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Synthesis of Polymers with Carboxy End Groups by Reaction of Polystyryl Anions with 4-Bromo-1,1,1-trimethoxybutane

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ABSTRACT: Well-defined polystyrenes with terminal carboxy groups were synthesized by the reaction of living polystyryl anions with 4-bromo-1,1,1-trimethoxybutane, followed by treatment with 0.1 N HCl at first and then with 0.2 N LiOH. The polymers thus obtained were carefully analyzed by size-exclusion chromatography (SEC), acid–base titration using potassium methoxide, ^{1}H and ^{13}C NMR, IR, and thin-layer chromatography (TLC)–flame ionization detection (FID). The analytical results indicated that the polymers had terminal carboxy groups with high degrees (>95%) as well as predictable molecular weights and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n < 1.1$). Chromatographic separation by TLC based on SiO_2 and quantitative analysis by FID for polymers with terminal carboxy groups were discussed.

Introduction

Anionic living polymers are very suitable precursors of telechelic polymers with ideal structures, since they have controlled molecular weights with nearly uniform distributions as well as highly reactive carbanionic species at their chain ends which allow reaction with electrophilic compounds. In fact, many examples have been reported for the synthesis of telechelic polymers by the reactions of anionic living polymers with a wide variety of electrophiles.[1–4] Unfortunately, most of the reported examples so far have been neither described in detail nor well characterized especially with respect to the degree of end functionalization. Up to the present time, reliable demonstrations with a degree of end functionalization more than 95% were quite limited.[5–10]

The introduction of carboxy groups at the polymer chain ends is of considerable interest since these groups undergo a variety of reactions and the polymers transform readily into ionomers with carboxylate anions. The polymers with terminal carboxy groups are one of the most industrially used telechelic polymers. They could be obtained anionically by the carbonation of anionic living polymers with carbon dioxide. However, there is a special problem pointed out by earlier research groups,[11,12] that the reaction yields the desired carboxylated polymer along with significant amounts of side products by subsequent reactions. They are the corresponding ketone (dimer) and tertiary alcohol (trimer) as follows:

$$\text{PSt-Li} \xrightarrow[\text{(2) H}^+]{\text{(1) CO}_2} \text{PSt-COOH} + (\text{PSt})_2\text{C{=}O} + (\text{PSt})_3\text{COH}$$

PSt-Li: polystyryllithium
PSt-COOH: carboxylated polystyrene
$(PSt)_2C{=}O$: ketone (dimer of polystyrene)
$(PSt)_3COH$: tertiary alcohol (trimer of polystyrene)

Several trials were attempted, with the intention of improving the yield of carboxy-terminated polymer. For example, the carbonation of polystyryllithium with solid, granulated carbon dioxide in benzene produced a 78% yield of the carboxylic acid, whereas a 60% yield was reported under the same conditions with use of gaseous carbon dioxide.[12] The addition of a polar solvent like THF exerted considerable influence to improve the yield. The conversion of polystyryllithium into the corresponding Grignard reagent was found also to be effective. Thus, the yields were increased up to more than 90% in some cases. Recently, Quirk and his co-workers have reinvestigated in detail the carbonation of polystyryl anions and have specified experimental conditions where the reaction quantitatively occurs.[6] Thus, well-defined carboxy-terminated polymers without byproducts could be successfully synthesized at the first time by the carbonation method.

Herein is reported an alternative synthesis of well-defined polystyrenes with terminal carboxy groups by the

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reaction of polystyryl anions with 4-bromo-1,1,1-trimethoxybutane (1), whose orthoester function is a pro-

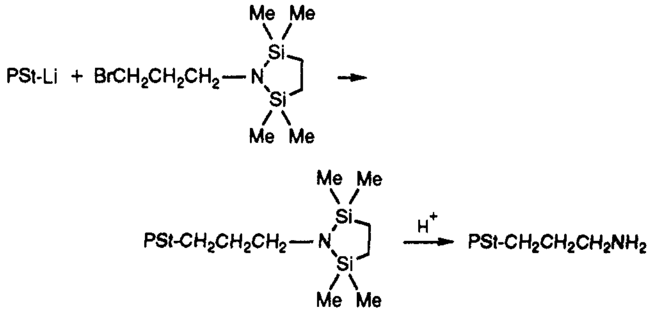
$$BrCH_2CH_2CH_2C(OCH_3)_3$$

1

tected form of the carboxy group. Furthermore, chromatographic isolation by TLC and quantitative analysis with flame ionization detection (FID) techniques for the resulting telechelic polymers with carboxy groups will be discussed.

