Synthesis of Novel Well-Defined Chain-End- and In-Chain-Functionalized Polystyrenes with One, Two, Three, and Four Perfluorooctyl Groups and Their Surface Characterization

Akira Hirao,* Gen Koide, and Kenji Sugiyama

Polymeric and Organic Materials Department, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ohokayama, Meguro-ku, Tokyo 152-8552, Japan

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ABSTRACT: Various chain-end and in-chain functionalized polystyrenes with one, two, three, and four perfluorooctyl (C_8F_{17}) groups with well-defined structures (M_n = (3.5−29) × 10^3 g/mol) were synthesized by the addition reaction of polystyryllithiums to phenol-functionalized agents such as 1-(4-bromobutyl)-4-*tert*-butyldimethylsilyloxybenzene, 1-(4-*tert*-butyldimethylsilyloxyphenyl)-1-phenylethylene, and 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene and the subsequent Williamson reaction with $C_8F_{17}(CH_2)_3$-Br to introduce C_8F_{17} groups via the phenol functions regenerated after deprotection. In addition, chain-end-functionalized polystyrene with C_8F_{17} group at both ends and in-chain-functionalized polystyrenes with one and two C_8F_{17} groups introduced at two positions in chains were synthesized in a similar fashion using difunctional living polystyrenes. Surface structures of annealed films prepared from such C_8F_{17}-chain-functionalized polystyrenes were characterized by angle-dependent XPS and contact angle measurements using water and dodecane droplets. Both measurements confirmed that the C_8F_{17} group segregated and preferentially enriched at the surfaces in virtually all films. The degree of surface enrichment increased with the number of C_8F_{17} groups and, on the other hand, decreased with the molecular weight of the functionalized polymer. The terminal C_8F_{17} group was usually much more effective for surface enrichment than the internal group in the same number. On the assumption that this moiety is highly ordered and oriented with the chain axis perpendicular to the surface, it can be speculated from the F/C values at 10° TOA by XPS in some polymers that all surface areas of these films are completely covered with the $C_8F_{17}C_3H_6OC_6H_4$ moiety.

Introduction

It has recently been well-known that the surface (or air−polymer interface) structures of multicomponent polymer systems such as block and random copolymers and polymer blends are different from those of the bulk.[1−4] Even in chain-end-functionalized polymers, the end groups are segregated to enrich at surfaces rather than they are randomly distributed through the bulk of the material.[5−11] The segregation effects may be more accentuated, when the chain-end functional groups are perfluoroalkyl (Rf) groups. It has indeed been observed by various analytical methods including contact angle, XPS, static SIMS, and neutron reflectivity measurements that the Rf groups are segregated from their main chains to preferentially enrich at the surface (or air−polymer interface) due to their low surface free energies.[12−17] The surface properties may be dominated by their Rf end groups, thus forming hydrophobic as well as lipophobic surfaces that originated from inherent characters of the Rf groups. In these polymers, the number of terminal Rf group is usually limited to one at each end or both ends. (In this case two Rf groups are present in the chain.)

For a recent few years, some research groups including ours have been developing general and versatile methodologies using functionalized 1,1-diphenylethylene (DPE) derivatives for the synthesis of well-defined chain-multifunctionalized polymers.[18−29] The methodologies involve diverse modes of addition reaction of either living anionic polymers or anionic initiators to functionalized DPE derivatives and further polymerization or reaction of appropriate electrophiles with the 1,1-diphenylalkyl anions generated after the addition reaction. Very recently, we have successfully synthesized chain-end-functionalized polystyrenes with one, two, three, and four perfluorooctyl (C_8F_{17}) groups by means of the above-mentioned methodology developed by us and characterized their surface structures.[17] It has been clearly observed for the first time that the degree of surface enrichment increases with an increase in number of the terminal C_8F_{17} group. Considering low surface free energy of perfluoroalkyl groups, the surface enrichment of C_8F_{17} groups is of certain expect. There is however so far no study on quantitative evaluation for the effect of number of terminal C_8F_{17} group on surface enrichment.

In this contribution, we report on the synthesis of C_8F_{17}-chain-functionalized polymers with various architectures and the more detailed surface characterization study of such polymers by XPS and contact angle measurements. We herein focus on the effects of the number and placement of C_8F_{17} groups as well as molecular weight on surface enrichment. The polymers herein synthesized involve chain-end- and in-chain-functionalized polystyrenes with one, two, three, and four C_8F_{17} groups, whose M_n values are in the range of (3.4−29) × 10^3 g/mol. In addition, chain-end-functionalized polystyrene with C_8F_{17} groups at both ends and in-chain-functionalized polystyrenes with one and two C_8F_{17} groups introduced at two positions in chains are synthesized and studied in surface characterization.

* Corresponding author: Tel 81-3-5734-2131; Fax 81-3-5734-2887; e-mail ahirao@polymer.titech.ac.jp.

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Experimental Section

Materials. Reagents used in this study were purchased from Aldrich Japan, unless otherwise stated. Dichloromethane was distilled over CaH_2 under an atmosphere of nitrogen. *N,N*-Dimethylformamide (DMF) was distilled over CaH_2 under reduced pressure. $CuCl_2$ (Tokyo Kasei, Japan), dibutylmagnesium (Bu_2Mg), *sec*-butyllithium (*sec*-BuLi) (Nakarai Chemicals, Japan), LiCl (Tokyo Kasei, Japan), imidazole (Tokyo Kasei, Japan), 4-bromophenol, 4-hydroxybenzophenone, 4,4′-dihydroxybenzophenone (Tokyo Kasei, Japan), potassium *tert*-butoxide, methyltriphenylphosphonium bromide, and *tert*-butyldimethylsilyl chloride (Shinetsu Chemical Co. Ltd., Japan) were used as received. 3-Perfluorooctyl-1-propanol was purchased from Daikin Co. Ltd., Japan. Li_2CuCl_4 was prepared by the reaction of $CuCl_2$ (1.25 g, 9.30 mmol) and LiCl (0.790 g, 18.6 mmol) in dry THF (20 mL) at room temperature for 1 h under an atmosphere of nitrogen. THF was refluxed over sodium wire and distilled over $LiAlH_4$ under an atmosphere of nitrogen. Heptane, after washing with H_2SO_4, was distilled over P_2O_5 under a nitrogen atmosphere. THF and heptane were finally distilled from the sodium naphthalenide and 1,1-diphenylhexyllithium solutions under high vacuum (10^{-6} Torr) in the reaction vessels, respectively. Styrene (Tokyo Kasei, Japan) was washed with 5% NaOH, dried over $MgSO_4$, and distilled over CaH_2 under reduced pressure. After adding Bu_2-Mg (3 mol %), styrene was finally distilled under high vacuum (10^{-6} Torr) in the reaction vessel. 1,1-Diphenylethylene (DPE) (Tokyo Kasei, Japan) was distilled over CaH_2 under reduced pressure and, after adding *n*-BuLi (3 mol %), was distilled under high vacuum (10^{-6} Torr) in the reaction vessel. 1,4-Dibromobutane (Tokyo Kasei, Japan) was distilled over CaH_2 under reduced pressure and, after addition of Bu_2Mg (3 mol %), again distilled under high vacuum (10^{-6} Torr) in the reaction vessel.

3-Perfluorooctylpropyl Bromide. This bromide was synthesized according to the procedure previously reported.[30] ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 2.10 (t, 2H, J = 5.4 Hz, $CH_2CH_2CH_2$), 2.21 (m, 2H, CF_2CH_2), 3.48 (t, 2H, J = 6.0 Hz, CH_2Br). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 24.0 (CH_2CH_2-CH_2), 30.1 (t, $^2J_{C-C-F}$ = 22.1 Hz, CF_2CH_2), 32.2 (CH_2Br), 114.0−118.9 (m, CF_2).

1-(4-*tert*-Butyldimethylsilyloxyphenyl)-1-phenylethylene (1). Compound **1** was synthesized according to the method previously reported.[31] ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.26 (s, 6H, $SiCH_3$), 1.04 (s, 9H, $C(CH_3)_3$), 5.41 (d, 2H, J = 7.2 Hz, $CH_2{=}C$), 6.83 (d, 2H, aromatic H′s ortho to OSi), 7.25 (d, 2H, aromatic H′s meta to OSi), 7.36 (m, 5H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): −4.30 ($SiCH_3$), 18.3 ($C(CH_3)_3$), 25.8 ($C(CH_3)_3$), 113.1 ($CH_2{=}C$), 119.7, 128.2, 129.4, 134.5, 141.9, 149.7 (Ar), 155.6 ($CH_2{=}C$).

