Functionalization of Poly(styryl)lithium with Styrene Oxide

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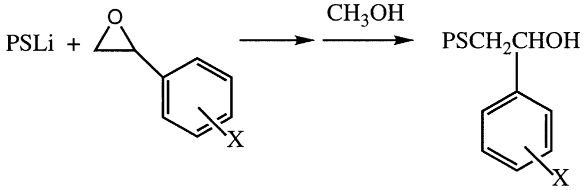
ABSTRACT: The functionalization of poly(styryl)lithium with styrene oxide as a route to functional polymers was investigated. When the reaction was performed in benzene at room temperature, analysis of the products by SEC and column chromatography indicated the presence of functional polymer (83.5 wt %), along with unfunctionalized polymer (9.0 wt %), dimeric product (5.6 wt %), and trimeric product (0.1 wt %). The structure of the dimeric product was determined to be head-to-head dimer from both ^{13}C NMR analysis and MALDI−TOF MS and was proposed to result from an electron-transfer mechanism. The dimeric product was eliminated when the functionalization was effected in the presence of tetrahydrofuran (>15 mol equiv). Under these conditions >99 wt % functionalized polymer was obtained as determined by column chromatography and MALDI−TOF MS. Addition of PSLi to the epoxide can occur by addition to the least hindered carbon or by addition to the most hindered carbon. Analysis of the regiochemistry of the chain end was performed by both ^{13}C NMR and APT ^{13}C NMR spectroscopy. It was determined that the product obtained in the presence of tetrahydrofuran contained 53 mol % of the product resulting from addition to the least hindered carbon and 47 mol % resulting from addition to the most hindered carbon.

Introduction

Alkyllithium-initiated anionic polymerization provides a facile route for the synthesis of functional polymers due to the living nature of the chain end.[1] Functional polymers can by synthesized by the use of either functional initiators or postpolymerization functionalization reactions.[2,3] The use of functional initiators in living anionic polymerization ensures that each polymer chain contains one functional group, but initiators of this type are of limited availability and generally require protection of the functional group.[1] Postpolymerization reactions require optimization of the reaction conditions to ensure quantitative functionalization.

The functionalization of poly(styryl)lithium with ethylene oxide has been well-studied.[4−7] Initial investigations into the functionalization of PSLi with ethylene oxide (4 mol equiv) indicated that the reaction proceeded efficiently in the absence of oligomerization to produce functional polymer (>99%).[7] Reinvestigation of the functionalization of PSLi with larger molar excesses of ethylene oxide (10 mol equiv) for extended periods of time indicated that oligomerization did in fact occur to a small extent as indicated by MALDI−TOF MS.[4−6] The functionalizations of PSLi with 1-butene oxide and propylene oxide have also been reported.[8,9] The functionalization of poly(styryl)lithium with a 2 M excess of propylene oxide in hydrocarbon solution formed the corresponding hydroxypropylated polymer in 93% yield accompanied by 7% of the unfunctionalized polymer.[9] In the presence of THF the functionalization reaction was complete in 5 h, and the yield of functionalized polymer was 94% with 6% unfunctionalized polymer formed. The reaction is regioselective, resulting in predominantly (97%) a secondary alcohol chain end, the product expected from attack of the organolithium on the least hindered carbon of the propylene oxide ring. The functionalization of PSLi with 1-butene oxide has also been reported.[8] The reaction of 1-butene oxide with PSLi yielded less than 1% of unfunctionalized polymer, while the functional product was isolated in >99% yield. The reaction was also regioselective to only form the secondary alcohol product, resulting from attack at the least hindered carbon. The functionalization of polymeric organolithium compounds with 3,4-epoxy-1-butene, a functional epoxide, has also been investigated as a route to functional polymers.[10] High yields of functional polymer (95%) were obtained, but the reaction was not regioselective. A highly regioselective 1,4-addition product was obtained when either triethylamine, poly(dienyl)lithium chain ends, low temperatures, or inverse addition was utilized.

Scheme 1. Potential Utility of Substituted Styrene Oxides To Form a Variety of Functional Polymers



These initial investigations indicated that epoxides may provide a facile route to a variety of functional polymers by substitution on the epoxide ring. Therefore, the functionalization of PSLi with styrene oxide was investigated. If this functionalization is quantitative, a variety of substituents can be placed on the benzene ring of the epoxide to form a variety of functional polymers (see Scheme 1). Previous work on the ring-opening chemistry of styrene oxide has been reported using a variety of nucleophiles.[11,12] The reaction of styrene oxide with sodium diethyl malonate resulted in the formation of two lactones.[11] The major product (60%) resulted from nucleophilic attack at the more hindered carbon, while

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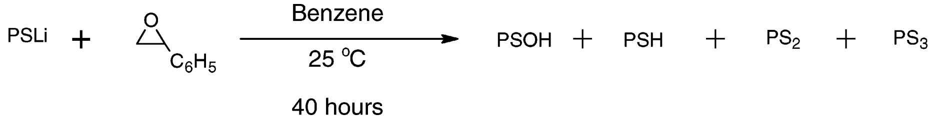
Scheme 2. Products from the Functionalization of Poly(styryl)lithium with Styrene Oxide in Benzene at Room Temperature



the minor product resulted from attack at the least hindered carbon. Subsequent work on the ring opening of para-substituted styrene oxides indicated that the substituent had a dramatic effect on the regiochemistry of the reaction.[12,13] In the presence of sodium diethyl malonate, substitution of a methoxy group in the para position favored attack at the more substituted carbon atom, while a nitro substitution favored attack at the least hindered carbon. Thus, both steric and electronic factors affect the regiochemistry of nucleophilic ring-opening of epoxides.

On the basis of the results from previous investigations of the functionalization of polymeric organolithium compounds with epoxides, the functionalization of PSLi with styrene oxide was investigated. The degree of functionalization and the regiochemistry of the chain end were investigated by the use of a variety of analytical techniques including SEC, NMR, and MALDI−TOF MS.

Experimental Section

Chemicals and Solvents. Benzene (Fisher, certified grade), THF (Fisher, certified grade), and styrene (Fisher, certified grade) were purified as previously described.[14] Benzene was distilled as needed into ampules and reactors from poly(styryl)lithium. Solutions of *sec*-butyllithium (12 wt % in cyclohexane, FMC, Lithium Division, or Chemetall Foote) were used as received after analysis by Gilman double titration with allyl bromide.[15] Styrene oxide (Aldrich, 97%) was stirred over freshly ground calcium hydride for 2 days on the vacuum line and was subjected to frequent degassing. The styrene oxide was then distilled onto neat dibutylmagnesium (12 wt % in hexanes, FMC, Lithium Division) using a short path distillation apparatus. Immediately prior to use, styrene oxide was distilled into calibrated ampules, and the ampules were flame-sealed from the vacuum line. Methanol (Fisher, certified ACS grade) was used as received.

Characterization. Size exclusion chromatography (SEC) was performed using a Waters HPLC component system equipped with an RI detector and six ultra-μ-styragel columns (two−500, two 10^3, 10^4, and 10^5 Å) at 30 °C in THF at a flow rate of 1.0 mL/min. The instrument was calibrated with polystyrene standards obtained from Polymer Laboratories. The concentration of polystyrene used for SEC analysis was 6−8 mg/mL. ^{1}H (200 MHz, 500−1000 scans) and ^{13}C (quantitative reverse-gate decoupled spectra, 7500 scans at 50 and 100 MHz, with $d_1 = 6$) NMR spectra were recorded in $CDCl_3$ (Aldrich, 99.8% D) on Varian Gemini-200 and Gemini-400 spectrometers. Infrared spectra were recorded on a Beckman FT2100 spectrometer by casting films of the polymers on KBr plates from chloroform solutions. The mass spectra were acquired using a Bruker REFLEX-III time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Billerica, MA), equipped with a LSI model VSL-337ND pulsed 337 nm nitrogen laser (3 nm pulse width), a single-stage pulsed extraction ion source, and a two-stage gridless reflector. Solutions of dithranol (20 mg/mL), polymer (10 mg/mL), and silver trifluoroacetate (10 mg/mL) were made in THF. These solutions were mixed in the ratios of matrix:cationizing salt:polymer (10:1:2), and 0.5 μL was deposited on the sample holder. The attenuation of the nitrogen laser was adjusted to maximize the sensitivity without causing any appreciable fragmentation of the polymer. The mass scale was calibrated externally using polystyrene standards.

