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Anionic Synthesis of Epoxide-Functionalized Macromonomers by Reaction of Epichlorohydrin with Polymeric Organolithium Compounds

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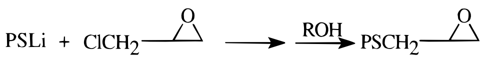
ABSTRACT: The efficient synthesis of ω-epoxide-functionalized macromonomers has been achieved by optimizing the reaction of polymeric organolithium compounds (PLi) with epichlorohydrin (EPC). The addition of epichlorohydrin to a benzene solution of poly(styryl)lithium ($M_n = 2 \times 10^3$g/mol) forms the ω-epoxide-functionalized polystyrene in only 9% yield; the major products correspond to dimeric species (70%). Inverse addition of epichlorohydrin reduces the yield of dimer to 22% (16% ring-opened dimer and 6% nonfunctional) and increases the epoxidation yield to 28%; the other products correspond to unfunctionalized polymer (18%) and the ring-opened product (32%). Addition of tetrahydrofuran (THF) to the solutions of PLi and EPC decreases the dimer yield to 10% and increases the epoxide functionalization to 74% for poly(styryl)lithium and to 80% for poly(styrene-*b*-butadienyl)lithium. By reaction of the polymeric chain ends with 1,1-diphenylethylene (DPE) to form the corresponding polymeric (1,1-diphenylalkyl)lithium, functionalization yields increase to 83% with 4% dimer in benzene. After DPE end-capping and in the presence of THF, the epoxide functionalization yields increase to 91−97% with < 1% dimer. The ω-epoxide-functionalized polymers have been purified by column chromatography, and the epoxide functional groups have been characterized by ^{1}H and ^{13}C NMR and FTIR spectroscopy. Quantitative determination of the amount of epoxide functional groups in polymers was effected by perchloric acid/tetraethylammonium bromide titration.

Introduction

Macromonomers are linear macromolecules carrying some polymerizable functional group at their chain ends; the polymerizable functional group can be at one chain end or at both chain ends.[1−5] Macromonomers are macromolecular monomers, often referred to as "Macromers".[1] The important feature of macromonomers is that they can undergo copolymerization with other monomers by a variety of mechanisms to form comb-type, graft copolymers. If the macromonomer has a well-defined structure, then the branches in the comb-type, graft copolymers will have well-defined structures also. The polymerizable functional group at the chain end of a macromonomer is often a vinyl group, but it can also be a heterocyclic ring such as an oxirane (epoxide) functionality. In contrast to the plethora of methods available for synthesis of well-defined macromonomers with vinyl-type functionality,[1−6] reliable methods for the efficient, direct synthesis of epoxide-functionalized macromonomers have not been available.

Living polymerizations provide reliable methods for the synthesis of macromonomers with predictable, well-defined structures.[5,7] Living anionic polymerization is one of the most reliable and useful methods for the routine synthesis of macromonomers.[8] Milkovich and Chiang[9,10] described the synthesis of epoxide-terminated macromonomers in their series of seminal patents defining the scope and limitations of the alkyllithium-initiated synthesis of well-defined macromonomers and their applications. Poly(styryl)lithium (PSLi) in benzene was terminated with a 1.5 molar excess of epichlorohydrin (EPC), presumably by normal addition to PSLi, to form an epoxide-functionalized polystyrene macromonomer (eq 1). The molecular weight distribution was described as "very narrow". However, as later work and the results reported herein show, this is a very



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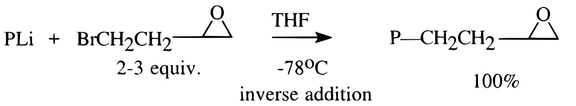
inefficient epoxide functionalization procedure. They also hydrolyzed this product to form the corresponding ω-diol-functionalized polystyrene macromonomer. Neither of these macromonomers was characterized with respect to functionality in these patents.

Xie and Sun[11,12] reexamined the epichlorohydrin functionalization of poly(styryl)lithium in detail. In the presence of a small amount of tetrahydrofuran (THF) ([THF]/[BuLi] $\approx$ 2) and using an inverse addition of PSLi to an excess of epichlorohydrin ([EPC]/[BuLi] $\approx$ 2), the maximum yield of epoxide-functionalized polystyrene macromonomer was only 35% under optimized conditions of mode of addition, temperature, solvent, and stoichiometry. The epoxide content was assayed using an argentimetric method.[13] In addition to the low yield of epoxide functionalization, a significant amount of dimer formation (10−15%) was reported. It was also reported that end-capping of poly(styryl)lithium with either 1,1-diphenylethylene or ethylene oxide gave no better yields of epoxide functionalization.

Mouzali, Lacoste, and Abadie[14] investigated the reaction of α,ω-dilithiopoly(styrene-*b*-isoprene-*b*-styrene) with epichlorohydrin in THF at −30 °C and reported a 40% yield of epoxide-functionalized polymer by ^{1}H NMR analysis. No detailed experimental procedures were provided, however. The reaction of poly(styryl)lithium with ethylene oxide prior to addition of epichlorohydrin (end-capping) produced a product mixture which included significant amounts of chlorine by elemental analysis and a yield of 50% of the epoxide-functionalized polymer. In contrast to the results reported by Xie and Sun,[11,12] a quantitative functionalization was reported for the reaction of epichlorohydrin with the small-molecule analog, (1,1-diphenylhexyl)lithium in THF; however, the functionalization reactions with 1,1-diphenylethylene end-capping by Xie and Sun[11,12] were apparently carried out in hydrocarbon solvent.

Youqing and Eping[15] reported that epoxide functionalization yields as high as 82% can be obtained by end-capping poly(styryl)lithium with propylene sulfide prior to addition of epichlorohydrin. Unfortunately, no detailed experimental procedures were provided. However, in support of the effectiveness of this end-capping procedure, Mancinelli[16] has reported that reaction of poly(styryl)lithium with ethylene sulfide prior to reaction with epichlorohydrin also provides the epoxide-functionalized macromonomer in 87% yield.

Takenaka, Hirao, and Nakahama[17] have developed an efficient synthesis of epoxide-functionalized polystyrenes and polyisoprenes by terminating the corresponding living polymers with (2-bromoethyl)oxirane at −78 °C in THF as shown in eq 2. Termination of either poly(styryl)lithium or poly(isoprenyl)lithium by inverse addition to 2−3 equiv of (2-bromoethyl)oxirane reportedly produced the corresponding epoxy-functionalized polymers in quantitative yields as determined by ^{1}H NMR and TLC-FID chromatography. The requirements of −78 °C and THF as solvent limit the usefulness of this procedure, however.



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Herein are reported our detailed investigations of the scope and limitations of the functionalization reactions of poly(styryl)lithium and poly(butadienyl)lithium with epichlorohydrin to prepare epoxide-functionalized macromonomers. The effects of mode of addition, solvent, Lewis base, end-capping with 1,1-diphenylethylene, end-capping with ethylene oxide, and stoichiometry have been examined.

