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Carbonation and Related Reactions of Poly(styryl)lithium

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ABSTRACT: The carbonation of polymeric organolithium compounds using carbon dioxide has been studied by a combination of acid titration, size-exclusion and thin-layer chromatography, and infrared and ultraviolet spectral analysis. In hydrocarbon solution, the hydrolysis products of this reaction were the carboxylated polymer, the corresponding ketone (dimer) and alcohol (trimer). In general, the addition of a Lewis base (e.g., tetrahydrofuran) was found to attenuate the yield of the dimeric and trimeric products. However, the total elimination of these higher molecular weight products was accomplished by the carbonation of freeze-dried material where the active centers were complexed with one or two molecules of *N,N,N′,N′*-tetramethylethylenediamine.

Introduction

Alkyllithium-initiated anionic polymerizations of certain monomers can be performed without the incursion of spontaneous termination or chain-transfer reactions.[1-4] When suitable initiators and procedures are used, these polymerizations yield polymers with predictable molecular weights and narrow molecular weight distributions.[1] Because of the absence of termination and chain-transfer reactions, these polymerizations generate stable, carbanionic chain ends which allow controlled termination reactions to be effected.[2] In principal, chains with a variety of functional groups at one or both ends can be prepared.[5] However, many of the reported examples of anionic chain-end functionalizations have not been well characterized.[2]

The carbonation of polymeric carbanions using carbon dioxide is one of the most useful and widely used functionalization reactions.[2] However, there are special problems associated with the simple carbonation of polymeric organolithium compounds. For example, it has been reported that the resulting carboxylated polymer is contaminated with significant amounts of the corresponding ketone (dimer) and tertiary alcohol (trimer) as shown in eq 1.[6,7]

$$\mathrm{PLi} \xrightarrow{\mathrm{CO_2}} \xrightarrow{\mathrm{H_3O^+}} \mathrm{PCO_2H} + \mathrm{P_2CO} + \mathrm{P_3COH} \tag{1}$$

We previously reported results of a study of the carbonation of polymeric organolithium compounds using high vacuum techniques and high-purity, gaseous carbon dioxide.[8] Carbonations of poly(styryl)lithium, poly(isoprenyl)lithium, and poly(styrene-*b*-isoprenyl)lithium in benzene were reported to produce a mixture of the polymer carboxylic acids (60% yields) and the corresponding ketone dimers (40% yields), but no tertiary alcohols were detected by size exclusion chromatography.[8] When analogous carbonations were carried out in the presence of 25/75 tetrahydrofuran (THF)/benzene (v/v) mixtures to eliminate chain-end association,[2] the carboxylation occurred essentially quantitatively (eq 2).[8] Furthermore, when a

$$\mathrm{PLi} \xrightarrow{\mathrm{CO_2}} \xrightarrow{\mathrm{H_3O^+}} \underset{100\%}{\mathrm{PCO_2H}} \tag{2}$$

freeze-dried sample of poly(styryl)lithium was carboxylated, it was reported that the ketone could be efficiently prepared (eq 3).[9]

$$\mathrm{PsLi} \xrightarrow[\text{freeze-drying from benzene}]{} \xrightarrow{\mathrm{CO_2}} \xrightarrow{\mathrm{H_3O^+}} \underset{90\%}{(\mathrm{Ps})_2\mathrm{CO}} \tag{3}$$

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Herein are reported the results of an extensive reinvestigation of the role of association and medium effects on the carbonation of polymeric organolithium compounds. A critical reexamination of the question of the role of adventitious moisture in the formation of trimeric alcohol is presented, as well as the effects of the strongly coordinating and dissociating base *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) on the carboxylated products. Attempts to develop a rational synthesis of dimeric ketones are also presented.

Experimental Section

Styrene, benzene, and THF were purified as described previously.[8] TMEDA (Aldrich Chemical Co., 99%) was stirred over calcium hydride and freeze-degassed several times on the vacuum line with liquid nitrogen; it was then vacuum distilled into calibrated ampules that were stored in a freezer at −20 °C. Solutions of *sec*-butyllithium (Lithium Corp., 12 wt % in cyclohexane) were analyzed by the double titration method with 1,2-dibromoethane.[10] A cylinder of carbon dioxide (Air Products, 99.99% pure <2 ppm H_2O) was connected directly to the vacuum line via Cajon Ultra-Torr fittings and flexible stainless steel tubing.[11]

Polymerizations were carried out at 30 °C in round-bottom all glass, sealed reactors using breakseals and standard high vacuum techniques.[12] Carbonations were effected by reattaching the reactor to the vacuum line and introducing gaseous CO_2 into the unstirred reactor through a breakseal. When THF was required, it was distilled into the reactor after completing the polymerization and before the introduction of CO_2. After the carbonations, solutions of polymeric carboxylate salts were hydrolyzed with methanol containing aqueous HCl (1 N) followed by precipitation into methanol.

