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Polymer 45 (2004) 3423–3428

polymer

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Investigation of ethylene oxide oligomerization during functionalization of poly(butadienyl)lithium using MALDI-TOF MS and ^{1}H NMR analyses

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Received 9 January 2004; received in revised form 2 March 2004; accepted 3 March 2004

Abstract

Oligomerization of ethylene oxide during the functionalization of poly(butadienyl)lithium in benzene and cyclohexane at 25 °C has been investigated by MALDI-TOF MS and ^{1}H NMR. Chemically significant amounts of oligomer were found using 4 equiv. of ethylene oxide ([EO]/[PLi]) after 12 h in both benzene and cyclohexane. No oligomer was observed when the reaction time was minimized.
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Keywords: Anionic polymerization; Hydroxyl functionalization; Oligomerization

1. Introduction

One of the unique and useful aspects of living polymerization is the ability to prepare chain-end functionalized polymers [1]. Alkyllithium-initiated, living anionic polymerization has proven to be a useful method for the synthesis of well-defined, chain-end functionalized polymers [2–4]. Because of the absence of chain transfer or termination reactions, polymers are formed with predictable molecular weights and narrow molecular weight distributions as long as initiation is competitive with propagation [2,5]. In principle, the living anionic chain ends produced after all of the monomer is consumed can react with electrophilic reagents to form well-defined, chain-end functionalized polymers. Although a variety of these functionalization reactions have been described in the literature [6–8], proper characterization has not always been included. In fact, many of these post-polymerization functionalization reactions are not efficient and a variety of side products are often formed [2,4].

In contrast, the reaction of polymeric organolithium compounds with ethylene oxide is one of the few simple, efficient functionalization reactions. The functionalization of poly(styryl)lithium with a small excess of ethylene oxide in benzene solution produces the corresponding hydroxyethylated polymer in quantitative yield without formation of detectable amounts of oligomeric ethylene oxide blocks [9]. Using model compounds, calculated ^{13}C NMR chemical shifts and ^{13}C-labeled ethylene oxide, it was concluded that no oligomerization had occurred [9,10]. The absence of oligomerization is surprising in view of the steric strain [11] and intrinsic reactivity of ethylene oxide toward nucleophiles [12]. Lithium alkoxides are the least reactive among the alkali metal alkoxides for anionic polymerization of ethylene oxide [12,13]. This unreactivity has been attributed to the high degree of association of lithium alkoxides [14]; however, other alkali metal alkoxides are also highly aggregated in solution [14]. Therefore, it has been concluded that the alkoxylithium chain ends are more strongly aggregated and have very low degrees of dissociation to form unassociated, unreactive species [15].

The functionalization of PSLi with ethylene oxide was recently reinvestigated by a combination of ^{1}H and ^{13}C NMR and MALDI-TOF mass spectral analysis [16]. Under the standard reaction conditions (4 molar equiv. of EO, benzene, 3–12 h, 25 °C), no oligomerization was detected. However, when the amount of ethylene oxide used was increased to 10 equiv. or the reaction proceeded for reaction times up to 4 weeks, oligomerization corresponding to addition of two or even three ethylene oxide units at the

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doi:10.1016/j.polymer.2004.03.022

chain end was clearly observed, especially by mass spectrometry.

