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Investigation of Ethylene Oxide Oligomerization during Functionalization of Poly(styryl)lithium Using MALDI−TOF MS and NMR

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ABSTRACT: The amount of ethylene oxide oligomerization for functionalization of poly(styryl)lithium in benzene at 25 °C has been determined using MALDI−TOF MS and ^{1}H and ^{13}C NMR. Chemically insignificant amounts of oligomer were found using 4 equiv of ethylene oxide ([EO]/[PLi]) after 12 h. For reactions times ranging from 12 h to 4 weeks using 10 equiv of ethylene oxide, the corresponding amounts of dimeric oligomerization varied from 4% to 34%. Trimeric oligomerization of ethylene oxide was detected after 1 week (1%) and 4 weeks (4%) by MALDI−TOF MS. The quantitative results from MALDI−TOF MS were in good agreement with results from both ^{1}H and ^{13}C NMR analyses. The quantitative aspects of MALDI−TOF MS compared to ^{1}H and ^{13}C NMR for the determination of the amount of EO oligomerization have been established through the synthesis and characterization of the model dimeric oligomer product, ω-(2-(2-hydroxyethoxy)ethyl)polystyrene.

Introduction

Synthesis of functional polymers is important for numerous applications, including colloidal stabilization, dispersion of fillers and synthesis of new block copolymers.[1−3] Living anionic polymerization provides a useful methodology for synthesis of a wide range of functionalized polymers with well-defined structures and low degrees of compositional heterogeneity.[4,5] Post-polymerization reactions of living anionic chain ends with electrophiles form the corresponding ω-functionalized polymers. Of particular importance is the synthesis of hydroxyl-functionalized polymers. ω-Hydroxy-functionalized polymers can be obtained by the reaction of polymeric organolithiums with ethylene oxide. This reaction is well-known in the literature and has been reported to give quantitative yields without detectable amounts of oligomerization in the absence of polar additives.[6] The prevailing wisdom has been that lithium alkoxides are unable to oligomerize ethylene oxide due to the unreactivity of the chain ends.[7] The apparent unreactivity of the chain ends is presumed to result from the high degree of aggregation of lithium alkoxides, even in a polar medium,[8] and the strength of the association.[9] Sodium and potassium alkoxides are also highly aggregated but will effect the polymerization of ethylene oxide.[10] Recently, a small amount of oligomer, which was previously not observed by ^{13}C NMR, was detected by matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS).[11] MALDI−TOF MS can detect small quantities of polymeric products that are not detected by ^{1}H and ^{13}C NMR and it is ideal for the detection of very small amounts of oligomerization.[11−13] This initial discovery of ethylene oxide oligomerization during functionalization of polymeric organolithium compounds has not been previously reported and has prompted a more thorough investigation into the effect of time and ethylene oxide concentration on oligomerization for the hydroxyethylation of polymeric organolithiums in hydrocarbon solution. Herein is reported a quantitative study by MALDI−TOF MS and NMR (^{1}H and ^{13}C) of ethylene oxide oligomerization during functionalization of poly(styryl)lithium in benzene.

Experimental Section

Materials. Benzene (Certified ACS, Fisher Scientific) and styrene (99%, Aldrich) were purified as described previously.[14] As needed, benzene was distilled directly from poly(styryl)lithium into polymerization reactors. Ethylene oxide (99+ %, Aldrich) was dried sequentially over CaH_2 and Bu_2Mg according to known procedures before being distilled into glass ampules.[6] *sec*-Butyllithium was used as received from FMC, Lithium Division, and the concentration was determined by the Gilman double titration method using allyl bromide.[15] The polymerizations were carried out in all-glass reactors using standard high-vacuum techniques.[16] Di(ethylene glycol) di-*p*-tosylate (98%, Aldrich) was used as received.

Characterization. Size exclusion chromatography (SEC) was performed using a Waters 150-C Plus instrument equipped with a differential refractometer, a viscosity detector (Viscotek model 150R) and four Phenomenex Phenogel columns (500, 10^3, 10^4, and 10^5 Å). The SEC analysis was run at 30 °C in THF at a flow rate of 0.5 mL/min after calibration with polystyrene standards (Polymer Laboratories). The concentration of polystyrene ($M_n = 2100-2400$ g/mol) used for SEC analysis was 6−8 mg/mL. ^{1}H (300 MHz, 500−1000 scans) and ^{13}C (quantitative reverse-gated decoupled spectra taken after 7500 scans at 400 MHz with $d_1 = 6$ s; routine spectra taken after 30 000 scans at 300 MHz) NMR spectra were recorded in $CDCl_3$ (99.8% D, Cambridge Isotope Laboratories) on Varian Mercury 300 and 400 MHz spectrometers, respectively, at room temperature. The NMR sample concentrations were 10 to 20 wt %.

