Carboxylation of Poly(styryl)lithium Using ^{13}C-Labeled Carbon Dioxide. Aromatic Ring Carboxylation

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ABSTRACT: The carboxylation of poly(styryl)lithium and the adduct of 1,1-diphenylethylene with poly(styryl)lithium ($M_n = 2 \times 10^3$) with $^{13}CO_2$ in the solid state produces the para-substituted ring-carboxylation products in 15% and 35% yields, respectively, as deduced by ^{13}C NMR. The ring-carboxylated product from the polymeric diphenylalkyllithium was separated and isolated from the aliphatic carboxyl derivative by SiO_2 column chromatography. Solution carboxylation produces the ring-carboxylated polymer in only 1–4% yield using a variety of experimental conditions; thus, solution carboxylation in the presence of Lewis bases such as THF and TMEDA is the recommended procedure. End-capping with 1,1-diphenylethylene prior to solution carboxylation is also efficient (>99%) and produces a minimum amount of ring substitution (1%). The variables which favor ring substitution are discussed.

Introduction

One of the most useful and important characteristics of living anionic polymerization is the generation of polymer chains with stable carbanionic chain ends.[1-4] In principle, these reactive anionic end groups can be readily converted into a diverse array of functional end groups.[1,2,5-10] These groups may then undergo a variety of further reactions including (1) chain extension, branching, or cross-linking reactions with polyfunctional reagents, (2) coupling and linking with reactive groups on other oligomer or polymer chains, and (3) initiation of polymerization of other monomers. In addition, polar functional groups can aid in the dispersion of reinforcing agents and fillers.

Unfortunately, many of the functionalization reactions which have been described for anionic polymers are not well characterized.[3] Thus, a variety of potentially useful functionalization reactions have not been well-defined in terms of specifics such as side reactions, solvent effects, and optimum conditions. One of the most useful and widely used functionalization reactions is the carboxylation of polymeric anions using carbon dioxide. In spite of the apparent simplicity of this reaction, a complex mixture of products including the dimeric ketone and trimeric alcohol is often obtained.[10] For example, the carboxylation of poly(styryl)lithium in benzene solution with high-purity, gaseous carbon dioxide at atmospheric pressure produces the carboxylated polymer in only 46–66% yield; the functionalized polymer is contaminated with dimeric ketone (25–30%) and trimeric alcohol (7–24%) as shown in eq 1 where P represents the polystyrene chain.[11,12] A

$$\mathrm{PLi} + \mathrm{CO_2} \xrightarrow{\mathrm{H_3O^+}} \mathrm{PCO_2H} + \mathrm{P_2CO} + \mathrm{P_3COH} \qquad (1)$$

recent careful investigation of the optimum conditions for carboxylation concluded that essentially quantitative carboxylation can be effected by adding sufficient quantities of Lewis bases such as tetrahydrofuran (THF) or *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) prior to the functionalization reaction.[12]

Herein are reported further studies of the carboxylation of poly(styryl)lithium with ^{13}C-labeled carbon dioxide which provide evidence for the formation of aromatic carboxylation products in significant yields under a variety of experimental conditions.

Experimental Section

Chemicals and Solvents. Styrene, benzene, and tetrahydrofuran were carefully purified as previously described.[11] 1,1-Diphenylethylene (97%; Aldrich) was stirred over freshly-crushed CaH_2, distilled onto a small amount of *sec*-butyllithium to form the dark red (1,1-diphenylhexyl)lithium, and then distilled directly into ampules which were heat sealed. Solutions of *sec*-butyllithium (Lithium Corp.; 12.0 wt % in cyclohexane) were analyzed using the double titration method with 1,2-dibromoethane.[13] Carbon dioxide (99.99%, $H_2O < 2$ ppm; Air Products) and ^{13}C-labeled carbon dioxide (99.99% pure, 99% ^{13}C-enriched; Isotech, Inc.) were used as received. Methanol (99.9%, acetone free, ACS certified; Fisher) for termination reactions was degassed on the vacuum line before heat-sealing in ampules.