1,1-Bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene (2). Compound **2** was synthesized according to the method previously reported.[21] ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.19 (s, 12H, $SiCH_3$), 0.97 (s, 18H, $C(CH_3)_3$), 5.26 (s, 2H, $CH_2{=}C$), 6.76 (d, 4H, aromatic H′s ortho to OSi), 7.18 (d, 4H, aromatic H′s meta to OSi). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): −4.29 ($SiCH_3$), 18.3 ($C(CH_3)_3$), 25.8 ($C(CH_3)_3$), 111.8 ($CH_2{=}C$), 119.7, 126.0, 129.5, 134.9 (Ar), 155.5 ($CH_2{=}C$).

1-(4-Bromobutyl)-4-*tert*-butyldimethylsilyloxybenzene (3). Under an atmosphere of nitrogen, to 4-bromophenol (7.03 g, 43.7 mmol) in DMF (10 mL) was added dropwise *tert*-butyldimethylsilyl chloride (10.4 g, 69.3 mmol) and imidazole (14.5 g, 213 mmol) in DMF (20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 24 h. The reaction was quenched with a small amount of water and extracted with hexanes. The organic layer was washed with water and dried with $MgSO_4$. After filtration and evaporation, 1-bromo-4-*tert*-butyldimethylsilyloxybenzene (8.25 g, 30.0 mmol) was obtained in 69% yield as a colorless liquid by distillation under reduced pressure (78−79 °C/3 Torr). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.17 (s, 6H, $SiCH_3$), 0.96 (s, 9H, $C(CH_3)_3$), 6.70, 7.30 (2d, 4H, J = 8.7 Hz, Ar).

Under an atmosphere of nitrogen, to a THF (10 mL) solution of 1-bromo-4-*tert*-butyldimethylsilyloxybenzene (7.03 g, 25.6 mmol) was added dropwise to magnesium (1.12 g, 46.1 mmol) in THF (40 mL) at 25 °C for 20 min. The reaction mixture was stirred at 25 °C for an additional 1 h. To a THF (10 mL) solution of 1,4-dibromobutane (13.7 g, 63.5 mmol) and Li_2CuCl_4 (0.253 M, 1.60 mL, 0.405 mmol) was added dropwise the Grignard reagent thus prepared at 25 °C for 30 min, and the reaction mixture was stirred for an additional 2 h. After usual workup, the crude product was purified by distillation under reduced pressure (122−124 °C/1 Torr) to afford **3** (2.72 g, 8.22 mmol) as a colorless liquid in 32% yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.16 (s, 6H, $SiCH_3$), 0.96 (s, 9H, $C(CH_3)_3$), 1.72 (pentad, 2H, J = 7.8 Hz, $PhCH_2CH_2$), 1.86 (pentad, 2H, J = 6.9 Hz, $BrCH_2CH_2$), 2.55 (t, 2H, J = 7.5 Hz, $PhCH_2$), 3.39 (t, 2H, J = 6.6 Hz, $BrCH_2$), 6.75, 6.98 (2d, 4H, J = 8.4 Hz, Ar).

Synthesis of Chain-End- and In-Chain Functionalized Polystyrenes with Phenol Functionalities. All the polymerization and phenol-functionalization reactions were carried out under high-vacuum conditions (10^{-6} Torr) in all-glass apparatus equipped with break-seals. The living anionic polymerization of styrene was carried out in THF at −78 °C for 30 min with *sec*-BuLi as an initiator. A portion of the resulting polystyryllithium was always taken prior to the phenol-functionalization reaction in order to determine the molecular weight and molecular weight distribution. For the synthesis of chain-functionalized polystyrenes, polystyryllithiums of 0.6−2.0 g and/or the prepolymers of 0.6−1.0 g were used. The synthetic routes will be illustrated in Schemes 1 and 2.

The addition reaction of polystyryllithium to either **1** or **2** was carried out in THF at −78 °C for 1 h. The reaction of polystyryllithium with **2** was performed in a similar manner. The reaction of polystyryllithium with **2** followed by treatment with a 1.5-fold excess of **3** was carried out in THF at −78 °C for 1 h. Each reaction was terminated with degassed methanol. The reaction mixtures were poured into methanol to precipitate the polymers. Yields of polymers were virtually quantitative in all cases. The polymers were purified by reprecipitation from THF solution to methanol two times and then freeze-dried from their absolute benzene solutions for 24 h. The M_n and M_w/M_n values were measured by SEC relative to polystyrene. The M_n values were also determined by ^{1}H NMR. The end-functionalization degrees were determined by ^{1}H NMR using two resonance at 0.60−0.80 ppm (CH_3 protons of the initiator fragment) and at 0.18−0.25 ppm ($Si{-}CH_3$ protons).

Prepolymer **P-1** was prepared by the addition reaction of polystyryllithium to **2** followed by treatment of a 10-fold excess of 1,4-dibromobutane in THF at −78 °C for 1 h. The end-functionalization degrees of the silyl-protected phenol and 4-bromobutyl groups determined by ^{1}H NMR were 2.0_0 and 1.0_0, respectively. For determination, three resonances at 0.28 ppm ($Si{-}CH_3$), 0.78 ppm (CH_3 of the initiator fragment), and 3.10 ppm ($BrCH_2$) were used.

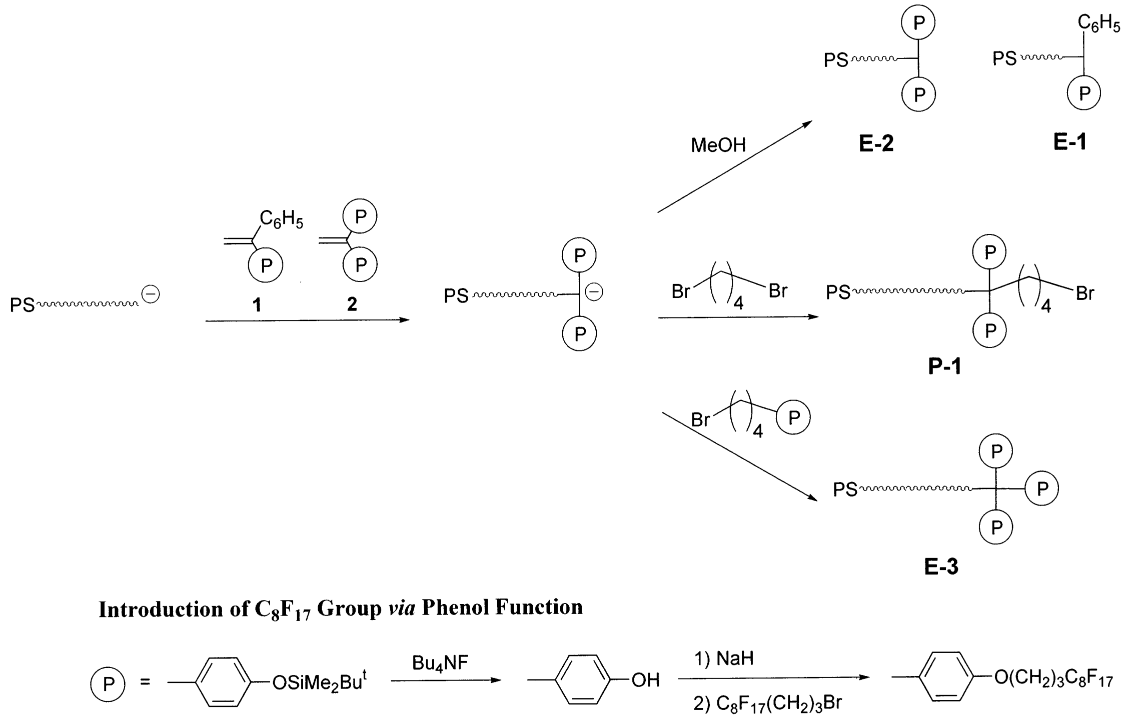
Chain-end-functionalized polystyrene with four phenols was synthesized by the reaction of **P-1** with the functionalized 1,1-diphenylalkyl anion prepared from **2** and *sec*-BuLi in THF at −78 °C for 5 h.

In-chain-functionalized polystyrene with two phenols was synthesized by the coupling reactions of **P-1** with polystyryllithium in THF at −78 °C for 24 h. The coupled polymer was isolated in 89% yield by fractionation with SEC. The isolated polymer was reprecipitated two times from THF to methanol and freeze-dried from its absolute benzene solution for 24 h.

