Anionic Synthesis of Model Ionomers. ω-Lithium Poly(styrene)sulfonates

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ABSTRACT: The chain end sulfoalkylation of poly(styryl)lithium and poly(styrene-*block*-α-methylstyryl)lithium using sultones, 1,3-propanesultone and 1,4-butanesultone, has been investigated by a combination of colorimetric titration with methylene blue, two-phase titration with Hyamine 1622, size-exclusion chromatography, TLC, column chromatography using annealed silica gel, infrared, and ^{1}H and ^{13}C NMR spectroscopic analyses. Low yields (<53%) of ω-lithium poly(styrene)sulfonate are obtained from the direct sulfoalkylation reaction under a variety of conditions. In contrast, the direct reaction of poly(styrene-*block*-α-methylstyryl)lithium with 1,3-propanesultone in THF at −78 °C produces the corresponding ω-sulfonated polymer in 94% yield; a yield of only 28% is obtained in toluene at −78 °C. High yields (>90%) of ω-sulfonated polystyrenes are produced by first reacting poly(styryl)lithium with ethylene oxide prior to reaction with 1,3-propanesultone or 1,4-butanesultone; however, this product is labile toward hydrolysis reactions. End-capping of poly(styryl)lithium with 1,1-diphenylethylene prior to the functionalization reaction with excess 1,3-propanesultone at 30 °C in THF/C_6H_6 produces the ω-sulfonated polymer in 93% yield; lower yields are obtained with 1,4-butanesultone. This end-capping procedure with 1,1-diphenylethylene is recommended as the best procedure for anionic functionalization with sultones since it is efficient and effected at room temperature.

Introduction

Ion-containing polymers are of considerable academic and industrial interest because of their unique chemical, thermal, rheological, and mechanical properties.[1-6] In general, structure–property relationships for these materials are based on the behavior of polymers that contain many ionic groups along the polymer backbone and with a statistically random distribution. In order to understand, control, and predict the properties of ion-containing polymers, it is essential to investigate the properties of a variety of model ion-containing polymers with well-defined structures.[7-15]

Anionic polymerization methodology provides a unique opportunity to prepare polymers with control of the major variables that affect polymer properties. Thus, from a variety of anionically polymerizable monomers, polymers can be prepared with controlled molecular weight, molecular weight distribution, copolymer composition and microstructure, stereochemistry, and molecular architecture.[16-22] Because many of these polymerizations proceed in the absence of chain termination and chain-transfer reactions, i.e., they are living polymerizations, the growing polymer chain retains its carbanionic chain end when all of the monomer is consumed.[23] These carbanionic chain ends can, in principle, be reacted with a variety of electrophilic reagents to generate a wide range of terminal functional groups.[17,24]

The use of termination reactions of polymeric carbanions with sultones to prepare the corresponding sulfonated polymers has been reported; however, several of these results appear to be conflicting. Thus, Eisenbach et al.[25] reported that the 1,3-propanesultone termination reaction of poly(α-methylstyryl)lithium in THF at −78 °C produced the corresponding sulfonated polymer in >90% yield. Similarly, Broze et al.[10] reported that the functionalization reaction of α,ω-disodium polystyrene with propanesultone in THF at −78 °C produced the corresponding α,ω-disulfonic acid with a functionality of 1.9. However, Omeiss et al.[26] reported that the corresponding reaction of poly(styryl)lithium and α,ω-dilithium polystyrene in THF provided the corresponding sulfonated polymers with maximum functionalities of 0.72 and 1.35, respectively. In view of these apparent discrepancies and the importance of the sulfonate groups in ionomer chemistry, a systematic investigation of the termination reaction of polymeric organolithium compounds with sultones to prepare the corresponding terminally-sulfonated polymers was undertaken and the results are reported herein.

Experimental Section

Chemicals and Solvents. Benzene and tetrahydrofuran (THF) were carefully purified as described previously.[27] Toluene was purified by procedures similar to those described for benzene,[27] except stirring with concentrated H_2SO_4 was for only 1 day. Styrene (Fisher Scientific, Certified) and α-methylstyrene (Matheson Coleman & Bell) were purified as described previously for styrene.[27] 1,1-Diphenylethylene (Aldrich, 97%) was stirred over Na–K alloy with degassing, followed by vacuum distillation into calibrated ampules, followed by dilution with benzene. Ethylene oxide (Kodak Laboratory & Research Products, 99.7%) was purified as described previously.[27] 1,3-Propanesultone and 1,4-butanesultone (Aldrich, 99+%) were dried and degassed on the vacuum line, followed by dilution with benzene and ampulization. *sec*-Butyllithium (Lithium Corporation, 12 wt % in cyclohexane) was analyzed by the double-titration method with 1,2-dibromoethane.[29]

Polymerizations. Anionic polymerizations of styrene with *sec*-butyllithium as initiator were carried out in benzene at 25 °C for 24 h in all-glass, sealed reactors, using break-seals and standard high vacuum techniques.[30] The volume ratio of monomer to solvent was usually 0.1–0.15. Poly(styrene-*block*-α-methylstyryl)lithium was prepared by removing the solvent from a benzene solution of poly(styryl)lithium (M_n = 4.7 × 10^3 g/mol) followed by distillations of either THF or toluene and then α-methylstyrene into the reactor at −78 °C.

Termination Reactions. The direct sulfonation reactions of poly(styryl)lithium were effected by addition of a solution of sultone via a break-seal and the reaction time was generally 24 h (see Table I). The solvent for the sultone was benzene or toluene when these were the solvents for the polymeric organolithium; the sultone was dissolved in THF when THF was used as solvent or cosolvent for the polymeric organolithium. The direct reaction of poly(styrene-*block*-α-methylstyryl)lithium in THF at −78 °C was effected by addition of a THF solution of sultone via a break-seal similar to the procedure described by Eisenbach et al.[25] The general procedure for workup of functionalized polymers was to

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Table I
Direct Sulfoalkylation of Poly(styryl)lithium and Poly(styrene-*block*-α-methylstyryl)lithium with 1,3-Propanesultone

run	solvent	[sultone]/[Li]	temp, °C	M_n, g/mol	M_w/M_n	functnalizatn yield, wt %
D1[a]	C_6H_6	3	3	2.7×10^3	1.06	25[b]
D2[a]	C_6H_6	3	40	4.2×10^3	1.08	30[b]
D2[a]	C_6H_6	3	80	4.2×10^3	1.08	24[b]
D3[a]	THF	2	−78	4.7×10^3	1.06	53[c]
D4[d]	toluene	3.7	−78	10.0×10^3	1.08	28[c]
D5[e]	THF	2	−78	6.0×10^3	1.16	94[c]

[a] Poly(styryl)lithium. [b] Colorimetric method with methylene blue. [c] SEC method. [d] Poly(styrene-*block*-α-methylstyryl)lithium; M_n(Ps) = 9.7×10^3 g/mol. [e] Poly(styrene-*block*-α-methylstyryl)lithium; M_n(Ps) = 4.7×10^3 g/mol.

