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Investigation of the Reaction of Poly(styryl)lithium with Propylene Oxide

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ABSTRACT: The room-temperature functionalization reaction between poly(styryl)lithium and propylene oxide in benzene was studied. The functionalized polymer was characterized by ^{1}H NMR, ^{13}C NMR, and APT-^{13}C NMR. ^{13}C-methyl-labeled propylene oxide-functionalized polystyrene was also synthesized and characterized. Hydroxylated polystyrene was obtained in only 93% yield, but with high regioselectivity (97% of addition of the anionic chain-end to the least substituted carbon of the propylene oxide ring) and no oligomerization. The lower than quantitative yield was ascribed to the proton-transfer reaction of poly(styryl)lithium from the methyl group of propylene oxide, which formed unfunctionalized polystyrene.

Introduction

Living anionic polymerization is a particularly suitable way to effect chain-end functionalization, given that it generates stable polymer chain ends, once all the monomer is consumed. Reactions of the living polymer chain end with a variety of electrophiles have been carried out to generate different functional groups.[1−3]

Polymeric organolithium compounds are often reacted with ethylene oxide to efficiently introduce a primary hydroxyl functional end group quantitatively and without oligomerization.[4−6] It was proposed that the high degree of aggregation of lithium alkoxides in hydrocarbon media[7] renders them unreactive toward further oligomerization at the chain end.[8,9]

Propylene oxide also reacts with poly(styryl)lithium to generate an alkoxide chain end. There are possible complications to achieving a quantitative functionalization reaction that arise from the acidic nature of the protons on the methyl substituent of the epoxide ring.[10] On the other hand, the asymmetry of the propylene oxide ring raises the question of the poly(styryl)lithium mode of attack. This question has been answered for the case of the metal alkoxide-initiated anionic polymerization of propylene oxide, where only 2% of head-to-head or tail-to-tail linkages is observed.[11] Steric reasons and the electron-donating inductive effect of the methyl substituent on the epoxide ring make the attack on the least substituted carbon the most favorable reaction pathway. It is the purpose of the present communication to report a systematic analysis of reaction efficiency, mode of attack, and assessment of oligomerization at the chain end for the aforementioned reaction.

Experimental Section

Materials. Styrene, benzene, and tetrahydrofuran (THF) were purified as described previously.[12] Propylene oxide (99+%, Aldrich) was stored with stirring over freshly crushed calcium hydride (Alfa). After being degassed on the vacuum line, the propylene oxide was vacuum distilled onto dibutylmagnesium (Alfa) and a slight excess of 1,10-phenanthroline (99+%, Aldrich) indicator (propylene oxide/dibutylmagnesium/1,10-phenanthroline: 2.86 mol/5.4 × 10^{-4} mol/3.52 × 10^{-4} mol). It was then immediately distilled into calibrated ampules, followed by heat sealing with a torch. 1,2-Propylene oxide (3-^{13}C, 99%, Cambridge Isotope Laboratories) was supplied in a carbon steel lecture bottle. This lecture bottle was fitted with a single-stage, noncorrosive, low flow, cga 170 regulator (Matheson, model No. 3322), useful for regulating pressures of up to 30 psi. The regulator outlet was attached to flexible steel tubing (3/8 in. o.d., 24 in. length) by a hexagonal coupling (female, $^{1}/_{8}$ in. NPT) and a male connector ($^{1}/_{8}$ in. NPT) (Akron Valve & Fitting Co.). The connection of this flexible tubing with the vacuum line was achieved via a union that was screwed onto the slightly greased end of a port that consisted of a glass tube of the appropriate diameter, connected to the vacuum line with a Rotaflo stopcock. 1,2-Propylene oxide (3-^{13}C) was used without further purification given the small volumes involved. It was condensed under vacuum into a small flask fitted with a breakseal and then heat sealed with a torch. Solutions of *sec*-butyllithium (FMC, Lithium Division) 1.4 M (12 wt %) in cyclohexane were analyzed by a direct titration method with 1,10-phenanthroline[13] as the indicator. Silica gel 60 (EM Science, 230−400 mesh) was used for column chromatography after activation by heating at 150 °C under vacuum for 2 h. Silica gel plates were used for thin-layer chromatography (TLC) (Whatman silica gel 60 Å, Diamond Series). Deuterated chloroform (99.8% D, Aldrich) and deuterated acetone (99.5% D_6, Aldrich) were used as NMR solvents.

Polymerization. Polymerizations of styrene in benzene were carried out at 30 °C using *sec*-butyllithium as initiator in all glass, sealed reactors using breakseals and standard high-vacuum techniques.[14] The concentration of styrene to benzene (mL/mL) was 10−11 vol %. The molar concentration of organolithium chain ends was (4−9) × 10^{-2} M. After 12 h, and prior to functionalization, an aliquot of poly(styryl)lithium (8−10% of the total volume) was removed from the reaction and terminated with degassed methanol.

