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Precise Synthesis of Novel Chain-End-Functionalized Polystyrenes with a Definite Number of Perfluorooctyl Groups and Their Surface Characterization

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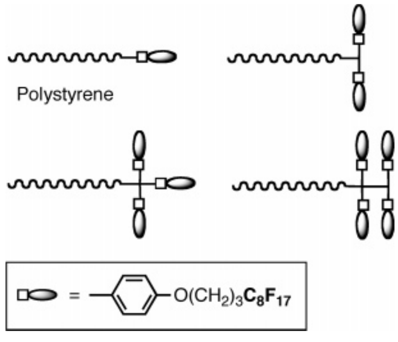
ABSTRACT: We have successfully synthesized two types of chain-end-functionalized polystyrenes with a definite number of C_8F_{17} groups that are dendritically distributed and linearly aligned in a double line. They are referred to as **D** and **L** types, respectively. In each type, there are three series of polymers whose C_8F_{17} groups are connected to the main polystyrene chains by phenyl ether, benzyl ether, and benzyl ester linkages. A definite number of C_8F_{17} groups from 2 to 32 and 1 to 10 are introduced at the chain ends of **D** and **L** type polymers, respectively. The resulting polymers all were well-defined in architecture and precisely controlled in chain length and degree of chain-end functionalization of C_8F_{17} group. These polymers were cast into film and, after annealing, examined the surface segregation behavior of C_8F_{17} group by angle-dependent X-ray photoelectron spectroscopy and contact angle measurements using water and dodecane droplets. All of the C_8F_{17}-chain-end-functionalized polymers showed fairly large surface segregation and enrichment of C_8F_{17} group. Furthermore, it was found that the segregation behavior strongly depended on the number and the alignment of C_8F_{17} group and the linkage between C_8F_{17} group and main chain. In general, the extent of the enrichment increased with increasing number of C_8F_{17} groups and appeared to be saturated at a certain number of C_8F_{17} groups, ranging from 4 to 16 depending on the polymer series.

Introduction

The surface (and/or polymer−air interfacial) properties of multicomponent polymer systems, such as polymer blends, random, graft, and block copolymers,[1−42] and chain-end-functionalized polymers,[43−49] can be quite different from those of the bulk by introducing particular functional groups into their polymer chains. It is now well established that a functional group that has a lower surface energy than its original polymer chain preferentially segregates to enrich at the surface. Such a segregation effect is particularly accentuated when a series of perfluoroalkyl (Rf) groups are employed as functional groups. In fact, significant segregation behaviors of Rf groups are observed in almost all multicomponent polymer systems containing Rf group(s) and/or Rf-functionalized polymer segments by various surface analytical methods, resulting in drastic change of their surface properties to hydrophobic as well as lipophobic characters.

Several research groups have recently demonstrated that chain-end-functionalized polymers with Rf group(s) serve as convenient model systems for fundamentally understanding the general behavior of Rf terminus on the surface.[50−57] However, the results achieved by using chain-end-functionalized polymers are generally difficult to compare with those obtained by block and random copolymers because they possess a few 10 or more Rf groups in a polymer chain, and on the other hand, the number of terminal Rf group is usually limited to one at each end in chain-end-functionalized polymers.

We have recently succeeded in synthesizing novel chain-end- and in-chain-functionalized polystyrenes with a definite number of 1, 2, 3, and 4 perfluorooctyl (C_8F_{17}) groups by various addition reactions of polystyryllithium (PSLi) with specially designed 1,1-diphenylethylene (DPE) derivatives, followed by the introduction of C_8F_{17} groups via the Williamson reaction.[58−60] Chain architectures of such polymers are illustrated below. They were characterized by X-ray photoelectron spectroscopy (XPS) and contact angle measurements.



As expected, these analytical results clearly demonstrated that C_8F_{17} group was significantly segregated to enrich at each of all film surfaces. The extent of enrichment dramatically increased with increasing the number of C_8F_{17} group from one to four.[61] It was also demonstrated that chain-end-functionalized polymer was always superior to in-chain-functionalized polymer