Table II
Termination of Poly(styryl)lithium with Ethylene Oxide Followed by Functionalization with 1,3-Propanesultone or 1,4-Butanesultone

run	solvent	[sultone]/[Li]	temp, °C	M_n,[a] g/mol	M_w/M_n[a]	functnalizatn yield, wt %
EO1[b]	C_6H_6	3	25	5.0×10^3	1.04	84[c]
EO2[d]	C_6H_6	4	25	6.0×10^3	1.08	23[c]
EO3[b]	C_6H_6	5	25	4.4×10^3	1.05	86[c]
EO4[b]	C_6H_6	1.2	40	5.0×10^3	1.06	47[c]
EO5[b]	C_6H_6	5.3	40	3.1×10^3	1.06	100[e]
EO6[b]	C_6H_6	5	40	3.2×10^3	1.06	98[e]
EO7[d]	C_6H_6	4.5	40	6.6×10^3	1.08	33[c]
EO8[d]	C_6H_6	9	40	2.5×10^3	1.08	93[c]
EO9[b]	THF/C_6H_6[f]	2	40	8.6×10^3	1.08	90[e]
EO10[b]	THF/C_6H_6[f]	4	40	2.8×10^3	1.07	96[e]

[a] SEC analysis using THF/DMF (10/1 v/v) containing 2 g/L $LiNO_3$. [b] Functionalization with 1,3-propanesultone. [c] SEC method (see Experimental Section). [d] Functionalization with 1,4-butanesultone. [e] Colorimetric method with methylene blue. [f] 1/10 vol/vol.

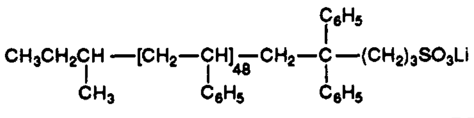
Table III
End-Capping of Poly(styryl)lithium with 1,1-Diphenylethylene Followed by Functionalization with 1,3-Propanesultone or 1,4-Butanesultone

run	solvent	[sultone]/[Li]	temp, °C	M_n,[a] g/mol	M_w/M_n[a]	functnalizatn yield, wt %[b]
DPE1[c]	C_6H_6	2	30	5.2×10^3	1.07	76
DPE2[c]	C_6H_6	10	30	4.2×10^3	1.05	54
DPE3[d]	C_6H_6	6	25	9.0×10^3	1.07	49
DPE4[c]	THF/C_6H_6[e]	1.5	30	4.7×10^3	1.06	93
DPE5[d]	THF/C_6H_6[f]	1.3	25	3.9×10^3	1.08	73
DPE6[c]	THF/C_6H_6[g]	5	25	13.7×10^3	1.02	89
DPE7[d]	THF/C_6H_6[g]	6.4	40	3.6×10^3	1.08	77

[a] SEC analysis using THF/DMF (10/1 vol/vol) containing 2 g/L $LiNO_3$. [b] SEC method. [c] Functionalization with 1,3-propanesultone. [d] Functionalization with 1,4-butanesultone. [e] 1/6 vol/vol. [f] 1/2 vol/vol. [g] 1/5 vol/vol.

remove the solvent(s) and then dissolve samples in toluene for column chromatographic purification.

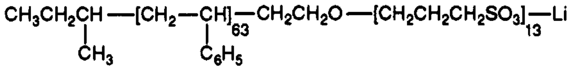
The procedures for ethylene oxide end-capping of poly(styryl)lithium have been described previously.[28] The resulting polymeric alkoxylithium was reacted with sultone solutions under vacuum, using a variety of procedures for periods of 16–48 h (see Table II). End-capping of poly(styryl)lithium in benzene with a stoichiometric amount of 1,1-diphenylethylene was effected by reaction at 25 °C for 24 h. The resulting polymeric (1,1-diphenylalkyl)lithium was reacted with sultone under vacuum using a variety of procedures for periods of 12–48 h (see Table III). A representative sample of this type of functionalized polymer [Table III, sample DPE4; M_n (SEC) base polymer = 5.2×10^3 g/mol] was submitted for elemental analysis after purification by column chromatography.



$$CH_3CH_2\underset{CH_3}{CH}-[CH_2-\underset{C_6H_5}{CH}]_{48}-CH_2-\overset{C_6H_5}{\underset{C_6H_5}{C}}-(CH_2)_3SO_3Li$$

$C_{405}H_{411}O_3SLi$ (M_n = 5365.8 g/mol). Anal. Calcd: C, 90.66; H, 7.72; S, 0.66. Found: C, 90.19; H, 7.91; S, 0.61.

The ring-opening block polymerization of 1,3-propanesultone was performed in a sealed glass reactor using a THF/benzene (1/1, vol/vol) solution of polymeric alkoxylithium (M_n = 6.6×10^3 g/mol) by addition of sultone via a break-seal ([sultone]/[Li] = 1240) and heating at 50 °C for 8 days. The following analytical data were obtained for this polymer after purification by column chromatography on annealed silica gel using a toluene/THF mixture (5/1 vol/vol) as eluent. The degree of sultone oligomerization was estimated from the elemental analysis data using the known molecular weight of the polystyrene block.



$$CH_3CH_2\underset{CH_3}{CH}-[CH_2-\underset{C_6H_5}{CH}]_{63}-CH_2CH_2O-[CH_2CH_2CH_2SO_3]_{13}-Li$$

$C_{549}H_{595}O_{40}S_{13}Li$ (M_n = 8257.6 g/mol). Anal. Calcd: C, 79.9; H, 7.26; S, 5.05. Found: C, 79.04; H, 7.65; S, 4.42.