Results and Discussion

Preparation of Polystyrenes with Terminal Carboxy Groups. *It is well-known that carbanions like* organolithium compounds react efficiently with primary alkyl halides to yield addition products via new C–C bond formation. Similarly, the reactions of anionic living polymers with alkyl halides (RXs) are expected to proceed to afford the polymers with terminal R groups. We previously demonstrated that the reaction occurred efficiently between either polystyryl anions or polyisopropenyl anions and the alkyl halides with a silyl-protected amino functionality as shown below:[8]



By the above reaction, followed by deprotection of the silyl groups, an amino group was introduced into the polymer chain ends in yields of generally more than 95%. The resulting polymers expectedly possessed predictable molecular weights and narrow molecular weight distributions. Thus, this method provides an excellent route for synthesizing well-defined telechelic polymers with terminal amino groups.

The above-mentioned method might be extended to a general methodology for synthesizing a variety of telechelic polymers if the haloalkanes with other functionalities appropriately protected could be used in the reaction. As an extension of the method, we describe here the reaction of living polystyrene with a haloalkane with a protected carboxy functionality for synthesis of polystyrenes with terminal carboxy groups. For this purpose, 4-bromo-1,1,1-trimethoxybutane is a reagent of choice as the haloalkane, because of the stability of the orthoester function toward highly reactive basic reagents like organolithium compounds and easy hydrolysis to generate carboxylic acid under mild conditions.[13-16] An outline of this synthetic route is as follows:

$$\text{PSt-Li} + BrCH_2CH_2CH_2C(OCH_3)_3 \rightarrow$$

$$\text{PSt-}CH_2CH_2CH_2C(OCH_3)_3 \xrightarrow{H^+} \xrightarrow{OH^-}$$

$$\text{PSt-}CH_2CH_2CH_2COOH$$

The reaction of either polystyryllithium or potassium with 1 was carried out in THF or THF/pentane mixtures (6/4 to 7/3, v/v). The general reaction conditions were being allowed at −78 °C for 12 h and then at 25 °C for 1 h to complete the reaction, although characteristic dark red and orange-red colors of polystyryl anions were observed to disappear within a few hours even at −78 °C. Lower temperatures are favored for avoiding the possible side reaction of polystyryl anions with the orthoester function of 1. A slight excess (1.2 equiv to the carbanion) of reagent was enough to complete the reaction. The reaction mixtures were poured into a large excess of methanol to precipitate polymers. The polymers were then purified by reprecipitation from THF to methanol at least four times. Both ^1H and ^{13}C NMR analysis of the polymers showed that end groups of the polymers were always a mixture of $C(OCH_3)_3$ (80–90 mol %) and $COOCH_3$ (10–20 mol %), indicating partial hydrolysis of the terminal orthoester function during these work-up steps. Treatment of the polymer with 0.1 N HCl afforded quantitatively the polymer with a terminal methyl ester group. It was found that the ester C=O stretching frequency was clearly observable at 1739 cm^{-1} in the polymer sample. Hydrolysis of the terminal methyl ester to the carboxy group could be accomplished by 0.2 N LiOH. The IR spectrum of the polymer showed a new strong band at 1707 cm^{-1} characteristic of carboxylic acid with disappearance of the band at 1739 cm^{-1} due to the ester group. Its ^1H, ^{13}C NMR, and TLC analyses also strongly indicated quantitative hydrolysis.

Table I
Reaction of Mono- and Difunctional Polystyryl Anions with 1[a]

initiator	functionality of polystyryl anion	carboxylated polystyrene $\bar{M}_n$[b]	carboxylated polystyrene degree of carboxylation,[c] %
BuLi[d]	1	4100	90
BuLi	1	6400	95
BuLi	1	10300	98
Li-Nap[e]	2	4700	91
Li-Nap	2	6500	97
Li-Nap	2	11000	99
K-Nap[f]	2	6600	96
K-Nap	2	10400	92

[a] Reactions were carried out in THF at −78 °C for 12 h and at 25 °C for 1 h. Yields of polymers were 90–95% in all cases after four reprecipitations. [b] The $\bar{M}_n$ values were determined by SEC using a standard polystyrene calibration curve. The $\bar{M}_w/\bar{M}_n$ values of all samples were less than 1.1. [c] Degrees of carboxylation were determined by the acid–base titration–$\bar{M}_n$ method. [d] *n*-Butyllithium. The reactions were carried out in THF–pentane mixtures (6/4 to 7/3). [e] Lithium naphthalenide. [f] Potassium naphthalenide.

