Sulfonium Ion Adducts from Quasiliving Polyisobutylene and Mono- or Disulfides

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ABSTRACT: Low-temperature-stable sulfonium ion adducts were generated by addition of mono- and disulfides to $TiCl_4$-catalyzed quasiliving polyisobutylene (PIB). The adducts were studied *in situ* via low temperature NMR in 50/50 (v/v) CS_2/CD_2Cl_2 using the initiator 2-chloro-2,4,4-trimethylpentane (TMPCl) and C_{16} and C_{20} *tert*-chloride oligo-isobutylenes as models for the PIB chain end. At temperatures less than or equal to −60 °C, quantitative 1:1 adducts were formed between the (di)sulfides and TMPCl or the oligo-isobutylenes. Adduct formation prevented further homopolymerization of isobutylene, but when a more reactive nucleophile such as an alcohol or amine was added to the reaction, the adducts were destroyed. Both elimination and substitution products were obtained at the PIB chain end. With PIB−monosulfide adducts, elimination was the principle decomposition pathway, and near-quantitative formation of *exo*-olefin PIB was achieved upon termination by a hindered tertiary amine, such as proton trap, 2,6-di-*tert*-butylpyridine. For PIB−disulfide adducts, decomposition was observed to occur principally through sulfur−sulfur cleavage, yielding useful thioether end groups, e.g., when terminated with triethylamine, the PIB−bis(2-bromoethyl) disulfide adduct yielded near-quantitative primary bromide-terminated PIB.

Introduction

In situ functionalization of quasiliving polyisobutylene (PIB) is an inherently difficult task due to the stability imparted by the low number of active or ionized chain ends. For a typical isobutylene polymerization catalyzed by $TiCl_4$, the dormant-active equilibrium constant is very low,[1] near 10^{-7} M^{-2}. When a nucleophilic quenching or capping agent is deliberately added to the polymerization, it is more likely to be rapidly consumed by interaction with the Lewis acid rather than reacting with the carbenium ion chain ends. The result is ion-pair collapse and production of unmodified *tert*-chloride terminated PIB. To date, only a few successful quenching reactions have been reported, including capping by nonpolymerizing olefins,[2−7] substitution at highly reactive aromatic substrates,[8−10] and those that lead to β-proton elimination.[11]

Here we report on a use of sulfides and disulfides as quenching/capping agents for $TiCl_4$-catalyzed isobutylene polymerizations. We show that when a (di)sulfide is added to an isobutylene polymerization, consumption of monomer ceases and a low-temperature-stable sulfonium ion adduct is formed. When a more reactive nucleophile is then added, such as an alcohol or amine, both substitution (ether or thioether) and elimination (*exo*-olefin) products are obtained at the PIB chain end. The stability of sulfonium ions has been used previously in other cationic polymerization systems to impart control but not as a means for chain end functionalization. For example, during the polymerization of epoxides,[12] styrenics,[13] or vinyl ethers[14,15] the carbenium or oxonium ions may be trapped as more stable trivalent sulfonium ions, either slowing or stopping monomer consumption.

The formation of small molecule alkyl sulfonium salts and subsequent nucleophilic decomposition was originally studied by Hughes, Ingold, and Maw.[16] They formed alkyl dimethyl-sulfonium iodides by reacting alkyl thiols with two equivalents of methyl iodide. The primary, secondary, and tertiary alkyl dimethyl sulfide adducts were reacted with sodium ethoxide in ethanol at or above room temperature. Typically, adduct decomposition resulted in elimination accompanied by nucleophilic substitution. When substitution occurred, either a methyl group of the sulfide moiety was displaced, creating a thioether, or the entire sulfide moiety was replaced with ethoxide, creating an ether.

Experimental Section

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

Initiators, Oligo-Isobutylenes, and tert-Chloride PIB Masterbatch. 2-Chloro-2,4,4-trimethylpentane (TMPCl), 2-chloro-2,4,4,6,6,8,8-heptamethylnonane (C_{16}PIBCl), and 2-chloro-2,4,4,6,6,8,8,10,10-nonamethylundecane (C_{20}PIBCl) were prepared by bubbling HCl gas through neat 2,4,4-trimethyl-1-pentene (Sigma-Aldrich), 2,4,4,6,6,8,8-heptamethyl-1-nonene (Chevron Oronite) in CH_2Cl_2, and 2,4,4,6,6,8,8,10,10-nonamethyl-undec-1-ene (Chevron Oronite) in CH_2Cl_2, respectively, at 0 °C. The HCl-saturated TMPCl was stored at 0 °C, and immediately prior to use it was neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$, and filtered. The HCl-saturated C_{16}PIBCl and C_{20}PIBCl were neutralized with $NaHCO_3$, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed under vacuum and the product stored at 0 °C. Low molecular weight polyisobutylene ($\bar{M}_n = 2.0 \times 10^3$ g/mol, $\bar{M}_w/\bar{M}_n = 1.03$ by GPC-MALLS) with tert-chloride end groups ("*tert*-chloride PIB masterbatch") was prepared via the BCl_3-catalyzed polymerization of isobutylene from TMPCl in methyl chloride[17] at −60 °C.

Sulfides, Disulfides, and Nucleophilic Terminators. Dimethyl sulfide (99%), diisopropyl sulfide (99%), dimethyl disulfide (99%), diethyl disulfide (99%), di-*tert*-butyl disulfide (97%), *n*-butylamine (99.5%), triethylamine (99.5%), 1,2,2,6,6-pentamethylpiperidine (97%), 2,6-di-*tert*-butylpyridine (>97%), and 2,5-dimethylpyrrole (98%) were used as received from Sigma-Aldrich. Diisopropyl disulfide (96%), di-*p*-tolyl disulfide (98%), and ethanol (99.5%)

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Table 1. Polyisobutylene Chain End Compositions Obtained after Addition of Various Nucleophiles to PIB−Sulfide and PIB−Disulfide Onium Ion Adducts

				fractional end group functionality					
entry	conditions[a]	sulfide	terminating nucleophile[b](excess)	*tert*-Cl	*endo*-olefin	*exo*-olefin	coupled	ether	thioether
1	MB	dimethyl sulfide	methanol	0.03	0.19	0.69	-	0.09	-
2	MB	diisopropyl sulfide	methanol	0.01	0.02	0.90	-	0.07	-
3	A		ethanol	0.03	0.03	0.90	0.03	0.01	-
4	A		2-propanol	0.03	0.03	0.91	0.03	-	-
5	A		*n*-butylamine	0.05	0.03	0.88	0.04	-	-
6	MB		triethylamine	0.12	0.02	0.85	0.01	-	-
7	MB		2,6-di-*tert*-butylpyridine	0.01	0.02	0.97	-	-	-

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

[a] See Experimental Section for specific reaction conditions A, B, C, D, and MB. All reactions conducted at −60 °C. [b] 2,6-lutidine included as an additional nucleophile at low concentration, except for reactions with *tert*-chloride PIB masterbatch (MB). [c] [diisopropyl disulfide]/[TMPCl] = 2.0. [d] Number average molecular weight $\bar{M}_n$ = 2450 g/mol; polydispersity $\bar{M}_w/\bar{M}_n$ = 1.1. [e] $\bar{M}_n$ = 1505 g/mol; $\bar{M}_w/\bar{M}_n$ = 1.19.