Polymer Purification. Excess sultone was removed from sulfonated polymer products either by elution chromatography or by solid–liquid extraction. Silical gel (EM Science, 220–400 mesh) was activated by heating at ca. 600 °C for at least 3 h in an annealing oven, followed by storage in a vacuum desiccator.[31,32] For purification of a 2-g sample of crude sulfonation products, 300 g of annealed silica gel was placed in a 5 cm × 50 cm column, washed with three column volumes of methanol (Fisher Scientific Co., certified ACS), and then replaced with toluene. The sulfonation mixture was dissolved in toluene, placed on the column, and eluted with THF/toluene (1/4 vol/vol) to obtain the polymeric reaction products. The excess sultone was eluted with THF/methanol (1/4 vol/vol).

A 3.0-g sample of crude sulfonation products was placed in a thimble in a Soxhlet extractor and extracted with petroleum ether (Fisher Scientific, Certified) at 80 °C for at least 48 h. The presence of residual 1,3-propanesultone was monitored by ^1H NMR using the CH_2O resonance at δ = 4.48 ppm.

Characterization. Size-exclusion chromatographic analyses (SEC) of homopolystyrenes, poly(styrene-*block*-α-methylstyrene), and hydroxy-terminated polystyrenes were performed at a flow rate of 1.0 mL/min in THF at 30 °C using a Waters HPLC component system (RI detector) equipped with a six Ultra-μ-styragel columns (two 500, two 10^3, 10^4, and 10^5 Å) after calibration with standard polystyrene samples (Polymer Laboratories). SEC analyses of terminally sulfonated polymers were performed at a flow rate of 1.0 mL/min in a ternary mixture of 10/1 (vol/vol) THF/dimethylformamide (DMF) containing 2 g/L of $LiNO_3$[33] using a Waters 150C SEC chromatograph with an RI detector and six Ultrastyragel columns (10^6, 10^5, 10^4, 10^3, 500, and 100 Å). SEC analyses in the ternary mixture utilized a polystyrene calibration curve generated in this solvent system. Infrared spectra of polymer films on NaCl plates were obtained on a Beckman Model FT 2100 FTIR spectrometer. ^1H and ^{13}C NMR spectra of polymers were obtained in $CDCl_3$ on a Varian Gemini-200 spectrometer. UV–visible spectroscopic analyses were performed on a Hewlett-Packard Model HP8452A diode array spectrophotometer.

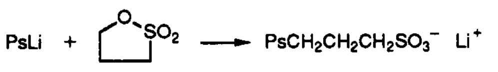
Qualitative characterization of functionalized polymers (0.5 wt % toluene solutions) was obtained by thin-layer chromatography (TLC, Eastman Kodak, Chromatogram sheet, 13181 silica gel with fluorescent indicator) using toluene as eluent. Quantitative analyses of the functionalization reactions and characterization of functionalized polymers were performed by using a colorimetric method,[34-37] a two-phase titration method,[34-37] and an SEC calibration procedure. The colorimetric method is based on the measurement of the absorption intensity of a complex of sulfonate groups with methylene blue (EM Science, MCB reagent); a chloroform solution of the complex absorbs at 652 nm. Analysis was based on a standard curve generated by using the methylene blue complex with sodium dodecyl sulfate (Aldrich, 98%), which was recrystallized from THF/H_2O and dried in a vacuum oven (mp 204 °C; lit.[38] mp 204–207 °C). The titration method is based on the titration of a $CHCl_3$ solution of a methylene blue complex of sulfonate groups with a standard 0.004 M aqueous solution of Hyamine 1622 (Sigma Chemical, reagent grade). The SEC method is based on the fact that the sulfonated polystyrenes do not elute when THF is used as the eluent; only the unfunctionalized polymer can be detected.

Therefore, from a standard linear plot of peak area versus weight percent of unfunctionalized polymer, which was generated by using weighed standard samples containing different, known amounts of homopolymer and sulfonated polymer, the measurement of the peak area for the SEC chromatogram of reaction mixtures from sulfonation reactions was related to the amount (weight percent) of unfunctionalized polymer contained in each sample.

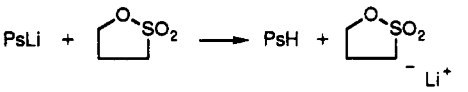
Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Results and Discussion

Direct Sultone Functionalization Reactions. The simplest procedure for the sulfonation of polymeric organolithium compounds is the direct reaction with sultones. Thus, the functionalization of poly(styryl)lithium ($M_n = (2.7-4.7) \times 10^3$ g/mol) with generally a 2-fold molar excess of 1,3-propanesultone (eq 1) was investigated as a function of solvent and temperature and the results are listed in Table I. At temperatures from 3 to 80 °C in benzene solution, only 25–30% of the terminally sulfonated polymer was formed; the remainder of the product was the unfunctionalized polymer. At −78 °C in THF with a molar excess of sultone, a yield of 53% of the terminally sulfonated polystyrene was obtained compared to the yields of 67–72% reported by Omeis et al.[26] using a 5-fold excess of sultone. Presumably the relatively low yields of sulfonated polymer are a result of the competing metalation reaction of poly(styryl)lithium with the acidic α-hydrogens of the sultone as shown in eq 2. Analogous reactions of butyllithium with 1,3-propanesultone produce the metalated sultone in 65–85% yields.[39,40]



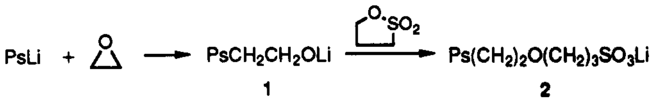
(1)



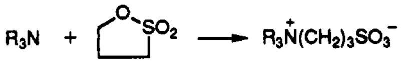
(2)