Polymerizations. Styrene polymerizations were carried out at room temperature in all-glass, sealed reactors using breakseals and standard high-vacuum techniques.[14] After polymerizations and prior to termination reactions, aliquots of poly(styryl)lithium were isolated in attached ampules, heat-sealed, and terminated with degassed methanol. Polymers were recovered by addition of the polymer solution dropwise into a 4-fold excess of methanol, filtration, and drying in a vacuum oven. Conversion to the (1,1-diphenylalkyl)lithium chain end was effected by addition of 1,1-diphenylethylene to the benzene solution of poly(styryl)lithium via an ampule and stirring for 2–3 days at room temperature.

Carboxylation. Before introducing gaseous CO_2 into the reactor without stirring, CO_2 was used to purge the connecting apparatus to the reactor several times by alternate evacuation and purging. The resulting functionalized polystyrenes in benzene were hydrolyzed with a 10% (by volume) hydrochloric acid–methanol mixture by stirring for several hours. After washing with distilled water, the functionalized polystyrenes were isolated by precipitation into excess methanol and dried in a vacuum oven. Solid-state carbonations were carried out as described previously.[12]

Characterization. Number-average molecular weights $<10 \times 10^3$ were determined using a vapor-pressure osmometer (VPO) (Knauer Type 11.00) in toluene (Fisher Scientific; ACS certified) which was distilled from freshly crushed CaH_2; sucrose octaac-

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etate (99%; Aldrich) was used as a calibration standard and was purified by two recrystallizations from methanol. Higher molecular weights were determined using a membrane osmometer (Mechrolab 503) in toluene at room temperature. Size-exclusion chromatographic analyses of polymers were performed at a flow rate of 1.0 mL min^{-1} in tetrahydrofuran at 30 °C using a Waters HPLC component system (RI detector) equipped with six ultra-μ-Styragel columns (two 500, two 10^3, 10^4, and 10^5 Å) for low molecular weight samples ($M_n < 20 \times 10^3$) or with four ultra-μ-Styragel columns (10^3, 10^4, 10^5, and 10^6 Å) for high molecular weight samples after calibration with standard polystyrene samples obtained from Polymer Laboratories. UV-visible, ^{1}H NMR ($CDCl_3$), ^{13}C NMR ($CDCl_3$), and FTIR spectra were recorded on HP8452A diode-array, Varian, Gemini-200, and Beckman Instruments FT-2100 spectrometers, respectively. For quantitative ^{13}C NMR analysis of carboxylation reaction products, spectra were obtained using 5000 transients with a delay time of 8 s between pulses. Thin-layer chromatographic analyses used silica gel plates (100-μm thickness, 131981 silica gel with a fluorescent indicator; Kodak) with toluene as eluent.

The concentrations of carboxyl chain ends were determined by titration of 0.5-g samples of functionalized polymer in 30 mL of toluene using 0.01 N KOH in methanol as the titrant and phenolphthalein as the indicator.

Results and Discussion

A variety of techniques including end-group titration have been used to characterize functionalized polymers and to determine the efficiency of functionalization reactions.[15] High-resolution ^{1}H and ^{13}C NMR spectrometers provide a powerful probe for determining the structures of functionalized polymers.[16-23] Since ^{1}H and especially the ^{13}C chemical shifts are sensitive to the local chemical environment, NMR can often be utilized to identify functional groups or atoms adjacent to these functional groups.[24-27] In principle, integration can be used to determine the concentration of a given type of atom or group of atoms in a given environment within the inherent error limits of the method. This is less ambiguous for ^{1}H NMR than for ^{13}C NMR determinations because of the complications caused by relaxation effects and nuclear Overhauser effects which affect the signal areas in the latter.[23] However, in spite of this proviso, NMR spectroscopy provides a unique opportunity to directly observe signals pertaining to a given functional group, whether or not quantitative data can be extracted.

For example, when the natural-abundance ^{13}C NMR spectrum of a purified, carboxyl-functionalized polystyrene ($M_n = 2 \times 10^3$; $M_w/M_n = 1.04$)[12] is examined, a very weak signal is observed at 179.1 ppm. The corresponding resonance for phenylacetic acid was observed at 178.5 ppm. This very low intensity signal is a consequence of the relatively low concentration of the functional groups at the polymer chain ends and also of the long relaxation times for carbonyl carbons.

