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Reaction of Polymeric Organolithium Compounds with Ethylene Oxide in Hydrocarbon Solution: Determination of Extent of Oligomerization

Roderic P. Quirk, *[1] *Robert T. Mathers,*[1] *Jing-Jing Ma,*[1]
Chrys Wesdemiotis,[2] *Mark A. Arnould*[2]

Departments of Polymer Science[1] and Chemistry[2], The University of Akron, Akron, Ohio USA 44325

Summary. The functionalization of poly(styryl)lithium with excess ethylene oxide in benzene solution has been reexamined to determine if oligomerization of ethylene oxide occurs under normal conditions. No ^{13}C NMR peaks were observed at $\delta = 69\text{-}70$ and 72-73 ppm as expected for a chain end with two ethylene oxide units. These peaks were not observed even when 3.3 equivalents of ^{13}C-labeled ethylene oxide (98 atom % ^{13}C) was utilized. No peak corresponding to two ethylene oxide units at the chain end (at m/z 104n + 210 + 44 Daltons) was observed in the MALDI-TOF mass spectrum of the functionalization product. The main series of peaks (Ag^+-cationized) appeared at m/z 104n + 210, corresponding to the expected C_4H_9 and CH_2CH_2OH end groups with a number average degree of polymerization of n. A small peak (ca. 3 %) corresponding to two ethylene oxide units at the chain end was observed in the mass spectrum of the functionalization product obtained using 10 equivalents of ethylene oxide

INTRODUCTION

One of the most useful aspects of living anionic polymerization, especially alkyllithium-initiated anionic polymerization, is the ability to prepare a variety of chain-end functionalized polymers by post-polymerization reactions of the resulting polymeric organolithiums with electrophilic reagents. [1-5] Despite the potentially vast array of possible functionalization reactions[6-11] relatively few functionalization reactions have been well characterized and provide the corresponding terminal chain-end functionalized polymers in quantitative yield. [1,3] A special challenge has been to prepare chain-end functionalized polymers in hydrocarbon solution at room temperature and above.

The reaction of polymeric organolithium compounds with ethylene oxide is one of the few simple, efficient functionalization reactions. Previous studies established that the reaction of poly(styryl)lithium with ethylene oxide in benzene produced the

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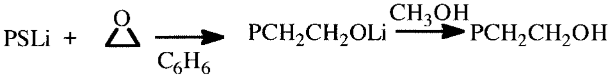
corresponding ω-hydroxyethylated polystyrene in quantitative yield without formation of detectable amounts of oligomeric ethylene oxide blocks as shown in Eq. 1. [12] This apparent inability of lithium bases to effect the anionic polymerization of ethylene oxide is unique among the alkali metals. [13] The unreactivity of lithium alkoxides has been ascribed to their strong association; lithium alkoxides are aggregated into tetramers and hexamers even in polar media as shown in Table 1. [14] However, this is not the only factor since sodium and potassium alkoxides are also highly associated in these media (see Table 1) and yet they are active initiators for the polymerization of ethylene oxide. It was concluded that lithium alkoxide unreactivity is not due to their association *per se*, but to the strength of the association, i.e., the lack of dissociation into reactive, unassociated species. [15] Mass spectrometric analysis of lithium alkoxides indicated that the only parent peak corresponded to the hexamer and that large increases in ionizing potential (eV) were necessary to observe fragmentation to lower degrees of aggregation. [16]



$$PSLi + \overset{O}{\triangle} \xrightarrow[C_6H_6]{} PCH_2CH_2OLi \xrightarrow{CH_3OH} PCH_2CH_2OH \quad (1)$$

Table 1. Degree of association of alkali metal alkoxides in various solvents.[14]