Thin-layer chromatographic (TLC) analyses were carried out on silica gel plates (Kodak Eastman silica gel chromagram sheet 13179) using mixtures of pentane and methylene chloride (4:5) as eluent. After development, different sections of the plate were removed, and then samples were dissolved in tetrahydrofuran, filtered, and analyzed quantitatively by UV spectroscopy at 254 nm.[8]

The concentration of carboxylic acid chain ends was determined by titrating a solution of 0.5 g of polymer in 30 mL of toluene with 0.01 M KOH in methanol to the phenolphthalein end point.[13] The solution of KOH in methanol was standardized with sulfamic acid (Fisher Scientific Co.).

Number-average molecular weights were determined by using a Knauer vapor pressure osmometer (VPO) in toluene (Fisher Scientific, certified ACS) which was distilled from freshly crushed CaH_2. Size exclusion chromatographic (SEC) analyses of the polymers were performed at a flow rate of 1.0 mL min^{-1} in THF at 30 °C using a Waters HPLC component system (RI detector) equipped with six ultra-Styragel columns (two 500, two 10^3, one 10^4, one 10^5 Å) after calibration with standard polystyrene samples obtained from Polymer Laboratories. Supplementary SEC characterization was undertaken with a Waters 150C instrument equipped with either six (set A) or four (set B) μ-Styragel columns. The continuous porosity ranges were 10^6–10^2 Å (set A) and 2 × 100, 500, and 10^3 Å (set B). The mobile phase was THF at 30 °C at a flow rate of either 1.0 or 0.1 mL min^{-1}. The lower rate of flow was used in order to enhance resolution.[14] Infrared spectra were recorded on a Beckman FT 2100 spectrometer while ultraviolet spectral analyses were performed on a Perkin-Elmer 559A UV–vis spectrophotometer.

Results and Discussion

Solution Carbonation. One of the major discrepancies between our previous studies[8] and the results of Wyman, Allen, and Altares[6] in benzene solution and that of Mansson[7] in methylcyclohexane was that we found no evidence for trimeric tertiary alcohol formation by size exclusion chromatographic analyses. These analyses were obtained by using three μ-Styragel columns (10^5, 10^4, and 10^3 Å) to study polymers with molecular weights <20 × 10^3 g/mol. Tertiary alcohol formation, as reported by others,[6,7] was attributed to the presence of adventious moisture[8] contamination during the workup procedure as shown in eq 4–7.

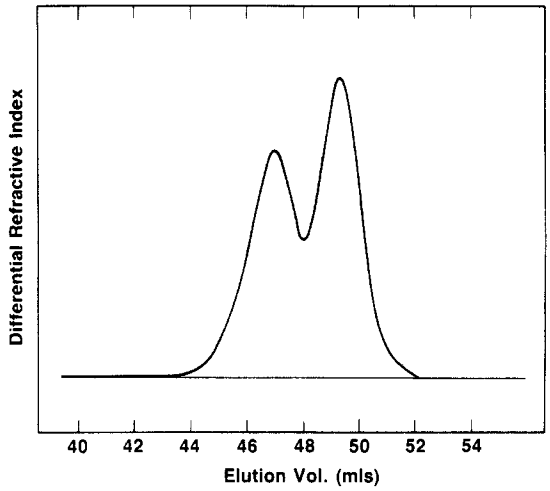


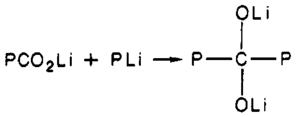
Figure 1. Size-exclusion chromatogram of carbonated polystyrene via the μ-Styragel column set B.

