Functionalization of Poly(styryl)lithium with Thiiranes: Sulfur Extrusion vs Ring-Opening Mechanisms

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ABSTRACT: Poly(styryl)lithiums (M_n = 1500−2200 g/mol) in benzene were reacted with propylene sulfide (1.3−3 equiv) to prepare the corresponding thiol chain-end-functionalized polymers. The resulting polymers were characterized by thin layer chromatography, elemental analysis, ^{1}H, ^{13}C, and DEPT NMR spectroscopy, and MALDI-TOF mass spectrometry. Analysis of the resulting polymers by MALDI-TOF mass spectrometry indicates that reaction occurs by a ring-opening mechanism, in contrast to precedents showing that the reaction of organolithium compounds with propylene sulfide occurs by a sulfur extrusion mechanism. Poly(styryl)lithium was also reacted with 1.3 equiv of ethylene sulfide. The results from MALDI-TOF mass spectrometry show that the structure of the polymer corresponds to the product resulting from a ring-opening mechanism analogous to the reaction of propylene sulfide with poly(styryl)lithium. More oligomerization was observed for functionalizations with 1.3 equiv of ethylene sulfide (34.6%) compared to propylene sulfide (3.8%). The experimental results are consistent with quantitative thiol functionalization for reactions of poly(styryl)lithium with thiiranes.

Introduction

Alkyllithium-initiated, living anionic polymerization is a useful method to prepare well-defined polymers with controlled, predictable molecular weights and narrow molecular weight distributions.[1] Because of the absence of chain termination and chain transfer steps, alkyllithium-initiated anionic polymerization provides an excellent methodology for the preparation of a variety of ω-chain-end functionalized polymers by reaction of the living carbanionic chain ends with appropriate electrophilic functionalizing agents.[1−3]

Among the types of functional polymers of synthetic interest are polymers with end-functional thiol groups (P-SH). These have found a range of applications including stabilization of gold nanoparticles,[4,5] spontaneous chemisorption onto gold surfaces to form monolayers,[6,7] preparation of semiconductor cadmium sulfide (CdS) nanocomposites,[8] and functional group attachment by chemical ligation[9] as well as potential applications for chain extension, reversible dimerization,[10] block copolymer formation by chain transfer,[11] and cross-linking reactions.[12]

Well-defined, thiol end-functionalized polymers have been prepared indirectly by atom transfer radical polymerization (ATRP).[13,14] There are few reports describing the anionic synthesis of well-defined, ω-thiol-functionalized polymers. Nakahama and co-workers[10] prepared ω-thiol-functionalized polystyrenes and polyisoprenes by termination of the corresponding anionic living polymers with *tert*-butyldimethylsilyl-3-chloropropyl sulfide. Although these functionalization reactions were reported to be quantitative, the polymers had to be deprotected under nitrogen (HCl/dioxane/water) to obtain the desired thiol functionality. The resulting deprotected ω-thiol-functionalized polymers were reported to undergo oxidative dimerization upon attempted SEC analysis. Furthermore, the reactions were carried out in the polar solvent tetrahydrofuran (THF) at −78 °C. The use of THF as solvent for the reaction is undesirable since poly(styryl)lithium chains decompose in the presence of THF;[1,15] in addition, the unique ability of alkyllithium compounds to produce polydienes with high 1,4 microstructure is lost in the presence of THF.[1]

The reaction of polymeric organolithium compounds with thiiranes (episulfides, alkylene sulfides) is reported to be a viable route for the preparation of thiol functional polymers.[5−8,11] Tung and co-workers[11] described the preparation of ω-thiol- and α,ω-dithiol-functionalized polybutadienes by reaction of poly(butadienyl)lithium and α,ω-dilithiumpolybutadiene, respectively, with excess propylene sulfide or ethylene sulfide in the presence of THF. The thiol end-functionalized polybutadienes were used as chain transfer agents in the free radical polymerizations of styrene, styrene/acrylonitrile, and methyl methacrylate. Stouffer and McCarthy[6] functionalized poly(styryl)lithium in THF by terminations with stoichiometric and excess amounts of propylene sulfide to prepare ω-thiol-functionalized polystyrene and polystyrene-*block*-poly(propylene sulfide), respectively. Kim and co-workers[8] prepared telechelic α,ω-dithiol functional polystyrene by reaction of an unspecified amount of ethylene sulfide with α,ω-dilithiopolystyrene synthesized with lithium naphthalenide in the presence of THF (95/5, v/v, benzene/THF). Thiol functionalization yields were reportedly >98% as determined by ^{1}H NMR analysis. These authors stated that formation of poly(propylene sulfide) blocks was unavoidable under their conditions. A number of research groups have utilized the reactions of polymeric organolithium compounds with excess propylene sulfide to prepare the corresponding diblock copolymers.[16−19] In all of this previous research on the functionalization of polymeric organolithium compounds with propylene sulfide and ethylene sulfide, the mechanisms of these functionalization reactions have not been elucidated. In addition, the efficiency of these functionalizations and the question of whether oligomerization occurs have not been determined, especially in hydrocarbon solution.

The only mechanistic information on the reactions of organolithium compounds with thiiranes is derived from studies of the reactions with simple alkyllithium and aryllithium compounds. The reaction of simple organolithium compounds with

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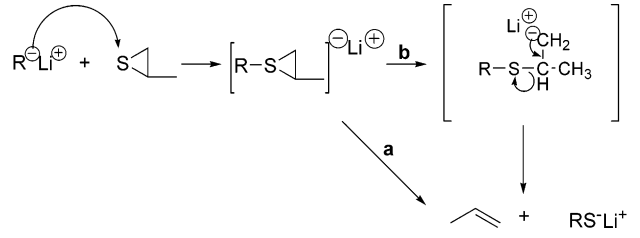
Scheme 1. Mechanisms for the Reaction of Alkyllithium Compounds with Propylene Sulfide by Sulfur Extrusion: (a) Direct Fragmentation of the Trigonal-Bipyramidal Sulfurane Intermediate and (b) Ring-Opening To Form a 1-Lithio-2-alkylthioalkane Intermediate Followed by Elimination of the Alkene and Formation of the Thiolate Anion



thiiranes was first studied by Bordwell and co-workers.[20] The "sulfur extrusion" reaction was reported to proceed by attack of the anion on sulfur to form a trigonal-bipyramidal intermediate, ring-opening to form an intermediate primary carbanion, and finally 1,2-elimination of the alkyl or aryl thiolate and an olefin corresponding to the thiirane, as shown in Scheme 1b. Schuetz and Jacobs[21] isolated alkyl allyl ethers and lithium mercaptides from the reactions of butyllithium and phenyllithium with 2-alkoxymethylthiiranes. Morton and Kammereck[22] confirmed the results of Bordwell et al.[20] for the reaction of ethyllithium with 2-methylthiirane at −78 °C in THF by identifying ethanethiol and propylene as the exclusive products. Trost and Ziman[23] as well as Bonini and co-workers[24] have shown that the desulfurization reaction of episulfides with *n*-butyllithium forms the corresponding alkenes derived from the episulfides with complete stereospecificity. On the basis of these results and experiments involving generation of the proposed intermediate 1-lithio-2-alkylthioalkanes, Trost and Ziman[23] concluded that the trigonal-bipyramidal intermediate fragments via a concerted (Scheme 1a) rather than stepwise process (Scheme 1b) to give the alkene and alkylthiolate directly.

To date, the sulfur extrusion mechanism has been the accepted mechanism for the reaction of organolithium compounds with cyclic sulfides irrespective of the structure of the carbanion. Herein, the mechanism and utility of the thiol functionalization reaction of poly(styryl)lithium with propylene sulfide (2-methylthiirane) or ethylene sulfide (thiirane) have been investigated in hydrocarbon solvent at room temperature. The structures of the resulting functionalized polymers were determined by ^{1}H and ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry.

