Synthesis of Well-Defined Functionalized Polystyrenes with a Definite Number of Chloromethylphenyl Groups at Chain Ends or in Chains by Means of Anionic Living Polymerization in Conjunction with Functional Group Transformation

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ABSTRACT: The syntheses of well-defined polystyrenes functionalized with a definite number (from one to four) of chloromethylphenyl groups at the chain ends or in the chains by means of anionic living polymerization in conjunction with functional group transformation are described. The synthetic method involves the introduction of anion-stable methoxymethylphenyl or *tert*-butyldimethylsilyloxymethylphenyl groups at the chain ends or in the chains and subsequent transformation reactions of these groups into chloromethylphenyl groups with BCl_3. It is also possible to transform the *tert*-butyldimethylsilyloxymethylphenyl group into bromomethylphenyl and iodomethylphenyl groups by treatment with $Me_3SiCl-LiBr$, and $Me_3SiCl-NaI$, respectively. Furthermore, the synthesis of well-defined polystyrenes having two, four, and six methoxymethylphenyl and six chloromethylphenyl termini via a new iterative approach using 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium is described. It involves repeated chemical transformations at the chain end from *tert*-butyldimethylsilyloxybutyl, bromobutyl, and methoxymethylphenyl groups to the chloromethylphenyl group. At each stage in the iteration, the number of chloromethylphenyl groups doubles. The resulting polymers all, after HPLC fractionation in some cases, possessed well-controlled molecular weights and narrow molecular weight distributions. Their functionalities were nearly quantitative in all cases.

Introduction

Anionic living polymers of styrene and 1,3-dienes are very attractive precursors for the synthesis of end-functionalized polymers with well-defined structures whose molecular weights are well-controlled with narrow distributions and whose end-functionalization degrees are quantitative. Many synthetic methodologies for such polymers have so far been developed and reviewed.[1−8] Well-characterized and quantitatively functionalized polymers with a variety of termini are presently available. α,ω-Difunctionalized polystyrenes, poly(1,3-butadiene)s, and polyisoprenes having two termini, such as diol, diamine, and dicarboxylic acid functions, are also synthesized from difunctional living polymers as macromonomers for the use of polyaddition and polycondensation reactions. Some of them are utilized for making model networks of synthetic rubbers.[9]

Several α,ω-heterodifunctionalized polystyrenes having different termini are synthesized by anionic living polymerizations of styrenes with functionalized initiators followed by treatment with functionalized terminating agents. Eisenbach and co-workers reported the synthesis of an α-(dimethylamino)-ω-lithium sulfonate-functionalized poly(α-methylstyrene) by the 1,3-propane sultone termination of poly(α-methylstyryl)lithium initiated with 3-dimethylaminopropyllithium.[10] Recently, two research groups have developed a new strategy with use of α,ω-heterodifunctional polystyrenes for the preparation of cyclic polystyrenes. For this purpose, Deffieux and co-workers have synthesized an α-diethyl acetal-ω-styrenyl polystyrene by the 3-lithiopropionaldehyde diethyl acetal initiated polymerization of styrene followed by treatment with 4-chloromethylstyrene after end-capping the resulting polystyryllithium with 1,1-diphenylethylene.[11] Similarly, Ito, Kubo, and their co-workers have synthesized an α-carboxy-ω-amino polystyrene with the use of 3-lithiopropionaldehyde diethyl acetal and 2,2,5,5-tetramethyl-1-(3-bromopropyl)-1-aza-2,5-disilacyclopentane as an initiator and a terminator in the anionic living polymerization of styrene.[12] Gnanou and co-workers have reported the synthesis of α-norbornene-ω-hydroxy polystyrenes as macromonomer precursors by the 5-(lithiomethyl)bicyclo[2.2.1]hept-2-ene initiated polymerization of styrene followed by termination with ethylene oxide.[13] In these polymers, all discussed as above, only one functional group is usually present at each chain end, although two of the same functions (or two different functions) are presented at both chain ends of α,ω-difunctionalized polymers.

It is possible in principle to introduce a centrally located functional group by terminating 2 equiv of anionic living polystyrene with a difunctional terminating agent containing the functional group. For example, Worsfold synthesized a polystyrene containing a centrally placed dimethylamino group by the reaction of polystyryllithium with 8-(dimethylamino)valeric acid methyl ester.[14] Hadjichristidis, Young, and their co-workers have reacted 2 equiv of polyisoprenyllithium with tetrachlorosilane to produce a polyisoprene functionalized with a dichlorosilyl group at the middle of the chain as precursors for making heteroarm (or miktoarm) star polymers.[15]

A more general, versatile method for introducing functional groups in the chains is to utilize the monoaddition reaction of functionalized 1,1-diphenylethylenes with anionic living polymers of styrene and dienes followed by sequential addition of the same or a different monomer to extend the chain or to form a new block.

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Thus, new polymers having functional groups in the chains and/or at the interface between blocks are produced. This functionalization reaction in conjunction with anionic living polymerization named as *a living functionalization reaction* by Quirk has been greatly developed by his research group.[16] Typically, a new functionalized block copolymer of styrene and 1,3-butadiene with the dimethylamino group at the interface between two blocks could be synthesized by reacting 1-(4-dimethylaminophenyl)-1-phenylethylene with polystyryllithium followed by addition of 1,3-butadiene.[17] Similarly, pyrene-labeled interfacial functionalized poly(styrene-*b*-ethylene oxide)s were synthesized using 1-phenyl-1-pyrenylethylene.[18]

In contrast, the syntheses of functionalized polymers with two or more groups at the chain ends or in the chains have been much less studied so far. Since we are here focusing on the synthetic methods mainly using anionic living polymers of styrenes and 1,3-dienes, discussion is limited only to well-controlled functionalized polystyrenes or poly(1,3-diene)s with such molecular architectures. Heitz and Hocker,[19] and Quirk and Wang,[20] have been independently reported the successful synthesis of polystyrenes with two phenol end functionalities. These polymers are obtained by reacting polystyryllithiums with 1,1-bis(4-methoxyphenyl)ethylene and 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)-ethylene followed by deprotection of the methyl and silyl groups. Eisenberg and Zhong have reported the synthesis of an end-functionalized polystyrene with two carboxy groups by reacting polystyryllithium with dimethyl maleate followed by hydrolysis of the ester groups.[21] Hadjichristidis and Iatrou have synthesized dichloro and trichlorosilanes terminated polyisoprenes polystyrenes by reacting the corresponding living polymers with large excesses of trichloromethylsilane and tetrachlorosilane.[22,23] We have demonstrated the synthesis of various well-defined polystyrenes end-functionalized with two, three, and four glucose residues that are obtained by reacting polystyryllithium with a DPE derivative with two acetal-protected glucofuranoses followed by methanol termination or further reactions with haloalkanes containing the same protected glucofuranoses.[24] A ω,ω'−α-methylstyrene-functionalized polystyrene macromonomer has recently been synthesized in an analogous fashion.[25] Gitsov and Frechet have reacted polystyryllithium with the benzyl bromides of dendrimers to successfully couple both macromolecules. Although the dendritic segments in this case are not functionalized, this is a promising method for making polystyrenes having polyfunctional end groups.[26]

Recently, we have been successful in making various regular and heteroarm star-branched polymers.[27] Well-defined polystyrene prepolymers multifunctionalized with chloromethylphenyl groups at the chain ends or in the chains were required in these star polymer syntheses. Therefore, we have developed a new method which involves the monoaddition reaction of 1,1-bis(3-methoxymethylphenyl)ethylene with living polymers of styrene followed by treatment with appropriate terminators to introduce plural anion-stable methoxymethylphenyl groups at the chain ends or in the chains and a subsequent transformation reaction into anion-reactive chloromethylphenyl groups.