These results with poly(styryl)lithium are quite different from the results of Eisenbach et al.[25] who reported sulfonation yields of >90% for the reaction of poly(α-methylstyryl)lithium with 1,3-propanesultone in THF at −78 °C. In order to examine this effect of chain end structure, poly(styryl)lithium ($M_n = 4.7 \times 10^3$ g/mol; $M_w/M_n = 1.03$) was reacted with α-methylstyrene at −78 °C in THF to form poly(styrene-*block*-α-methylstyryl)lithium [M_n (SEC, apparent) = 6.0×10^3 g/mol; $M_w/M_n = 1.16$]. When this block copolymeric organolithium compound was reacted with a molar excess of 1,3-propanesultone, the corresponding sulfonated diblock copolymer was obtained in 94% yield as shown in Table I. This is in excellent agreement with the reported results of Eisenbach et al.[25] However, when the sulfonation reaction of an analogous diblock copolymeric organolithium compound was effected in toluene under analogous conditions with almost a 3-fold excess of sultone, the corresponding sulfonated product was obtained in only 28% yield. It appears that the competition between ring opening and metalation is quite sensitive to solvent and chain-end structure. These results indicate that although the direct sulfonation of poly(α-methylstyryl)lithium with 1,3-propanesultone is an efficient reaction in THF at −78 °C,[25] this is not a generally useful procedure for poly(styryl)lithium since only 53–72% yields can be obtained.[26] This dramatic effect of chain-end structure suggested that other methods of attenuating the reactivity of the polymeric organolithium chain end might also be effective. A sulfonation procedure that could be effected at room temperature was also desirable.

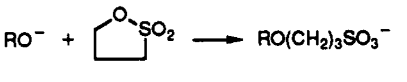
Scheme I



Ethylene Oxide End-Capping. 1,3-Propanesultone and 1,4-butanesultone are very reactive sulfoalkylating agents. It has been reported that a variety of nucleophiles react with these sultones to open the ring and produce the corresponding sulfoalkylation product.[41] For example, even tertiary amines react efficiently to produce the corresponding sulfonated zwitterionic product as shown in eq 3.[42,43] In addition, since it has been reported that alkoxides are sufficiently reactive to open the sultone ring[41,44,45] (eq 4), it was envisioned that an effective method for attenuating the reactivity of the anionic chain end would be to first carry out the hydroxylethylation reaction with ethylene oxide prior to reaction with the sultone as shown in Scheme I. This approach has been used effectively to generate macromonomers by reaction of poly(styryl)lithium with ethylene oxide prior to reaction with methacroyl chloride.[46,47] It is well established that the reaction of polymeric organolithium compounds with ethylene oxide is an efficient functionalization reaction, which produces the corresponding hydroxyethylation product in essentially quantitative yield without oligomerization of the excess ethylene oxide in benzene solution.[28]



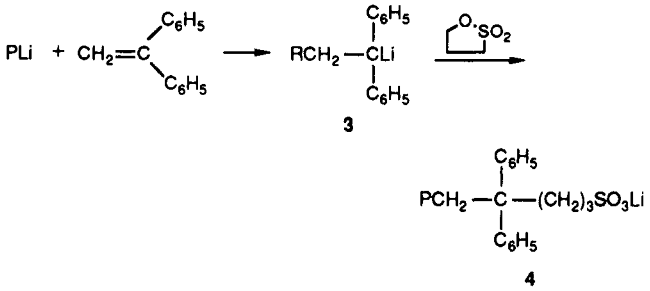
(3)



(4)

A series of hydroxyethylated polystyrenes were prepared by reaction of poly(styryl)lithium with excess ethylene oxide at room temperature in benzene followed by methanol quenching of aliquots for analyses. Thin-layer chromatographic analyses of the resulting hydroxyl-functionalized polymers ($R_f = 0.7$) indicated that no unfunctionalized polystyrene ($R_f = 1.0$) was formed (<1%), in accord with previous studies.[28] The corresponding lithium alkoxide derivatives (1, Scheme I) were reacted with either 1,3-propanesultone or 1,4-butanesultone under a variety of conditions and these results are shown in Table II. The reaction of the polymeric lithium alkoxide derivative with 1,3-propanesultone produced the corresponding sulfonated polymer in quantitative yield in benzene solution using a 4-fold excess of sultone at 40 °C after approximately 16 h as determined by colorimetric titration (Table II, run EO5). A 96% yield was obtained in a 1/10 (vol/vol) mixture of THF/benzene with 3-fold excess of sultone at 40 °C (Table II, run EO10). Lower yields were obtained by using a smaller excess of sultone, lower temperatures, or 1,4-butanesultone. These results are consistent with previous work that has shown that 1,4-butanesultone is less reactive toward nucleophiles compared to 1,3-propanesultone.[41] However, it was possible to obtain a 93% yield when an 8-fold excess of 1,4-butanesultone was used in benzene solution (Table II, run EO8). It should be noted that irreproducible amounts (5–10% as determined by SEC) of dimeric products were sometimes obtained from these functionalization reactions. This may be due to a spurious atmospheric contamination consistent with previous observations with polymeric alkoxides.[48,49]

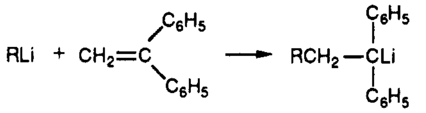
Scheme II



$$PLi + CH_2{=}C(C_6H_5)_2 \longrightarrow RCH_2{-}CLi(C_6H_5)_2\ (\mathbf{3}) \xrightarrow{\text{sultone}} PCH_2{-}C(C_6H_5)_2{-}(CH_2)_3SO_3Li\ (\mathbf{4})$$

Attempted silica gel column chromatographic purification of the sulfonated polymers synthesized as shown in Scheme I indicated that these polymers were not stable to the chromatographic conditions. TLC analyses of the products eluting from the silica gel column indicated the formation of the hydroxyethylated polymer ($R_f = 0.7$) and a spot corresponding to an unfunctionalized product ($R_f = 1.0$) in addition to the sulfonated product ($R_f = 0$). Analogous results, i.e., desulfonation, were observed when the sulfonation products were treated with an alcoholic hydrochloride acid solution (1 M) at room temperature for 24 h. Pure sulfonated polymer obtained via the lithium alkoxide route could be purified and separated from the excess sultone without desulfonation by using a modified silica gel that had been annealed at ca. 600 °C and stored in a desiccator;[31,32] the effluents were toluene followed by THF.

