Synthesis and Characterization of Well-Defined Chain-End- and In-Chain-Functionalized Polystyrenes with a Definite Number of D-Glucose and/or D-Galactose

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ABSTRACT: The synthetic methodologies for various well-defined chain-end- and in-chain-functionalized polystyrenes with a definite number of D-glucose and/or D-galactose residues have been described. They are based on diverse modes of addition reactions of polystyryllithium with substituted 1,1-diphenylethylene derivatives with acetal-protected α-D-glucofuranose and α-D-galactopyranose residues, followed by deprotection. By employing these methodologies, chain-end-functionalized polystyrenes with 4, 6, and 8 D-glucose and/or D-galactose residues and in-chain-functionalized polystyrenes with 2, 4, 8, and 12 D-glucose residues were synthesized. These polymers all were precisely controlled with regard to molecular weight, molecular weight distribution, degree of functionalization, and functionalized position in a chain. Such functionalized polymers with monosaccharide residues aggregated possibly to form reversed micelles in cyclohexane at 39 °C. It was observed that the aggregation number increased as increasing with the number of monosaccharide residue of both chain-end- and in-chain-functionalized polymers.

Introduction

Chain-end-functionalized polymers such as telechelic and semitelechelic polymers and macromonomers are industrially important prepolymers for the preparation of multiblock copolymers, graft copolymers, and crosslinked polymers with network structures.[1] Recently, it has been demonstrated that the intentional addition of special functional groups into polymer chain end can profoundly influence the solution, interfacial, and surface structures and properties of the resulting polymers.[2−17] Although almost all chain-end-functionalized polymers currently utilized have usually one functional group per each chain end, little attention has been, however, paid to the synthesis and application of chain-end-functionalized polymers with multifunctional or even two functional groups,[18] which are expected to more dramtically influence aggregated and surface structures and properities of the polymers. Moreover, such multifunctionalized polymers are of more interest as building blocks for polymers with complex architectures.

We have recently synthesized well-defined chain-end-functionalized polystyrenes with not only 1 but also 2, 3, and 4 D-glucose residues by using reactions of living anionic polymers with the substituted benzyl chloride and 1,1-diphenylethylene (DPE) derivatives with acetal-protected α-D-glucofuranose residues, followed by deprotection.[19] It was observed that the functionalized polystyrenes with one and two glucose residues aggregated possibly to form reverse micelles in cyclohexane at 39 °C, and interestingly the aggregation number increased from 3.6 to 7.1 with increasing the number of D-glucose residue from one to two.[20]

As an extended part of our program to the synthesis of functionalized polymers with a definite number of functional groups,[19,21,22] we employ herein a tetrasubstituted DPE derivative, 1,1-bis[3′,5′-bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose-3-oxymethyl)phenyl]-ethylene (**3**), and a special designed terminator, **4**, having four D-glucose residues and two 4-bromobutyl groups as two new functionalized agents in order to synthesize various well-defined chain-end- and in-chain-functionalized polystyrenes with four or more monosaccharide derivatives. These synthetic methodologies are based on diverse modes of addition reactions of using polystyryllithium, functionalized DPE derivatives such as 1,1-bis[3′-(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose-3-oxymethyl)phenyl]ethylene (**1**), 1,1-bis[3′-(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-oxymethyl)-phenyl]ethylene (**2**), **3**, their monoadduct anions prepared from **1**−**3** and *sec*-BuLi, and **4**. The aggregation behaviors of the series of chain-end- and in-chain-multifunctionalized polystyrenes with monosaccharide residues were studied in terms of solvent, structure of monosaccharide residue, number of monosaccharide residue, and position of monosaccharide residue in a polymer chain.

Experimental Section

Materials. All chemicals (>95%) were purchased from Tokyo Kasei Kogyo Co., Ltd., unless otherwise stated. 1,1-Bis-[3′-(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose-3-oxymethyl)phenyl]ethylene (**1**) was synthesized by a Williamson reaction of 1,1-[bis(3′-chloromethyl)phenyl]ethylene and the sodium salt of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose according to our method previously reported.[19] 3,5-Bis(methoxymethyl)-bromobenzene was synthesized according to the literature[23] and used for the synthesis of 1,1-bis[3′,5′-bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose-3-oxymethyl)phenyl]ethylene (**3**). 1-(4′-Bromobutyl)-4-(*tert*-butyldimethylsilyloxy)methylbenzene was synthesized according to the literature[22] and used for the synthesis of a chain-end-functionalized polystyrene with one hydroxy group. Boron trichloride as a 1.0 M solution in CH_2Cl_2 and tetrabutylammonium fluoride as a 1.0 M solution in THF from Aldrich were used without purification. Potassium naphthalenide was prepared by the reaction of a small excess amount of naphthalene with potassium in dry THF. Styrene was washed with 10% NaOH and H_2O and dried over $CaCl_2$. It was then distilled over calcium hydride under reduced pressure and further purified by distillation on a vacuum line after addition of dibutylmagnesium (ca. 5 mol %). THF was refluxed over Na wire for 5 h, distilled over $LiAlH_4$ under an atmosphere of nitrogen, and finally distilled through vacuum line from its sodium naphthalenide solution. Commercially available *sec*-BuLi as a 1.3 M solution in cyclohexane from Aldrich was used without purification,

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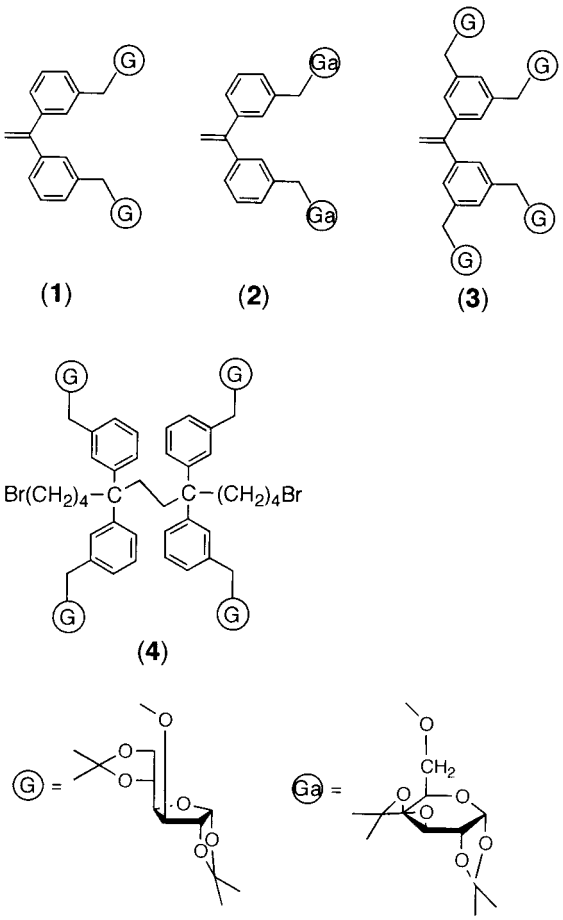


diluted with *n*-heptane, and stored at −30 °C. The exact concentration of *sec*-BuLi was determined by reaction with 1,1-diphenylethylene, followed by colorimetric titration to colorless end point with standardized 1-octanol in a sealed reactor in a vacuum at −78 °C prior to use.[24]

Measurements. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX spectrometer operating at 300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR in $CDCl_3$. Chemical shifts were reported in ppm downfield relative to tetramethylsilane (δ 0) for ^{1}H NMR and to $CDCl_3$ (δ 77.1) for ^{13}C NMR as standards.

Size-exclusion chromatography (SEC) was performed on a Tosoh HLC 8020 instrument with UV (254 nm) and refractive index detection. THF was used as a carrier solvent at a flow rate of 1.0 mL/min. Two kinds of polystyrene gel columns (measurable molecular weight ranges: 1×10^3−2×10^4 and 1×10^4−4×10^6 g/mol) were used.

The TLC-FID instrument was an Iatroscan New MK-5 TS equipped with an Iatrocorder TC-21 from Iatron Co., Ltd. Specially designed quartz rods (150 mm × 2.0 mm) were used on which silica gel was sintered.

Fractionation by HPLC was performed at 40 °C using a Tosoh HLC8020 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 10−20% (w/v).

Static light scattering (SLS) measurements were performed on an Ootsuka Electronics SLS-600R equipped with a 5 mW He−Ne laser operating at $\lambda = 633$ nm. At the beginning of the measurement, the solvent offset was recorded. Cyclohexane was dried with molecular sieves. Benzene and THF were distilled over CaH_2. The polymer solutions and the solvents were filtered through 0.22 μm Millipore filters. The stock solutions were placed at 60 °C for 3 h in order to achieve equilibrium structures and then left for 1 day at measurement temperature of 39 °C (cyclohexane) or 25 °C (benzene and THF) before conducting the appropriate measurements.

Refractive index increments, d*n*/d*c*, were measured with an Ootsuka Electronics DRM-1020 double-beam differential refractometer operating at $\lambda = 633$ nm. The d*n*/d*c* values of the functionalized polystyrenes with 4, 6, 8, and 12 D-glucose and/or D-galactose residues were in the range 0.1635−0.1715 in cyclohexane at 39 °C. The d*n*/d*c* values of the chain-end-functionalized polystyrene with four D-glucose residues (M_w = 14 0.9 kg/mol) were 0.0931 in benzene at 25 °C and 0.1847 in THF at 25 °C.

1,1-Bis[3′-(1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose-6-oxymethyl)phenyl]ethylene (2). To a stirred solution of 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (5.10 g, 19.6 mmol) in dry DMF (30 mL) was added sodium hydride (0.560 g, 23.3 mmol) at 0 °C, and the mixture was stirred for 2 h at room temperature. Then, 1,1-[bis(3′-chloromethyl)-phenyl]ethylene (2.00 g, 7.22 mmol) in dry DMF (10 mL) was added dropwise at room temperature, and the mixture was stirred at 50 °C for 5 h. Water was added to decompose excess sodium hydride, and the resulting mixture was extracted with ether three times. The organic layer was dried over magnesium sulfate. After evaporation, the crude product was purified by flash column chromatography on silica gel (hexanes/EtOAc, 8/2, v/v) to afford **2** in 88% yield (4.60 g, 6.35 mmol) as a pale yellow syrup. ^{1}H NMR: δ 7.33−7.20 (m, 8H, Ar), 5.54 (d, 2H, $J = 5.01$ Hz, α-pyranose H-1), 5.46 (s, 2H, C=CH_2), 4.65−3.64 (m, 16H, H-2−H-6 and ArCH_2−), 1.52−1.33 (m, 24H, CH_3). ^{13}C NMR: δ 149.9 (*C*=CH_2), 141.6, 138.4, 127.7, 127.6, 127.2, and 126.0 (Ar), 114.6 (C=*C*H_2), 109.3 and 108.6 (*C*(O)(O)), 96.4 (C-1), 73.3, 71.2, 70.7, 69.0, and 66.9 (C-2−C-6), 26.2, 26.1, 25.0, and 24.5 (*C*H_3).