Thin-layer chromatography (TLC) with silica gel plates (Eastman Kodak, chromatograms sheet 13179 with fluorescent indicator) and a toluene/hexane (75/25, vol/vol) mixture as the eluent was performed on the functionalized polymer samples. Quantitative column chromatography was also performed using silica gel (EM Science, 220−400 mesh) to separate the unfunctionalized polystyrene, polystyrene dimer, and/or polystyrene trimer from the functionalized products using toluene/hexane (75/25, vol/vol) as the eluent, followed by THF to remove the functionalized polymer.

Fractionation of the polystyrene dimer and/or trimer from the unfunctionalized polymer was performed by dissolving 2 g of the first fraction from column chromatography in 800 mL of toluene. Methanol was slowly added until the solution became turbid. The turbid solution was heated slightly until it became clear, and the solution was allowed to cool to room temperature undisturbed overnight. The concentrated phase in the bottom of the container contained the polystyrene dimer and/or polystyrene trimer. The two phases were separated using a pipet. The dilute phase was fractionated twice to ensure complete separation.

Polymerizations. Poly(styryl)lithium (PSLi) was prepared by the anionic polymerization of styrene in benzene (10−15 vol %) at room temperature using *sec*-butyllithium as the initiator. The reaction was performed in all-glass, sealed reactors with break-seals and high-vacuum techniques.[16] An aliquot of PSLi was removed and terminated with degassed methanol prior to functionalization.

Functionalizations. The reactions of benzene solutions of styrene oxide (1.04−2.95 mol equiv) with PSLi were carried out in vacuo under a variety of conditions. In the absence of additives, the reaction was performed by the addition of styrene oxide directly to the PSLi solution by smashing the corresponding break-seal. When the functionalization was performed in the presence of THF, THF (5−50 mol equiv) was added to PSLi immediately prior to functionalization followed by styrene oxide. The functionalization reactions were performed at room temperature unless otherwise noted for 11−40 h. Upon addition of the styrene oxide to the PSLi solution, the color of the solution changed immediately from the characteristic orange-red of PSLi to a light yellow color. Before quenching with methanol, the reaction mixture was colorless.

Results and Discussion

Functionalization with Styrene Oxide. Poly(styryl)lithium (PSLi, $M_n = 1.9 \times 10^3$ g/mol, $M_w/M_n = 1.08$) was reacted with 1.3 mol equiv of styrene oxide in benzene at room temperature for 40 h as shown in Scheme 2. The color of the solution changed from the characteristic orange-red of PSLi to light yellow almost immediately upon addition of styrene oxide. After termination with methanol, the resulting polymer was characterized by SEC. The SEC chromatogram is shown in Figure 1. The lower molecular weight peak corresponded to the adduct of poly(styryl)lithium with styrene oxide, while the higher molecular weight peak corresponded to twice the molecular weight of the base polystyrene. It also appears that a higher molecular weight product is present in the product mixture.

Analysis of the crude polymer by TLC (silica gel plates, toluene/hexane, 75/25, vol/vol) indicated the presence of two species. One spot was observed with an R_f of 0.7 while the other had an R_f of 0.3. Silica gel chromatography of the crude sample yielded two frac-

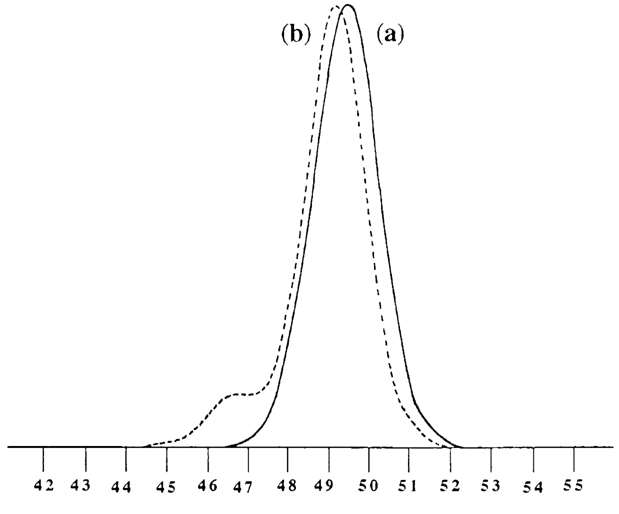


Figure 1. SEC chromatograms of (a) base polystyrene and (b) products from functionalization of PSLi with styrene oxide.

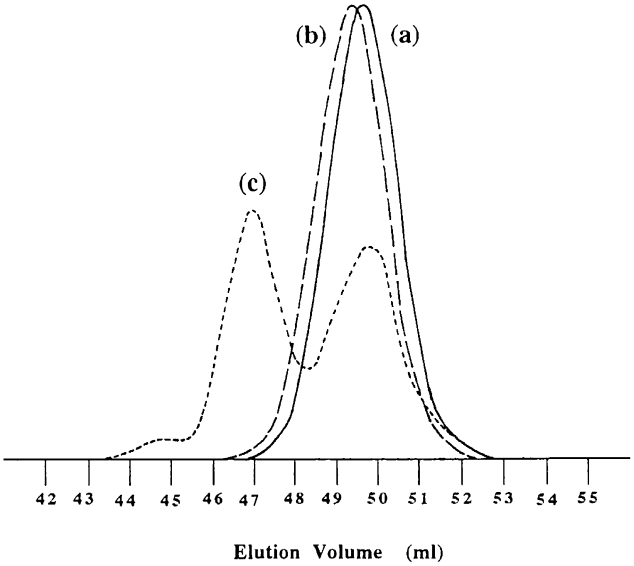
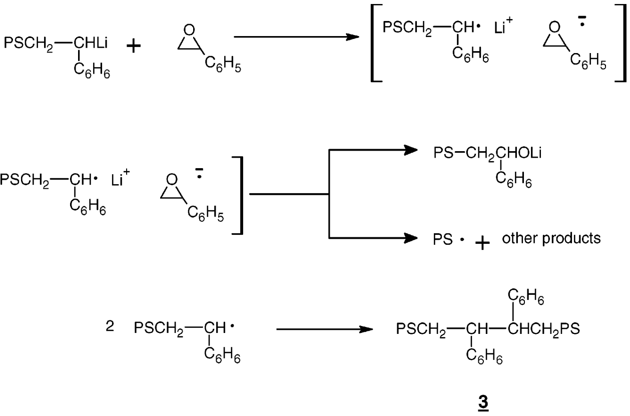


Figure 2. SEC chromatograms of (a) base polymer, (b) THF fraction from column chromatography, and (c) toluene/hexane fraction from column chromatography.

tions. The first fraction was eluted with a toluene/hexane mixture while the second fraction was eluted with THF. The SEC chromatograms of the two fractions are shown in Figure 2. The second fraction eluted from the column corresponded to the styrene oxide-functionalized polystyrene, and the peak is monomodal, indicating removal of the high molecular weight byproducts (Figure 2b). The toluene/hexane fraction contained three different molecular weight products as indicated by SEC (Figure 2c). The lowest molecular weight product corresponded to unfunctionalized polymer, the second to a dimeric product, and the higher molecular weight species to a trimeric product. Utilizing both SEC and the results from quantitative column chromatography, it was determined that 83.5 wt % of the product was ω-hydroxy-functionalized polystyrene. The unfunctionalized polystyrene, polystyrene dimer, and polystyrene trimer accounted for 9.0, 5.6, and 0.1 wt %, respectively.