Functionalized Polystyrene. Termination reactions with propylene oxide (×2 molar excess) were effected by smashing the breakseal of the ampule containing this terminating agent. For the case of the functionalization reaction carried out in the presence of THF, the THF ampule's breakseal was smashed first, followed by the addition of propylene oxide. The color of the solution quickly changed from orange to yellow and became lighter with time. The extent of the functionalization reaction was monitored by UV−vis spectroscopy by measuring the absorbance at 350 nm and at 286 nm. After completion of the reaction, the reactor was scored open and the reaction terminated with methanol/concentrated hydrochloric acid, 37% (5/1 v/v). The crude polymer was isolated in quantitative yield by precipitating the product into excess methanol and drying under vacuum at room temperature. The pure hydroxylated polymer was isolated by running column chromatography of the crude polymer, isolating the corresponding fraction, precipitating the product into excess metha-

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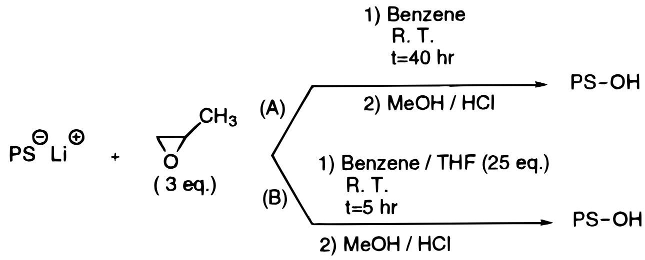
Scheme 1



nol, and drying under vacuum at room temperature.

Characterization. Number-average molecular weights were determined using size exclusion chromatography (SEC). Polymer molecular weights and molecular weight distributions were obtained by SEC using a Waters model gel permeation chromatograph (501 HPLC pump and U6K injector) equipped for detection with a differential refractometer (Waters, model R401) (RI detector). The column setup consisted of six ultra-μ-Styragel columns with average pore sizes of 10^5, 10^4, 10^3, (two) and 500 Å (two). The eluting solvent was tetrahydrofuran at flow rates of 1 and 0.4 mL/min. The runs were made at 30 °C. The sample concentration was 5 mg/mL. A strip chart recorder (Yokogawa Hokushiu Electric, Model 79994A) was used to present the information. Curve calibration was achieved with standard polystyrene samples obtained from Polymer Laboratories.

Routine ^{1}H and ^{13}C NMR spectra were measured on a Varian Gemini 200, using deuterated chloroform or deuterated acetone and 5 mm diameter tubes. The sample concentration for ^{1}H NMR was approximately 30 mg/mL and was 70−80 mg/mL for ^{13}C NMR. Quantitative ^{1}H NMR spectra were measured with a delay time of 20 s. Special ^{13}C NMR experiments were run using a Varian XL-400 NMR spectrometer, using deuterated chloroform as the solvent and 10 mm diameter sample tubes. Chemical shifts were referenced to the deuterated chloroform chemical shift value of 77.0 ppm. Sample concentrations of 70−80 mg/mL were used. Routine ^{13}C NMR spectra and ^{13}C NMR-APT[15] (attached proton test) spectra of polymers were obtained with a 3 s delay time, 10 ms pulse width, and approximately 12 000 transients. A T_1 experiment was run on a Varian Gemini 200 NMR spectrometer, with a sample concentration of 300 mg/mL and experimental parameters of P1 = 45 ms, PW = 22.5 ms, D1= 5 s, and D2(1) = 0.01, 0.05, 0.1, 0.5, 1, 2, 3, 4 s.

Silica gel glass plates (Whatman Diamond Series) with fluorescent indicator (λ = 254 nm) were used for thin-layer chromatographic (TLC) analyses with toluene as eluent. In this system, polystyrene has an $R_f = 1$ and propylene oxide-functionalized polystyrene has an $R_f \approx 0.35$.

The amount of unfunctional polymer was determined by column chromatography using flash chromatography techniques.[16] Quantitation of functional and unfunctional polymer was achieved by collecting the fractions and weighing them after solvent removal. For example, 10 g of functional polymer was chromatographed on 6 in. of activated silica gel in a 2 in. diameter column. Toluene and THF were used as the eluents. The column was prepared in toluene. Once the front running polystyrene eluted out of the column the eluent was gradually changed to pure THF to elute the remaining functional polymer. The flow rate was 1 in./2 min under an Ar_g pressure of 5 psi.