1,1-Bis[3′,5′-bis(methoxymethyl)phenyl]ethanol. To a solution of Grignard reagent from 3,5-bis(methoxymethyl)-bromobenzene (4.01 g, 16.4 mmol) and Mg (0.870 g, 36.0 mmol) in 40 mL of dry THF was added dry ethyl acetate (0.800 mL, 8.19 mmol) dropwise at 0 °C. The reaction mixture was stirred at room temperature overnight. After removal of the solvent under vacuum, 2 N HCl was added to the residue. The resulting mixture was then extracted with ether three times, and the organic layer was washed with water and dried over magnesium sulfate. After evaporation by vacuum pump, a crude 1,1-bis[3′,5′-bis(methoxymethyl)phenyl]ethanol was obtained in 72% yield (2.17 g, 5.83 mmol) as a viscous oil. It was used without further purification. ^{1}H NMR: δ 7.30 and 7.22 (2s, 6H, Ar), 4.42 (s, 8H, CH_2OCH_3), 3.38 (s, 12H, CH_2OCH_3), 1.95 (s, 3H, CH_3).

1,1-Bis[3′,5′-bis(methoxymethyl)phenyl]ethylene. A solution of 2.17 g (5.83 mmol) of 1,1-bis[3′,5′-bis(methoxymethyl)-phenyl]ethanol and 0.30 g of *p*-toluenesulfonic acid in dry benzene (30 mL) was refluxed. After 3 h, aqueous sodium bicarbonate was added to neutralize the reaction mixture. It was extracted with ether, dried over magnesium sulfate, and concentrated. Flash column chromatography on silica gel (hexanes/EtOAc, 8/2, v/v) afforded 1.92 g (5.42 mmol, 93%) of pure 1,1-bis[3′,5′-bis(methoxymethyl)phenyl]ethylene as a viscous oil. ^{1}H NMR: δ 7.29 and 7.22 (2s, 6H, Ar), 5.47 (s, 2H, C=CH_2), 4.44 (s, 8H, CH_2OCH_3), 3.39 (s, 12H, CH_2OCH_3). ^{13}C NMR: δ 149.6 (*C*=CH_2), 141.9, 138.4, 127.1, and 126.6 (Ar), 115.1 (C=*C*H_2), 74.6 (*C*H_2OCH_3), 58.3 (CH_2O*C*H_3).

1,1-Bis[3′,5′-bis(chloromethyl)phenyl]ethylene. To a CCl_4 (40 mL) solution of 1,1-bis[3′,5′-bis(methoxymethyl)-phenyl]ethylene (1.92 g, 5.42 mmol) at 0 °C was added BCl_3 (1.0 M in CH_2Cl_2, 44.0 mL, 44.0 mmol) dropwise with stirring. The reaction mixture was stirred for additional 20 h at 0 °C and quenched with methanol. The reaction mixture was basified with NaOH(aq), extracted with CCl_4, dried over $MgSO_4$, and concentrated. Flash column chromatography on silica gel (hexanes/EtOAc, 9.5/0.5, v/v) afforded 1.93 g (5.19 mmol, 96%) of 1,1-bis[3′,5′-bis(chloromethyl)phenyl]ethylene as a white solid; mp 93−94 °C. ^{1}H NMR: δ 7.35 and 7.16 (2s, 6H, Ar), 5.55 (s, 2H, C=CH_2), 4.58 (s, 4H, CH_2Cl). ^{13}C NMR: δ 148.1 (*C*=CH_2), 142.1, 138.3, 128.5, and 126.0 (Ar), 116.5 (C=*C*H_2), 45.7 (*C*H_2Cl).

1,1-Bis[3′,5′-bis(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose-3-oxymethyl)phenyl]ethylene (3). To a stirred solution of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (5.42 g, 20.8 mmol) in dry DMF (30 mL) was added sodium hydride (0.600 g, 25.0 mmol) at 0 °C, and the mixture was stirred for 2 h at 25 °C. 1,1-Bis[3′,5′-bis(chloromethyl)phenyl]ethylene (1.42 g, 3.82 mmol) in dry DMF (10 mL) was then added dropwise at room temperature, and the mixture was stirred at 50 °C for 5 h. Water was added to decompose excess sodium hydride, and the resulting mixture was extracted with ether three times. The organic layer was dried over $MgSO_4$. After evaporation, the crude product was purified by flash column chromatography on silica gel (hexanes/EtOAc, 6/4, v/v) to afford **3** in 83% yield (3.93 g, 3.17 mmol) as a white solid; mp 69−70 °C. The purity of **3** was confirmed to be more than 99% by TLC coupled with FID detector. ^{1}H NMR: δ 7.29 and 7.22 (2s, 6H, Ar), 5.88 (d, 4H, J = 3.60 Hz, α-furanose H-1), 5.48 (s, 2H, C=CH_2), 4.65−3.97 (m, 32H, H-2−H-6 and ArCH_2−), 1.50−1.31 (m, 48H, CH_3). ^{13}C NMR: δ 149.3 (*C*=CH$_2$), 141.8, 138.1, 127.0, and 126.2 (Ar), 114.2 (C=*C*H$_2$), 111.9 and 109.1 (⟩*C*(O)(O)), 105.3 (C-1), 82.6, 82.0, 81.4, 72.6, and 67.4 (C-2−C-6), 72.2 (Ar*C*H$_2$), 26.9, 26.9, 26.3, and 25.5 (*C*H$_3$). Anal. Calcd for **3**, $C_{66}H_{92}O_{24}$: C, 62.45; H, 7.30; O, 30.25. Found: C, 62.43; H, 7.08; O, 30.82.

5,5,8,8-{Tetra{3′-[(1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose-*O*-3-oxy)methyl]phenyl}}-1,12-dibromododecane (4). Under high-vacuum conditions (10^{-6} Torr), a solution of **1** (5.39 g, 7.45 mmol) in THF (40.0 mL) was added at once to potassium naphthalenide (6.82 mmol) in THF (15.0 mL) at −78 °C with stirring. After 30 min, the resulting mixture was then added dropwise to 1,4-dibromobutane (47.0 mmol) in THF (30.0 mL) at −78 °C with stirring for a period of 30 min, and the reaction was continued for an additional 30 min. After removal of the solvent under vacuum, the resulting mixture was then extracted with ether three times, and the organic layer was washed with water, dried over $MgSO_4$, and concentrated. Flash column chromatography on silica gel (hexanes/EtOAc, 5/5, v/v) afforded 2.98 g (1.73 mmol, 51%) of **4** as a white solid; mp 66−67 °C. The purity of **4** was confirmed to be more than 99% by TLC coupled with an FID detector. ^{1}H NMR: δ 7.36−6.92 (m, 16H, Ar), 5.84 (d, 4H, J = 3.51 Hz, α-furanose H-1), 4.56−3.96 (m, 32H, H-2−H-6 and ArCH_2O−), 3.23 (t, 4H, J = 6.75 Hz, CH_2Br), 2.04 (b, 4H, −CCH_2CH_2CH_2C−), 1.75−1.64 (m, 8H, −CCH_2CH$_2$− and −CH_2CH$_2$Br), 1.48, 1.42, 1.34, and 1.29 (4s, 48H, CH_3), 0.80 (b, 4H, −CH_2CH$_2$-CH$_2$Br). ^{13}C NMR: δ 148.4 (Ar*C*Ar), 137.4, 128.1, 126.8, and 125.2 (Ar), 111.8 and 109.0 (⟩*C*(O)(O)), 105.3 (C-1), 82.6, 82.1, 81.3, 72.6, and 67.3 (C-2−C-6), 72.7 (*C*H$_2$Br), 49.1 (C*C*H$_2$*C*H$_2$C), 33.5 (*C*H$_2$CH$_2$Br), 33.2 (C*C*H$_2$CH$_2$), 26.9, 26.9, 26.4, and 25.6 (*C*H$_3$), 22.4 (*C*H$_2$CH$_2$CH$_2$Br). Anal. Calcd for **4**, $C_{88}H_{120}O_{24}$-Br_2: C, 61.39; H, 7.03; O, 22.30; Br, 9.28. Found: C, 62.54; H, 6.97; O, 22.49; Br, 9.00.

Anionic Polymerization of Styrene and Reaction of Polystyryllithium with 1−4. All polymerization and reactions were carried out in an all-glass apparatus equipped with break-seals with vigorous shaking under high-vacuum conditions (10^{-6} Torr) in THF at −78 °C.[25]

Synthesis of Chain-End-Functionalized Prepolymers with Acetal-Protected Monosaccharide Residues and One 4-Bromobutyl Group (P1−P3). The prepolymers, **P1**−**P3**, were prepared by the monoaddition reactions of polystyryllithiums to **1**−**3**, followed by treatment with a 7-fold or more excess of 1,4-dibromobutane in THF at −78 °C. A typical procedure for the synthesis of **P1** is as follows: To a solution of polystyryllithium (M_n = 12.1 kg/mol, 0.185 mmol) in THF (19.0 mL) was added **1** (0.228 mmol) in THF (7.00 mL) at −78 °C with stirring. After 0.5 h, the resulting mixture was then added dropwise to 1,4-dibromobutane (1.37 mmol) in THF (12.2 mL) at −78 °C with stirring for a period of 1 h or more, and the reaction was continued for an additional 30 min. The mixture was poured into a large amount of methanol to precipitate the polymer. Reprecipitation twice from the THF solution to methanol, followed by freeze-dried from its benzene solution, gave 2.22 g (93% yield) of a chain-end-functionalized polystyrene with two acetal-protected α-D-glucofuranose residues and one 4-bromobutyl group. The M_n value was determined to be 13.0 kg/mol by comparing the ^{1}H NMR peak intensity of the methyl protons of the *sec*-butyl group with that of the aromatic protons of main chains. The M_w/M_n value determined from SEC calibration using polystyrene standards was 1.07. The degrees of end-functionalities of α-D-glucofuranose residue and 4-bromobutyl group were determined to be 2.0_2 and 1.0_1 by comparing ^{1}H NMR peak intensities of the α-furanose H-1 protons of the acetal-protected glucofuranoses at 5.8 ppm and the bromomethylene protons at 3.0 ppm with that of the methyl protons of the initiator fragment at 0.7 ppm.