Experimental Section

Chemicals and Solvents. Benzene, tetrahydrofuran (THF), and styrene (all Fisher, Certified A.C.S.) were carefully purified as described previously.[18] 1,1-Diphenylethylene (Aldrich, 97%) was stirred over calcium hydride with periodic degassing, followed by reduced-pressure distillation into a calibrated ampule, dilution with benzene, and flame-sealing. 1,3-Butadiene (Matheson, C.P., 99%) was condensed in the vacuum line at −78 °C into a flask containing freshly ground CaH_2. The butadiene was then stirred over CaH_2 at −78 °C with repeated degassing for 24 h, followed by distillation under reduced pressure into a flask containing neat *n*-butyllithium (FMC, Lithium Division). The monomer was stirred over *n*-butyllithium at −78 °C for 5 h and then was distilled into an ampule followed by flame-sealing. This monomer ampule was used immediately. Epichlorohydrin (Aldrich, 99 +%) was stirred over calcium hydride for at least 2 days with degassing, followed by reduced-pressure distillation into calibrated ampules just before use. Ethylene oxide (Kodak Laboratory & Research Products, 99.7%) was purified as described previously.[19] *sec*-Butyllithium (FMC, Lithium Division, 12 wt % in cyclohexane) was analyzed by the double titration method with 1,2-dibromoethane.[20]

Polymerization. Anionic polymerization of styrene with *sec*-butyllithium as initiator was carried out in benzene at 25 °C for 24 h in all-glass, sealed reactors, using breakseals and standard high-vacuum techniques.[21] The volume ratio of monomer to solvent was usually 0.1−0.15. The resulting solution of poly(styryl)lithium (PSLi) was used for further reactions after a small aliquot was removed and terminated with degassed methanol to form a base polymer sample for analysis.

Synthesis of poly(styrene-*b*-butadienyl)lithium (PS-*b*-PBDLi) was effected by addition of butadiene (BD) monomer (calculated M_n of butadiene block = 216 g/mol; [BD]/[PSLi] = 4) to poly(styryl)lithium (M_n = 1500 g/mol, M_w/M_n = 1.06) in benzene at 25 °C and polymerization for 24 h. The crossover reaction from PSLi (λ_{max} = 334 nm)[22] to PBDLi (λ_{max} = 290 nm)[23] was monitored by UV−visible spectroscopy. 1,1-Diphenylethylene (DPE) end-capping of poly(styryl)lithium was carried out by addition of a benzene solution of 1,1-diphenylethylene ([DPE]/[PLi] = 1.2/1) to a benzene solution of PSLi. The crossover reaction to the corresponding polymeric (1,1-diphenylalkyl)lithium (λ_{max} = 446 nm)[24] was monitored by UV−visible spectroscopy. 1,1-Diphenylethylene end-capping of poly(styrene-*b*-butadienyl)lithium was carried out by addition of a benzene solution of 1,1-diphenylethylene ([DPE]/[PLi] = 1.2/1) into a benzene solution of PS-*b*-PBDLi, followed by addition of a small amount of THF ([THF]/[PLi] = 30/1) at room temperature. The crossover reaction to form the polymeric (1,1-diphenylalkyl)lithium (λ_{max} = 452 nm)[24] was monitored by UV−visible spectroscopy.

Epoxide Functionalization. The reactions of epichlorohydrin (EPC) with polymeric organolithium compounds were carried out under vacuum using a variety of procedures (see Table 1). For direct addition, a solution of epichlorohydrin ([EPC]/[PLi] = 30/1) in benzene in an ampule was added to the polymer solution by fracturing the breakseal. For inverse additions, ampules containing a benzene solution or a benzene/THF (90/10, vol/vol) solution of the polymeric organolithium were added, by shattering the respective breakseals, to either benzene, benzene/THF (1/1, vol/vol), or THF solutions of epichlorohydrin ([EPC]/[PLi] = 30/1) which were stirred vigorously. The optimum addition time was 5 min. THF was only added to the solutions of polymeric organolithium just before the functionalization reaction. In general, the reactions were stirred for 2 h at 0 °C and for 5 h at 25 °C and then quenched by addition of degassed methanol.

End-capping of poly(styryl)lithium with ethylene oxide (EO) prior to epichlorohydrin functionalization was effected by addition of a benzene solution of ethylene oxide ([EO]/[PSLi]

= 1/1) and stirring for 24 h.[19] A benzene/THF (9/1, vol/vol) solution of the resulting polymeric lithium alkoxide (POLi) was added to a benzene/THF (1/1, vol/vol) solution of EPC ([EPC]/POLi] = 30). The resulting mixture was stirred at 0 °C for 5 h and at room temperature for 12 h prior to quenching with degassed methanol.

The general workup procedure for the functionalized polymers was to concentrate the reaction solution by removing half of the solvent using a rotary evaporator and then to precipitate the concentrated solution into methanol. The polymeric solids were isolated by filtration or decantation and were dried under vacuum.

Characterization. Size exclusion chromatographic analyses (SEC) of polymers were performed at a flow rate of 0.4 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). ^{1}H NMR and ^{13}C NMR spectra of the polymers were obtained in $CDCl_3$ on a Varian Gemini-200 spectrometer. UV–visible spectroscopic analysis was performed on a Hewlett-Packard Model HP8452A diode array spectrometer. Infrared spectra of polymer films on NaCl plates were obtained on an ATI Mattson Genesis Series FTIR spectrometer. Vapor pressure osmometry measurements were made at 45 °C using a Knauer Type 11.00 vapor pressure osmometer with toluene (Fisher, dried over 4 Å molecular sieves) as the solvent and sucrose octaacetate (Aldrich) as the calibration standard.

Qualitative characterization of functionalized polymers (0.5 wt % in toluene) was obtained by thin-layer chromatography (TLC, Eastman Kodak, chromatogram sheet, 13181 silica gel with fluorescent indicator) using toluene as eluent. Quantitative determination of epoxide groups in the polymers was carried out by chemical titration using the following procedure described in ASTM D 1652-90:[25] the epoxide-containing polymer (2 g) was dissolved in 30 mL of methylene chloride and treated with a 20 wt % solution of tetraethylammonium bromide in glacial acetic acid, prepared previously. After addition of 6–8 drops of crystal violet indicator solution in acetic acid, the mixture was titrated with 0.1 N perchloric acid solution in acetic acid. Hydrobromic acid formed *in situ* by the exchange reaction between perchloric acid and tetraethylammonium bromide reacted instantaneously with the epoxide group, leading to bromohydrin formation. The end point of the titration was determined by the change of the color of the solution from a sharp blue to green.

Results and Discussion

Functionalization in Benzene Solution. The reaction of poly(styryl)lithium ($M_n = 2 \times 10^3$ g/mol) with excess epichlorohydrin ([EPC]/[PLi] = 30) in hydrocarbon solution was reexamined using both direct and inverse addition procedures in view of the conflicting results reported in the literature for this reaction (eq 1).[9–12,14] The addition of a benzene solution of EPC to poly(styryl)lithium (normal addition procedure) produced a mixture of products as shown by SEC analysis. The major product (70 wt % by SEC) consisted of a dimeric species. Epoxide end group determination by perchloric acid/tetrabutylammonium bromide titration according to ASTM D 1652-90[25] indicated that the product mixture contained only 9 wt % of epoxide-functionalized polymer. When a benzene solution of poly(styryl)lithium was added to a benzene solution of epichlorohydrin (inverse addition procedure), the yield of epoxide-functionalized polystyrene increased to 28 wt % and the yield of dimer was reduced to 22 wt % (see Figure 1). Although these results stand in sharp contrast to the implication from the patents of Milkovich and Chiang[9,10] that quantitative functionalization is obtained from a direct addition process, these results are in good agreement with the work of Xie and Sun,[11,12] who reported that the yield of epoxide-functionalized polymer was 22 wt % in benzene via an inverse addition procedure.