Results and Discussion

Molecular Weight Characterization and Extent of Reaction. The functionalization of poly(styryl)lithium in benzene with propylene oxide was carried out at room temperature in the absence of THF (A) and in the presence of 25 equivalents of THF (B) (Scheme 1). The UV absorbance of the living polymer versus time was monitored for the two functionalization reactions. The strong absorption at λ = 334 nm, characteristic of the poly(styryl)lithium chain end in benzene, decreases in intensity as the crossover reaction to propylene oxide proceeds. Figure 1 shows plots for the ratio of the absorbance at 334 nm to the absorbance at 286 nm, which is invariant given that it corresponds to the phenyl ring[17] in the polystyrene chain, versus time. The data from these plots indicated that the functionalization reaction had reached completion in 40 h in benzene, compared to 5 h in the presence of THF. It is also interesting to observe that the slopes of the two plots are very similar at the beginning of the reaction but become very different after approximately an 1 h. This effect could be due to the initial solvating effect of propylene oxide. Propylene oxide can interact with the lithium cation as a Lewis base, in the same fashion as THF can,[18] therefore influencing the propagation rate constant (k_p) or the equilibrium constant for the dimer−ion pair dissociation (K_{diss}) and consequently increasing the overall rate of reaction.

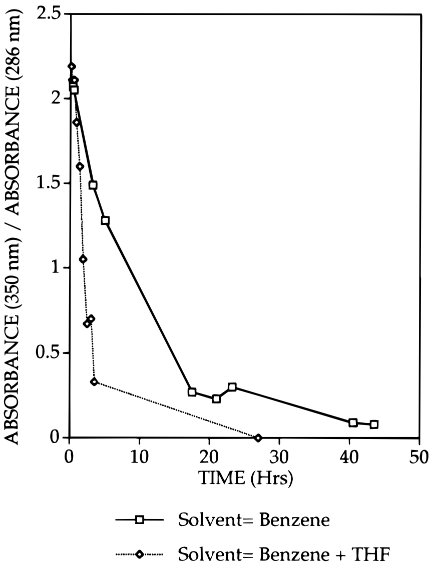


Figure 1. Rate of addition for the functionalization reaction of poly(styryl)lithium with propylene oxide in the presence and in the absence of THF.

SEC-RI analysis was carried out on the products of the two hydroxylation reactions. Figure 2 shows these two chromatograms superimposed on the corresponding base polystyrene. The polymers obtained had the molecular weights and molecular weight distributions shown in Table 1.

TLC analysis was carried out for these two crude polymers and the resulting plates showed two spots. One of these spots had the same R_f value as polystyrene and the second one was ascribed to functionalized polystyrene.

Flash column chromatography was used to separate the two components of the crude polymer mixture. The percentage of material recovered after separation was over 99%. Table 2 shows the percentage yield of functionalized polystyrene as calculated from the weights of the functionalized and unfunctionalized material eluted from the column chromatographic separation. These values suggest that even though the addition of a polar additive such as THF produced a more reactive poly(styryl)lithium chain end[12] that led to a faster rate of chain-end functionalization, this higher reactivity was not a factor in the extent of hydroxylation. Overall, the amount of unfunctionalized polystyrene did not exceed 8% in either case.

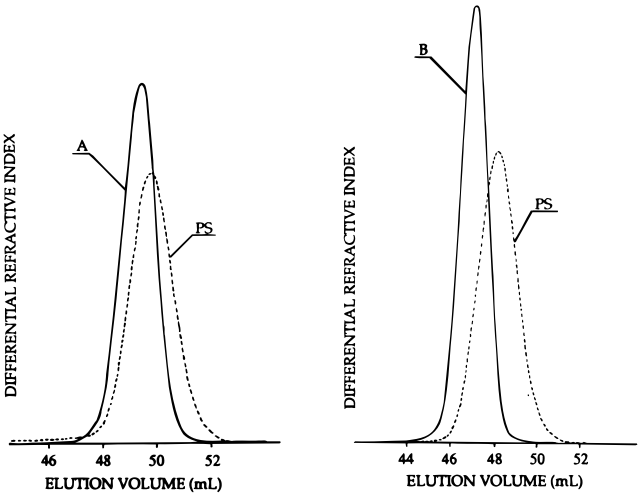


Figure 2. SEC-RI chromatogram of the crude products of the reactions of poly(styryl)lithium with propylene oxide in benzene (A) and in benzene/THF (B), superimposed to their corresponding base polystyrene.

Table 1. Molecular Weight and PDI (M_w/M_n) for the Crude Products of the Functionalization Reaction of Poly(styryl)lithium with Propylene Oxide and for Their Corresponding Base Polystyrenes

reacn	$10^{-3}M_n$ of crude polymer[b]	M_w/M_n[b]	$10^{-3}M_n$ of base polystyrene[b]	M_w/M_n[b]
A	2.2	1.05	2.1	1.04
B[a]	2.2	1.04	2.1	1.04

[a] THF added to the reaction. [b] By SEC.

Table 2. Isolated Yields of Products for the Reaction of Poly(styryl)lithium with Propylene Oxide

	isolated yield of products (%)[b]	
reacn	unfunctionalized polymer	functional polymer
A	7.4	92.6
B[a]	5.6	94.4

[a] THF added to the reaction. [b] From column chromatography.