The resulting polymers with terminal carboxy groups thus obtained were first evaluated by a combination of acid–base titration of the terminal carboxy group and $\bar{M}_n$ determined by size-exclusion chromatography (SEC). It should be noted that $\bar{M}_n$ was that of the base polymer obtained by degassed methanol quenching prior to the reaction, since difficulty was encountered by direct determination of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values of the polystyrene with terminal carboxy groups by SEC measurement. Their SEC chromatograms always showed asymmetrical single peaks with low molecular weight tails, and the values of $\bar{M}_w/\bar{M}_n$ were in the range of 1.2–1.3. The values of $\bar{M}_n$ were definitely lower than the base polymers in all cases.

The results are summarized in Table I. As can be seen, the contents of terminal carboxy groups are reasonably excellent, indicating that the reaction of polystyryl anions with 1 proceeds in high efficiency to introduce carboxy groups at the polymer chain ends. Furthermore, the polystyrenes with one or two terminal carboxy groups could be obtained by choosing living polystyrenes produced with either mono- or difunctional initiators.

As mentioned before, difficulty was encountered by SEC measurement of polystyrenes with terminal carboxy groups, since their chromatograms showed asymmetrical peaks eluted at unexpected molecular weight regions. However, they go back to symmetrical peaks with unimodal distributions by esterification of the terminal carboxy groups with diazomethane. They are completely identical to those of the polystyrenes with terminal methyl ester groups before hydrolysis with LiOH. The molecular weight distributions were narrow and almost the same as those of base polystyrenes. The $\bar{M}_{\rm w}/\bar{M}_{\rm n}$ values were less than 1.1. The results strongly indicate that the reactions of polystyryl anions with 1 proceed without side reactions. Accordingly, the resulting polymers thus obtained have well-regulated chain lengths and excellent degrees of terminal carboxy groups that are ideal structures as a telechelic polymer. The representative SEC chromatograms of the base polystyrene, the polystyrene with terminal ester groups, the polystyrene with carboxy groups, and the diazomethane esterified polystyrene sample are shown in Figure 1. The molecular weight distributions are almost identical among these polymers except for that with terminal carboxy groups, indicating no side reactions leading to degradation or cross-linking during treatments with 0.1 N HCl, 0.2 N LiOH, and diazomethane.

Characterization of Polystyrenes with Terminal Carboxy Groups By Thin Layer Chromatography (TLC). Earlier work by Law suggested the possibility of the separation of carboxy-terminated polybutadiene by column chromatography based on silica gel (SiO_2).[17] The distribution of the carboxy functionality was found to be an important factor for separation. Later, Månsson demonstrated successful chromatographic separation of the mixed products obtained by the carbonation of polystyryl anions with carbon dioxide.[12] A polystyrene with carboxy groups ($\bar{M}_{\rm n}$ = 2500) could be isolated by column chromatography and preparative TLC based on SiO_2. Similarly, Quirk and Cheng have recently reported that pure amine-terminated polystyrenes can be isolated from unfunctionalized polystyrenes by SiO_2 column chromatography.[18] In our previous paper,[8] we examined the behaviors of various telechelic polystyrenes with amino groups on TLC. It was found that in addition to the successful separation of polystyrenes with amino groups from unfunctionalized polystyrene by TLC, more importantly, the polystyrenes with one amino end group could possibly be separated from those with two amino end groups. Also, the chromatographic technique to separate these telechelic polymers by the difference of molecular weights was established. Furthermore, it has been demonstrated that the TLC–FID method is successfully applied to quantitative analysis of these telechelic polystyrenes with terminal amino groups which will be discussed in the next section. Thus, column and thin-layer chromatographies should be extremely useful for the separation of telechelic polymers by their specified structures.

Since we have obtained here a variety of polystyrenes with one and two terminal carboxy groups having different molecular weights, we have examined the behaviors of these polymers on TLC to aim at finding the conditions for separating each of these polymers by their structural variables. For this purpose, we have prepared nine polymer samples listed in Table II, in which symbols S, M, and D indicate polystyrene and mono- and dicarboxylated polystyrenes at their end groups, respectively. Their $\bar{M}_{\rm n}$ values are about 4000, 6000, and 10 000, respectively, and the $\bar{M}_{\rm w}/\bar{M}_{\rm n}$ values are less than 1.1 for all samples.