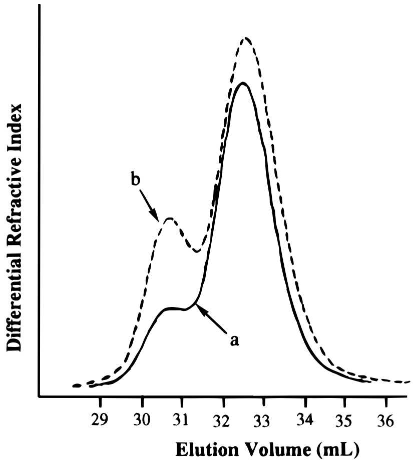
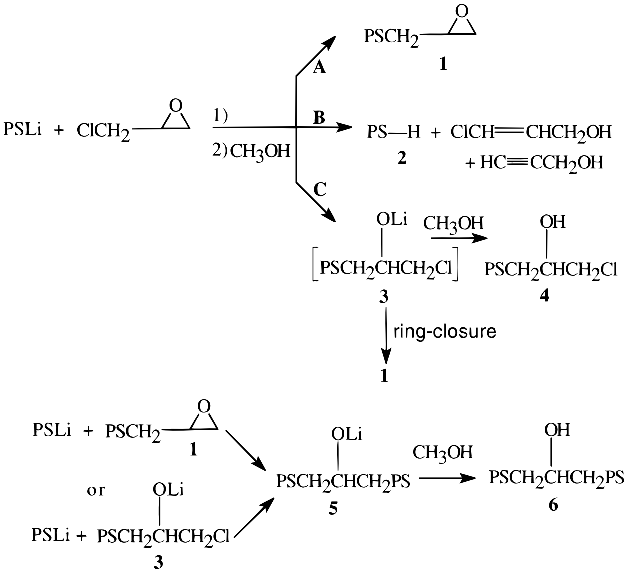


Figure 1. SEC (RI) chromatograms of (a) the crude reaction product obtained from the inverse addition of poly(styryl)lithium (M_n = 2100 g/mol; M_w/M_n = 1.05) in benzene to an excess of epichlorohydrin in benzene and (b) the unfunctionalized polymer products separated by silica gel column chromatography.

Scheme 1



A number of competing reactions can be occurring in these epichlorohydrin functionalization reactions as outlined in Scheme 1. The Wurtz-like coupling reaction (A) to form the desired epoxide-functionalized polymer (**1**) is only one of at least three competing reactions. A metalation reaction (B) at the relatively acidic hydrogen geminal to chloride and β to the epoxide ring would lead to unfunctionalized polymer (**2**); this is apparently the primary reaction mode for *n*-butyllithium.[26a,27] The epoxide ring provides another favorable site for reaction of organolithium compounds,[19] and this pathway (C) would lead to formation of the ring-opened product, **4**; this could also be the pathway for formation of **1** by ring closure of intermediate **3**. Thus, it is not surprising that such low yields of epoxide-functionalized polymers are obtained.

Dimer formation (**6**) can result from secondary reactions of either of the first-formed functionalized polymeric products (**1** or **3**) with poly(styryl)lithium as shown in Scheme 1. These dimer-forming reactions

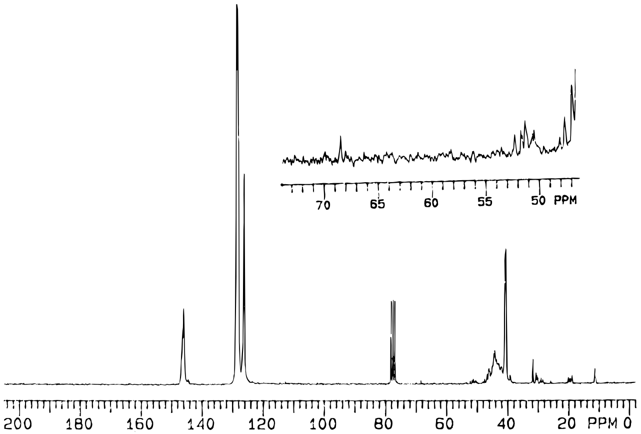
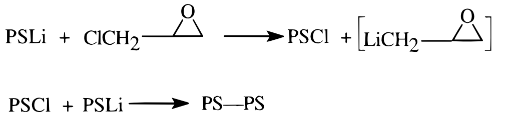


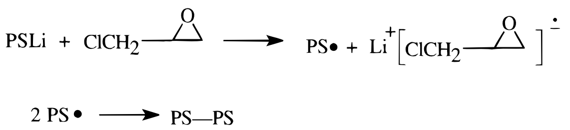
Figure 2. ^{13}C NMR spectrum ($CDCl_3$) of the polymer products obtained from the inverse addition of poly(styryl)lithium with excess epichlorohydrin in benzene.

Scheme 2

D. Wurtz-coupling pathway for dimer formation.



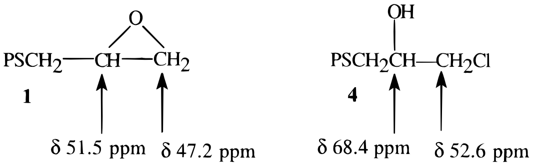
E. Single electron transfer pathway for dimer formation.



would be minimized by the inverse addition procedure with excess epichlorohydrin which reduces the probability of these secondary reactions of added PSLi compared with reaction with epichlorohydrin. Thus, dimer formation is reduced from 70 wt % for the direct addition mode to only 22 wt % for the inverse addition mode. However, the yield of epoxide-functionalized polymer is still low (28 wt %), although it is higher than the yield for the direct reaction addition mode (9 wt %).

Insight into the chemistry involved in these functionalization reactions was provided by silica gel column chromatography and ^{13}C NMR spectroscopic analysis of the products from the functionalization using the inverse addition mode. Separation of the nonpolar, unfunctionalized polymer products (24 wt % isolated) from the polar, functionalized polymer products was achieved by silica gel column chromatography using toluene as eluent. From the SEC trace of this fraction (see Figure 1 (b)), significant amounts of both unfunctionalized dimer product (6 wt %) and polymer with the same elution volume as the base polystyrene (**2**, 18 wt %) were obtained. This large amount of isolated, unfunctionalized polymer product, **2**, suggests that in benzene a major reaction pathway for reaction of poly(styryl)lithium with epichlorohydrin is hydrogen abstraction (reaction mode B in Scheme 1). The formation of unfunctionalized dimer is consistent with lithium–halogen exchange, followed by Wurtz-type coupling (alkylation)[26b] (see mode D in Scheme 2). Another possibility is that the reaction of poly(styryl)lithium with epichlorohydrin proceeds by a single electron transfer process[28] to form polystyryl radicals which subsequently dimerize (reaction mode E in Scheme 2). Precedent for this mode of dimer formation has been obtained for the reaction of poly(styryl)lithium with styrene oxide, which produces an analogous unfunctionalized dimer with the expected head-to-head type unit as determined by ^{13}C NMR analysis[29] ($\delta = 49.5$ ppm).[30,31] Based on the yield of unfunctionalized dimer isolated by column chromatography (6 wt %) and the total amount of dimer product in the crude reaction mixture (22 wt %), the amount of ring-opened, functionalized dimer product (**6**) is estimated to be 16 wt %.