The assessment of percent functionality was made qualitatively by TLC, which showed a single spot for the functionalized polymer. Further evidence of the purity of the hydroxylated polystyrene is provided by the fact that the resonance corresponding to the terminal carbon of polystyrene ($-CH_2-Ph$) at δ 33.6 ppm is not observed in the corresponding ^{13}C NMR spectrum (Figure 4).[8] The quantitative determination of functionality was made by integration from the ^1H NMR and ^{13}C NMR spectra (Figures 3 and 4), and it will be discussed later in the paper.

Regiochemistry at the Chain End. It was expected that the majority of the hydroxylated polystyrene formed by reaction of poly(styryl)lithium with propylene oxide had the regiochemistry that corresponds to the attack of the chain end on the least hindered site of attack of the propylene oxide ring. The chain end generated in this case would have a secondary hydroxyl end group. Nevertheless, the high reactivity and low selectivity of the benzyllithium-type chain end could make the alternative mode of attack possible.

The functionalization reactions carried out in the presence (B) and in the absence (A) of THF gave the same ^1H NMR results and will therefore be analyzed as a single set of data. The ^1H NMR spectrum of the pure hydroxylated polystyrene with $M_n = 2.5 \times 10^3$ and $M_w/M_n = 1.02$ is shown in Figure 3.

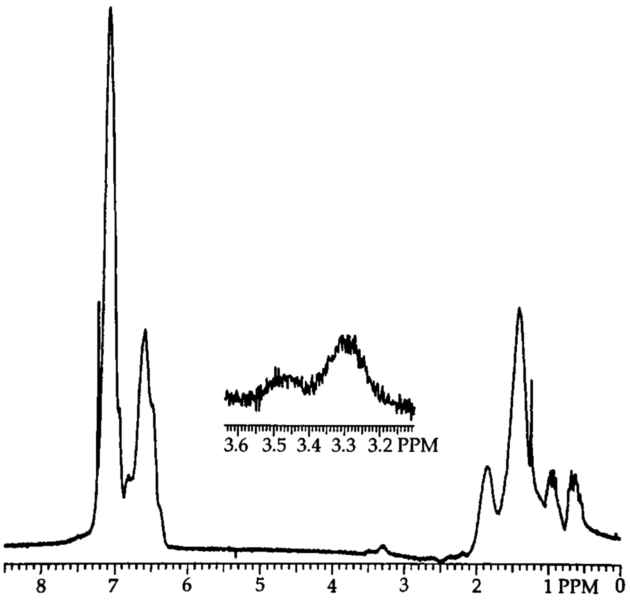


Figure 3. ^1H NMR spectrum of the pure hydroxylated polystyrene from the reaction of poly(styryl)lithium with propylene oxide in benzene, obtained in $CDCl_3$.

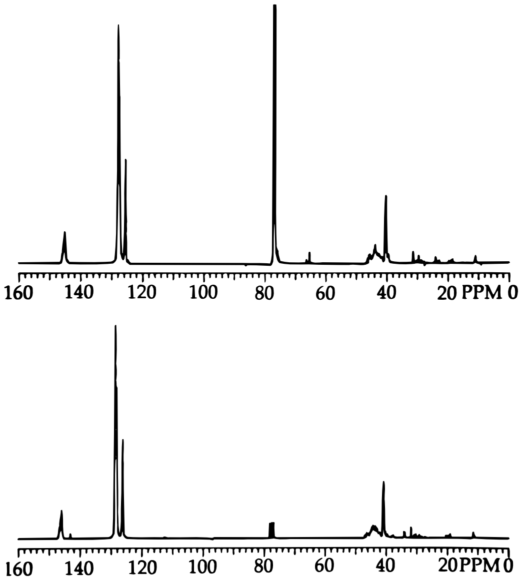
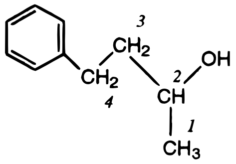


Figure 4. ^{13}C NMR spectrum of the pure hydroxylated polystyrene from the reaction of poly(styryl)lithium with propylene oxide (above), compared to the ^{13}C NMR spectrum of base polystyrene, obtained in $CDCl_3$.

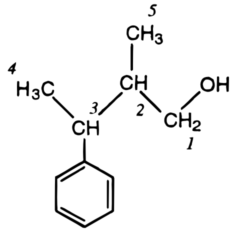
This spectrum showed two broad peaks centered at δ 3.32 and 3.47 ppm. A possible assignment would have these two signals correspond to methylene and methine protons bonded to carbon atoms next to the terminal hydroxyl group. Such would be the case if reaction products with different regiochemistries at the propylene oxide chain end had been formed. This is demonstrated by the chemical shifts of similar carbons in the model compounds for the two regiochemically different chain ends shown in Table 3.