Experimental Section

Chemicals and Solvent. Benzene (Certified ACS, EM Science) and styrene (99%, Aldrich) were purified as previously described.[25] Benzene was distilled as needed from poly(styryl)lithium directly into the polymerization reactor. *sec*-Butyllithium (Chemetall Foote Corp., 12 wt % in cyclohexane) was used as received after double titration with allyl bromide.[26] Propylene sulfide (≥96%, Aldrich) and ethylene sulfide (98%, Aldrich) were purified by stirring over calcium hydride with periodic degassing for 12 h followed by distillation into calibrated ampules and flame-sealing with a torch. Methyl iodide (≥96%, Aldrich) was purified by stirring over phosphorus pentoxide with periodic degassing for 12 h followed by vacuum distillation into calibrated, flame-sealed ampules. Methanol (Fisher Scientific, reagent grade) was degassed on the vacuum line before distillation into ampules with or without degassed glacial acetic acid (100%, Fisher Scientific) and flame-sealed with a torch.

Polymerizations. Poly(styryl)lithiums (ca. 1500−2500 g/mol) were prepared under high-vacuum conditions in sealed, all-glass reactors using break-seals and with *sec*-butyllithium as the initiator in benzene (10−15 vol % styrene) at 30 °C.[27] Before addition of the thiirane, a 10 mL aliquot of the poly(styryl)lithium solution was transferred into an attached, empty ampule followed by removal by sealing with a hand torch. This base sample was then quenched with degassed methanol for characterization by SEC.

Functionalization of Poly(styryl)lithium. Functionalization of poly(styryl)lithium was effected directly in the polymerization reactor by smashing the break-seal for the ampule containing the thiirane in benzene at room temperature. A change of color from orange to light yellow was observed almost immediately. After 15 min, a 25 mL aliquot of the functionalized poly(styryl)lithium solution was removed by flame-sealing an ampule from the reactor with a hand torch. The sample was then quenched with methyl iodide. The rest of the reaction mixture was quenched with a 1:1 methanol/acetic acid mixture. Solvent was removed from the resulting polymers using a rotary evaporator, followed by further drying on the high-vacuum line for 48 h. Elemental analysis was performed on the sample obtained when poly(styryl)lithium (PSLi, $M_n = 2.0 \times 10^3$ g/mol, $M_n/M_w = 1.05$) was reacted with 1.3 equiv of propylene sulfide and quenched with a 1:1 methanol/acetic acid mixture. Elemental Analysis: Calcd for 1 propylene sulfide unit [$C_4H_9(C_8H_8)_{18}CH_2CH(CH_3)SH$]: C, 90.36; H, 8.04, S 1.60; Calcd for 2 propylene sulfide units {$C_4H_9(C_8H_8)_{18}[CH_2CH(CH_3)S]_2H$}: C, 88.89; H, 8.04, S, 3.07. Found: C, 89.84; H, 7.74; S, 2.42 (by difference).

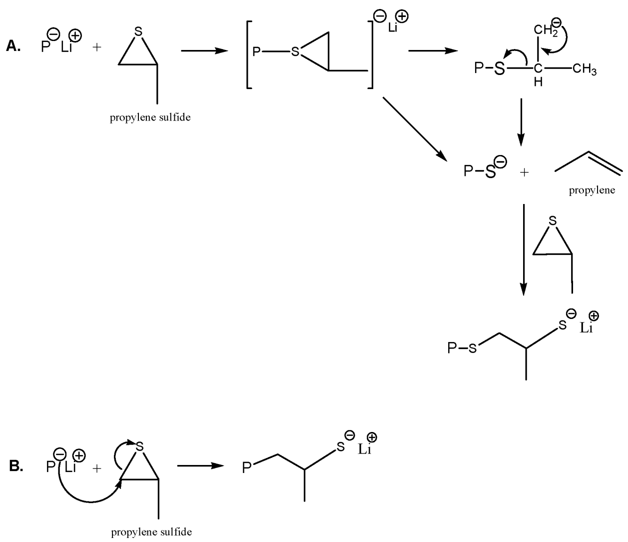
Oxidation of Thiol-Functionalized Polymers. Oxidation of the terminal thiol group with iodine was carried out in benzene under a dry nitrogen atmosphere in the dark. An excess amount of iodine (100 mol) was added to the functional polymer solution (1 g/250 mL of benzene) and stirred for 24 h. The resulting polymer was washed with a 10% solution of aqueous sodium bisulfite to remove excess iodine and analyzed by SEC.

Characterization. Size-exclusion chromatographic analyses (SEC) for the base polymers and functionalized polymers were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/10^3/10^4 Å), mixed bed (10^3/10^4/10^6 Å)] and a triple detector system with THF as eluent at a flow rate of 1.0 mL/min at 30 °C; the detector system consisted of a differential refractometer (Waters 410), a differential viscometer (Viscotek 100), and a laser light scattering detector (Wyatt Technology, DAWN EOS, $\lambda = 670$ nm). Regular SEC calibrations were conducted with polystyrene standards (Polymer Laboratories). All ^{1}H (300 MHz), ^{13}C (quantitative reverse-gate decoupled spectra, 12 500 scans at 75 MHz with $d_1 = 6$ s), and DEPT ($\theta = 135°$) NMR spectra were acquired in $CDCl_3$ (Aldrich, 99.8% D) using a Varian Mercury 300 spectrometer.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Reflex-III TOF mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with an LSI model VSL-337ND pulsed 337 nm nitrogen laser (3 nm pulse width), a single-stage pulsed ion extraction source, and a two-stage gridless reflector. Solutions of dithranol (20 mg/mL) (Alfa Aesar, 1,8,9-anthracenetriol, 97+%), polymer sample (10 mg/mL), and silver trifluoroacetate (10 mg/mL) (Aldrich, 98%) or sodium iodide (10 mg/mL) (MCD, 99%) were prepared in THF (Aldrich, 99.9%). These solutions were mixed in the ratio of matrix/cationizing salt/polymer (10:1:2), and 0.5 μL of the mixture was applied to the MALDI sample target and allowed to dry. To minimize undesirable polymer fragmentation and to achieve optimal intensity, the intensity of the nitrogen laser pulses was frequently attenuated and adjusted. Mass spectra were measured in the linear and reflection modes, and the mass scale was calibrated externally using the peaks of a polystyrene standard at the molecular weight under consideration.

Thin-layer chromatographic analyses (TLC) were carried out on the functionalized polymers by spotting and developing polymer samples on flexible silica gel plates (Selecto Scientific, Silica Gel 60, F-254 with fluorescent indicator), using a 50/50 (vol/vol) mixture of toluene and cyclohexane as eluent. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS/O analyzer in the laboratory of Professor C. Pugh at The University of Akron.

Scheme 2. Mechanisms for the Reaction of Poly(styryl)lithium and Propylene Sulfide (A) with Sulfur Extrusion and (B) by Ring-Opening



Results and Discussion

Functionalization of Poly(styryl)lithium with 3 mol equiv of Propylene Sulfide. For the initial experiments, poly(styryl)lithium (PSLi, $M_n = 2.2 \times 10^3$ g/mol, $M_n/M_w = 1.04$) was functionalized with 3 mol equiv of propylene sulfide in benzene at 30 °C to investigate the questions of the mechanism of the reaction and the extent of oligomerization. The characteristic orange color of the poly(styryl)lithium disappeared within minutes and turned light yellow. The reaction was allowed to proceed for 1 h. Since the base-catalyzed oxidation of thiols to disulfides in the presence of oxygen is well-known,[28] the reaction was quenched with acidic methanol (methanol/acetic acid). The SEC chromatogram for the resulting thiol-functionalized polystyrene ($M_n = 2.5 \times 10^3$ g/mol; $M_w/M_n = 1.04$) showed a narrow, monomodal distribution. The stability of the prepared thiol-functional polymer toward oxidation was further confirmed by performing another SEC chromatogram after 1 month, resulting again in a narrow, monomodal curve ($M_n = 2.4 \times 10^3$ g/mol; $M_w/M_n = 1.04$). These results stand in sharp contrast to the reports of Nakahama and co-workers[10] that thiol-functionalized polystyrenes and polyisoprenes underwent oxygen-catalyzed dimerization reactions during SEC analysis in THF.