Recently, Mays and coworkers [17] also studied the functionalization of both poly(styryl)lithium and poly(butadienyl)lithium with ethylene oxide in benzene at room temperature. The resulting functionalized polymers were characterized by MALDI-TOF MS. The functionalization with PSLi with 4 equiv. of ethylene oxide and a 24 h reaction time were reported to produce only one distribution of peaks, corresponding to functionalization without oligomerization, by MALDI-TOF MS analysis. When these functionalizations were allowed to proceed for periods up to one month, peaks corresponding to addition of two ethylene oxide units to the chain end were detected. The functionalization of PBDLi ([ethylene oxide]/[PBDLi] = 4, 24 h reaction time) was reported to produce hydroxyethyl-functionalized polymer as the main product by MALDI-TOF MS. However, a second distribution was also detected with a mass which corresponded to a terminal hydroxyethoxyethyl group resulting from addition of two ethylene oxide units at the chain end. It was concluded that oligomerization of ethylene oxide does occur for functionalization of PBDLi under standard conditions in contrast to all previous work [15] and the results reported by Mays and coworkers [17] in the same paper for functionalization of poly(styryl)lithium. Mays and coworkers [17] concluded that 'the degree of ethylene oxide oligomerization depends on the type of living anion, and is much more pronounced with PBD than PS'. If this result is correct, then the ability of a polymeric alkoxide to oligomerize with ethylene oxide depends on the nature of the backbone chain. Because of this unexpected result for functionalization of poly(butadienyl)lithium, we have reinvestigated the functionalization of poly(butadienyl)lithium with ethylene oxide under standard conditions using high purity reagents, standard high vacuum techniques and ^{1}H NMR and MALDI-TOF mass spectral analysis of the products.

2. Experimental

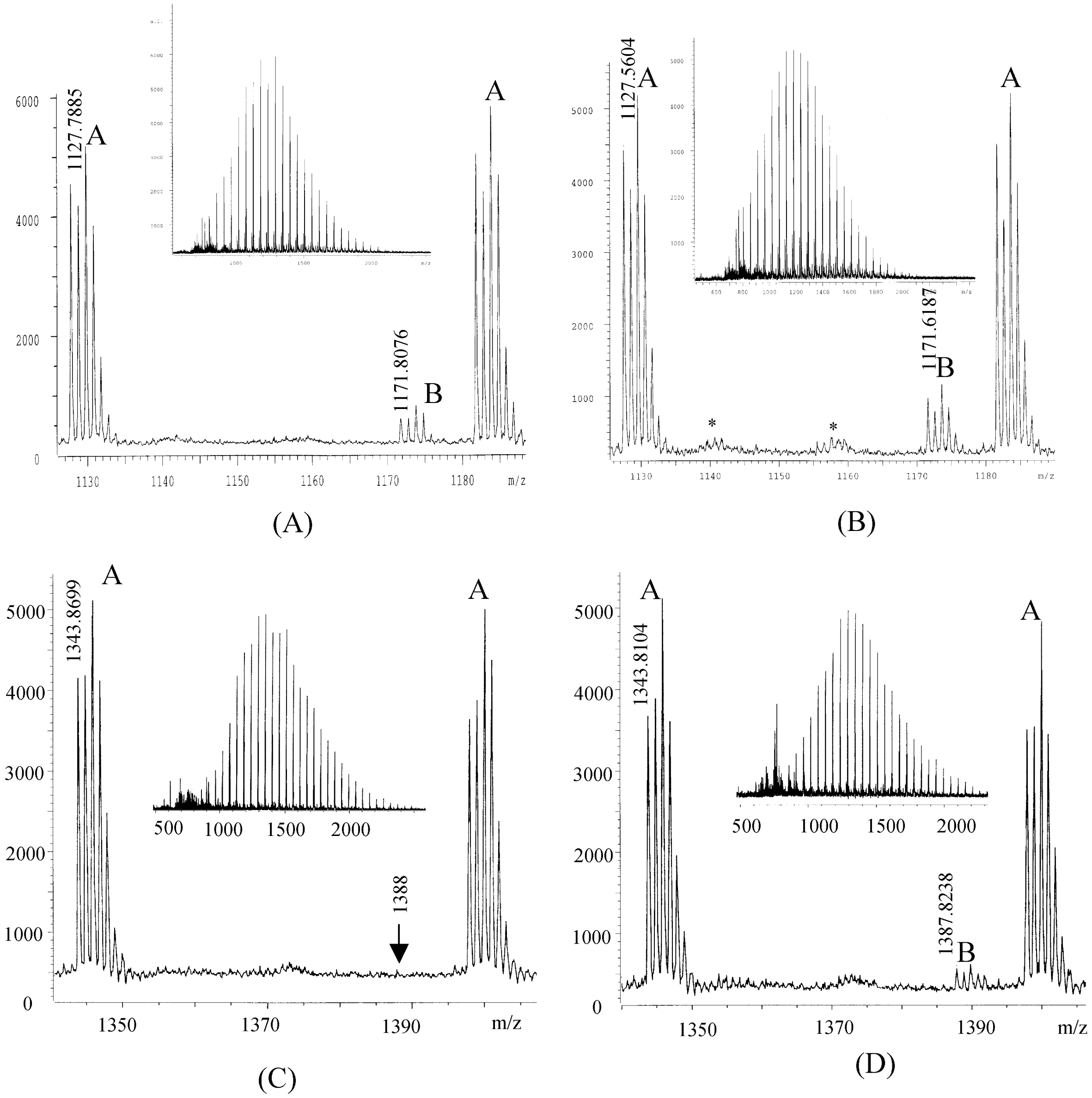
All chemicals used were purchased from Aldrich Chemical Co. (Milwaukee, WI) unless addressed separately. *sec*-Butyllithium (FMC, Lithium Division, 12.0 wt% in cyclohexane) was used without further purification after double titration analysis [18]. Benzene [19], cyclohexane [20], butadiene [21] and ethylene oxide [9] were purified as described previously. The polymerizations were carried out in all-glass reactors using standard high-vacuum techniques [22]. Chain end hydroxylation was effected by reacting poly(butadienyl)lithium with 4 equiv. of ethylene oxide ([EO]/[PBDLi] = 4) for various times as described in Section 3. The reaction was terminated by degassed methanol and the samples were precipitated into methanol, collected and dried on the vacuum line.