The polymer product mixture was characterized by ^{13}C NMR (see Figure 2). It was instructive to calculate the expected chemical shifts for the functionalized polymer products (**1** and **4**) using the general additivity equations developed by Grant and Paul[32] for **4** and the additivity equations for epoxide compounds of Paulson et al.[33] for **1**. The calculated chemical shifts for the carbons of interest are shown with the structures below.



It is noteworthy that Nakahama and co-workers[17] have reported that an epoxidized polyisoprene exhibited resonances at $\delta = 46.9$ (CH_2) and at 52.1 ppm (CH) which are in good agreement with the calculated values for **1** above. From the ^{13}C NMR spectrum in Figure 2, the resonance observed at $\delta = 68.38$ ppm can be assigned to the methine carbon bonded to the hydroxyl group in **4**. The resonance at $\delta = 47.5$ ppm is assigned to the methylene carbon of the epoxide ring in **1**. The multiplet of peaks observed in the range of $\delta = 50-52$ ppm (specifically $\delta = 50.4$, 51.2, 51.64, and 52.2 ppm) presumably includes both the methine carbon in the epoxide ring of **1** (diastereomeric; may exist as a multiplet) and the methylene group bonded to chlorine in **4**. The peak observed at $\delta = 50.4$ ppm is consistent with the resonance expected for the methine carbons for the head-to-head dimer product discussed previously; the methine carbons of these head-to-head units have been observed in the $\delta = 48.5-51$ ppm region.[29-31] This structural information together with the yields of unfunctionalized polymer (**2**, 18 wt %), epoxide-functionalized polymer (**1**, 28 wt %), and polymer with the same retention volume as the base polystyrene (nondimer product, 78 wt %) can be used to calculate the yield of ring-opened product (**4**, 32 wt %) by difference.

These results show that the reaction of poly(styryl)lithium with epichlorohydrin is not efficient with respect to formation of the desired epoxide-functionalized polystyrene in hydrocarbon solution. The reaction is complicated by hydrogen abstraction from epichlorohydrin, Wurtz-coupling, and ring-opening reactions with the epoxide group even when using an inverse addition mode in the presence of a 30-fold excess of epichlorohydrin.

Functionalization in the Presence of Tetrahydrofuran (THF). Polymeric organolithium compounds are associated into dimers, tetramers, and even higher aggregates in hydrocarbon solution.[8,34] It has been observed for many functionalization reactions that the presence of Lewis bases such as THF, which promote dissociation of the polymeric organolithium aggregates, can exert a dramatic effect on the course of the reaction and often minimize side reactions.[35] However, it should be noted that polymeric organolithium compounds can react with THF and terminate by proton abstraction,[8]

Table 1. Effect of THF on the Functionalization of Poly(styryl)lithium (PSLi)[a] and Poly(styrene-*b*-butadienyl)lithium (PS-*b*-PBDLi)[b] with Epichlorohydrin (EPC)[c]

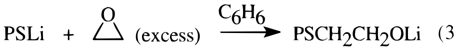
run	PLi	PLi solvent	EPC solvent	PS-epoxide[d] (wt %)	dimer (wt %)[e]
1	PSLi	C_6H_6	C_6H_6	28	22
2	PSLi	C_6H_6	THF/C_6H_6 (1/1, vol/vol)	66	19
3	PSLi	THF/C_6H_6 (1/9, vol/vol)	THF/C_6H_6 (1/1, vol/vol)	69	14
4	PSLi	THF/C_6H_6 (1/9, vol/vol)	THF	74	10
5	PS-*b*-PBDLi	C_6H_6	C_6H_6	29	44
6	PS-*b*-PBDLi	THF/C_6H_6 (1/9, vol/vol)	THF/C_6H_6 (1/1, vol/vol)	80	3

[a] $M_n = 2.0 \times 10^3$ g/mol, $M_w/M_n = 1.06$, [PSLi] = 0.049 M. [b] M_n(PS) = 1500 g/mol, M_n(PBD) = 260 g/mol M_n(VPO) = 1800 g/mol. [c] Termination by inverse addition mode with 30-fold excess of EPC for 2 h at 0 °C and for 5 h at 25 °C; [PLi] ≈ 0.05 M. [d] Determined by titration using ASTM D 1652-90. [e] Determined by SEC.

analogous to the chemistry of simple organolithium compounds.[26c] Furthermore, the presence of THF during polymerization would result in the loss of high 1,4-polydiene stereospecificity, which is a unique and desirable feature of alkyllithium-initiated polymerizations in hydrocarbon solution.[8] Therefore, in order to study the effect of added THF and preserve the desirable and unique features of alkyllithium-initiated polymerizations, all polymerizations were carried out in hydrocarbon solution, and THF was either added in the epichlorohydrin solution or after polymerization to the solution of the polymeric organolithium compound.

The effects of added THF on the functionalization of poly(styryl)lithium with epichlorohydrin are listed in Table 1. The addition of THF (THF/C_6H_6 = 1/1, vol/vol) to the solution of epichlorohydrin ([EPC]/[PLi] = 30) prior to addition of PSLi to this solution resulted in a dramatic increase in the epoxide functionalization yield to 66 wt % but only decreased the amount of dimer formation to 19 wt %. Quite surprisingly, the addition of THF to the PSLi solution only increased the epoxide functionalization yield slightly (69 wt %) and further decreased the dimer yield to 14 wt %. The best epoxide functionalization yields (74 wt %) with minimum dimer formation (10 wt %) were obtained with THF as solvent for EPC and with THF added to PSLi (run 4, Table 1).

Effects of Chain-End Structure. Another method to optimize functionalization reactions and to promote nucleophilic displacement reactions is to convert the chain end to a lithium alkoxide prior to reaction with an electrophilic functionalizing agent, such as an alkyl halide.[35] The reaction of poly(styryl)lithium with ethylene oxide is a simple, quantitative functionalization reaction which forms the corresponding polymeric lithium alkoxide (**7**) quantitatively without oligomerization of ethylene oxide (see eq 3).[8,19,35] It was expected that



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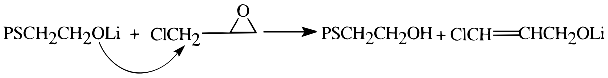
many of the side reactions documented for the functionalization of PSLi with EPC (see Scheme 1) would not occur; however, it should be noted that proton abstraction of the acidic hydrogen geminal to chlorine (see eq 4) has precedent in the monomer chain-transfer reaction of polymeric alkoxides with propylene oxide.[36]



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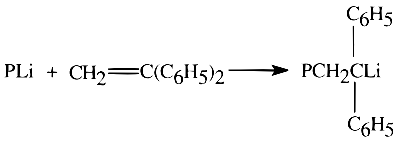
The functionalization of the polystyrene lithium alkoxide (**7**) (dissolved in 10 vol % THF/benzene) with excess epichlorohydrin ([EPC]/[POLi] = 30; dissolved in THF/benzene, 1/1, vol/vol) formed the corresponding epoxide-functionalized polystyrene in only 46 wt % yield. However, this procedure did eliminate dimer formation. These results are in good agreement with the previous studies of Mouzali, Lacoste, and Abadie,[14] who reported a 50% yield of epoxide-functionalized polymer from the reaction of the ethylene oxide adduct of α,ω-dilithiopoly(styrene-*b*-isoprene-*b*-styrene) with epichlorohydrin in THF at −30 °C.