In order to investigate the mechanism of the functionalization reaction of poly(styryl)lithium with propylene sulfide, i.e., ring-opening vs sulfur extrusion (see Scheme 2), precise information on the nature of the end groups was required. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) has been shown to be one of the most useful tools for the characterization of chain-end-functionalized polymers.[29−33] The MALDI-TOF mass spectrum for the thiol-functionalized polymer (Figure 1) obtained using silver as cationizing agent showed five series of peaks. Within each series, the peaks were separated by *m*/*z* 104, corresponding to a styrene repeat unit. The *m*/*z* difference between each series was 74 corresponding to a propylene sulfide unit, which indicates that oligomerization was occurring during these functionalizations. The analysis of the mass spectral results was further complicated by the recognition that there was ambiguity in the assignment of structures to the peaks because of isobaric structures corresponding to the either sulfur extrusion and propylene sulfide oligomerization or ring-opened structures with oligomerization and exchange of the thiol proton with a silver ion. For example, the peak at *m*/*z* 1979.6 could correspond to [$C_4H_9-(C_8H_8)_{15}-S-(C_3H_6S)_3-H{\cdot}Ag^+$], i.e., the silver complex of the 15-mer of polystyrene, with a sulfur from sulfur extrusion, three units of propylene sulfide, and a terminal proton; the calculated monoisotopic mass {57.07 (C_4H_9) + 15 × 104.06 [$(C_8H_8)_9$] + 31.97 (S) + 3 × 74.02 [$(C_3H_6S)_3$] + 1.008 (H) + 106.90 (Ag^+)} = 1979.91 Da. However, the peak at *m*/*z* 1979.6 could also correspond to [$C_4H_9-(C_8H_8)_{15}-(C_3H_6S)_2-Ag{\cdot}Ag^+$], i.e., the silver complex of the 15-mer of polystyrene, two units of propylene sulfide, and a terminal silver; the calculated monoisotopic mass {57.07 (C_4H_9) + 15 × 104.06 [$(C_8H_8)_9$] + 2 × 74.02 [$(C_3H_6S)_3$] + 2 × 106.90 (Ag^+)} = 1979.81 Da. Thus, the calculated monoisotopic masses cannot distinguish between these two isobaric structures. In order to distinguish between these two structures, the experimental isotopic distribution (Figure 2) was compared with the theoretical isotopic distributions (Figure 3) calculated using Bruker XTOF 5.0.2 software. It is clear from this comparison that the correct structure corresponds to the disilver structure without sulfur extrusion (Figure 3B). This assignment was confirmed by measuring the MALDI-TOF mass spectrum using sodium as the cationizing agent (Figure 4). Although the whole mass spectrum appears to be complicated, the expanded spectrum between *m*/*z* 1860 and 1970 can be readily assigned to series of polystyrene oligomers with 1−5 mers of propylene sulfide. For example, the peak at *m*/*z* 1864.3 corresponds to [$C_4H_9-(C_8H_8)_{15}-(C_3H_6S)_3-H{\cdot}Na^+$]; the calculated monoisotopic mass

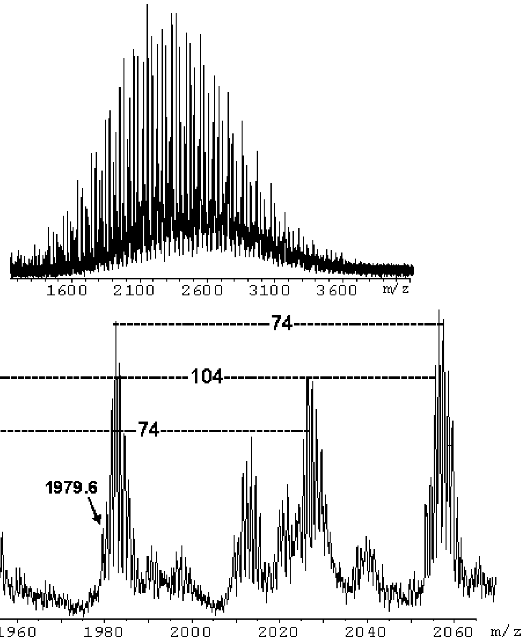


Figure 1. MALDI-TOF mass spectrum of product from the reaction of poly(styryl)lithium and 3 equiv of propylene sulfide using silver as cationizing agent.

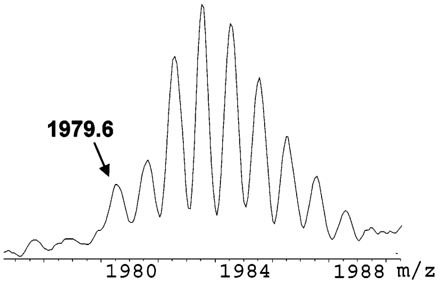


Figure 2. Expanded region of the experimental MALDI-TOF mass spectrum corresponding to the isotopic peaks at *m*/*z* 1979.6.

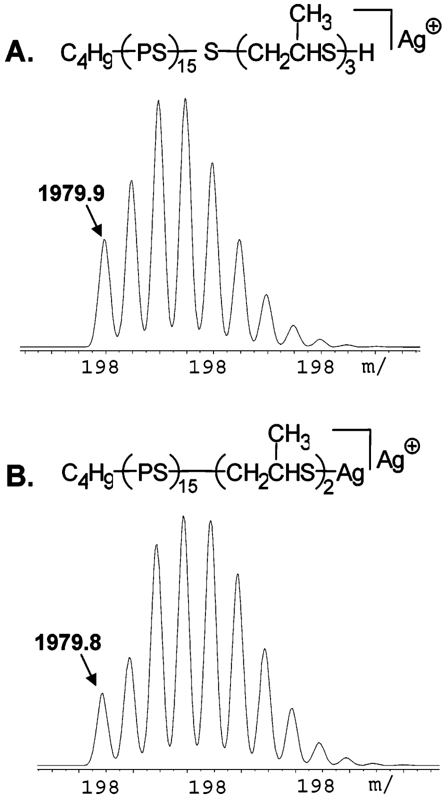


Figure 3. Expanded region of the theoretical isotopic distributions for (A) the silver complex of the 15-mer of polystyrene, with sulfur from sulfur extrusion, three units of propylene sulfide, and a terminal proton [$C_4H_9-(C_8H_8)_{15}-S-(C_3H_6S)_3-H\cdot Ag^+$] and (B) the silver complex of the 15-mer of polystyrene, with two units of propylene sulfide and a terminal silver [$C_4H_9-(C_8H_8)_{15}-(C_3H_6S)_2-Ag\cdot Ag^+$].