Synthesis of Chain-End-Functionalized Polystyrenes with Four, Six, and Eight Acetal-Protected α-D-Glucofuranose and/or α-D-Galactopyranose Residues. The prepolymer with either two or four acetal-protected monosaccharide residues and one 4-bromobutyl group at the chain end was reacted with ca. 1.2−1.3-fold excess of the monoadduct anions prepared from **1** or **3** and *sec*-BuLi in THF at −78 °C to afford the corresponding chain-end-functionalized polystyrenes with four, six, and eight acetal-protected monosaccharide residues. A typical procedure for the synthesis of chain-end-functionalized polystyrene with six acetal-protected α-D-glucofuranose residues is as follows: A solution of **1** (55.9 mg, 0.0772 mmol) in THF (2.30 mL) chilled to −78 °C was added at once to *sec*-BuLi (0.0622 mmol) in heptane (2.40 mL) at −78 °C with stirring. After 30 min, the prepolymer with four acetal-protected α-D-glucofuranose residues and one 4-bromobutyl group at the chain end (M_n = 13.1 kg/mol, 0.621 g, 0.0474 mmol) in THF (11.3 mL) was added slowly at −78 °C with stirring, and the reaction was continued for an additional 24 h. After quenching with degassed methanol, the mixture was poured into a large amount of methanol to precipitate the polymer. Reprecipitation twice from the THF solution to methanol followed by freeze-dried from its benzene solution gave a chain-end-functionalized polystyrene with six acetal-protected α-D-glucofuranose residues (0.646 g, 99% yield). The M_n value was determined to be 13.8 kg/mol by comparing the ^{1}H NMR peak intensity of the methyl protons of the *sec*-butyl group with that of the aromatic protons of main chains. The M_w/M_n value determined from SEC calibration using polystyrene standards was 1.08. The degree of end-functionality of α-D-glucofuranose residue was determined to be 6.0_6 by comparing ^{1}H NMR peak intensity of the α-furanose H-1 protons of the acetal-protected glucofuranoses at 5.8 ppm with that of the methyl protons of the initiator fragment at 0.7 ppm. Chain-end-functionalized polystyrenes with four monosaccharide (two d-glucose and two D-galactose, four D-galactose) residues and eight D-glucose residues were also synthesized in a similar manner.

Synthesis of Chain-End-Functionalized Polystyrene with Four Acetal-Protected α-D-Glucofuranose Residues by Monoaddition Reaction of Polystyryllithium to 3. The polymerization of styrene followed by monoaddition reaction of the resulting polystyryllithium to **3** was carried out in THF at −78 °C. A typical procedure is as follows: Polystyryllithium (M_n = 11.7 kg/mol, 0.100 mmol) was obtained by adding a solution of styrene (1.16 g, 11.2 mmol) in THF (9.90 mL) chilled to −78 °C at once to *sec*-BuLi (0.100 mmol) in heptane (2.40 mL) at −78 °C with stirring. After 15 min, **3** (155 mg, 0.113 mmol) in THF (2.10 mL) was added at −78 °C with stirring, and the reaction was continued for an additional 30 min. After quenching with degassed methanol, the mixture was poured into a large amount of methanol to precipitate the polymer. Reprecipitation twice from the THF solution to methanol, followed by column chromatography on silica gel (hexanes/EtoAc, 7/3, v/v), and freeze-dried from its benzene solution gave 1.22 g (94% yield) of a chain-end-functionalized polystyrene with four acetal-protected α-D-glucofuranose residues. The M_n value determined by comparing the ^{1}H NMR peak intensity of the methyl protons of the *sec*-butyl group with that of the aromatic protons of main chains was 14.4 kg/mol. The M_w/M_n value determined from SEC relative to polystyrene standards was 1.05. The degree of end-functionality of α-D-glucofuranose residue was determined to be 4.0_7 by comparing ^{1}H NMR peak intensity of the α-furanose H-1 protons of the acetal-protected

glucofuranoses at 5.8 ppm with that of the methyl protons of the initiator fragment at 0.7 ppm.

Synthesis of In-Chain-Functionalized Polystyrenes with Two and Four Acetal-Protected α-D-Glucofuranose Residues at the Desired Position in Chains. In-chain-functionalized polystyrenes with two and four acetal-protected α-D-glucofuranose residues at the desired position in the chains were synthesized by the following two reaction steps: First, a chain-end-functionalized prepolymer with two acetal-protected α-D-glucofuranose residues and one 4-bromobutyl group was prepared as mentioned above. Second, a small excess of the prepolymer thus synthesized was reacted with polystyryllithium or living end-functionalized polystyrene with two α-D-glucofuranose residues in THF at −78 °C. A typical procedure for the synthesis of an in-chain-functionalized polystyrene with two acetal-protected α-D-glucofuranose residues at one-fifth of the chain is as follows: To a solution of polystyryllithium (M_n = 2.53 kg/mol, 0.583 mmol) in THF (15.0 mL) was added **1** (0.635 mmol) in THF (4.80 mL) at −78 °C with stirring. After 0.5 h, the resulting polymerization mixture was then added dropwise to 1,4-dibromobutane (4.46 mmol) in THF (7.50 mL) at −78 °C with stirring for a period of 1 h, and the reaction was continued for an additional 30 min. The mixture was poured into a large amount of methanol to precipitate the polymer. Reprecipitation from the THF solution to methanol and freeze-dried from its benzene solution gave 1.87 g (94% yield) of a chain-end-functionalized prepolymer with two acetal-protected α-D-glucofuranose residues and one 4-bromobutyl group. The prepolymer (M_n = 3.41 kg/mol, 0.228 mmol) dissolved in THF (20.0 mL) was then added to a solution of polystyryllithium (M_n = 9.88 kg/mol, 0.217 mmol) in THF (26.0 mL) in THF at −78 °C. After 0.5 h, the resulting mixture was poured into a large amount of methanol to precipitate the polymer. Reprecipitation from the THF solution to methanol, fractionation with SEC, and freeze-dried from its benzene solution gave 2.91 g (95% yield) of an in-chain-functionalized polystyrene with two acetal-protected α-D-glucofuranose residues at one-fifth of the chain. The M_n value was determined to be 14.1 kg/mol by comparing the ^{1}H NMR peak intensity of the methyl protons of the *sec*-butyl groups with that of the aromatic protons of main chains. The M_w/M_n value determined from SEC calibration using polystyrene standards was 1.04. The degree of end-functionality of α-D-glucofuranose residue was determined to be 2.0_0 by comparing ^{1}H NMR peak intensity of the α-furanose H-1 protons of the acetal-protected glucofuranoses at 5.8 ppm with that of the methyl protons of the initiator fragment at 0.7 ppm.

Synthesis of In-Chain-Functionalized Polystyrenes with 4, 8, and 12 Acetal-Protected Monosaccharide Residues at the Middle of the Chain. Polystyrenes having 4, 8, and 12 acetal-protected monosaccharide residues at the middle of the chain were synthesized by the coupling reactions of 2 equiv of polystyryllithium or living end-functionalized polystyrenes with two and four α-D-glucofuranose residues with **4** in THF at −78 °C. A typical procedure for the synthesis of an in-chain-functionalized polystyrene with four acetal-protected α-D-glucofuranose residues at the middle of the chain is as follows: To a solution of polystyryllithium (M_n = 6.16 kg/mol, 0.164 mmol) in THF (13.0 mL) was added **4** (0.0779 mmol) in THF (3.20 mL) at −78 °C with stirring, and the reaction was continued for an additional 24 h. The mixture was then poured into a large amount of methanol to precipitate the polymer. Reprecipitation twice from the THF solution to methanol, fractionation with SEC, and freeze-dried from its benzene solution gave 0.946 g (91% yield) of an in-chain-functionalized polystyrene with four acetal-protected α-D-glucofuranose residues at the middle of the chain. The M_n value was determined to be 13.3 kg/mol by comparing the ^{1}H NMR peak intensity of the methyl protons of the *sec*-butyl groups with that of the aromatic protons of main chains. The M_w/M_n value determined from SEC calibration using polystyrene standards was 1.04. The degree of end-functionality of α-D-glucofuranose residue was determined to be 3.9_4 by comparinig ^{1}H NMR peak intensity of the α-furanose H-1 protons of the acetal-protected glucofuranoses at 5.8 ppm with that of the methyl protons of the initiator fragment at 0.7 ppm.

Deprotection of Acetal-Protected Monosaccharide Residues Introduced at Chain Ends or in Chains. Deprotection of the acetal-protected α-D-glucofuranose and α-D-galactopyranose residues introduced at chain ends or in chains were carried out by treatment with 6 N HCl in 1,4-dioxane. A typical procedure is as follows: A solution of the chain-end-functionalized polystyrene with four acetal-protected α-D-glucofuranose residues (M_n = 14.4 kg/mol, 200 mg, 0.0552 mmol for glucofuranose unit) and 3.00 mL of 6 N HCl in 1,4-dioxane (20.0 mL) was stirred at room temperature for 24 h. The mixture was then concentrated and poured into a large amount of methanol to precipitate the polymer. Reprecipitation twice from the THF solution to methanol followed by freeze-dried from its benzene solution gave 194 mg (100% yield) of the chain-end-functionalized polystyrene with four D-glucose residues. The M_n value was determined to be 14.1 kg/mol by comparing the ^{1}H NMR peak intensitiy of the methyl protons of the *sec*-butyl group with that of the aromatic protons of main chains. The M_w/M_n value determined from SEC calibration using polystyrene standards was 1.06. The resulting polymer was characterized by ^{1}H and ^{13}C NMR and TLC-FID measurements. All of the analytical data confirmed that the acetal functions were completely deprotected to regenerate D-glucose residues.

Synthesis of Chain-End-Functionalized Polystyrene with One Hydroxy Group. Polystyryllithium (M_n = 9.92 kg/mol) was obtained by adding a solution of styrene (1.15 g, 11.1 mmol) in THF (12.4 mL) chilled to −78 °C at once to *sec*-BuLi (0.117 mmol) in heptane (2.35 mL) at −78 °C with stirring. After 15 min of the polymerization, 1-(4′-bromobutyl)-4-(*tert*-butyldimethylsilyloxy)methylbenzene (64.6 mg, 0.181 mmol) in THF (1.20 mL) was added to the polystyryllithium at −78 °C with stirring for 5 min. Then, the polymer was precipitated in methanol, reprecipitated twice from THF to methanol, and freeze-dried. The resulting polymer (1.15 g, 0.113 mmol) was dissolved in THF (10 mL) and then treated with tetrabutylammonium fluoride (1.0 M in THF, 0.60 mL, 0.60 mmol) at 0 °C for 6 h. The reaction mixture was then poured into a large amount of methanol containing a small amount of ice to precipitate the polymer. Reprecipitation twice from the THF solution to methanol followed by freeze-dried from its benzene solution gave 1.14 g (100% yield). The M_n value determined by comparing the ^{1}H NMR peak intensity of the methyl protons of the *sec*-butyl group with that of the aromatic protons of main chains was 10.6 kg/mol, which was comparable to the predicted M_n value of 10.1 kg/mol. The M_w/M_n value determined from SEC calibration using polystyrene standards was 1.04. The end-functionality was determined to be 1.0_0 by comparing ^{1}H NMR peak intensity of the benzyl protons with that of the methyl protons of the initiator fragment.