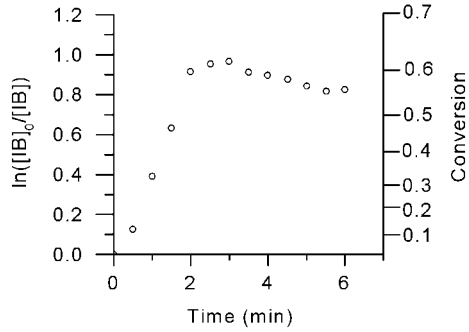


Figure 1. First order kinetic plot of an isobutylene polymerization in which diisopropyl disulfide was added at approximately 60% monomer conversion. Conditions were as follows: −60 °C in 60/40 (v/v) hexane/methyl chloride, [TMPCl] = 0.015 M, [IB] = 0.5 M, [26Lut] = 0.005 M, [$TiCl_4$] = 0.09 M, and [diisopropyl disulfide] = 0.03 M.

were used as received from Acros Organics. Bis(2-chloroethyl) disulfide was prepared using a published procedure.[18]

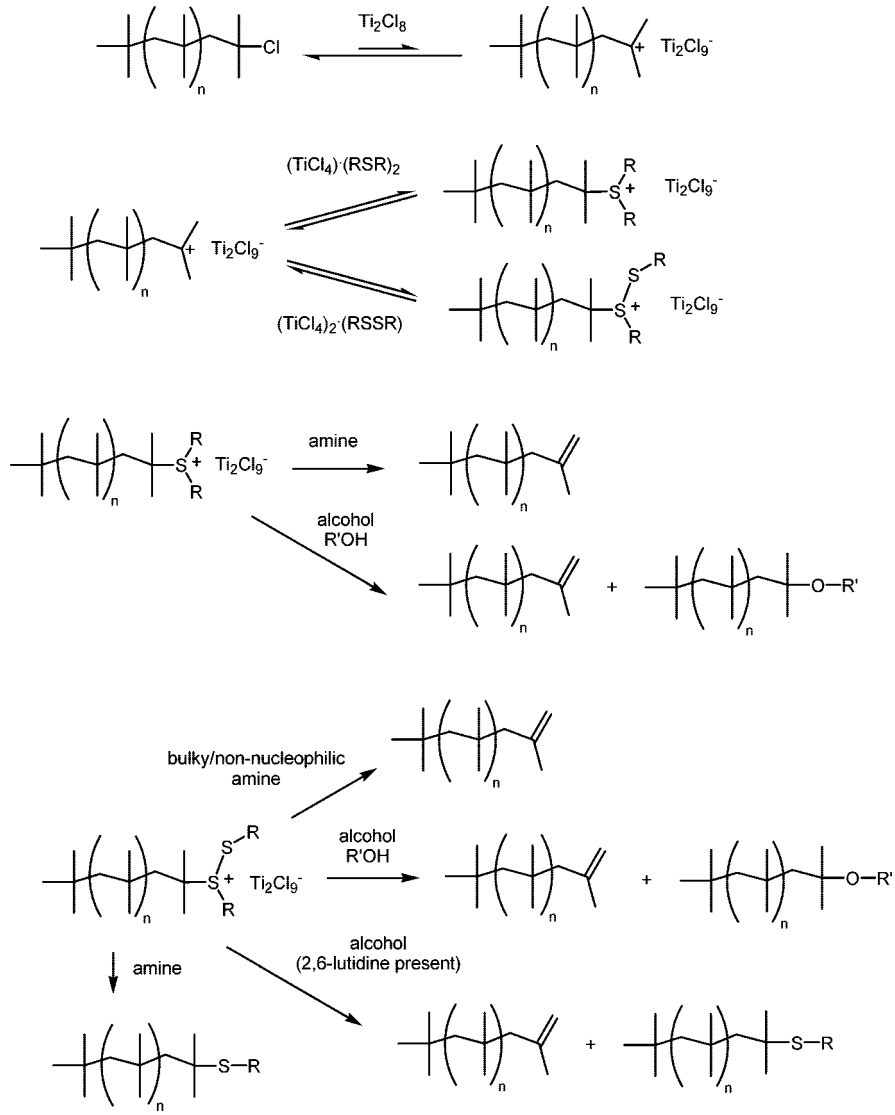
Bis(2-bromoethyl) disulfide was prepared using a variation of a published procedure.[19] To a round-bottom flask at room temperature were added 113 mL (1.0 mol) of 48% hydrobromic acid, followed by 13 mL of concentrated sulfuric acid, in portions with stirring. Using a syringe, 30.85 g (0.20 mol) of bis(2-hydroxyethyl) disulfide (Sigma-Aldrich, technical grade) was charged to the reactor, followed by an additional 11 mL of concentrated sulfuric acid, in portions with stirring. The resulting biphasic mixture was refluxed for 2−3 h. Upon cooling, the organic layer was taken up into 200 mL of diethyl ether. The ether solution was washed with saturated $NaHCO_3$ solution and then with distilled water, dried by stirring over $MgSO_4$, filtered, and finally concentrated on a rotary evaporator to yield 52.72 g (94%) of crude bis(2-bromoethyl) disulfide. The product was dissolved in hexane and passed through a silica gel column. Removal of the hexane on a rotary evaporator afforded 44.47 g (79%) of a clear, oily liquid: ^{1}H NMR δ 3.10 (t, 4H, SCH_2), δ 3.62 (t, 4H, CH_2Br).