It is known that poly(dienyl)lithiums tend to be associated more strongly and/or to higher degrees of aggregation compared to poly(styryl)lithium;[8,34] therefore, it was of interest to investigate the epoxide functionalization of poly(butadienyl)lithium. For this purpose, poly(styryl)lithium (M_n = 1500 g/mol, M_w/M_n = 1.06) in benzene was converted to poly(styrene-*b*-butadienyl)lithium (PS-*b*-PBDLi) by a crossover reaction with butadiene monomer [calculated M_n (BD) = 216 g/mol]. Complete crossover to butadienyllithium was documented by UV−visible spectroscopy (see Experimental Section). When a benzene solution of PS-*b*-PBDLi was added via inverse addition to a benzene solution of epichlorohydrin (30-fold molar excess), the yield of epoxide-functionalized polymer was only 29 wt % and the amount of dimer product was 44 wt % (see run 5, Table 1); using the same procedure for poly(styryl)lithium, the functionalization yield was comparable (28 wt %) but the amount of dimer was much less (22 wt %) (see run 1, Table 1). Thus, it appears that the stronger association of dienyllithium chain ends promotes dimer formation; similar effects have been observed in carbonation reactions where significantly more dimer and trimer formation is obtained for dienyllithium compared to styryllithium chain ends.[37]

Based on the previously discussed effects of THF on poly(styryl)lithium functionalization (see Table 1), it was anticipated that optimum functionalization yields would be obtained by addition of THF to both the dienyllithium solution and the EPC solution. When a THF/benzene (10/90, vol/vol) solution of PS-*b*-PBDLi was added to a THF/benzene (1/1, vol/vol) solution of excess epichlorohydrin ([EPC]/[PLi] = 30), the yield of epoxide-functionalized polymer increased to 80 wt % with only 3 wt % dimer (see run 6, Table 1). Under comparable conditions, poly(styryl)lithium was functionalized in only 69 wt % yield with 14 wt % dimer (run 3, Table 1). The small increase in yield for poly(dienyl)lithium may be a consequence of the differences in association behavior of dienyllithiums versus styryllithiums.[8,34]

One of the most effective end-capping procedures for decreasing side reactions for functionalizations of polymeric organolithiums is to react the chain ends with 1,1-diphenylethylene.[35] 1,1-Diphenylethylene reacts with poly(styryl)lithium and poly(dienyl)lithiums to form the corresponding polymeric (1,1-diphenylalkyl)lithiums, which are more stable and more sterically hindered (see eq 5). This simple, quantitative reaction proceeds without oligomerization when stoichiometric amounts



$$\mathrm{PLi} + \mathrm{CH_2{=}C(C_6H_5)_2} \longrightarrow \mathrm{PCH_2\overset{C_6H_5}{\underset{C_6H_5}{C}}Li} \qquad (5)$$

of 1,1-diphenylethylene are added.[8,38,39] The quantitative end-capping of poly(styryl)lithium in benzene with 1,1-diphenylethylene (0.2 molar excess) was monitored by UV−visible spectroscopy (see Experimental Section). The resulting polymeric (1,1-diphenylalkyl)lithium in benzene was added (inverse addition) to a benzene solution of epichlorohydrin ([EPC]/[PLi] = 30) and the results are shown in Table 2. Even in the absence of THF, 1,1-diphenylethylene end-capping produced the highest yield of epoxide-functionalized polymer (83 wt %) with only 4 wt % dimer (see Table 2, run 1) when compared to poly(styryl)lithium (see Table 1, runs 1−4) or poly(butadienyl)lithium chain ends (see Table 1, runs 5 and 6) even in the presence of THF.

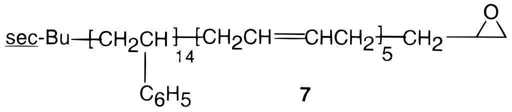
The epoxide functionalizations utilizing the 1,1-diphenylethylene end-capping procedure for both poly(styryl)lithium and poly(styrene-*b*-butadienyl)lithium were very efficient in the presence of THF (see runs 2−5, Table 2). In the presence of THF, no significant dimer formation was observed, and the yield of epoxide-functionalized polymer was 91−97 wt %. A small amount of unfunctionalized polymer constituted the remainder of the polymer products as determined by TLC. A typical SEC curve for the products of these functionalizations is shown in Figure 3. This dramatic effect of chain end structure stands in sharp contrast to the results of Xie and Sun,[12] who reported that 1,1-diphenylethylene end-capping did not improve the yield of epoxide-functionalized polymer. However, these results are in accord with the preliminary observations of Mouzali, Lacoste, and Abadie,[14] who reported that efficient functionalization by epichlorohydrin was observed for the adduct of butyllithium and 1,1-diphenylethylene in THF at −30 °C.

Characterization of Epoxide-Functionalized Polymers. The ability to prepare low molecular weight (M_n <2000 g/mol), narrow molecular weight distribution (M_w/M_n < 1.1), epoxide-functionalized polymers in high yield and separate them from any nonfunctionalized polymer by silica gel column chromatography has provided a unique opportunity to characterize the epoxide functional end group. From TLC analysis (see Experimental Section) for a purified, epoxy-functionalized polystyrene, the R_f value for the functionalized polymer was 0.56 compared to the R_f value of 0.92 for the unfunctionalized polystyrene base polymer. These results further confirm the utility of TLC to qualitatively analyze the purity of functionalized polymer and the ability to utilize chromatography to purify functionalized polymers.[35]

The ^{1}H NMR spectra of epoxide-functionalized polystyrenes all exhibited a broad peak in the region of δ = 2.5−2.6 ppm. An analogous peak at δ = 2.6 ppm was reported for the epoxide-functionalized polystyrenes synthesized by Mouzali, Lacoste, and Abadie.[14] Hild and Lamps[40] have assigned peaks at δ = 3.28 (methine), 2.88 (*cis* methylene CH), and 2.69 ppm (*trans* methylene CH) to the epoxide ring protons in poly(glycidyl methacrylate). The ^{1}H NMR spectrum of epoxidized polybutadiene is characterized by resonances at δ = 2.6 (*trans* methylene CH) and 2.85 ppm (*cis* methylene CH).[41,42] The ^{1}H NMR spectrum of the purified, epoxide-functionalized poly(styrene-*b*-butadiene) is shown in Figure 4. By analogy with previous studies of polymers with epoxide functional groups, the three new resonances which are observed at δ = 2.90, 2.72, and 2.45 ppm are assigned to the methine and *cis* and *trans* methylene protons of the oxirane ring, respectively. The ^{1}H NMR spectrum of the epoxide-functionalized polystyrene which was end-capped with 1,1-diphenylethylene prior to functionalization is shown in Figure 5. Compared to the epoxide-functionalized poly(styrene-*b*-butadiene) (Figure 4), the resonances for the epoxide group are shielded and observed in the region of δ = 2.2−2.8 ppm. It is noteworthy that the peak corresponding to the methine proton of the terminal 1,1-diphenylmethine group at δ = 3.52 (lit.[14] δ = 3.8 ppm; lit.[24] δ = 3.5 ppm) is not observed in the spectrum of the functionalized polymer.

