butyl sulfide]/[CE] = $[TiCl_4]/[CE]$ = 4.0 (Table 5, entry 2), terminated with methanol at −60 °C.

sulfonium cations are decomposed by alcohols,[16] but it is not the exclusive reaction for alkyl substituents other than *tert*-butyl, with substitution (ether formation) usually also observed, as well as some *endo*-olefin. Apparently, with D*t*BS, steric strain in the sulfonium cation is so great that regiospecific E2 elimination is the only reaction observed, even with weak bases such as alcohols.

Comparison of entries 1 and 3 in Table 5 shows that with D*t*BS, the quencher/chain end ratio can be reduced downward toward 1:1 without apparent harm to the yield of *exo*-olefin functionality. This is in direct contrast to the results obtained with DIPS (Table 1). For DIPS, reduction of the sulfide/chain end ratio leads to coupling, which indicates that some reversal (E1 elimination) back to the carbenium ion with rising temperature had occurred prior to completion of the E2 elimination reaction. With D*t*BS, the E2 elimination reaction is more favorable and able to reach completion before rising temperature causes reversal.

Technological Aspects of Sulfide Quenching. We next examined certain technological aspects of the sulfide quenching method, including the effect of [CE], [sulfide]/[CE] ratio, $TiCl_4$ demand, and reaction scale. In all cases, D*t*BS was used as the quencher and methanol was used as the base/terminating agent at −60 °C. Reaction conditions and results are shown in Table 6. In previous work, we have shown that the formation of coupled PIB is the major side reaction when hindered amines are used as quenching agents to produce *exo*-olefin PIB.[14] We demonstrated that this side reaction can be largely avoided with sulfide quenching by appropriate choice of quencher and reaction conditions; however, since coupling is bimolecular in chain ends, its rate of occurrence is expected to increase with the square of the chain end concentration. As shown in entries 1−3 of Table 6, increasing the [CE] from 0.039 to 0.10 M caused no loss in the desired *exo*-olefin functionality. This shows that the sulfide quenching method is exceptionally resistance to the formation of coupled PIB, and this is the first report wherein quantitative *exo*-olefin-terminated PIB has been obtained at such high [CE]. This is made possible by the fact that the living chains are first quantitatively converted to a more stable species, *i.e.*, PIB sulfonium ion, which has no tendency to react with *exo*-olefin product.

Entries 3−5 of Table 6 demonstrate the effect of systematically lowering the [D*t*BS]/[CE] ratio toward 1:1. The results show that under these conditions the sulfide excess can be diminished to as little as 20% over stoichiometry with only a barely detictible deterioration in the chain end functionality, *i.e.*, contamination of the chain ends with 1% *endo*-olefin.

Entries 3, 6, and 7 of Table 6 address the issue of $TiCl_4$ demand of the sulfide quenching process. According to Lewkebandara et al.[21] a sulfide and $TiCl_4$ form a 2:1 complex in solution. Therefore, the theoretical quantity of $TiCl_4$ required to convert all of the chain ends to sulfonium ions is given by eq 4.

$$[TiCl_4] = 2[CE] + 0.5([sulfide] - [CE]) \tag{4}$$

If a base such as TEA is used, it will require approximately 1 equiv of $TiCl_4$ in addition to the above. For entries 3, 6, and 7, where no base was used, the required $[TiCl_4]$ is predicted to be 0.25 M, or 2.5 times [CE]. Surprisingly, the data show that the actual $[TiCl_4]$ required is less than this amount. Entry 3 used a large excess of $TiCl_4$; however, entry 6 only used 2.2 times [CE], but produced perfect *exo*-olefin functionality. Entry 7, which used $[TiCl_4]$ = 1.54[CE], did indeed exhibit the effect of insufficient $TiCl_4$, producing only 82.6% *exo*-olefin functionality, with the balance consisting solely of *tert*-chloride. This is precisely the mode of failure one would expect. Sulfonium ion formation proceeds until $TiCl_4$ is depleted, but it is incomplete and some chains remain as *tert*-chloride. Upon introduction of methanol, the sulfonium ions decompose to form *exo*-olefin, and the *tert*-chloride end groups are unchanged, *i.e.*, coupling is not observed since ionization cannot take place in the absence of Lewis acid.