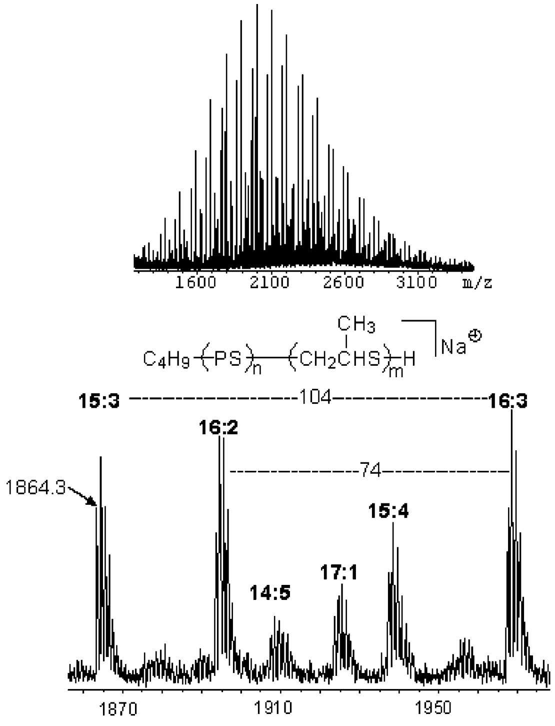


Figure 4. MALDI-TOF mass spectrum of product from the reaction of poly(styryl)lithium and 3 equiv of propylene sulfide using sodium as cationizing agent.

{57.07 (C_4H_9) + 15 × 104.06 [$(C_8H_8)_{15}$] + 3 × 74.02 [$(C_3H_6S)_3$] +1.008 (H) + 22.99 (Na^+)} = 1864.03 Da.

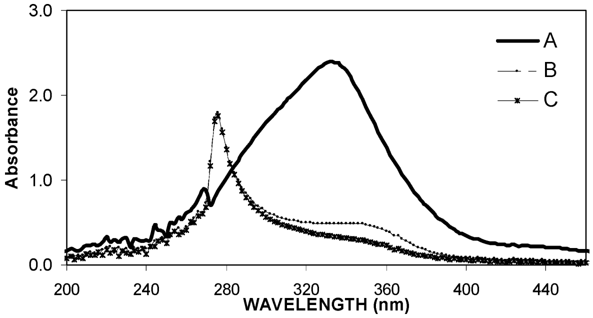


Figure 5. UV−vis spectra of (A) poly(styryl)lithium in benzene prior to addition of 2.2 mol equiv of propylene sulfide, (B) 5 min after addition of propylene sulfide, and (C) 15 min after addition of propylene sulfide.

The structural information from MALDI-TOF mass spectral analysis of the products of the reaction of poly(styryl)lithium with propylene sulfide (3 equiv) unambiguously shows that the functionalization reaction occurs by direct ring-opening to form the corresponding 1-methylethenylthiolate end group. This result is rather surprising, especially since the previous reports on the mechanisms of reactions of organolithium compounds with propylene sulfide found evidence only for attack on the sulfur with elimination of propylene, i.e., no functionalization by direct ring-opening occurred for simple alkyl- and aryllithium compounds.[20−24] For the reactions of polymeric organolithium compounds with propylene sulfide, researchers have implicitly ignored the question of the nature of the end groups beyond the fact that a lithium thiolate end group was formed. The observation of significant amounts of oligomerization of propylene sulfide during functionalization of poly(styryl)lithium with propylene sulfide also stands in sharp contrast to the analogous functionalization reactions with ethylene oxide.[30,34] For room temperature functionalizations of poly(styryl)lithium using 3−5 equiv of ethylene oxide in benzene for 12 h, no oligomerization was observed by MALDI-TOF mass spectral analysis.[30,34] Although lithium thiolate end groups would be expected to be aggregated analogous to lithium alkoxides,[35] a weaker interaction between the hard lithium cation and the softer thiolate anion compared to the hard alkoxide anion would be expected.[36,37] This would tend to result in more dissociation of the lithium thiolate aggregates to more reactive, unassociated species that could participate in oligomerization. Because of the discrepancy found between our results and the previous literature, it was decided to further investigate the mechanism of this reaction, especially the effects of stoichiometry and the presence of Lewis base additives such as THF, since many of the previous functionalizations were carried out in the presence of ethyl ether or THF.[6−8,11,20,22−24]

Functionalization with 2.2 mol equiv of Propylene Sulfide. In order to better control the structure of the resulting functionalized polymers and to simplify the analysis of the functionalization products, it was desirable to attempt to eliminate the oligomerization of the propylene sulfide. To achieve this objective, the effects of both the reaction time and the amount of propylene sulfide relative to chain ends were investigated. Poly(styryl)lithium (PSLi, $M_n = 1.5 \times 10^3$ g/mol, $M_n/M_w = 1.05$) was reacted with 2.2 mol equiv of propylene sulfide in benzene at 30 °C while monitoring the reaction by UV−vis spectroscopy. Prior to the addition of the propylene sulfide to the PSLi, the λ_{max} was observed at 334 nm. After the addition of the propylene sulfide the color of the solution changed from bright orange to light yellow, and the λ_{max} shifted to 280 nm (Figure 5). The reaction was followed for a few hours but it was noted that after 15 min there was no further changes in the

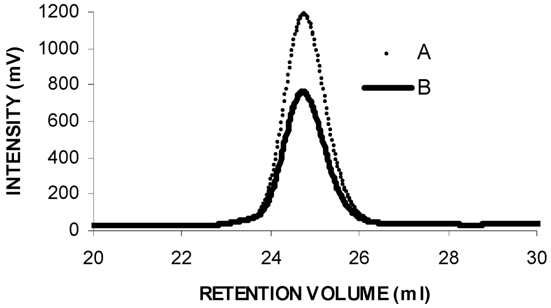


Figure 6. SEC chromatograms of the reaction products from the functionalization of poly(styryl)lithium (M_n = 2000 g/mol) with 1.3 equiv of propylene sulfide after quenching with (A) acidic methanol and (B) methyl iodide.

UV−vis spectrum. From this experiment it was determined that 15 min was sufficient time for the poly(styryllithium) to crossover to propylene sulfide.

Functionalization with 1.3 mol equiv of Propylene Sulfide. In order to minimize oligomerization of propylene sulfide during functionalization, poly(styryl)lithium (PSLi, $M_n = 2.0 \times 10^3$ g/mol, $M_n/M_w = 1.05$) was reacted with 1.3 mol equiv of propylene sulfide for 15 min, at which time the solution was divided into two parts. The two living polymer aliquots were quenched with acidic methanol and methyl iodide, respectively. The SEC chromatograms for the thiol- and methylthio-functionalized polystyrenes ($M_n = 2.1 \times 10^3$ g/mol; $M_w/M_n = 1.06$) both showed narrow, monomodal curves (Figure 6).

The characteristic peak expected for the SH proton in the ^{1}H NMR spectrum at δ 1.2−1.6 ppm[38] was not observed because it overlaps with the methylene protons in the polystyrene backbone and the methyl protons in the propylene sulfide unit. The ^{13}C NMR spectrum of the thiol-functionalized polystyrene (Figure 7) shows characteristic peaks at δ 24.6 and 32.8−33.8 ppm corresponding to the methyl (b) and methine (a) carbons of the functional group, respectively.[39] It is noteworthy that there are no resonance peaks at δ 33.8 or 142.7 ppm arising from the terminal methylene carbon and terminal *ipso* carbon in unfunctionalized polystyrene.[40] These assignments were confirmed by a ^{13}C DEPT-135 spectrum which showed positive peaks for both the δ 24.6 and 32.8−33.8 ppm peaks which establishes that they correspond to $-CH_3$ and $-CH$ carbons (Figure 8). From a quantitative ^{13}C NMR spectrum, an integration ratio of 1.03 was obtained for the area of the resonance corresponding to the methine carbon in the propylene sulfide unit at δ 32.8−33.8 ppm relative to the area corresponding to the initiator methyl carbon at δ 11.0−11.4 ppm. This result is consistent with quantitative functionalization of poly(styryl)lithium with propylene sulfide. Furthermore, the thin layer chromatographic (TLC) analysis using a toluene:cyclohexane mixture (50/50, v/v) as eluent, which is capable of separating the nonfunctionalized polystyrene from the functionalized polystyrene, resulted in observation of only one spot; i.e., no spot corresponding to unfunctionalized polymer was observed. This is consistent with the quantitative nature of the functionalization of PSLi with propylene sulfide.[41] Elemental analysis was consistent with a product mixture consisting of 45% of the product corresponding to monoaddition of propylene sulfide [$P-CH_2CH(CH_3)SH$] and 55% of the product corresponding to diaddition of propylene sulfide {$P-[CH_2CH(CH_3)S]_2H$}.