Table I
Carbonation of Poly(styryl)lithium in Benzene[a,b]

entry	monomer concn (vol %)	SEC yield (wt %)			acid titratn yield (wt %)
		acid	ketone[c]	alcohol[d]	
1	2.7	66	27	7	64
2	11	63	25	12	
3	15	47	29	24	48
4	29	54	30	16	52
5	31	52	30	18	54
6	53	46	42	12	48
7	2.7[e]	94	4	2	96
8	11[e]	99	1	0	97
9	15[e]	98	2	0	96
10	15	97	3	0	95[f]
11	13[g]	29	20	51	25
12	56[g]	40	14	46	40

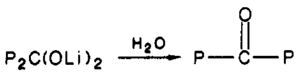
[a] Poly(styryl)lithium: $M_n = 4 \times 10^3$ g mol^{-1}. [b] 760-mm pressure of CO_2 except for runs 11 and 12. [c] Dimer. [d] Trimer. [e] Poly(styryl)lithium freeze-dried from benzene solution before carbonation. [f] A 97% yield of carboxylated polymer was determined from TLC plus UV analysis. [g] 130-mm pressure of CO_2.

$$PLi + CO_2 \longrightarrow PCO_2Li \qquad (4)$$



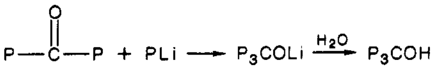
$$PCO_2Li + PLi \longrightarrow P-\underset{\displaystyle OLi}{\overset{\displaystyle OLi}{C}}-P \qquad (5)$$

1



$$P_2C(OLi)_2 \xrightarrow{H_2O} P-\overset{\displaystyle O}{\overset{\|}{C}}-P \qquad (6)$$

1



$$P-\overset{\displaystyle O}{\overset{\|}{C}}-P + PLi \longrightarrow P_3COLi \xrightarrow{H_2O} P_3COH \qquad (7)$$

In this study the products from the carbonation of poly(styryl)lithium ($M_n = 4 \times 10^3$) in benzene solution were reexamined by size exclusion chromatography using a set of six ultra-Styragel columns. Figure 1 shows the SEC chromatogram of the previously prepared carbonation sample[8] for poly(styryl)lithium ($M_n = 9 \times 10^3$) in benzene using four μ-Styragel columns (set B). The trimer peak is not apparent using this column set. The SEC of the same sample analyzed by using the six ultra-Styragel columns is shown in Figure 2. The trimer peak is clearly observed as a distinct shoulder on the dimer peak using

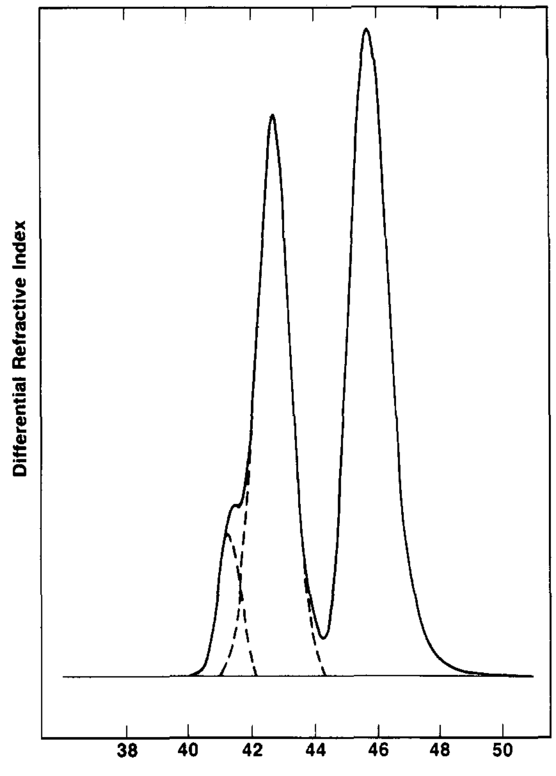


Figure 2. Size-exclusion chromatogram of the carbonated polystyrene of Figure 1 via the ultra-Styragel column set.

these columns. The SEC chromatogram for entry 11 in Table I is shown in Figure 3. With use of a lower pressure of carbon dioxide, the trimer alcohol is the major product.