1,1-Diphenylethylene End-Capping. Because of the apparent hydrolytic instability of the sulfonation product from the lithium alkoxide reaction (Scheme I), an alternative method of attenuating the reactivity of the carbanionic chain end was sought. End-capping of simple alkyl or polymeric organolithium compounds with 1,1-diphenylethylene produces the corresponding 1,1-diphenylalkyllithium compound quantitatively without homopolymerization as shown in eq 5.[18,20,50-54]



$$RLi + CH_2{=}C(C_6H_5)_2 \longrightarrow RCH_2{-}CLi(C_6H_5)_2 \qquad (5)$$

The decreased basicity and increased steric requirements of this carbanion have been used effectively to generate an efficient initiator for the anionic polymerization of alkyl methacrylates.[55-57] Thus, end-capping of poly(styryl)lithium with 1,1-diphenylethylene prior to reaction with a sultone (see Scheme II) was investigated as a method for increasing the efficiency of the sulfonation reaction as well as generating a hydrolytically stable sulfonation product. The results of the sulfonation reaction of the polymeric diphenylalkyllithium compounds (3) with 1,3-propanesultone and 1,4-butanesultone are shown in Table III. By use of a 1/6 (vol/vol) ratio of THF/benzene and at least a 0.5-fold excess of 1,3-propanesultone at 25–30 °C, a 93% yield of the sulfonated polymer 4 could be obtained via the 1,1-diphenylethylene end-capping route for poly(styryl)lithium (Table III, run DPE4). Lower sulfonation yields (54–76%) were obtained in benzene solution (Table III, runs DPE1,2) and the yield decreased when a large excess of sultone (9-fold) was used (Table III, run DPE2). Sulfonation yields with 1,4-butanesultone were generally lower than the corresponding sulfonations with 1,3-propanesultone under analogous conditions (Table III, runs DPE4 versus DPE5; runs DPE6 versus DPE7); however, the effects of solvent and excess sultone were similar to the effects observed with 1,3-propanesultone.

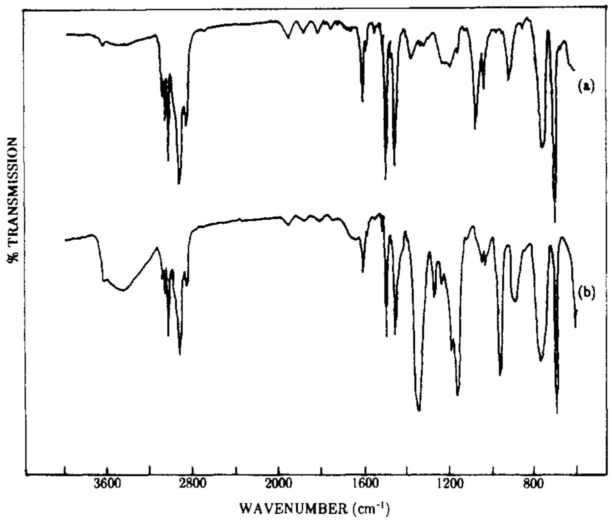


Figure 1. Comparison of FTIR spectra of (a) ω-lithium poly(styrene)sulfonate (sample DPE5 in Table III) and (b) poly(styrene-*block*-1,3-propanesulfone).

Characterization of End-Sulfonated Polymers. Qualitative information regarding the efficiency of sulfoalkylation reactions and the purity of sulfonated polymers can be readily obtained by TLC using silica gel coated plates with toluene as eluent. The lithium salts of the sulfonated polymers have R_f values of 0.0, while the unfunctionalized polymers exhibit R_f values of ca. 1.0.

It is reported that sulfonic acid salts show a strong infrared absorption band in the region 1150–1250 cm^{-1} and a medium-intensity absorption near 1050 cm^{-1}.[25,58,59] Thus, the end-sulfonated polystyrene salts prepared in this research exhibited a broad IR absorption band from 1150 to 1250 cm^{-1} and a medium-intensity absorption at 1052 cm^{-1}, as shown in Figure 1a. These bands were used to qualitatively indicate the presence of the sulfonated polymers. It is noteworthy that sulfonate esters show IR SO_2 stretching bands in the region 1335–1175 cm^{-1} and a strong S–O–C stretching absorption between 1000 and 770 cm^{-1}.[59] An authentic poly(styrene-*block*-1,3-propanesultone) diblock copolymer was prepared by heating a solution of the polymeric alkoxylithium, 1 ($M_n = 6.6 \times 10^3$ g/mol), with excess sultone ([sultone]/[Li] = 1240) in a THF/benzene solution (1/1 v/v) at 50 °C for 8 days. The resulting diblock copolymer ($M_n = 7.6 \times 10^3$ g/mol) exhibited IR bands at 1350, 1167, and 958 cm^{-1} as shown in Figure 1b. The clear separation and distinction between the sulfonate salt IR bands (Figure 1a) and those for poly(sultone) oligomeric units in the block copolymer (Figure 1b) provide qualitative evidence for the expected lack of oligomerization of the sultone under the functionalization reaction conditions.

The ^1H NMR spectra of the sulfonated polymers all exhibited a characteristic absorption at ca. $\delta = 2.3$ ppm, which has been assigned to the methylene protons on the carbon α to the lithium sulfonate group.[25] For the sulfonated products incorporating the ethylene oxide unit, a peak was observed at $\delta = 3.8$ ppm, which is tentatively assigned to the methylene units adjacent to the ether oxygen group [CH_2OCH_2]. The sulfonated products incorporating the diphenylethylene unit exhibited a peak at $\delta = 3.8$ ppm, which is tentatively assigned to the methylene units adjacent to the diphenylmethyl group [$CH_2C(C_6H_5)_2$] as shown in Figure 2. The ^1H NMR spectrum for the poly(styrene-*block*-1,3-propanesultone) is shown in Figure 3.