Previous work on the reaction of ketones or halides with Grignard reagents,[17,18] metal hydrides,[19] and organometallic reagents[20,21] indicated that the reactions often involved a single electron-transfer pathway (ET) under certain reaction conditions. This ET pathway can result in formation of a mixture of other products in competition with the formation of the desired nucleophilic ring opening product as shown in Scheme 3. If the reaction of PSLi with styrene oxide proceeds via an ET pathway to form dimer, the dimeric product should have the characteristic head-to-head structure in the middle of the chain as shown in Scheme 3. The head-to-head dimer (**3**) results from coupling of two polystyryl radicals after diffusion from the cage. The structure of the dimeric species was investigated by ^{1}H and ^{13}C NMR spectroscopy and MALDI−TOF MS in order to surmise the pathway by which the dimer was formed and to develop methods to eliminate its formation.

Scheme 3. Formation of Head-to-Head Dimer by an Electron-Transfer Mechanism



To determine the structure of the dimeric product, the unfunctionalized fraction from column chromatography was fractionated to obtain only the dimeric and trimeric products. By SEC, the high molecular weight fraction contained 77 wt % of the dimeric polystyrene and 23 wt % of the trimeric polystyrene. Structural analysis of the dimeric product was performed using ^{1}H and ^{13}C NMR spectroscopy and MALDI−TOF MS. The ^{1}H NMR spectrum of dimeric fraction was the same of that of the base polystyrene; therefore, no information about the structure was obtained. Structural characterization of the dimeric fraction was possible by ^{13}C NMR spectroscopy as shown in Figure 3. One can calculate the chemical shifts of a carbon based on the additivity principles outlined by Grant and Paul.[22,23] A peak corresponding to unfunctionalized polymer was expected at δ 34.1 ppm ($-C\text{H}_2\text{Ph}$) due to the terminal carbon.[24] No peak was observed in this region, indicating that all unfunctionalized polymer was removed upon fractionation. The ^{13}C NMR assignments for head-to-head dimer have been elucidated by Rinaldi and co-workers[25,26] and are given in Table 1. A peak was observed at δ 49.5 ppm, which was assigned to the methine carbon (carbon 1 in Table 1) due to head-to-head dimer as shown in Table 1 and Figure 3. The peak due to the methylene carbon (carbon 2 in Table 1), which was expected to appear at δ 42 ppm, overlaps with the methylene and methine carbons of the polystyrene main chain.

The crude sample from the reaction of PSLi with styrene oxide in benzene at room temperature was also analyzed by MALDI−TOF mass spectrometry. MALDI−TOF MS allows for structural determination of the chain end and has become an essential tool for the characterization of functional polymers.[27] The MALDI−TOF

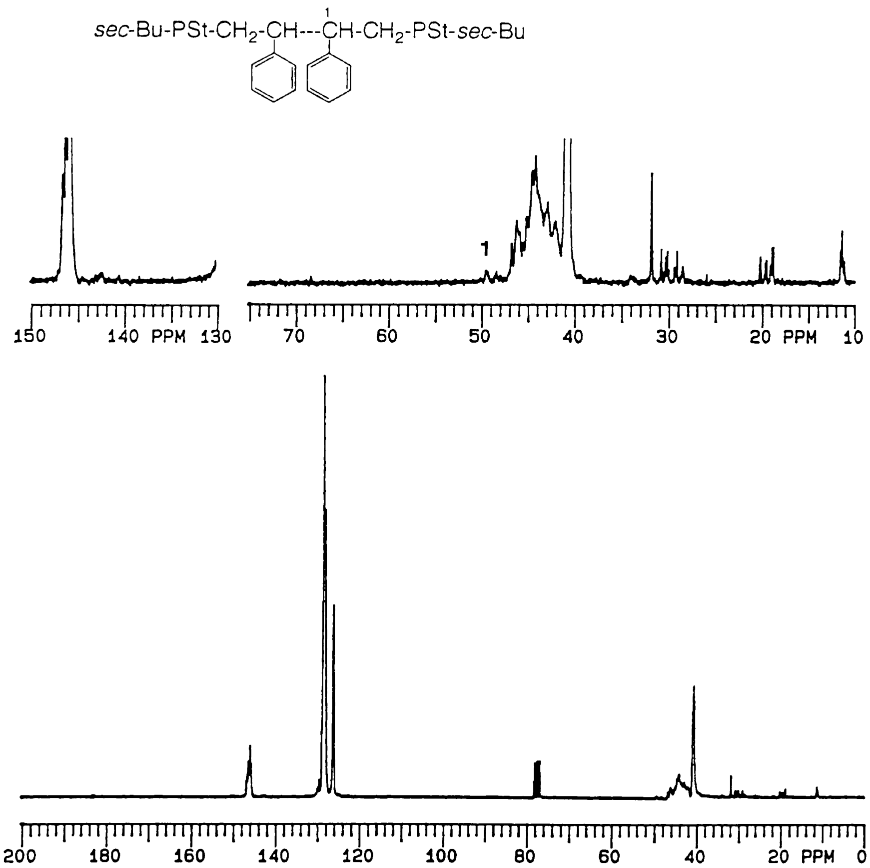
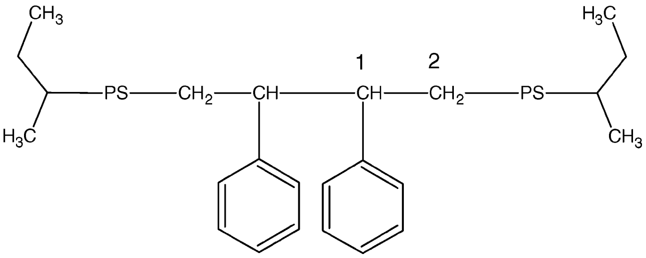


Figure 3. ^{13}C NMR spectrum of fractionated polystyrene dimer from the reaction of PSLi with styrene oxide in benzene.

Table 1. ^{13}C NMR Calculated and Observed Chemical Shifts for Polystyrene Head-to-Head Dimer



	chemical shift (ppm)	
carbon	calculated	observed
1	52.3	49.5
2	42.3	42–45[a]

[a] Overlapped with absorptions of methylene and methane carbon of polystyrene main chain.

mass spectrum of the crude sample of styrene oxide-functionalized polymer is shown in Figure 4. In the spectrum several distributions are observed. There are two lower molecular weight distributions and one higher molecular weight distribution. The major lower molecular weight distribution was attributed to the styrene oxide-functionalized polymer [e.g., $C_4H_9-(C_8H_8)_{10}-C_8H_9O{\cdot}Ag^+$, calcd monoisotopic mass = 1325.7 Da, obsd $m/z = 1325.7$] The minor distribution was attributed to nonfunctional polymer [e.g., $C_4H_9\text{-}(C_8H_8)_{12}-H{\cdot}Ag^+$, calcd monoisotopic mass = 1413.7 Da, obsd $m/z = 1413.8$]. Two minor distributions are also visible in the spectrum. The distribution at $m/z = 27.9$ above the major distribution is metastable peaks since they disappeared when the spectrum was obtained in the linear mode. Metastable peaks result from fragmentation of the oligomer ions after leaving the ion source. The distribution observed at $m/z = 10.8$ above the major distribution was observed in both the linear and reflector modes. These peaks are most likely due to fragmentation of the polymer at the time of ionization due to the high laser power used to obtain the spectrum. With the current instrument, the use of lower laser power did not provide a useable spectrum.