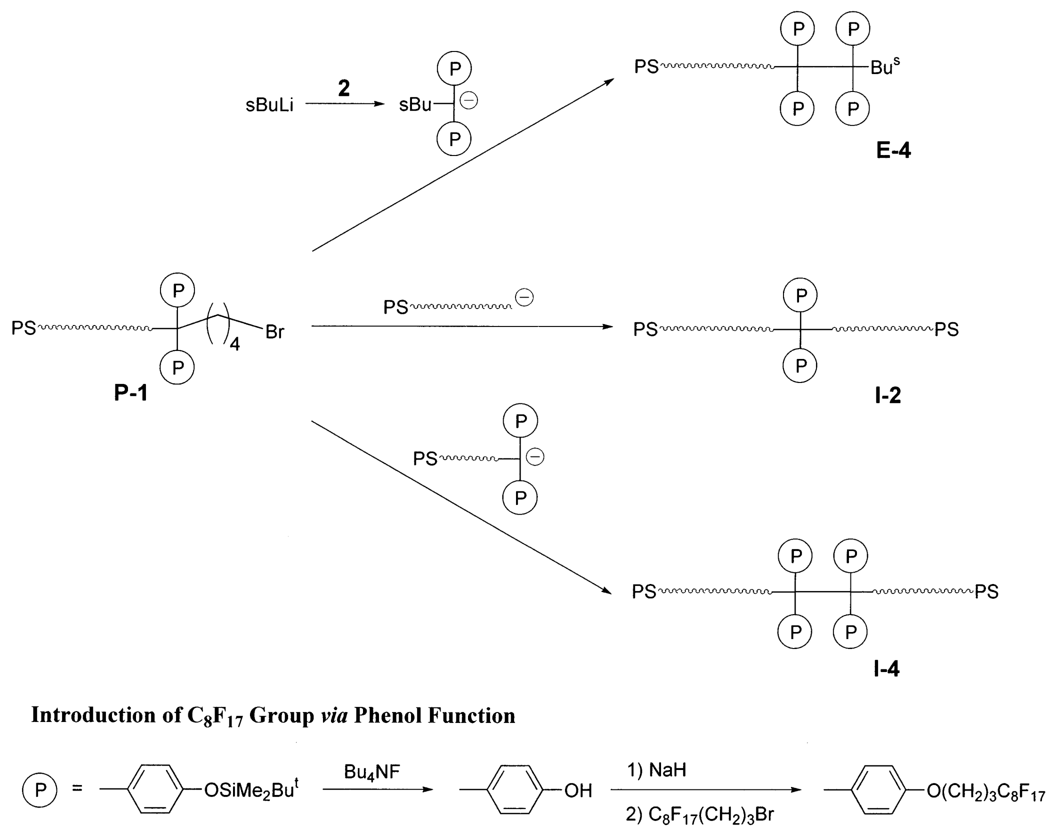
Similarly, in-chain-functionalized polystyrene with four phenols was synthesized by the reaction of **P-1** with polystyryllithium end-capped with **2** in THF at −78 °C for 48 h.

The silyl-protecting groups of the polymers were quantitatively deprotected with $(C_4H_9)_4NF$ (ca. 5-fold excess) in THF at 25 °C for 2 h. The polymers were precipitated in 1 N HCl aqueous solution and purified by reprecipitation from THF to methanol two times and freeze-drying from their absolute benzene solutions for 24 h. Yields of polymers were around 95%. The resulting polymers, after freeze-drying twice from their absolute benzene solutions, were used in the next Williamson reaction within 1 h. All of the phenol-functional-

Scheme 1. Synthetic Procedures for the Synthesis of Chain-Functionalized Polystyrens with One, Two, and Three C_8F_{17} Groups and ω-Bromoalkylated Polystyrene



Scheme 2. Synthetic Procedures for the Synthesis of Chain-End- and In-Chain-Functionalized Polystyrenes with Two and Four C_8F_{17} Groups



ized polymers showed sharp monomodal SEC distributions similar to those of their parent polymers.

Introduction of C_8F_{17} Group via Phenol Function by Williamson Reaction. C_8F_{17} groups were introduced via phenol functions by a Williamson reaction of the phenol-functionalized polystyrenes with $C_8F_{17}(CH_2)_3Br$. In a typical reaction, under an atmosphere of nitrogen, NaH (2.40 mmol) was added to a DMF (35 mL) solution of chain-end-functionalized polystyrene with two phenols (0.720 g, $M_n = 5.9_8 \times 10^3$ g/mol, phenol moiety = 0.241 mmol). The reaction mixture was allowed to stir for an additional 1 h at 25 °C. Then, $C_8F_{17}(CH_2)_3$-Br (2.65 g, 4.90 mmol) in DMF (5 mL) was added dropwise to this suspension at 0 °C. The mixture was allowed to gradually warm to 25 °C and stir for further 12 h. Water was cautiously added to quench unreacted NaH. The reaction mixture was then poured into 1 N HCl methanolic solution to precipitate the polymer. The polymer was further purified by column chromatography with hexanes and benzene to remove unreacted $C_8F_{17}(CH_2)_3Br$. After evaporation, the residual polymer (0.716 g, 90% yield) was reprecipitated from THF to methanol two times and freeze-dried from its benzene solution for 24 h. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.60−0.80 (broad, 6H, CH_3), 1.2−2.2 (broad, 234H, CH_2), 3.9−4.0 (m, 8H, OCH_2), 6.2−7.2 (broad, 341H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 20.6 (s, $CH_2CH_2CF_2$), 27.9 (t, CH_2CF_2, $^2J_{C-C-F} = 20.5$ Hz), 41.9−46.8 (broad, CH_2CHAr), 66.1 (s, OCH_2), 106.0−125.7 (m, CF_2), 127.5−128.9 (broad, ArC2−C5), 145.2−146.1 (m, ArC1). Similarly, the reactions of other phenol-functionalized polymers with $C_8F_{17}(CH_2)_3Br$ were carried out under the same conditions. All of the polymers were purified by column chromatography, reprecipitation, and freeze-dried from their benzene solutions for 24 h. Isolate yields of polymers were usually more than 90%. The M_n values were determined by ^{1}H NMR as follows: The molecular weight of polystyrene part was determined by comparing peak area of the resonance at 6.2−7.2 ppm for the aromatic protons and that at 0.60−0.80 ppm (CH_3 protons of the initiator fragment). The total molecular weight of the polymer was obtained by adding molecular weight of the introduced C_8F_{17} moieties to that of the polystyrene part.

Synthesis of Chain-End-Functionalized Polystyrene with C_8F_{17} Group at Both Ends and In-Chain-Functionalized Polystyrene with One and Two C_8F_{17} Groups Introduced at Two Positions in Chains. Chain-end-functionalized polystyrene with C_8F_{17} group at both ends was synthesized by the reaction of difunctional living polystyrene initiated with potassium naphthalenide, followed by end-capping with DPE and by subsequent treatment with **2** in THF at −78 °C for 1 h.

For the synthesis of the title in-chain-functionalized polystyrenes, a new prepolymer (**P-2)** was prepared by the reaction of the above-mentioned difunctional living polystyrene with **1**, followed by treatment with a 10-fold excess of 1,4-dibromobutane under the same conditions used for the preparation of **P-1**. Difunctional living polystyrene, **1**, and 1,4-dibromobutane were used for the synthesis of **P-2**. The **P-2** thus prepared was reacted with either polystyryllithium end-capped with DPE or **1** in THF at −78 °C for 24 h to afford the title in-chain-functionalized polymers. Similarly, the coupling reaction of **P-2** with polystyryllithium end-capped with **1** was carried out under the same conditions. Deprotection and introduction of C_8F_{17} groups of the chain-functionalized polymers were carried out under the identical conditions mentioned before.