The ^{13}C NMR spectra of 1,3-propanesultone and the poly(styrene-*block*-1,3-propanesultone) have been used as

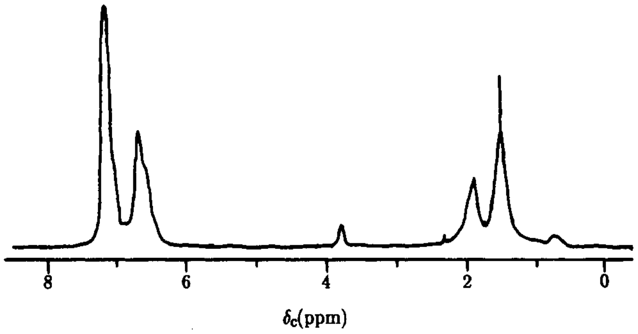


Figure 2. ^{1}H NMR spectrum of diphenylethylene-attenuated ω-lithium poly(styrene)sulfonate (sample DPE4 in Table III) in $CDCl_3$.

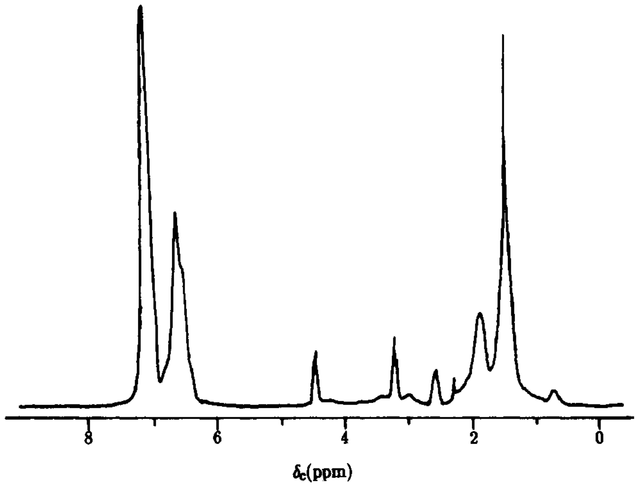


Figure 3. ^{1}H NMR spectrum of poly(styrene-*block*-1,3-propanesultone) in $CDCl_3$.

calibrations for the interpretation of the spectra for the functionalized polymers. The ^{13}C NMR resonances for 1,3-propanesultone occur at δ 68.9, 43.5, and 23.0 ppm for the OCH_2, CH_2SO_2, and CCH_2C methylene carbons, respectively. The chemical shifts for the analogous sultone-derived repeat units in poly(styrene-*block*-1,3-propanesultone) were observed at δ = 68.5, 43.8, and 23.36 ppm as shown in Figure 4. The close correspondence between the resonances for these two compounds was used to tentatively assign resonances for the functionalized polymers. The ^{13}C NMR spectrum for the purified ω-lithium poly(styrene)sulfonate (30% yield) obtained by the direct reaction of 1,3-propanesultone ([sultone]/[Li] = 3) with poly(styryl)lithium ($M_n = 4.2 \times 10^3$ g/mol) in benzene at 40 °C showed a distinct resonance at δ = 68 ppm as shown in Figure 5; this peak is assigned to the methylene carbon α to the lithium sulfonate group (CH_2SO_3Li) based on the above analogies. The ^{13}C NMR spectrum for the ethylene oxide attenuated ω-lithium poly(styrene)sulfonate exhibited resonances at δ = 69.5, 67.5, and 22.0 ppm. The assignments for the CH_2SO_3Li and CH_2O are tentatively assigned to the 69.5 or the 67.5 ppm peaks, respectively. The ^{13}C NMR spectrum for the 1,1-diphenylethylene attenuated ω-lithium poly(styrene)sulfonate (see Figure 6) exhibited pertinent resonances at δ = 68.0, 50.0, 28.0, and 24.5 ppm, which have been assigned to the CH_2SO_3Li, $C(Ph)_2$, $CH_2C(Ph)_2$, and CCH_2C units. Thus, a ^{13}C NMR resonance at δ = 68–70 ppm appears to be characteristic for a methylene carbon adjacent (α) to the lithium sulfonate chain-end functionality. Although no conclusions regarding the efficiency of functionalization reactions or the purity of functionalized polymers have been drawn from these ^{13}C NMR data, it is significant to note that the absorption at δ = 33.6 ppm corresponding to the terminal carbon ($CH_2C_6H_5$) in unfunctionalized polystyrene[28] is not observed in the ^{13}C NMR spectra of any of the purified, lithium sulfonate functionalized polymers.

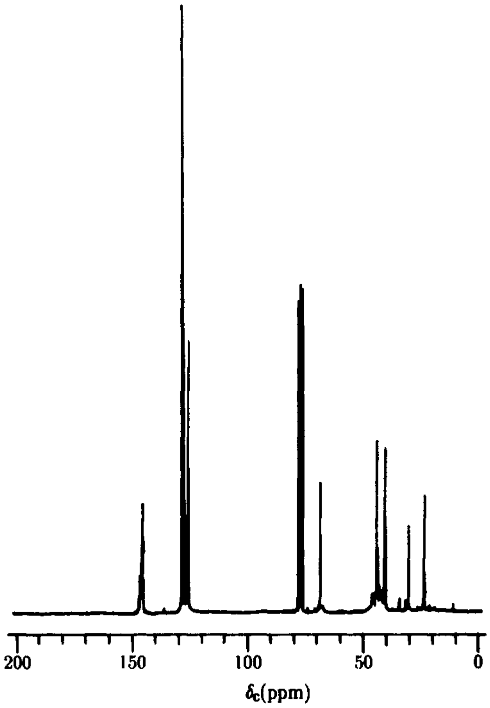


Figure 4. ^{13}C NMR spectrum of poly(styrene-*block*-1,3-propanesultone) in $CDCl_3$.