Another important technological issue concerns the facility with which a chemical process can be scaled to larger batch sizes. Entry 8, Table 6, demonstrates that the sulfide quenching process can be readily scaled to produce about 800 g olefin-terminated PIB (98/2 *exo*/*endo*) in a 3.6 L reaction volume.

***Telechelic* (Difunctional) *exo*-Olefin-Terminated PIB.** We successfully adapted the above-discussed quenching method to produce near-quantitative telechelic (difunctional) *exo*-olefin

Table 6. Polyisobutylene End-Group Composition: Effect of [CE], [Sulfide]/[CE], [$TiCl_4$]/[CE], and Batch Reaction Volume[a]

					PIB end-group composition (mol %) determined using ^1H NMR			
entry	rxn vol (mL)	[CE] (M)	[sulfide]/[CE]	[$TiCl_4$]/[CE]	*exo*-olefin	*endo*-olefin	coupled	^{t}Cl
1	120	0.039	4.0	4.0	100.0	0.0	0.0	0.0
2	120	0.077	4.0	4.0	100.0	0.0	0.0	0.0
3	120	0.10	2.0	4.4	100.0	0.0	0.0	0.0
4	120	0.10	1.5	3.30	99.0	1.0	0.0	0.0
5	120	0.10	1.2	2.64	99.0	1.0	0.0	0.0
6	120	0.10	2.0	2.20	100.0	0.0	0.0	0.0
7	120	0.10	2.0	1.54	82.6	0.0	0.0	17.4
8	3560	0.10	1.2	2.64	98.0	2.0	0.0	0.0

[a] Hexane/methyl chloride, 60/40 (v/v); sulfide = di-*tert*-butyl sulfide; initiator = TMPCl; [CE] ≅ [TMPCl]; [IB]/[TMPCl] = 38.7; [2,6-lutidine] = 0.005 M; termination temperature (methanol) = −60 °C.

Table 7. Difunctional Polyisobutylene End-Group Composition[a]

			PIB end-group composition (mol %) determined using ^1H NMR				
entry	[CE]	sulfide (M)	*exo*-olefin	*endo*-olefin	coupled	^{t}Cl	ether
1	0.042	di-*tert*-butyl sulfide (0.164)	100.0	0.0	0.0	0.0	0.0
2	0.042	diisopropyl sulfide (0.164)	98.0	1.0	1.0	0.0	0.0

[a] Hexane = 60 mL, methyl chloride = 40 mL; initiator = bDCC; [CE] ≅ 2 × [bDCC]; [IB] = 0.77 M; [2,6-lutidine] = 0.005 M; [sulfide]/[CE] = [$TiCl_4$]/[CE] = 4.0; [TEA]/[CE] = 1.2; [2,6-lutidine] = 0.005 M; polymerization and quenching temperature = −60 °C; termination temperature = −20 °C.

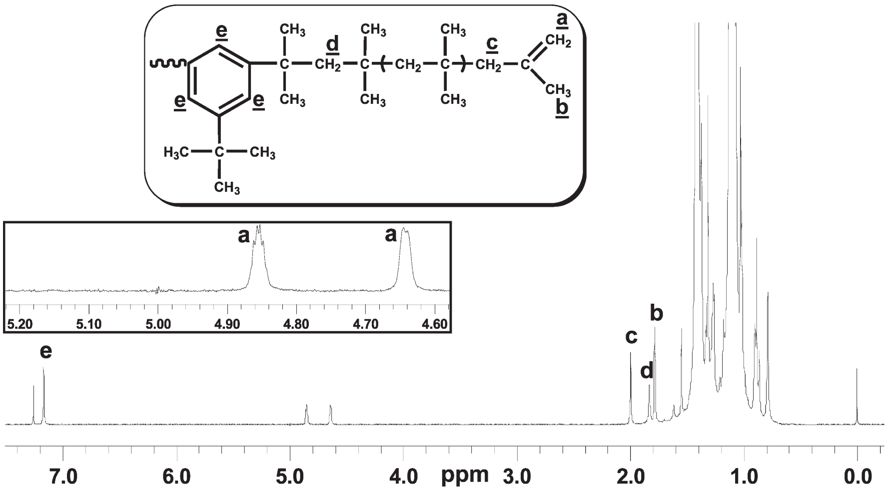


Figure 4. ^1H NMR spectrum of *telechelic* (difunctional) *exo*-olefin-terminated PIB (entry 1, Table 7).