The ^{13}C NMR spectra of epoxide-functionalized polymers provide good qualitative evidence for this functional group. As discussed previously with respect to the functionalization reactions in benzene solution (see structure **1** and Figure 2), the ^{13}C NMR spectra for epoxide-functionalized polymers would be expected to exhibit resonances at δ = 51.5 and 47.2 ppm for the methine and methylene carbons of the oxirane ring, respectively, according to the additivity equations for epoxide compounds developed by Paulson et al.[33] The ^{13}C NMR spectrum ($CDCl_3$) of purified, epoxidize-functionalized polystyrene (M_n = 2.1 × 10^3 g/mol; see run 3, Table 1) is shown in Figure 6. Compared with the ^{13}C NMR spectrum of unfunctionalized polystyrene base polymer,[19] the epoxide-functionalized polymer exhibits two new, characteristic resonances at δ = 47.5 and 51.6 ppm, as expected, which are assigned to the methylene and methine carbons of the oxirane ring, respectively. It is also noteworthy that the resonance for the terminal benzylic carbon in unfunctionalized polystyrene, at δ = 34.9 ppm[19] is not observed in the ^{13}C NMR spectrum of the epoxide-functionalized polymers which further supports the purity of these samples.

The ^{13}C NMR spectrum of the purified, epoxide-functionalized poly(styrene-*b*-polybutadiene) copolymer (**7**) is shown in Figure 7b. By comparison with the corresponding spectrum of the unfunctionalized base polymer (Figure 7a)), the epoxide-functionalized polymer exhibits resonances at δ = 47.5, 48.0, 51.2, and 52.3 ppm. Using the empirical additivity equations developed by Paulson et al.,[33] the calculated chemical shifts for the methylene and methine oxirane carbons would be expected at δ = 47.0 and 52.4 ppm, respectively, for the 1,4-butadiene penultimate unit and at δ = 47.2 and 51.5 ppm, respectively, for the 1,2-butadiene penultimate unit. Based on these calculations, the resonance at δ = 52.3 ppm is assigned to the functionalized 1,4-unit and the resonance at δ = 51.2 ppm is assigned to the functionalized 1,2-unit.



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The ^{13}C NMR spectrum of the purified, epoxide-functionalized polystyrene (**8**) which had been end-

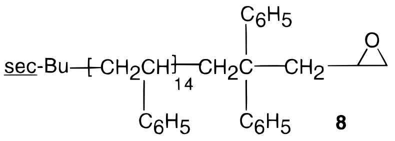

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Table 2. Effect of 1,1-Diphenylethylene End-Capping on the Functionalization of Poly(styryl)lithium and Poly(styrene-*b*-butadienyl)lithium with Epichlorohydrin (EPC)[a]

run	PLi	PLi solvent	EPC solvent	P-epoxide[b] (wt %)	dimer (wt %)[c]
1	PS-DPELi[d,e]	C_6H_6	C_6H_6	83	4
2	PS-DPELi[d,f]	10 vol % THF in C_6H_6	THF/C_6H_6 (1/1, vol/vol)	94	<1
3	PS-DPELi[d,g]	10 vol % THF in C_6H_6	THF/C_6H_6 (1/1, vol/vol)	91	<1
4	PS-DPELi[d,h]	10 vol % THF in C_6H_6	THF/C_6H_6 (1/1, vol/vol)	95	<1
5	PS-*b*-PBD-DPELi[i]	10 vol % THF in C_6H_6	THF/C_6H_6 (1/1, vol/vol)	97	<1

[a] Termination by inverse addition mode with 30-fold molar excess of EPC for 2 h at 0 °C and for 5 h at 25 °C; [PLi] $\approx$ 0.05 M unless otherwise noted. [b] Epoxide-functionalized polymer; determined by titration using ASTM D 1652-90. [c] Determined by SEC. [d] Product of end-capping of poly(styryl)lithium with 1,1-diphenylethylene. [e] M_n(SEC) = 1900 g/mol; M_n(VPO) = 2100 g/mol. [f] M_n(SEC) = 1500 g/mol, M_w/M_n = 1.05; M_n(VPO) = 1600 g/mol (functionalized polymer); [PLi] = 0.077 M. [g] M_n(SEC) = 2000 g/mol, M_w/M_n =1.06; M_n(VPO) = 2300 g/mol (functionalized polymer). [h] M_n(SEC) = 4500 g/mol, M_w/M_n = 1.05; M_n(VPO) = 4800 g/mol (functionalized polymer); [PLi] = 0.021 M. [i] Product of end-capping of poly(styrene-*b*-butadienyl)lithium with 1,1-diphenylethylene; M_n(PS) = 1.1×10^3 g/mol; M_w/M_n =1.07); M_n(PBD) = 260 g/mol; M_n(VPO) = 1600 g/mol (functionalized polymer).

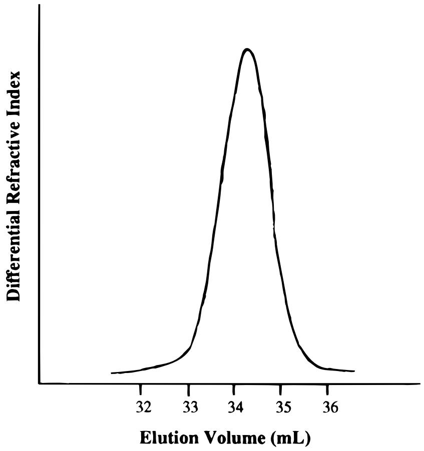

Figure 3. SEC (RI) chromatogram for the crude reaction products obtained for the functionalization of the adduct of 1,1-diphenylethylene with poly(styryl)lithium (M_n = 1600 g/mol) with epichlorohydrin (run 2, Table 2).

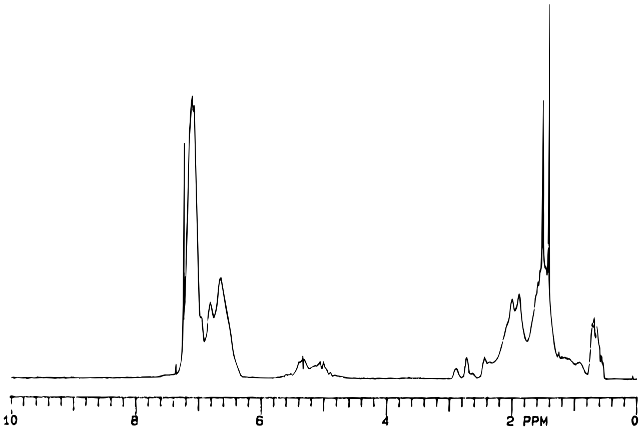

Figure 4. ^{1}H NMR spectrum ($CDCl_3$) of purified, epoxide-functionalized poly(styrene-*b*-butadiene) copolymer (see run 6, Table 1).

capped with 1,1-diphenylethylene prior to functionalization is shown in Figure 8b. Compared with the corresponding spectrum of the unfunctionalized base polymer (Figure 8a)), the epoxide-functionalized polymer (**8**) exhibits resonances at δ = 50.0 and 47.5 ppm. Based on the empirical chemical shift equations, three peaks would be expected at δ = 50.5, 50.6, and 47.4 ppm for the diphenyl-substituted carbon, the methine carbon of the oxirane, and the methylene carbon of the oxirane, respectively. Because of the expected overlap of resonances for the diphenyl-substituted carbon and the methine carbon of the epoxide ring,[13] NMR analysis for this functionalized polymer is less definitive.