Mass Spectroscopy. The mass spectra were acquired using a Bruker REFLEX-III time-of-flight (TOF) mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with a 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. Mass spectra were obtained in linear and reflector mode. Solutions of dithranol (20 mg/

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mL), end-functional polymer (10 mg/mL), and silver trifluoroacetate (10 mg/mL) were made in tetrahydorfuran (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 70%. 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.

Synthesis of Hydroxy-Functionalized Polystyrene (10 equiv of EO). Polymerization of styrene (6.15 mL) was initated with *sec*-BuLi (1.86 mL, 2.8 mmol) in benzene (65 mL). The resulting poly(styryl)lithium (M_n = 2300 g/mol, M_w/M_n = 1.01, 2.8 mmol) was split into four side ampules. The ampules were sealed with a hand torch, and 10 equiv of ethylene oxide in benzene (5−6 mL) was added and allowed to react for different time periods. The first ampule was quenched with degassed methanol after 12 h, the second after 1 week, and the third after 4 weeks. The polymers were precipitated into methanol, filtered and dried overnight in a vacuum oven. The yield of polymer was > 99%.

Synthesis of Hydroxy-Functionalized Polystyrene (4 equiv of EO). Styrene (6.6 mL) was initiated with *sec*-BuLi (2.1 mL, 3.0 mmol, 1.43 M) in benzene (65 mL). The resulting poly(styryl)lithium (M_n = 2400 g/mol, M_w/M_n = 1.04, 3.0 mmol) was functionalized by the addition of ethylene oxide (0.60 mL, 12 mmol, in 7 mL of benzene) for 12 h. The reaction was quenched with degassed methanol (0.5 mL) and the polymer was precipitated in methanol, filtered, and dried overnight in a vacuum oven. The polymer yield was > 99%.

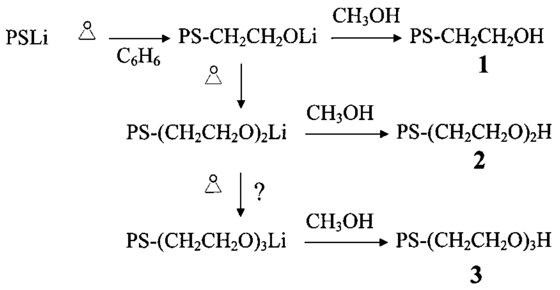
Synthesis of Hydroxy-Functionalized Polystyrene (10 equiv of EO) and ω-[2-(2-Tosyloxyethoxy)ethyl]polystyrene. Styrene (10.0 mL) was initiated with *sec*-BuLi (3.18 mL, 5.0 mmol) in benzene (114 mL). The resulting poly(styryl)lithium (M_n = 2100 g/mol, M_w/M_n = 1.04, 5.0 mmol) was split into several ampules. The first ampule containing PSLi (14.5 mL, 0.7 mmol) was treated with ethylene oxide (0.31 mL, 10 equiv) in benzene (5 mL) for 12 h before quenching with methanol. The second ampule (22 mL, 0.88 mmol) was taken into the drybox and added to di(ethylene glycol) di-*p*-tosylate (50 equiv, 18.2 g, 44 mmol). After 1 h, the resulting ω-[2-(2-tosyloxyethoxy)ethyl]polystyrene was precipitated into methanol, filtered, and dried.

Deprotection of ω-[2-(2-Tosyloxyethoxy)ethyl]polystyrene. ω-[2-(2-Tosyloxyethoxy)ethyl]polystyrene (1.0 g, 0.48 mmol) in THF (7 mL) was added dropwise to sodium naphthalide (8.0 mmol) in THF (27 mL). The sodium naphthalide was prepared by adding sodium metal (0.21 g, 9.1 mmol) and naphthalene (1.2 g, 9.5 mmol) to anhydrous THF (30 mL) and stirring for 2 h. After quenching with deionized water (0.1 mL) the polymer was precipitated into MeOH, filtered and dried in a vacuum oven. The resulting $PSCH_2CH_2OCH_2CH_2OH$ was purified by silica gel column chromatography using toluene as the first eluent and then THF.

Results and Discussion

The reaction of polymeric organolithium compounds with excess ethylene oxide (4 equiv) is a quantitative functionalization reaction (> 99% yield) in hydrocarbon solution at room temperature as shown in Scheme 1.[6] The reaction is completed in a matter of minutes, but the mixture is often allowed to react for periods up to 12 h. Quantitative functionalization has been established by a combination of thin-layer chromatography (<1% nonfunctional polymer) and analysis by ^1H and ^{13}C NMR spectroscopy. The absence of any oligomerization products was deduced from ^{13}C NMR spectroscopy, calculated ^{13}C chemical shifts for oligomeric products, and model compounds. Thus, in the ^{13}C NMR spectrum of the functionalization products, no resonances are observed at δ = 69.5 and 71.8 ppm, as expected for the corresponding dimeric oligomer product (**4**) as shown in Scheme 2. When ω-hydroxyethylpolystyrene was prepared using ^{13}C-labeled ethylene oxide ([^{13}C-ethylene oxide]/[PSLi] = 3.3), the ^{13}C spectrum of the functionalized polystyrene (M_n = 2000 g/mol) exhibited a doublet at δ = 61 ppm and no peaks at δ = 69.5 or 71.8 ppm.[17]