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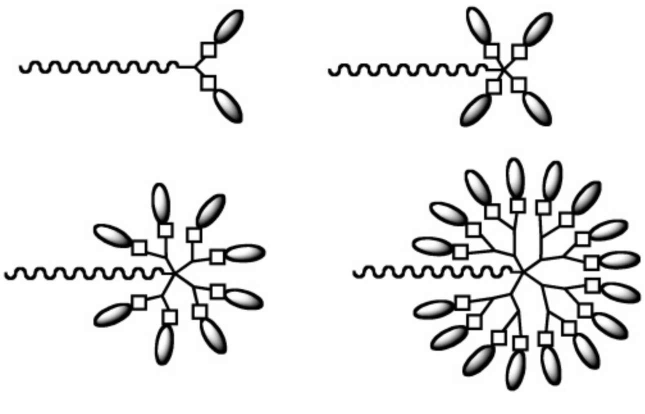
in degree of surface enrichment by C_8F_{17} group by comparing both chain-functionalized polymer having the same number of C_8F_{17} groups. The effect of functional group location on surface properties has been recently studied by several groups.[62−64]

More recently, we have synthesized a new series of chain-end-functionalized polystyrenes with a definite number of C_8F_{17} groups dendritically distributed by a novel methodology based on the iterative divergent approach.[65] With this method, more C_8F_{17} groups up to 16 in number could be introduced at the polymer chain ends as illustrated below.



In these polymers, the fluorine (F) atomic % at outmost top surface greatly increased with increasing the number of C_8F_{17} group from two to four. However, the value remained unchanged between four and eight in number, and then the value slightly increased with the increase of C_8F_{17} groups to 16 in number. Interestingly, the value observed for 16 dendritically C_8F_{17}-functionalized polymer was consistent with that of the above-mentioned chain-end-functionalized polystyrene with four C_8F_{17} groups, although the number and the alignment of C_8F_{17} group are quite different between those two polymers as shown above. A similar trend was observed by the contact angle measurement using either water or dodecane droplets. Thus, the influence of the number of C_8F_{17} groups on surface enrichment seems interesting and indicative. It is however essential to synthesize chain-end-functionalized polymers with more numbers of C_8F_{17} groups in order to quantitatively elucidate how many numbers of C_8F_{17} groups are required to satisfy the surface enrichment.

Herein, we first report on the synthesis of two types of chain-end-functionalized polystyrenes with more numbers of C_8F_{17} groups that are dendritically distributed and linearly aligned in a double line. In each type, we will synthesize three different polymer series whose C_8F_{17} groups are connected to the main chains by phenyl ether, benzyl ether, and benzyl ester linkages. Second, the surface segregation phenomena of C_8F_{17} groups are explored to associate with the number of C_8F_{17} group and discussed together with the previous results.

Experimental Section

Materials. All chemicals (>98% purities) were purchased from Tokyo Kasei Co. Ltd., Japan, and used as received unless otherwise noted. Both styrene and 1,1-diphenylethylene (DPE) were washed with 5% NaOH, dried over $MgSO_4$, and distilled twice over CaH_2 under reduced pressure. Styrene was finally distilled from its dibutylmagnesium solution (3 mol %, Aldrich, Japan) on a high-vacuum line (10^{-6} Torr). DPE was distilled from its 1,1-diphenylhexyllithium on the high-vacuum line. 1,4-Dibromobutane was distilled twice over CaH_2 under nitrogen and then distilled over CaH_2 on the high-vacuum line. Tetrahydrofuran (THF) was refluxed over sodium wire for 5 h and then distilled over $LiAlH_4$ under nitrogen. It was finally distilled from its sodium naphthalenide solution on the vacuum line. Both dibutylmagnesium and *sec*-butyllithium (*sec*-BuLi) (Aldrich, Japan) were used without further purification. *tert*-Butyldimethylsilyl chloride (99%, Shinetsu Chemical Co., Ltd.) was used as received. *N,N*-Dimethylformamide (DMF), dichloromethane, pyridine, chloroform, acetonitrile, and trimethylsilyl chloride were distilled over CaH_2 under nitrogen. LiBr (99%, Koso Chemical Co., Ltd.) was dried on the high-vacuum line at 100 °C for 24 h. Both 3-perfluorooctyl-1-propanol ($C_8F_{17}(CH_2)_3OH$) (98%, Daikin Co., Ltd., Japan) and perfluorononanoic acid ($C_8F_{17}COOH$) (98%, Daikin Co., Ltd., Japan) were used as received. 3-Perfluorooctylpropyl bromide ($C_8F_{17}(CH_2)_3Br$) was synthesized by the reaction of $C_8F_{17}(CH_2)_3$-OH with carbon tetrabromide/triphenylphosphine in THF/dichloromethane according to the modified procedure previously reported.[66] Perfluorononanoyl chloride ($C_8F_{17}COCl$) was synthesized by the reaction of $C_8F_{17}COOH$ with $SOCl_2$ according to the procedure previously reported.[67] Both 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**)[68] and 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene (**2**)[69,70] were synthesized according to procedures previously reported. Chain-end-functionalized polystyrenes with 2, 4, 8, and 16 benzyl bromide moieties ($PS(BnBr)_2$, $PS(BnBr)_4$, $PS(BnBr)_8$, $PS(BnBr)_{16}$) were synthesized according to our method reported elsewhere.[71,72] All polymerizations and functionalization reactions of polymers were carried out under high-vacuum conditions (10^{-6} Torr) in sealed glass reactors with breakable seals on the high-vacuum line.