In this paper, we would like to describe more details and the extension of our method that permits one to synthesize well-defined functionalized polystyrenes with a definite number of halomethylphenyl groups at the chain ends or in the chains. Furthermore, a new iterative approach for the synthesis of well-defined polystyrenes having two, four, and six methoxymethylphenyl and six chloromethylphenyl termini is reported. In addition to general uses as functionalized polymers, these polymers can be purposely used as suitable building blocks for the preparation of well-defined macromolecules with various architectures such as block and graft copolymers and star, cyclic, and branched polymers as well as supramolecular assemblies.[28] Needless to say, the halomethylphenyl groups are versatile functions capable of undergoing a wide variety of transformations into other functionalities.[29]

Experimental Section

Materials. Styrene was purified according to the usual procedure and was finally distilled over dibutylmagnesium (5 mol % was added) on the vacuum line into ampules with break seals that were prewashed with (1,1-diphenylhexyl)lithium in heptane. 1,3-Dibromopropane, 1,3-diiodopropane, and 1,4-dibromobutane were first distilled over CaH_2 under an atmosphere of nitrogen and then distilled over phenylmagnesium chloride on the vacuum line. THF was carefully purified according to the usual procedure and distilled from a sodium naphthalenide solution on the vacuum line. Acetone, CH_2Cl_2, $CHCl_3$, CCl_4, acetonitrile, and pyridine were distilled over CaH_2 under nitrogen atmosphere. 3-(*tert*-Butyldimethylsilyloxy)-1-propyllithium was purchased from Asia FMC Corporation, Osaka, Japan. Commercially available BCl_3 (Aldrich, 1.0 M in CH_2Cl_2), *tert*-butyldimethylsilyl chloride, $(C_4H_9)_4NF$ (Aldrich, 1.0 M in THF), and methanesulfonyl chloride (MsCl) were used without purification. Trimethylsilyl chloride was distilled over CaH_2 under nitrogen atmosphere. Both LiBr and NaI were dried under high vacuum at 100 °C for 10 h.

1-(4′-Bromobutyl)-4-methoxymethylbenzene (1). 1 was synthesized by the Li_2CuCl_4-mediated coupling reaction of (4-methoxymethylphenyl)magnesium bromide and 1,4-dibromobutane. To an ice-cooled THF solution (50 mL) containing 1,4-dibromobutane (20.9 g, 96.7 mmol) and Li_2CuCl_4 (0.149 g, 0.68 mmol) was added dropwise (4-methoxymethylphenyl)magnesium bromide, prepared from 1-bromo-4-methoxymethylbenzene (6.25 g, 31.1 mmol) and Mg (1.14 g, 47.4 mmol) in THF (30 mL). The reaction mixture was stirred at 25 °C for 20 h. It was then acidified with 2 N HCl, extracted with ether, and dried over $MgSO_4$. Removal of solvent under reduced pressure followed by fractional distillation yielded **1** (5.52 g, 69%) as a colorless liquid: bp 112−113 °C (3.3−3.6 Torr); 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.23 (m, 4H, HAr), 4.45 (s, 2H, $-C_6H_4-CH_2-O$), 3.42 (m, 5H, $-OCH_3$, $-CH_2Br$), 2.65 (t, 2H, $-C_6H_4-CH_2-$), 1.78 (m, 4H, $-CH_2CH_2CH_2-CH_2Br$).

1-(4′-Bromobutyl)-4-(*tert*-butyldimethylsilyloxy)methylbenzene (2). 2 was synthesized by the Li_2CuCl_4-mediated coupling reaction of 4-(*tert*-butyldimethylsilyloxy)methylphenylmagnesium bromide with 1,4-dibromobutane. To a solution of 4-bromobenzyl alcohol (10.4 g, 55.5 mmol) and imidazole (8.63 g, 127 mmol) in *N*,*N*-dimethylformamide (DMF) (60 mL) was added *tert*-butyldimethylsilyl chloride (9.53 g, 64.9 mmol) in DMF (80 mL) dropwise at 0 °C. The mixture was allowed to stand at 0 °C for 1 h and then at 25 °C for an additional 3 h. The reaction mixture was poured into water, and the product was extracted with $CHCl_3$, washed with 5% NaOH, and dried over $MgSO_4$. Removal of solvent followed by fractional distillation under reduced pressure yielded 1-bromo-4-(*tert*-butyldimethylsilyloxy)methylbenzene (14.81 g, 90%) as a colorless liquid: bp 105−7 °C (5.0 Torr); 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.55−7.23 (m, 4H, HAr), 4.71 (s, 2H, $-C_6H_4-CH_2-O$), 0.96 (s, 9H, $-Si-C-CH_3$), 0.12 (s, 6H, $Si-CH_3$).

The Grignard reagent, prepared from 1-bromo-4-(*tert*-butyldimethylsilyloxy)methylbenzene (5.10 g, 17.1 mmol) and Mg (0.64 g, 26.3 mmol) in THF (40 mL) for 3 h, was reacted with 1,4-dibromobutane (10.5 g, 48.4 mmol) in the presence of a catalytic amount of Li_2CuCl_4. The mixture was stirred at 25

°C for 20 h. After usual workup, fractional distillation under reduced pressure gave **2** (3.77 g, 64%) as a colorless liquid: bp 135−138 °C (2.0 Torr); 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.28−7.14 (m, 4H, HAr), 4.77−4.73 (s, 2H, $-C_6H_4-CH_2-O$), 3.56−3.41 (t, 2H, $-CH_2Br$), 2.68−2.63 (t, 2H, $-C_6H_4-CH_2-$), 1.96−1.75 (m, 4H, $-CH_2-CH_2-$), 0.96 (s, 9H, $-Si-C-CH_3$), 0.12 (s, 6H, $Si-CH_3$).

1,1-Bis(3-methoxymethylphenyl)ethylene (3). 3 was synthesized according to a method previously reported by us.[17]

1,1-Bis[(3-*tert*-butyldimethylsilyloxy)methylphenyl]-ethylene (4). To synthesize **4**, 1,1-bis(3-hydroxymethylphenyl)ethylene was at first synthesized by the reaction of ethyl acetate with 3-(1,3-dioxolan-2-yl)phenylmagnesium bromide followed by dehydration with *p*-toluenesulfonic acid, according to the usual procedure employed for 1,1-diphenylethylene derivatives. To a stirred solution of the Grignard reagent, prepared from 3-(1,3-dioxolan-2-yl)phenyl bromide (9.02 g, 39.6 mmol) and Mg (1.44 g, 59.3 mmol) in THF (100 mL), was added ethyl acetate (1.80 mL, 18.4 mmol) in THF (5 mL) dropwise at 0 °C, and the mixture was stirred at 25 °C for 10 h. The reaction mixture was acidified by 2 N HCl, extracted with ether, and dried over $MgSO_4$. After removal of solvent under reduced pressure, the residual oil was reacted with $NaBH_4$ (0.81 g, 21.4 mmol) in ethanol (50 mL) to give crude 1,1-bis-(3-hydroxymethylphenyl)ethanol (4.43 g, 17.2 mmol, 93%). It was then dehydrated with a catalytic amount of *p*-toluenesulfonic acid in $CHCl_3$ (30 mL) at 60∼70 °C for 3 h. After the usual workup, 1,1-bis(3-hydroxymethylphenyl)ethylene (3.67 g, 15.3 mmol) was obtained in 89% yield as a pale yellow liquid. The resulting 1,1-bis(3-hydroxymethylphenyl)ethylene was used in the further silylation reaction without purification. To a solution of 1,1-bis(3-hydroxymethylphenyl)ethylene (3.67 g, 15.3 mmol) and imidazole (3.02 g, 44.1 mmol) in DMF (20 mL) was added *tert*-butyldimethylsilyl chloride (4.60 g, 30.7 mmol) in DMF (10 mL) dropwise at 0 °C. The mixture was allowed to stand at 25 °C for 3 h. After the usual workup, flash column chromatography (hexanes/benzene, 1:1) afforded 1.58 g (3.38 mmol, 22%) of **4** as a viscous syrup. It was freeze-dried several times to remove water from its benzene solution prior to use; 300 MHz ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 8H, $-C_6H_4-$), 5.47 (s, 2H, $C=CH_2$), 4.76 (s, 4H, $-CH_2O-$), 0.99 (d,18H, $C-CH_3$), 0.12 (d, 12H, $Si-CH_3$); 75 MHz ^{13}C NMR ($CDCl_3$) δ 141.3, 141.2, 127.9, 126.8, 125.8, 125.3, 114.0, 76.5, 64.8, 25.8, 18.3, −5.4.

Synthesis of Polystyrenes Functionalized with a Definite Number of Methoxymethylphenyl and (*tert*-Butyldimethylsilyloxy)methylphenyl Groups at the Chain Ends or in the Chains. The polymerizations and reactions were carried out under high vacuum condition (10^{-6} Torr) in sealed glass reactors with break seals. The reactors were always prewashed with the initiator solutions after being sealed off from a vacuum line and were used for the polymerizations and reactions. The anionic polymerization of styrene was performed with either *s*-BuLi or potassium naphthalenide in THF at −78 °C for 10 min. About 1 g of polymer was used in each functionalization reaction.

The polystyrene end-functionalized with either one methoxymethylphenyl (MMP) or (*tert*-butyldimethylsilyloxy)methylphenyl (SMP) group was synthesized by adding polystyryllithium dropwise into a THF solution of ca. 1.5-fold excess of **1** or **2** at −78 °C over a period of 10 min, and the mixture was allowed to stand at −78 °C for an additional 10 min. The polystyrene end-functionalized with either two MMP or two SMP groups was synthesized by reaction of polystyryllithium with ca. 1.2-fold excess of **3** or **4** in THF at −78 °C for 1 h.