The expanded region of the high molecular weight product is shown in Figure 5. The high molecular weight product was attributed to head-to-head dimer [e.g., $C_4H_9-(C_8H_8)_{24}-C_4H_9{\cdot}Ag^+$, calcd monoisotopic mass = 2718.6 Da, obsd $m/z = 2718.6$]. This structural assignment confirms the conclusion based on ^{13}C NMR analysis of the dimer fraction. A trimeric product was not observed by MALDI–TOF MS. This may be due to the lower volatility of the trimeric product or the small concentration of the trimeric product in the crude sample. Despite this, the results from MALDI–TOF MS correlate well with the results from SEC and column chromatography.

Optimization of Functionalization Reaction. The functionalization of PSLi with styrene oxide has been shown to produce a mixture of products, including functionalized polymer, unfunctionalized polymer, dimeric polystyrene, and trimeric polystyrene. Because of the structure of the dimeric product formed, it was proposed that the dimer resulted from a single electron pathway mechanism (Scheme 3). Therefore, it was desirable to determine the reaction conditions under which formation of nonfunctional products is minimized relative to the formation of the hydroxyl-functionalized polymer. The functionalization of PSLi with styrene oxide was

Table 2. Effect of Styrene Oxide Stoichiometry on the Functionalization of Poly(styryl)lithium with Styrene Oxide

sample	$M_n \times 10^{-3}$ (g/mol)[a]	M_w/M_n	reagent ratio ([SO]/[PSLi])[b]	products (wt %)[c]			
				PSOH[d]	PSH[e]	$(PS)_2$[f]	$(PS)_3$[g]
1	1.9	1.05	2.95	83.3	10.1	6.4	0.2
2	1.9	1.05	1.31	85.3	9.0	5.6	0.1
3	1.9	1.05	1.17	83.2	10.1	6.4	0.3
4	1.8	1.05	1.04	76.3	12.6	10.4	0.7

[a] Determined by SEC. [b] [SO]/[PSLi] = [styrene oxide]/[poly(styryl)lithium]. [c] Product yields determined by a combination of SEC and product isolation by silica gel column chromatography. [d] Styrene oxide-functionalized polystyrene. [e] Unfunctionalized polystyrene. [f] Polystyrene dimer. [g] Polystyrene trimer.

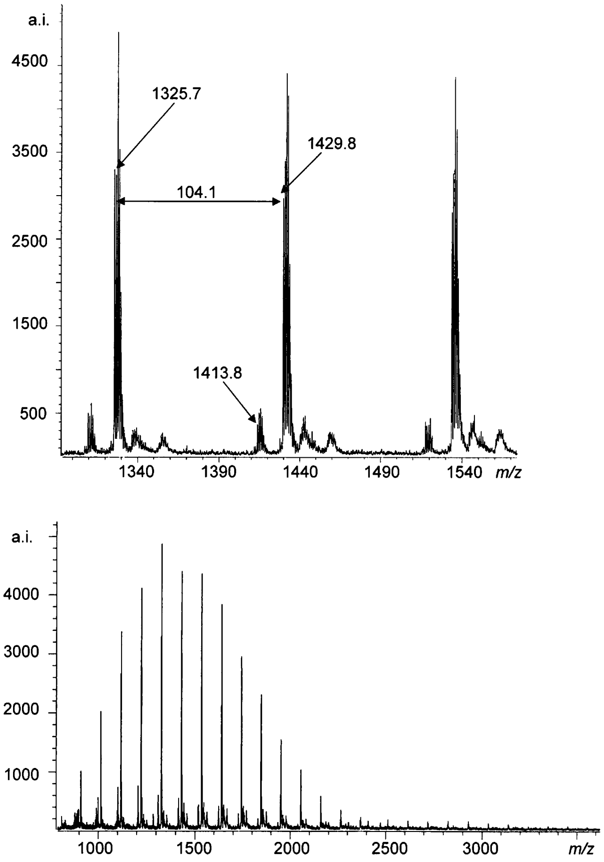


Figure 4. MALDI−TOF mass spectrum of the crude polymer sample prepared by the functionalization of PSLi with styrene oxide.

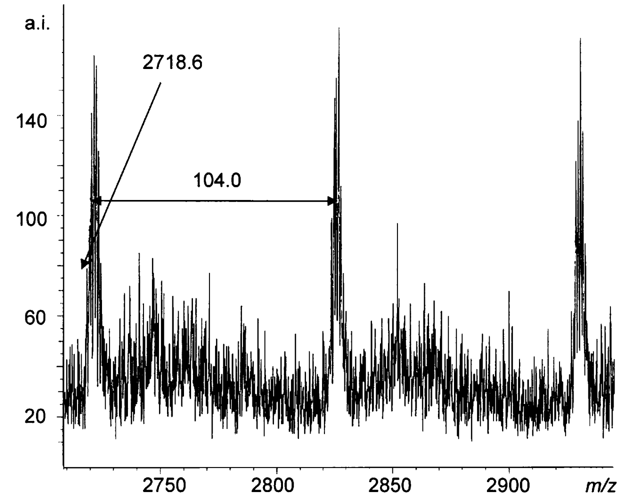


Figure 5. Expanded high molecular weight region of the MALDI spectrum of the crude polymer sample prepared by the functionalization of PSLi with styrene oxide.

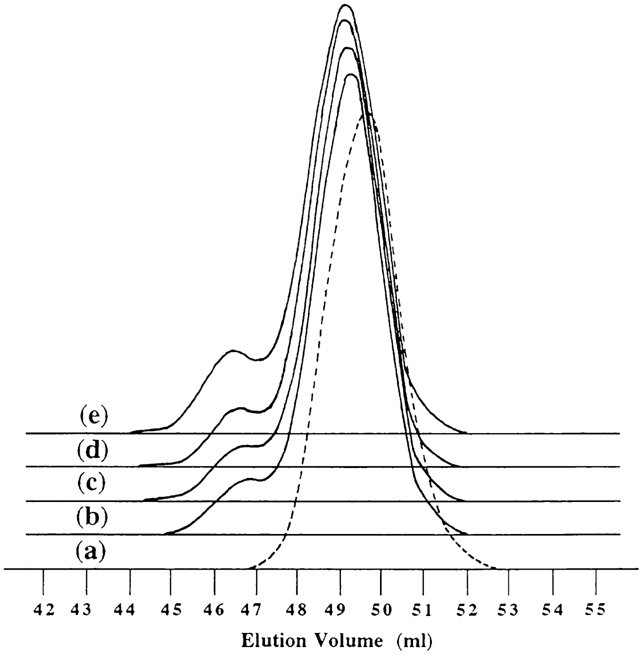


Figure 6. SEC chromatograms of (a) base polystyrene; (b) sample 1, Table 2; (c) sample 2, Table 2; (d) sample 3, Table 2; and (e) sample 4, Table 2.

investigated under a variety of conditions, including variations in temperature, styrene oxide equivalents, and addition of polar additives.

Effect of Styrene Oxide Stoichiometry. The reaction of PSLi with varying amounts of styrene oxide (1.04−2.95 mol equiv) was investigated in benzene at 25 °C (see Table 2). The resulting products were analyzed by SEC in order to determine whether the high molecular weight byproducts were eliminated or reduced. The SEC chromatograms of the products are shown in Figure 6. From the SEC chromatograms, it was concluded that variation of the stoichiometry had no significant effect on the amount of higher molecular weight products. Separation of the functionalized and unfunctionalized products by column chromatography indicated that the stoichiometry of the reaction did not have a significant effect on the yield of functionalized product or the product distribution, as shown in Table 2.