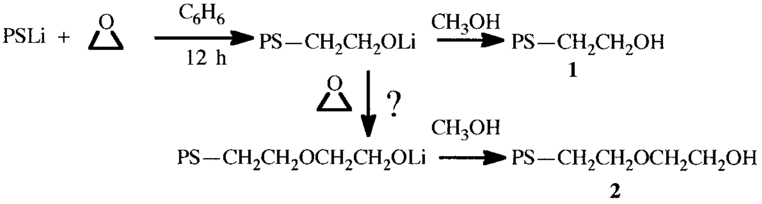
	Degree of Association				
Alkoxide	Cyclohexane	Benzene	Diethyl ether	Tetra-hydrofuran	pyridine
Lithium *t*-butoxide	5.8	6.2	5.9	4.1	4.0
Sodium *t*-butoxide	8.2	8.2	4.3	3.9	2.9
Potassium *t*-butoxide	--	--	3.9	4.	--

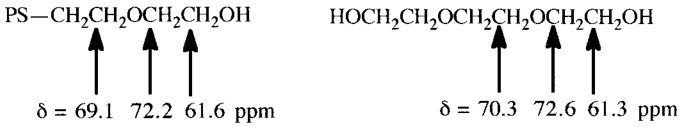
However, a recent reexamination of the products of this reaction by matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF MS) reported the detection of a peak corresponding to a dimeric ethylene oxide unit at the chain end.[17] These results prompted a reexamination of the question of whether or not a chemically significant amount of oligomerization occurs during the functionalization of poly(styryl)lithium in benzene solution with excess ethylene oxide.

Characterization of Functionalization Products from the Reaction of Poly(styryl)lithium with Four Equivalents of Ethylene Oxide for Twelve Hours in Benzene

The detection of a peak by MALDI-TOF MS corresponding to the addition of two ethylene oxide units during functionalization of poly(styryl)lithium in benzene prompted a reexamination of the spectral evidence indicating the absence of oligomerization during this functionalization reaction. This conclusion was based primarily on ^{13}C NMR characterization of the functionalized products, comparision of the observed resonances with calculated ^{13}C NMR chemical shifts for the expected oligomeric product (**2**, Scheme 1) and comparison with the chemical shifts of a model for the oligomer. The calculated ^{13}C NMR shifts expected for **2** and the chemical shifts for a model of the oligomer (triethylene glycol) are shown below. Thus, it can be concluded that if oligomeric products are formed during this functionalization, then resonances should be observed at δ = 69-70 and 72-73 ppm. It is noteworthy that no peaks were detected in this region for a natural abundance ^{13}C NMR spectrum of the products of poly(styryl)lithium (M_n = 1,300) with a four-fold excess of ethylene oxide and a reaction time of 12 h in benzene at room temperature.[12]

Scheme 1.





A clear demonstration of the absence of ethylene oxide oligomerization products for this functionalization procedure was provided by effecting the functionalization of poly(styryl)lithium (M_n = 2,000) with 3.3 equivalents of ^{13}C-labeled ethylene oxide (98 atom % ^{13}C) for 12 hours in benzene at room temperature. The ^{13}C NMR spectrum of the functionalization products (see Figure 1) showed no resonances corresponding to the dimeric ethylene oxide unit at the chain end in the regions of δ = 69-70 and 72-73 ppm. The ^{13}C NMR spectrum of the functionalized product showed only a doublet at 61 ppm corresonding to the monohydroxyethylated product, **1**; the doublet results from the splitting of the carbon bonded to the hydroxyl group by the adjacent labeled carbon.

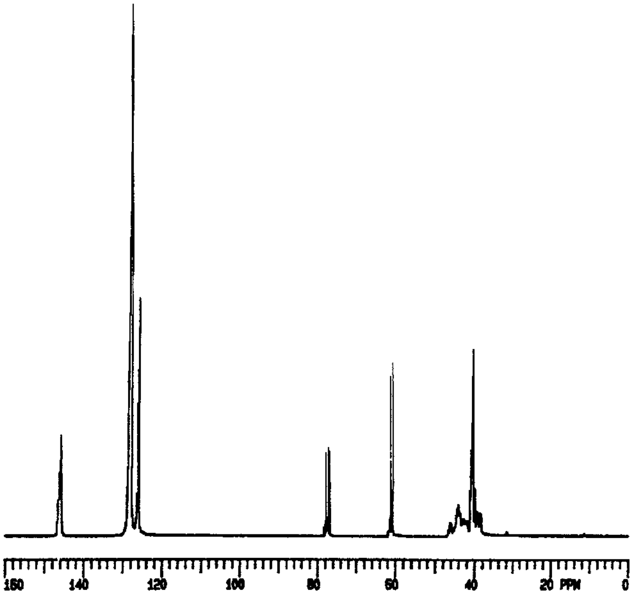


Figure 1. ^{13}C NMR spectrum of hydroxyl-functionalized polystyrene prepared using ^{13}C-labeled ethylene oxide.