The polystyrene end-functionalized with three MMP groups was synthesized by reaction of polystyryllithium with a 1.2-fold excess of **3** in THF at −78 °C for 1 h, followed by treatment with a 1.5-fold excess of **1** in THF at −78 °C for 0.5 h. The polystyrene end-functionalized with four MMP groups was synthesized by the following two reaction steps: First, an end-functionalized polystyrene with two MMP and one bromobutyl groups was prepared by reaction of polystyryllithium with a 1.2-fold excess of **3** in THF at −78 °C for 1 h, followed by treatment with a 7.0-fold excess of 1,4-dibromobutane in THF at −78 °C for 0.5 h. The resulting prepolymer was purified by repeated precipitation from THF to methanol three times and freeze-drying three times from the absolute benzene solution for the next reaction. Second, the polymer thus purified was reacted with a functionalized organolithium reagent with two MMP groups, prepared from *s*-BuLi and a 1.2-fold excess of **3** in THF at −78 °C for 1 h. The reaction was carried out with use of a 1.5-fold excess of the lithium reagent in THF at −78 °C for 24 h to afford a polystyrene end-functionalized with four MMP groups.

The polystyrene having two MMP groups in the chain was synthesized by the following two reaction steps: First, the polystyrene end-functionalized with two MMP groups and one bromobutyl group was reacted with a 1.2-fold excess of polystyryllithium in THF at −78 °C for 24 h to afford the desired polystyrene with two MMP groups in the chain. Similarly, the polystyrene with four MMP groups in the chain was synthesized in the above-mentioned reaction in which, instead of polystyryllithium, a living end-functionalized polystyrene, prepared from polystyryllithium with **3**, was used. The polystyrenes having four MMP groups in the chain was also synthesized in more than 90% yield by coupling 1,3-dibromopropane with 2 equiv of the living end-functionalized polystyrene having two MMP termini in THF at −78 °C for 72 h. A similar result was obtained by the reaction using 1,3-diiodopropane with a living functionalized polystyrene, prepared from polystyrylpotassium and **3**, under the same condition. In both cases, the MMP groups were always placed at the middle of the chains.

The functionalities of MMP groups were determined by comparing the relative intensities of the ^{1}H NMR resonances at 3.2 and 4.3 ppm for methyl and benzyl protons of the MMP groups with those at 0.7 ppm for methyl protons of the *sec*-butyl groups (initiator residue). The resonances at 6.2−7.4 ppm for aromatic protons of the polystyrenes were also used for the same purpose.

Synthesis of Polystyrenes Functionalized with Two, Four, and Six Methoxymethylphenyl Groups at the Chain Ends by Use of 3-(*tert*-Butyldimethylsilyloxy)-1-propyllithium. The title functionalized polystyrenes with MMP groups were synthesized by a new iterative approach using 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium. As a first starting prepolymer, we synthesized the polystyrene end-functionalized with one bromobutyl group by reacting polystyryllithium with 1,1-diphenylethylene, followed by treatment with a 10-fold excess of 1,4-dibromobutane in THF at −78 °C for 20 min. The resulting polymer was then reacted with a 1.5-fold excess of the reagent prepared from 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium and a 1.2-fold excess of **3** in THF. The reaction mixture was allowed to stand at −78 °C for 10 h. The *tert*-butyldimethylsilyloxybutyl group introduced at the chain end was deprotected by treatment with a 5.0-fold excess of $(C_4H_9)_4NF$ in THF at 0 °C for 10 h. After the reaction, the purified polymer (1.00 g) was mesylated by treatment with a 10-fold excess of methanesulfonyl chloride in pyridine (20 mL) at 0 °C for 10 h. After the polymer was isolated and purified, the polymer (0.90 g) was then reacted with a 20-fold excess of LiBr in acetone (20 mL) at 60 °C for 48 h. In each reaction step, prior to the reaction the polymer was carefully purified by repeated reprecipitation from THF to methanol three times and freeze-drying three times from its absolute benzene solution. At this stage, the polystyrene with two MMP and one bromobutyl groups was obtained.

The terminal bromobutyl group was again reacted with the reagent prepared from 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium and **3**. The 4-(*tert*-butyldimethylsilyloxy)butyl group introduced at the chain end was then deprotected, mesylated, and brominated under the same conditions. Four MMP and one bromobutyl groups could be thus introduced.

The resulting polymer was finally reacted with a 1.5-fold excess of the organolithium reagent prepared *s*-BuLi and a 1.2-fold excess of **3** in THF at −78 °C for 10 h. By this reaction, the polystyrene end-functionalized with six MMP groups was obtained.

The end functionalities of bromobutyl groups were determined by comparing the relative intensities of the ^{1}H NMR

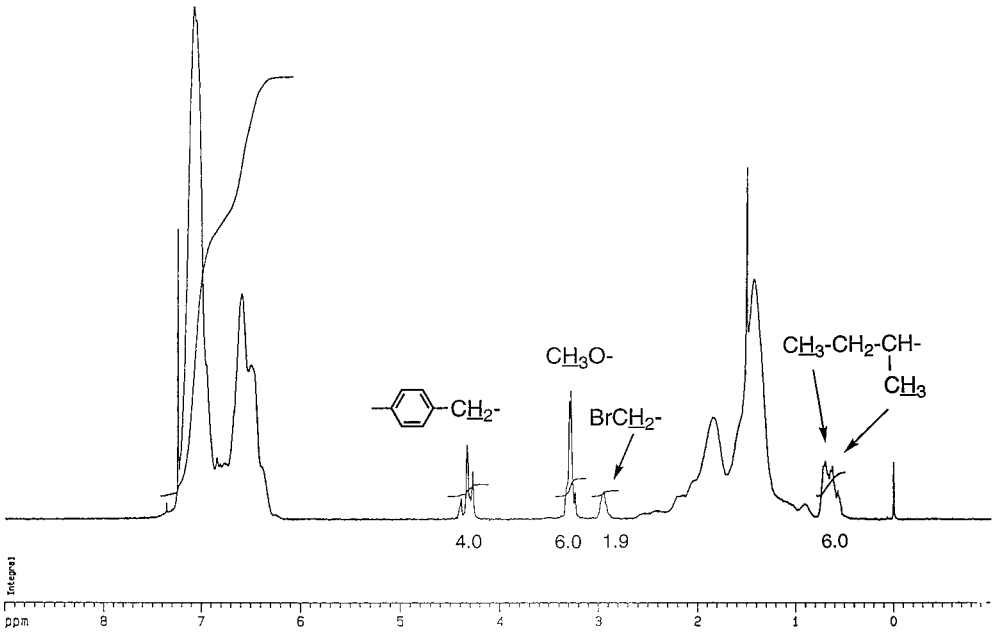


Figure 1. ^{1}H NMR spectrum of end-functionalized polystyrene with two MMP and bromobutyl groups.

resonances at 2.9−3.1 ppm for the bromomethylene protons with those at 6.2−7.4 ppm for aromatic protons of the polystyrenes based on M_n values determined by SEC. Similarly, characteristic resonances at 3.44 ppm for O−CH_2 protons of the hydroxybutyl groups, those at 0.05 and 0.91 ppm for silylmethyl and *tert*-butyl protons of the *tert*-butyldimethylsilyloxybutyl group and those at 2.60 ppm for methyl protons of the mesyl groups were used to determine the end functionalities of polymers obtained in the syntheses. Analytical errors are generally less than 5%. A typical ^{1}H NMR spectrum of the polystyrene end-functionalized with two MMP and one bromobutyl groups is shown in Figure 1.

Transformation Reactions of Methoxymethylphenyl and (*tert*-Butyldimethylsilyloxy)methylphenyl Groups into Halomethylphenyl Groups. All polymers used in the reactions were purified by repeated reprecipitation three times and freeze-drying from their benzene solutions. About 1 g of polymer was used in each reaction. All transformation reactions were carried out under an atmosphere of nitrogen.