Scheme 1. Functionalization of Polymeric Organolithiums with Ethylene Oxide



Scheme 2. Synthesis of ω-[2-(2-hydroxyethoxy)ethyl]polystyrene

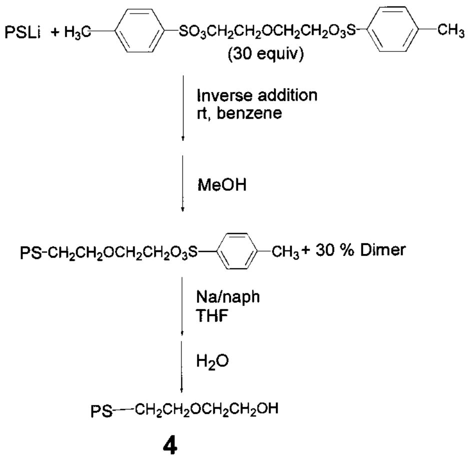


Table 1. Degree of Aggregation for Alkali Metal Alkoxides[8,9]

	cyclohexane	benzene	diethyl ether	THF	Py[b]
lithium *tert*-butoxide	5.8	6.2, 6.06[a]	5.9	4.1	4.0
sodium *tert*-butoxide	8.2	8.3	4.3	3.9	3.9
potassium *tert*-butoxide			3.9	4.0	

[a] See ref 9. [b] Pyridine.

Since ethylene oxide has an exothermic enthalpy of polymerization similar to cyclopropane and it is readily polymerizable using a variety of other alkali-metal alkoxides,[10] the unreactivity of lithium alkoxides as ethylene oxide polymerization initiators is surprising. High degrees of aggregation for lithium alkoxides even in polar solvents as shown in Table 1[8,9] contribute to the unreactivity of lithium salts. As seen in Table 1, sodium and potassium alkoxides are also highly aggregated, but they effect polymerization of ethylene oxide.[10] Evidently, the strength of aggregation for lithium alkoxides is the main contributor to their unreactivity. Mass spectrometry results for lithium *t*-butoxides show that the hexamer is the only species present to any significant extent.[9] The high stability of the hexamer is evident from the fact that large increases in ionizing potential (eV) were required to observe fragmentation to lower degrees of aggregation.[9] The strength and degree of aggregation of lithium alkoxides can be altered by the addition of Lewis bases. Polar