Effect of Reaction Temperature. The functionalization of PSLi with styrene oxide (1.04 mol equiv) at −78 and 60 °C was also investigated to determine the effect of temperature on the product distribution. At −78 °C the reaction was performed in toluene due to the high freezing point of benzene. At lower temperature, the color change from orange to yellow was slow compared to room temperature. Upon analysis of the products by SEC (Figure 7) and column chromatography, it was found that there was a remarkable decrease in the amount of dimer formed (1.2 wt %), and no trimer was

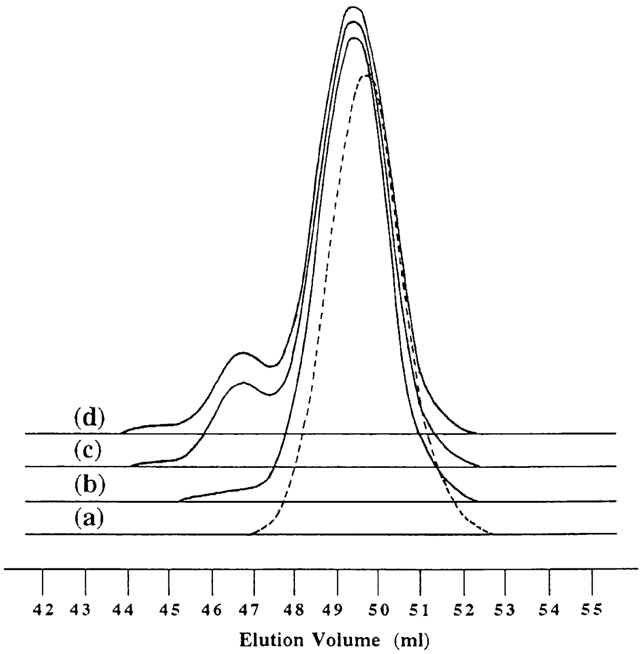


Figure 7. SEC chromatograms of (a) base polystyrene; (b) PSLi functionalized with styrene oxide at −78 °C (sample 5, Table 3); (c) 25 °C (sample 1, Table 3); and (d) 60 °C (sample 6, Table 3).

Table 3. Effect of Reaction Temperature on the Functionalization of Poly(styryl)lithium with Styrene Oxide

		products (wt %)[c]			
sample	temp (°C)	PSOH[d]	PSH[e]	$(PS)_2$[f]	$(PS)_3$[g]
1	25[a]	76.3	12.6	10.4	0.7
5	−78[b]	94.4	4.4	1.2	0
6	60[a]	74.2	13.9	11.2	0.7

[a] Functionalization of PSLi ($M_n = 1.8 \times 10^3$ g/mol) with styrene oxide (1.04 mol equiv) in benzene. [b] Functionalization of PSLi ($M_n = 1.8 \times 10^3$ g/mol) with styrene oxide (1.04 mol equiv) in toluene. [c] Product yields determined by a combination of SEC and product isolation by silica gel chromatography. [d] Styrene oxide functionalized polystyrene. [e] Unfunctionalized polystyrene. [f] Polystyrene dimer. [g] Polystyrene trimer.

observed. The amount of unfunctionalized polystyrene also decreased (4.4 wt %) at lower temperature. On the other hand, at 60 °C slightly larger amounts of the side products were observed (Table 3, sample 6). Clearly, the use of low temperature has a dramatic effect on the product distribution and may aid in choosing conditions for quantitative functionalization. Thus, lower temperatures provided more selectivity as expected.

Table 4. Effect of THF on the Functionalization of Poly(styryl)lithium with Styrene Oxide[a]

		products (wt %)[b]			
sample	[THF]/[PSLi]	PSOH[c]	PSH[d]	$(PS)_2$[e]	$(PS)_3$[f]
1	0	76.3	12.6	10.4	0.7
7	5	97.0	2.7	0.3	0
8	15	>99	<1	<1	0
9	50	>99	<1	<1	0

[a] Functionalization of PSLi ($M_n = 1.8 \times 10^3$ g/mol) with styrene oxide (1.04 mol equiv) in benzene at 25 °C for >40 h. [b] Product yields determined by a combination of SEC and product isolation by silica gel chromatography. [c] Styrene oxide functionalized polystyrene. [d] Unfunctionalized polystyrene. [e] Polystyrene dimer. [f] Polystyrene trimer.

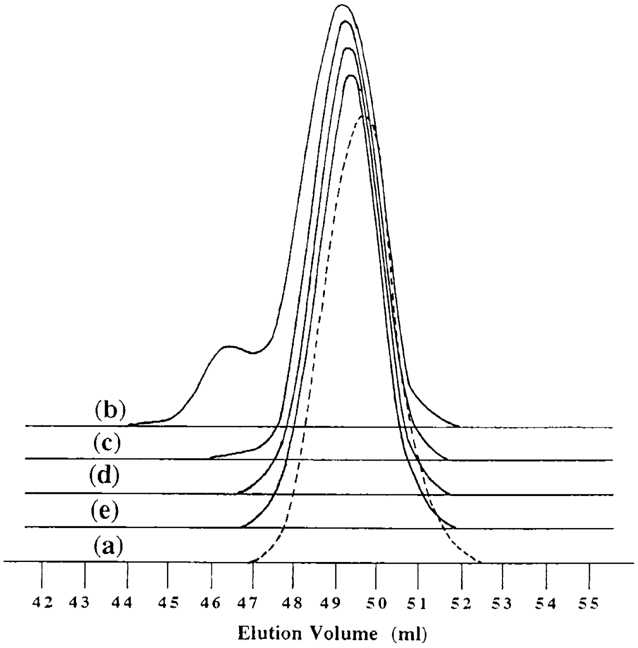


Figure 8. SEC chromatograms of (a) base polystyrene; (b) PSLi functionalized with styrene oxide at 25 °C, [THF]/[PSLi] = 0 (sample 1, Table 4); (c) [THF]/[PSLi] = 5 (sample 7, Table 4); (d) [THF]/[PSLi] = 15 (sample 8, Table 4); and (e) [THF]/[PSLi] = 50 (sample 9, Table 4).

Effect of Lewis Bases. Lewis bases such as tetrahydrofuran (THF) and *N*,*N*,*N*,*N*-tetramethylethylenediamine (TMEDA) are known to reduce or eliminate the association of simple and polymeric organolithium chain ends.[1,28a,29] Although useful when attempting to change the reactivity of polymeric organolithium compounds, Lewis bases also have a dramatic effect on the stereochemistry of polydienes.[30,31] When 1,3-dienes are polymerized in the presence of Lewis bases, the high 1,4-stereospecificty of alkyllithium-initiated polymerization is lost. Organolithium compounds also have reduced stability in the presence of Lewis bases, resulting in decomposition of chain ends at fast rates at room temperature.[32−34] Since the reactivity of organolithium compounds is strongly dependent on their degree of aggregation, if the formation of dimer is favored by the association of PSLi chain ends, one would expect that the addition of Lewis base would decrease the formation of dimer. Therefore, varying amounts of THF (0−50 mol equiv) were added to benzene solutions of PSLi prior to the addition of styrene oxide, and the results are shown in Table 4.