Size exclusion chromatography (SEC) analyses were performed at a flow rate of 1.0 ml/min in THF at 30 °C using a Waters 150-C plus model gel permeation chromatography system equipped with six Ultra-Styragel columns (500, 2×10^3, 10^4, 10^5, and 10^6 Å), a Waters differential refractometer, and a Viscotek viscosity detector after calibration with polystyrene standards from Polymer Laboratories, Ltd. UV analyses of living polymer solutions were obtained using a single-beam Hewlett Packard 8452A diode array spectrophotometer coupled with a Gateway 2000 computer. UV cells (Helma) with 0.1 mm path length were attached directly to the polymerization reactors. ^{1}H NMR spectra were recorded on a Gemini-300 NMR spectrometer in $CDCl_3$. MALDI-TOF mass spectra were acquired using a Bruker REFLEX-III time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with an LSI model VSL-337ND pulsed 337 nm nitrogen laser (3 nm pulse width), a single-stage pulsed extraction ion source and a two-stage grid-less reflector. Solutions of dithranol (20 mg/ml), end-functional polymer (10 mg/ml), and silver trifluoroacetate (10 mg/ml) were made in tetrahydrofuran (THF). These solutions were mixed in the ratio matrix: cationizing salt: polymer (10:1:2), and 0.5 μl of the solution was deposited on the sample holder. The attenuation of the nitrogen laser was set at 69%. The mass scale was calibrated externally, using polystyrene standards; the mass accuracy was better than ±0.05%. All mass-to-charge (*m*/*z*) ratios quoted are monoisotopic, referring to the species containing the lowest-mass isotope of each element.