1,12-Dibromo-5,5,8,8-(tetra(3-(*tert*-butyldimethylsilyloxymethyl)phenyl))dodecane. Under high-vacuum conditions, a THF solution (40 mL) of **1** (3.99 g, 8.33 mmol) was added to potassium naphthalenide (8.33 mmol) in THF (15 mL) at −78 °C with stirring. After allowing to stir for an additional 30 min, the resulting dianion was added dropwise to 1,4-dibromobutane (26.1 mmol) in THF (30 mL) at −78 °C with vigorous stirring for a period of 20 min. The resulting mixture was allowed to stir for 30 min and then quenched with methanol. After evaporation, the residue was extracted with ether, and the organic layer was washed with water, aqueous $NaHCO_3$, and brine, and dried over anhydrous $MgSO_4$. After filtration and evaporation, the objective dibromide was purified by flash column chromatography on silica gel (hexane/ethyl acetate/triethylamine; 100/5/2, v/v/v) to afford 3.50 g (70% yield) of the dibromide as a white solid. ^1H NMR: δ 7.35−6.84 (m, 16H, Ar), 4.60 (s, 8H, $ArCH_2O$), 3.21−3.17 (m, 4H, CH_2Br), 2.05−1.99 (m, 4H, $ArCC\mathit{H}_2C\mathit{H}_2CAr$), 1.74−1.54 (m, 8H, $C\mathit{H}_2C\mathit{H}_2CH_2Br$), 0.89−0.76 (br, 40H, $(CH_3)_3CSi$ and $C\mathit{H}_2$-$CH_2CH_2CH_2Br$), 0.10 (s, 24H, $SiCH_3$). ^{13}C NMR: δ 148.57 (C5 and C8), 140.84, 127.74, 126.37, 125.36, 123.33 (Ar), 65.15 (ArCO), 48.90 (C1 and C12), 36.37 (C2 and C11), 33.59 and 33.34 (C-6 and C-7), 30.90 (C4 and C9), 26.03 ($SiC(\mathit{C}H_3)_3$), 22.57 (C3 and C10), 18.42 ($Si\mathit{C}(CH_3)_3$), −5.10 ($SiCH_3$).

Preparation of Polystyryllithium (PSLi). PSLi was prepared by the polymerization of styrene with *sec*-BuLi in THF at −78 °C for 0.5 h, in which styrene in THF was added at once to *sec*-BuLi in heptane with vigorous stirring. In some cases, PSLi was end-capped with a 1.5-fold excess of DPE in THF at −78 °C for 1 h for further modification.

Synthesis of Chain-End-Functionalized Polystyrenes with a Definite Number of C_8F_{17} Groups Dendritically Distributed (D Type). There are three polymer series in chain-end-functionalized polystyrenes with a definite number of C_8F_{17} groups dendritically distributed (**D** type polymers). In these polymer series, phenyl ether, benzyl ether, and benzyl ester linkages were used to connect C_8F_{17} groups to the main polystyrene chains. They are referred to as **DP-*n***, **DB-*n***, and **D′B-*n***, respectively. The "*n*" indicates the number of C_8F_{17} groups in each polymer series. The **DP** polymer series were synthesized by the following two reaction steps: In the first reaction, a series of chain-end-functionalized polystyrenes with phenol moieties ($PS(PhOH)_n$) were prepared by the coupling reaction of PS(BnBr)$_n$ with the 1,1-diphenylalkyl anion generated from **2** and *sec*-BuLi, followed by deprotection of the introduced *tert*-butyldimethylsilyl-protecting groups with $(C_4H_9)_4NF$. In each case, the number of phenol moieties becomes twice that of the BnBr moieties by the coupling reaction. In the second reaction, C_8F_{17} groups were introduced by the Williamson reaction of $C_8F_{17}(CH_2)_3Br$ with the PS(PhOH)$_n$, resulting in the formation of **DP** polymer series. A series of chain-end-functionalized polystyrenes with a definite number of benzyl alcohol moieties (PS(BnOH)$_n$) for the precursory polymers of **DB** and **D′B** polymer series were obtained by the coupling reaction of PS(BnBr)$_n$ with the 1,1-diphenylalkyl anion generated from **1** and *sec*-BuLi, followed by deprotection of the introduced *tert*-butyldimethylsilyl-protecting groups with $(C_4H_9)_4NF$. Then, both **DB** and **D′B** polymer series were synthesized by the reactions of the corresponding PS(BnOH)$_n$ with $C_8F_{17}(CH_2)_3Br$ and $C_8F_{17}COCl$, respectively.