The transformation reactions to chloromethylphenyl groups were carried out by treating MMP or SMP groups introduced in the chains or at the chain ends with a 5-fold excess of BCl_3 for each MMP or SMP functionality according to the method previously reported.[30] The reactions were performed in dry CH_2Cl_2 or CCl_4 at −20 ∼ 30 °C for 0.5−5 h under nitrogen atmosphere. After the reactions, polymers were precipitated in a mixture of MeOH and 2 N HCl ($^8/_2$, v/v), purified by repeated precipitation from THF to methanol three times, and freeze-dried from their benzene solutions. The transformation reactions of the SMP groups introduced at the chain ends into bromomethylphenyl or iodomethylphenyl groups were carried out with a 10-fold excess of either TMS−Cl/LiBr or TMS−Cl/NaI in a mixture of dry $CHCl_3$ and CH_3CN (1/1, v/v) at 40 °C for 48 h under an atmosphere of nitrogen according to the methods previously reported.[31−33]

Under the conditions employed in this study, it was observed by ^{1}H NMR analysis that all transformation reaction proceeded quantitatively. The characteristic resonances at 3.2 and 4.3 ppm for MMP groups or at 0.05 and 0.91 ppm for SMP groups were observed to be completely replaced by new resonances at 4.45, 4.35, and 4.32 ppm corresponding to benzyl protons of the chloromethylphenyl, bromomethylphenyl, and iodomethylphenyl groups, respectively.

Molecular characteristics (M_n and M_w/M_n) of the resulting polymers were determined by SEC. Functionalized polymers with controlled molecular weights and narrow molecular weight distributions were usually, although not always, obtained by fractionating with HPLC to remove their high molecular weight byproducts.

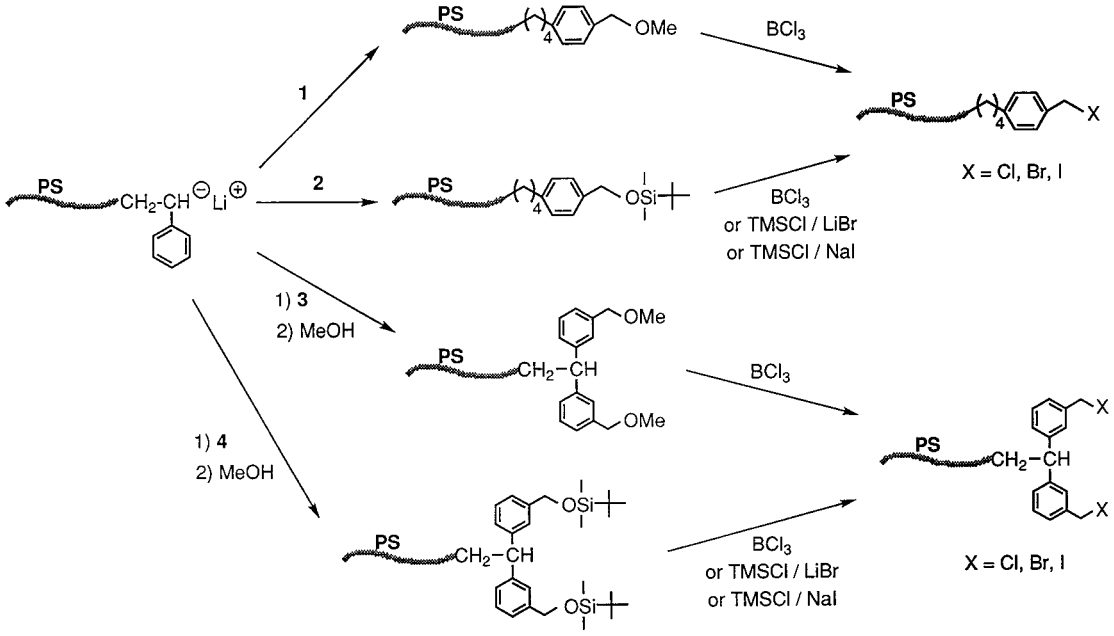
Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX (300 MHz for ^{1}H and 75 MHz for ^{13}C) in $CDCl_3$. Size-exclusion chromatography (SEC) chromatogram was obtained at 40 °C with a Tosoh HLC 8020 instrument with UV (254 nm) or refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 mL/min. Three polystyrene gel columns (TSK_{gel} $G4000H_{XL}$, $G3000H_{XL}$, $G2000H_{XL}$ or TSK_{gel} $G5000H_{XL}$, $G4000H_{XL}$, $G3000H_{XL}$) were used. A calibration curve was made to determine M_n and M_w/M_n values with standard polystyrene samples. Fractionation by HPLC was performed at 40 °C using an Tosoh HLC 8020 Type fully automatic instrument equipped with a TSK-$G4000H_{HR}$ column (300 mm in length and 7.8 mm in diameter). All runs for fractionation were made with THF as an eluent. The concentration of the polymer solution for fractionation was adjusted to 10−20 w/v %, depending on the molecular weight of the sample.

Results and Discussion

Several attempts were previously made on the synthesis of polymers having halomethylphenyl termini by reacting living polymer anions with halogens or α,α′-dihalo-*p*- (or *m*-) xylenes. However, these reactions, in general, proceeded competitively with the Wurtz-type coupling reactions to yield considerable amounts of dimeric byproducts. Richards and co-workers were successful in reducing the degree of coupling by transforming polystyryllithium into the corresponding Grignard reagent.[34] In the reaction with bromine, for example, the yield of brominated polystyrene was increased from 58 to 93% yield. Unfortunately, the dimer formation by coupling could not be completely suppressed even in this case.

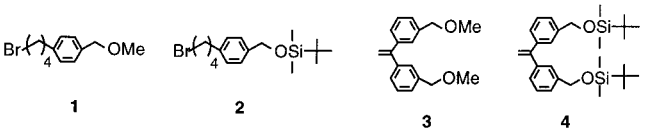
The same research group also reported the synthesis of end-functionalized polystyrenes with bromomethylphenyl groups by reaction of either polystyryllithium or polystyrylmagnesium bromide with α,α′-dibromo-*m*-xylene.[34−36] It was again observed that the coupling to produce dimer occurred during the reactions. The maximum yield never exceeded 77%. Watanabe and coworkers reported that an end-functionalized poly(styrene-*b*-2-vinylpyridine) with a chloromethylphenyl group was

Scheme 1. Reactions of Polystyryllithium with 1−4 Followed by Transformation Reactions



synthesized by reaction of the corresponding anionic living block copolymer with a large excess of α,α′-dichloro-*p*-xylene.[37] In this paper, however, neither the formation of coupling byproduct nor the end-functionalization degree of the resulting polymer was described. We also attempted to synthesize the end-functionalized polystyrene with chloromethylphenyl group by adding polystyryllithium slowly to a 1.5-fold excess of α,α′-dichloro-*p*-xylene in THF at −78 °C. Similar to the results previously reported, a considerable amount of dimeric byproduct was formed, while the desired end-functionalized polystyrene was obtained only in 39% yield.[38] Thus, unfortunately, all synthetic methods so far reported were not sufficient to obtain quantitatively well-defined polystyrenes having halomethylphenyl termini.

Synthesis of Polystyrenes Having One and Two Halomethylphenyl Termini. (1) Introduction of Methoxymethylphenyl and (*tert*-Butyldimethylsilyloxy)methylphenyl Groups at Polystyrene Chain Ends. As mentioned above, the Wurtz-type coupling reactions to produce byproducts were not completely suppressed in the reactions of living polystyrene with halogens and α,α′-dihaloxylenes. Instead of these electrophiles, we have proposed here the use of specially designed terminators possessing precursory functions that are anion stable and transformable into halomethylphenyl groups. They are the following bromides (**1** and **2**) and DPE derivatives (**3** and **4**):



Their precursor functions are the methoxymethylphenyl (MMP) and (*tert*-butyldimethylsilyloxy)methylphenyl (SMP) moieties, respectively. Our synthetic procedure consists of reacting a polystyryl anion with each of **1**−**4** followed by transformation reactions of their precursory functions into halomethylphenyl groups as illustrated in Scheme 1.

The reaction of polystyryllithium with either **1** or **2** was very fast and finished within a few seconds in THF at −78 °C as soon as the living polymer anion was mixed with the bromides. Under the same conditions, an immediate color change for orange red to dark red occurred upon addition of **3** or **4** to polystyryllithium, indicating rapid generation of the 1,1-diphenylalkyl anions derived from **3** and **4**. The reactions were then quenched with degassed methanol after 0.3−1 h.