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

In some cases, the polymerization mixture was quenched with a (di)sulfide and then divided into glass tube reactors so that a common PIB−sulfonium ion adduct could be terminated with different nucleophiles (condition A). In another case, the mixture was divided prior to quenching so that a common quasiliving PIB could be quenched with different (di)sulfides (condition B). Two preparative-scale reactions were conducted to produce larger quantities of primary halogen-terminated PIB (conditions C and D). Finally, *tert*-chloride-terminated PIB ("*tert*-chloride PIB masterbatch") prepared in a separate BCl_3-catalyzed reaction was divided into tubes, reactivated with $TiCl_4$, and quenched with various disulfides and terminating agents (condition MB). The various conditions used were dictated by the objectives of the experiments; for example, in the preparative-scale experiments, to achieve appropriate reaction rates both during polymerization and quenching, total $TiCl_4$ was added in two separate charges, a first charge to catalyze the polymerization and a second charge, after addition of the (di)sulfide, to catalyze the sulfonium ion formation. Details of the conditions used for the samples in Table 1 were as follows:

Condition A (Table 1). Polymerization reaction mixtures were quenched with a (di)sulfide and then divided into several glass tube reactors, each of which received a different terminating nucleophile. Reaction concentrations were as follows: [IB] = 0.82 M; [TMPCl]

Scheme 1. Chain End Functionalities That Can Be Obtained upon Decomposition of Polyisobutylene−(Di)Sulfide Onium Ion Adducts by Contact with Excess Alcohol and/or Amines



= 0.021 M; [26Lut] = 0.010 M; [$TiCl_4$]/[TMPCl] = 5.0; [(di)sulfide]/[TMPCl] = 1.5. Condition A is representative of those polymerization reactions divided into glass tubes and is therefore described in detail for the case of quenching with diisopropyl sulfide: A four-necked 500 mL round-bottom flask, equipped with an overhead mechanical stirrer and platinum resistance thermometer, was charged with 165 mL of hexane (−60 °C), 110 mL of methyl chloride (−60 °C), 1.06 mL of TMPCl (room temperature, 6.2 mmol), 0.35 mL of 26Lut (room temperature, 3.0 mmol), and 19.9 mL of IB (−60 °C, 0.244 mol). The contents were stirred and equilibrated at −60 °C. Then, with continued stirring, 3.42 mL of $TiCl_4$ (room temperature, 31.1 mmol) was charged to the flask to initiate polymerization. The reaction was allowed to proceed for 17 min, and then 1.36 mL (9.3 mmol) of diisopropyl sulfide was charged to the reactor. After 30 s, 35 mL of the polymerization solution was charged to each of several 60 mL test tubes. The tubes were sealed with threaded caps and immersed in the heptane bath maintained at −60 °C. Quenching was allowed to proceed for 17 min. Then, into individual tubes were added one of the following terminating nucleophiles, pre-equilibrated to −60 °C and at approximately 60-fold excess relative to chain ends: 2.55 mL of ethanol (43.7 mmol), 3.34 mL of 2-propanol (43.6 mmol), or 4.53 mL of *n*-butylamine (45.8 mmol). The terminated reaction mixtures were allowed to warm to room temperature, and low boiling components were volatilized. A volume of hexane (2−3 mL) was added to each sample to dissolve the PIB, and then the polymers were precipitated into methanol. Finally, the isolated PIBs were washed with fresh methanol to remove any remaining salts and dried by vacuum stripping.

Condition B (Table 1). Polymerization reaction mixtures were catalyzed (*vide supra*), divided into several glass tube reactors, and after 26 min, each tube was quenched with a different (di)sulfide. After 15 min quenching time, each tube was charged with a large excess of methanol. Reaction concentrations were as follows: [IB] = 1.03 M; [TMPCl] = 0.014 M; [26Lut] = 0.010 M; [$TiCl_4$]/[TMPCl] = 9.8; [(di)sulfide]/[TMPCl] = 2.0.

Condition C (Table 1). Primary bromide-terminated PIB was prepared using the following concentrations: [IB] = 3.02 M; [TMPCl] = 0.076 M; [26Lut] = 0.007 M; [$TiCl_4$] (pzn.) = 0.034 M; [$TiCl_4$] (quench) = 0.500 M; [disulfide]/[TMPCl] = 1.2; 47/53 (v/v) hexane/methyl chloride. Condition C is representative of a preparative-scale batch reaction and is therefore described in detail: A four-necked 1 L round-bottom flask, equipped with an overhead mechanical stirrer and platinum resistance thermometer, was charged with 189 mL of hexane (−60 °C), 216 mL of methyl chloride (−60 °C), 6.25 g of TMPCl (42.0 mmol), 0.48 mL of 26Lut (room temperature, 4.1 mmol), and 135 mL of IB (−60 °C, 1.66 mol). The contents were mixed and equilibrated at −60 °C. Then, 2.03 mL of $TiCl_4$ (room temperature, 18.5 mmol) was charged to the flask to initiate polymerization. The polymerization was allowed to proceed for 90 min (conversion >0.98), at which time 14.13 g of bis(2-bromoethyl) disulfide (50.5 mmol) and an additional 30.24

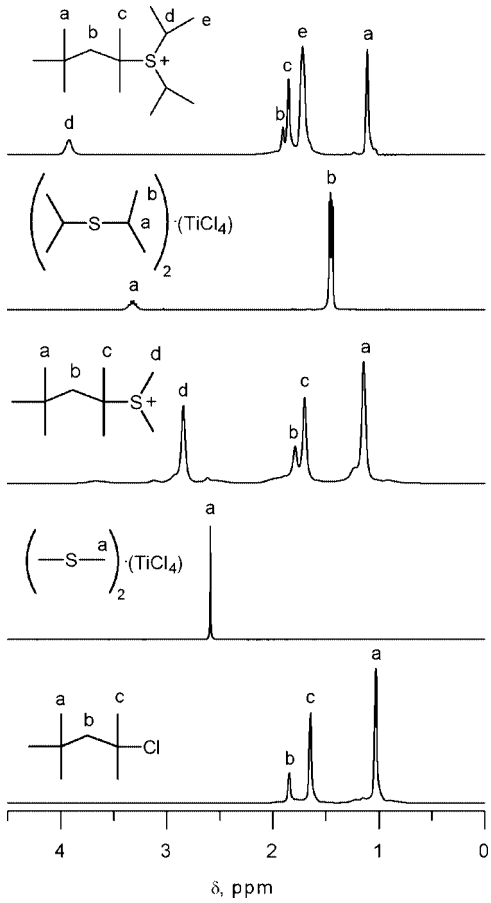


Figure 2. 500 MHz ^{1}H NMR spectra of TMPCl and TMPCl/monosulfide adducts with dimethyl sulfide and diisopropyl sulfide in the presence of 5 equiv of $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 at −60 °C. Spectra of dimethyl sulfide and diisopropyl sulfide complexes with $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 at 20 °C are also shown for comparison. $Ti_2Cl_9^-$ counterions are not shown with the sulfonium ions for simplicity.

mL of $TiCl_4$ (room temperature, 0.275 mol) were charged to the reactor. The mixture was allowed to react 22 min and was then terminated by addition of 29.3 mL of triethylamine (0.21 mol) pre-equilibrated at −60 °C. The mixture was stirred for 10 min, and then 73.2 mL of methanol, pre-equilibrated at −60 °C, was slowly charged to the reactor. The flask was removed from the glovebox, and the volatile components were allowed to evaporate under ambient conditions. The hexane/polyisobutylene layer was washed with 5% HCl (aq) and then deionized H_2O until the extracts were neutral. The hexane solution was dried over $MgSO_4$, filtered, and concentrated using rotary evaporation.