In order to enhance the sensitivity of the ^{13}C method as a method of characterizing carboxyl-functionalized polymers, ^{13}C-labeled carbon dioxide was used as the functionalizing agent. For example, the direct carboxylation of poly(styryl)lithium ($M_n = 2 \times 10^3$) with $^{13}CO_2$ in benzene produced the corresponding functionalized polymer in only 47% yield, but the signal for the carboxyl-group carbonyl carbon was clearly observed at 179.5 ppm in the ^{13}C NMR spectra (Figure 1), as were the signals corresponding to the dimeric ketone at 208.8 and 210 ppm by analogy with the resonance at 206 ppm observed for 1,3-diphenylacetone. The absence of a resonance at 33.6 ppm corresponding to the terminal benzylic carbon in the base polystyrene[24] indicates that there is no unfunctionalized polystyrene formed under these experimental conditions.

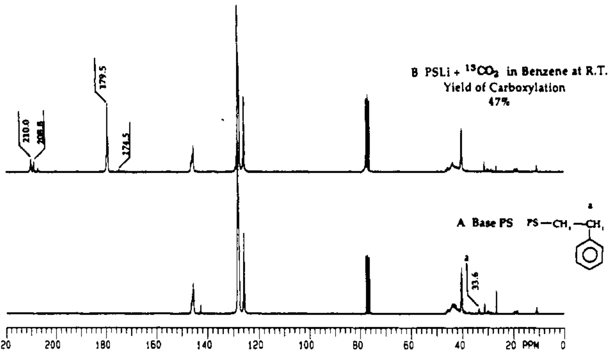
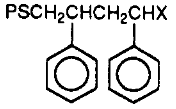


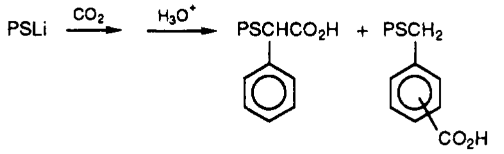
Figure 1. ^{13}C NMR spectra ($CDCl_3$) of unfunctionalized, base polystyrene (A) and the carboxylation products of PSLi in benzene with $^{13}CO_2$ (B).

We have observed that multiple resonances are often observed for both ^{1}H and ^{13}C NMR resonances for functional groups in functionalized polystyrenes with the general structure shown below.[26]



The terminal diad unit can exist as a diastereomeric pair of stereoisomers because the carbons indicated with asterisks represent chiral carbon atoms which can exhibit chemical shift nonequivalence.

It was noted in this ^{13}C NMR spectrum of the $^{13}CO_2$ carboxylation products (Figure 1) that there there was an additional resonance absorption in the carbonyl carbon region at 174.5 ppm. The ^{13}C NMR spectra of several model compounds were examined in order to assign this anomalous peak. For example, *o*-toluic acid exhibits a carboxyl carbon resonance at 174.0 ppm. This suggested that previously unobserved ortho ring carboxylation may be occurring during carboxylation as shown in eq 2. In addition, the ^{13}C spectra of *p*-toluic acid and 4-ethylbenzoic acid with absorbances for carbonyl carbons at 172.8 and 172.9 ppm suggest that, if para ring carboxylation occurs, it will be characterized by an absorption in this region (173 ppm) which is separated from the absorbance for the ortho ring-carboxylation product (174 ppm).



(2)

It should be noted that the direct products of ring carboxylation would be the reactive cyclohexadiene intermediates shown in Scheme I. These intermediates would be expected to rearomatize in the presence of acid or base catalysis, perhaps by a conducted tour mechanism.[28-30]

In order to confirm that ring substitution was occurring, a series of carboxylation experiments was carried out under a variety of conditions to attempt to maximize the yield of these products. The ^{13}C NMR spectra for the products of carboxylation of poly(styryl)lithium ($M_n = 2 \times 10^3$; $M_w/M_n = 1.04$) with ^{13}C-labeled CO_2 in aromatic solvents at various temperatures are shown in Figure 2.