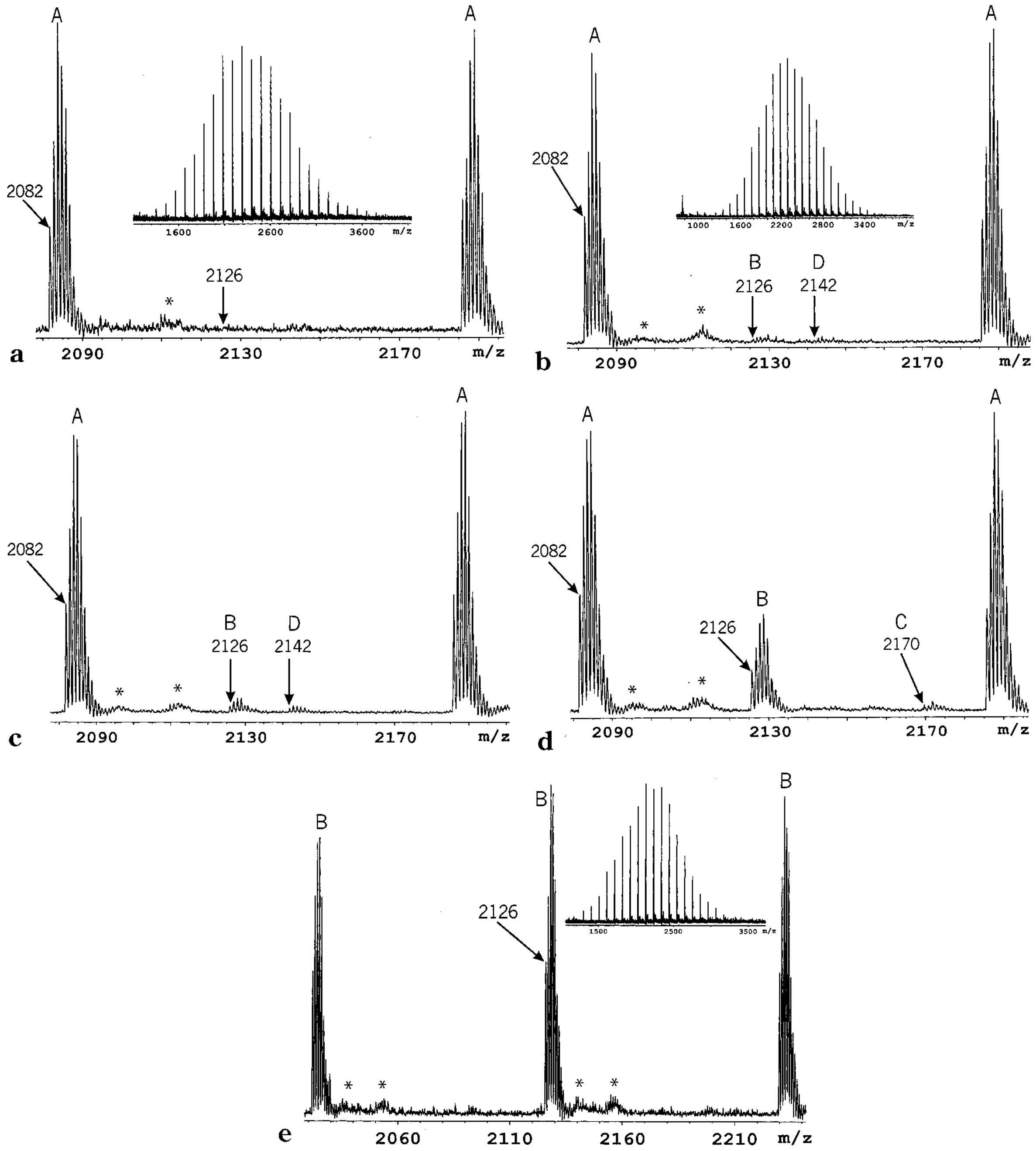


Figure 1. (a) MALDI−TOF mass spectrum of the product from the reaction of poly(styryl)lithium with 4 equiv of ethylene oxide ([EO]/[PSLi]) after a 12 h reaction time. (b) MALDI−TOF mass spectrum of the product from the reaction of poly(styryl)lithium with 10 equiv of ethylene oxide ([EO]/[PSLi]) after a 12 h reaction time. (c) MALDI−TOF mass spectrum of the product from the reaction of poly(styryl)lithium with 10 equiv of ethylene oxide ([EO]/[PSLi]) after a reaction time of 1 week. (d) MALDI−TOF mass spectrum of the product from the reaction of poly(styryl)lithium with 10 equiv of ethylene oxide ([EO]/[PSLi]) after a reaction time of 4 weeks. (e) MALDI−TOF mass spectrum of the model dimeric oligomer (**4**).

additives such as dimethyl sulfoxide (DMSO)[7,18] and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) will complex lithium and promote the dissociation of lithium alkoxides necessary for oligomerization and polymerization. Since ethylene oxide is expected to act as a stronger Lewis base than tetrahydrofuran (THF),[19] increasing the amount of ethylene oxide relative to the concentration of chain ends would be expected to promote oligomerization.

Typically, functionalization reaction products are characterized by end-group titration, size-exclusion chromatography (SEC), vapor phase osmometry, thin-layer chromatography (TLC), NMR, and FTIR.[1] However, the subtleties of ethylene oxide oligomerization are not detectable by routine methods such as end-group titration, size-exclusion chromatography (SEC), vapor phase osmometry, and thin-layer chromatography (TLC). As a result, a technique such as MALDI−TOF mass spectrometry was necessary to detect not only minute amounts of side-products but also small changes in mass in order to investigate ethylene oxide oligomerization as a function of time and amount of ethylene oxide ([EO]/[PSLi]).

MALDI−TOF mass spectrometry is an ideal technique for the detection of extremely small quantities of side reaction products.[11−13] MALDI MS is many thousands of times more sensitive than ^{1}H NMR. Under the MALDI conditions used, polystyrene (PS) oligomers (M)

Table 2. Calculated Mass-to-Charge (*M/z*) Ratios of PS Oligomers Appearing in the *M/z* 2050−2200 Range of the MALDI−TOF Mass Spectrum (Experimental Uncertainty ± = 0.05 %)

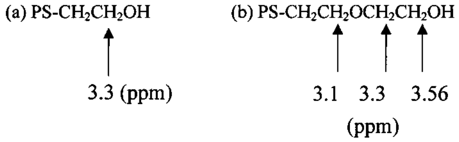
	$Bu(C_8H_8)_{19}H(Ag^+)$	$Bu(C_8H_8)_{18}CH_2CH_2OH(Ag^+)$	$Bu(C_8H_8)_{18}(CH_2CH_2O)_2H(Ag^+)$	$Bu(C_8H_8)_{18}(CH_2CH_2O)_3H(Ag^+)$
m/z (calcd)	2142.2	2082.1	2126.2	2170.2
m/z (obsd)	2141.8	2081.8	2125.8	2169.7