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

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

^{1}H NMR spectra of the purified polymers in $CDCl_3$ (20−50 mg/mL) at room temperature were recorded on a 300 MHz Varian Mercury^{plus} NMR (VNMR 6.1C) spectrometer. Relative molar quantities of the various chain end functionalities were determined using peak integration and converted to absolute percentages by assuming that the following constitute 100% of the chain ends: *tert*-chloride, *exo*-olefin, *endo*-olefin, coupled, and if appropriate, methoxy (or ethoxy) and/or thio ether (methyl, isopropyl, *p*-tolyl, 2-bromoethyl, or 2-chloroethyl). The various resonances integrated were as follows: *tert*-chloride, δ 1.69 (s, 6H, terminal *gem*-dimethyl); *exo*-olefin, δ 4.64 (m, 1H, olefin); *endo*-olefin, δ 5.15 (s, 1H, olefin); coupled, δ 4.82,[21] obtained as the difference between the 4.85 and 4.64 *exo*-olefin resonances; methoxy, δ 3.17 (s, 3H, OCH_3); ethoxy, δ 3.37 (m, 2H, OCH_2); methyl thio ether, δ 2.03 (s, 3H, SCH_3); isopropyl thio ether, δ 2.93 (m, 1H, SCH)), *p*-tolyl thio ether, δ 2.36 (s, 3H, methyl), δ 7.13 (d, 2H, *o*-phenyl), or δ 7.40 (d, 2H, *m*-phenyl); 2-bromoethyl thio ether, δ 3.10 (t, 2H, SCH_2) or δ 3.62 (t, 2H, CH_2Br); 2-chloroethyl thio ether, δ 3.03 (t, 2H, SCH_2) or δ 3.77 (t, 2H, CH_2Cl).

Low-Temperature in situ NMR Investigation of Sulfonium Ion Adducts. Sulfonium ion adducts were formed by reacting TMPCl or oligo-isobutylenes with (di)sulfides in the presence of $TiCl_4$. A 0.02 M solution of TMPCl (or oligo-isobutylene) in a 50/50 (v/v) mixture of CS_2/CD_2Cl_2 was prepared within a N_2-atmosphere glovebox and chilled to −60 °C. The *tert*-chloride groups were then activated by the addition of 5 equiv of $TiCl_4$ (room temperature, neat). A portion of the activated solution was charged to a 5 mm o.d. NMR tube fitted with a screw-on septum cap. The sealed tube was placed in a spinner, removed from the dry box and transported at dry ice temperature (approximately −78 °C) to the probe of a Varian Inova 500 MHz spectrometer. The (di)sulfide was added to the tube through the septum with a microliter syringe to achieve the necessary concentration, and the contents of the tube were briefly mixed by swirling and inverting before inserting the tube into the probe. The tube was equilibrated at the desired temperature (calibrated with a methanol standard) before recording spectra. All chemical shifts were referenced to the residual solvent resonances of CD_2Cl_2, i.e., 5.32 ppm for ^{1}H and 53.8 ppm for ^{13}C.

Results and Discussion

When a sulfide or disulfide is charged to an active $TiCl_4$-catalyzed isobutylene polymerization in an equivalent or excess amount relative to the number of chain ends, consumption of monomer immediately ceases, as shown in Figure 1 for diisopropyl disulfide. This occurs as the sulfide or disulfide immediately complexes $TiCl_4$, and the complex reacts with the carbenium ion chain ends to form sulfonium ion adducts as outlined in Scheme 1. Lewkebandara et al.[22] found that sulfide-$TiCl_4$ complexes in solution likely exist as a 6-coordinate $TiCl_4$ having two sulfide ligands. However, disulfide-$TiCl_4$ complexes were different, consisting of dimeric Ti_2Cl_8 and a single disulfide ligand. The difference was thought to occur because the η^2-disulfide ligand cannot bind strongly in bidentate fashion to the small titanium center; rather it coordinates with two faces of Ti_2Cl_8 forming a bridge. Regardless of the exact (di)sulfide-$TiCl_4$ complexation stoichiometry, there appears to be minimal effect on the overall PIB−(di)sulfide adduct formation when excess $TiCl_4$ is present. Under typical polymerization conditions with temperatures between −60 and −80 °C, adduct formation is quantitative even when only one equivalent of (di)sulfide relative to chain chains is present.

The sulfonium ion at the PIB chain end, though unreactive with isobutylene under typical quasiliving polymerization condi-