3. Results and discussion

The molecular weights of poly(butadienyl)lithiums [M_n (SEC) = 1500 g/mol, $M_w/M_n = 1.04$] were designed to be the same as that used by Mays and coworkers [17] to obtain a reliable comparison with their work. The mass spectrum obtained from the product of the reaction of poly(butadienyl)lithium with 4 equiv. of ethylene oxide ([EO]/[PSLi]) in benzene after a reaction to time of 12 h is shown in Fig. 1(A). It contains one major distribution (A), whose *m*/*z* values correspond to the Ag^+ adducts of PBD oligomers with C_4H_7 and CH_2CH_2OH end groups, and one minor distribution (B) corresponding to oligomers with one extra C_2H_4O unit (+44 Da). For example, for the 17-mer of distribution A the calculated monoisotopic mass is {57.06 (C_4H_7) + 17 × 54.05 ($(C_4H_6)_{17}$) + 45.03 (CH_2CH_2OH) + 106.90 ($^{107}Ag^+$) = 1127.84 Da}, as indeed is observed at *m*/*z* 1127.79 for series A in Fig. 1(A). The 17-mer with dimeric oligomerization in distribution B exhibited a monoisotopic peak at *m*/*z* 1171.80 while the calculated mass is {57.06 (C_4H_7) + 17 × 54.05 ($(C_4H_6)_{17}$) + 44 (CH_2CH_2O) + 45.03 (CH_2CH_2OH) + 106.90 ($^{107}Ag^+$) = 1171.84 Da}.

The same two distributions were observed in the MALDI-TOF spectrum [Fig. 1(B)] of the product obtained



(A)

(B)

(C)

(D)

Fig. 1. Complete MALDI-TOF mass spectra (inset) and the expanded MS spectra of the products from the reaction of poly(butadienyl)lithium with 4 equiv. of ethylene oxide ([EO]/[PBDLi]). (A) In benzene after a 12 h reaction time; (B) in benzene after a 24 h reaction time; (C) in cyclohexane monitored by UV–vis; (D) in cyclohexane after a 12 h reaction time.

by the functionalization reaction of poly(butadienyl)lithium with 4 equiv. of ethylene oxide ([EO]/[PSLi]) in benzene after a reaction to time of 24 h. The intensity of the distribution B (e.g. for the 17-mer at $m/z = 1171$) increased relative to A (e.g. for 17-mer at $m/z = 1127$), indicating that as the reaction time increased, the amount of chain-end ethylene oxide oligomerization also increased. The weak, unresolved metastable peaks in Fig. 1(B) are marked by an asterisk (*). It is concluded that oligomerization of ethylene oxide does indeed take place during functionalization of poly(butadienyl)lithium with 4 equiv. of ethylene oxide under normal reaction conditions which did not produce oligomerized product in the functionalization of poly(styryl)lithium with ethylene oxide [10,16,17].

Cyclohexane was chosen as another solvent to investigate for the functionalization because it is less polar than benzene. Thus, organolithium compounds in general, and poly(butadienyl)lithium chain ends in particular, are less reactive in cyclohexane compared to benzene, presumably because they are either more associated (higher degree of aggregation) or more strongly associated (e.g. less dissociation to unassociated species) in cyclohexane compared to benzene [2,6,23]. However, oligomerization during functionalization of poly(butadienyl)lithium with ethylene oxide in cyclohexane was also detected, although to a lesser extent, after a reaction time of 12 h [see Fig. 1(D)]. The peaks for the functionalized polybutadienes with dimeric ethylene oxide, chain-end oligomerization (series B) appeared in the MALDI-TOF mass spectrum [Fig. 1(D)] at m/z 1388 for the 21-mer. The calculated monoisotopic mass is {57.06 (C_4H_7) + 21 × 54.05 ($(C_4H_6)_{21}$ + 44 (CH_2CH_2O) + 45.03 (CH_2CH_2OH) + 106.90 ($^{107}Ag^+$) = 1388.04 Da}. Therefore, changing the solvent from benzene to cyclohexane did decrease the amount of ethylene oxide oligomerization during functionalization of PBDLi with ethylene oxide; however, significant amounts of oligomerization were detectable by mass spectrometry.