Upon addition of THF to the PSLi solutions, the color of the solution changed from orange to dark red. Also, the reaction time was greatly reduced to 4−5 h compared to the reactions in the absence of THF. The SEC chromatograms of the products are shown in Figure 8. When even small amounts of THF were used (5 mol equiv), the amounts of dimeric, trimeric, and unfunctionalized polymer were dramatically decreased to 0.30, 0, and 2.7 wt %, respectively, as determined by column chromatography and SEC. When larger amounts of THF were used (≥15 mol equiv), only one spot was observed by TLC analysis on silica gel plates. Analysis by SEC and column chromatography indicated that the ω-hydroxy-functionalized polymer was obtained in high yield (>99%) with very small amounts of unfunctionalized and dimeric products present. This suggests that the course of the reaction of PSLi with styrene oxide may be related to the degree of association of PSLi. Addition

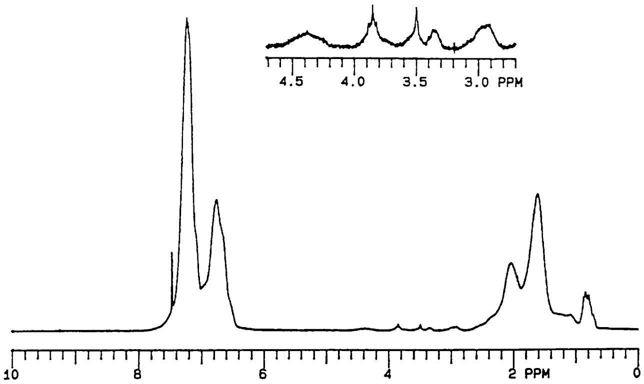
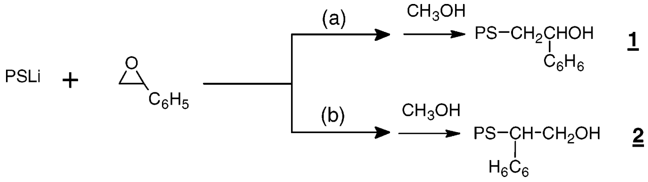


Figure 9. ^{1}H NMR spectrum of poly(styryl)lithium functionalized with styrene oxide in the presence of 50 mol equiv of THF (sample 9, Table 4).

Scheme 4. Addition of PSLi to (a) the Least Hindered Carbon of Styrene Oxide and (b) the Most Hindered Carbon of Styrene Oxide



of THF results in a decrease in the average degree of aggregation of the PSLi chain ends, and this system does not form significant amounts of dimer upon reaction with styrene oxide.

Determination of Functionality and Regiochemistry. After determining the reaction conditions which produced functional polymer in high yield, it was important to characterize the functionality of the polymer and the regiochemistry of addition of PSLi to styrene oxide. Because of the asymmetry of styrene oxide, it is possible for PSLi to attack at either the least hindered carbon to form a secondary alcohol (**1**) or the most hindered carbon to form a primary alcohol (**2**) (see Scheme 4). On the basis of previous work on the functionalization of polymeric organolithium compounds with epoxides such as propylene oxide[9] and 1-butene oxide,[8] attack at the least hindered carbon was expected to be the major product. Investigations into the behavior of styrene oxide in the presence of nucleophiles indicated that a mixture of products may be expected due to the electronic contributions of the benzene ring.[11,12] Oligomerization of the epoxide at the chain end is also possible, as has been observed for ethylene oxide under certain conditions.[4−6] A variety of analytical tools were utilized to determine the functionality, regiochemistry, and degree of oligomerization, including ^{1}H and ^{13}C NMR spectroscopy and MALDI−TOF MS.

FT-IR spectroscopy provides qualitative information about the functionality of a polymer. By FT-IR, the functionalized polymer exhibited an absorption at 3540 cm^{-1} which did not appear in the base polystyrene spectrum. This absorption was attributed to the hydroxyl group at the chain end. Therefore, the chain end has been functionalized by the styrene oxide, but neither the degree of functionalization nor the chain end regiochemistry can be obtained from IR.

The ^{1}H NMR spectrum of the ω-hydroxy-functionalized polymer is shown in Figure 9. The peaks centered at δ 2.93, 3.35, 3.50, and 4.40 ppm are not observed in the ^{1}H NMR spectrum of the base polystyrene. These peaks were assigned to the methylene protons [$-CH(C_6H_5)-CH_2-OH$] and methine protons [$-CH_2-CH(C_6H_5)-OH$] attached to the carbons that are adjacent to the hydroxyl group of the functional polymer. The peak centered at δ = 3.85 ppm was assigned to the proton of the hydroxyl group, since its position shifted upon shaking with D_2O due to the rapid exchange of the protons with deuterium.[23]

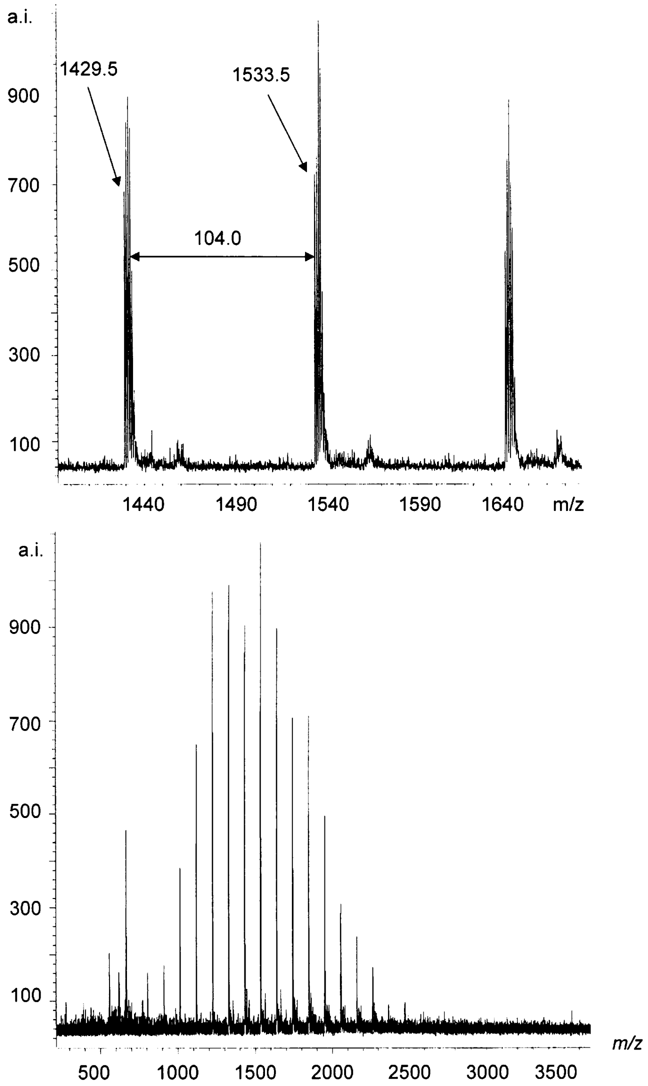
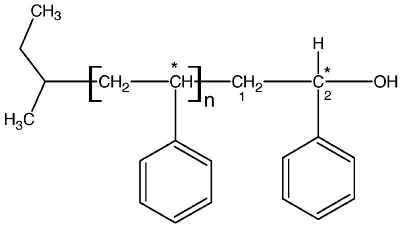


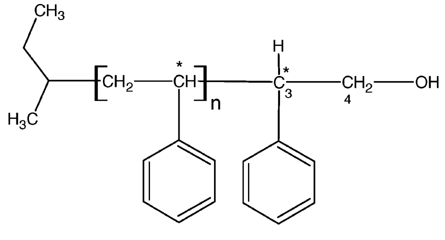
Figure 10. MALDI−TOF mass spectrum of PSLi functionalized with styrene oxide in the presence of 15 mol equiv of THF.

MALDI−TOF mass spectrometry provided information concerning the functionality of the chain end. The mass spectrum of ω-hydroxy-functionalized polymer prepared in the presence of 15 mol equiv of THF is shown in Figure 10. No high molecular weight distribution was observed in the spectrum. The expanded region also shows only one distribution whose peaks differ by m/z 104.0, which corresponds to one styrene unit. This distribution of peaks was attributed to a polystyrene chain with one styrene oxide unit at the chain end [e.g., $C_4H_9-(C_8H_8)_{11}-C_8H_9O\cdot Ag^+$, calcd monoisotopic mass = 1429.7 Da, obsd m/z = 1429.5]. There is no evidence for oligomerization of the styrene oxide at the chain end or unfunctionalized polymer. The mass spectrum indicates that the functionalization of PSLi with styrene oxide in the presence of 15 mol equiv of THF is quantitative, yielding only the functionalized polymer.