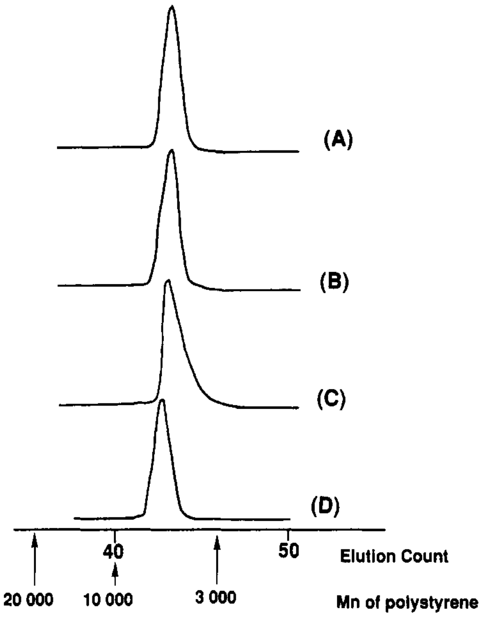


Figure 1. SEC curves of base polystyrene (A), polystyrene–$CH_2CH_2CH_2COOCH_3$ (B), polystyrene–$CH_2CH_2CH_2COOH$ (C), and polystyrene–$CH_2CH_2CH_2COOCH_3$ (D). $\bar{M}_{\rm w}/\bar{M}_{\rm n}$ values of polymers A, B, D were less than 1.1, whereas that of polymer C was 1.37.

Table II
Lists of Samples of Polystyrenes and Polystyrenes with Terminal Carboxy Groups for TLC and TLC–FID Measurements

PSt[a]		PSt-COOH[b]		HOOC-PSt-COOH[c]	
no.	$\bar{M}_{\rm n}$	no.	$\bar{M}_{\rm n}$	no.	$\bar{M}_{\rm n}$
S-1	4100	M-1	4100	D-1	4700
S-2	6200	M-2	6400	D-2	6500
S-3	10100	M-3	10300	D-3	10400

[a] Polystyrenes. [b] Polystyrenes with one terminal carboxy group. [c] Polystyrenes with two terminal carboxy groups. The values of $\bar{M}_{\rm w}/\bar{M}_{\rm n}$ of these samples were less than 1.1.

Figure 2 illustrates some representative chromatograms of the polymer samples on SiO_2-based TLC using various elution solvents. When THF was used as the eluent, the samples all were well mobile with high R_f values (R_f = 0.90–0.95), whereas the spots were not moved at all with methanol as expected. Interestingly, the spots of polystyrenes show up at values of R_f of approximately 0.90–0.93 with toluene as a developing solvent, and, on the other hand, the samples with terminal carboxy groups remained on the starting points on TLC. A similar behavior was observed with the use of chloroform. These results clearly indicate that the polystyrenes with carboxy groups are separable from unfunctionalized polymers by preparative TLC and probably column chromatography based on SiO_2 using either toluene or chloroform.

Of more interest are the behaviors of polymer samples on TLC developed with toluene/methanol (98/2, v/v) and chloroform/methanol (98/2, v/v). With these mixed solvents, polystyrenes were moved up easily with R_f values of 0.95 and the polystyrenes with two terminal carboxy groups remained almost at the starting points. The samples with one terminal carboxy group were found to be mobile to some extent, showing up at an R_f of 0.22–0.67 whose values were dependent on molecular weight. These results lead to the possibility that three polymers with different terminal groups are separable by TLC and column chromatography. For example, S3, M3, and D3 of which have $\bar{M}_{\rm n}$s of about 10 000 are separable, estimating