All polymers obtained exhibited symmetrical unimodal peaks with narrow molecular weight distributions from SEC analysis. Neither shoulder nor tailing was observed in each case. The molecular weights of these polymers were very close to those predicted as expected. The polymers were characterized by ^{1}H NMR spectroscopy to examine the functionalities. In the case with **1**, the NMR spectrum of the resulting polymer showed two characteristic resonances at 3.2 and 4.3 ppm assigned to methyl and methylene protons of the methoxymethyl groups of **1**. The resonances assigned to *tert*-butyldimethylsilyloxymethyl group were observed at 0.05, 0.91, and 4.61 ppm in NMR spectrum of the resulting polymer obtained by the reaction with **2**. From integration ratios of these peaks with multiplet peak at 0.7 ppm for the methyl protons of the initiator (*s*-BuLi) residue, both MMP and SMP groups were introduced at the polystyrene chain ends in yields of more than 95%. The polystyrene with MMP groups at both ends was also obtained by reaction of **1** with difunctional living polystyrene initiated with potassium naphthalenide. Similarly, two MMP and SMP groups were introduced quantitatively (> 99%) at the chain ends by reactions with **3** and **4**. The results are summarized in Table 1 in addition to molecular characteristics by SEC.

The reactions with **1**−**4** usually proceeded cleanly and quantitatively in THF at −78 °C. However, in the reaction of **3** with polystyryllithium for a longer reaction time, up to 24 h, a small amount (ca. 8%) of high molecular weight shoulder, which seemed to have double the molecular weight of the starting living polymer, was observed in the SEC curve of the resulting polymer as shown in Figure 2. In addition, the degree

Table 1. Reaction of Polystyryllithium with 1−4 in THF at −78 °C[a]

reagent	[reagent]/[anion]	polymers $\bar{M}_n$(calcd)	$\bar{M}_n$(obsd)	$\bar{M}_w/\bar{M}_n$	functionality NMR
1	1.50	2700	2800	1.05	1.00
1[b]	2.16	6600	7100	1.06	0.98
2	1.18	3000	3000	1.09	0.95
3	1.35	5200	5100	1.04	0.99
4	1.98	5200	5000	1.07	1.00

[a] Yields of polymers: 100% in all cases. [b] Difunctional living polystyrene initiated with potassium naphthalenide was used in the reaction.

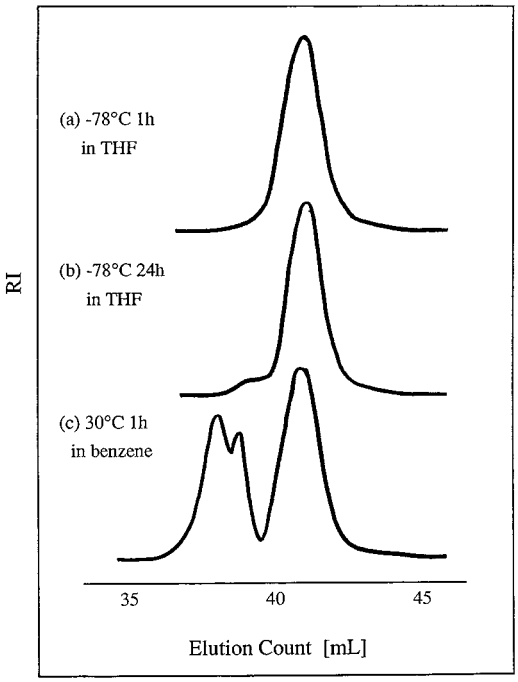
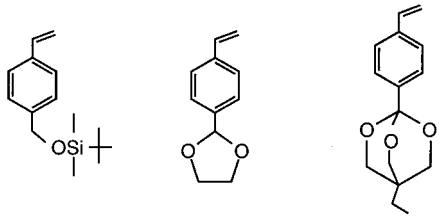


Figure 2. SEC curves of polystyrenes obtained by reaction of polystyryllithium with **3**. (a) in THF at −78 °C for 1 h (b) in THF at −78 °C for 24 h (c) in benzene at 30 °C for 1 h.

of MMP functionality was reduced to 0.92 in this polymer sample. Accordingly, the active chain end anion of 1,1-diphenylalkyl-type substituted with two methoxymethyl groups seems not to be stable enough for a long time of up to 24 h even at −78 °C.

A more serious problem was encountered in the reaction of polystyryllithium with **3** in benzene at 30 °C. The benzene solution immediately turned dark red upon adding **3** to polystyryllithium. The red color remained after 1 h, but disappeared immediately after quenching with degassed methanol. It was observed from SEC of the resulting polymer that large quantities of dimeric, trimeric, and even oligomeric products of the starting living polymer were formed as also shown in Figure 2. Obviously, an undesirable coupling reaction among polymer chains occurred significantly in benzene at 30 °C. The degree of the MMP group in the product mixture was determined to be 0.60 by ^{1}H NMR analysis. We are now considering the following two possibilities accounting for the coupling reaction: either the living polymer anion may attack the benzyl carbon of the MMP group introduced at another chain end in a nucleophilic way, or the anion at the chain end may induce 1,5-elimination to generate the very reactive biradical intermediate which reacts readily by radical combination to couple another polymer chain as shown in Scheme 2:

The latter process was often observed in the anionic polymerization systems with *p*-methoxymethylstyrene[39] and the following para-substituted styrenes



possessing benzyl ether skeletons,[40−42] but not those with the corresponding meta-isomers in THF at −78 °C. Therefore, the latter process as shown in Scheme 2 is not reasonable in this respect, but we consider that it may possibly occur in our systems using **3**. We are presently investigating the reactions of polystyryllithium with DPEs para- and ortho-substituted with methoxymethyl groups to elucidate how their methoxymethyl groups participate in the reactions.

(2) Transformation Reactions of Methoxymethylphenyl and (*tert*-Butyldimethylsilyloxy)methylphenyl Groups into Halomethylphenyl Groups. The terminal group and two MMP groups were readily and quantitatively transformed into chloromethylphenyl (CMP) groups with BCl_3 in CH_2Cl_2 at 0 °C for 30 min.[30] ^{1}H NMR spectra of the products showed that multiplets at 3.2 and 4.3 ppm were completely replaced by a new resonance at 4.45 ppm assigned to chloromethyl protons. Analysis of the resulting polymers by SEC showed them to possess similar narrow molecular weight distributions of the starting polystyrenes with one and two MMP groups. However, small shoulders (ca. 5%) were usually observed on the high molecular weight sides of the major peaks. They are probably produced as a result of the BCl_3-catalyzed Friedel−Crafts reaction among the polymer chains. We have therefore optimized the reaction condition for suppressing the formation of these higher molecular weight byproducts. The results are listed in Table 2.

Contrary to our expectation, the byproduct portion was not increased even in the reactions carried out either at a high temperature of 30 °C or for a longer reaction time of 5 h. It was not reduced by replacing CH_2Cl_2 with the less polar CCl_4. Working at −20 °C for 0.5 h proved to be the best system in this study. Under such conditions, the extent of the side reaction was minimized to be 2%. Similarly, the SMP group was quantitatively transformed into the CMP group with BCl_3 in CH_2Cl_2 at −20 °C for 0.5 h. Also in this case, the higher molecular weight byproduct was formed in 3% yield. Thus, it can most probably not be completely suppressed in the reaction with use of BCl_3.

The SMP group was also transformable into bromomethylphenyl or iodomethylphenyl group by treatment with Me_3SiCl−LiBr or Me_3SiCl−NaI. Their functionalities were found by ^{1}H NMR to be quantitative when the reactions were carried out at 40 °C for 48 h. The resulting polymers were observed to exhibit narrow molecular weight distributions. It should be noted that higher molecular weight byproducts were not formed in both reactions. Accordingly, these transformation reactions are clean and quantitative. The well-defined end-functionalized polystyrenes with one and two halomethylphenyl (halogen: Br and I) groups were thus successfully obtained. These results are summarized in Table 3.