Synthesis of PS(PhOH)*$_n$*. A series of PS(PhOH)$_n$ were prepared by the coupling reaction of PS(BnBr)$_n$ with the 1,1-diphenylalkyl anion generated from **2** and *sec*-BuLi, followed by treatment with $(C_4H_9)_4NF$. Since the phenol functionalities are not stable in the air, the polymers thus prepared are stored under nitrogen and used in the next reaction within 24 h. A typical example carried out under high-vacuum conditions is as follows: A THF solution (7.65 mL) of **2** (0.196 mmol) chilled at −78 °C was added to *sec*-BuLi (0.151 mmol) in heptane solution (2.30 mL) at −78 °C, and the reaction mixture was stirred for 30 min at −78 °C. Subsequently, to this solution was added PS(BnBr)$_4$ (0.494 g, $M_n = 19.6 \times 10^3$ g/mol, BnBr moiety = 0.101 mmol) dissolved in THF (8.55 mL) chilled at −78 °C, and the reaction mixture was stirred at −78 °C for 7 h. After the excess 1,1-diphenylalkyl anion was quenched with a small amount of degassed methanol, the resulting mixture was poured into a large amount of methanol to precipitate the polymer. The polymer was then purified by reprecipitation with THF/methanol twice and freeze-drying from its absolute benzene solution for 24 h. The chain-end-functionalized polystyrene with eight silyl-protected phenol moieties (0.490 g) was obtained in 84% yield. The resulting polymer was characterized by ^{1}H NMR, SEC, and VPO to determine the functionality and molecular weight (M_n) and the distribution (M_w/M_n). ^{1}H NMR: δ 0.1−0.2 (br, 48H, $Si(CH_3)_2$), 0.6−0.8 (br, 48H, CH_3), 0.9−1.1 (br, 72H, $SiC(CH_3)_3$), 1.1−2.2 (br, 420H, CH_2), 3.1−3.2 (br, 14H, $ArCH_2$), 6.0−7.1 (br, 1060H, Ar).

The resulting polystyrene with eight silyl-protected phenol moieties (0.390 g, $M_n = 23.0 \times 10^3$ g/mol, silyl-protected phenol moiety = 0.140 mmol) was dissolved in dry THF (6.50 mL) under a nitrogen atmosphere. To this solution was added $(C_4H_9)_4NF$ (0.702 mmol) in THF (0.702 mL), and the reaction mixture was stirred at 25 °C for 12 h. The reaction was quenched with a small amount of water, and the reaction mixture was poured into 1 N HCl to precipitate the polymer. After purification by reprecipitation with THF/methanol and freeze-drying from its absolute benzene solution for 24 h, the objective PS(PhOH)$_8$ (3.86 g) was obtained in quantitative yield. ^{1}H NMR: δ 0.5−0.7 (br, 48H, CH_3), 1.1−2.3 (br, 425H, CH_2), 3.1−3.2 (br, 14H, $ArCH_2$), 6.3−7.2 (br, 1100H, Ar). Similarly, PS(PhOH)$_2$, PS(PhOH)$_4$, PS(PhOH)$_{16}$, and PS(PhOH)$_{32}$ were prepared and characterized by ^{1}H NMR, SEC, and VPO, respectively.

Synthesis of PS(BnOH)*$_n$*. Similar to the synthesis of PS(PhOH)$_n$, a series of PS(BnOH)$_n$ were obtained by the treatment of PS(BnBr)$_n$ with a 5-fold excess of $(C_4H_9)_4NF$. The resulting polymers were purified by reprecipitation using THF/methanol twice and freeze-drying from their absolute benzene solutions for 24 h. All of the benzyl alcohol-functionalized polymers showed sharp monomodal SEC distributions similar to those of their parent polymers. In each case, quantitative deprotection of the silyl-protecting group was confirmed by the complete disappearances of *tert*-butyldimethylsilyl protons (0.1 and 0.9 ppm) in ^{1}H NMR.