are ionized to $[M + Ag]^+$ ions. The mass spectrum obtained from the product of the reaction of poly(styryl)lithium ($M_n = 2000$ g/mol) with 4 equiv of ethylene oxide ([EO]/[PSLi]) after a reaction to time of 12 h is shown in Figure 1a. It contains one major distribution (A), whose *m/z* values correspond to the Ag^+ adducts of PS oligomers with C_4H_7 and CH_2CH_2OH end groups (Table 2). For example, the 18-mer of this distribution is expected to produce a signal at *m/z* $18 \times 104.06\ (C_8H_8)_{18} + 57.06\ (C_4H_7) + 45.03\ (CH_2CH_2OH) + 106.90\ (^{107}Ag^+) = 2082$, as indeed is observed. Dimeric oligomerization, which would have led to oligomers with one extra C_2H_4O unit (+44 Da), is absent (no *m/z* 2126 detected in Figure 1a). The presence of weak, unresolved peaks is noticed in Figure 1a (marked by ∗). Such broad signals are mainly due to fragments of $[M + Ag]^+$, generated either in the ion source or in the flight tube of the mass spectrometer; they can readily be distinguished from actual product signals because (a) they are broad, (b) they disappear or diminish upon detection in linear TOF mode,[20] and (c) their abundance is strongly dependent on laser power.

It was found that as the reaction time increased or the amount of ethylene oxide increased ([EO]/[PSLi]), the amount of oligomerization also increased. The MALDI−TOF mass spectrum of the product of the functionalization using 10 equiv of EO and a reaction time of 12 h (Figure 1b) clearly shows a second distribution, B, besides the main series A. The oligomers of series B appear at 44 Da higher than those of series A, as shown for the 18-mers in Figure 1b (*m/z* 2126 vs 2082), consistent with incorporation of two ethylene oxide units in products B (see Table 2). As the functionalization time increased to 1 week (Figure 1c), distribution B markedly increased in intensity relative to A (cf. *m/z* 2126 vs 2082) and a further, more dramatic increase was seen after 4 weeks (Figure 1d). In fact, after 4 weeks, an additional product distribution (C) appears, corresponding to the incorporation of three EO units at the ω-end; the 18-mer of series C can be seen at *m/z* 2170 in Figure 1d (see Table 2). Finally, traces of ω-unfunctionalized polymer are sometimes observed (series D), most notably in Figure 1c; this minor product presumably results from adventitious protic termination during functionalization.

To better characterize the extent of oligomerization, a model oligomer of polystyrene with two terminal ethylene oxide units (**4**) was synthesized as outlined in Scheme 2. Characterization of the model oligomer was expected to more conclusively establish peak assignments and to help correlate NMR and MALDI MS results. Poly(styryl)lithium ($M_n = 2100$ g/mol) in benzene was added to excess di(ethylene glycol) di-*p*-tosylate to prepare the model compound. After deprotection of the model oligomer and purification by column chromatography, no dimer or unfunctionalized polymer was detected by MALDI MS (only distribution B in Figure 1e). The model oligomer, **4**, (shown in Scheme 2) exhibited a peak at *m/z* 2126 (Figure 1e) that corresponds exactly to the peak (*m/z* 2126) that increased in intensity with increasing reaction time as shown in Figure 1, parts b−d and that was assigned to the dimeric oligomerization product (**2**).

Scheme 3. Assignment of ^1H NMR Peaks for Monoaddition (a) and Oligomer (b)



Although oligomerization was detected by MALDI−TOF MS, it was of interest to determine whether chemically significant amounts of oligomerization products could also be detected by conventional NMR methods (^1H and ^{13}C). For this purpose, the NMR spectra of the model dimeric oligomer, **4**, were compared with NMR spectra for ethylene oxide oligomerization reactions utilizing various amounts of ethylene oxide ([EO]/[PLi]) with reaction times ranging from 12 h to 4 weeks. The ^1H NMR resonance for the hydrogens on the methylene carbon bonded to the hydroxyl group for monoaddition (**1**) is observed at 3.3 ppm (Figure 2a) and the hydrogens on the methylene carbon next to the hydroxyl group for the dimeric model oligomer (**4**) come at 3.56 ppm (Figure 2e). On the basis of the absence of ^1H NMR resonances at $\delta = 3.56$ ppm, EO oligomerization was not observed by ^1H NMR (Figure 2a) for reaction of poly(styryl)lithium with 4 equiv of EO after a reaction time of 12 h. However, when the amount of ethylene oxide was increased ([EO]/[PLi]) to 10 equiv, the ^1H NMR spectrum of the products showed a small peak at 3.56 ppm (Figure 2b) after 12 h. This peak increased in intensity in the ^1H NMR spectra of functionalized polystyrenes obtained with increasing reaction times as shown in Figure 2, parts c (1 week) and d (4 week). Thus, from the ^1H NMR assignments of the functionalization products obtained using 10 equivalents of ethylene oxide, it is clear that ethylene oxide oligomerization can be detected by ^1H NMR.