The ^1H NMR also shows three small peaks centered at δ 2.2, 2.35, and 2.6 ppm, respectively. After comparison with the two possible chain-end model compounds, it can be observed that these peaks could correspond to the hydroxylic chain-end proton and to a benzylic proton of the chain end, either H4 for the

Table 3. ^{1}H NMR Chemical Shifts of Model Compounds for the Two Different Regiochemistries at the Chain End of the Product of the Reaction between Poly(styryl)lithium and Propylene Oxide



4-Phenyl-2-butanol

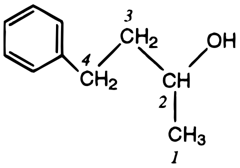


2-Methyl-3-phenyl butanol

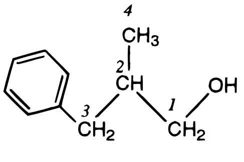
	multiplicity; chemical shift (ppm)			
compd	H1	H2	H3	H4
4-phenyl-2-butanol[a]	d; 1.17	m; 3.75	m; 1.49−1.92 2.53−2.9	
2-methyl-3-phenyl-butanol[b]	d; 3.27 & 3.48	m; 1.77 & 1.78	d; 2.65 & 2.75	d; 1.22 & 1.28

[a] Reference 19. [b] Reference 20.

Table 4. ^{13}C NMR Chemical Shifts of Model Compounds for the Two Regiochemically Different Hydroxylated Polystyrene Chain Ends



4-Phenyl-2-butanol



2-Methyl-3-phenyl propanol

	carbon no., chemical shift (ppm)		
model compd	δ 21.5−26 ppm	δ 64−67.5 ppm	δ 10−20 ppm
4-phenyl-2-butanol[a]	C1, 23.50	C2, 67.30	none
2-methyl-3-phenyl-propanol[a]	none	C1, 67.26	C4, 16.39

[a] Reference 21.

4-phenyl-2-butanol-like chain end or H3 for the 2-methyl-3-phenylbutanol-like one. The rest of the signals in the spectrum can be assigned to polystyrene protons.

The ^{13}C NMR spectrum of the pure hydroxylated polystyrene with $M_n = 2.5 \times 10^3$ and the corresponding unfunctionalized polystyrene are shown in Figure 4. The functionalization reactions carried out in the presence and in the absence of THF gave the same ^{13}C NMR results and will therefore be analyzed as a single set of data. Upon comparison of the two spectra in Figure 4 it can be observed that there are two regions in the ^{13}C NMR spectrum of pure hydroxylated polystyrene that show peaks which do not appear in the spectrum of polystyrene: δ 21.5−26 ppm and δ 64−67.5 ppm. These two spectral regions ought to contain the chain-end carbons. Given the possibility for two different regiochemistries at the chain end, two model compounds were used to compare their chemical shifts within the two regions of interest with those found experimentally (see Table 4).

The chemical shift values for carbons 1 and 2 of 4-phenyl-2-butanol lie within the two regions of interest of the ^{13}C NMR spectrum of pure hydroxylated polystyrene. This evidence is consistent with the presence of propylene oxide terminated polystyrene chains possessing the regiochemistry that corresponds to the expected mode of attack. As to the presence of any chains with the regiochemistry generated by the second mode of attack, the absence of any peaks in the region between δ 21.5−26 ppm of the 2-methyl-3-phenylpropanol model compound's spectrum suggests that none of the hydroxylated polystyrene produced in the reaction between poly(styryl)lithium and propylene oxide had the same regiochemistry as the model compound in question. Further evidence for this conclusion is that no peaks can be observed near δ 16 ppm in the spectrum of the hydroxylated polymer; this region would contain the chain-end methyl carbon (C4 of 2-methyl-3-phenyl propanol, Table 4) for the propylene oxide-terminated polystyrene chains possessing the regiochemistry that corresponds to the attack on the most substituted carbon of the propylene oxide ring.

An attached-proton-test ^{13}C NMR (APT-^{13}C NMR) experiment, also called the J-modulated-spin−echo technique (JMSET),[15] was carried out on the same pure hydroxylated polystyrene samples (Figure 5). The pulse sequence applied in this type of experiment produces modulated peak intensities for methine, methylene, and methyl type carbons such that the signals for methylene carbons appear with a normal phase and those for methine and methyl carbons appear with an inverted phase. Quaternary carbons are unmodulated. It can be observed from Figure 5 that the two spectral regions that contain the signals from the functional chain-end carbons, δ 21.5−26 and δ 64−67.5 ppm, show inverted-phase peaks. Upon reexamination of the values of Table 4, we can say that this spectrum shows evidence for the signal of the methine carbon belonging to the most probable type of chain end modeled by 4-phenyl-2-butanol, given that the multiplet signal found between δ 64 and 67.5 ppm shows an inverted phase. On the other hand, we do not see any evidence for normal-phase peaks within this spectral region, which would suggest the absence of any methylene-type carbon at the chain end, as the one corresponding to the type of chain-end modeled by 2-methyl-3-phenylpropanol (C1). This would suggest the absence of any polymer chain ends formed by way of the attack of poly(styryl)lithium on the most substituted methine carbon of the propylene oxide ring.