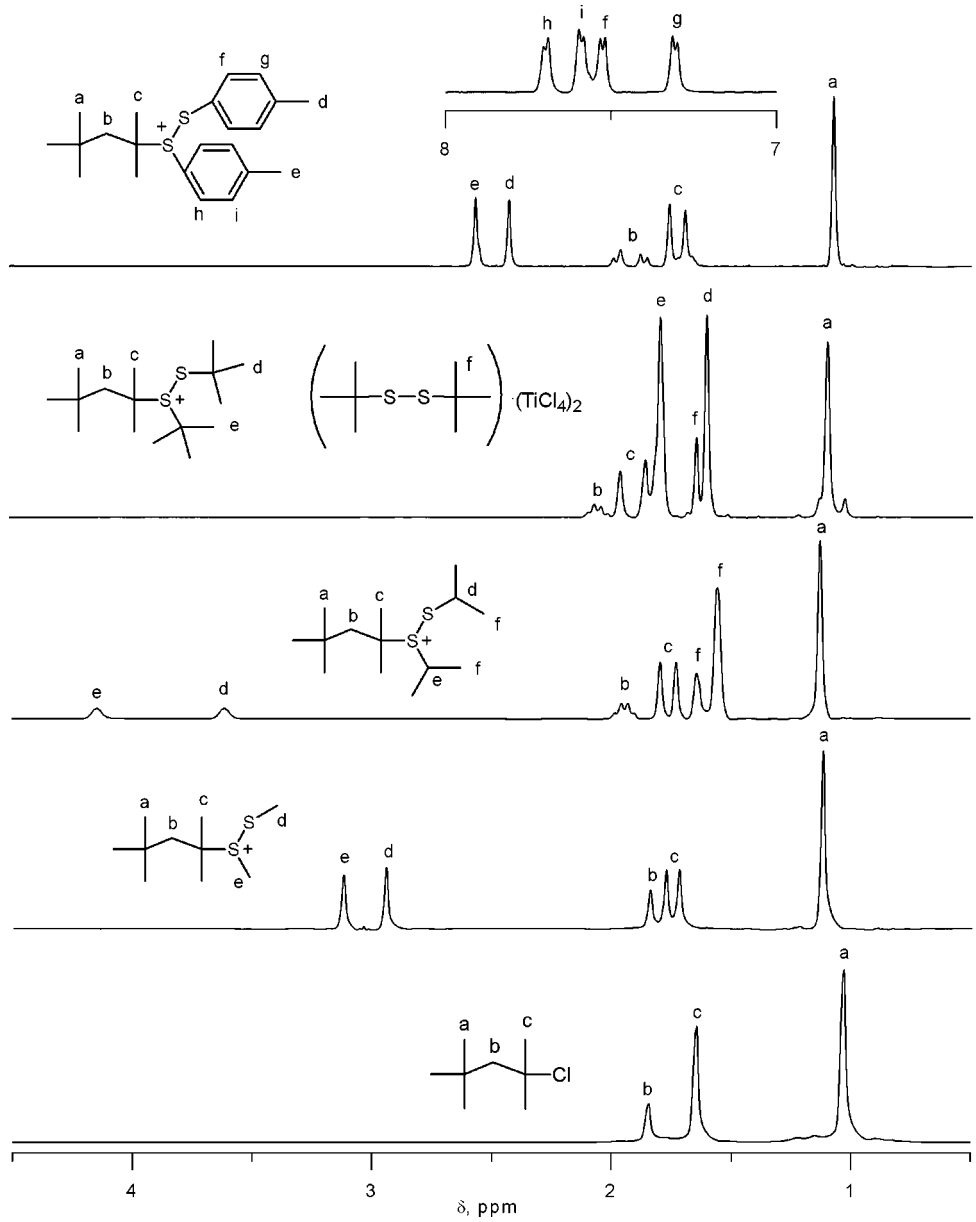


Figure 3. 500 MHz ^{1}H NMR spectra of TMPCl and TMPCl/disulfide adducts in the presence of 5 equiv of $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 at −60 °C. Shown are adducts from dimethyl disulfide, diisopropyl disulfide, di-*tert*-butyl disulfide, and di-*p*-tolyl disulfide.

tions, represents an excellent leaving group for reaction with stronger nucleophiles such as alcohols or amines. As illustrated in Scheme 1, when sulfonium ion adducts are contacted with excess alcohol or amine a mixture of elimination and substitution products results. The predominant decomposition pathway for PIB−sulfide adducts is elimination to form *exo*-olefin PIB; however, in some cases alcohols can displace the sulfide moiety resulting in concomitant formation of ether endgroups. With PIB−disulfide adducts high yields of *exo*-olefin are also possible, but the situation is complicated by an additional reaction pathway where the sulfur−sulfur linkage of the disulfide moiety is cleaved to provide thioether endgroups.

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

Figure 3 shows the ^{1}H NMR spectra of sulfonium ion adducts formed from the reaction of various disulfides with TMPCl in the presence of $TiCl_4$ at −60 °C. The disulfide adducts are similar to the sulfide adducts in that resonances of the TMP moiety are shifted downfield; however, the *gem*-dimethyl protons (c) now appear nonequivalent due to the asymmetric sulfonium ion and hindered rotation about the newly formed carbon−sulfur bond. In the spectrum for the dimethyl disulfide adduct the methylene protons of the TMP moiety are equivalent. As the size of the groups attached to sulfur increases, rotation about the carbon−carbon bond between the neopentyl moiety of TMP and the remainder of the adduct is further hindered. In the spectra for diisopropyl, di-*tert*-butyl, and di-*p*-tolyl disulfide, the methylene protons of the TMP moiety (b) appear as a