The ^1H NMR results provided an opportunity to determine whether the amounts of oligomeric product determined by ^1H NMR correlate with the amounts determined by MALDI−TOF MS. ^1H NMR results for ω-[2-(2-hydroxyethoxy)ethyl]polystyrene (Scheme 2) also show that the peak at 3.3 ppm (Figure 2, parts b−d) has a contribution from the dimeric end group. When the amount of dimer was calculated from ^1H NMR peak areas, the peak area at 3.3 ppm for the CH_2OH group of the monoaddition product was adjusted by subtracting the contribution to this peak area from this dimeric oligomer (see Scheme 3 and Figure 2, parts b and e). Since the integration of the peak areas in Figure 2e for the three methylene groups are equivalent, the oligomer contribution at 3.3 ppm is the same as the peak area at 3.56 ppm. The peak at ca. 3.7 ppm, as seen in Figure 2d, is assumed to result from oligomer groups with three or more EO units; this peak is absent for the model of the dimeric oligomer functionalization product **(4)**. These results are compared to the amounts of dimer determined by using MALDI MS peak heights, as shown in Table 3. The peak heights of the ionized 18-mers of

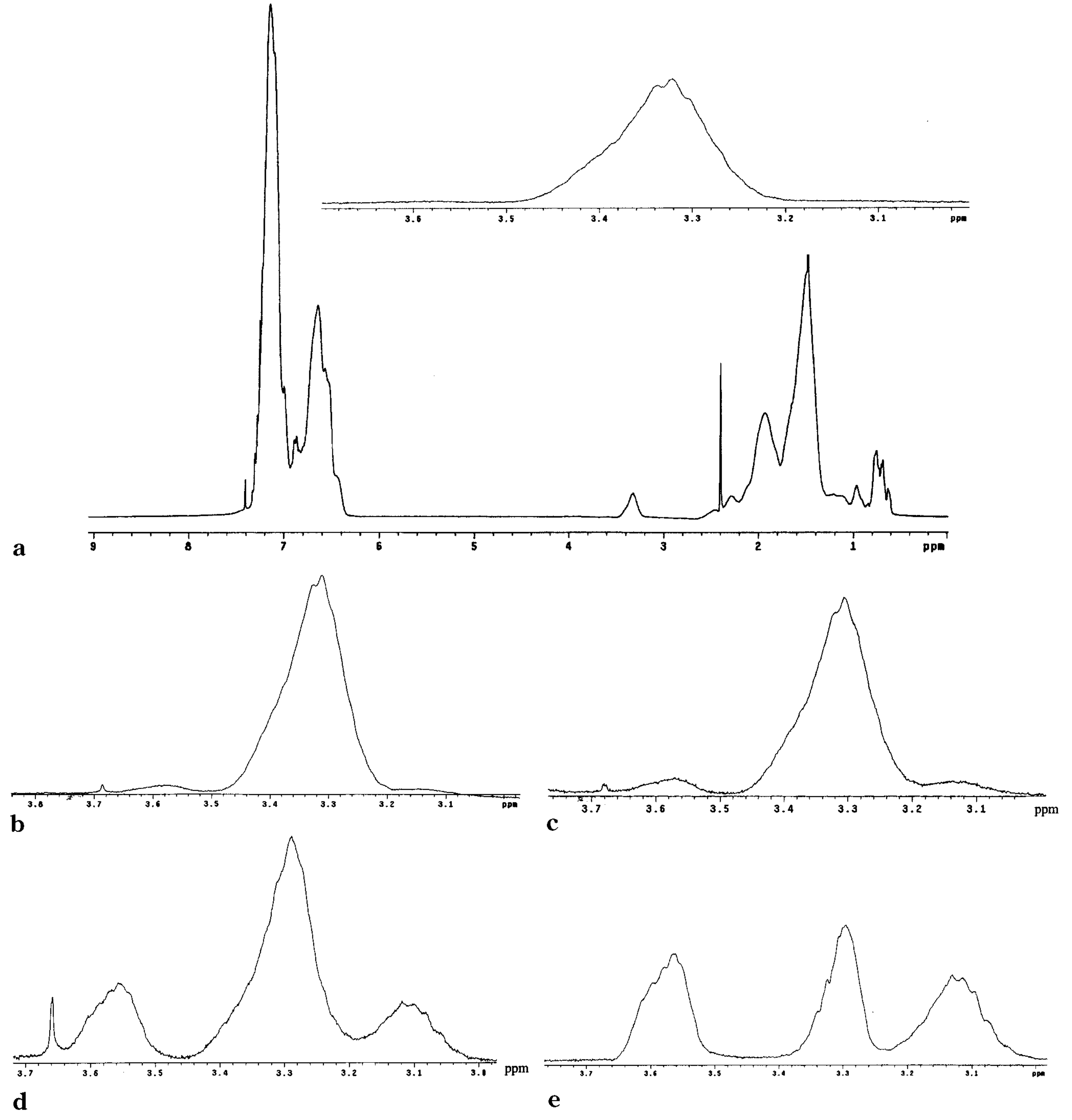


Figure 2. (a) ^{1}H NMR spectrum of the product from the reaction of poly(styryl)lithium with 4 equiv of ethylene oxide ([EO]/[PSLi]) after a reaction time of 12 h. (b) ^{1}H NMR spectrum of the product from the reaction of poly(styryl)lithium with 10 equiv of ethylene oxide ([EO]/[PSLi]) after a reaction time of 12 h. (c)^{1}H NMR spectrum of the product from the reaction of poly(styryl)-lithium with 10 equiv of ethylene oxide ([EO]/[PSLi]) after a reaction time of 1 week. (d) ^{1}H NMR spectrum of the product from the functionalization reaction using 10 equiv of ethylene oxide ([EO]/[PSLi]) and a reaction time of 4 weeks. (e)^{1}H NMR spectrum of the model dimeric oligomer (**4**).

series A and B (displayed in the expanded traces of Figure 1) were recorded directly from the mass spectra using software provided with the instrument. Note that the MALDI MS peaks used (*m/z* 2126 and *m/z* 2082) are 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 ^{1}H NMR results correlate well with the MALDI MS results within experimental error (±1%).

The ^{13}C NMR spectrum of the model polymeric oligomer (**4**) exhibits a peak at $\delta = 62.0$ ppm and shows no peak at $\delta = 61.3$ ppm [Figure 3b(3)]. The ^{13}C NMR spectrum for the hydroxy-functionalized polystyrene prepared using 10 equiv of ethylene oxide and a 12 h reaction time does not show evidence of oligomerization at either $\delta = 69.3$ or 71.9 ppm (Figure 3a). As expected, routine ^{13}C NMR (300 MHz) is not as sensitive as either MALDI MS or ^{1}H NMR (300 MHz) for the determination of the extent of oligomerization, since oligomerization