The spectral region between δ 21.5 and 26 ppm corresponds to the methyl carbon region. It was therefore not surprising to find an inverted-phase multiplet at the expected chemical shift (see Table 4, C1 of 4-phenyl-2-butanol) that corresponds to the methyl carbon at the chain end.

It was of interest to investigate the occurrence of the "abnormal" type of chain end in the propylene oxide functionalization of poly(styryl)lithium with a technique that pushed the limits of detection to higher levels. The strategy chosen was to effect the functionalization reaction using a ^{13}C-methyl-labeled propylene oxide to enhance the sensitivity of the ^{13}C NMR experiment by increasing the concentration of the methyl carbons at the chain-end above the level of natural abundance. ^{13}C NMR was run on the purified ^{13}C-labeled polymer, and the corresponding spectrum is shown in Figure 6. The spectral region between δ 11 and 27 ppm (see Figure 6) shows the peaks corresponding to the initiator fragment and two extra multiplets that correspond to the propylene oxide chain-end methyl carbons, centered at δ 24.1 and 14.8 ppm, respectively. We have already assigned the multiplet centered at δ 24.1 ppm as corresponding

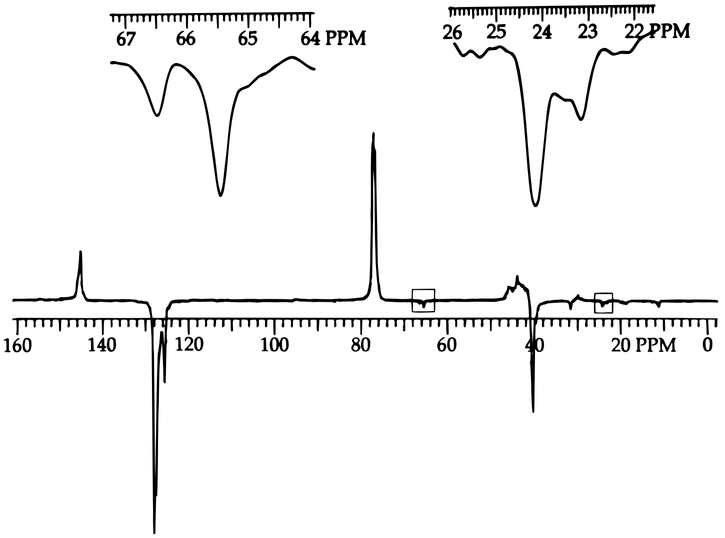


Figure 5. Attached-proton-test-^{13}C NMR (APT-^{13}C NMR) spectrum of the pure hydroxylated polystyrene from the reaction of poly(styryl)lithium with propylene oxide, obtained in $CDCl_3$.

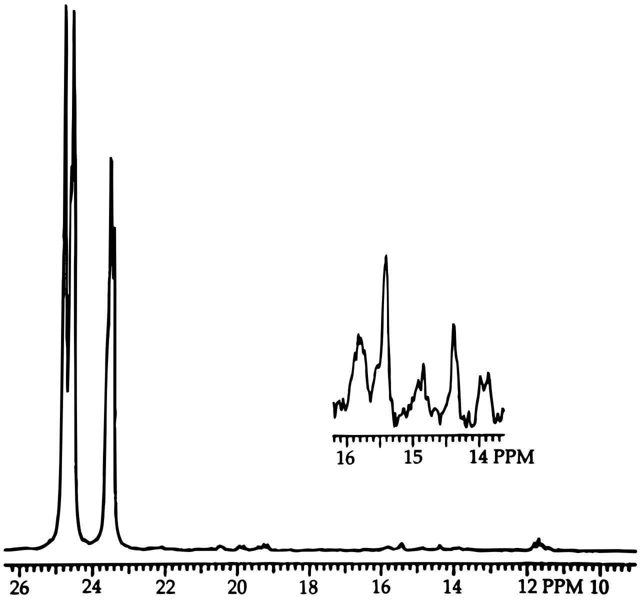
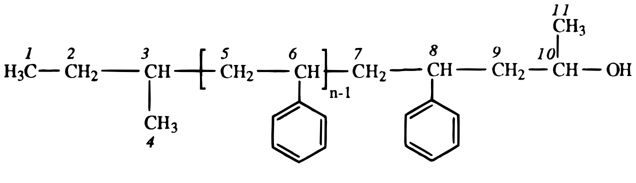
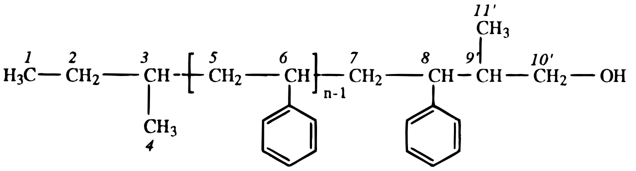


Figure 6. Insert of the ^{13}C NMR spectrum of the purified ^{13}C-labeled hydroxylated polystyrene from the reaction of poly(styryl)lithium with 1,2-propylene oxide (3-^{13}C), obtained in $CDCl_3$.