Table 5. ^{13}C NMR Calculated and Observed Chemical Shifts for the Two Regiochemically Different Chain Ends[a]



1



2

carbon	calcd chemical shift (ppm)[b,c]	obsd chemical shift (ppm)
1	50.8 (47.1)	52.3
2	77.4 (72.5)	72.2 and 73.3
3	56.8 (46.4)	55.3
4	67.4 (67.2)	65.1 and 66.5

[a] Chiral carbons are indicated by an asterisk. [b] Calculated using parameters in ref 23. [c] Numbers in parentheses calculated using ChemNMR C-13 Estimation software in ChemDraw Ultra 8.

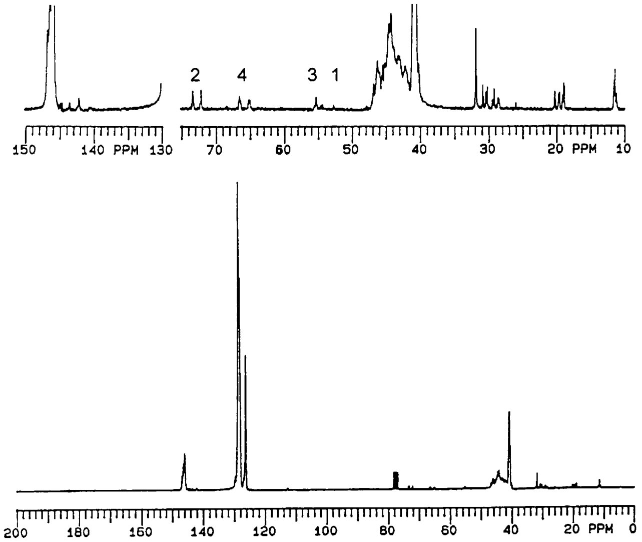


Figure 11. ^{13}C NMR spectrum of ω-hydroxy-functionalized polystyrene from the reaction of PSLi with styrene oxide in the presence of 50 mol equiv of THF.

Unfortunately, MALDI−TOF MS does not provide information about the regiochemistry of the chain end.

The regiochemistry of the chain end was best determined by ^{13}C NMR spectroscopy. One is able to calculate the chemical shifts for the carbons of the chain end using the empirical additivity rules proposed by Grant and Paul.[22,23] The calculated and observed chemical shifts for the two regiochemically different chain ends are shown in Table 5. In the ^{13}C NMR spectrum (Figure 11) of the ω-hydroxy-functionalized polystyrene prepared in the presence of THF, several peaks were observed between δ 65 and 73 ppm. The peaks observed at δ 72.2 and 73.3 ppm were assigned to the terminal benzylic carbon adjacent to the hydroxyl group (carbon 2, Table 5), resulting from addition to the least hindered carbon (**1**). The peaks observed at δ 65.1 and 66.5 ppm were assigned to the terminal methylene carbon adjacent to the hydroxyl group (carbon 4, Table 5), resulting from addition to the most hindered carbon (**2**). Two peaks are observed in this region due to the possibility of diastereomers resulting from the chiral benzylic methine carbons from the styrene oxide chain end and the chiral methine carbons of the adjacent styryl groups. The chiral centers are marked with an asterisk in Table 5.

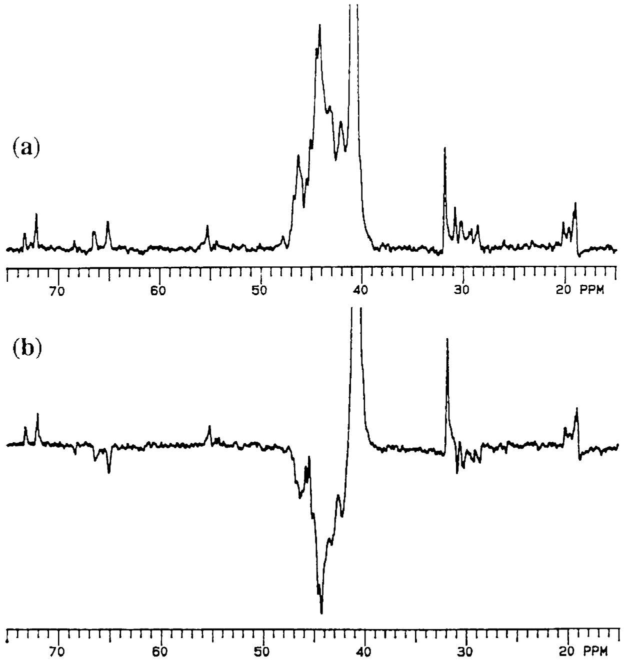


Figure 12. Proton coupled ^{13}C NMR spectrum of styrene oxide-functionalized polymer (a) and the APT spectrum of the styrene oxide-functionalized polymer (b) in the region between 15 and 75 ppm.

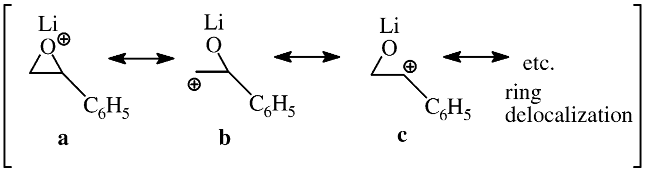
These assignments were confirmed using the attached proton test (APT). The attached proton test separates the methyl and methine carbons from the methylene carbons.[35] In the spectrum, the methyl and methine carbons are pointing up and the methylene carbons are pointing down. Both the proton coupled ^{13}C NMR spectrum and the APT ^{13}C NMR spectrum are shown in Figure 12. The peaks observed at δ 72.2 and 73.3 ppm which were assigned to carbon 2 of structure **1** were pointing up, which is consistent with a methine carbon. The peaks at δ 65.1 and 66.5 ppm assigned to carbon 4 of structure **2** were pointing down, which is consistent with a methylene carbon. The peak pointing up at 55.3 ppm was assigned to carbon 3 of structure **2**, a methine carbon, and the peak pointing down at 52.3 (see Figure 11) was assigned to carbon 1 of structure **2**, a methylene carbon.

From ^{13}C NMR analysis it is clear that the reaction is not regiospecific. In fact, products resulting from both attack at the least hindered carbon (**1**) and attack at the most hindered carbon (**2**) were observed by ^{13}C NMR spectroscopy. After assignment of the peaks, quantitative information could be gained by obtaining a quantitative ^{13}C NMR spectrum. Comparison of the integration of the peaks corresponding to carbons 2 and 4 indicated that the product resulting from addition to the least hindered carbon (**1**) accounted for 53 mol % of the product while the remaining 47 mol % resulted from addition to the most hindered carbon.

Previous studies have shown that the regiochemistry of addition of nucleophiles with styrene oxide depends on the steric and electronic nature of the nucleophile, the coordinating ability of any additional Lewis acids, and the electronic nature of the substituents on the aromatic ring. For example, the reaction of triphenylsilyllithium[36] and 1-lithio-1-methyl-1,3-dithian[37] with styrene oxide exclusively gives the product of addition to the least hindered, terminal α- carbon in THF. However, the reaction with phenyllithium gives only the product of addition to the more hindered, β-carbon.[28b] For the reaction of amines with styrene oxide in the presence of lithium perchlorate, addition to the least-hindered α-position predominates for anilines (87−95%), while aliphatic amines such as diisopropylamine give exclusively the product resulting from addition to the more substituted, β-position.[38] However, the analogous zinc chloride-catalyzed reactions result in predominant addition to the more substituted β-carbon with various types of amines.[39] The reactions of the lithium enolates of pinacolone and acetophenone give predominantly (88−94%) addition to the least-hindered oxirane carbon in THF in the presence of lithium perchlorate;[40] however, in the presence of yterbium triflate, the lithium enolate of acetophenone added predominantly to the more-substituted oxirane carbon (85%).[41] Thus, for a given set of reaction conditions, the regiochemistry is very sensitive to the steric and electronic nature of the nucleophile. Also, the presence of coordinating Lewis acid salts dramatically affects the regiochemistry.