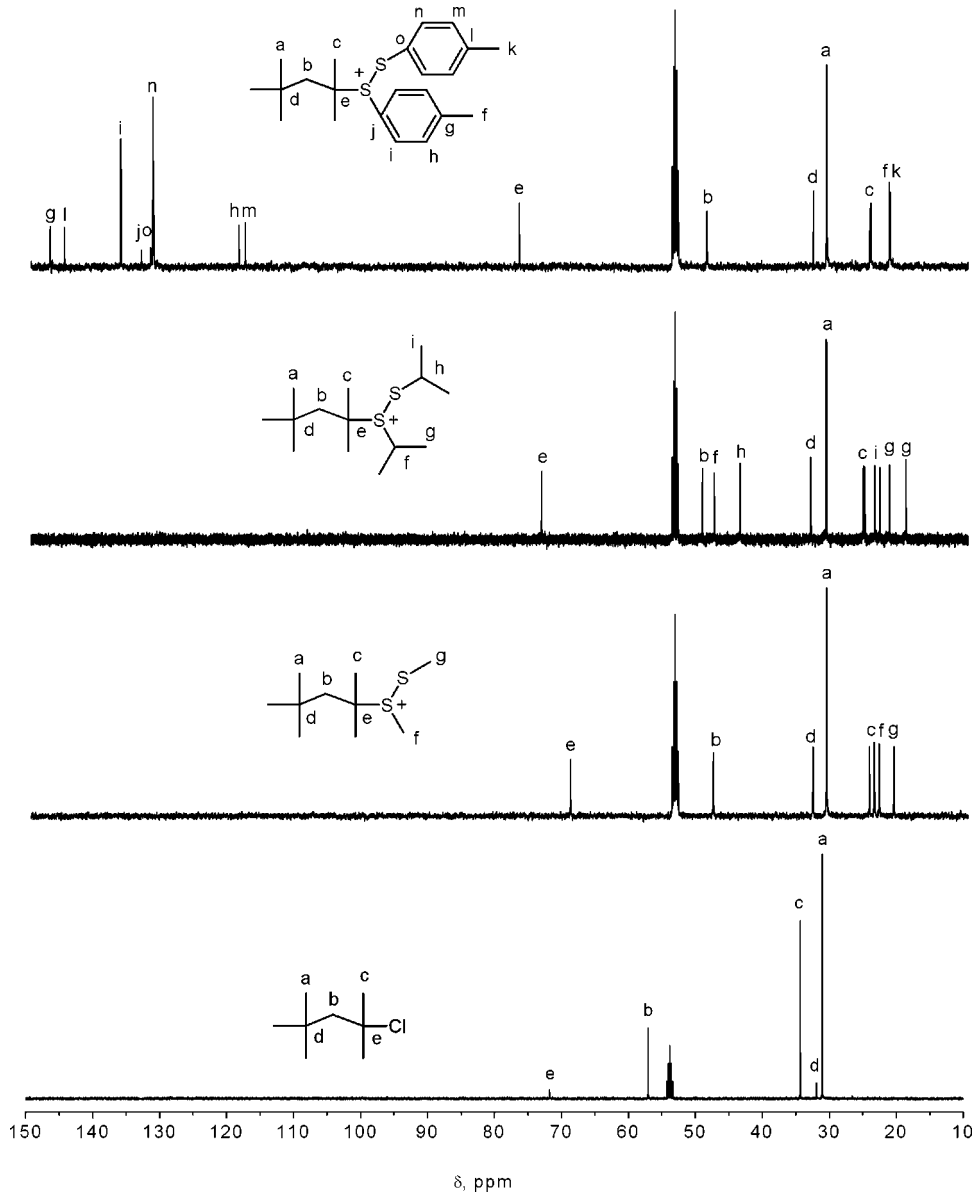


Figure 4. 125 MHz ^{13}C NMR spectra of TMPCl and its adducts with dimethyl disulfide, diisopropyl disulfide, and di-*p*-tolyl disulfide in the presence of 5 equiv of $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 at −60 °C.

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

Figure 4 shows the ^{13}C NMR spectra of the sulfonium ion adducts formed from the reaction of dimethyl, diisopropyl, and di-*p*-tolyl disulfide with TMPCl in the presence of $TiCl_4$ at −60 °C. These ^{13}C spectra more clearly show the nonequivalence imparted by hindered rotation from steric bulk and asymmetry in the disulfide moiety.

To confirm that equivalent sulfonium ion adducts are formed with higher molecular weight oligo-isobutylenes, a series of *tert*-chloride functional oligo-isobutylenes was reacted with dimethyl disulfide in the presence of $TiCl_4$ at −60 °C. Figure 5 shows the resulting ^1H NMR spectra. As with the TMPCl-dimethyl disulfide adduct, the ultimate dimethyl resonances of the oligo-isobutylenes are split and shifted downfield. Also, the methyl resonances of the disulfide moiety are split, consistent with asymmetric sulfonium ion formation.

Sulfonium ion adduct formation has a significant dependence on temperature. Figure 6 illustrates this temperature dependence for the 1:1 TMPCl/dimethyl disulfide (MDS) adduct. In the range of −60 to −20 °C adduct formation is essentially quantitative. Above −20 °C, adduct formation becomes reversible, and with increasing temperature, increasing amounts of MDS-$TiCl_4$ complex and TMPCl are observed in equilibrium with the adduct (e.g., see the 10 or 20 °C spectrum). Over the temperature range where the sulfonium ion adduct, TMPCl, and $(MDS).(TiCl_4)_2$ species coexist, the ^1H NMR resonances for each

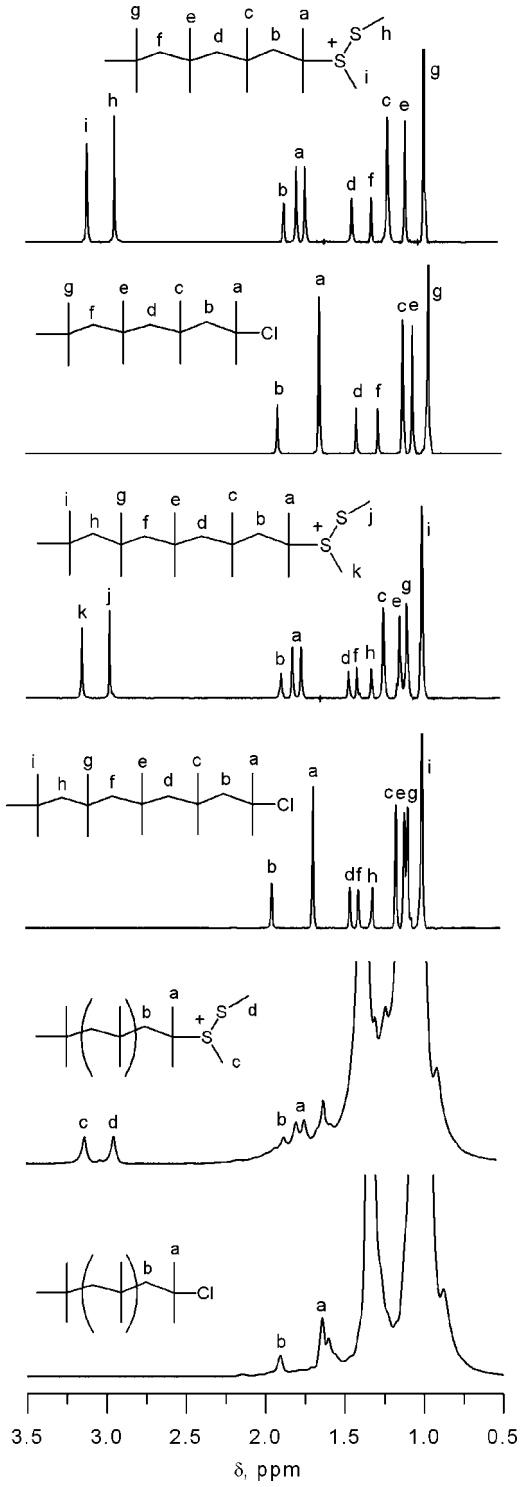


Figure 5. 500 MHz ^{1}H NMR spectra of dimethyl disulfide adducts in the presence of 5 equiv of $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 at −60 °C. Shown are adducts of dimethyl disulfide with *tert*-chloride PIB masterbatch, C_{16}PIBCl and C_{20}PIBCl.

species are resolved indicating a slow rate of exchange in reference to the NMR time scale.[14,23] If the system is further warmed, for example, to room temperature or above, irreversible side reactions begin to occur and the adduct cannot be fully recovered by cooling. Figure 6 also shows that the *gem*-dimethyl resonances of TMP that appeared nonequivalent below −20 °C begin to coalesce into a single resonance at higher temperatures, indicating increased rotation about the carbon−sulfur bond between the TMP and disulfide moiety.