Measurements. ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $(CH_3)_4Si$ (δ 0 ppm) for ^{1}H NMR and relative to $CDCl_3$ (δ 77.1 ppm) for ^{13}C NMR as standards. Size-exclusion chromatograms (SEC) were measured with a TOSOH HLC-8020 at 40 °C with ultraviolet (254 nm) or refractive index detection. THF was 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. Measurable molecular weight ranges are 10^3−4×10^5 and 10^4−4×10^6, respectively. Calibration curves were made with standard polystyrene to determine M_n and M_w/M_n values. Fractionation with SEC was performed with a TOSOH HLC-8020 type fully automatic instrument equipped with a TSKgel G5000H_{HR} column (measurable molecular weight range: 10^3−4×10^6). All runs for fractionation were made with THF at a flow rate of 5.0 mL/min at 40 °C. The concentration of the polymer solution for fractionation was adjusted to 10−20 g/L, depending on the molecular weight of the sample. TLC coupled with flame ionization detector (FID) was performed by IATRON IATROSCAN NEW MK-5 equipped with IATROCORDER TC-21 from Iatron Laboratories, Inc. Specially designed quartz rods (150 mm × 2.0 mm) were used on which silica gel was sintered. Contact angles of the polymer films were measured with a Kyowa Interface Science CA-A using water and dodecane droplets. Angle-dependent X-ray photoelectron spectroscopy (XPS) was performed on Perkin-Elmer 5500MT with a monochromatic Al Kα X-ray source. The polymer films for contact angle and XPS measurements were prepared by spin-coating (4000 rpm, 20 s) onto cover glasses from 3 to 5.0 wt % benzene solution of polymer. The thickness of the film was 100 nm. The sample was dried at 25 °C for 24 h and annealed for 2 h at 110 °C under vacuum to allow the chains to reach their equilibrium configurations.

Results and Discussion

Synthesis of Chain-End- and In-Chain-Functionalized Polystyrenes with One, Two, Three, and Four C_8F_{17} Groups. We have recently reported elsewhere on the synthesis of chain-end-functionalized polystyrenes with one, two, three, and four C_8F_{17} groups (M_n = ca. 20×10^3 g/mol).[17] However, the synthetic procedures have been described only briefly; in this section the more detailed procedures for such polymers and new other related functional polymers have been described from a synthetic point of view. The synthetic procedures are illustrated in Scheme 1. All of the chain-end-functionalized polymers with C_8F_{17} groups were synthesized by the addition reaction of polystyryllithium to phenol-functionalized agents whose phenol functions were protected with *tert*-butyldimethylsilyl groups, followed by deprotection with $(C_4H_9)_4NF$ and the subsequent Williamson reaction with $C_8F_{17}(CH_2)_3Br$. Two kinds of polystyryllithiums having M_n values of around 5×10^3 and 25×10^3 g/mol were usually employed. As phenol-functionalized agents, 1-(4-*tert*-butyldimethylsilyloxyphenyl)-1-phenylethylene (**1**), 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene (**2**), and 1-(4-bromobutyl)-4-*tert*-butyldimethylsilyloxymethylbenzene (**3**) were used.

Similar to the procedures previously reported by Quirk and co-workers,[21,31] chain-end-functionalized polystyrene with one or two phenols was synthesized by adding either **1** or **2** to polystyryllithium, followed by deprotection with $(C_4H_9)_4NF$. To examine the effect of molecular weight on surface structure in more detail, three more polymer samples with different M_n values were also synthesized in the polymers with two phenols. Chain-end-functionalized polystyrene with three phenols was obtained by the reaction of polystyryllithium with **2**, followed by treatment with **3** to introduce one more phenol at the chain end. For the synthesis of chain-end-functionalized polystyrene with four phenols, we first prepared a prepolymer **P-1** by the reaction of polystyryllithium with **2**, followed by treatment with a 10-fold excess of 1,4-dibromobutane. The functionalized polystyrene with four phenols was synthesized by the reaction of **P-1** with the functionalized 1,1-diphenylalkyl anion from **2** and *sec*-BuLi, followed by deprotection with $(C_4H_9)_4NF$. Since phenol functions were not very stable in the air, the functionalized polymers were characterized by ^{1}H NMR and SEC prior to the deprotection step of the silyl groups. The results are summarized in Table 1.

All of the polymers were observed to exhibit symmetrical monomodal SEC peaks with narrow molecular weight distributions. The M_n values observed by SEC using polystyrene calibration curve were in good agreement with those calculated. There were however some deviations in the M_n values between calculated and observed by SEC in a series of relatively low molecular weight polymers having M_n values of around (2.3−9.4) $\times 10^3$ g/mol. The M_n values were also determined by ^{1}H NMR using three resonance at 6.2−7.2 ppm (aro-

Table 1. Synthesis of End-Functionalized Polystyrenes with One, Two, Three, and Four *tert*-Butyldimethylsilyloxyphenyl Groups[a]

code	*sec*-BuLi (mmol)	styrene (mmol)	DPE[b] type (mmol)	R−Br[c] (mmol)	$M_n \times 10^{-3}$ calcd	SEC[d]	NMR[e]	M_w/M_n	functionality calcd	obsd[e]
E-1 (6.3K)	0.268	13.9	**1**, 0.318		5.76	6.00	5.98	1.04	1	0.98_4
E-1 (28K)	0.0429	9.86	**1**, 0.0677		24.6	26.8		1.05	1	1.0_0
E-2 (3.4K)	0.811	14.1	**2**, 0.990		2.31	2.51	2.72	1.05	2	1.9_9
E-2 (6.6K)	0.212	10.8	**2**, 0.240		5.67	5.94	5.91	1.03	2	2.0_0
E-2 (9.2K)	0.174	14.9	**2**, 0.199		9.40	8.81	8.55	1.02	2	1.9_2
E-2 (20K)	0.0851	16.8	**2**, 0.107		21.7	19.6		1.04	2	2.0_0
E-2 (28K)	0.0447	9.37	**2**, 0.0622		22.3	28.6		1.05	2	2.0_0
E-3 (8.5K)	0.183	11.8	**2**, 0.257	**3**, 0.280	7.47	6.62	7.43	1.04	3	3.0_0
E-3 (20K)	0.0762	14.5	**2**, 0.116	**3**, 0.171	21.2	19.3		1.03	3	2.8_8
E-4 (8.4K)	0.301		**2**, 0.343	**P-1**,[f] 0.0907	8.11	6.95	8.43	1.02	4	4.0_0
E-4 (24K)	0.177		**2**, 0.248	**P-1**,[g] 0.0225	21.1	22.1		1.02	4	4.0_2
1-E-1 (24K)	0.0946[h]	9.48	**1**, 0.360		21.3	22.8		1.07	2	2.0_0

[a] Yields of polymers were quantitative in all cases. [b] **1**: 1-(4-*tert*-butyldimethylsilyloxyphenyl)-1-phenylethylene. **2**: 1,1-bis[4-(*tert*-butyldimethylsilyloxy)phenyl]ethylene. [c] **3**: 1-(4-bromobutyl)-4-(*tert*-butyldimethylsilyloxy)benzene. **P-1**: ω-bromobutylated polystyrene. [d] Determined by SEC using polystyrene calibration. [e] Determined by ^{1}H NMR. [f] $M_n = 7.72 \times 10^3$ (g/mol). [g] $M_n = 21.0 \times 10^3$ (g/mol). [h] Potassium naphthalenide.

Table 2. Synthesis of In-Chain-Functionalized Polystyrenes with One, Two, Three, and Four *tert*-Butyldimethylsilyloxyphenyl Groups[a]

code	*sec*-BuLi (mmol)	styrene (mmol)	DPE[b] type (mmol)	R−Br[c] (mmol)	$M_n \times 10^{-3}$ calcd	SEC[d]	NMR[e]	M_w/M_n	functionality calcd	obsd[e]
I-2 (6.2K)	0.299	8.24	DPE, 0.359	**P-1**,[f] 0.269	6.13	5.52	5.55	1.03	2	2.0_2
I-2 (29K)	0.0782	9.34	**1**, 0.124	BrC_4H_8Br, 0.0453	25.6	27.0	-	1.02	2	2.0_6
I-4 (7.4K)	0.217	5.79	**2**, 0.239	**P-1**,[f] 0.194	6.30	6.19	6.45	1.02	4	3.9_1
I-4 (24K)	0.177	20.9	**2**, 0.279	BrC_4H_8Br, 0.0998	25.4	22.4		1.02	4	4.0_0
1-I-1 (24K)	0.116	2.20	DPE, 0.135	**P-2**,[g] 0.0456	24.1	23.2		1.05	2	2.0_5
2-I-2 (25K)	0.132	2.17	**1,** 0.287	**P-2**,[g] 0.0443	24.1	23.1		1.09	4	4.0_0

[a] Yields of polymers were around 90% after SEC fractionaltion in all cases. [b] **1**: 1-(4-*tert*-butyldimethylsilyloxyphenyl)-1-phenylethylene. **2**: 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene. [c] **P-1**: ω-bromobutylated polystyrene. **P-2**: α,ω-dibromoalkylated polystyrene. [d] Determined by SEC using polystyrene calibration. [e] Determined by ^{1}H NMR. [f] $M_n = 3.03 \times 10^3$ (g/mol). [g] $M_n = 19.8 \times 10^3$ (g/mol).

matic protons of the polymer side chain and the phenol-functionalized agent), at 0.60−0.80 ppm (CH_3 protons of the initiator fragment), and at 0.18−0.25 ppm (Si−CH_3 protons). These values well agreed with those calculated. The functionalization degrees were determined by ^{1}H NMR using two resonances at 0.18−0.25 and 0.60−0.80 ppm just mentioned above. Agreement between values observed and expected is quite satisfactory in every sample as shown in Table 1.