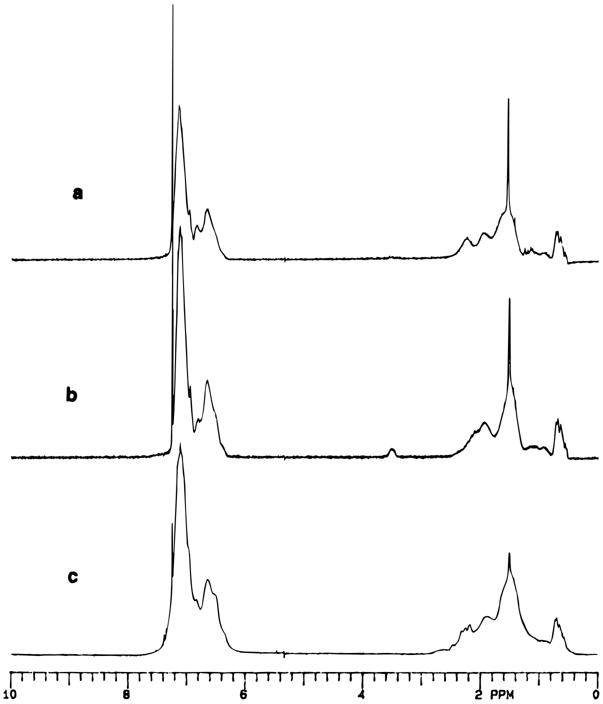

Figure 5. ^{1}H NMR spectra ($CDCl_3$) of (a) polystyrene base polymer,; (b) 1,1-diphenylethylene end-capped polystyrene base polymer, and (c) purified, epoxide-functionalized polystyrene with 1,1-diphenylethylene end cap (see run 2, Table 2).

With respect to the infrared spectra of the epoxide-functionalized polymers, it is noteworthy that Mouzali, Lacoste, and Abadie[14] previously reported that medium-intensity infrared absorption bands corresponding to the epoxide group in epoxide-functionalized polystyrene were observed at 1410, 1260, 1130, and 920 cm^{-1} for a low molecular weight analog of a 1,1-diphenylethylene end-capped polymer. Although there are weak bands at 1411, 1135, and 930 cm^{-1} which were discerned in the FTIR spectrum of the functionalized polymer compared to the corresponding spectrum for the unfunctionalized polymer, stronger absorption bands were observed at 1269 and 828 cm^{-1}. It has been stated that epoxy ring compounds absorb at 1280−1230 cm^{-1} due to the ring breathing vibration (symmetrical C−O−C stretching) and that another ring vibration is observed at 880−775 cm^{-1}.[43] Thus, it appears that the presence of the FTIR bands at 1269 and 828 cm^{-1} may be useful for characterizing epoxide-functionalized macromonomers.

Conclusion

The functionalization reaction of polymeric organolithium compounds with epichlorohydrin (EPC) to form

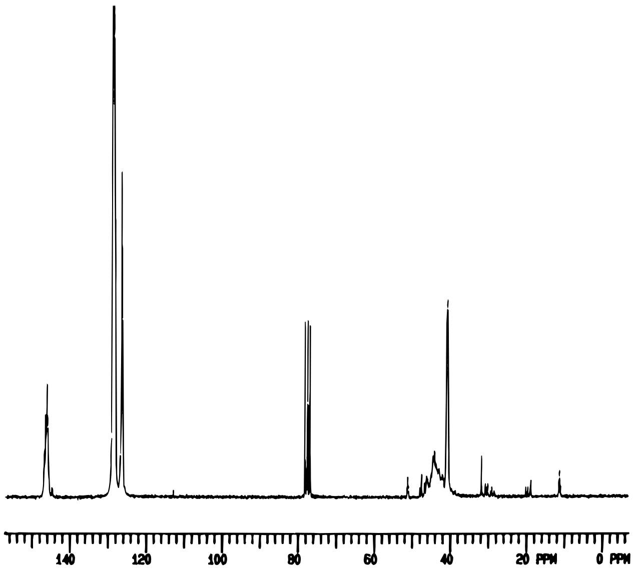

Figure 6. ^{13}C NMR spectrum ($CDCl_3$) of purified, epoxide-functionalized polystyrene (**1**) (see run 3, Table 1).

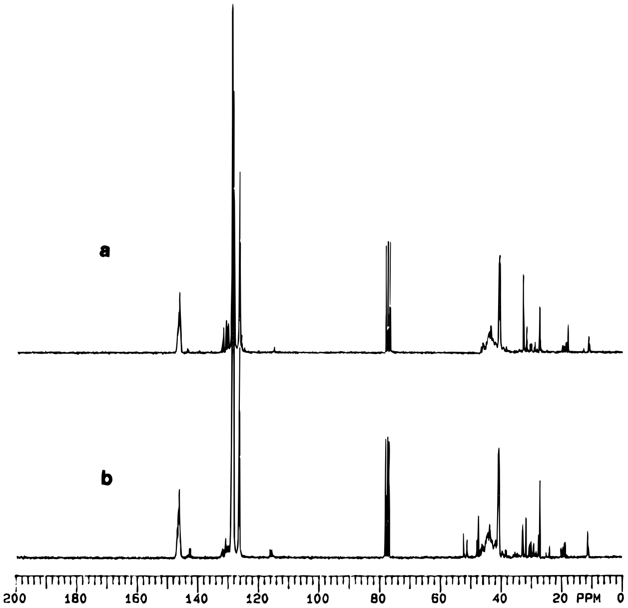

Figure 7. ^{13}C NMR spectra ($CDCl_3$) of (a) poly(styrene-*b*-butadiene) base polymer and (b) purified, epoxide-functionalized poly(styrene-*b*-butadiene) (**7**) (see run 6, Table 1).

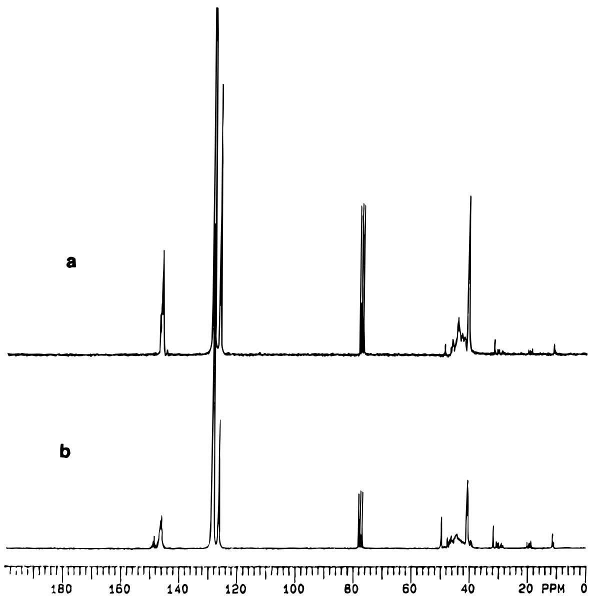

Figure 8. ^{13}C NMR spectra ($CDCl_3$) of (a) 1,1-diphenylethylene end-capped polystyrene base polymer and (b) purified, epoxide-functionalized, 1,1-diphenylethylene end-capped polystyrene (**8**) (see run 2, Table 2).