For benzene solutions of poly(styryl)lithium with M_n = 6.2 × 10^4, Wyman, Allen, and Altares[6] reported yields of dimeric ketone and trimeric alcohol of 28% and 12%, respectively, when carbonation was effected by allowing gaseous carbon dioxide to diffuse into the system. These results are in good agreement with the data in Table I for 11 volume percent monomer concentration (run 2). Similarly, SEC analysis of the carbonation of poly(isoprenyl)lithium (M_n = 6.3 × 10^4) in benzene showed a product distribution of 59% carboxylic acid, 25% ketone dimer, and 16% trimeric alcohol. Thus, the formation of trimer is general for poly(styryl)lithium and poly(isoprenyl)lithium. It is obvious that trimeric alcohol is formed even under rigorous high vacuum conditions using high purity gaseous carbon dioxide, in contrast to our earlier conclusion.[8] The presence of the polymeric ketone (eq 6) and tertiary alcohol (eq 7) was demonstrated as described in the Appendix. Clearly these previous, erroneous conclusions were caused by the inability of the SEC column set in use[8] to detect the presence of trimer. A complex dependence of trimer yield on monomer (chain end) concentration is apparent from the data in Table I. The yield of trimer increases with monomer concentration in the range of 3–15 vol % and then decreases at higher concentrations. A dramatic effect of carbon dioxide pressure on trimer formation is evident when runs 11 and 12 are compared with runs 2 and 6, which were terminated with CO_2 pressures of 130 mm and 760 mm, respectively. Trimer formation is promoted by lower concentrations of carbon dioxide, consistent with trimer formation competing with direct carbonation of the active carbanionic chain ends. A similar effect is observed when the polymer solution is stirred during carbonation; only a 60% yield of carboxylated polymer is obtained with stirring even in the presence of 25% THF/75% benzene. The overall trend is a decrease in the yield of carboxylated polymer with increasing monomer concentration (chain end concentration), presumably increasing viscosity and decreasing concentration of carbon dioxide.

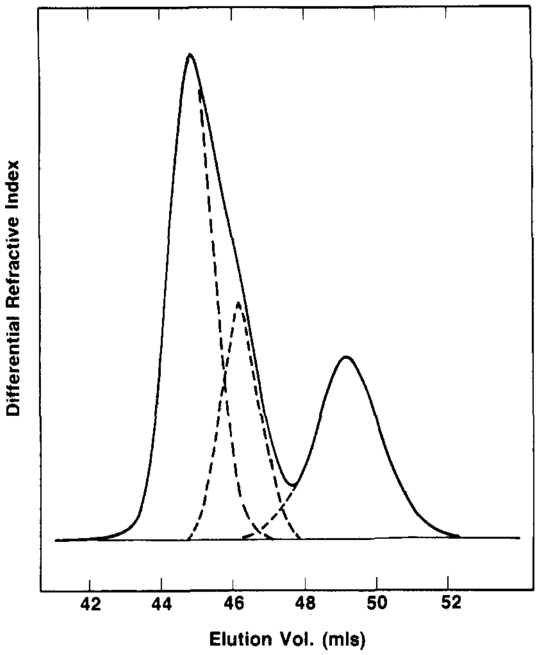
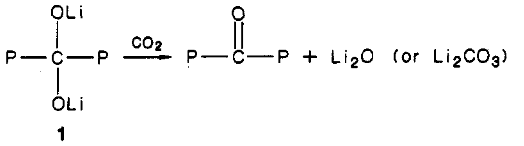


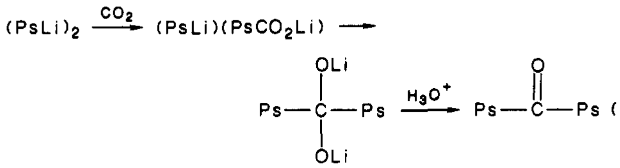
Figure 3. Size exclusion of chromatogram of carbonated polystyrene (ultra-Styragel) (entry 11 of Table I).

Jorgenson[15] concluded that the dilithium acetal salt 1 is inert toward further reaction; i.e., 1 is stable under the conditions for carboxylation and ketone formation. On the basis of this assumption, Jorgenson[15] proposed that trimeric alcohol products result from introduction of adventious moisture (or the presence of carboxylic acid) during the reaction or workup procedures. The data presented in Table I refute both of these conclusions. It is observed that increasing chain end concentration (monomer concentration at constant molecular weight) and decreasing carbon dioxide pressure increase the yield of trimer. This indicates that the dilithium acetal salt 1 is not stable under the reaction conditions and that 1 decomposes to form the ketone, and either Li_2O or Li_2CO_3, during the carboxylation reaction as shown in eq 8.