It was observed that the total yield of carboxylated polymer (determined by end-group titration and SEC analyses) increased with decreasing temperature; the car-

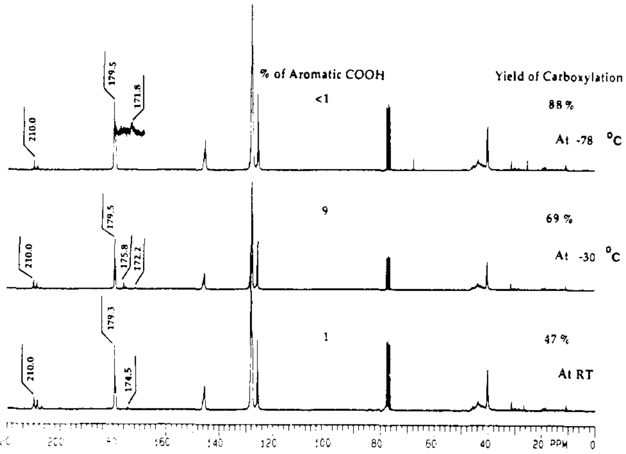
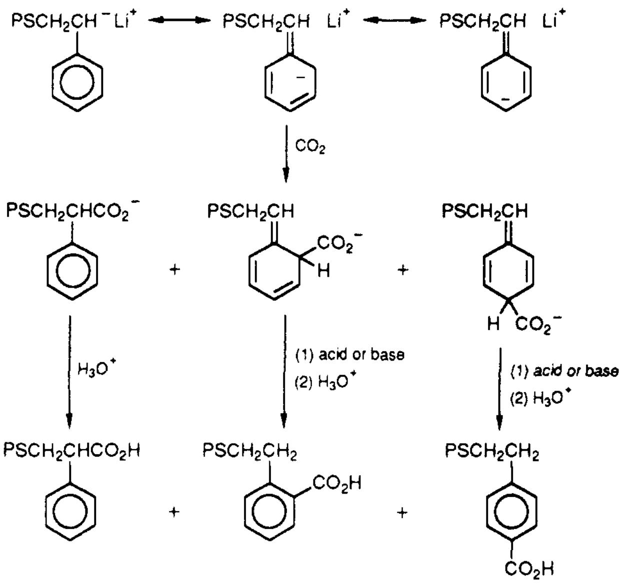


Figure 2. ^{13}C NMR spectra ($CDCl_3$) of the carboxylation products of PSLi with $^{13}CO_2$ in aromatic solvents at various temperatures.

Scheme I



boxylation yields were determined to be 47%, 69%, and 88% at +25, −30, and −78 °C, respectively. However, the dependence of the amount of ring-carboxylated products on temperature was minor. The amount of ring carboxylation as a function of temperature was deduced from the relative intensity of the peaks at 174 and 172 ppm relative to the normal product absorption at 179.5 ppm. It was estimated that approximately 1% ring carboxylation occurred both at +25 °C (predominantly ortho) and at −78 °C (predominantly para); however, at −30 °C, the yield of aromatic ring products was estimated to be 9% (predominantly ortho).

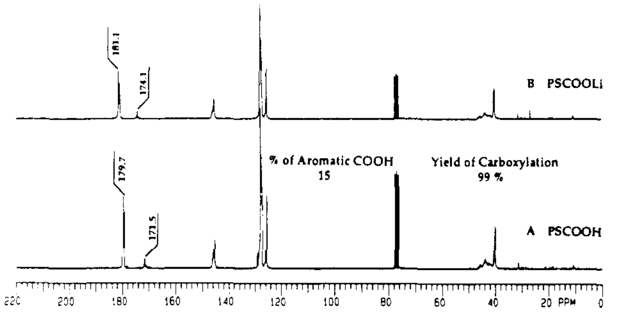
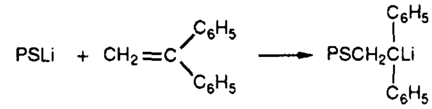


Figure 3. ^{13}C NMR spectra ($CDCl_3$) of the solid-state carboxylation products from PSLi with $^{13}CO_2$ after (A) and before (B) hydrolysis.

Carboxylations with $^{13}CO_2$ were also carried out in the solid state by freeze-drying benzene solutions of poly(styryl)lithium ($M_n = 2 \times 10^3$; $M_w/M_n = 1.04$) to form a porous, orange solid. As described previously,[12] the yield of carboxylated polymer from solid-state carboxylation was essentially quantitative (99%). No evidence for unfunctionalized polymer (<1%) was obtained by TLC analyses. The ^{13}C NMR spectra of the lithium salt of the carboxylic acid and the carboxyl-functionalized polystyrene are shown in Figure 3. Only one main carbonyl carbon absorption is observed, and this resonance at 171.5 ppm is assigned to the para-substitution product. The yield of ring-functionalized product was estimated to be 15%. It is interesting to note that for the corresponding lithium carboxylate salt the carbonyl resonances at 181.1 and 174.1 ppm for the aliphatic and aromatic substitution products, respectively, were deshielded relative to the resonances for the corresponding carboxylic acids.