In an attempt to minimize oligomerization by minimization of the reaction time, UV–vis spectroscopy was used to monitor the functionalization reaction. The solution of poly(butadienyl)lithium [M_n (SEC) = 1740 g/mol, M_w/M_n = 1.03] in cyclohexane was light yellow in color and showed an absorption at 284 nm (see Fig. 2). The light yellow color disappeared immediately after addition of ethylene oxide as did the peak at 284 nm in the UV–vis spectrum. The reaction was then immediately terminated by addition of methanol and the product was analyzed by MALDI-TOF MS and ^1H NMR. Only one major distribution (A), whose m/z values correspond to the Ag^+ adducts of PBD oligomers with C_4H_7 and CH_2CH_2OH end groups, is present in the MALDI-TOF spectrum of this product [see Fig. 1(C)]. For example, for the 21-mer of the distribution A the calculated monoisotopic mass is {57.06 (C_4H_7) + m/z 21 × 54.05 ($(C_4H_6)_{21}$ + 45.03 (CH_2CH_2OH) + 106.90 ($^{107}Ag^+$) = 1344.04 Da}, and the corresponding peak was observed at m/z 1343.87 for series A in Fig. 1(C). Dimeric oligomerization, which would have led to oligomers with one extra C_2H_4O unit (+44 Da), is absent [no m/z 1388 peak is observed in Fig. 1(C)].

The amounts of dimer formed during the functionalization reactions were determined by using MALDI MS peak heights for the isotopomers containing only ^{12}C and ^{107}Ag (from the cationizing agent) which are free of discriminating isotope effects and the least likely to include isobaric contaminants; the peak heights of the ionized 17-mers of series A and B (e.g. m/z 1128 and m/z 1172) were recorded directly from the mass spectra using software provided with the instrument and the results are shown in Table 1. The results show that the amounts of dimer formation increased as the reaction time increased and less dimer was formed in cyclohexane than in benzene at the same reaction time as expected [2,6,23].

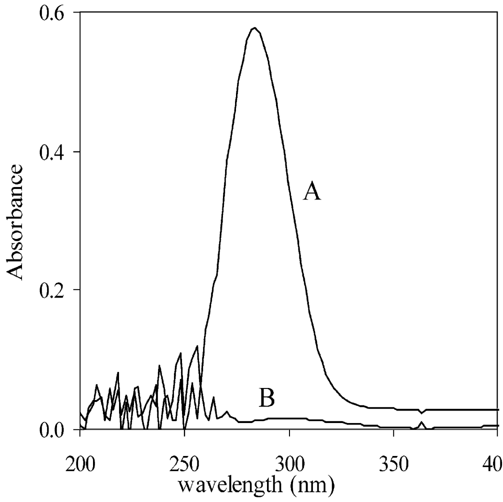


Fig. 2. UV–vis spectra of poly(butadienyl)lithium (A) and the alkoxide formed after addition of ethylene oxide; (B) for the reaction of poly(butadienyl)lithium with 4 equiv. of ethylene oxide ([EO]/[PBDLi]) in cyclohexane.

^1H NMR is another method which was used previously to investigate dimer formation during the functionalization reaction of poly(styryl)lithium with ethylene oxide (see Fig. 3) [16]. The calculated chemical shifts for the protons at the chain ends for monoaddition and oligomer are shown in Scheme 1.