Results and Discussion

Synthesis of Chain-End-Functionalized Polystyrenes with 4, 6, and 8 Monosaccharide Derivatives. To precisely synthesize a variety of multifunctionalized polymers with monosaccharide residues, we have been developing general and versatile methodologies of using monosaccharide-functionalized DPE derivatives by which one can place a definite number of monosaccharide residues at essentially any position in a polymer chain. Previously, we were successful in synthesizing well-defined chain-end-functionalized polystyrenes with 1, 2, 3, and 4 D-glucose residues. In this report, we focused on the synthesis of chain-end-functionalized polystyrenes with 4, 6, and 8 D-glucose and/or D-galactose residues. For such polymer syntheses, we have herein developed a more general and convenient methodology as illustrated in Scheme 1. By using this method, chain-end-functionalized polymers with not only 4 but also 6 and 8 D-glucose and/or D-galactose residues could be synthesized. At first, a

Scheme 1

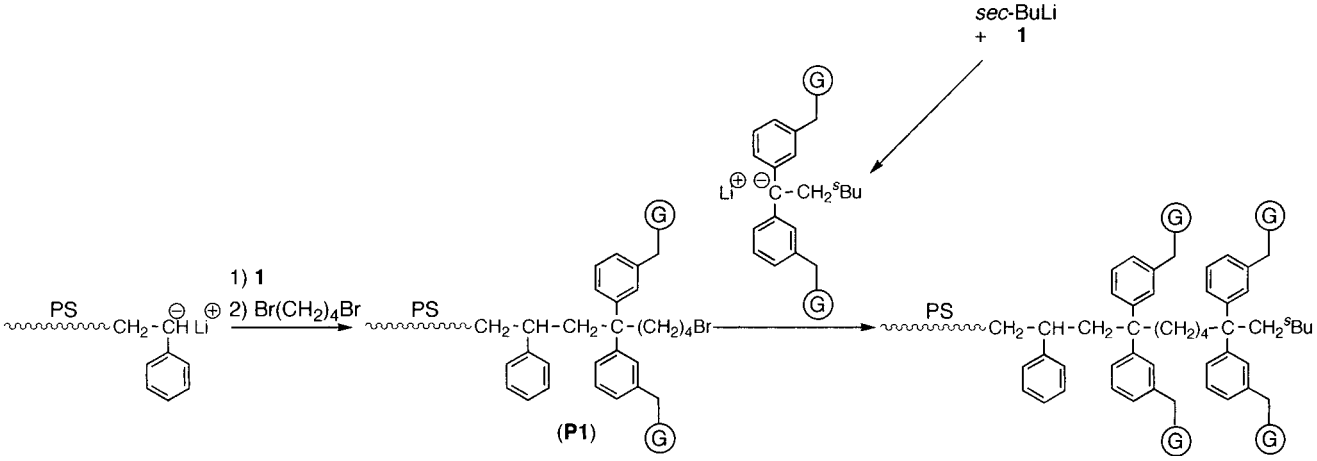


Table 1. Synthesis of P1−P3[a]

pre-polymer	$[sec\text{-BuLi}]_0$ (mmol/L)	$[styrene]_0$ (mmol/L)	$[DPE]_0$ (mmol/L)	$[Br(CH_2)_4Br]_0$ (mmol/L)	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ SEC[b]	$M_n \times 10^{-3}$ NMR[c]	M_w/M_n[b]	funtionality: protected monosacharide[d]	funtionality: bromobutyl group[e]
P1	4.85	560	**1**, 5.97	35.9	12.9	12.3	13.0	1.07	2.0_2 (G)[f]	1.0_1
P1′	13.0	560	**1**, 19.6	119	5.40	5.36	5.47	1.05	2.0_0 (G)[f]	1.0_0
P1″	21.4	509	**1**, 23.3	163	3.40	3.08	3.41	1.08	2.0_3 (G)[f]	1.0_1
P2	4.84	560	**2**, 6.35	38.5	13.0	12.7	13.3	1.08	2.0_4 (Ga)[g]	1.0_1
P3	5.49	559	**3**, 6.57	38.5	12.0	10.9	13.1	1.07	4.0_7 (G)[f]	1.0_2

[a] Reaction was carried out in THF at −78 °C. [b] M_n(SEC) and M_w/M_n values were estimated from SEC calibration using polystyrene standards in THF. [c] M_n(NMR) values were determined by ^{1}H NMR area ratios of signals corresponding to main chain and initiator fragment. [d] Functionalities of acetal-protected glucofuranoses and galactopyranoses were estimated by ^{1}H NMR area ratios of acetal-protected glucofuranoses and galactopyranoses signals with those corresponding to main chain and initiator fragment. [e] Functionality of bromobutyl group was estimated by ^{1}H NMR area ratios of bromobutyl group signal with those corresponding to main chain and initiator fragment. [f] Glucose residue. [g] Galactose residue.

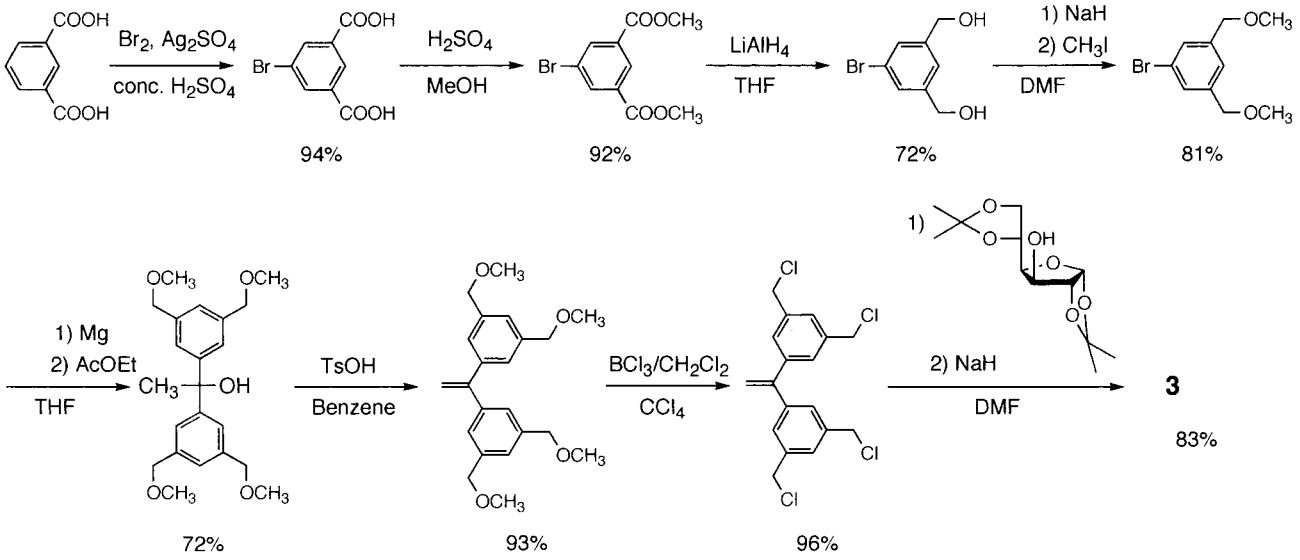
chain-end-functionalized polystyrene with two acetal-protected α-D-glucofuranose residues and one 4-bromobutyl group was prepared as a prepolymer (**P1**) by the addition reaction of polystyryllithium to **1**, followed by treatment with 1,4-dibromobutane. Seven or more excess of 1,4-dibromobutane was required for undergoing a selective monocoupling reaction. The addition order from the living functionalized polystyrene to 1,4-dibromobutane, but not vice versa, and the addition period (1 h or more) were also key factors for the monocoupling reaction. The reaction of 1,4-dibromobutane with the living functionalized polystyrene, prepared from polystyryllithium and **1**, was quite rapid as evidenced by immediate disappearance of a characteristic dark red color of the polymer anion upon addition of the living polymer to 1,4-dibromobutane. The results are summarized in Table 1. The polymer showed a symmetrical monomodal SEC peak with a narrow molecular weight distribution. The SEC-estimated M_n value was 12.3 kg/mol and agreed with that calculated (12.9 kg/mol). The M_n value determined by ^{1}H NMR (13.0 kg/mol) was in even better agreement with the calculated one, although the analytical error of the M_n value determined by ^{1}H NMR was within ±5%. However, the polymer often showed only a small amount of high molecular weight shoulder (<2%), which seemed double the molecular weight. It is possible to completely suppress such a shoulder by slowly adding the polymer anion with **1** to 1,4-dibromobutane for the period of 1 h or more.[26] ^{1}H NMR of the resulting polymer clearly showed two resonances at 5.8 and 3.0 ppm characteristic of the α-glucofuranose H-1 proton and the bromomethylene protons, respectively. The degrees of end-functionalities for both α-D-glucofuranose residues and 4-bromobutyl group were determined to be 2.0_2 and 1.0_1 by comparing both peak intensities with that of the methyl protons of the *sec*-butyl group at 0.7 ppm. Under the same conditions, two more prepolymers of different molecular weights, **P1′** and **P1″**, were synthesized, and the results are also listed in Table 1. Similarly, a chain-end-functionalized polystyrene with two α-D-galactopyranose residues, and 4-bromobutyl group could be synthesized by using **2** instead of **1** in the first reaction step with polystryllithium. This polymer was used as a prepolymer (**P2**). In the next reaction step, the prepolymers (**P1** and **P2**) were reacted with the monoadduct anion prepared from either **1** or **2** with *sec*-BuLi for the further introduction of two same or different monosaccharide residues at the chain ends. For example, **P1** was reacted with the monoadduct anion from **1** and *sec*-BuLi in THF at −78 °C to afford a chain-end-functionalized polystyrene with four D-glucose residues after deprotection. The reaction was relatively slow as evidenced by the observation that a dark red color of the polymer anion gradually faded. The reaction was therefore allowed to stand at −78 °C for 24 h. The results are summarized in Table 2. SEC analysis showed the resulting polymer to have a sharp unimodal peak without any shoulders and tailings. It was observed that the resonance at 3.0 ppm for the bromomethylene protons completely disappeared in the ^{1}H NMR spectrum. The end-functionality was determined to be 4.0_0 by comparing two peak intensities at 5.8 and 0.7 ppm. All results clearly indicate that the reaction proceeds quantitatively to introduce additional two D-glucose residues at the chain end. The M_n value (13.7 kg/mol) determined by ^{1}H NMR exactly agreed with that calculated (13.7 kg/mol), although the M_n value (11.6