$$\underset{\mathbf{1}}{P-\overset{\displaystyle OLi}{\underset{\displaystyle OLi}{C}}-P} \xrightarrow{CO_2} P-\overset{\displaystyle O}{\overset{\|}{C}}-P + Li_2O \text{ (or } Li_2CO_3) \quad (8)$$

Solid-State Carbonation. If association of the chain ends promotes coupling to form ketone (eq 9), it was expected[9] that ketone formation would be promoted by conditions that maximize chain-end association. In general, higher degrees of association of organolithium compounds are favored by higher active center concentrations, lower temperatures, and the absence of Lewis bases.[5] It was therefore anticipated that chain-end association effects, i.e., ketone formation, could be maximized by freeze-drying benzene solutions of poly(styryl)lithium.



$$(PsLi)_2 \xrightarrow{CO_2} (PsLi)(PsCO_2Li) \longrightarrow Ps-\overset{\displaystyle OLi}{\underset{\displaystyle OLi}{C}}-Ps \xrightarrow{H_3O^+} Ps-\overset{\displaystyle O}{\overset{\|}{C}}-Ps \quad (9)$$

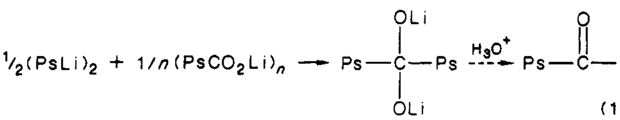
Table II
Reactions of Poly(styryl)lithium with Lithium Poly(styryl)carboxylate[a]

entry	PSLi/ PSCOOLi[b]	THF concn (vol %)	SEC yield (wt %)				acid titratn yield (wt %)
			acid	ketone	alcohol	calcd	
A	*c*	22.5	93	3	4	93	95
B	*d*	0	99	1	0	99	99
C	*d*	0	98	2	0	98	99
1	1 (A)	12.6	87	2	11	44	46
2	1 (B)	3.9	93	5	2	47	48
3	1 (B)	42.2	95	4	1	47	49
4[e]	2 (C)	0	59	34	7	14	16
5[e]	1 (C)	0	60	40	0	30	32
6[f]	1 (C)	0	56	44	0	28	29
7[g]	1 (C)	0	57	43	0	28	30

[a] Polystyrene molecular weights were 4.1 × 10^3 g mol^{-1}. Monomer concentration of 13 vol %. [b] Mole ratio. The letter in parentheses indicates the source of $\mathrm{PSCO_2Li}$. [c] Carbonation carried out in the presence of THF. [d] Carbonation carried out in solid state without polar additives. [e] By addition of $\mathrm{PSLi/C_6H_6}$ into $\mathrm{PSCOOLi/C_6H_6}$. [f] By addition of $\mathrm{PSLi/C_6H_6}$ to solid PSCOOLi. [g] By addition of PSCOOLi/$\mathrm{C_6H_6}$ to solid PSLi.

Quite unexpectedly, and contrary to a preliminary report,[9] carbonation of freeze-dried samples of poly(styryl)lithium gave minimal amounts (1–4%) of ketone dimer formation as shown by entries 7, 8, and 9 in Table I. In fact, these results are comparable to the carbonation results in the presence of tetrahydrofuran[8] that minimizes chain-end association effects. This reexamination of the solid-state carbonation of poly(styryl)lithium was prompted, in part, by findings made by one of us[16] in 1972. At that time observations similar to those of Wyman, Allen, and Altares[6] were recorded. However, carbonation in the solid state at ca. −78 °C (dry ice–2-propanol) after 1 month was found to yield product essentially devoid of the polymeric ketone and tertiary alcohol. Two of these samples were subsequently evaluated and studied by Norrby,[17,18] whose findings were compatible with carboxylation efficiencies of close to one for these monofunctional chains.

Ketone Synthesis. The complexity of the actual mechanism for dimer and trimer formation was apparent from attempts to develop a rational synthesis of the ketone dimer. By analogy with the synthesis of ketones from reactions of organolithium compounds with lithium carboxylates as described in the review by Jorgenson,[15] we reacted an aliquot of poly(styryl)lithium with the corresponding poly(styryl)lithium carboxylate. The formation of the expected dimeric ketone product is shown in eq 10.



$$\tfrac{1}{2}(\mathrm{PsLi})_2 + 1/n(\mathrm{PsCO_2Li})_n \longrightarrow \mathrm{Ps{-}C(OLi)_2{-}Ps} \xrightarrow{\mathrm{H_3O^+}} \mathrm{Ps{-}C({=}O){-}Ps} \qquad (10)$$