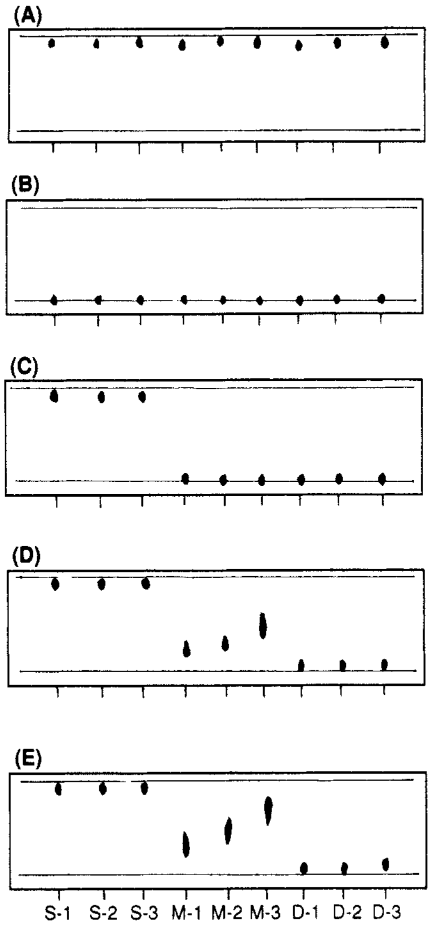


Figure 2. SiO_2-based thin layer chromatograms of polystyrene (S), polystyrene with one carboxy end group (M), and polystyrene with two carboxy end groups (D): (A) THF; (B) methanol; (C) toluene; (D) toluene–methanol (98/2, v/v); (E) chloroform–methanol (98/2, v/v).

from their R_f values, 0.95, 0.67, and 0.07, respectively. In addition, the polystyrenes with one terminal carboxy group can possibly be separated by the difference of $\bar{M}_n$ values, although their spots are not very well-separated from each other and the optimum conditions should be explored in more detail. Thus, the carboxy groups at the polymer ends seem to strongly interact with SiO_2, and therefore the polystyrenes with carboxy groups can be separated from unfunctionalized polymers.

Similar tendencies were observed on TLC based on alumina (Al_2O_3). Reproducibility of R_f values within ±10% is always obtained when the operation is carefully carried out. All the results obtained here clearly indicate the validity of the TLC method for the separation of telechelic polymers with terminal carboxy groups. The predominant factors for separation are the elution solvent, content of carboxylic acid in the polymer (0, 1, and 2), and molecular weight.

Quantitative Analysis of Polystyrenes with Terminal Carboxy Groups by the TLC–Flame Ionization Detection (FID) Method. The advantages of TLC have thus been recognized, but the method using TLC plates seems to not be suitable for direct quantification of chromatograms. For this purpose, we have employed the TLC–FID method developed previously by Padley.[19] This method used a specially designed thin quartz rod covered with SiO_2 or Al_2O_3 instead of a TLC plate on which the chromatographic separation was made. Almost the same spot distribution was realized between the rod and plate. The rod was then scanned with sufficient heating to ionize each component of the spots separated. The ions were quantitatively detected by FID. The use of a scanning apparatus equipped with FID eliminates the isolation step of polymer which is laborious and time consuming and causes some operation errors.

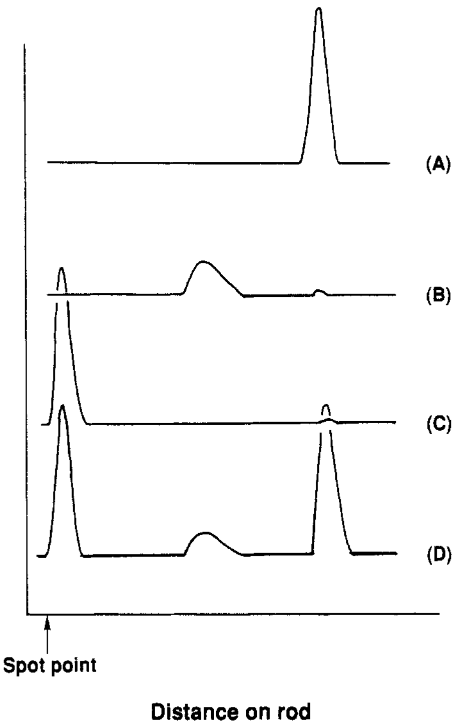


Figure 3. Chromatograms (Iatroscan) of polystyrene (A), polystyrene with one carboxy end group (B), polystyrene with two carboxy end groups (C), and a mixture of the three samples (D).

In order to investigate the feasibility of applying TLC–FID to quantitative analysis of polymers with terminal carboxy groups, we have prepared three samples of S2, M2, and D2. They are a polystyrene ($\bar{M}_n$ = 6200, $\bar{M}_w/\bar{M}_n$ = 1.05), a polystyrene with one terminal carboxy group ($\bar{M}_n$ = 6400, $\bar{M}_w/\bar{M}_n$ = 1.05, F_{COOH} = 0.95), and a polystyrene with carboxy groups at both ends ($\bar{M}_n$ = 6500, $\bar{M}_w/\bar{M}_n$ = 1.10, F_{COOH} = 0.97), respectively. On four Al_2O_3 rods, S2, M2, D2, and the 1/1/1 mixture of these three samples were spotted and developed in a toluene/methanol (98/2, v/v) mixed solvent. The chromatograms obtained by FID are shown in Figure 3.