Table 2. Synthesis of Chain-End-Functionalized Polystyrenes with 4, 6, and 8 Acetal-Protected Monosaccharide Residues[a]

$[sec\text{-BuLi}]_0$ (mmol/L)	$[DPE]_0$ (mmol/L)	$[prepolymer]_0$ (mmol/L)	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ SEC[b]	$M_n \times 10^{-3}$ NMR[c]	M_w/M_n[b]	functionality of protected monosaccharide calcd	functionality of protected monosaccharide NMR[d]
4.33	**1**, 5.97	**P1**, 3.51	13.7	11.6	13.7	1.08	4 (G)[e]	4.0_0 (G)
4.76	**1**, 19.6	**P2**, 3.25	14.0	12.1	14.0	1.07	2 (G), 2 (Ga)[f]	2.0_4 (G), 1.9_3 (Ga)
4.80	**2**, 23.3	**P2**, 3.32	14.0	12.2	14.0	1.07	4 (Ga)	3.8_8 (Ga)
3.89	**1**, 6.35	**P3**, 2.96	13.8	11.3	13.8	1.08	6 (G)	6.0_6 (G)
3.81	**3**, 6.57	**P3**, 2.96	14.3	11.0	14.3	1.07	8 (G)	7.8_4 (G)

[a] Reaction was carried out in THF at −78 °C. [b] M_n(SEC) and M_w/M_n values were estimated from SEC calibration using polystyrene standards in THF. [c] M_n(NMR) values were determined by ^{1}H NMR area ratios of signals corresponding to main chain and initiator fragment. [d] Functionalities of acetal-protected glucofuranoses and galactopyranoses were estimated by ^{1}H NMR area ratios of acetal-protected glucofuranoses and galactopyranoses signals with those corresponding to main chain and initiator fragment. [e] Glucose residue. [f] Galactose residue.

Scheme 2



kg/mol) estimated by SEC was somewhat smaller than that calculated. Thus, the well-defined chain-end-functionalized polystyrene with four D-glucose residues could be synthesized by the procedure illustrated in Scheme 1. Similarly, a chain-end-functionalized polystyrene with four D-galactose residues was synthesized by the reaction of **P2** with the monoadduct anion from **2** and *sec*-BuLi, followed by deprotection of the acetal functions. It was again observed that the calculated M_n value was in good agreement with that determined by ^{1}H NMR but somewhat higher than the M_n value estimated by SEC. This tendency ($M_{n,calcd} = M_{n,NMR} > M_{n,SEC}$) was always observed in a series of the functionalized polystyrenes with four or more monosaccharide residues synthesized in this study. One of the advantages of this procedure is to be able to introduce two D-glucose and two D-galactose residues into the chain end by the reaction of **P1** with the monoadduct anion from **2** and *sec*-BuLi. Very fortunately, both degrees of chain-end-functionalities of α-D-glucofuranose and α-D-galactopyranose residues can be measured by ^{1}H NMR because their resonances for α-furanose and α-pyranose 1H protons are separately observed at 5.8 and 5.5 ppm. Their functionality degrees were thus determined to be 2.0_4 (102%) and 1.9_3 (97%), respectively.

To synthesize chain-end-functionalized polystyrenes with six and eight D-glucose residues, we have synthesized a new tetrasubstituted DPE derivative, **3**, via eight reaction steps starting from isophthalic acid as illustrated in Scheme 2. Since all steps were high yielding

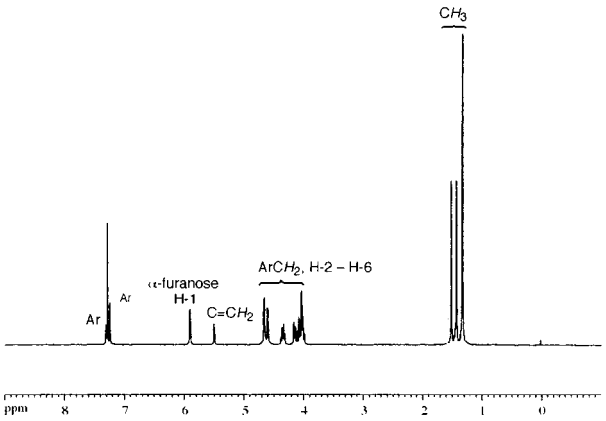


Figure 1. ^{1}H NMR (sol. $CDCl_3$) spectrum of **3**.

reactions, **3** was finally obtained only in ca. 10% isolated yield based on the starting material. The objective DPE, **3**, was a colorless semisolid and could be neither distilled nor recrystallized. It was therefore carefully purified by column chromatography and freeze-dried three times from its absolute benzene solution under high-vacuum conditions (10^{-6} Torr). The ^{1}H NMR spectrum of **3** after the purification is shown in Figure 1.

To examine the reactivity of **3**, the addition reaction of polystyryllithium to a 1.2-fold excess of **3** was first attempted in THF at −78 °C for 0.5 h. Upon addition of the THF solution of **3** to *sec*-BuLi, an immediate color

Table 3. Synthesis of Chain-End-Functionalized Polystyrenes with Four Acetal-Protected α-D-Glucofuranose Residues by Monoaddition Reaction of Polystyryllithium to 3[a]

[*sec*-BuLi]$_0$ (mmol/L)	[styrene]$_0$ (mmol/L)	[**3**]$_0$ (mmol/L)	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ SEC[c]	$M_n \times 10^{-3}$ NMR[d]	M_w/M_n[c]	functionality of protected glucose calcd	functionality of protected glucose NMR[e]
13.1	642	15.4	6.39	5.81	6.84	1.04	4	4.0_3
6.94	778	7.85	13.0	12.7	14.4	1.05	4	4.0_7
1.39	817	2.79[b]	62.4	71.7	71.6	1.04	4	4.0_1

[a] Reaction was carried out in THF at −78 °C for 30 min. [b] Bu_2Mg (ca. 10 mol %) was added to **3** prior to the reaction. [c] M_n(SEC) and M_w/M_n values were estimated from SEC calibration using polystyrene standards in THF. [d] M_n(NMR) was determined by ^{1}H NMR area ratio of signals corresponding to main chain and initiator fragment. [e] Functionalities (NMR) were estimated by ^{1}H NMR area ratios of acetal-protected glucofuranoses signals with those corresponding to main chain and initiator fragment.

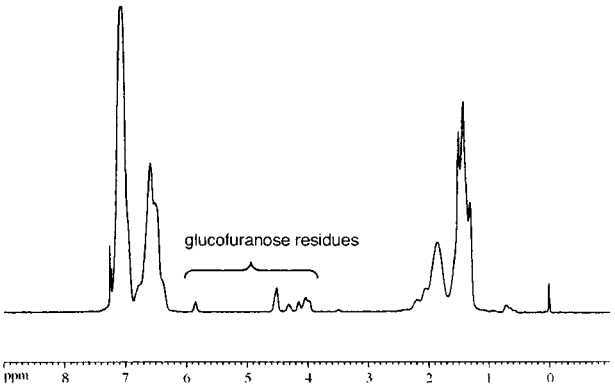


Figure 2. ^{1}H NMR (sol. $CDCl_3$) spectrum of the chain-end-functionalized polystyrene with four acetal-protected α-D-glucofuranose residues synthesized by the addition reaction of polystyryllithium to **3**.

change for reddish orange to deep magenta occurred. The color remained unchanged during the reaction but disappeared instantaneously by quenching with degassed methanol as expected. A polymer yield was quantitative. TLC-FID analysis showed that a small amount (ca. 3%) of unfunctionalized polystyrene was included in the resulting polymer. It is likely formed by the partial termination of polystyryllithium presumably with water in **3**, since complete removal of water from **3** is very difficult. This was not a serious problem. The unfunctionalized polystyrene could be completely removed from the functionalized polymer by column chromatography on silica gel (hexanes/ethyl acetate = 7/3, v/v). The functionalized polymer was isolated in 94% yield. Another way to avoid the formation of unfunctionalized polystyrene is the addition of ca. 10 mol % dibutylmagnesium to **3** prior to the reaction. Indeed, dibutylmagnesium has proven effective in minimizing the formation to nearly zero in this case. The results are listed in Table 3.

The polymer showed a single monomodal SEC peak with a narrow molecular weight distribution (M_w/M_n = 1.05). As shown in Figure 2, characteristic resonances at 5.8 and 4.0−4.5 ppm assigned to the α-glucofuranose H-1 proton and H2−H6 and benzyl ether protons are observed in the ^{1}H NMR spectrum. From the peak intensity ratio of the resonances at 5.8 ppm and the multiplet at 0.7 ppm mentioned above, the degree of end-functionality of the glucofuranose residue was determined to be 4.0_7. Accordingly, the reaction of polystyryllithium with **3** proceeded cleanly and quantitatively in a monoaddition manner. Similarly, two more chain-end-functionalized polystyrenes with four D-glucose residues of different molecular weights could be synthesized by the monoaddition reaction of polystyryllithiums to **3**. Thus, the new DPE derivative, **3**, has proven effective to end-functionalize polystyryllithium with four D-glucose residues in one step.

By utilizing the procedure similar to Scheme 1, we have attempted to synthesize chain-end-functionalized polystyrenes with six and eight D-glucose residues as illustrated in Scheme 3. At first, a chain-end-functionalized polystyrene with four acetal-protected α-D-glucofuranose and 4-bromobutyl groups was prepared as a prepolymer, **P3**, by the addition reaction of polystyryllithium to **3**, followed by treatment with an 8-fold excess of 1,4-dibromobutane. The degrees of both end-functionalities were quantitative within the analytical limit ($f = 4.0_7$ and 1.0_2) (see Table 1).