The main difference between this procedure and the reactions that lead directly to ketone formation during the carboxylation reaction (eq 9) is that in this procedure the reactants are not cross-associated as indicated in eq 10. The results of these experiments are shown in Table II. The lithium carboxylate salt was formed in high yield by performing the carboxylation either in a tetrahydrofuran/benzene mixture (entry A, Table II) as described previously[7] or using the freeze-drying technique (entries B and C, Table II). The size-exclusion chromatograms of the base polystyrene (obtained by methanol quenching), the carboxylated polystyrene, and the products of the reactions of the lithium carboxylated polymer with polystyryllithium in the presence of THF (entry 1, Table II) are shown in Figure 4. Contrary to expectations based on analogies to the high-yield (80%) ketone syntheses described for low molecular weight organolithium compounds,[15] the yield of dimeric ketone from this reaction was only 2%. In the presence of 42% THF (entry 3, Table II), the yield of dimeric ketone was only about 4%. Better yields of dimeric ketone product (34–44%) were obtained when the reactions were carried out in benzene in the absence of THF (entries 4–7, Table II). The formation of ketone dimer product did not seem to depend on the mode of addition of the reactants or the presence of a 2-fold excess of poly(styryl)lithium. One possible explanation for these results is that the lithium carboxylate salts are highly associated into relatively unreactive aggregates under these conditions.[19] An analogous lack of reactivity of associated heteratom lithium salts is presumably responsible for the lack of polymerizability of epoxides in the presence of lithium alkoxide salts under most experimental conditions.[20-22] Another possible explanation for the lack of higher yields of ketone dimer under these conditions is the metalation of the lithium poly(styrene)carboxylate by poly(styryl)lithium as shown in eq 11. Metalation via the

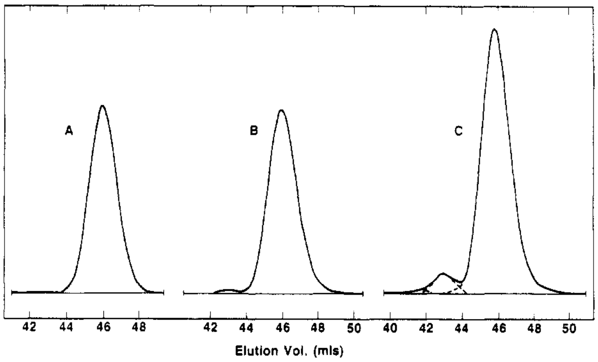
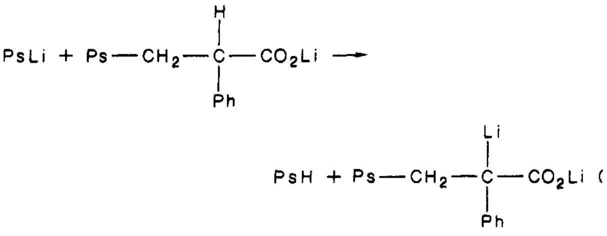


Figure 4. Size-exclusion chromatogram of Carbonated Polystyrene (ultra-Styragel) (entry 3 of Table II). See text for description of samples.



$$\mathrm{PsLi} + \mathrm{Ps{-}CH_2{-}CH(Ph){-}CO_2Li} \longrightarrow \mathrm{PsH} + \mathrm{Ps{-}CH_2{-}C(Li)(Ph){-}CO_2Li} \qquad (11)$$

2

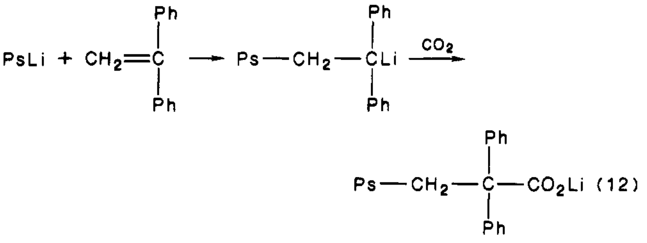
enolizable protons adjacent to the carboxylate group would render the resulting dilithiated species **2** much less reactive toward addition of poly(styryl)lithium to form the dilithium acetal salt 1. Evidence for this side reaction was