As can be seen, the peaks due to S2, D2, and M2 appeared at different distances on the rod, and, obviously, they were separated in the mixed sample. In the mixed sample, the ratio of the three peak areas was found to be nearly 1/1/1 which was in good agreement with that of the composition mixture. Similarly, fair agreements were observed in other mixed samples with different compositions. Duplicates usually agreed to less than 5% error for each peak area in all runs under careful operation. Furthermore, in the samples with carboxy groups (M2 and D2) small peaks corresponding to unfunctionalized polystyrene were always observed in addition to main peaks. The area percentages of main peaks to small ones are calculated to be both 98%. These values are closely equal to those of 95% and 97% estimated by acid–base titration and $\bar{M}_n$ by SEC analysis. The results thus obtained unequivocally indicate that the TLC–FID method is applicable to quantitative analysis of the polymer samples with terminal carboxy groups. With toluene/methanol (98/2, v/v) as a developing solvent, broad peaks were always observed for a series of the polystyrenes with one terminal carboxy group. When toluene was instead used to analyze these samples by FID, the samples

Table III
Results of Degrees of Carboxylation by the TLC–FID and Titration–$\bar{M}_n$ Methods

functionality of carboxylated polystyrene	$\bar{M}_n$	degree of carboxylation, %	
		TLC–FID	titration–$\bar{M}_n$
1	4100	96	90
1	6400	98	95
1	10300	96	98
2	4700	91	91
2	6500	98	97
2	10400	95	92

appeared as sharper peaks in the chromatograms. Similarly, toluene/methanol (99/1, v/v) was preferable in the case where the $\bar{M}_n$ values of the samples were more than 10 000.

Attempts to analyze our polymer samples with terminal carboxy groups were indeed successful. The results are summarized in Table III. The degrees of carboxylation estimated by TLC–FID are observed to be excellent to nearly quantitative and are in good agreement with the values determined on the basis of titration and $\bar{M}_n$ values, again indicating high efficiency of the reaction of polystyryl anions with 1. Thus, the results demonstrate obviously the validity of the TLC–FID method for quantitative analysis of polymers with terminal carboxy groups. The advantages of the TLC–FID method are as follows: First, microgram quantities of samples are enough for this method, whereas the titration of the carboxy group with potassium methoxide requires gram quantities, especially with the samples having $\bar{M}_n$s higher than 10 000. Second, the degree of functionalization can be directly determined by the ratio of peaks in the chromatogram without using $\bar{M}_n$ values of the samples. This is attractive considering the fact that it is often difficult to determine the exact $\bar{M}_n$ values of the polymers. Third, the ratio of polystyrene with one terminal carboxy group to that with carboxy groups at both ends can be estimated in some cases by the TLC–FID method. Such information, which is difficult to obtain by any other methods, is especially important in the case of chain extension reactions, since the presence of a monofunctionalized sample causes a serious termination reaction.

In conclusion, we have successfully obtained well-defined telechelic polystyrenes with terminal carboxy groups by the reaction of living polystyrenes with 4-bromo-1,1,1-trimethoxybutane, followed by deprotection. In addition to our previous result on the synthesis of telechelic polymers with amine groups, this result strongly suggests that the reaction of anionic living polymers with specially designed haloalkanes with appropriate protected functionalities can provide a general and convenient method for the synthesis of well-defined polymers with a variety of end functional groups.

Experimental Section

Materials. Styrene was purified according to a standard procedure. It was then distilled twice over CaH_2 under a nitrogen atmosphere. Phenyl chloride free phenylmagnesium chloride (2.0 mL, 0.5 M THF solution) was added to styrene (10 g) at 0 °C, and the mixture was degassed and stirred at room temperature for 1 h. Styrene was then distilled with THF on a vacuum line into ampules with break-seals that were prewashed with sodium naphthalenide in THF. THF was refluxed over a sodium wire for 5 h and then distilled from its sodium naphthalenide solution under an atmosphere of nitrogen. LIthium and potassium naphthalenides were prepared by the reaction of either lithium or potassium with 1.2 times excess of naphthalene in THF. *n*-Butyllithium (BuLi) from Kanto Chemical Co., Ltd., was used without purification. These anionic initiators were diluted with THF or *n*-heptane at appropriate concentrations and stored in ampules with break-seals. The concentrations of the initiators were determined by colorimetric titration with standardized 1-octanol in a sealed reactor under vacuum. 4-Bromo-1,1,1-trimethoxybutane was purchased from Aldrich. It was purified over CaH_2 by repeated fractional distillation under reduced pressure to remove completely methyl 4-bromobutyrate which was a possible source of side reaction. It was readily hydrolyzed even with the moisture in the air to methyl 4-bromobutyrate and therefore treated carefully under an atmosphere of nitrogen. Phenyl chloride free phenylmagnesium chloride (1.0 mL, 0.15M THF solution) was added to 4-bromo-1,1,1-trimethoxybutane (3.6 g, 16 mmol), degassed, stirred for 1 h at 25 °C, and then distilled on a vacuum line into ampules with break-seals that were prewashed with sodium naphthalenide.