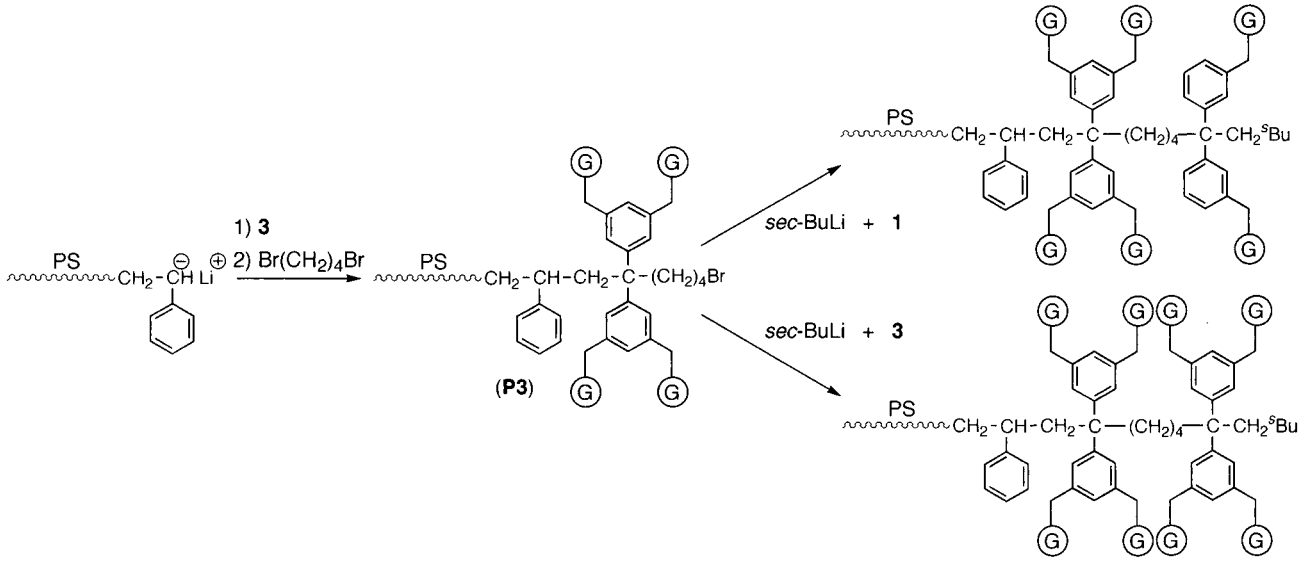
The prepolymer, **P3**, was then reacted with the monoadduct anion from **1** and *sec*-BuLi in THF at −78 °C for 24 h. The resulting polymer showed a sharp symmetrical unimodal SEC peak without any shoulders. The M_n value by ^{1}H NMR agreed well with that calculated. It was again observed that the SEC-estimated M_n value was somewhat smaller than that calculated. The degree of end-functionality determined by ^{1}H NMR was quantitative ($f = 6.0_6$, 101%). A chain-end-functionalized polystyrene with eight D-glucose residues was also synthesized by the addition reaction of **P3** to the monoadduct anion from **3** and *sec*-BuLi under the same conditions. All of the analytical results by SEC and ^{1}H NMR confirm the expectation that the reaction proceeds cleanly and quantitatively to afford the corresponding chain-end-functionalized polystyrene with eight D-glucose residues. The results are listed in Table 2.

The acetal groups of the glucofuranose and galactopyranose residues introduced at chain ends were always quantitatively deprotected by treatment with 6 N HCl at room temperature for 24 h. In all the polymer samples thus hydrolyzed, the resonances at 1.2−1.5 ppm corresponding to the isopropylidene groups completely disappeared in their ^{1}H NMR spectra. ^{13}C NMR analysis also showed complete disappearance of the resonances associated with the acetal carbons. Moreover, complete deprotection was supported by TLC-FID analysis. Typical TLC-FID chromatograms are shown in Figure 3. As you can see, the chain-end-functionalized polystyrene with four D-glucose residues remains near at the spotting point, while the spot of the corresponding polystyrene having four acetal-protected α-D-glucofuranose residues moves to near the top position. Importantly, no spot is observed at the top position in the polymer sample obtained after deprotection.

Solubilities of all polystyrenes chain-end-functionalized with D-glucose residues resembled that of polystyrene. They were soluble in THF, 1,4-dioxane, chloroform, benzene, and even cyclohexane but insoluble in methanol, ethanol, hexane, and water.

Synthesis of In-Chain-Functionalized Polystyrenes with Two and Four D-Glucose Residues. We

Scheme 3



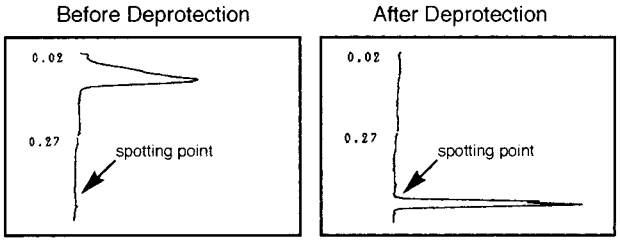


Figure 3. TLC-FID (sol. toluene/THF, 9.5/0.5 v/v) charts of the chain-end-functionalized polystyrene with four acetal-protected α-D-glucofuranose residues before and after deprotecton.

have extend the methodology illustrated in Scheme 1 to the synthesis of in-chain-functionalized polystyrenes with two and four D-glucose residues that are placed at any desired position in a polymer chain as illustrated in Scheme 4.

To synthesize in-chain-functionalized polystyrenes with two or four D-glucose residues at the middle of the chain, a 1.4-fold excess of **P1′** (M_n = 5.47 kg/mol) was reacted with either polystyryllithium or the living functionalized polystyrene with **1** that possessed the molecular weight very similar to that of **P1′**. Typically, the reaction of **P1′** with polystyryllithium occurred very fast and complete within a few minutes in THF at −78 °C. On the other hand, the reaction of **P1′** with the polymer anion from polystyryllithium and **1** proceeded very slowly under the same conditions. The characteristic dark red color of the polymer anion faded gradually and almost disappeared after 24 h. The reactivity difference between polystyryllithium and the living functionalized polystyrene with **1** was thus evident. Since the objective polymers obtained in both cases were contaminated with small amounts of unreacted **P1′** used in excess in the reactions, they were isolated in ca. 90% yield by HPLC fractionation. Figure 4A,B shows SEC traces of the resulting polymers before and after SEC fractionation. The polymers before fractionation exhibited two distinct SEC peaks that corresponded to the coupled polymers and unreacted **P1′**, respectively. After fractionation, the isolated polymers showed single monomodal SEC peaks with narrow molecular weight distributions. The results are summarized in Table 4.

The M_n values determined by ^{1}H NMR agreed quite well with those calculated, while the SEC-estimated M_n values were somewhat smaller than the calculated ones. ^{1}H NMR spectra of both polymers showed that the resonance at 3.0 ppm assigned to the bromomethylene protons observed in **P1′** completely disappeared. The functionalities of D-glucose residue were determined from these spectra to be 2.0_1 and 4.0_2. All of the results clearly indicate that the resulting polymers are the expected polystyrenes in-chain-functionalized with two and four D-glucose residues. Their D-glucose residues may possibly be placed nearly at the middle of the polymer chains, since polymer segments to be coupled were very similar in molecular weight.

In principle, D-glucose residues can be placed at any desired position in a polymer chain simply by changing the molecular weights of prepolymers and polymer anions. For example, the coupling product obtained by the reaction of another prepolymer, **P1″** (M_n = 3.41 kg/mol). In this polymer, the M_n of the polystyrene segment was only 2.55 kg/mol, with polystyryllithium (M_n = 9.88 kg/mol) an in-chain-functionalized polystyrene with two D-glucose residues placed at one-fifth of the chain. Similarly, an in-chain-functionalized polystyrene with four D-glucose residues at one-fifth of the chain was successfully synthesized by the reaction of **P1″** with the living functionalized polystyrene with **1** in THF at −78 °C for 24 h. The functionality degrees of D-glucose residue of the polymers isolated by SEC fractionation were 2.0_0 and 4.0_1. As expected, they possessed the expected molecular weights with narrow molecular weight distributions. These results are also listed in Table 4.

Synthesis of In-Chain-Functionalized Polystyrenes with 4, 8, and 12 D-Glucose and/or D-Galactose Residues. The methodology illustrated in Scheme 4 is an all-around procedure with which two and four D-glucose and possibly other monosaccharide residues can be introduced into the desired position of the chain. To synthesize in-chain-functionalized polystyrenes with more than four D-glucose residues, we have synthesized a new terminator, **4**, a functionalized α,ω-dibromide with four D-glucose residues, from **1**, potassium naphthalenide, and 1,4-dibromobutane (see Experimental Section). Figure 5 shows the ^{1}H NMR spectrum of **4**.

Scheme 4

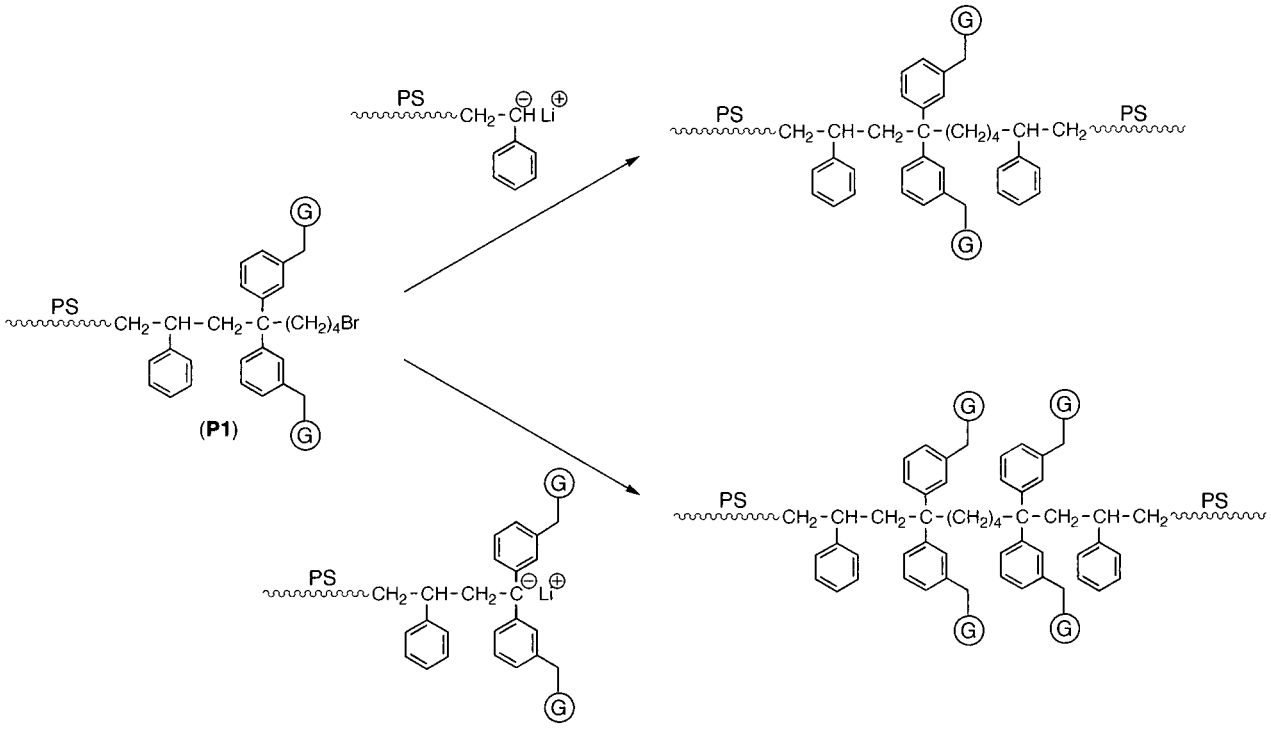


Table 4. Synthesis of In-Chain-Functionalized Polystyrenes with Two and Four Acetal-Protected α-D-Glucofuranose Residues at Desired Position in Chains[a]

[*sec*-BuLi]$_0$ (mmol/L)	[styrene]$_0$ (mmol/L)	[**1**]$_0$ (mmol/L)	[prepolymer]$_0$ (mmol/L)	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ SEC[b]	$M_n \times 10^{-3}$ NMR[c]	M_w/M_n[b]	functionality of protected glucose calcd	functionality of protected glucose NMR[d]	functionality of protected glucose placement
4.72	312		**P1′**, 6.55	12.3	12.0	12.1	1.04	2	2.0_1	middle of chain
4.51	235	6.99	**P1′**, 5.41	11.6	10.7	11.8	1.05	4	4.0_2	middle of chain
4.72	446		**P1″**, 4.96	13.2	13.9	14.1	1.04	2	2.0_0	one-fifths of chain
3.76	373	4.91	**P1″**, 4.13	14.4	12.7	14.0	1.05	4	4.0_1	one-fifths of chain

[a] Reaction was carried out in THF at −78 °C. [b] M_n(SEC) and M_w/M_n values were estimated from SEC calibration using polystyrene standards in THF. [c] M_n(NMR) values were determined by ^{1}H NMR area ratios of signals corresponding to main chain and initiator fragment. [d] Functionalities of acetal-protected glucofuranoses were estimated by ^{1}H NMR area ratios of acetal-protected glucofuranoses signals with those corresponding to main chain and initiator fragment.