Another important variable affecting the yield of carboxylated polymers is the presence of polar additives such as tetrahydrofuran and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA).[12] The carboxylation of poly(styryl)lithium ($M_n = 2 \times 10^3$; $M_w/M_n = 1.04$) in benzene in the presence of 20 equiv of TMEDA produced the carboxylated polystyrene in 97% yield; however, the yield of aromatic carboxylation products was estimated from the intensity of the resonance at 170.2 ppm to be only 4%. Solid-state carboxylation[12] in the presence of 2 equiv of TMEDA produced the carboxylated polystyrene in quantitative yield (100%) but with only 6% ring carboxylation as estimated from the resonance observed at 172.1 ppm. In contrast, solid-state carboxylation in the absence of added TMEDA produced the carboxylated polymer in 99% yield and the para-substituted ring-carboxylation product in 15% yield. Thus, ring substitution was promoted in the solid state in the absence of TMEDA.

Another important variable affecting the yield of the carboxylation reaction is the structure of the chain end. The chain-end modification reaction with 1,1-diphenylethylene is very useful to modify both the steric and electronic nature of the chain end; this reaction proceeds in essentially quantitative yield to form a (1,1-diphenylalkyl)lithium chain end as shown in eq 3. Quite surprisingly, it was observed that carboxylation of this (diphenylalkyl)lithium species ($M_n = 2 \times 10^3$) produced the carboxylated polymer in essentially quantitative yield. These results are in sharp contrast to the low efficiency for carboxylation of poly(styryl)lithium (47%) at the same chain-end concentration. These results suggest that the carboxylation reaction is quite sensitive to the steric and electronic nature of the chain end.



$$\mathrm{PSLi} + \mathrm{CH_2{=}C(C_6H_5)_2} \longrightarrow \mathrm{PSCH_2C(C_6H_5)_2Li} \qquad (3)$$

^{13}C NMR analysis of the solution carboxylation products of the polymeric (1,1-diphenylalkyl)lithium chain end using $^{13}CO_2$ indicated that very little ring carboxylation (1–2%) is present in these samples as shown by the small intensities for the peaks at 171.7 and 171.5 ppm for carboxylations at +25 and −78 °C, respectively. The carbonyl carbon resonance for the main product is observed at 180.7 ppm compared to 179.5 ppm for the normal polystyrene product.

The most dramatic increase in ring substitution was observed when the adduct of 1,1-diphenylethylene and

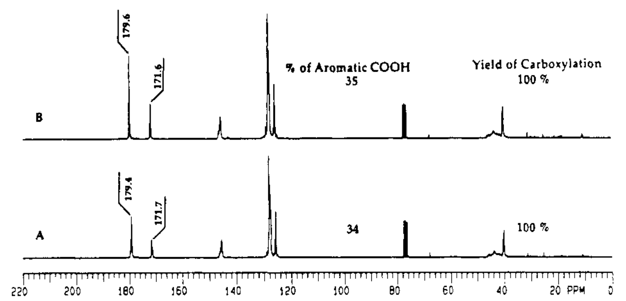


Figure 4. ^{13}C NMR spectra (CDCl$_3$) of the carboxylation products from two solid-state carboxylation reactions of the adduct of PSLi with 1,1-diphenylethylene using ^{13}CO$_2$.

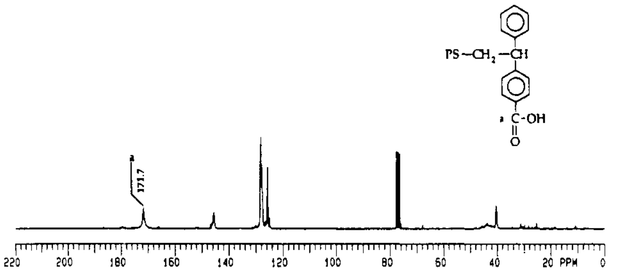


Figure 5. ^{13}C NMR spectrum (CDCl$_3$) of the purified ring-substitution product from the solid-state carboxylation of the adduct of PSLi with 1,1-diphenylethylene using ^{13}CO$_2$.