Table III
Carbonation of Poly(styryl)lithium in the Presence of TMEDA[a-c]

entry	R ([TMEDA]/[Li])	SEC yield (wt %) acid	ketone[d]	alcohol[e]	acid titratn yield (wt %)
1	1	80	8	12	81
2	2	86	6	8	85
3[f]	2	75	6	19	
4	5	93	4	3	91
5	7	93	4	3	92
6	10	98	2	0	97
7	12	99	1	0	98
8[g]	1	100			98
9[g]	2	100			100

[a] Poly(styryl)lithium: $M_n = 4 \times 10^3$ g/mol. [b] Monomer concentration: ca. 13.5 vol %. [c] 760-mm pressure of CO_2. [d] Dimer. [e] Trimer. [f] The poly(styryl)lithium solution ($M_n = 2 \times 10^3$) was stirred during carbonation. [g] Poly(styryl)lithium freeze-dried from benzene solution before carbonation.

obtained by end capping poly(styryl)lithium with diphenylethylene prior to carbonation (eq 12).



$$\mathrm{PsLi} + \mathrm{CH_2{=}CPh_2} \longrightarrow \mathrm{Ps{-}CH_2{-}CPh_2Li} \xrightarrow{CO_2} \mathrm{Ps{-}CH_2{-}CPh_2{-}CO_2Li} \quad (12)$$

3

Reaction of the resulting lithium carboxylate (3) with poly(styryl)lithium in the presence of 5.2 vol % THF in benzene gave a 40% yield of ketone dimer (compare this result with entry 2, Table II). Thus, the increase in ketone yield can be explained by the absence of enolizable α protons in the lithium carboxylate 3.

Lewis Base Effects. One of the most important variables in the carbonation of polymeric organolithium compounds is the presence of Lewis bases. Although only a 60% yield of carboxylated polymer is obtained in benzene solutions, identical functionalization reactions in a 75/25 (v/v) mixture of benzene and tetrahydrofuran provide essentially quantitative carbonation of poly(styryl)lithium, poly(isoprenyl)lithium, and poly(styrene-*b*-isoprenyl)lithium.[8] These effects were rationalized in terms of the ability of tetrahydrofuran to promote deaggregation of the organolithium chain ends and the postulate that association of the chain ends promotes intraaggregate coupling to form the dimeric ketone as shown in eq 9. If these concepts are correct, it would be expected that other Lewis bases which dissociate the organolithium chain ends would also be effective in promoting carboxylation and minimizing the side reactions leading to dimeric and trimeric products.

N,N,N′,N′-Tetramethylenediamine (TMEDA) is one of the most strongly coordinating ligands for organolithium compounds.[23] TMEDA causes dramatic changes in kinetics and stereochemistry for alkyllithium-initiated polymerizations of styrene and diene monomers.[2] Viscometric studies have shown that TMEDA causes a sharp drop in the apparent degree of association of poly(butadienyl)lithium chain ends at low ratios of R([TMEDA]/[PLi]).[24] Calorimetric studies have shown that the interaction of TMEDA with polymeric organolithium chain ends is strongly exothermic and exhibits sharp concentration dependencies which are consistent with kinetic effects.[25,26] All of the evidence is consistent with the ability of TMEDA to complex strongly with the organolithium chain ends and dissociation of the chain ends at low values of R (e.g., $R \geq 1$).[24] Thus, it was expected that TMEDA, like THF, would promote carboxylation and minimize dimer and trimer formation at low R values. The results of an investigation of the effects of TMEDA on the carbonation of poly(styryl)lithium in benzene solution are shown in Table III. TMEDA does favor carbonation since at an R value of 1.0 an 80% yields of acid was obtained compared to only a 60% yield in benzene[6] (also see Table I). These results are consistent with the report by Rovers[27] that ca. 9% dimer formation is observed in the carbonation of poly(styryl)lithium in the presence of TMEDA at an R value of 1.5. In contrast to expectations based on viscometric, spectroscopic, kinetic, and calorimetric studies of the stoichiometric dependence of TMEDA effects on polymeric organolithium chain ends,[2,24-26,28-30] very large R values ($R \geq 10$) were required to minimize dimeric ketone and trimeric alcohol formation (see entries 5 and 6 in Table III). Similarly, carboxylation of poly(isoprenyl)lithium ($M_n = 6.3 \times 10^4$ g/mol) complexed with TMEDA ($R = 43$) produced the corresponding carboxylated polymer in quantitative yield as deduced by SEC and TLC analysis. Essentially quantitative yields of carboxylated polystyrene were obtained from freeze-dried solutions of poly(styryl)lithium complexed with only 1 or 2 equiv TMEDA (see entries 7 and 8 in Table II). The yield of carboxylated polymer was lowered (entry 3) when the solution was stirred during carbonation as discussed previously.