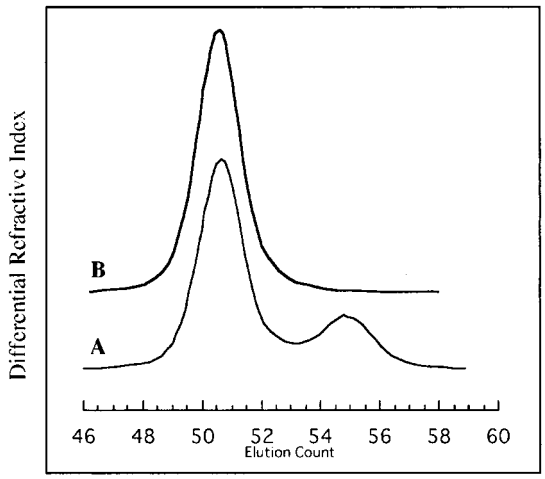


Figure 4. SEC curves of in-chain-functionalized polystyrene with two acetal-protected α-D-glucofuranose residues before SEC fractionation (A) and after SEC fractionation (B).

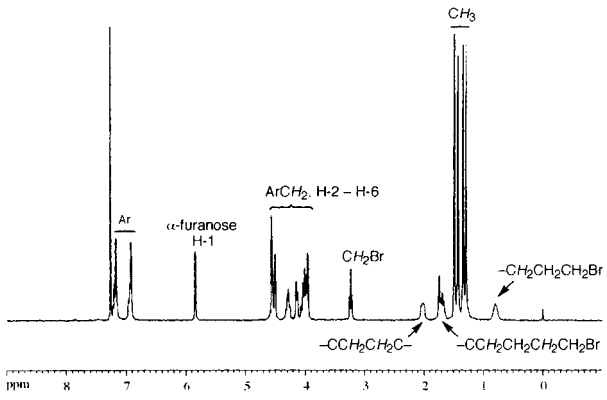


Figure 5. ^{1}H NMR (sol. $CDCl_3$) spectrum of **4**.

As illustrated in Scheme 5, an in-chain-functionalized polystyrene with four D-glucose residues was synthesized by the coupling reaction of **4** with a 2.1-fold excess of polystyryllithium in THF at −78 °C for 24 h. Similarly, for the introduction of eight D-glucose residues, a 2.2-fold excess of living functionalized polystyrene with **1** was reacted with **4** under the same conditions. The resulting polymers were isolated in ca. 90% yields by SEC fractionation to remove unreacted living polymers used in excesses in the reactions. The results are summarized in Table 5.

Both isolated polymers showed single monomodal SEC peaks with narrow molecular weight distributions. It was again observed that their M_n values determined by ^{1}H NMR were in a fair agreement with those calculated, but the SEC-estimated M_n values were somewhat smaller than the calculated values. The

Scheme 5

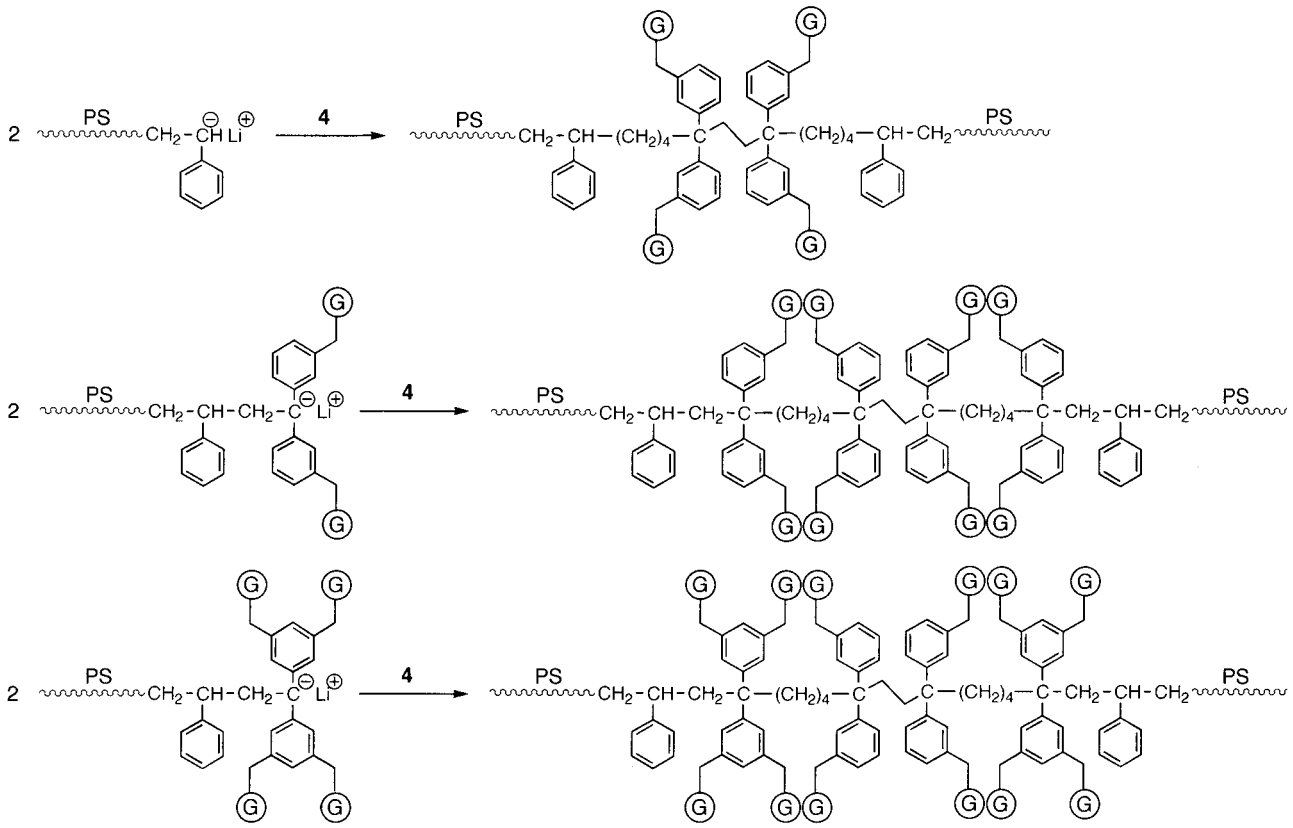


Table 5. Synthesis of In-Chain-Functionalized Polystyrenes with 4, 8, and 12 Acetal-Protected Monosaccharide Residues at Middle of Chain[a]

[*sec*-BuLi]$_0$ (mmol/L)	[styrene]$_0$ (mmol/L)	[DPE]$_0$ (mmol/L)	[**4**]$_0$ (mmol/L)	$M_n \times 10^{-3}$ calcd	$M_n \times 10^{-3}$ SEC[b]	$M_n \times 10^{-3}$ NMR[c]	M_w/M_n[b]	functionality of protected monosaccharide calcd	functionality of protected monosaccharide NMR[d]	total material used (g)	yield of purified polymer (%, g)
10.1	594		4.81	13.9	12.1	13.3	1.04	4 (G)[e]	3.9_4 (G)	1.14	91, 0.946
8.23	473	**1**, 9.87	3.74	15.1	13.4	16.1	1.04	8 (G)	8.0_5 (G)	1.42	90, 1.22
9.09	500	**2**, 10.4	3.50	14.6	13.2	15.6	1.07	4 (G)	4.0_1 (G)	1.60	93, 1.23
								4 (Ga)[f]	3.98 (Ga)		
9.03	492	**3**, 10.4	3.55	15.5	11.8	15.7	1.07	12 (G)	$12._1$ (G)	1.69	88, 1.17

[a] Reaction was carried out in THF at −78 °C. [b] M_n(SEC) and M_w/M_n values were estimated from SEC calibration using polystyrene standards in THF. [c] M_n(NMR) values were determined by ^{1}H NMR area ratios of signals corresponding to main chain and initiator fragment. [d] Functionalities of acetal-protected glucofuranoses and galactopyranoses were estimated by ^{1}H NMR area ratios of acetal-protected glucofuranoses and galactopyranoses signals with those corresponding to main chain and initiator fragment. [e] Glucose residue. [f] Galactose residue.

functionalization degrees of D-glucose residue were determined by ^{1}H NMR to be 3.9_4 and 8.0_5. In these polymers, the D-glucose residues introduced were placed exactly at the middle of the chains. It is also possible to introduce two D-galactose, four D-glucose, and two D-galactose residues in this order into the middle of the chain by the reaction of **4** with the living functionalized polystyrene with **2** instead of **1**.

For the synthesis of an in-chain-functionalized polystyrene with 12 D-glucose residues at the middle of the chain, polystyryllithium was first reacted with **3** in THF at −78 °C for 1 h, followed by coupling with **4** under the same conditions for 24 h. In this case, a 2.5-fold excess of polystyryllithium was used to force the coupling reaction to completion. The isolated polymer after SEC fractionation was the expected in-chain-functionalized polystyrene with 12 D-glucose residues at the middle of the chain as was seen in Table 5.

In summary, our developed methodologies illustrated in Schemes 1 and 3−5 work satisfactorily to quantitatively afford various chain-end- and in-chain-functionlaized polystyrenes with a definite number of plural monosaccharide residues. The resulting polymers all possessed well-defined and controlled structures with respect to degree of functionalization, functionalized position in a chain, molecular weight, and molecular weight distribution. One attractive feature of the methodologies is to use only two kinds of the reaction involving a monoaddition reaction of polystyryllithium with DPE derivatives and a coupling reaction of various bromides and anions, both of which are quantitative nature of reactions. In addition, all the prepolymers and/or building blocks used in the synthesis can be prepared by various modes of reactions of using DPE derivatives.