The silyl groups were then deprotected with ca. 5-fold excess of $(CH_3)_4NF$ in THF at 25 °C for 2 h. Quantitative deprotection was confirmed by complete disappearance of the resonances at 1.02 and 0.21 ppm characteristic of methyl protons of the *tert*-butyldimethylsilyl group in ^{1}H NMR spectra of all polymers obtained after deprotection. SEC profiles of the resulting polymers showed symmetrical monomodal peaks. Their molecular weight distributions remained narrow. Typical ^{1}H NMR spectra of the polystyrenes with four phenols before and after deprotection are shown in parts A and B of Figure 1, respectively.

The synthetic procedures for in-chain-functionalized polystyrenes with two and four phenols are illustrated in Scheme 2. In-chain-functionalized polystyrene with two phenols was obtained by the reaction of **P-1** with polystyryllithium end-capped with DPE, followed by deprotection with $(C_4H_9)_4NF$. Similarly, in-chain-functionalized polystyrene with four phenols was synthesized by the reaction of **P-1** with polystyryllithium end-capped with **2**. In these reactions, both prepolymers and polystyryllithiums were very similar in molecular weight, and therefore the introduced phenols were placed nearly at the middle of the chains. It is of course possible to place phenols at essentially any desired position in a polymer chain by changing the molecular weights of these polymers.

In the two reactions mentioned above, small excesses of polystyryllithiums were used to force the reactions to completion. The objective in-chain-functionalized polymers were therefore isolated in ca. 90% yields by fractionation with SEC. The SEC peaks of in-chain-functionalized polystyrenes with four silyl-protected phenols before and after fractionation are shown in parts A and B of Figure 2. As can be seen, the isolated polymer is pure and free of its prepolymer and polystyrene. Both in-chain-functionalized polymers were well controlled in chain length and quantitatively functionalized as summarized in Table 2. These polymers were then deprotected with $(CH_3)_4NF$ in THF.

Next, the reaction was carried out between the phenol-functionalized polystyrene and $C_8F_{17}(CH_2)_3Br$ for introducing the C_8F_{17} group via phenol function placed at chain end or in-chain. The phenol function of chain-functionalized polystyrene was first reacted with a 5-fold excess of NaH in DMF for 1 h at 25 °C, followed by in-situ treatment with a 20-fold excess of $C_8F_{17}(CH_2)_3Br$ for 12 h at 25 °C. The results are summarized in Tables 3 and 4.

The polymers all obtained by the Williamson reaction showed sharp symmetrical monomodal SEC distributions. Typically, the SEC profile of in-chain-functionalized polystyrene with four C_8F_{17} groups is shown in Figure 2C. The M_n values measured by SEC agreed with those predicted in all of the C_8F_{17}-functionalized polymers. In the polymers having M_n values of (3−8) × 10^3 g/mol, their molecular weights were also determined by ^{1}H NMR since the portions of segments including C_8F_{17} moieties were relatively large in comparison with their

Table 3. Synthesis of End-Functionalized Polystyrenes with One, Two, Three, and Four C_8F_{17} Groups[a]

code	$M_n \times 10^{-3}$ calcd[b]	$M_n \times 10^{-3}$ SEC[c]	$M_n \times 10^{-3}$ NMR[d]	M_w/M_n	functionality calcd	functionality obsd[d]
E-1 (6.3K)	6.35	6.40	6.32	1.05	1	0.98_4
E-1 (28K)	27.7	27.6		1.02	1	1.0_0
E-2 (3.4K)	3.41	3.52	3.42	1.04	2	2.0_1
E-2 (6.6K)	6.63	6.56	6.60	1.04	2	2.0_0
E-2 (9.2K)	9.24	9.34	9.18	1.02	2	1.9_4
E-2 (20K)	20.3	20.2		1.02	2	2.0_5
E-2 (28K)	29.3	28.2		1.02	2	2.0_0
E-3 (8.5K)	8.45	7.10	8.48	1.05	3	3.0_0
E-3 (20K)	20.5	20.4		1.02	3	3.1_9
E-4 (8.4K)	9.81	7.96	8.36	1.02	4	3.9_6
E-4 (24K)	21.2	23.8		1.06	4	3.9_0
1-E-1 (24K)	23.5	24.1		1.09	2	2.0_0

[a] Yields of polymers were around 90% in all cases. [b] Calculated from the observed molecular weight of the silyl-protected polymer ($M_{n,SEC}$ or $M_{n,NMR}$ in Table 1). [c] Determined by SEC using polystyrene calibration. [d] Determined by ^{1}H NMR.

Table 4. Synthesis of In-Chain-Functionalized Polystyrenes with One, Two, Three, and Four C_8F_{17} Groups[a]

code	$M_n \times 10^{-3}$ calcd[b]	$M_n \times 10^{-3}$ SEC[c]	$M_n \times 10^{-3}$ NMR[d]	M_w/M_n	functionality calcd	functionality obsd[d]
I-2 (6.2K)	6.21	6.10	6.24	1.03	2	2.0_7
I-2 (29K)	27.7	29.0		1.02	2	1.7_8
I-4 (7.4K)	7.57	7.30	7.43	1.02	4	3.9_5
I-4 (24K)	23.8	23.6		1.03	4	4.0_0
1-I-1 (24K)	23.9	24.4		1.06	2	2.2_4
2-I-2 (25K)	24.5	24.7		1.04	4	4.0_0

[a] Yields of polymers were around 90% in all cases. [b] Calculated from the observed molecular weight of the silyl-protected polymer ($M_{n,SEC}$ or $M_{n,NMR}$ in Table 2). [c] Determined by SEC using polystyrene calibration. [d] Determined by ^{1}H NMR.

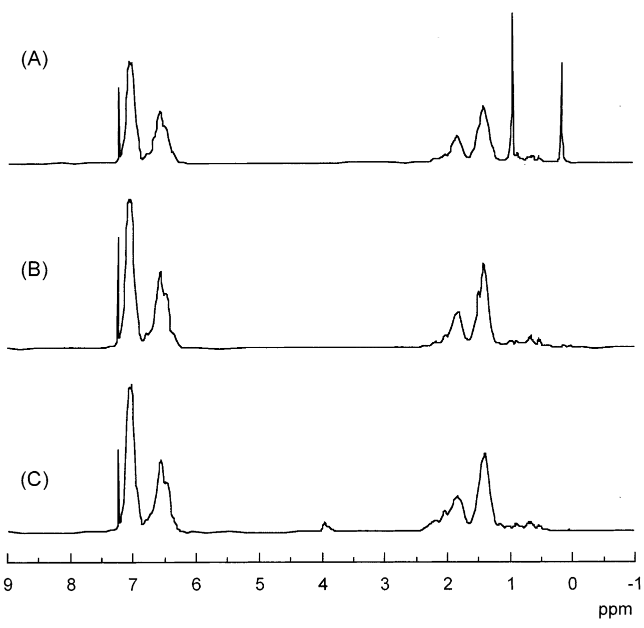


Figure 1. ^{1}H NMR spectra of polystyrenes with (A) four *tert*-butyldimethylsilyloxyphenyl groups, (B) four phenol groups (after deprotection), and (C) four C_8F_{17} groups (after Williamson reaction).

main chains. The M_n values thus determined also agreed with those predicted.

The degree of C_8F_{17}-functionalization was determined by ^{1}H NMR analysis. Figure 1C shows a typical ^{1}H NMR spectrum of chain-end-functionalized polystyrene with four C_8F_{17} groups. As can be seen, a new resonance at 4.0 ppm corresponding to the methylene protons attached to the phenoxy group clearly appears after the Williamson reaction. The degree of C_8F_{17} functionalization was determined by comparing this resonance with the resonance at 0.60−0.80 ppm for methyl protons of the initiator fragment. The ^{1}H NMR spectra of all polymers indicated that the introduced C_8F_{17} groups via phenol functions corresponded to the expected numbers within experimental errors.