Polymerizations and Reactions of Polystyryl Anions with 4-Bromo-1,1,1-Trimethoxybutane. Polymerizations and reactions were carried out under high-vacuum conditions in sealed glass reactors with break-seals. The reactors were always prewashed with the initiator solution after being sealed off from a vacuum line and were used for polymerizations, followed by reactions. Anionic polymerization of styrene, initiated with either metal naphthalenide or BuLi, was carried out in THF or THF/heptane mixed solvents at −78 °C for 0.5 h. The polymer solution was then divided into two portions, one of which was terminated with degassed methanol to determine the $\bar{M}_n$ value. An excess (1.2–2.0 equiv to initiator) of a dried 4-bromo-1,1,1-trimethoxybutane in THF solution (0.2–0.3 M) was added dropwise at −78 °C to the remaining living polystyrene solution, and the reaction mixture was allowed to stand at −78 °C for 12 h and then at 30 °C for 1 h. The mixture was poured into a large excess of methanol to precipitate the polymer. It was purified by repeated reprecipitation from THF solution to methanol at least four times to remove unreacted 4-bromo-1,1,1-trimethoxybutane completely. The polymer thus purified was freeze-dried from its benzene solution and characterized by ^1H NMR, ^{13}C NMR, and IR spectroscopies. Hydrolysis of $C(OCH_3)_3$ to $COOCH_3$ was always observed to some extent (ca. 10–20 mol %) in the ^1H NMR spectrum of the polymer.

Transformation of an Orthoester End Group to a Methyl Ester End Group of Polystyrene. The polystyrene with a methyl ester end group was quantitatively obtained by treating the polymer ($\bar{M}_n$ = 6400) with an orthoester end group (1.40 g, ca. 0.43 mmol for the orthoester group) with 0.1 N HCl in a mixture of 1,4-dioxane/H_2O (14/1, v/v) at 25 °C for 1.5 h. The quantitative transformation was confirmed by ^1H NMR, ^{13}C NMR, and IR spectroscopies.

Hydrolysis of a Methyl Ester End Group to a Carboxy End Group of Polystyrene. The polystyrene ($\bar{M}_n$ = 6400) with a methyl ester end group (0.800 g, ca. 0.25 mmol for two ester end groups) dissolved in THF (10 mL) and LiOH (0.0814 g, 1.94 mmol) was added to the solution. The reaction mixture was stirred at 30 °C for 20 h and then neutralized by adding 0.1 N HCl. The polymer was collected by precipitation in methanol, purified by repeated reprecipitation from THF to methanol, and freeze-dried from its benzene solution. The yield of polymer was generally more than 90%. The complete hydrolysis to a carboxy end group was confirmed by ^1H NMR, ^{13}C NMR, and IR spectroscopies and the TLC–FID method.

Reesterification of a Carboxy End Group to a Methyl Ester End Group of Polystyrene. An ether solution of diazomethane (0.2 mL, ca. 0.08 mmol) was added to the polystyrene ($\bar{M}_n$ = 6400) with a carboxy end group (30.0 mg, 0.0093 mmol for a carboxy group) in benzene solution (10 mL) at 25 °C for overnight. After decomposition of unreacted diazomethane with acetic acid, the polymer was collected by precipitation in methanol and purified by reprecipitation from THF to methanol. The polymer was found to be methylated completely by the ^1H NMR and ^{13}C NMR spectroscopies. The observed values of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ were identical with those of the polystyrene with a methyl ester end group obtained by the original polymer sample.

Characterization of Polystyrene with a Carboxy End Group. The content of a carboxy group at the polystyrene chain ends was directly determined by acid–base (standard potassium methoxide in benzene/methanol (9/1, v/v) titration with thymol blue as an indicator in dry pyridine under an atmosphere of nitrogen. Color change from orange to green was an end point. The degree of functionalization (F_{COOH}) was evaluated by a combination of the carboxy group content thus obtained and the $\bar{M}_n$ value of polystyrene determined by SEC. The F_{COOH} was also estimated by the TLC–FID method. The results by both methods were compared and found to be identical within experimental errors for each of all the samples.