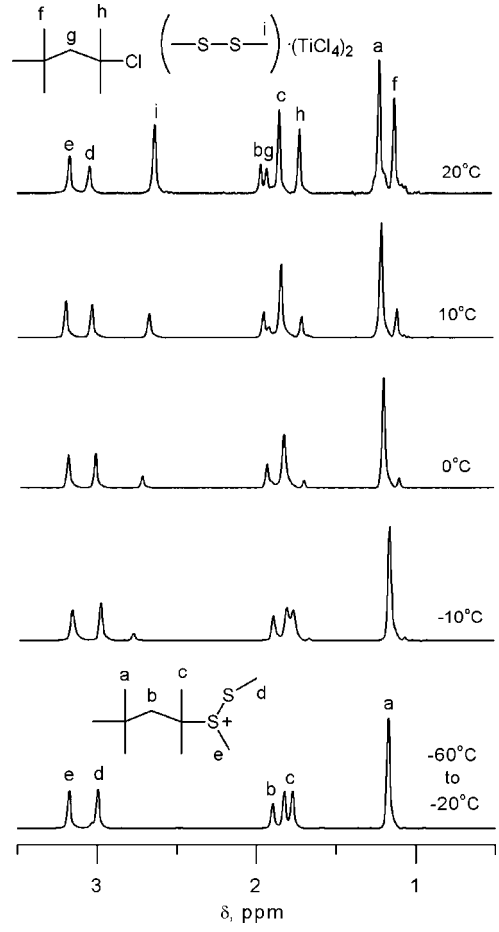


Figure 6. 500 MHz ^{1}H NMR spectra of the TMPCl/dimethyl disulfide adduct in the presence of 5 equiv of $TiCl_4$ in 50/50 (v/v) CS_2/CD_2Cl_2 from −60 to +20 °C.

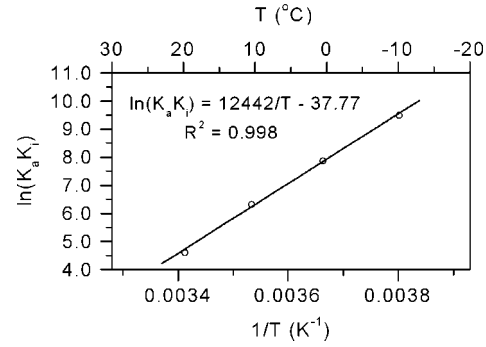


Figure 7. van't Hoff plot of TMPCl−dimethyl disulfide adduct formation reaction.

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

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

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

Combining these two equilibria, and assuming quantitative complexation of the disulfide in the presence of excess $TiCl_4$ (i.e., no free MDS) and equimolar charges of TMPCl and MDS,

Table 2. Estimated Apparent Equilibrium Constant (K_aK_i) for Adduct Formation between Dimethyl Disulfide (MDS) and TMPCl Based on Integration of the ^{1}H NMR Spectra of Figure 6 and $[TMPCl]_0 = 0.02$ M

temperature (°C)	reciprocal temperature (K^{-1})	extent of adduct formation, ε	equilibrium constant, $K_aK_i \times 10^{-2}$ (M^{-1})	$\ln(K_aK_i)$
−20		1.00		
−10	0.00380	0.94	130.6	9.5
0	0.00366	0.87	25.7	7.9
10	0.00353	0.74	5.5	6.3
20	0.00341	0.50	1.0	4.6

i.e. $[TMPCl]_0 = [MDS]_0$, the overall adduct formation equilibrium constant may be written as

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

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

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

The apparent equilibrium constant (K_aK_i) can be estimated by integration of the methyl resonances of $(MDS)\cdot(TiCl_4)_2$ versus those of the adduct in Figure 6 and assuming $[TiCl_4]$ remains roughly constant and equal to its initial nominal concentration, $[TiCl_4]_0$. This assumption becomes valid for $[TiCl_4]_0 \gg [TMPCl]_0$. Calculated values of the apparent equilibrium constant (K_aK_i) are shown in Table 2. The values are quite large and increase with decreasing temperature, indicating energetically favorable formation of the sulfonium ion adduct. The data from Table 2 are shown as a van't Hoff plot in Figure 7. The apparent standard enthalpy change for adduct formation is estimated from the slope of the plot to be −24.7 kcal/mol.

Decomposition of Sulfonium Ion Adducts. To be useful as an *in situ* PIB functionalization method, addition of the sulfide or disulfide should be timed to coincide with approximately full