Table 5. Observed Chemical Shifts for the Two Regiochemically Different Pure Hydroxylated Polystyrene Products of the Reaction of Poly(styryl)lithium and Propylene Oxide





	chemical shifts (ppm)	
carbon no.	obsd	calcd
1	11.0	11.3[a]
2	28–31	32.1[a]
3	31.7	29.9[a]
4	18–20	19.7[a]
5	41–47	44.3[a]
6	39.5–41	43.3[a]
7	*b*	45.2[a]
8	*b*	40.2[a]
9	*b*	40.8[c]
9′	*b*	37.7[c]
10	64.3–67	67.3[c]
10′	*d*	67.3[c]
11	23–25.4	23.5[c]
11′	14–16	16.4[c]

[a] Reference 8. [b] Overlapped with other signals. [c] Reference 21. [d] Not observed.

to the methyl carbon of the chain-end product of the poly(styryl)lithium expected mode of attack on the least hindered carbon of the propylene oxide ring. This multiplet has a largely increased intensity due to the ^{13}C-labeling. The second multiplet centered at δ 14.8 ppm was not visible in the ^{13}C NMR spectrum shown in Figure 4. This multiplet is assigned to the chain-end methyl carbon that corresponds to the alternate chain-end regiochemistry, namely that resulting from the attack of poly(styryl)lithium on the most hindered carbon of the propylene oxide ring. The chemical shift found corresponds to the theoretical one, according to the model compound 2-methyl-3-phenylpropanol (see Table 4), whose methyl carbon (C4 in the 2-methyl-3-phenylpropanol model compound) peak appears at δ 16.4 ppm. After having elucidated the nature of the chain end, it was possible to give a complete assignment for all the peaks found in the ^{13}C NMR spectrum of the product of the reaction between poly(styryl)lithium and propylene oxide (Figure 4). This peak assignment is shown in Table 5.

It is possible to get an approximate quantitation of the percentage of "abnormal" attack of poly(styryl)lithium on propylene oxide with respect to the expected mode of attack. The cut-and-weigh method was used on the areas of the two methyl carbon multiplets of the ^{13}C NMR spectrum shown in Figure 6. A delay between pulses of 3 s was considered sufficiently long (equivalent to $5T_1$ or more) in order to allow enough time for the

Table 6. Chemical Shifts, T_1 Values, and Corresponding Errors for Peaks from the Chain-End Methyl Carbon Multiplets That Correspond to the Two Different Regiochemistries at the Chain End

peak	chemical shift (ppm)	T_1	error
1[a]	24.4	0.469	0.006
2[a]	23.4	0.597	0.002
3[b]	15.2	0.522	0.156

[a] Carbon 11, Table 5. [b] Carbon 11′, Table 5.

Table 7. Chemical Shifts, T_1 Values, and Corresponding Errors for Peaks from the Methyl Carbon Multiplets That Correspond to the Secondary Methyl Group of the Initiator Segment (C4 in Table 5)

peak	chemical shift (ppm)	T_1	error
1	20.3	0.564	0.047
2	20.0	0.510	0.072
3	19.2	0.574	0.409
4	18.9	0.747	0.094

methyl carbons to relax. This assessment was based on the T_1 determination for the methyl carbons of the two methyl carbon multiplets in question. The values of T_1 found and the corresponding errors in their determination are shown in Table 6. The results showed that 97% of the propylene oxide end-functionalized polystyrene had the expected regiochemistry at the chain end and only 3% of the chains were formed through the least probable attack of the polystyryl anion on the methine carbon of the propylene oxide molecule.

Multiplet absorbances are observed in both the ^{1}H NMR and ^{13}C NMR spectra. This is not surprising given the diastereomeric nature of the chain end.

Quantitation on the Extent of Functionalization. To get an approximate quantitation of the extent of functionalization in the purified propylene oxide-functionalized polystyrene by ^{1}H NMR, the cut-and-weigh method was used on selected areas of the corresponding spectrum (Figure 3). Given that this chain end is 97% regiochemically regular, the broad doublet between δ 3.2 and 3.6 ppm was already assigned to the methine protons belonging to the chain-end, which is demonstrated by comparison to the model compound 4-phenyl-2-butanol (see Table 3). The fact that it appears as a doublet instead of a singlet is probably due to the different magnetic environments provided by the two diastereomerically different configurations at the chain end. The integration for the two components of this doublet is not the same, which suggests that there is selective stereoisomer formation.[22] The integration value for the one methine proton of the chain end was then compared to the integration value for the broad multiplet between δ 6.2 and 7.6 ppm, which was ascribed to the five phenyl ring protons in each unit of the polymer chain. This calculation yielded a value of 97% propylene oxide chain-end functionality.