Synthesis of Chain-End-Functionalized Polystyrenes with a Definite Number of C_8F_{17} Groups Linearly Aligned in a Double Line (L Type). There are also three polymer series in chain-end-functionalized polystyrenes with a definite number of C_8F_{17} groups linearly aligned in a double line (**L** type polymers). Similar to **D** type polymers, phenyl ether, benzyl ether, and benzyl ester linkages were used to connect C_8F_{17} groups to the main polystyrene chains in these polymers. They are referred to as **LP-*n***, **LB-*n***, and **L′B-*n***, respectively. The "*n*" indicates the number of C_8F_{17} group in each polymer series. The polymers of **LP** series were synthesized by the Williamson reaction of chain-end-functionalized polystyrenes with a definite number of phenol moieties linearly aligned in a double line (PS′(PhOH)$_n$) with $C_8F_{17}(CH_2)_3Br$. On the other hand, both **LB** and **L′B** polymer series were synthesized by the reaction of chain-end-functionalized polystyrenes with a definite number of benzyl alcohol linearly aligned in a double line (PS′(BnOH)$_n$) with $C_8F_{17}(CH_2)_3Br$ and $C_8F_{17}COCl$, respectively.

Synthesis of Chain-End-Functionalized Polystyrene with Two or Four Silyl-Protected Benzyl Alcohol Moieties and 4-Bromobutyl Terminus (P-1 and P-2). Under high-vacuum conditions, PSLi (1.92 g, $M_n = 21.0 \times 10^3$ g/mol, 0.0959 mmol) in THF (18.9 mL) was added to **1** (0.143 mmol) in THF (3.2 mL) at −78 °C, and the reaction mixture was stirred at −78 °C for 1 h. The resulting living polymer solution was added slowly to 1,4-dibromobutane (1.30 mmol) in THF (4.0 mL) at −78 °C, and the reaction mixture was stirred at −78 °C for an additional 1 h. The polymer was precipitated in methanol and purified by reprecipitation with THF/methanol twice and freeze-drying from its absolute benzene solution for 24 h. The polymer yield was 97%. The ^{1}H NMR spectrum showed that the end-functionalization degrees of silyl-protected benzyl alcohol moiety and 4-bromobutyl terminus were 2.0_2 and 1.0_2, respectively. The M_n and M_w/M_n values were 21.5×10^3 g/mol and 1.02, respectively. Thus, the chain-end-functionalized polystyrene with two silyl-protected benzyl alcohol moieties and 4-bromobutyl terminus (**P-1**) was obtained. ^{1}H NMR: δ 0.1−0.2 (br, 12H, $Si(CH_3)_2$), 0.6−0.8 (br, 6H, CH_3), 1.0−1.2 (br, 18H, $SiC(CH_3)_3$), 1.2−2.4 (br, 642H, CH_2), 3.1−3.2 (br, 2H, CH_2Br), 4.5−4.7 (br, 4H, $ArCH_2$), 6.3−7.2 (br, 1020H, Ar).

Similarly, the chain-end-functionalized polystyrene with six silyl-protected benzyl alcohol moieties and 4-bromobutyl terminus (**P-2**, $M_n = 23.0 \times 10^3$ g/mol, $M_w/M_n = 1.02$) was prepared by the coupled reaction of a 8-fold excess of 1,12-dibromo-5,5,8,8-(tetra(3-(*tert*-butyldimethylsilyloxymethyl)phenyl))dodecane with the living polymer obtained from PSLi and **1** under the same conditions. It was observed by SEC analysis that ca. 10% of the dimeric product was formed by reacting 2 equiv of the living polymer with the dibromide. The dimeric product was removed by fractional precipitation with a mixture of cyclohexane and hexane. The objective **P-2** was isolated in 70% yield. ^{1}H NMR: δ 0.1−0.2 (br, 36H, $Si(CH_3)_2$), 0.4−0.8 (br, 6H, CH_3), 1.0−1.2 (br, 54H, $SiC(CH_3)_3$), 1.2−2.4 (br, 689H, CH_2), 3.1−3.2 (br, 2H, CH_2Br), 4.5−4.7 (br, 12H, $ArCH_2$), 6.3−7.2 (br, 1120H, Ar).