Scheme 2. Possible Side Reaction Candidates

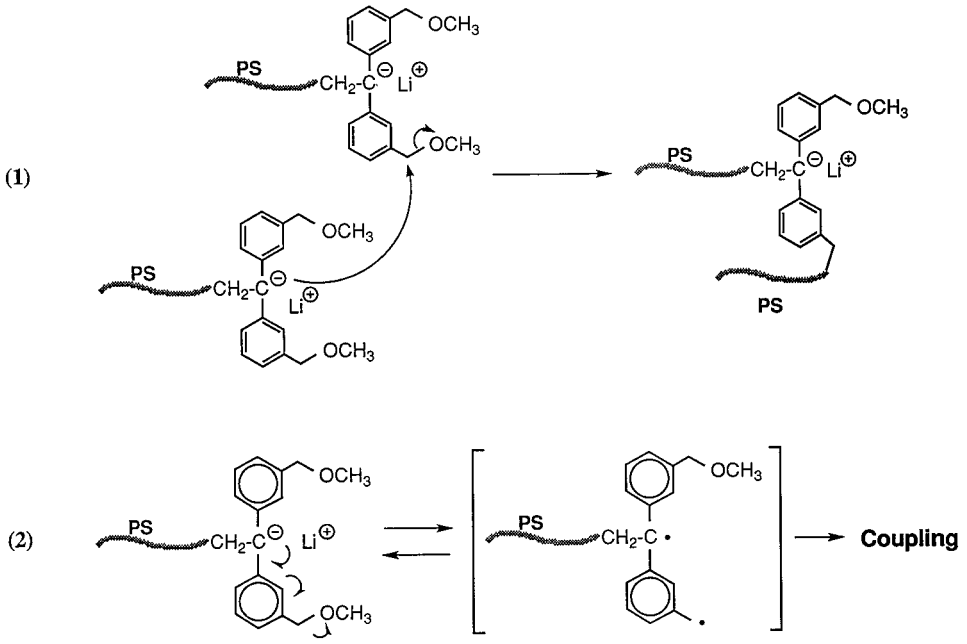


Table 2. Transformation Reactions of Methoxymethylphenyl Termini with BCl_3[a]

conditions			
solvent	temp (°C)	time (h)	dimer (%)
CH_2Cl_2	30	0.5	5
CH_2Cl_2	0	0.5	5
CH_2Cl_2	0	5	5
CH_2Cl_2	−20	0.5	2
CCl_4	0	0.5	4

[a] End functionality of chloromethylphenyl group: 100% in all cases.

Table 3. Transformation Reactions of (*tert*-Butyldimethylsilyloxy)methylphenyl Termini into Halomethylphenyl Groups[a]

	conditions				
reagent	solvent	temp (°C)	time (h)	dimer (%)	halogen atom[b]
BCl_3	CH_2Cl_2	−20	0.5	3	Cl
$Me_3SiCl/LiBr$	$CHCl_3/CH_3CN$	40	48	0	Br
Me_3SiCl/NaI	$CHCl_3/CH_3CN$	40	48	0	I

[a] End-functionalities of halomethylphenyl groups: 100% in all cases. [b] In halomethylphenyl group.

Synthesis of Polystyrenes Functionalized with Three and Four Chloromethylphenyl Termini. The synthesis of polystyrenes with three and four CMP termini is illustrated in Scheme 3. As was seen, three MMP groups were first introduced at the chain end by reacting polystyryllithium with **3** followed by treatment with **1**. The resulting polymer had a symmetrical SEC distribution composed of a single sharp peak. Subsequent reaction with BCl_3 provided the desired well-defined polystyrene end-functionalized with three CMP groups. Fortunately in this case, the higher molecular weight byproduct mentioned as above was not formed. The degree of end-functionalization was 3.10 based on ^{1}H NMR spectrum. The results are listed in Table 4.

For the synthesis of polystyrene with four CMP termini, a prepolymer end-functionalized with two MMP and one bromobutyl groups was prepared by reacting polystyryllithium with **3** followed by treatment with 1,4-dibromobutane. In the latter step, the living end-functionalized polystyrene was added slowly to the dibromide at −78 °C for 20 min. Both end-functionalization reactions were confirmed to proceed quantitatively by ^{1}H NMR analysis. The prepolymer thus prepared was then reacted with a new functionalized organolithium with two MMP groups derived from **3** and *s*-BuLi (see Scheme 3). The polystyrene with four CMP termini was obtained by further reaction with BCl_3 in CH_2Cl_2 at 0 °C for 1 h.

SEC analysis was performed on three of the polymers to verify that the molecular weight characteristics remained constant through the subsequent reactions. They are shown in Figure 3. The prepolymer and the polystyrene with four MMP termini exhibited narrow molecular weight distributions without shoulders, whereas a small amount (ca. 5%) of higher molecular weight shoulder was observed in the polystyrene having four CMP termini. A pure polymer sample was finally obtained in 90% yield by HPLC fractionation (see also Figure 3). Estimated from ^{1}H NMR spectrum of this sample, the end-functionality of the CMP group was determined to be 3.99.

Synthesis of Well-Defined Polystyrenes Functionalized with Two and Four Chloromethylphenyl Groups in the Polymer Chains. Currently, the method based on the living functionalization reaction seems to be the most convenient approach to synthesize polymers having functional groups in the chains.[16−18] Unfortunately, this very useful reaction was not directly applied to our reaction system. Under the successful conditions reported by Quirk and co-workers,[24] the living end-functionalized polystyrene, prepared from polystyryllithium with **3**, was not stable as mentioned before. We therefore devised alternative strategies with use of the living end-functionalized polystyrene as illustrated in Scheme 4.

The polystyrene having two CMP groups in the chain could be obtained from two reaction steps. At first, polystyryllithium was reacted with the prepolymer having two MMP termini and one bromobutyl terminus as shown before in Scheme 3. A polystyrene having two MMP groups in the chain was thus synthesized. In this

Scheme 3. Synthesis of Polystyrenes Functionalized with Three and Four Chloromethylphenyl Termini

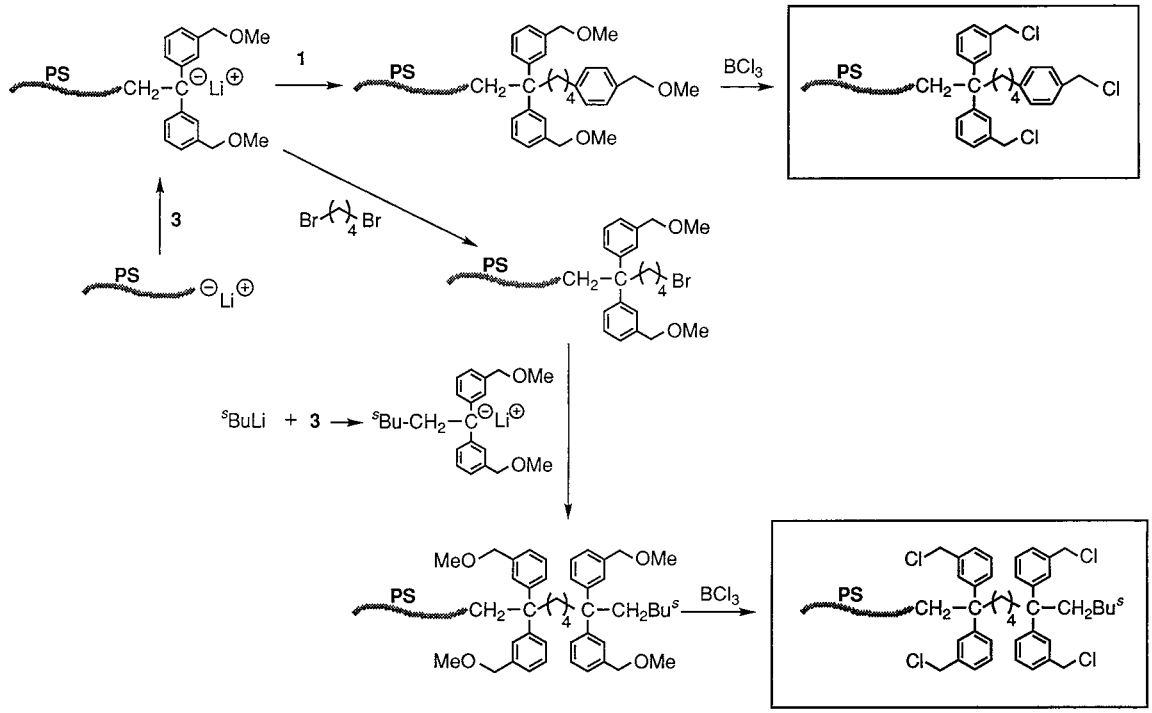


Table 4. Synthesis of Polystyrenes Functionalized with Three and Four Chloromethylphenyl Termini[a]

no. of chloromethylphenyl groups	reagent	polymers $\bar{M}_n$(calcd)	polymers $\bar{M}_n$(obsd)	polymers $\bar{M}_w/\bar{M}_n$	functionality NMR
3	**3** and **1**	6500	6200	1.09	3.10
4	**3** and (**3** + ^{s}BuLi)	6500	6900	1.09	3 99

[a] Yields of polymers: 100% in all cases.

reaction, the MMP group can be in principle placed at essentially any position in a polymer chain by changing the molecular weights of the prepolymer and polystyryllithium used in the reaction. Treatment with BCl_3 in the second step provided the desired polystyrene having two CMP groups in the chain. A small quantity of unreacted polystyrene was contaminated in the product, because a slight excess of polystyryllithium was used to complete the reaction. In addition, a higher molecular weight shoulder (ca. 5%) was observed as usual after the treatment with BCl_3. A pure polymer was finally obtained by fractionating with HPLC. The resulting polymer was shown by SEC and ^{1}H NMR to possess a narrow molecular weight distribution (M_w/M_n = 1.05) as well as a reasonable functionality (f = 2.00). The results are listed in Table 5.