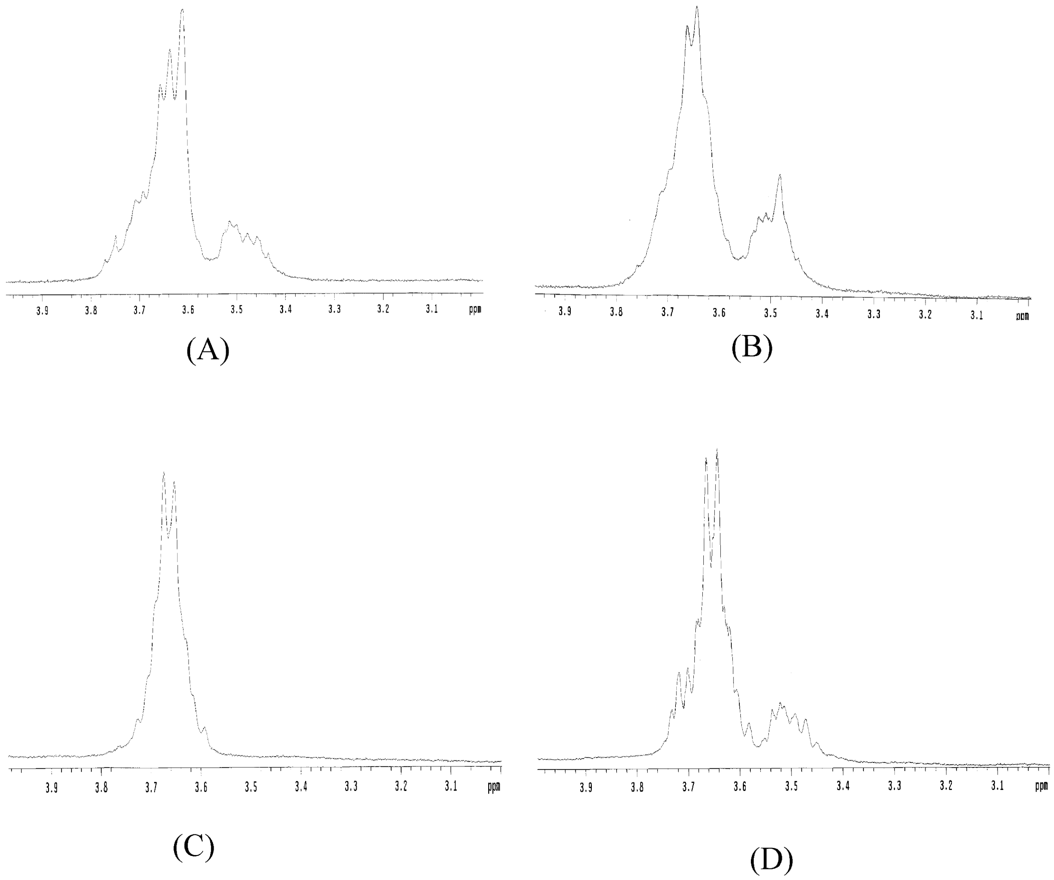
In the expanded ^1H NMR spectrum of sample 3 [Fig. 3(C)], which is the monoaddition sample as determined by mass spectral analysis [see Fig. 1(C)], only one broad peak is observed at δ 3.65 ppm corresponding to the terminal methylene protons (a in Scheme 1). It was predicted from the calculation results shown in Scheme 1 that three peaks at around δ 3.37, 3.56 and 3.7 ppm should be observed in the ^1H NMR spectrum of the dimeric ethylene oxide oligomer. However, only two broad peaks centered at δ 3.65 and 3.48 ppm are present in the ^1H NMR spectrum [see Fig. 3(A), (B) and (D)] of samples 1,2 and 4 which contained detectable amounts of dimeric oligomerization products as determined by mass spectrometry (see Fig. 1). Based on the calculations, the resonances centered at about δ 3.48 ppm are assigned to the methylene protons labeled b in Scheme 1. The peaks centered at about δ 3.65 ppm for these three samples are broader compared to those of sample 3 and exhibit shoulders on the higher chemical shift side of this peak. Based on these observations and the predicted chemical shifts, it was concluded that the peaks for the methylene protons bonded to the hydroxyl group (d in Scheme 1) in the oligomer and the adjacent methylene group (c in Scheme 1) are overlapped with the methylene peak for the monoaddition peak centered at δ 3.65 ppm. If x corresponds to the number moles of monoaddition product and y corresponds to the number of moles of diaddition product, then the areas of the peaks centered at 3.65 ppm

Table 1
Ethylene oxide oligomerization during functionalization of poly(butadienyl)lithium using MALDI-TOF MS and ^1H NMR

Reaction time	Solvent	Dimer (wt%) (MALDI-TOF MS)[a]	Dimer (wt%) (^1H NMR)[b]
12 h (Sample 1)	Benzene	11	14
24 h (Sample 2)	Benzene	16	17
1 min (Sample 3)	Cyclohexane	0.0	0.0
12 h (Sample 4)	Cyclohexane	7.6	6.5

[a] Ratio of ^{12}C peak heights; m/z = 1172 (dimer) and m/z = 1128 (monoaddition).