epoxide-functionalized macromonomers is strongly affected by the addition mode of reagents, the solvent, and the structure of the polymeric chain end. Even using an inverse addition mode with excess EPC, only low yields ($<$ 30%) of functionalization are observed for poly(styryl)lithium and for poly(butadienyl)lithium, while reasonable yields (83%) are observed for polymeric (1,1-diphenylalkyl)lithiums formed by 1,1-diphenylethylene (DPE) end-capping. Addition of THF to both the polymeric organolithium and the EPC solutions increases the yields to 80 and 74% for poly(butadienyl)-lithium and poly(styryl)lithium, respectively. Almost quantitative yields (91−97%) with $<$1% dimer are observed for polymeric (1,1-diphenylalkyl)lithiums in the presence of THF. Pure epoxide-functionalized polymers can be separated from any unfunctionalized polymer by silica gel column chromatography. Epoxide-functionalized polymers exhibit characteristic ^1H NMR resonances ($\delta = 2.2-3.3$ ppm), ^{13}C NMR resonances ($\delta = 47-52.5$ ppm), and FTIR absorption bands (1269 and 828 cm^{-1} regions).

Although these epoxide functionalizations were effected in benzene, analogous results would be expected in cyclohexane based on the solvent effects reported by Xie and Sun.[12] The chemistry of these epoxide-functionalized macromonomers is currently under investigation and will be reported in subsequent publications.

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References and Notes

(1) Milkovich, R. In *Anionic Polymerization. Kinetics and Mechanism*; McGrath, J. E., Ed.; ACS Symposium Series No. 166; American Chemical Society: Washington, DC, 1981; p 41.
(2) Rempp, P. F.; Franta, E. *Adv. Polym. Sci.* **1984**, *58*, 1.
(3) Kawakami, Y. In *Encyclopedia of Polymer Science and Engineering*; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1987; Vol. 9, p 195.
(4) Percec, V.; Pugh, C.; Nuyken, O.; Pask, S. D. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Elmsford, NY, 1989; Vol. 6, p 281.
(5) Gnanou, Y. *Indian J. Technol.* **1993**, *31*, 317.
(6) Quirk, R. P.; Zhuo, Q.; Tsai, Y.; Yoo, T.; Wang, Y. In *Macromolecular Engineering. Recent Advances*; Mishra, M. K., Nuyken, O., Kobayashi, S., Yagci, Y., Sar, B., Eds.; Plenum Press: New York, 1995; p 197.
(7) Quirk, R. P.; Kim, J. *Rubber Chem. Technol.* **1991**, *64*, 450.
(8) Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization. Principles and Practical Applications*; Marcel Dekker: New York, 1996; Chapter 11.
(9) Milkovich, R.; Chiang, M. T. (assigned to CPC International); U.S. Patent 3,786,116, 1974.
(10) Milkovich, R.; Chiang, M. T. (assigned to CPC International), U.S. Patent 3,846,393, 1974.
(11) Xie, H.; Sun, W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25* (2), 67.
(12) Xie, H.; Sun, W. In *Advances in Polymer Synthesis*; Culbertson, B. M., McGrath, J. E., Eds.; Plenum Press: New York, 1985;, p 461.
(13) Stenmark, G. A. *Anal. Chem.* **1957**, *29*, 1367.

(14) Mouzali, M.; Lacoste, J.; Abadie, M. J. M. *Eur. Polym. J.* **1989**, *25*, 491.
(15) Youqing, J.; Eping, L. *Polymer* **1992**, *33*, 5076.
(16) Mancinelli, P. A. (assigned to Atlantic Richfield), U. S. Patent 4,544,711, 1985.
(17) Takenaka, K.; Hirao, A.; Nakahama, S. *Polym. Int.* **1995**, *37*, 291.
(18) Quirk, R. P.; Chen, W.-C. *Makromol. Chem.* **1982**, *183*, 2071.
(19) Quirk, R. P.; Ma, J.-J. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 2031.
(20) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447.
(21) Morton, M.; Fetters, L. J. *Rubber Chem. Technol.* **1975**, *48*, 359.
(22) Bywater, S.; Johnson, A. F.; Worsfold, D. J. *Can. J. Chem.* **1964**, *42*, 1255.
(23) Tsai, Y. Ph.D. Thesis, University of Akron, 1995.
(24) Lee, B.; Ph.D. Thesis, University of Akron, 1991.
(25) ASTM D 1652-90, *1993 Annual Book of ASTM Standards*; Fazio, P. C., et al., Eds.; American Society for Testing and Materials: Philadelphia, PA, 1993; Vol 0801, plastic (1):C177-D2343, p 504.
(26) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: Elmsford, NY, 1974; (a) p 201; (b) p 144; (c) p 199.
(27) Fabris, H. J. *J. Org. Chem.* **1967**, *32*, 2031.
(28) Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414.
(29) (a) Quirk, R. P.; Kuang, J. J.; Hasegawa, H.; Han, K. *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1994**, *53*, 15. (b) Hasegawa, H. M. S. Thesis, University of Akron, 1994.
(30) Hensley, D. R.; Goodrich, S. D.; Harwood, H. J.; Rinaldi, P. L. *Macromolecules* **1994**, *27*, 2351.
(31) Bangerter, F.; Serafini, S.; Pino, P.; Vogl, O. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 109.
(32) Grant, D. M.; Paul, E. G. *J. Am. Chem. Soc.* **1964**, *86*, 2984.
(33) Paulson, D. R.; Tang, F. Y. N.; Moran, G. F.; Murray, A. S.; Pelka, B. P.; Vasquez, E. M. *J. Org. Chem.* **1975**, *40*, 184.
(34) Fetters, L. J.; Balsara, N. P.; Huang, J. S.; Jeon, H. S.; Almdal, K.; Lin, M. Y. *Macromolecules* **1995**, *28*, 4996.
(35) Quirk, R. P. In *Comprehensive Polymer Science. First Supplement*; Aggarwal, S. L., Russo, S., Eds.; Pergamon Press: Oxford, UK, 1992; pp 83−106.
(36) Boileau, S. In *Comprehensive Polymer Science*; Eastmond, G. C., Ledwith, A., Russo, S., Sigwalt, P., Eds.; Pergamon Press: Oxford, UK, 1989; Vol. 3, pp 467−487.
(37) Quirk, R. P.; Yin, J. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 2349.
(38) Quirk, R. P.; Ren, J. In *Macromolecules 1992*; Kahovek, J., Ed; VSP International Science Publishers: Zeist, The Netherlands, 1993; pp 133−148.
(39) Quirk, R. P. *Makromol. Chem., Macromol. Symp.* **1992**, *63*, 259.
(40) Hild, G.; Lamps, J.-P. *Polymer* **1995**, *36*, 4841.
(41) Maenz, K.; Schutz, H.; Stadermann, D. *Eur. Polym. J.* **1993**, *29*, 855.
(42) Burfield, D. R.; Lim, K. L.; Law, K. S.; Ng, S. *Polymer* **1984**, *25*, 995.
(43) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to Infrared and Raman Spectroscopy*; Academic Press: New York, 1964; p 273.

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