The importance of electronic effects on regiochemistry was demonstrated in the reaction of sodium ethyl malonate with ring-substituted styrene oxides in ethanol. The electron-releasing p-methoxy group promoted exclusive nucleophilic attack at the secondary (more highly substituted) carbon atom, while the electron-withdrawing p-nitro group promoted exclusive attack at the terminal carbon atom.[13]

For the reaction of poly(styryl)lithium with styrene oxide described herein, the fact that both substitution products are observed in similar yields suggests that both steric and electronic factors are affecting the regiochemistry. Steric effects of PSLi would certainly favor reaction at the least-hindered, terminal carbon. However, lithium coordination and the electron-delocalizing effect of the phenyl ring would promote reaction at the more hindered, secondary carbon as illustrated by the favorable resonance structure **c**.



Another factor to be considered is the nature of the transition state. If the reaction of PSLi with styrene oxide is an exothermic reaction, as expected, according to the Hammond postulate,[42] the transition state would resemble the reactants. Under these conditions, there would be very little bond making or bond breaking, and this could explain the fact that both products are obtained in comparable yields; i.e., the reaction is quite unselective. This would also be consistent with the electron-transfer mechanism shown in Scheme 3.

Conclusions

The functionalization of PSLi ($M_\mathrm{n} = 1.9 \times 10^3$ g/mol) with styrene oxide (1.5 mol equiv) in benzene yielded a mixture of products including functional polymer (83.5 wt %), unfunctionalized polymer (9.0 wt %), polystyrene dimer (5.6 wt %), and polystyrene trimer (0.1 wt %) as determined by SEC and column chromatography. The structure of the dimeric species was found to be head-to-head dimer by both ^{13}C NMR and MALDI−TOF MS and was proposed to result from an electron-transfer mechanism. The effects of styrene oxide stoichiometry, reaction temperature, and Lewis base on the functionalization reaction were investigated. While the stoichiometry of styrene oxide relative to the chain end had little effect on the functionalization reaction products, both temperature and Lewis base resulted in favorable changes in the product distribution. At lower temperatures the amount of functionalized polymer was increased, but the formation of dimer and unfunctionalized polymer was not eliminated. The addition of THF as a Lewis base (≥15 mol equiv) resulted in only functionalized polymer being formed as determined by MALDI−TOF MS and SEC. The regiochemistry of the chain end was determined to result from both addition to the least hindered carbon (53 mol %) and addition to the most hindered carbon (47 mol %) by the use of quantitative ^{13}C NMR spectroscopy and the calculated chemical shifts.

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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) Quirk, R. P.; Yin, J.; Guo, S. H.; Hu, X. W.; Summers, G. J.; Kim, J.; Zhu, L. F.; Ma, J. J.; Takizawa, T.; Lynch, T. *Rubber Chem. Technol.* **1991**, *64*, 648.
(3) Quirk, R. P. In *Comprehensive Polymer Science, First Supplement*; Aggarwal, S. L., Russo, S., Eds.; Pergamon Press: Oxford, 1992; p 83.
(4) Ji, H.; Sato, N.; Nondez, W. K.; Mays, J. W. *Polymer* **2002**, *43*, 7119.
(5) Quirk, R. P.; Mathers, R. T.; Ma, J.-J.; Wesdemiotis, C.; Arnould, M. A. *Macromol. Symp.* **2002**, *183*, 17.
(6) Quirk, R. P.; Mathers, R. T.; Wesdemiotis, C.; Arnould, M. A. *Macromolecules* **2002**, *35*, 2912.
(7) Quirk, R. P.; Ma, J.-J. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2031.
(8) Quirk, R. P.; Ge, Q.; Arnould, M. A.; Wesdemiotis, C. *Macromol. Chem. Phys.* **2001**, *202*, 1761.
(9) Quirk, R. P.; Lizarraga, G. M. *Macromolecules* **1998**, *31*, 3424.
(10) Quirk, R. P.; Gomochak, D. L.; Wesdemiotis, C.; Arnould, M. A. *J. Polym. Sci., Part A: Polym. Chem.* **2003**, *41*, 947.
(11) DePuy, C. H.; Breitbeil, F. W.; Eilers, K. L. *J. Org. Chem.* **1964**, *29*, 2810.
(12) Cristol, S. J.; Helmreich, R. F. *J. Am. Chem. Soc.* **1952**, *74*, 4083.
(13) Kayser, M. M.; Morand, P. *Can. J. Chem.* **1980**, *58*, 302.
(14) Quirk, R. P.; Chen, W. C. *Makromol. Chem.* **1982**, *183*, 2071.

(15) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447.
(16) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 3.
(17) Ashby, E. C. *Pure Appl. Chem.* **1980**, *32*, 545.
(18) Ashby, E. C.; Wiesemann, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 3101.
(19) Ashby. E. C.; Goel, A. B.; DePrist, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 7779.
(20) Alnajjar, M. S.; Kuivila, H. G. *J. Am. Chem. Soc.* **1985**, *107*, 416.
(21) Yamataka, H.; Fujimura, N.; Kawafuji, Y.; Hanafusa, T. *J. Am. Chem. Soc.* **1987**, *109*, 4305.
(22) Paul, E. G.; Grant, D. M. *J. Am. Chem. Soc.* **1963**, *85*, 1701.
(23) Silverstein, R. M.; Webster, F. X. *Spectrometric Identification of Organic Compounds*, 6th ed.; John Wiley & Sons: New York, 1998.
(24) Quirk, R. P.; Ma, J. J. *J. Polym. Sci., Part A: Polym. Chem.* **1988**, *26*, 2031.
(25) Hensley, D. R.; Goodrich, S. D.; Harwood, H. J.; Rinaldi, P. L. *Macromolecules* **1994**, *27*, 2351.
(26) Hensley, D. R.; Goodrich, S. D.; Huckstep, A. Y.; Harwood, H. J.; Rinaldi, P. L. *Macromolecules* **1995**, *28*, 1586.
(27) Rader, H. J.; Schrepp, W. *Acta Polym.* **1998**, *49*, 272.
(28) (a) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: New York, 1974; p 9. (b) p 201.
(29) Morton, M.; Fetters, L. J.; Pett, R. A.; Meier, J. F. *Macromolecules* **1970**, *3*, 327.
(30) Bywater, S.; Firat, Y.; Black, P. E. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 669.
(31) Worsfold, D. J.; Bywater, S. *Can. J. Chem.* **1964**, *42*, 2884.
(32) Honeycutt, S. C. *J. Organomet. Chem.* **1971**, *29*, 1.
(33) Glasse, M. D. *Prog. Polym. Sci.* **1983**, *9*, 133.
(34) Bhattacharyya, D. N.; Lee, C. L.; Smid, J.; Szwarc, M. *J. Phys. Chem.* **1965**, *69*, 612.
(35) Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535.
(36) Gilman, H.; Aoki, D.; Wittenberg *J. Am. Chem. Soc.* **1959**, *81*, 1107.
(37) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 1075.
(38) Chini, M.; Crotti, P.; Macchia, F. *J. Org. Chem.* **1991**, *56*, 5939.
(39) Pachon, L. D.; Gamez, P.; van Brussel, J. J. M.; Reedijk, J. *Tetrahedron Lett.* **2003**, *44*, 6025.
(40) Chini, M.; Crotti, P.; Favero, L.; Pineschi, M. *Tetrahedron Lett.* **1991**, *51*, 7583.
(41) Crotti, P.; Bussolo, V. D.; Favero, L.; Macchia, F.; Pineschi, M. *Tetrahedron Lett.* **1994**, *35*, 6537.
(42) Hammond, G. S. *J. Am. Chem. Soc.* **1955**, *77*, 334.

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