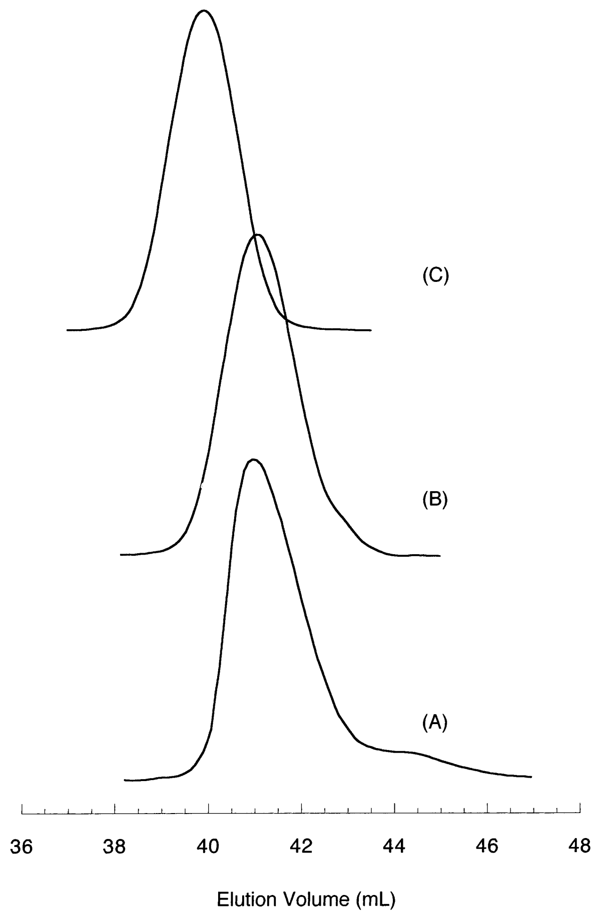
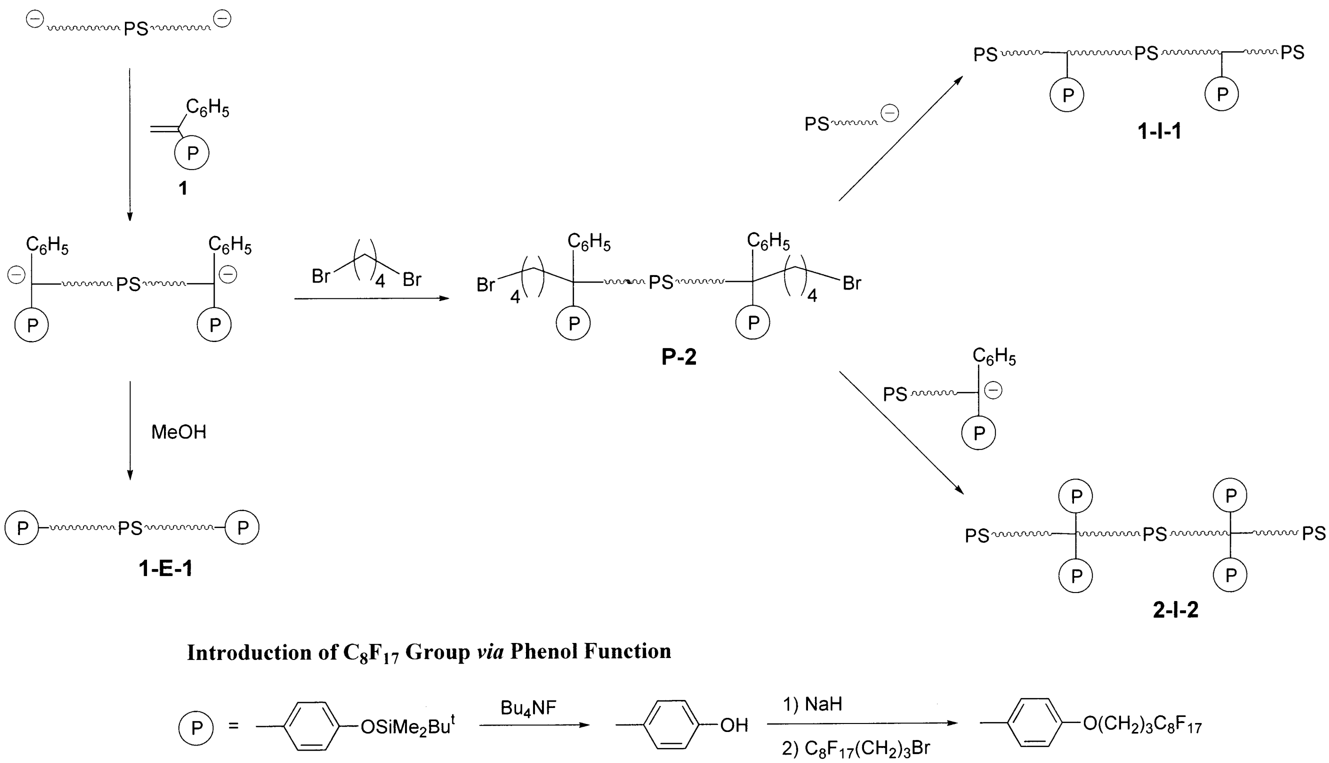


Figure 2. SEC profiles for polystyrenes with four *tert*-butyldimethylsilyloxyphenyl groups (A) before and (B) after fractionation and (C) polystyrene with four C_8F_{17} groups.

TLC-FID analysis was also very effective for determining the functionalization degree of the C_8F_{17} group. With use of toluene as an eluent, for example, chain-functionalized polystyrenes with C_8F_{17} groups were developed to reach to almost the top positions, while any polystyrene with phenol remained near at the spotting points. All of the functionalized polystyrenes showed only one spot at the top position and no spot at all at the spotting point, indicating that they were quantitatively functionalized with C_8F_{17} groups.

All analytical results clearly indicate that the chain-functionalized polymers with C_8F_{17} groups synthesized here were precisely controlled in chain length and quantitatively functionalized. The results also indicate that each reaction step is an essentially quantitative reaction. Two series of C_8F_{17}-functionalized polystyrenes with M_n values of around (6−9) × 10^3 and (20−28) × 10^3 g/mol were prepared for surface characterization study. In addition, five chain-end-functionalized polystyrenes with two C_8F_{17} groups were prepared. Their M_n values were in the range of (3.4−28) × 10^3 g/mol.

Scheme 3. Synthetic Procedures for the Synthesis of Chain-Functionalized Polystyrenes with Two and Four C_8F_{17} Groups at Both Chain Ends and Two Positions in Chain



In the C_8F_{17}-functionalized polystyrenes, chain-end, in-chain, number of C_8F_{17} groups, and molecular weight (10^{-3} g/mol) are abbreviated to E, I, number, and (number), respectively. E-2 (6.6 K), for example, means a chain-end-functionalized polystyrene with two C_8F_{17} groups. The M_n value of this sample was 6.6×10^3 g/mol. Such well-defined architectures of the functionalized polymers may be well-suited to elucidate the influence of molecular weight, number, and/or placement of C_8F_{17} group in a polymer chain on the surface structure.

Synthesis of Chain-End-Functionalized Polystyrene with C_8F_{17} Group at Both Ends and In-Chain-Functionalized Polystyrenes with One and Two C_8F_{17} Groups Introduced at Two Positions in Chains. The synthetic procedures of the title polymers are illustrated in Scheme 3. Chain-end-functionalized polystyrene with one phenol function at both ends was synthesized by the addition reaction of **1** to difunctional living polystyrene initiated with potassium naphthalenide, followed by deprotection. For the synthesis of the title in-chain-functionalized polystyrenes, a new prepolymer, **P-2**, was first prepared by the reaction of the above-mentioned difunctional living polystyrene with **1**, followed by treatment with a 10-fold excess of 1,4-dibromobutane under the same conditions used for the preparation of **P-1**. The in-chain-functionalized polymers were synthesized by the reaction of **P-2** with polystyryllithiums end-capped with DPE and **1**, respectively. A 1.2-fold excess of each living polystyrene was used. Therefore, the objective polymers were isolated by SEC fractionation. Although the resulting polymers possess total two and four C_8F_{17} groups in the chains, each one and two C_8F_{17} groups are separated by the polystyrene chain ($M_n = 20 \times 10^3$ g/mol).