To facilitate analysis by MALDI-TOF mass spectrometry, the methyl iodide-quenched sample was investigated. The $-S-CH_3$ end group is stable in the presence of silver, thus avoiding the complication from the silver−hydrogen exchange observed previously for the −SH group. Two distributions can be observed in the mass spectrum of this sample (Figure 9). A representative peak in the major distribution at *m*/*z* 1814.0 corresponds to the methylthio-functionalized polystyrene 15-mer with one propylene sulfide unit [$C_4H_9-(C_8H_8)_{15}-CH_2CH(CH_3)S-CH_3\cdot Ag^+$]; the calculated monoisotopic mass {57.07 (C_4H_9) + 15 × 104.06 [$(C_8H_8)_{15}$] + 74.02 (C_3H_6S) + 15.02 (CH_3) + 106.90 (Ag^+)} = 1813.91 Da. The peaks in the minor

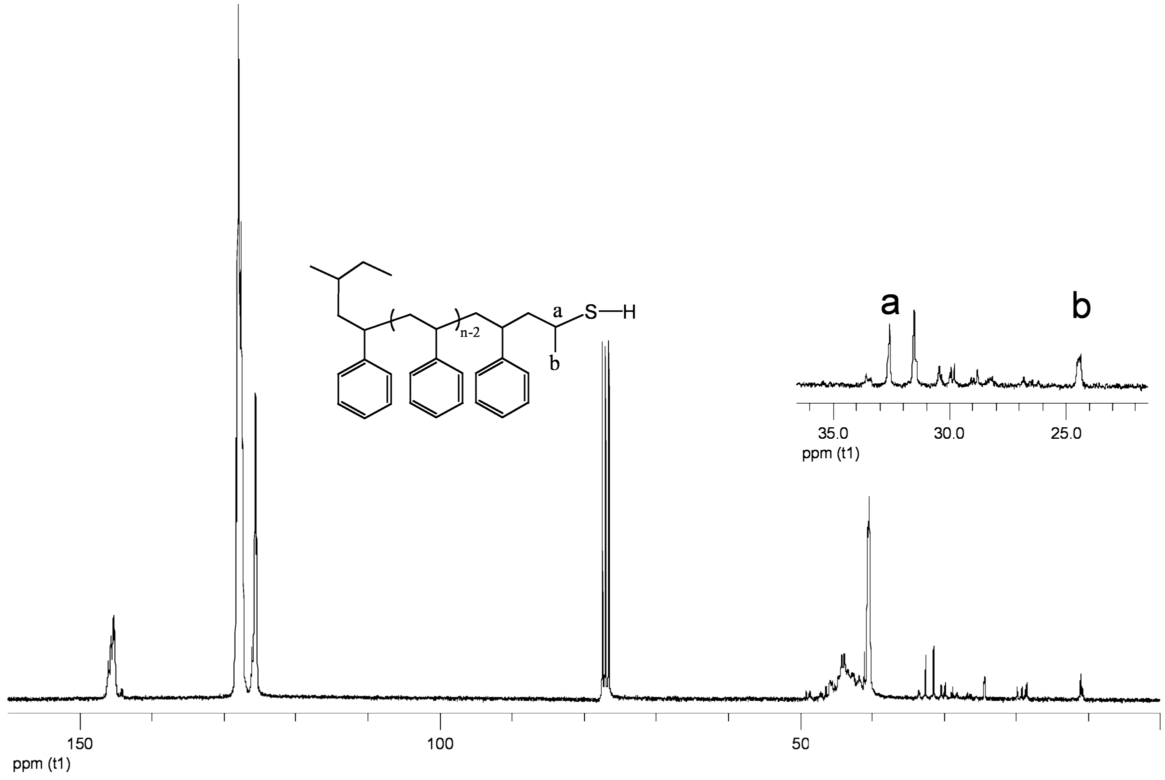


Figure 7. ^{13}C NMR spectrum of thiol-functionalized polystyrene ($M_n = 2.1 \times 10^3$ g/mol) with propylene sulfide.

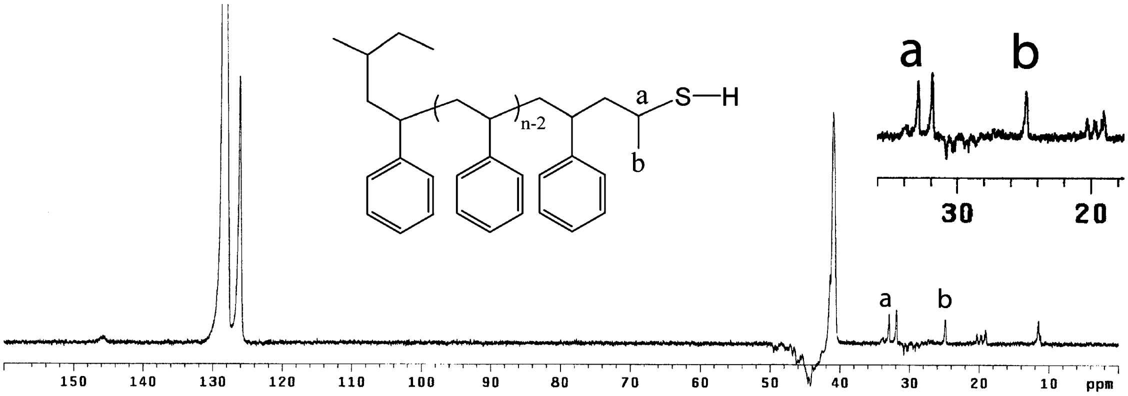


Figure 8. DEPT-135 spectrum of thiol-functionalized polystyrene ($M_n = 2.1 \times 10^3$ g/mol) with propylene sulfide.

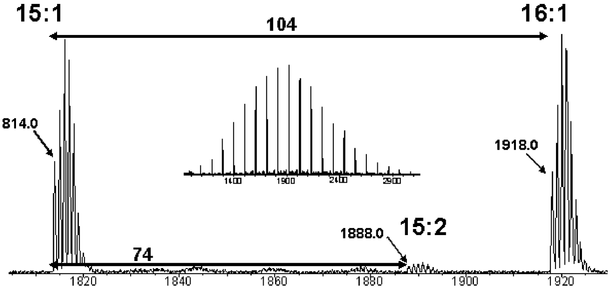


Figure 9. MALDI-TOF MS of the product from methyl iodide-quenched, thiol functionalization of poly(styryl)lithium ($M_n = 2.1 \times 10^3$ g/mol) with 1.3 equiv of propylene sulfide in benzene.