The absence of oligomerization products was also confirmed by MALDI-TOF mass spectrometric analysis of the products from functionalization of poly(styryl)lithium with 4 equivalents of ethylene oxide for 12 hours at room temperature in benzene as shown in Figure 2. No peaks were observed at 44 Daltons higher than the main series of

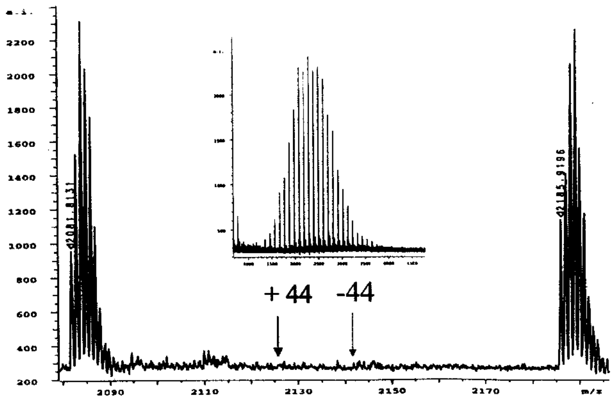


Figure 2. MALDI-TOF mass spectrum of hydroxyl-functionalized polystyrene prepared using 4 equivalents of ethylene oxide at room temperature for a 12 hour reaction time.

peaks (all ions were Ag^+-cationized polymers) that appeared at m/z 104n + 210, corresponding to the expected C_4H_9 and CH_2CH_2OH end groups. Thus, under these conditions oligomerization of ethylene oxide did not occur. Furthermore, no significant peaks were observed at 44 Daltons lower than the main series of peaks; this indicates the absence of significant amounts of unfunctionalized polymer (only C_4H_9 and H end groups). However, when ten equivalents of ethylene oxide were used to functionalize poly(styryl)lithium in benzene for the same reaction time, a significant peak corresponding to the addition of two ethylene oxide units to the chain end was observed as shown in Figure 3. No peaks corresponding to non-functional polymer (-44 Daltons) were observed in the mass spectrum of the products for this functionalization.

Thus, all of the available evidence indicates that no significant amounts of oligomerized ethylene oxide units are detected by either ^{13}C NMR or MALDI-TOF mass spectrometric analysis for the normal procedure for functionalization of poly(styryl)lithium in benzene with 3-4 equivalents of ethylene oxide for a 12 hour reaction time. However, oligomerization is observed when 10 equivalents are used.

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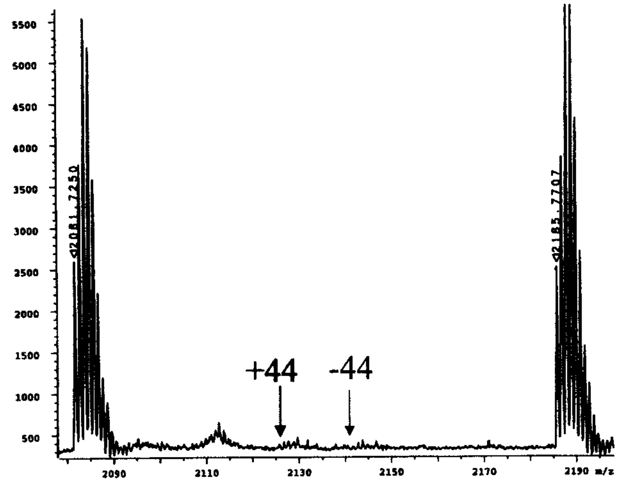

Figure 3. MALDI-TOF mass spectrum of hydroxyl-functionalized polystyrene prepared using 10 equivalents of ethylene oxide at room temperature for 12 hours.

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