terminated PIB. 1,3-*bis*(1-Chloro-1-methylethyl)-5-*tert*-butylbenzene (bDCC) was used as difunctional initiator for IB polymerization. As shown in Table 7, both diisopropyl sulfide and di-*tert*-butyl sulfide quenching were used under optimized conditions. Approximately 98% *exo*-olefin, 1% *endo*-olefin, and 1% coupled product were observed for DIPS/TEA with a −20 °C termination temperature. For D*t*BS with a −60 °C termination temperature, 100% *exo*-olefin was obtained. The ^1H NMR spectrum of the resulting *telechelic exo*-olefin-terminated PIB is depicted in Figure 4. Resonances observed at 7.2 ppm (e) and at 4.64 and 4.85 ppm (a) are due to the aromatic initiator residue and the vinylidene protons, respectively. For the theoretical case of 100% *exo*-olefin terminated PIB, the ratio of aromatic (3H)/vinylidene (2 + 2) protons =0.75; the theoretical ratio was observed for the D*t*BS-quenched sample. For the DIPS/TEA sample, the ratio was 0.746, yielding functionality, F_n (*Exo*) = 1.99.

CONCLUSIONS

We have demonstrated that *in situ* quenching of living PIB with a sulfide, followed by decomposition (E2 elimination) of the resulting PIB sulfonium salt with a base, produces *exo*-olefin end groups in yields approaching and including 100%, depending on choice of sulfide and reaction conditions. The most effective sulfides studied were those with bulky, electron donating (aliphatic) substituents, such as di-*tert*-butyl sulfide and diisopropyl sulfide. Other sulfides such as diphenyl, dimethyl, diethyl, methyl isopropyl, and di-*n*-butyl gave poorer results. The best performing sulfide, and the only one that yielded 100% *exo*-olefin end groups, was di-*tert*-butyl sulfide. A unique characteristic of di-*tert*-butyl sulfide, to which its high performance largely owes, is that the resulting PIB−di-*tert*-butyl sulfonium salt undergoes E2 elimination with weakly basic, protic nucleophiles such as methanol, and hence decomposition may be carried out at low temperature. Less bulky sulfides yielded mixed end groups, *i.e.*, *exo*-olefin, *endo*-olefin, coupled, *tert*-chloride, and methyl ether, when methanol was used to decompose the resulting PIB sulfonium salt.

E2 elimination with less sterically strained PIB sulfonium ions, that is, all sulfides except those derived from di-*tert*-butyl sulfide, was thought to require the presence of a strong tertiary amine base such as TEA, accompanied by an increase in temperature, *e.g.*, −20 °C, to produce a sufficient concentration of free base in the presence of $TiCl_4$. However, this strategy proved satisfactory only for diisopropyl sulfide. For less bulky sulfides, such as di-*n*-alkyl sulfides, higher free base concentration proved to be moot; the resulting PIB sulfonium ions were relatively free of steric strain and apparently stable toward TEA. Decomposition of PIB di-*n*-alkyl sulfonium ions only occurred upon final termination with methanol, resulting in significant proportions of *tert*-chloride and methyl ether end groups. For all sulfides, higher temperatures tended to cause E1 elimination at the PIB sulfonium cation, which resulted in coupling in the presence of excess $TiCl_4$, or *tert*-chloride end groups in its absence. The only practical way to combat this tendency was to use an excess of sulfide relative to chain ends.

The sulfide quenching method is exceptionally resistance to the formation of coupled PIB, since under the proper conditions, PIB carbenium ions never coexist with *exo*-olefin product. With di-*tert*-butyl sulfide, we obtained 100% *exo*-olefin-terminated PIB at a chain-end concentration of 0.1 M, without a large excess of quencher or $TiCl_4$. To our knowledge, this is the first report of quantitative *exo*-olefin formation by an *in situ* quenching method in such a highly concentrated system.

ASSOCIATED CONTENT

Supporting Information. Molecular weight data (GPC) for all PIB samples obtained by sulfide/base quenching, PIB end-group composition as a function of sulfide structure for aliquots removed at various temperatures during warming of the reaction after addition of base, and PIB end-group composition from dimethyl sulfide quenching as a function of the presence or absence of base, for aliquots removed at various temperatures during warming of the reaction. This material is available free of charge via the Internet at http://pubs.acs.org.

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ACKNOWLEDGMENT

Financial support by Chevron Oronite Company is gratefully acknowledged.

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