A more accurate determination for the chain-end functionality was obtained by integration from the ^{13}C NMR spectrum shown in Figure 4. The areas compared were that corresponding to the chemical shift assigned to the secondary methyl carbon from the initiator-end, between δ 18 and 20 ppm (C4 in Table 5), and the area assigned to the chain-end methyl carbon (C11 in Table 5), between δ 23 and 25.4 ppm. The values of T_1 for these two regions are shown in Tables 6 and 7. A delay of 3 s was considered sufficiently long to allow enough time for these two methyl carbons to relax and hence allow for accurate integration. The results indicated a value of 100% functionality.

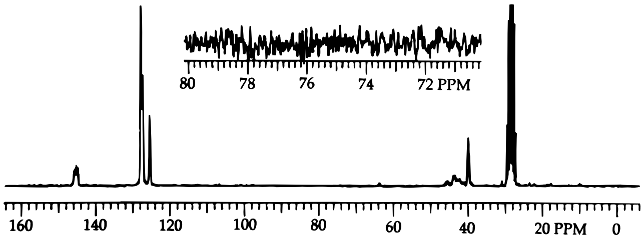
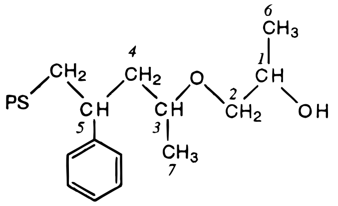


Figure 7. ^{13}C NMR spectrum of the pure hydroxylated product of the reaction of poly(styryl)lithium with propylene oxide, obtained in $(CD_3)_2CO$.

Table 8. Calculated Chemical Shifts for the Case in Which Two Propylene Oxide Units Were Added to the Chain End during the Reaction of Poly(styryl)lithium and Propylene Oxide



carbon no.	calcd chemical shift[a] (ppm)	carbon no.	calcd chemical shift[a] (ppm)
1	72.4	5	42.8
2	74.3	6	24.0
3	71.7	7	22.3
4	46.8		

[a] Reference 23.

Homopolymerizability or Oligomerization at the Chain End. ^{13}C NMR spectroscopy was used to analyze for the possibility of oligomerization at the propylene oxide chain end, given that this reaction was carried out with a 3-fold excess of propylene oxide. Figure 7 shows the ^{13}C NMR spectrum of the pure hydroxylated product of the reaction between poly(styryl)lithium and propylene oxide using deuterated acetone as the solvent. Table 8 shows the calculated chemical shifts[23] for the hypothetical case in which two propylene oxide units were added to the chain end during the functionalization reaction, for the chain-end regiochemistry that occurs with a 97% yield. Obtaining the ^{13}C NMR spectrum shown in Figure 7 in deuterated acetone as the solvent, instead of deuterated chloroform, allowed us to observe the spectral region between δ 70 and 80 ppm free from the chloroform solvent signal (δ 78 ppm). The calculated values for the hypothetical chain-end product of oligomerization shown in Table 8 suggest that, if indeed oligomerization occurred, carbons 1, 2, and 3 would produce signals with chemical shifts between δ 70 and 75 ppm. Observation of the ^{13}C NMR experiment shown in Figure 7 indicates the absence of any peaks in that region. This suggests the absence of oligomerization of propylene oxide.

Further proof against the occurrence of oligomerization came from the ^{13}C NMR spectrum of the ^{13}C-methyl-labeled hydroxylated polystyrene, whose spectrum is shown in Figure 6. It was expected that given its higher natural abundance it would be easier to identify the signal for the methyl carbon labeled C7 on the structure of Table 8. The calculated chemical shift for this carbon was δ 22.3 ppm. Observation of the spectrum in Figure 6 reveals no peaks between δ 21 and 23 ppm, which further suggests that oligomerization did not occur in the reaction under discussion.

Conclusion

The results found for the efficiency of the functionalization reaction of poly(styryl)lithium with propylene oxide at room temperature, with or without the addition of tetrahydrofuran to the hydrocarbon medium were surprisingly good. Despite the potential for loss of functionality due to proton abstraction, this functionalization reaction was shown to be of synthetic value given that high functionality (higher than 90%) was found under the conditions used. Also, it was shown that the addition of a Lewis base produced a more reactive poly(styryl)lithium chain end,[1,12] which led to a faster rate of chain-end functionalization without any significant change of the extent of functionalization. The regiochemistry at the chain end was shown to be 97% the product of the expected attack of poly(styryl)lithium on the least hindered carbon of the propylene oxide ring and 3% the product of the least probable attack on the methine carbon of propylene oxide. No evidence of oligomerization at the propylene oxide chain end was observed. This is consistent with the results found for the case of the reaction of poly(styryl)lithium with ethylene oxide,[8] where only monoaddition occurs.

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