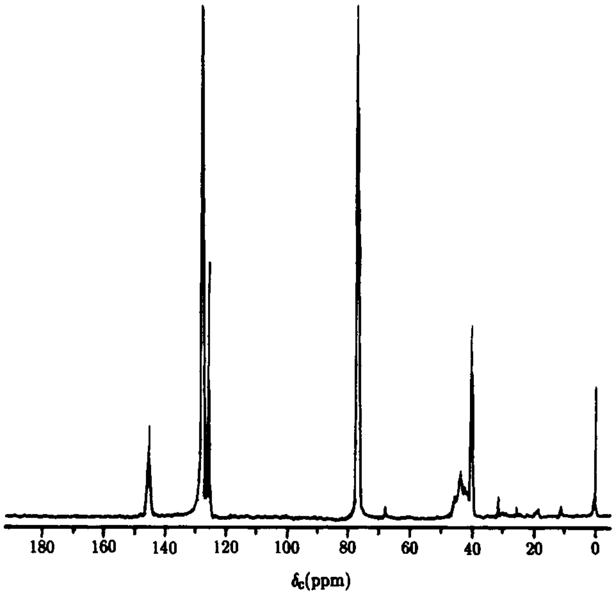


Figure 5. ^{13}C NMR spectrum of ω-lithium poly(styrene)sulfonate (sample D2 in Table I) in $CDCl_3$.

Size-exclusion chromatography (SEC) methodology has been utilized to characterize the molecular weight and molecular weight distributions for the ω-lithium poly(styrene)sulfonates and related polymers. However, the standard solvent, THF, which is generally used for SEC analysis of functionalized polymers, could not be employed. The SEC curves in THF for a crude sulfonation reaction mixture compared to curves of the corresponding base polystyrene homopolymer at the same concentration are shown in parts b and a of Figure 7, respectively. A broad, low molecular weight tail is apparent in the SEC of the reaction mixture. In addition, the signal intensity (RI) is

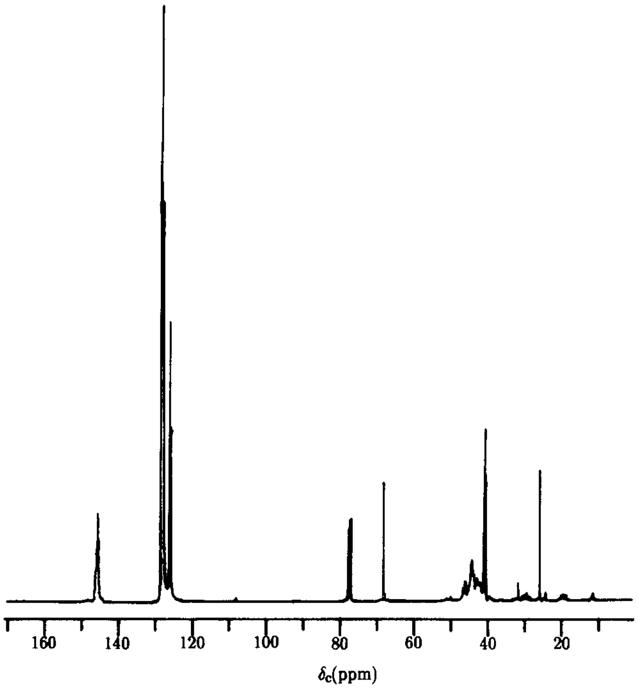


Figure 6. ^{13}C NMR spectrum of diphenylethylene-attenuated ω-lithium poly(styrene)sulfonate (sample DPE4 in Table III) in $CDCl_3$.

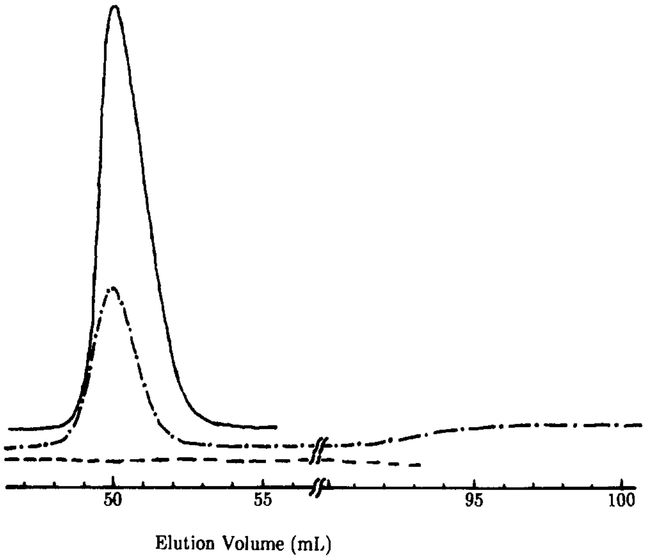


Figure 7. SEC curves in THF for (a) polystyrene homopolymer (—), (b) a crude sulfonation reaction mixture containing ω-lithium poly(styrene)sulfonate (- · -) (sample D3 in Table I), and (c) purified ω-lithium poly(styrene)sulfonate (- - -) (sample EO10 in Table II).

much lower for the functionalized product compared to that of the same sample weight for the polystyrene homopolymer. When a purified sample of ω-lithium poly(styrene)sulfonate was similarly analyzed by SEC using THF as solvent, no peak was observed as shown in Figure 7c. It was concluded that only the polystyrene homopolymer was being separated and detected in the SEC of the crude reaction mixture (Figure 7b) and that the ω-functionalized sulfonate polymer was strongly adsorbed on the column and eluted slowly without being resolved. This behavior was utilized to measure the functionalization yield by generating a calibration curve for signal intensity versus the weight of unfunctionalized polystyrene homopolymer. This, in turn, was used to estimate the yield of functionalized polymer by carefully weighing samples of crude reaction mixtures and these results are compared with other methods for determining the functionalization yield in Table IV.

Table IV
Comparison of Sulfonation Yields Determined by the Two-Phase Titration, Colorimetric Method and SEC Analysis

	functionalization yield, %		
run	two-phase titration,[a] mol %	colorimetric method,[b] mol %	SEC anal,[c] wt %
EO9	90	90	
EO10		78	96
EO5	94	100	91
EO6	96	98	92
EO8	95	101	93
DPE4	94		95

[a] Titration with the cationic titrant Hyamine 1622. [b] Colorimetric method using complexation with methylene blue using the calibration curve. [c] SEC analysis in THF for unfunctionalized polymer using the calibration curve.