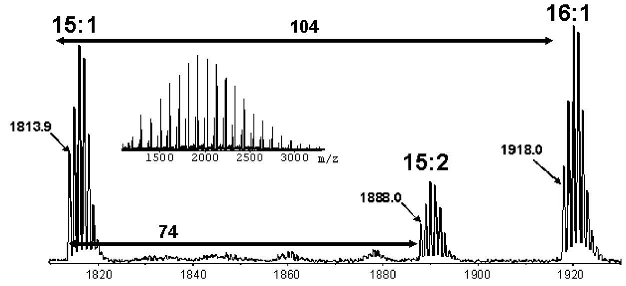


Figure 10. MALDI-TOF MS of product from methyl iodide−quenched, thiol functionalization of poly(styryl)lithium ($M_n = 2.0 \times 10^3$ g/mol) with propylene sulfide in benzene in the presence of 22 mol equiv of THF.

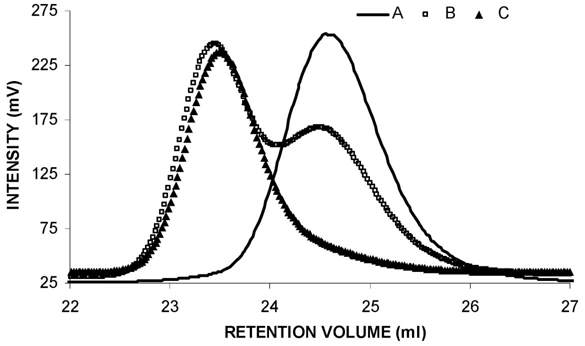


Figure 11. SEC chromatograms for the thiol-functionalized polystyrene (A) before addition of iodine, (B) 10 min after addition of iodine, and (C) 6 h after addition of iodine.

distribution are observed *m/z* 74 above the corresponding peaks in the main distribution. A representative peak at *m/z* 1888.0 corresponds to the methylthio-functionalized polystyrene 15-mer with two propylene sulfide units $\{C_4H_9-(C_8H_8)_{15}-[CH_2\text{-}CH(CH_3)S]_2-CH_3 \cdot Ag^+\}$; the calculated monoisotopic mass $\{57.07\ (C_4H_9) + 15 \times 104.06\ [(C_8H_8)_{15}] + 2 \times 74.02\ (C_3H_6S)_2 + 15.02\ (CH_3) + 106.90\ (Ag^+)\} = 1887.93$ Da. From the peak size it is evident that oligomerization only occurred to a small extent (3.8 ± 0.5%). Thus, once again it is concluded that the structure of the thiol-functionalized polymer corresponds to the product arising from a ring-opening mechanism and not a sulfur extrusion mechanism (see Scheme 2). This indicates that poly(styryl)lithium attacks a ring carbon (presumably the less-hindered methylene carbon) in propylene sulfide followed by ring opening and the formation of a thiolate anion. This result was rather surprising, especially since the previous reports on the reactions of organolithium compounds with propylene sulfide suggested attack on the sulfur with elimination of propylene.[6,8,20−24] A possible explanation for the differences in the mechanism of the reaction can be deduced by considering the energetics of the reaction. For the reactions of propylene sulfide with primary alkyllithium compounds (RLi) reported by Bordwell et al.[20] as well as Morton and Kammereck,[22] the results were interpreted in terms of a mechanism involving attack of RLi on sulfur, opening of the ring to form another primary carbanion, and then elimination of the stable thiolate to form propene (see Scheme 1b). In contrast, for the reaction of PSLi with propylene sulfide (see Scheme 2), attack at sulfur followed by ring-opening via the stepwise mechanism would form a less stable primary carbanion intermediate (conjugate acid pK_a > 56)[42] from a much more stable benzylic carbanion (conjugate acid pK_a 43).[42] This step would be expected to be very unfavorable energetically in spite of the exothermic ring-opening contribution and the ultimate formation of a stable thiolate anion.

Effects of Tetrahydrofuran (THF). Since the previous investigations[6−8,11,20,22−24] of organolithium compounds with propylene sulfide were all carried out in ethyl ether or THF at low temperatures, it was desired to investigate the effect of Lewis base additives such as THF on the course of the reaction of poly(styryl)lithium with propylene sulfide. It was considered that the mechanistic course of this reaction could be altered by the presence of Lewis bases which are known to promote dissociation of the organolithium aggregates and increase their reactivity.[1,43] Thus, Morton and co-workers[44] reported that poly(styryl)lithium, which is associated into dimers in benzene, is completely converted to the unassociated organolithium chain ends in the presence of 10 equiv of THF ([THF]/[PSLi] = 10). Therefore, poly(styryl)lithium (PSLi, $M_n = 2.2 \times 10^3$ g/mol, $M_n/M_w = 1.05$) was reacted with 1.3 mol equiv of propylene sulfide in the presence of 22 mol equiv of tetrahydrofuran (THF). The MALDI-TOF mass spectrum of the methyl iodide quenched sample showed two distributions (Figure 10). A representative peak in the major distribution at *m/z* 1813.9

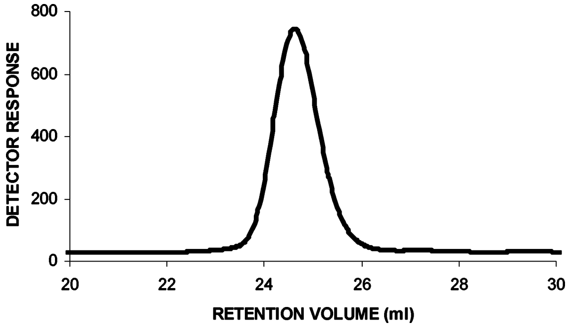


Figure 12. SEC chromatogram of acidic methanol quenched thiol-functionalized polystyrene by reaction of poly(styryl)lithium (M_n = 2700 g/mol) with 1.3 equiv of ethylene sulfide.

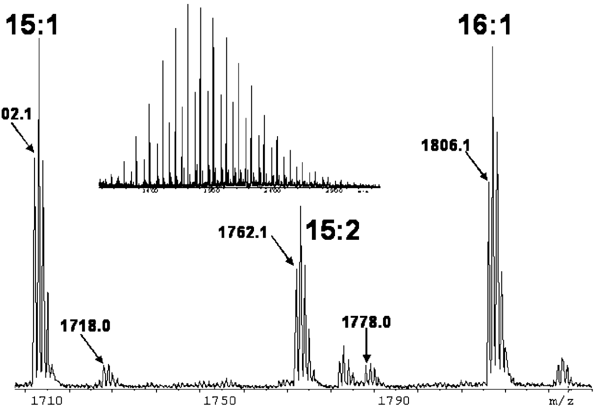


Figure 13. MALDI-TOF MS of product from methanol-quenched, thiol functionalization of poly(styryl)lithium (M_n = 2.7 × 10^3 g/mol) with ethylene sulfide in benzene.

corresponds to the methylthio-functionalized polystyrene 15-mer with one propylene sulfide unit [$C_4H_9-(C_8H_8)_{15}-CH_2CH(CH_3)S-CH_3\cdot Ag^+$]; the calculated monoisotopic mass {57.07 (C_4H_9) + 15 × 104.06 [$(C_8H_8)_{15}$] + 74.02 (C_3H_6S) + 15.02 (CH_3) + 106.90 (Ag^+)} = 1813.91 Da. The peaks in the minor distribution are observed at *m*/*z* 74 above the main distribution. A representative peak at *m*/*z* 1888.0 corresponds to the methylthio-functionalized polystyrene 15-mer with two propylene sulfide units {$C_4H_9-(C_8H_8)_{15}-[CH_2CH(CH_3)S]_2-CH_3\cdot Ag^+$}; the calculated monoisotopic mass {57.07 (C_4H_9) + 15 × 104.06 [$(C_8H_8)_{15}$] + 2 × 74.02 [$(C_3H_6S)_2$] + 15.02 (CH_3) + 106.90 (Ag^+)} = 1887.93 Da. The relative abundance of the minor distribution with respect to the major propylene sulfide monoaddition distribution was calculated to be 26.4 ± 1.4%. From the comparisons of the abundance for the oligomerized chain ends relative to the major propylene sulfide monoaddition distributions in Figures 9 and 10 (3.8 ± 0.5% and 26.4 ± 1.4%, respectively), it is evident that the oligomerization is promoted by the presence of THF. This is possibly due to the lower degree of aggregation of the lithium thiolate chain ends in the presence of a Lewis base, THF.[35,43] It is noteworthy that the structure of the resulting polymer is the same as that obtained in the absence of THF, which indicates that the mechanism of reaction of PSLi with propylene sulfide in hydrocarbon solution does not change in the presence of THF.