Measurements. Infrared spectra were recorded on a JEOL JIR-AQS20M FT-IR spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-90Q (89.6-MHz ^{1}H and 22.53-MHz ^{13}C) in $CDCl_3$. Size-exclusion chromatograms (SEC) for the determination of $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values were obtained at 40 °C with a Toyosoda HLC 8020 instrument with UV (254 nm) or refractive index detection. THF was the carrier solvent at a flow rate of 1.4 mL min^{-1}. Three polystyrene gel columns (TOSOH G5000H$_{X-1}$, G4000H$_{X-1}$, G3000H$_{X-1}$) were used after calibration with standard polystyrene samples obtained from Toyosoda Co., Ltd. Thin-layer chromatography (TLC) was carried out on SiO_2 plates (Merck Art 5554) or Al_2O_3 plates (Merck Art 5550) with a fluorescent indicator. The instrument for the TLC–FID method was an Iatron Thinchrograph Model TH-10 from Iatron Co., Ltd. Specially designed quartz rods (150 × 2.0 mm) were employed on which silica gel or alumina particles were sintered in advance. They were commercially available as SII, SIII, and A rods. Air flow rate (200 mL min^{-1}) and hydrogen pressure (0.85 kg cm^{-2}) were set for analysis. The principles and equipment for this method as well as schematic diagram of the instrument were described in detail in previous literature.[19–24]

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References and Notes

(1) Morton, M.; Fetters, L. J. *Macromol. Rev.* **1967**, *2*, 71.
(2) French, D. M. *Rubber Chem. Technol.* **1969**, *42*, 71.
(3) Young, R. N.; Quirk, R. P.; Fetters, L. J. *Adv. Polym. Sci.* **1984**, *56*, 1.
(4) Quirk, R. P.; Yin, J.; Guo, S.-H.; Hu, X.-W.; Summers, G.; Kim, J.; Zhu, L.-F.; Schock, L. E. *Makromol. Chem. Macromol. Symp.* **1990**, *32*, 47.
(5) Morton, M.; Fetters, L. J.; Inomata, J.; Rubio, D. C.; Young, R. N. *Rubber Chem. Technol.* **1976**, *49*, 303.
(6) Quirk, R. P.; Yin, J.; Fetters, L. J. *Macromolecules* **1989**, *22*, 85.
(7) Quirk, R. P.; Zhu, L.-F. *Makromol. Chem.* **1989**, *190*, 487.
(8) Ueda, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1990**, *23*, 939.
(9) Quirk, R. P.; Kim, J. *Macromolecules* **1991**, *24*, 4515.
(10) Quirk, R. P.; Yin, J.; Fetters, L. J.; Kastrup, R. V. *Macromolecules* **1992**, *25*, 2262.
(11) Wyman, D. P.; Allen, V. R.; Altares, T., Jr. *J. Polym. Sci.* **1964**, *A2*, 4545.
(12) Månsson, P. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 1945.
(13) Corey, E. J.; Kang, J. *Tetrahedron Lett.* **1982**, *23*, 1651.
(14) Nájera, C.; Yus, M. *J. Org. Chem.* **1988**, *53*, 4708.
(15) Burkholder, T. P.; Fuchs, P. L. *J. Am. Chem. Soc.* **1988**, *110*, 2341.
(16) Bee, T. G.; McCarthy, T. J. *Macromolecules* **1992**, *25*, 2093.
(17) Law, R. D. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 175.
(18) Quirk, R. P.; Cheng, P.-L. *Macromolecules* **1986**, *19*, 1291.
(19) Padley, F. B. *J. Chromatogr.* **1969**, *39*, 37.
(20) Szakasits, J. J.; Peurifoy, P. V.; Woods, L. A. *Anal. Chem.* **1970**, *42*, 351.
(21) Mukherjee, K. D.; Spanns, H.; Haahti, E. *J. Chromatogr.* **1971**, *61*, 317.
(22) Min, T. I.; Miyamoto, T.; Inagaki, H. *Rubber Chem. Technol.* **1977**, *50*, 63.
(23) Ogawa, T.; Ishitoki, M. *J. Polym. Sci., Polym. Chem. Ed.* **1983**, *21*, 781.
(24) Tax, J. C. J. F.; German, A. L. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 817.