The polystyrene having four CMP groups in the chain was obtained by reacting the same living end-functionalized polystyrene having two MMP groups with the prepolymer having two MMP termini and one bromobutyl terminus, followed by treatment with BCl_3 as was seen in Scheme 4. Similar to the case mentioned above, the position of the CMP groups introduced can be readily controlled by changing the molecular weights of two polymers used in the reaction.

The polystyrene having four CMP groups in the chain could also be synthesized by coupling 2 equiv of the living end-functionalized polystyrene having two MMP groups with 1,3-dibromopropane followed by treatment with BCl_3. The first reaction proceeded efficiently in THF at −78 °C to give the polystyrene having four MMP groups in more than 90% yield. A similar result was obtained by the reaction of 1,3-diiodopropane with the living end-functionalized polystyrene prepared from **3** and polystyrylpotassium. The resulting polymers were then reacted with BCl_3 followed by HPLC fractionation to give the polystyrenes having four CMP groups. In these cases, the CMP groups were always placed at the

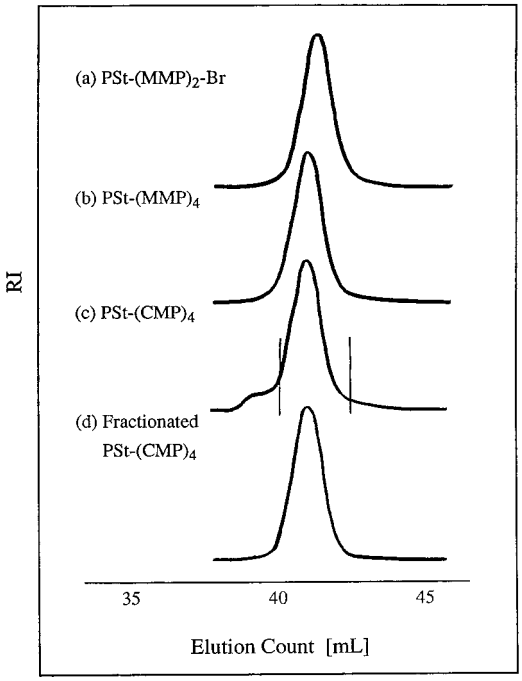
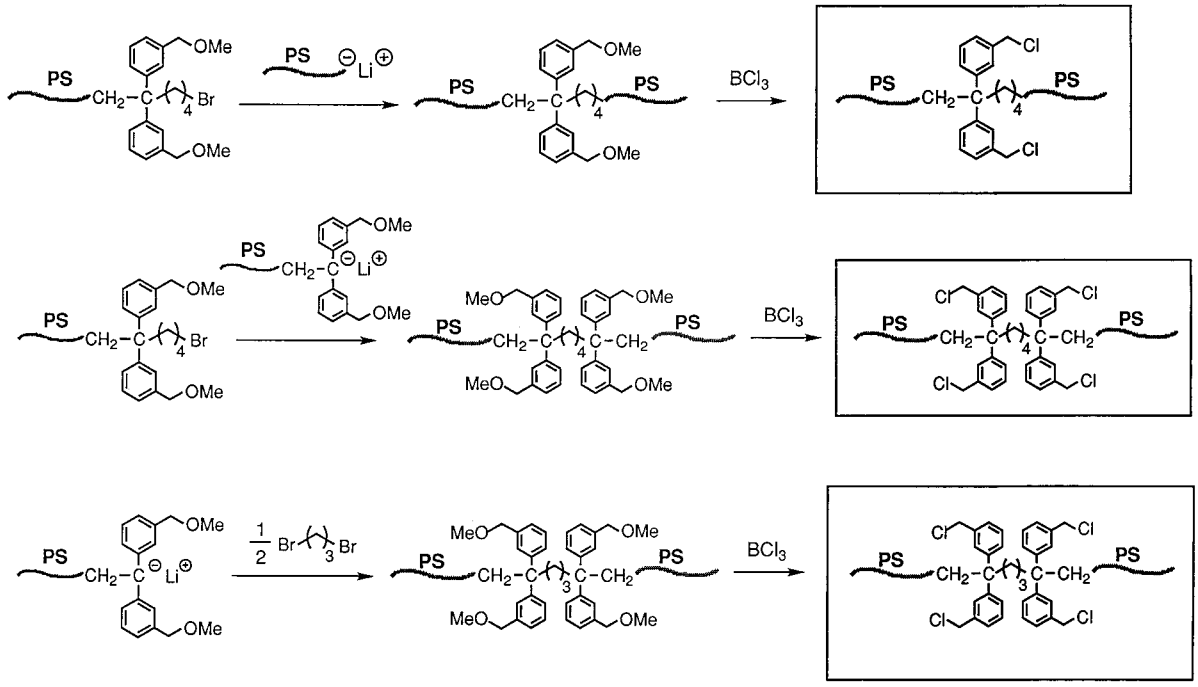
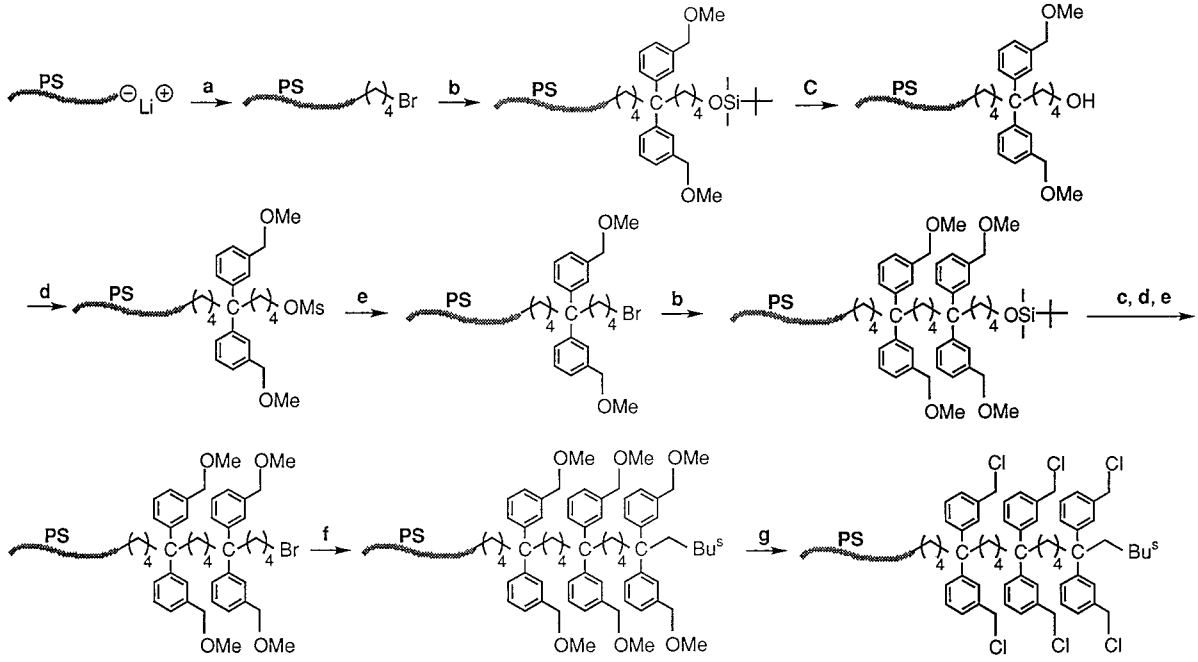


Figure 3. SEC curves of end-functionalized polystyrenes: (a) polystyrene with two MMP and bromobutyl groups; (b) polystyrene with four MMP groups; (c) polystyrene with four CMP groups; (d) polystyrene with four CMP groups after HPLC fractionation.

Scheme 4. Synthesis of Polystyrenes Functionalized with Two and Four Chloromethylphenyl Groups in Chains



Scheme 5. Iterative Approach for Synthesis of Polystyrene with Six Chloromethylphenyl termini[a]



[a] Key: (a) (1) DPE, (2) 1,4-dibromobutane; (b) **5**; (c) Bu_4NF: (d) MsCl; (e) LiBr; (f) **3**, *s*-BuLi; (g) BCl_3.

middle of the polymer chains. A typical example of functionalized polymer having four CMP groups in the middle of the chain was also listed in Table 5. A narrow molecular weight distribution as well as a nearly quantitative functionality were confirmed by SEC and ^{1}H NMR analyses.