poly(styryl)lithium was carboxylated in the solid state. The quantitative carboxylation was accompanied by approximately 34–35% of the ring-substitution products as shown in Figure 4 for two solid-state carboxylation reactions. The ring-substitution product exhibits an absorption at ca. 171.6 ppm which suggests that this is primarily the para substitution product. It is important to compare this result with the 15% ring substitution observed for carboxylation of poly(styryl)lithium in the solid state. Thus, the maximum yields of ring-substitution products, predominantly para, were observed for carbonations of both poly(styryl)lithium and the corresponding polymeric (1,1-diphenylalkyl)lithium in the solid state.

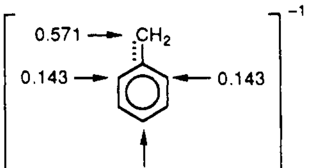
Because of the dfferent electronic effects in aliphatic and aromatic carboxylic acids, the difference in acidity among these two types of acids has been reported to be significant; in general, there is a higher acidity for aromatic carboxylic acids compared with aliphatic acids. The pK_a values for acetic acid and benzoic acid in water are estimated to be 4.75 and 4.19, respectively;[31] in nonaqueous solvents, such as dimethyl sulfoxide, the pK_a values are reported to be 11.4 and 10.0, respectively.[32] These effects suggested that it might be possible to separate the aliphatic substitution product from the aromatic carboxylation product by both TLC and column chromatography.

TLC analysis of the product of carboxylation of PS–DPELi in the solid state which contained an estimated 35% ring carboxylation displayed only one spot which did not move on silica gel plates with toluene as eluent. However, when a mixture of THF and toluene (50/50, v/v) was used as eluent, two distinct spots were observed with R_f values of 0.7 and 0.2. These two components were separated and isolated by column chromatography on silica gel using first a mixture of toluene and THF (50/50, v/v) to elute the first component, followed by elution with THF to remove the second component. The second component (30% isolated yield) was identified as the pure ring-substituted carboxylation product from its ^{13}C NMR spectrum which exhibited only one carbonyl carbon resonance at 171.7 ppm as shown in Figure 5.

All of the isomeric carboxylation results discussed herein are summarized in Table I. The most important conclusion from these data is that under certain experimental conditions the carboxylation of poly(styryl)lithium and polymeric (1,1-diphenylalkyl)lithium compounds with gaseous carbon dioxide under high-vacuum conditions gives rise to significant amounts of aromatic ring-substituted carboxylic acid end groups. Obviously, these results further complicate the already difficult task of characterizing chain-end-functionalized polymers synthesized via living alkyllithium-initiated polymerizations. For low molecular weight functionalized polymers, the degree of functionalization can be investigated by a variety of techniques including ^{1}H and ^{13}C NMR spectroscopy, FTIR spectroscopy, UV–visible spectroscopy, elemental analysis, thin-layer chromatography, separation and isolation of components by column chromatography, and end-group titration.[15] The results reported herein indicate the type of sophisticated characterization which may be required to thoroughly characterize functionalized polymers. Furthermore, ring-substitution products may be formed with a variety of other electrophilic functionalization agents and could give rise to anomalous results in subsequent reactions of the functionalized polymers.

Because of this potential complicating aspect of ring substitution for other anionic functionalization reactions, it is worthwhile to attempt to deduce what factors promote aromatic substitution reactions in poly(styryl)lithium. Several features of the data in Table I are interesting. It would be expected that a more ionic, delocalized carbanion would tend to give more aromatic substitution product; however, no significant effect of TMEDA in promoting aromatic substitution is apparent in spite of the general expectation that organolithium compounds are less associated and more ionic in the presence of this bidentate complexing ligand.[3,4] Temperature was not a significant variable in promoting ring substitution. The most important variable was the use of solid-state carboxylation, and the (1,1-diphenylalkyl)lithium chain end was most effective compared to the poly(styryl)lithium chain end.