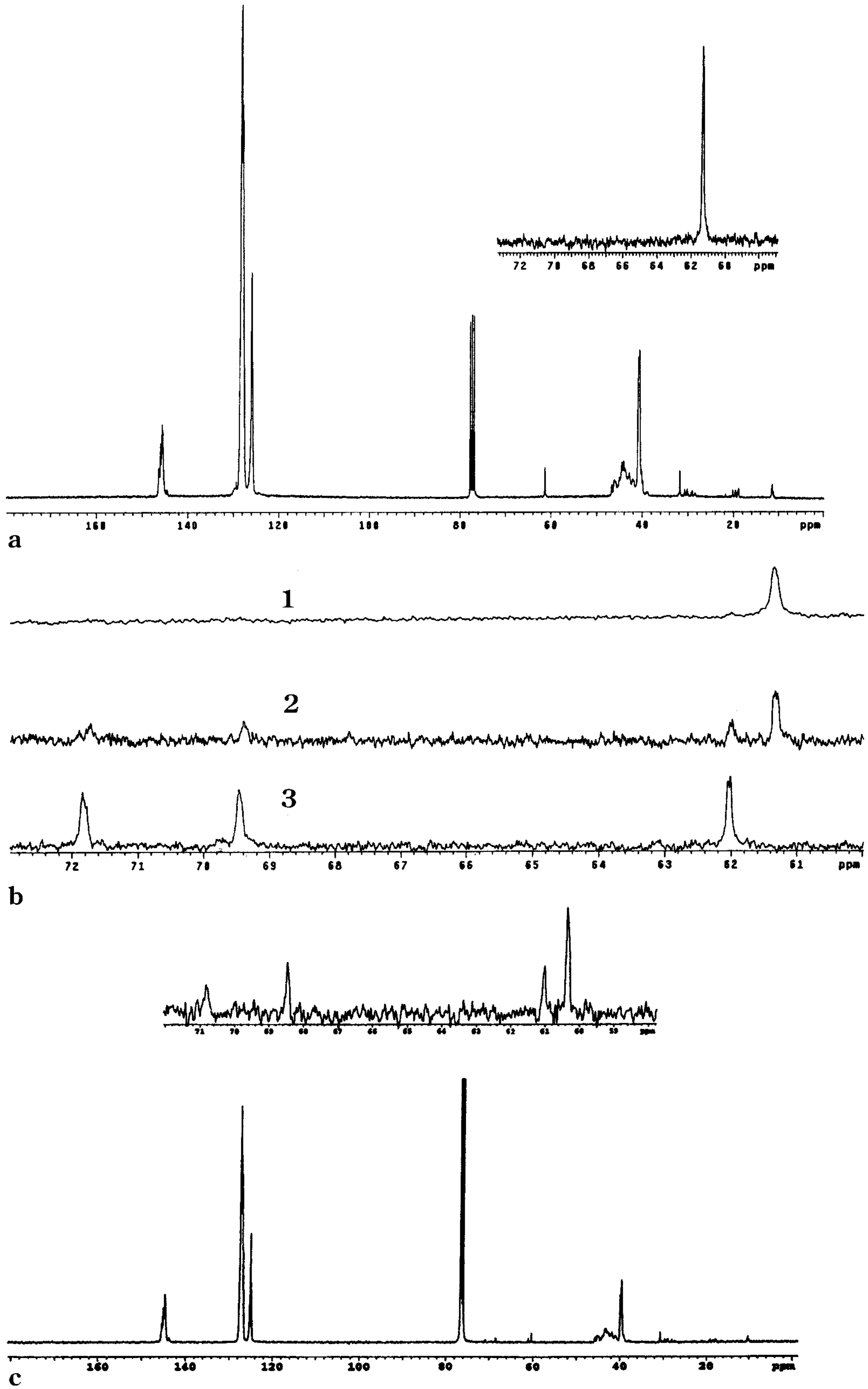


Figure 3. (a) ^{13}C NMR spectrum of the product from the reaction of poly(styryl)lithium with 10 equiv of ethylene oxide ([EO]/[PSLi]) after a reaction time of 12 h. (b) ^{13}C NMR spectra of the products from the reaction of poly(styryl)lithium with 10 equiv of ethylene oxide ([EO]/[PSLi]) after (1) 1 and (2) 4 weeks and (3) of the model dimeric oligomer (**4**). (c) ^{13}C NMR (400 MHz) quantitative ($d_1 = 6$ s) spectrum of the product from the reaction of poly(styryl)lithium with 10 equiv of ethylene oxide ([EO]/[PSLi]) after a reaction time of 4 weeks.

was detected by these techniques for this sample. The lack of oligomerization for experiments with 4 equiv of ethylene oxide as probed by ^{13}C NMR has also been documented using ^{13}C-labeled ethylene oxide. No oligomerization was detected using 4 equiv of ^{13}C-labeled ethylene oxide (98 atom %) after 12 h.[6] The ^{13}C overlay

Table 3. Oligomerization Comparison Using ^{1}H NMR and MALDI−TOF MS

reaction time	dimer (wt %) (^{1}H NMR)[a]	dimer (wt %) (MALDI−TOF MS)[b]	trimer (wt %) (MALDI−TOF MS)[c]
12 h (sample 1)	3.7	3.4	-
12 h (sample 2)	3.4	3.6	-
1 week (sample 3)	5.5	4.9	1.0
4 week (sample 4)	33	35	5.0

[a] Ratio of peak areas from integration. [b] Ratio of ^{12}C peak heights; $m/z = 2126$ (dimer) and $m/z = 2082$ (monoaddition). [c] Ratio of ^{12}C peak heights; $m/z = 2170$ (trimer) and $m/z = 2082$ (monoaddition).

in Figure 3b shows the spectra for reaction times of 1 (10 equiv) and 4 weeks (10 equiv) and for the model dimeric oligomer product (see Scheme 2). As time increased, additional ^{13}C NMR peaks are seen that correlate with the model dimeric ethylene oxide oligomer at $\delta = 62.0$, 69.3, and 71.9 ppm. The ^{13}C NMR peak at $\delta = 61.3$ ppm corresponds to the monoaddition product. The small ^{13}C NMR peak