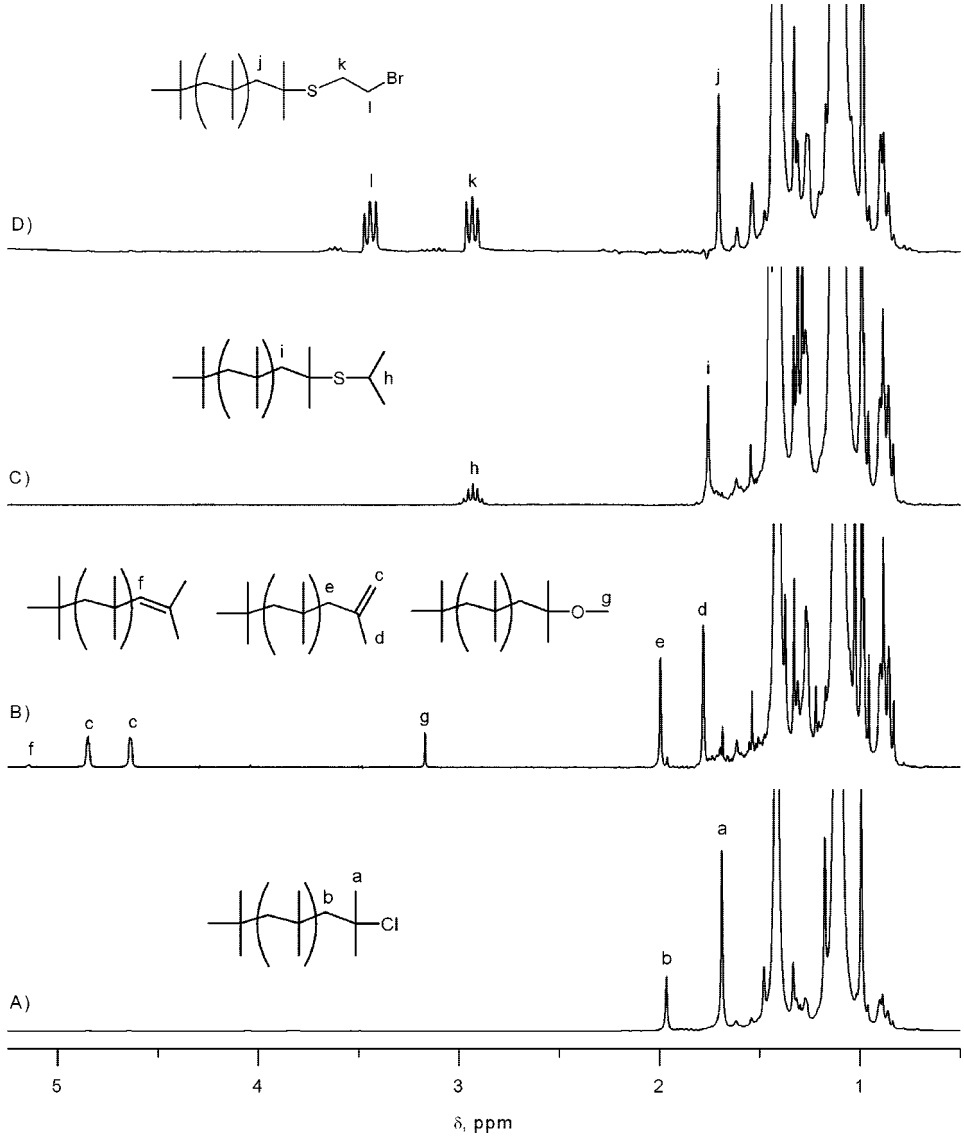


Figure 8. 300 MHz ^{1}H NMR spectra of polyisobutylene with representative chain end functionalities at 25 °C in $CDCl_3$. Shown are (A) *tert*-chloride chain ends, (B) *exo*-olefin, *endo*-olefin, and methoxy chain ends from termination of the PIB−diisopropyl sulfide adduct with methanol, (C) isopropyl thioether chain ends from termination of the PIB−diisopropyl disulfide adduct with triethylamine, and (D) 2-bromoethylsulfanyl chain ends from termination of the PIB−bis(2-bromoethyl) disulfide adduct with triethylamine.

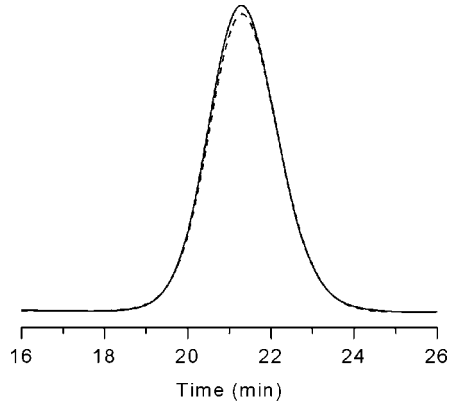


Figure 9. Differential refractive index traces for GPC of PIB immediately before addition of bis(2-bromoethyl) disulfide (---) and of the final primary bromide functional polymer (−) obtained from triethylamine decomposition of the PIB− bis(2-bromoethyl) disulfide adduct.

monomer conversion, and the terminating nucleophile should be selected to yield exclusively one type of chain end. As shown in Table 1, the product distribution is effected by both the (di)sulfide and the terminating nucleophile. In general, sulfides can be used to obtain high yields of *exo*-olefin PIB, and disulfides produce high yields of thioether-capped PIB.

For PIB−monosulfide adducts, when methanol or ethanol is used as the terminating nucleophile, the major product is *exo*-olefin, but some substitution occurs to yield alkoxy chain end functionality. Figure 8, spectrum B, shows a ^{1}H NMR spectrum of PIB obtained through methanol termination of a PIB−diisopropyl sulfide adduct (entry 2, Table 1); a *tert*-chloride-terminated PIB spectrum is shown for comparison (spectrum A). Switching to a bulkier alcohol, such as 2-propanol (entry 4, Table 1), eliminates the substitution product. Amines are also efficient at converting monosulfide-capped chain ends to *exo*-olefin; however, in some cases reformation of *tert*-chloride chain ends is observed (e.g., entry 6, Table 1) suggesting competitive complexation/reaction with $TiCl_4$, leading to collapse of the sulfonium ion adduct. The best results are obtained with highly hindered amines such as 2,6-di-*tert*-butylpyridine, which in combination with diisopropyl sulfide results in near-quantitative formation of *exo*-olefin chain ends (entry 7, Table 1).

For a PIB−disulfide adduct, the terminating nucleophile can attack the sulfonium ion, rupture the sulfur−sulfur linkage, and yield a potentially useful thioether end group. For example, Figure 8 shows isopropyl thioether (spectrum C) and primary bromide-terminated PIB (spectrum D) obtained through triethylamine termination of the PIB−diisopropyl disulfide adduct (entry 15, Table 1) and the PIB−bis(2-bromoethyl) disulfide adduct (entry 17, Table 1). As shown in Table 1, cleavage of the sulfur−sulfur linkage to produce thioether is the dominant decomposition pathway for PIB−disulfide adducts; it fails to occur only for bulky disulfides such as diisopropyl disulfide in combination with a weakly nucleophilic and/or bulky terminator (entries 11−13, Table 1). For these cases, *exo*-olefin is the major product. One principle exception to this generalization is that decomposition to thioether can also fail even for slender disulfides when an alcohol is used for termination in the absence of a proton trap/electron donor, such as 2,6-lutidine (compare entry 8, with 26Lut, to entry 9, without 26Lut, Table 1). This suggests that 2,6-lutidine, if present, may be the actual nucleophile responsible for decomposition of the adduct. Even in the presence of 2,6-lutidine, the fraction of thioether produced by methanol termination drops from 0.75 to 0.55 to zero when the bulkiness of the disulfide is systematically changed from methyl to ethyl to isopropyl (compare entries 8, 10, and 11, Table 1).

In general, nucleophilic amines such as triethylamine and 2,5-dimethylpyrrole provide very high yields of thioether without inducing chain coupling (see GPC trace for primary bromide functionalized PIB in Figure 9). Non-nucleophilic proton traps, such as 2,6-di-*tert*-butylpyridine and 1,2,2,6,6-pentamethylpiperidine, are presumably too bulky to attack the disulfide moiety directly, and therefore yield mostly olefin.

Conclusions

Sulfonium ion adducts are quantitatively produced when a mono- or disulfide is added to $TiCl_4$-catalyzed quasiliving polyisobutylene. The adducts are stable at −60 °C and lower, and they possess a well defined structure as elucidated by low-temperature NMR spectroscopy. PIB−sulfide and PIB−disulfide adducts provide an excellent platform for chain end functionalization. Near-quantitative yield of *exo*-olefin functionalized polyisobutylene can be obtained by addition of 2,6-di-*tert*-butylpyridine to the PIB−diisopropyl sulfide adduct. In this regard, the sulfonium ion adducts may offer significant advantage in terms of *exo*-olefin functionalization because they may reduce chain coupling at high chain end concentrations. Addition of an amine such as triethylamine to a PIB−disulfide adduct gives near-quantitative yield of the corresponding thioether functionalized PIB. This latter reaction is tolerant of the presence of other functional groups on the disulfide, including halogen, thus offering a method for introducing other useful functionality onto the PIB chain end.

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