Oxidation of Thiol-Functionalized Polymers. The thiol-functionalized polymer was oxidized under inert atmosphere in the presence of iodine. The reaction was followed by SEC, and the appearance of a different peak at double the molecular weight of the original polymer evidences the formation of dimer as expected (see Figure 11). These results corroborate the existence of −SH end group which is known to dimerize to the disulfide linkage (−SS−) in the presence of an oxidizing agent.[10,28]

Functionalization with Ethylene Sulfide. In order to study the generality of the mechanism of the reaction of PSLi with thiiranes, poly(styryl)lithium (M_n = 2.7 × 10^3 g/mol, M_n/M_w = 1.08) was reacted with 1.3 mol equiv of ethylene sulfide at 30 °C in benzene for 15 min. The SEC chromatogram for the thiol-functionalized polystyrene (M_n = 2.1 × 10^3 g/mol; M_w/M_n = 1.06) showed a narrow, monomodal curve (Figure 12). The MALDI-TOF mass spectrum of the acidic methanol quenched sample with sodium as cationizing agent showed two major distributions (Figure 13). A representative peak in the major distribution at *m*/*z* 1702.1 corresponds to the sodiated (Na^+) thiol-functionalized polystyrene 15-mer with one ethylene sulfide unit [$C_4H_9-(C_8H_8)_{15}-CH_2CH_2S-H\cdot Na^+$]; the calculated monoisotopic mass {57.07 (C_4H_9) + 15 × 104.06 [$(C_8H_8)_{15}$] + 60.00 (C_2H_4S) +1.008 (H) + 22.99 (Na^+)} = 1701.97 Da. The peaks in the minor distribution observed at *m*/*z* 60 above

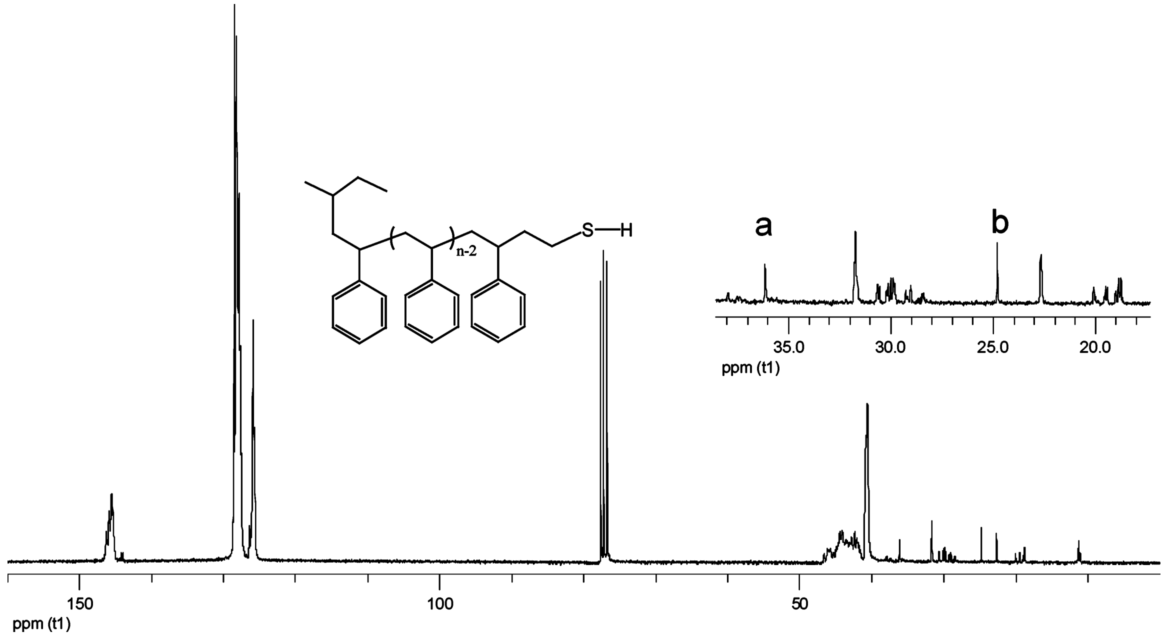


Figure 14. ^{13}C NMR spectrum of thiol-functionalized polystyrene (M_n = 2.1 × 10^3 g/mol) with ethylene sulfide.

the main distribution correspond to the products from oligomerization of ethylene sulfide at the chain end. Thus, the peak at *m*/*z* 1762.1 corresponds to the thiol-functionalized polystyrene 15-mer with two ethylene sulfide units $[C_4H_9-(C_8H_8)_{15}-(CH_2CH_2S)_2-H{\cdot}Na^+]$; the calculated monoisotopic mass $\{57.07\ (C_4H_9) + 15 \times 104.06\ [(C_8H_8)_{15}] + 2 \times 60.00\ [(C_2H_4S)_2] + 1.008\ (H) + 22.99\ (Na^+)\} = 1761.97$ Da. These results show that the mechanism of reaction between PSLi and ethylene sulfide is through ring opening by attack of the PSLi on one of the methylene carbons of ethylene sulfide, analogous to the reaction of poly(styryl)lithium and propylene sulfide. From the comparisons of the abundance for the oligomerized chain ends relative to the major propylene sulfide and ethylene sulfide monoaddition distributions in Figures 9 and 13 (3.8 ± 0.5% and 34.6 ± 1.0%, respectively), it is evident that significantly more oligomerization is occurring during the functionalization of ethylene sulfide vs propylene sulfide. It is anticipated that lower extents of oligomerization would result from the use of a smaller excess of either thiirane. There are two minor distributions 16 *m*/*z* units above the main distributions (peaks *m*/*z* 1718.0 and 1778.0) which could represent two isobaric structures: (1) the corresponding potassiated (K^+) thiol-functionalized polystyrene 15-mer with 1 and 2 ethylene sulfide units, respectively; the calculated monoisotopic masses are $\{57.07\ (C_4H_9) + 15 \times 104.06\ [(C_8H_8)_{15}] + 60.00\ (C_2H_4S) + 1.008\ (H) + 38.96\ (K^+)\} = 1717.94$ Da and $\{57.07\ (C_4H_9) + 15 \times 104.06\ [(C_8H_8)_{15}] + 2 \times 60.00\ [(C_2H_4S)_2] + 1.008\ (H) + 38.96\ (K^+)\} = 1777.94$ Da, respectively; or (2) the sodiated (Na^+) thiol-functionalized polystyrene 14-mer with 3 and 4 ethylene sulfide units, respectively; the calculated monoisotopic masses are $\{57.07\ (C_4H_9) + 14 \times 104.06\ [(C_8H_8)_{14}] + 3 \times 60.00\ [(C_2H_4\ S)_3] + 1.008\ (H) + 22.99\ (Na^+)\} = 1717.91$ Da and $\{57.07\ (C_4H_9) + 14 \times 104.06\ [(C_8H_8)_{14}] + 4 \times 60.00\ [(C_2H_4\ S)_4] + 1.008\ (H) + 22.99\ (Na^+)\} = 1777.91$ Da. Although we cannot distinguish between these possibilities, a small amount of contamination by potassium ions is a reasonable possibility.