Obviously, ring-substitution products can be considered as deriving from kinetic control as opposed to thermodynamic control since the ring-substitution reaction destroys the aromatic ring in the first-formed cyclohexadienyl intermediate as shown in Scheme I. In general, it is assumed that the electrophile will add to the carbon having the highest electron density.[33-35] The charge distribution for a free benzyl anion is shown below.[33]



The results in Table I are in accord with this charge distribution since predominant substitution at the benzylic carbon is observed. The charge density for the benzyl carbanion also indicates that there is significant charge delocalization into the aromatic ring, predominantly at the ortho and para positions. In terms of the Hammond postulate,[36] for exothermic reactions in which the transition state is early on the reaction coordinate (i.e., resembles reactants), it would be expected that some substitution would occur at the ortho and/or para positions. In contrast, for endothermic reactions, the transition state would

Table I
Yields of Isomeric Carboxylation Products as a Function of Chain-End and Reaction Conditions

PLi	carboxylation medium	temp, °C	carboxylation product yield: total	aliphatic	aromatic[a]	aromatic substitution
PSLi	benzene	25	47	46	1	ortho
	toluene	-30	69	60	9	ortho
	toluene	-78	88	87	1	para
	solid state[b]	25	99	84	15	para
	benzene–TMEDA[c]	25	97	93	4	para
	solid state–TMEDA[d]	25	100	94	6	para
PS-DPELi[e]	benzene	25	99	98	1	para
	toluene	-78	99	97	2	para
	solid state	25	100	65	35	para
		25	100	66	34	para

[a] Relative intensity of the ^{13}C NMR peak for an aromatic carbonyl carbon resonance compared to an aliphatic carbonyl carbon resonance. [b] Freeze-dried from C_6H_6 (see ref 12). [c] [TMEDA]/[Li] = 20. [d] [TMEDA]/[Li] = 2. [e] Adduct of PSLi plus 1,1-diphenylethylene.

resemble the products and the relative stabilities of the products would tend to favor benzyl substitution versus formation of ring-substituted products and loss of the aromaticity of the benzene ring.[36] These considerations predict that other examples of ring substitution will be observed for exothermic functionalization reactions using very reactive electrophilic species. Thus, Russell[37] reported that while neutralization of (α,α-dimethylbenzyl)-potassium with D_2O gave only deuterium substitution at the benzyl (α) position, reaction with DCl in diethyl ether produced up to 25% ring deuteration. With regard to the carboxylation reaction in the solid state, the reaction occurs almost immediately upon introduction of the gaseous carbon dioxide into the reactor, which is consistent with carboxylation being a fast, exothermic reaction.

The consideration of the charge distribution in the benzyl anion does not provide an explanation for the fact that very little ring substitution is observed in solution, while 15–35% ring substitution is observed in the solid state. Two factors could provide explanations for these results. First, it is important to consider the fact that the benzyl carbanions under discussion are actually associated with lithium as the counterion. As discussed by Schade and Von Rague Schleyer,[38] it is expected that the negative charge will tend to concentrate in the vicinity of the small lithium cation; consequently, if the equilibrium position of the lithium cation is different in the solid state versus solution, then this factor could favor ring substitution in the solid state by having more charge distributed onto the ring carbons in the solid state versus solution. The only available X-ray crystallographic structural information for benzyllithium in the solid state is for the quinuclidine complex, which does have the lithium cation located partially over the aromatic ring carbons.[39] The second factor which may be important in the solid state is the relative importance of steric factors. It is readily envisioned that the benzyl carbon may be in a more sterically restricted local environment vis-à-vis the para position of the aromatic ring. The fact that the ring substitution is almost exclusively para without significant amounts of ortho substitution, in spite of the fact that there are two ortho positions with approximately equivalent amounts of charge, does suggest that steric factors may play a role in directing substitution to the para position in the solid-state reactions.

Conclusions. The structure of functionalized polystyrenes cannot be deduced simply from titration results and routine functional group analysis. Evidence has been presented herein which shows that significant amounts (15%) of ring-substitution products are formed in the solid-state carboxylation of poly(styryl)lithium; the yield of the ring-substitution product increases to 35% for the corresponding (1,1-diphenylalkyl)lithium species. Thus, although the solid-state carboxylation reaction produces a quantitative yield of carboxylated polymers, it is not the recommended procedure because of the significant amounts of ring-substituted products which are formed. Solution carboxylation in the presence of Lewis bases such as THF and TMEDA is the recommended procedure;[12] using these procedures the amount of ring carboxylation is minimized (4%). End-capping with 1,1-diphenylethylene prior to solution carboxylation is also efficient and produces a minimum amount of ring substitution (1%).

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