at $\delta = 62.0$ ppm for products from a reaction time of 1 week increased in intensity from the 4 week reaction time indicating an increase in the amount of oligomerization. The reverse-gated decoupled ^{13}C spectrum shown in Figure 3c shows that the peak at $\delta = 61.3$ ppm has increased in intensity for the products obtained after 4 weeks relative to the product from the 1 week reaction. Since the reverse-gated decoupled ^{13}C spectrum was obtained with a sufficiently large relaxation delay time ($d_1 = 6$ s), quantitative information can be obtained. On the basis of the peak areas at $\delta = 62.0$ and 61.3 ppm, the extent of dimeric oligomerization was calculated to be 38% for the 4 week reaction time. This amount of dimeric oligomerization agrees well with values from Table 2 for MALDI MS (35%) and ^{1}H NMR (33%).

Conclusion

To our knowledge this is the first report of a quantitative MALDI−TOF MS study for polymer chain-end functionalization chemistry. This investigation is the first instance where quantitative results from MALDI−TOF MS have been correlated with other spectroscopic methods. MALDI MS, ^{13}C and ^{1}H NMR have provided consistent quantitative data in good agreement which suggests that no chemically significant amounts of oligomerization are detected for the functionalization of poly(styryl)lithium in benzene for 3−4 equiv of ethylene oxide after a 12 h reaction time, i.e., under normal functionalization conditions. Oligomerization was detectable by MALDI MS, ^{13}C NMR, and ^{1}H NMR as the amount of ethylene oxide increased ([EO]/[PLi]) to 10 equiv and as the reaction time increased from 12 h to 4 weeks. Thus, longer reaction times and larger excesses of ethylene oxide should be avoided to prepare pure ω-hydroxyethylated functionalization products.

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