The ^{13}C NMR spectrum of the product from ethylene sulfide functionalization of poly(styryl)lithium (Figure 14) shows characteristic peaks for the methylene carbons in the ethylenethiol chain-end unit at 36.1 and 24.8 ppm. Once more, it is noteworthy the absence of resonance peaks at 33.8 or 142.7 ppm arising from the terminal methylene carbon and terminal *ipso* carbon in unfunctionalized polystyrene.[40]

Thin-layer chromatographic (TLC) analysis of the ethylene sulfide functionalization product using a toluene:cyclohexane mixture (50/50, v/v) as eluent resulted in observation of only one spot; i.e., no spot corresponding to unfunctionalized polymer was observed. This is in accord with the quantitative nature of the functionalization of PSLi with ethylene sulfide.[41] It is also noteworthy that no distribution corresponding to unfunctionalized polystyrene was detected in the MALDI-TOF mass spectrum. Thus, these results are consistent with quantitative functionalization of poly(styryl)lithium with ethylene sulfide analogous to the results for propylene sulfide functionalization.

Conclusions

The reactions of alkyl- and aryllithium reagents with propylene sulfide in THF and ethyl ether have been shown previously to proceed by a mechanism involving sulfur extrusion. In contrast, the reaction of poly(styryl)lithium with propylene sulfide and ethylene sulfide was found to proceed by a conventional ring-opening mechanism. The functionalization of poly(styryl)lithium with propylene sulfide or ethylene sulfide produces the ω-thiol-functionalized polymer in quantitative yield. It was also found that the presence of THF does not change the mechanism of the reaction of propylene sulfide with poly(styryl)lithium.

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References and Notes

(1) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel Dekker: New York, 1996.
(2) Hirao, A.; Hayashi, M. *Acta Polym.* **1999**, *50*, 219−231.
(3) Quirk, R. P. In *Comprehensive Polymer Science, First Supplement*; Aggarwal, S. L., Russo, S., Eds.; Pergamon Press: Oxford, 1992; pp 83−106.
(4) Gonsalves, K. E.; Carlson, G.; Chen, X.; Kumar, J.; Aranda, F.; Perez, R.; Jose-Yacaman, M. *J. Mater. Sci. Lett.* **1996**, *15*, 948−951.
(5) Bockstaller, M.; Kolb, R.; Thomas, E. L. *Adv. Mater.* **2001**, *13*, 1783−1786.
(6) Stouffer, J.; McCarthy, T. *Macromolecules* **1988**, *21*, 1204−1208.
(7) Koutsos, V.; van der Vegte, E. W.; Hadziioannou, G. *Macromolecules* **1999**, *32*, 1233−1236.
(8) Kim, J.; Kim, S. S.; Kim, K. H.; Jin, Y. H.; Hong, S. M.; Hwang, S. S.; Cho, B. G.; Shin, D. Y.; Im, S. S. *Polymer* **2004**, *45*, 3527−3533.
(9) Crich, D.; Krishnamurthy, V.; Hutton, T. K. *J. Am. Chem. Soc.* **2006**, *128*, 2544−2545.
(10) Tohyama, M.; Hirao, A.; Nakahama, S.; Takenaka, K. *Macromol. Chem. Phys.* **1996**, *197*, 3135−3148.
(11) Tung, L. H.; Lo, G. Y. S.; Griggs, J. A. *J. Polym. Sci., Polym. Chem. Ed.* **1985**, *23*, 1551−1568.
(12) *The Chemistry of the Thiol Group*; Patai, S., Ed.; John Wiley and Sons: London, 1974.
(13) Tsarevsky, N. V.; Matjaszewski, K. *Macromolecules* **2002**, *35*, 9009−9014.
(14) Garamszegi, L.; Donzel, C.; Carrot, G.; Nguyen, T. Q.; Hilborn, J. *React. Polym.* **2003**, *55*, 179−183.
(15) Ogle, C. A.; Strickler, F. H.; Gordon, B. *Macromolecules* **1993**, *26*, 5803−5805.
(16) Nevin, R. S.; Pearce, E. M. *Polym. Lett.* **1965**, *3*, 487−490.
(17) Morton, M.; Kammereck, R. F.; Fetters, L. J. *Br. Polym. J.* **1971**, *3*, 120−128.
(18) Morton, M.; Kammereck, R. F.; Fetters, L. J. *Macromolecules* **1971**, *4*, 11−15.
(19) Morton, M.; Kammereck, R. F. *J. Macromol. Sci., Chem.* **1973**, *A7*, 1391−1397.
(20) Bordwell, F. G.; Andersen, H. M.; Pitt, B. M. *J. Am. Chem. Soc.* **1954**, *76*, 1082−1085.
(21) Schuetz, R. D.; Jacobs, R. L. *J. Org. Chem.* **1961**, *26*, 3467−3471.
(22) Morton, M.; Kammereck, R. F. *J. Am. Chem. Soc.* **1970**, *92*, 3217−3218.
(23) Trost, B. M.; Ziman, S. D. *J. Org. Chem.* **1973**, *38*, 932−936.
(24) Bonini, B. F.; Maccagnani, G.; Mazzanti, G.; Zani, P. *Gazz. Chim. Ital.* **1990**, *120*, 115−121.
(25) Quirk, R. P.; Chen, W. C. *Makromol. Chem.* **1982**, *183*, 2071−2076.
(26) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447−454.
(27) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359−409.
(28) Capozzi, G.; Modena, G. Oxidation of Thiols. In *The Chemistry of the Thiol Group*; Patai, S., Ed.; John Wiley and Sons: London, 1974.
(29) Quirk, R. P.; Ge, Q.; Arnould, M. A.; Wesdemiotis, C. *Macromol. Chem. Phys.* **2001**, *202*, 1761−1767.
(30) Quirk, R. P.; Mathers, R. T.; Ma, J.-J.; Wesdemiotis, C.; Arnould, M. A. *Macromol. Symp.* **2002**, *183*, 17−22.
(31) Quirk, R. P.; Gomochak, D. L.; Wesdemiotis, C.; Arnould, M. A. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 947−957.
(32) Quirk, R. P.; Guo, Y.; Wesdemiotis, C.; Arnould, M. A. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 2435−2453.
(33) Arnould, M. A.; Polce, M. J.; Quirk, R. P.; Wesdemiotis, C. *Int. J. Mass Spectrom.* **2004**, *238*, 245−255.
(34) Quirk, R. P.; Mathers, R. T.; Wesdemiotis, C.; Arnould, M. A. *Macromolecules* **2002**, *35*, 2912−2918 and references cited therein.
(35) Ruhlandt-Senge, K.; Englich, U.; Senge, M. O.; Chadwick, S. *Inorg. Chem.* **1996**, *35*, 5820−5827.
(36) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533−3539.
(37) Pearson. R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827−1836.

(38) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; Wiley: New York, 1998; p 168.

(39) Boileau, S.; Cheradame, H.; Lapeyre, W.; Sousselier, L.; Sigwalt, P. *J. Chim. Phys. Phys.-Chim. Biol.* **1973**, *70*, 879−883.

(40) Quirk, R. P.; Ma, J. J. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2031−2037.

(41) Quirk, R. P.; Lynch, T. *Macromolecules* **1993**, *26*, 1206−1212.

(42) Bordwell, F. G.; Algrim, D. J. *J. Am. Chem. Soc.* **1988**, *110*, 2964−2968.

(43) Wakefield, B. L. *The Chemistry of Organolithium Compounds*; Pergamon Press: Oxford, 1974.

(44) Morton, M.; Fetters, L. J.; Pett, R. A.; Meier, J. F. *Macromolecules* **1970**, *3*, 327−332.

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