[b] Ratio of peak areas from integration.



(A)

(B)

(C)

(D)

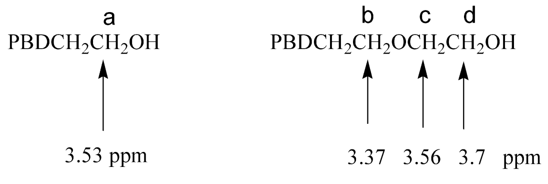
Fig. 3. The expanded ^{1}H NMR spectra of the products from the reaction of poly(butadienyl)lithium with 4 equiv. of ethylene oxide ([EO]/[PBDLi]). (A) In benzene after a 12 h reaction time; (B) in benzene after a 24 h reaction time; (C) in cyclohexane monitored by UV–vis; (D) in cyclohexane after a 12 h reaction time.

(labeled as A) and at 3.48 ppm (labeled as B) can be used to calculate the relative number of moles of diaddition product as shown in the following equation. The results of these calculations are shown in column four of Table 1 for comparison with the corresponding

$$\text{Mole\%diaddition} = 100[y/(x+y)] = 100[B/(A-B)]$$

quantitative results obtained by mass spectrometry shown in column three. These results show reasonable agreement between the ^{1}H NMR results and the MALDI MS results within ± 15%, and they show the same trends of amounts of dimer formation for different reactions.

The results reported herein and also previously reported by Mays and coworkers [17] are unexpected. In general, the reactivity of a functional group, e.g. the polymeric lithium alkoxide end group, does not depend on the nature of the backbone chain. However, it is obvious that a lithium alkoxide connected to a polybutadiene backbone is more reactive with respect to ethylene oxide oligomerization than is an analogous lithium alkoxide group attached to a polystyrene backbone. The general lack of reactivity of lithium alkoxides with respect to polymerization of ethylene oxide has been attributed to formation of aggregated chain ends that do not dissociate significantly to form the reactive, unassociated lithium alkoxide groups [14,15]. It is known that dissociation of organolithium chain ends is promoted by Lewis bases and that the degree of aggregation is sensitive to the steric requirements of the groups attached to lithium [2]. Thus, this unexpected phenomenon may be related to the degree of aggregation of the chain ends, the steric environment around the chain ends, and/or the ability of the chain ends to interact with the strong Lewis base, ethylene oxide. The absence of kinetic data for these processes limits any further explanation to the category of mere speculation.



$$\overset{a}{\text{PBDCH}_2\text{CH}_2\text{OH}} \qquad \text{PBDCH}_2\overset{b}{\text{CH}_2}\text{OCH}_2\overset{c}{\text{CH}_2}\overset{d}{\text{OH}}$$

Scheme 1.

4. Conclusions

The extent of oligomerization of ethylene oxide during the functionalization of poly(butadienyl)lithium was investigated by MALDI-TOF MS and ^{1}H NMR. Contrary to expectations, it was confirmed that dimeric ethylene oxide oligomerization products were formed during the functionalization reaction of poly(butadienyl)lithium with 4 equiv. of ethylene oxide in benzene and cyclohexane for a 12 h reaction time. The amount of dimeric oligomer product increased with increasing reaction time in both solvents as determined by MALDI-TOF MS and ^{1}H NMR. The oligomerization can be avoided if the reaction time is short, i.e. minutes instead of hours.

Acknowledgements

The authors are grateful to the FMC, Lithium Division, for providing samples of *sec*-BuLi and to Dynasol and Sartomer for financial support.

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