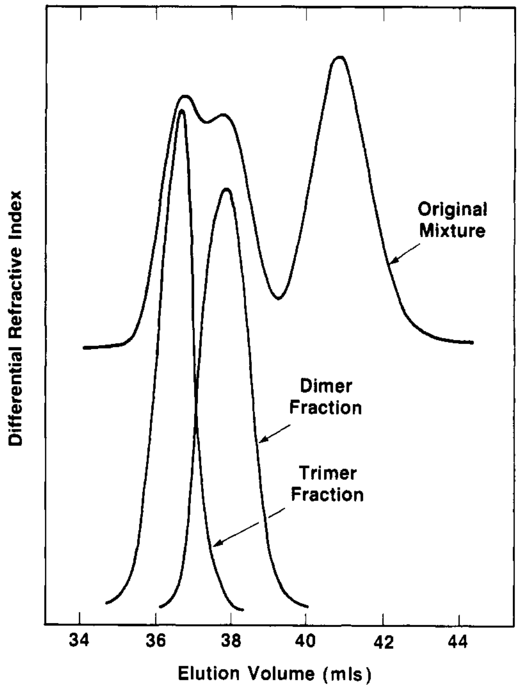


Figure 5. Size-exclusion chromatograms of carbonated polystyrene (ultra-Styragel) (entry 3 of Table I) and fractionated products.

Summary

In conclusion, the carbonation of poly(styryl)lithium, poly(isoprenyl)lithium, and presumably other polymeric organolithium compounds[8] produces both the dimeric ketone and the trimeric alcohol directly in benzene solution. The formation of these side reaction products is promoted by higher chain-end concentrations and a low concentration of carbon dioxide. Essentially quantitative yields of chain-end carboxylated polymers can be obtained by carrying out the carboxylation in the presence of sufficient Lewis bases ($R > 10$) such as THF and TMEDA. The most efficient carboxylation procedure utilizes a freeze-drying technique to generate a porous solid sample of poly(styryl)lithium in the presence of a Lewis base such as TMEDA. Only low efficiencies of ketone dimer formation can be achieved by reacting stoichiometric quantities of poly(styryl)lithium with lithium poly(styrene)-carboxylate.

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Appendix

The presence of the ketone and tertiary alcohol functionalities in the coupled and three-arm star polystyrenes was demonstrated as follows. Sample 3 of Table I was fractionated by the use of a toluene/methanol mixture. These two components were successfully separated as shown in Figure 5 where the fractionation results are shown in detail.

In order to minimize the potential influence of association of the hydroxyl group on the infrared analysis, the FT-IR measurements were carried out at a functional group concentration of 10^{-5} M. A 10-cm cell was used with carbon tetrachloride as the solvent. The trimer product exhibited several sharp adsorption peaks around 3615 cm^{-1}; a criterion[31] for free alcohols. The linear uncoupled polystyrene chain isolated in a chromatographic fractionation process did not show any signal in the 3600 cm^{-1} region. These observations demonstrate that the trimer product carries the tertiary alcohol structure (eq 7) at the core of the star-shaped polystyrene. The FT-IR analysis for the ketone group in the coupled polystyrene was carried out in chloroform. An adsorption peak at 1712 cm^{-1} was observed that is characteristic of the ketone unit. This conclusion was fortified by the observation that 1,3-diphenylacetone at an equivalent concentration of the ketone unit in the polystyrene dimer showed the same adsorption.

A supplementary characterization of the polymeric ketone was its reaction with 2,4-dinitrohyphenyldrazine.[32] The UV-visible spectrum of this material yielded a λ_{max} of 360 nm—which was in accord with that λ_{max} of 362 nm, found for the product of the model reaction between 1,3-diphenylacetone and 2,4-dinitrophenylhydrazine. This finding serves as an additional demonstration of the presence of the carbonyl group in the coupled polystyrene.

Registry No. Tetrahydrofuran, 109-99-9; *N,N,N′,N′*-tetramethylethylenediamine, 36345-04-7; poly(styryl)lithium, 36345-04-7; CO_2, 124-38-9.

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