The introduction of C_8F_{17} groups into the three chain-functionalized polymers with phenols were carried out under the identical conditions mentioned above. The results are also summarized in Tables 3 and 4. As was seen in this table, the resulting chain-functionalized polystyrenes possessed precisely controlled chain lengths and the expected degrees of chain functionalization. Abbreviations of these polymers are 1-E-1 (24K), 1-I-1 (24K), and 2-I-2 (25K). All of the chain-functionalized polystyrenes with C_8F_{17} groups synthesized in this study are illustrated in Figure 3. In these syntheses, it should be emphasized that well-defined C_8F_{17}-chain-functionalized polystyrenes with various architectures can readily and quantitatively be synthesized only by simple addition reactions with appropriate combinations of living anionic polymers of styrene, **1**, **2**, **3**, and 1,4-dibromobutane. The quantitative nature of the addition reaction, deprotection, and the Williamson reaction is also a key factor for achieving the synthesis of well-defined functionalized polymers.

In summary, a variety of chain-end- and in-chain-functionalized polystyrenes with a definite number of C_8F_{17} groups have been successfully synthesized. For these polymer syntheses starting from living anionic polystyrenes, multistep reactions including the addition, deprotection, and Williamson reactions were employed. Very fortunately, it was observed that all of these reactions proceeded virtually quantitatively under the conditions employed, since excess reagents toward the reaction sites on the polymers were always used. In each reaction step, however, two or more times of reprecipitation were needed for isolation and purification of the polymers. Therefore, all operations should be carefully performed. Yields of the purified polymers were generally in the range of 80−90%.

In addition, SEC fractionation was required for isolation of the in-chain-functionalized polymers. In these cases, the objective polymers were isolated in 85−90%, although the polymer yields in the reactions were almost quantitative on the basis of SEC measurement.

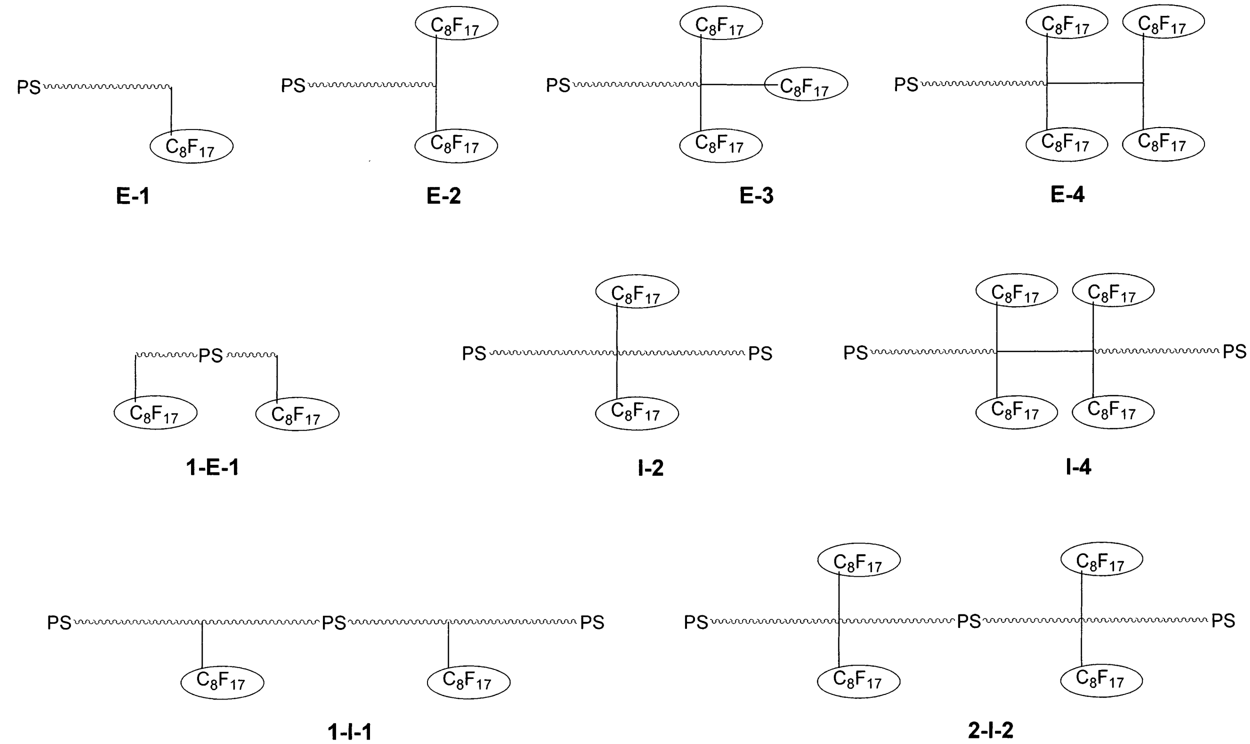


Figure 3. Chain-functionalized polystyrenes with C_8F_{17} groups synthesized in this study.

Table 5. Angle-Dependent XPS Atomic Percent on Film Surface Film Surface of Functionalized Polystyrenes with One, Two, Three, and Four C_8F_{17} Groups

	XPS atomic ratio (F/C)		
code	10° TOA[a]	80° TOA	bulk[b]
E-1 (6.3K)	32.2/66.0	10.3/88.8	3.4/96.4
E-1 (27K)	12.9/86.1	3.7/96.2	0.8/99.2
E-2 (3.4K)	50.2/48.1	26.8/71.6	13.7/85.5
E-2 (6.6K)	47.5/49.6	23.4/74.8	6.9/93.1
E-2 (9.2K)	33.2/65.2	13.5/85.4	4.8/94.9
E-2 (21K)	26.9/71.5	10.3/87.4	2.2/97.6
E-2 (28K)	25.1/73.1	8.2/91.5	1.6/98.3
E-3 (8.5K)	62.2/35.3	48.8/48.6	9.1/90.4
E-3 (20K)	39.0/59.3	13.9/84.7	3.1/96.7
E-4 (8.4K)	53.6/44.3	31.3/65.9	9.8/89.7
E-4 (24K)	53.9/43.3	30.9/67.0	4.0/95.8
1-E-1 (23K)	24.5/72.9	8.2/88.4	1.9/98.0
I-2 (6.2K)	27.8/70.3	11.1/86.9	10.9/88.4
I-2 (27K)	20.3/78.7	6.7/93.0	1.7/98.2
I-4 (7.4K)	49.1/48.4	27.2/70.9	18.8/80.1
I-4 (25K)	27.2/71.3	9.6/89.0	3.8/96.0
1-I-1 (23K)	15.3/83.6	5.2/93.5	1.9/98.0
2-I-2 (27K)	31.4/65.7	12.5/85.8	3.7/96.0

[a] 10° and 80° TOA (takeoff angle) corespond to 20 and 100 Å depth, respectively. [b] Calculated from chemical compositions of polymers.

All data listed in tables are those of the purified polymer samples.

Surface Characterization of C_8F_{17}-Functionalized Polymer Films by XPS Measurement. The surface composition as a function of depth can quantitatively be measured by angle-dependent XPS at takeoff angles of 10° and 80° on each of the annealed films. Takeoff angles (TOA) of 10° and 80° approximately correspond to 20 and 100 Å depths from the top surface, respectively. The results are summarized in Table 5.

It was observed that the atomic percent ratios of F/C measured at 10° TOA were much higher than they were in the bulk in virtually all films prepared from C_8F_{17}-chain-functionalized polymers. In addition, the F/C values at 10° TOA were always higher than those at 80° TOA. These results clearly indicate that C_8F_{17} groups placed either at chain-ends or in-chains are preferentially enriched at the film surfaces.

In the polymers with the same number and position of C_8F_{17} group in chains, the F/C value at 10° TOA always decreased with increasing the molecular weight. However, the enrichment factor calculated from F/C values at 10° TOA and of bulk was observed to increase with molecular weight in all polymer samples. The influence of molecular weight on F/C value was clearer in the E-2 series polymers with different molecular weights ((3.4−28) × 10^3 g/mol).

In both E and I series, the F/C value at 10° TOA progressively increased with increasing the number of C_8F_{17} group. The only an exception and of particular interest was E-3 (8.5K), which showed the highest value in all samples herein examined. The reason was not understood at the present time. The E series polymers always showed higher values than the corresponding I series polymers having the same numbers of C_8F_{17} groups. For example, the difference of surface enrichment by the placement of the C_8F_{17} group can be seen by comparing E-2 (6.6K) and E-2 (20K) with those of I-2 (6.2K) and I-2 (29K) in F/C values at 10° TOA. This is presumably due to the difference in mobility between terminal and internal C_8F_{17} groups, the former being more mobile than the latter.