We were thus successful to synthesize new functionalized polystyrenes having two and four CMP groups in the chains. Their chain structures were well-controlled with respect to molecular weight and molecular weight distribution. The functionalities of all polymers were nearly quantitative. SEC traces of the resulting polymers and all prepolymers strongly indicate that each reaction step used in the synthesis had proceeded very efficiently. The disadvantage of the procedures developed in this section is a tedious separation by HPLC fractionation, since excess amounts of living polymers were always used in the coupling reaction steps to force the reactions to completion.

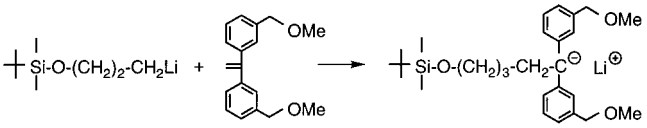
Synthesis of Polystyrenes Having Two, Four, and Six Methoxymethylphenyl and Six Chloromethylphenyl Termini by an Iterative Approach with Use of 3-(*tert*-Butyldimethyl-silyloxy)-1-propyllithium. Here we propose a new iterative approach for the synthesis of polystyrenes end-functionalized with a definite number (two, four, and six) of MMP and six CMP groups. The outline is illustrated in Scheme 5. A key feature of this approach is to utilize a functionalized

Table 5. Synthesis of Polystyrenes Functionalized with Two and Four Chloromethylphenyl Groups in the Polymer Chains[a]

no. of chloromethylphenyl groups	polymers			functionality
	$\bar{M}_n$ calcd	$\bar{M}_n$ obsd	$\bar{M}_w/\bar{M}_n$	NMR
2	11 000[b]	10 000	1.05	2.00
4	12 000[c]	10 000	1.05	4.00
4	11 000	10 000	1.09	4.10[d]

[a] Yields of polymers: 100% in all cases. [b] M_n values calculated of for the first and second polystyrenes were 5400 and 5300, respectively. [c] M_n values calculated of for the first and second polystyrenes were 6000 and 6000, respectively. [d] The polystyrene was obtained by reacting 2 equiv of living end-functionalized polymer with 1,3-dibromopropane.

organolithium compound **5**, prepared from 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium and **3**, in each step.



3 **5**

As can be seen in Scheme 5, the polystyrene with a bromobutyl terminus as a first prepolymer is prepared by reacting polystyryllithium with DPE followed by treatment with 1,4-dibromobutane. This prepolymer is then reacted with **5** to introduce two MMP groups and one 4-(*tert*-butyldimethylsilyloxy)butyl group at the chain end. The 4-(*tert*-butyldimethylsilyloxy)butyl group is transformed into a bromobutyl group by subsequent three reaction steps (deprotection, mesylation, and bromination). Thus, the same end group that was present in the first prepolymer is now again present at the polymer chain end. The procedure can be therefore repeated with an increase of two MMP groups at each iteration by using the same quantitative reactions throughout the sequence.

Specifically, the first prepolymer was prepared by slowly adding polystyryllithium end capped with DPE to 1,4-dibrombutane. The resulting polymer was then treated with a new functionalized organolithium **5**. Both end functionalities of MMP and 4-(*tert*-butyldimethylsilyloxy)butyl groups were observed by ^{1}H NMR to be 2.00 and 0.95, respectively. The 4-(*tert*-butyldimethylsilyloxy)butyl group thus introduced at the chain end was deprotected with $(C_4H_9)_4NF$, mesylated with methanesulfonyl chloride, and treated with LiBr. In each transformation reaction, a large excess of reagent was used to force the reaction to completion. It was confirmed by ^{1}H NMR spectra that all reactions proceeded quantitatively within analytical errors. Furthermore, two MMP groups remained unchanged during these reaction steps. All polymers isolated exhibited similar unimodal peaks with narrow molecular weight distributions by SEC traces. Thus, a polystyrene having two MMP termini and one bromobutyl terminus was obtained at this stage.[43]

The terminal bromobutyl group was again reacted with **5** under the same condition. The end functionalities of MMP and 4-(*tert*-butyldimethylsilyloxy)butyl groups were determined by ^{1}H NMR to be 3.90 and 1.00, respectively, indicating that the reaction proceeded satisfactorily. Having this polymer in hand, the reactions mentioned as above were repeated. ^{1}H NMR spectra of these polymer samples are shown in parts a−d of Figure 4, which demonstrate that each reaction undergoes expectedly the same reactions also in the second iteration. In the iteration, at the final reaction step another functionalized organolithium instead of **5**, prepared from **3** and *s*-BuLi, was used.

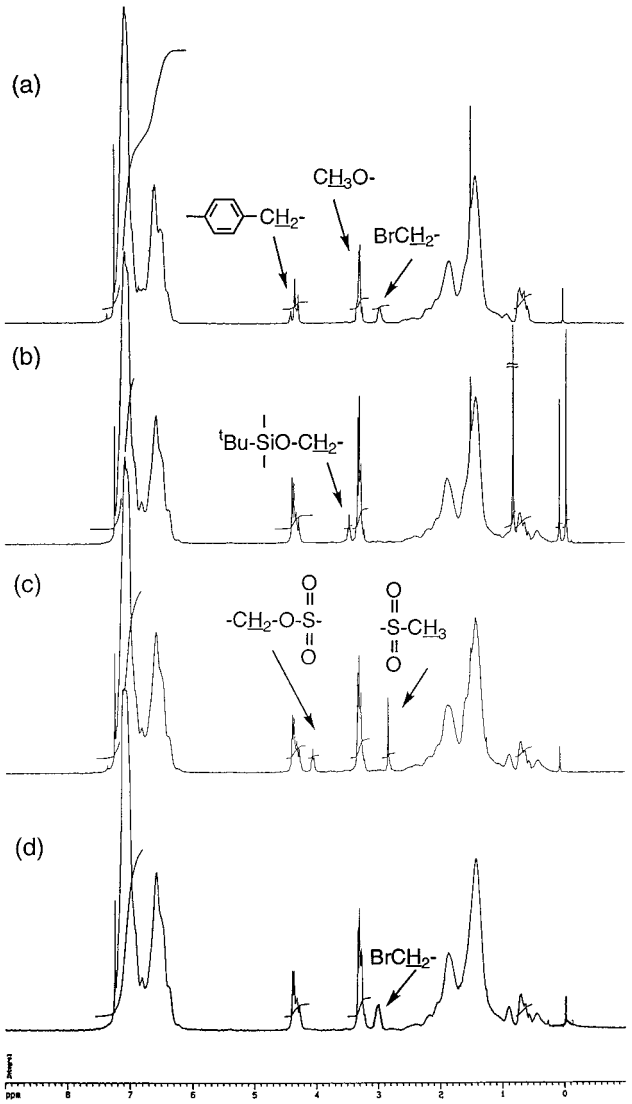


Figure 4. ^{1}H NMR spectra of end-functionalized polystyrenes: (a) with two MMP and bromobutyl groups; (b) with four MMP and *tert*-butyldimethylsilyl groups, (c) with four MMP and mesyl Groups, (d) with four MMP and bromobutyl groups.

Table 6. Synthesis of Polystyrenes with Two, Four, and Six Methoxymethylphenyl Termini by an Iterative Approach[a]

polymers			functionality	
$\bar{M}_n$(calcd)	$\bar{M}_n$(obsd)	$\bar{M}_w/\bar{M}_n$	MMP	*t*-BuMe_2SiO$(CH_2)_4$
2900	2900	1.08	2.00	0.95
3200	3300	1.06	3.90	1.00
3500	3700	1.06	5.90	

[a] Yields of polymers: 100% in all cases.

The resulting polymer obtained after the iteration was analyzed carefully by ^{1}H NMR and SEC. The MMP end functionality was found to be 5.90. Examination of the polymer by SEC showed it to have a reasonable molecular weight and to possess a narrow molecular weight distribution. These results are summarized in Table 6.

The MMP groups thus introduced were transformed into CMP groups with BCl_3 in CH_2Cl_2 at 0 °C for 1 h.

Complete conversion was confirmed from ^{1}H NMR that the resonances at 3.2 and 4.3 ppm disappeared and a new multiplet at 4.45 ppm assigned to chloromethyl protons appeared. As usual, a small amount (ca. 5%) of higher molecular weight shoulder in addition to a sharp major peak was observed in the SEC of the resulting polymer. A pure polymer sample was obtained in 90% yield by HPLC fractionation.

We have developed a new iterative approach which allowed us to synthesize well-defined polystyrenes having two, four, six MMP, and six CMP termini. Potentially, this approach provides a general method for the synthesis of functionalized polymers with a definite number of not only CMP groups but also other useful functional groups. The synthesis of polystyrenes functionalized with eight or more CMP groups at the chain ends and in the chains will be in progress.

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