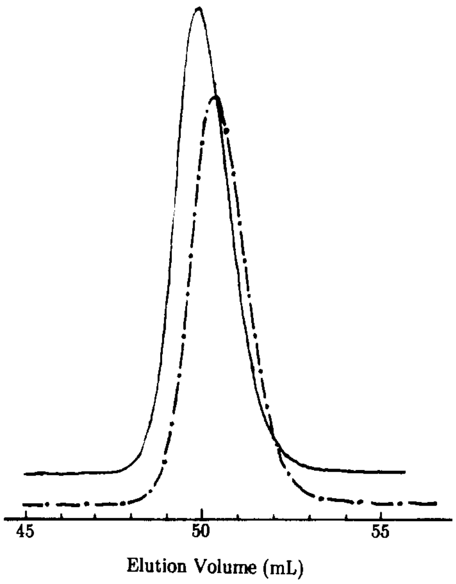


Figure 8. SEC curve for (a) polystyrene homopolymer (—) and (b) corresponding pure ω-lithium poly(styrene)sulfonate (- · -) in the ternary mixture of THF/DMF (10/1 vol/vol) containing 2 g/L $LiNO_3$ (sample D3 in Table I).

In order to obtain meaningful SEC curves for the ω-lithium poly(styrene)sulfonate polymers, it was necessary to utilize a ternary mixture of THF, DMF, and $LiNO_3$ as elution solvent, which was developed in previous work with randomly sulfonated polystyrene ionomers.[33] From a mixture of THF/DMF (10/1 vol/vol) containing 2 g/L $LiNO_3$, the SEC curves shown in Figure 8 were obtained for the same polymers that exhibited the unusual behavior shown in Figure 7. In general, the purified ω-lithium poly(styrene)sulfonate polymers displayed elution volumes in this ternary mixture that were larger than the corresponding polystyrene homopolymers; however, this difference decreased with increasing molecular weight. It is noteworthy that the observed elution volume for the ω-lithium poly(styrene)sulfonate polymers was sensitive to the salt concentration in the elution solvent. In order to characterize these polymers, a separate calibration curve was generated in the THF/DMF/$LiNO_3$ solvent mixture from standard polystyrene samples; however, in view of the sensitivity of the elution volume for the functionalized polymers to salt concentration, these values should be considered as only relative measures of molecular weight.

The quantitative analysis of the functionalization reactions was determined by using (a) quantitative size-exclusion chromatographic determination of the amount of unfunctionalized polymer, (b) a colorimetric method using complexation with methylene blue,[34-37] and (c) a two-phase titration using the cationic titrant Hyamine 1622.[34,36] These methods were used for determination of all functionalization reaction yields because the standard basic titration of the functionalized polymers could not be applied to the ethylene oxide attenuated polymers because of their observed hydrolytic instability. The results of application of these quantitative methods of analysis for a variety of functionalization reactions are shown in Table IV. It is important to note that the presence of unreacted sultone interferes with both the methylene blue colorimetric method and the two-phase titration with Hyamine 1622. Therefore, it was necessary to first remove the unreacted sultone either by solid–liquid extraction with petroleum ether as solvent or by column chromatography on annealed silica gel using a toluene/THF mixture. The general correspondence between the results obtained by SEC chromatographic analyses and those from the colorimetric method and the two-phase titration procedure suggests that no significant losses occur during these pretitration purification procedures.

Conclusions

The direct sulfoalkylation reaction of poly(styryl)lithium with excess 1,3-propanesultone provided only modest yields (<53%) of the ω-lithium poly(styrene)sulfonate under the optimum experimental conditions of −78 °C in THF. Under the same experimental conditions, poly(styrene-*block*-α-methylstyryl)lithium provides the ω-sulfonated polymer in 94% yield. End-capping of poly(styryl)lithium with ethylene oxide to generate the polymeric lithium alkoxide followed by reaction with either 1,3-propanesultone or 1,4-butanesultone provides an efficient method (>90% yields) under a variety of experimental conditions. However, this method is not recommended because hydrolytic instability of the functionalized polymer was observed upon attempted silica gel column chromatography of these polymers or upon treatment with methanolic hydrochloric acid. This functionalized polymer could be purified and isolated by using an annealed silica gel that had been pretreated by heating at 600 °C for at least 3 h and cooling in a vacuum desiccator. Hydrolytically stable ω-sulfonated polystyrenes could be obtained in high yield (93%) by reaction of poly(styryl)lithium with 1,1-diphenylethylene prior to reaction with 1,3-propanesultone at room temperature in a mixture of THF/C_6H_6 (1/6 vol/vol) and this is the procedure that is recommended. The ω-lithium poly(styrene)sulfonates can be qualitatively identified by SiO_2 thin layer chromatography (R_f = 0.0), FTIR absorption bands at 1150–1250 (br) and 1052 cm^{-1}, an ^{1}H NMR resonance at δ = 2.3 ppm for the methylene protons on the carbon α to the lithium sulfonate group, and a ^{13}C NMR resonance in the region δ = 68–70 ppm that is characteristic for the methylene carbon α to the lithium sulfonate chain-end functionality. Quantitative determination of the efficiency of sulfoalkylation reactions and the purity of ω-lithium poly(styrene)sulfonate polymers can be readily determined by an SEC method developed in this work whereby in THF only the nonfunctionalized polystyrene is observed. It is necessary to generate a calibration curve with known mixtures of functionalized and unfunctionalized polymers to take advantage of this simple method. Other quantitative methods that have been utilized and give comparable results include the colorimetric method with methylene blue and the two-phase titration method with Hyamine 1622. The SEC characteristics of the ω-lithium poly(styrene)sulfonate polymers in a ternary mixture of THF/DMF (10/1 vol/vol) containing 2 g/L $LiNO_3$ are analogous to previous work with ionomers.[33] These results and our unpublished work on the concentration dependences of their solution viscosities suggest that these ω-lithium poly(styrene)sulfonates may serve as useful models for ionomers and their unique solution behavior. Studies of the solution properties of these model ionomers are in progress and will be reported in a subsequent publication.

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Registry No. 1,3-Propane sultone, 1120-71-4; 1,4-butane sultone, 1633-83-6; ethylene oxide, 75-21-8; 1,1-diphenylethylene, 530-48-3; (styrene)(1,3-propane sultone) (block copolymer), 134311-44-7.