Surprisingly, a high F/C value was attained in I-4 (7.4K). It was definitely higher than that of E-1 (6.3K) and comparable to that of E-2 (6.6K) or even E-4 (8.4K). A similar trend was observed in a series of higher molecular weight polymers. As was seen, the F/C value of I-4 (24K) was higher than that of E-1 (28K) and equal to that of E-2 (20K). It is indicative that the surface enrichment by the inner C_8F_{17} group is usually less effective than that by the terminal one but becomes comparable by introducing more C_8F_{17} groups.

Table 6. Contact Angle Measurements Using Water and Dodecane Droplets on Film Surface of Functionalized Polystyrenes with One, Two, Three, and Four C_8F_{17} Groups

	contact angle [deg]	
code	water	dodecane
E-1 (6.3K)	101	32.8
E-1 (27K)	95.4	15.7
E-2 (3.4K)	110	49.2
E-2 (6.6K)	105	43.0
E-2 (9.2K)	107	35.7
E-2 (21K)	99.4	32.8
E-2 (28K)	99.2	22.5
E-3 (8.5K)	110	56.9
E-3 (20K)	105	40.4
E-4 (8.4K)	116	55.4
E-4 (24K)	111	47.8
1-E-1 (23K)	96.5	23.5
I-2 (6.2K)	97.4	18.3
I-2 (27K)	92.7	16.6
I-4 (7.4K)	109	49.7
I-4 (25K)	99.8	30.0
1-I-1 (23K)	95.5	5.2
2-I-2 (27K)	101	26.8

The value of 1-E-1 (24K) was comparable to that of E-2 (28K). Both 1-I-1 (24K) and 2-I-2 (25K) were similar in F/C value to I-2 (29K) and I-4 (24K), respectively. Thus, the surface enrichment of these C_8F_{17} groups was not affected by the presence of the polystyrene chain ($M_n = 20 \times 10^3$ g/mol) between C_8F_{17} group(s) in each case. The C_8F_{17} group(s) may possibly appear on the surfaces by folding the polystyrene chains.

Interestingly, E-2 (3.4K), E-2 (6.6K), E-4 (8.4K), and I-4 (7.4K) showed high F/C values in the range of 47.5/49.6 to 53.6/44.3. These values are very close to the value of 48.6/48.6 calculated from the $C_8F_{17}(CH_2)_3OC_6H_4$ moiety. This moiety is approximately 20−25 Å in length based on simple molecular model. As mentioned before, the outmost surface analyzable at 10° TOA by XPS is about 20 Å. It can be therefore speculated that these film surfaces are covered completely with the C_8F_{17}-functionalized moiety on the assumption that the moiety is highly ordered and oriented with the chain axis perpendicularly to the surface. Additional evidence for this speculation is provided by the agreement between oxygen atomic percents observed (2.5−2.9%) and calculated (2.9%) and the presence of peak arising from aromatic carbon. Again, the reason for the higher value of E-3 (8.5K) than the expected value (48.6/48.6) cannot be explained.

The F/C values of E-2 (20K), E-2 (28K), E-3 (20K), and I-4 (24K) were lower than the value of 48.6/48.6 mentioned above. The molecular size of the C_8F_{17}-functionalized moiety relative to high molecular weight main chains ($M_n = (20-28) \times 10^3$ g/mol) may be too small to cover all surface areas and thereby requiring more C_8F_{17} groups. On the other hand, four terminal C_8F_{17} groups may be sufficient to cover all surface area estimating from the F/C value of E-4 (24K). It is tentatively supposed that the orientation and the packing of C_8F_{17} groups may be prevented by the excluded volume of high molecular weight main chain.

Contact Angle Measurements of C_8F_{17}-Functionalized Polystyrene Films. Contact angle measurements using both water and dodecane droplets were carried out in order to study the surface character of films prepared from the C_8F_{17}-functionalized polystyrenes. The results are summarized in Table 6.

Contact angles using water droplet showed values in the range of 92.7°−116° for all films. These values are higher than 91.3° of the film of DPE-end-capped polystyrene ($M_n = 23 \times 10^3$ g/mol) under the same conditions. This indicates that C_8F_{17} groups are more or less enriched to form more hydrophobic surfaces covered with C_8F_{17} groups.

The value of contact angle increased with number of C_8F_{17} groups and decreased with increasing molecular weight. Moreover, the E series polymers always showed higher values than the corresponding I series polymers. However, I-4 (7.4K) showed a value higher than that of E-1 (6.3K) or E-2 (6.6K) and comparable to that of E-3 (8.5K). A similar trend was found in a series of high molecular weight polymers. Thus, four internal C_8F_{17} groups appear as effective as two and three terminal ones for surface enrichment. These observations are similar to the analytical results by XPS mentioned in the preceding section. The contact angle value of E-3 (8.5K) obtained here seems to be reasonable in contrast to the result by XPS. Both 1-E-1 (24K) and 1-I-1 (24K) were comparable in contact angle value to E-1 (28K). The value of 2-I-2 (25K) was almost equal to that of I-4 (24K).

The influence of number and placement of C_8F_{17} group on surface structure is also indicated by the contact angles using dodecane droplet. The contact angle of DPE-end-capped polystyrene ($M_n = 23 \times 10^3$ g/mol) could not be measured by getting wet with dodecane, whereas all C_8F_{17}-functionalized polystyrene samples showed measurable contact angle values. This indicates that the lipophobic surfaces covered with C_8F_{17} groups apparently formed.

The results are also summarized in Table 6. All things considered from the results of contact angle using dodecane droplet are almost consistent with those using water droplet. It should be mentioned that dodecane droplets on the film surfaces were not stable, and the contact angle values measured gradually decreased with time and reached 10−25° after 20 min in every sample. Therefore, the reproducible values after 1 min are listed in Table 6. Dodecane may gradually soak into the film inside from the surface and possibly dissolve the second layer mainly consisting of polystyrene under the surface layer covered with C_8F_{17} groups. More C_8F_{17} groups may be required for forming stable lipophobic surfaces toward organic solvents dissolving polystyrene like dodecane.

Conclusions

Chain-end- and in-chain-functionalized polystyrenes with one, two, three, and four C_8F_{17} groups with various architectures have been successfully synthesized by means of the methodology using functionalized DPE derivatives and living anionic polymers of styrene. The resulting polymers all synthesized in this study are precisely controlled in chain length and quantitatively C_8F_{17}-functionalized. By using annealed films prepared from such well-defined functionalized polymers, we have demonstrated that the surface enrichment of C_8F_{17} group is strongly influenced by the number and placement of C_8F_{17} groups as well as the molecular weight of the functionalized polymer. In general, the degree of surface enrichment is found to increase with the number of C_8F_{17} groups and, on the other hand, decrease with the molecular weight. The terminal C_8F_{17} group is much more effective for surface enrichment than the internal one, indicating that the former is more mobile than the latter in molecular motion as expected. However, a high degree of surface enrichment can be achieved by introducing more C_8F_{17} groups in number at the middle of the chain. For example, the internal four C_8F_{17} groups of I-4 (7.4K) are more effective than the terminal one group and comparable to the terminal two C_8F_{17} groups of polymers having the almost same molecular weights. Supporting evidence for the degree of surface enrichment of C_8F_{17} group is also provided by contact angle measurements using water and dodecane droplets. In some functionalized polymers on the assumption that the moiety is highly ordered and oriented with the chain axis perpendicularly to the surface, it is strongly suggested that all surface areas of such polymer films are completely covered with the functionalized moiety represented as the $C_8F_{17}(CH_2)_3OC_6H_4$ group. The importance of this study is to be able to quantitatively evaluate for the first time the effect of the number and placement of C_8F_{17} group as well as the molecular weight on surface enrichment by using well-defined C_8F_{17}-chain-functionalized polystyrenes.

Although the results herein obtained seems indicative and interesting, more detailed study will be needed to elucidate the fundamental understanding regarding the effect of number and placement of C_8F_{17} group on surface enrichment. Current research therefore focuses on the synthesis of chain-end- and in-chain-functionalized polymers with five or more C_8F_{17} groups. In addition, the synthesis of chain-functionalized polymers possessing low T_g and hydrophilic segments and block copolymers and their surface characterization are now under investigation.

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