Aggregation Behaviors of Chain-End- and In-Chain-Functionalized Polystyrenes with Monosaccharide Residues. All of the functionalized polystyrenes with monosaccharide residues synthesized here were observed to have single monomodal SEC peaks, which were very similar to those of the corresponding polymers with acetal-protected monosaccharide residues before deprotection. Their molecular weights estimated

Table 6. Characterization of Chain-End- and In-Chain-Functionalized Polystyrenes with Glucose and Galactose Residues

position of monosaccharide	no. of monosaccharide		$M_n \times 10^{-3}$			M_w/M_n[d]
	G	Ga	calcd	SEC[d]	NMR[e]	
chain end	4[a]		6.02	5.61	6.52	1.04
	4[a]		12.7	11.8	14.1	1.06
	4[a]		62.1	70.4	71.3	1.05
	4[b]		13.4	10.8	13.4	1.08
		4	13.7	11.3	13.7	1.07
	2	2	13.7	11.2	13.7	1.08
	6		13.3	10.3	13.3	1.08
	8		13.7	10.1	13.7	1.08
middle of chain	2		12.0	11.8	11.9	1.04
	4[c]		13.6	12.3	13.0	1.05
	8		14.5	12.7	15.5	1.04
	4	4	14.0	12.5	15.0	1.08
	12		14.5	10.9	14.7	1.07
one-fifth of chain	2		13.0	13.8	13.9	1.04
	4		14.1	12.5	13.7	1.05

[a] Polymer synthesized by the monoaddition reaction of polystyryllithium to **3**. [b] Polymer synthesized by the reaction of **P1** with the monoadduct anion prepared from **1** and *sec*-BuLi. [c] Polymer synthesized by the reaction of polystyryllithium with **4**. [d] M_n(SEC) and M_w/M_n values were estimated from SEC calibration using polystyrene standards in THF. [e] M_n(NMR) values were determined by ^{1}H NMR area ratios of signals corresponding to main chain and initiator fragment.

Table 7. Aggregation Number of Chain-End-Functionalized Polystyrenes with Four Glucose Residues[a]

SLS measurement conditions		$M_w \times 10^{-3}$		
solvent	temp (°C)	calcd[b]	SLS	aggregation no.[c]
cyclohexane	39	6.78	146	22
		14.9	184	12
		74.9	213	2.8
benzene	25	14.9	83.1	5.6
THF	25	14.9	14.9	1.0

[a] Polymers synthesized by the monoaddition reaction of polystyryllithium to **3**. [b] M_w(calcd) values were calculated from M_n values determined by NMR and M_w/M_n by SEC. [c] Aggregation numbers were calculated from M_w(SLS) values divided by M_w(calcd) values.

by SEC corresponded nearly to those calculated as summarized in Table 6. Accordingly, all functionalized polystyrenes did not aggregate in THF at 40 °C under the conditions measured by SEC.

To determine directly the molecular mass of the aggregate, static light scattering (SLS) measurement was carried out with our samples in cyclohexane, benzene, or THF. The molecular masses of the aggregates were nearly constant in the measured ranges (0.563−4.50 g/L), suggesting that the critical micelle concentrations are lower than 0.563 g/L in each case. The aggregation number can be calculated from the molar mass of the aggregates determined by SLS divided by that of the corresponding chain-end functionalized polystyrene determined by ^{1}H NMR. The M_n values by ^{1}H NMR were therefore converted to M_w value by using the M_w/M_n values estimated from SEC.

With the chain-end-functionalized polystyrene with four D-glucose residues (M_w = 14.9 kg/mol, M_w/M_n = 1.06) synthesized by the monoaddition reaction of polystyryllithium to **3**, SLS measurements were carried out in cyclohexane at 39 °C, benzene at 25 °C, and THF at 25 °C. As cyclohexane is a Θ solvent for polystyrene at 34.5 °C, the SLS measurement is always performed in cyclohexane at 39 °C. The results are summarized in Table 7. The functionalized polymer was observed to aggregate in either cyclohexane or benzene, possibly to form reverse micelles. The aggregation numbers were 12 and 5.6, respectively, in these solvents. In contrast, no aggregation was found in THF as expected by the results of SEC measurement. Both the second virial coefficient (A_2) and the squared radius of gyration ($\langle S^2 \rangle$) of the aggregate of the chain-end-functionalized polystyrene with four D-glucose residues in cyclohexane at 39 °C ($M_{w\ SLS}$ = 184 kg/mol, $\langle S^2 \rangle = 2.86 \times 10^{-12}$ cm^2, $A_2 = 9.53 \times 10^{-5}$ mol cm^3/g^2) were lower than those of linear polystyrene with a similar molecular weight ($M_{w\ SLS}$ = 190 kg/mol, $\langle S^2 \rangle = 7.67 \times 10^{-12}$ cm^2, $A_2 = 2.52 \times 10^{-4}$ mol cm^3/g^2). As reviewed by Douglas et al., similar trends were observed when the A_2 and $\langle S^2 \rangle$ values of star-branched polymers were compared with those of linear polymers.[27]

The results of the measurements of two more chain-end-functionalized polystyrenes having different molecular weights are also listed in Table 7. The aggregation number of the polystyrene with M_w value of 6.78 kg/mol was 22, while the aggregation number decreased to only 2.8 with increasing M_w value to 74.9 kg/mol. This molecular weight effect seemed reasonable, and in fact micelles made from block copolymers showed similar trends that the aggregation number decreases as the length of the soluble block increases.[28]

The aggregation numbers of chain-end-functionalized polystyrenes with 1, 2, 4, 6, and 8 D-glucose residues having similar molecular weights around 14 kg/mol were measured in cyclohexane by SLS. Two more chain-end-functionalized polystyrene with two D-glucose and two D-galactose residues as well as with four D-galactose residues were also added in SLS measurement. The results are listed in Table 8. In contrast to the polystyrene with one hydroxy terminus that does not aggregate in cyclohexane ($M_{w,calcd}$ = 12.1 kg/mol, $M_{w,SLS}$ = 12.5 kg/mol), the chain-end-functionalized polystyrene with even one D-glucose residue aggregated under the same conditions and the aggregation number was 3.6. It is thus obvious that the structure of D-glucose residue and/or the number of hydroxy group are important factors for the aggregation to form reverse micelle. As expected, the aggregation number increased to 7.0, 12, 16, and

Table 8. Aggregation Number of Chain-End- and In-Chain-Functionalized Polystyrenes with Glucose and Galactose Residues[a]

position of monosaccharide	no. of monosaccharide		$M_w \times 10^{-3}$		aggregation no.[g]
	G	Ga	calcd[f]	SLS	
chain end	1[b]		12.5	45.4	3.6
	2[b]		13.3	92.5	7.0
	4[c]		14.9	184	12
	4[d]		14.5	178	12
		4	14.7	179	12
	2	2	14.8	172	12
	6		14.4	225	16
	8		14.8	302	20
middle of chain	2		12.4	44	3.5
	4[e]		13.7	136	9.9
	8		16.1	244	15
	4	4	16.2	253	16
	12		15.7	337	21
one-fifth of chain	2		14.5	34.8	2.4
	4		14.4	23.0	1.6

[a] Measurement was carried out in cyclohexane at 39 °C. [b] Reference 19. [c] Polymer synthesized by the monoaddition reaction of polystyryllithium to **3**. [d] Polymer synthesized by the reaction of **P1** with the monoadduct anion prepared from **1** and *sec*-BuLi. [e] Polymer synthesized by the reaction of polystyryllithium with **4**. [f] M_w(calcd) values were calculated from M_n values determined by NMR and M_w/M_n by SEC. [g] Aggregation numbers were calculated from M_w(SLS) values divided by M_w(calcd) values.

20 as the number of D-glucose residue increased from 2, 4, 6, to 8. No influence on the aggregation was thus observed by the structural difference of the terminal monosaccharide residues under the conditions employed here.

With in-chain-functionalized polystyrenes with 2, 4, 8, and 12 D-glucose residues at the middle of the chains and with two and four D-glucose residues at the position of one-fifth of the chains, SLS measurements were performed in cyclohexane at 39 °C. The results are also listed in Table 8. Similar to the trend observed with chain-end-functionalized polymers, the aggregation number increased with increasing the number of D-glucose residue. The number was definitely smaller than that of the chain-end-functionalized polymer with the same number of D-glucose residue. Even with the in-chain-functionalized polystyrene with 12 D-glucose residues, the aggregation number was 21. Very surprisingly, the in-chain-functionalized polystyrene with either two or four D-glucose residues at the position of one-fifth of the chain showed to aggregate to a very little extent, the numbers being only 2.4 and 1.6, respectively. Thus, the placement of D-glucose residue seems to be a very important factor affecting the aggregation and/or micelle formation, although the reason is not understood at the present time.

In the previous paper reported by Eisenberg and Zhong,[3] the aggregation number of the chain-end functionalized polystyrene with two sodium carboxylate groups was roughly estimated by using the model proposed by Halperin ($f \sim N_B^{4/5}$, where f is the aggregation number and N_B is the chain length of insoluble block).[29] In this model, Halperin assumed the micelles to be completely spherical and monodispersed for simplicity. Although the distributions of the micelles in this study were not clear at the present time, we tentatively calculated the aggregation numbers of the chain-end-functionalized polystyrenes with 2, 4, 6, and 8 glucose residues by using his model. The calculated numbers were 3.6, 6.3, 11, 15, and 19. Very fortunately, the agreement was excellently good in the observed numbers.

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(25) We previously found that the anionic polymerization of styrene derivatives with acetal-protected monosaccharide residues proceeded in a living manner in THF at −78 °C, however, failed in benzene at either 0 or 30 °C. Under such conditions, isopropylidene protecting groups and glucofuranose framework might be attacked by anionic initiators and/or propagating chain-end anions.[30] Therefore, all the reactions in this study were carried out in THF at −78 °C.

(26) Several attempts were previously made on this method of addition to be more effective. Richards and co-workers were successful in reducing the degree of coupling by transforming polystyryllithium into the corresponding Grignard reagent.[31] Watanabe and co-workers reported that a chain-end-functionalized poly(styrene-*b*-2-vinylpyridine) with a chloromethylphenyl group was synthesized by reaction of the corresponding living polymer with a large excess of α,α′-dichloro-*p*-xylene.[32] Our group reported the synthesis of chian-end-functionalized polystyrenes with haloalkyl groups by end-capping the polystyryl anion with 1,1-diphenylethylene.[33]

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