Synthesis of PS′(BnOH)$_4$ and PS′(BnOH)$_8$. Under high-vacuum conditions, a THF (12.0 mL) solution of **P-1** (1.17 g, $M_n = 21.5 \times 10^3$ g/mol, bromobutyl terminus = 0.0544 mmol) was added slowly to the 1,1-diphenylalkylanion prepared from **1** (0.151 mmol) and *sec*-BuLi (0.116 mmol) in THF (10.0 mL) at −78 °C for 1 h. The reaction mixture was stirred at −78 °C for 2 h. After quenching with degassed methanol, the polymer was precipitated into a large amount of methanol and purified by the same procedure mentioned above. The chain-end-functionalized polystyrene with four silyl-protected benzyl alcohol moieties was thus obtained in 90% yield. ^{1}H NMR: δ 0.1−0.2 (br, 24H, $Si(CH_3)_2$), 0.4−0.8 (br, 12H, CH_3), 0.8−1.0 (br, 36H, $SiC(CH_3)_3$), 1.1−2.4 (br, 686H, CH_2), 4.5−4.7 (br, 8H, $ArCH_2$), 6.3−7.2 (br, 1120H, Ar).

Similarly, the chain-end-functionalized polystyrene with eight silyl-protected benzyl alcohol moieties was prepared by the same reaction using **P-2** in place of **P-1**. ^{1}H NMR: δ 0.1−0.2 (br, 48H, $Si(CH_3)_2$), 0.4−0.8 (br, 12H, CH_3), 1.0−1.2 (br, 72H, $SiC(CH_3)_3$), 1.2−2.4 (br, 686H, CH_2), 4.5−4.7 (br, 16H, $ArCH_2$), 6.3−7.2 (br, 1130H, Ar). Both polymers were treated with a 5-fold excess of $(C_4H_9)_4NF$ in THF at 25 °C for 12 h. By this treatment, PS′(BnOH)$_4$ and PS′(BnOH)$_8$ were obtained quantitatively. They were purified by the same procedures mentioned above and obtained in 90% and 92% yields. The assignments of ^{1}H NMR spectra were shown below. PS′(BnOH)$_4$: δ 0.3−0.8 (br, 12H, CH$_3$), 1.2−2.3 (br, 686H, CH$_2$), 4.4−4.6 (br, 8H, ArCH$_2$), 6.3−7.2 (br, 1120H, Ar). PS′(BnOH)$_8$: δ 0.4−0.8 (br, 12H, CH$_3$), 1.2−2.4 (br, 686H, CH$_2$), 4.4−4.6 (br, 16H, ArCH$_2$), 6.3−7.2 (br, 1130H, Ar).

Synthesis of PS′(BnOH)$_6$ and PS′(BnOH)$_{10}$. Under high-vacuum conditions, **P-1** (0.847 g, M_n = 21.5 × 10^3 g/mol, bromobutyl terminus = 0.0394 mmol) dissolved in THF (12.2 mL) was added slowly to the dianion generated from **1** (0.250 mmol) and potassium naphthalenide (0.245 mmol) in THF (5.05 mL) at −78 °C for 30 min, and the reaction mixture was stirred at −78 °C for 1 h. After quenching with degassed methanol, the polymer was precipitated into a large amount of methanol and purified by the same procedure mentioned above. The chain-end-functionalized polystyrene with six silyl-protected benzyl alcohol moieties was thus obtained in 90% yield. ^{1}H NMR: δ 0.1−0.2 (br, 36H, Si(CH$_3$)$_2$), 0.5−0.8 (br, 6H, CH$_3$), 0.8−0.9 (br, 54H, SiC(CH$_3$)$_3$), 1.1−2.3 (br, 745H, CH$_2$), 4.5−4.7 (br, 12H, ArCH$_2$), 6.2−7.2 (br, 1210H, Ar). Similarly, the chain-end-functionalized polystyrene with 10 silyl-protected benzyl alcohol moieties was obtained by the same reaction using **P-2** in place of **P-1**. ^{1}H NMR: δ 0.1−0.2 (br, 60H, Si(CH$_3$)$_2$), 0.5−0.8 (br, 6H, CH$_3$), 0.9−1.1 (br, 90H, SiC(CH$_3$)$_3$), 1.2−2.4 (br, 733H, CH$_2$), 4.5−4.7 (br, 20H, ArCH$_2$), 6.3−7.2 (br, 1230H, Ar).

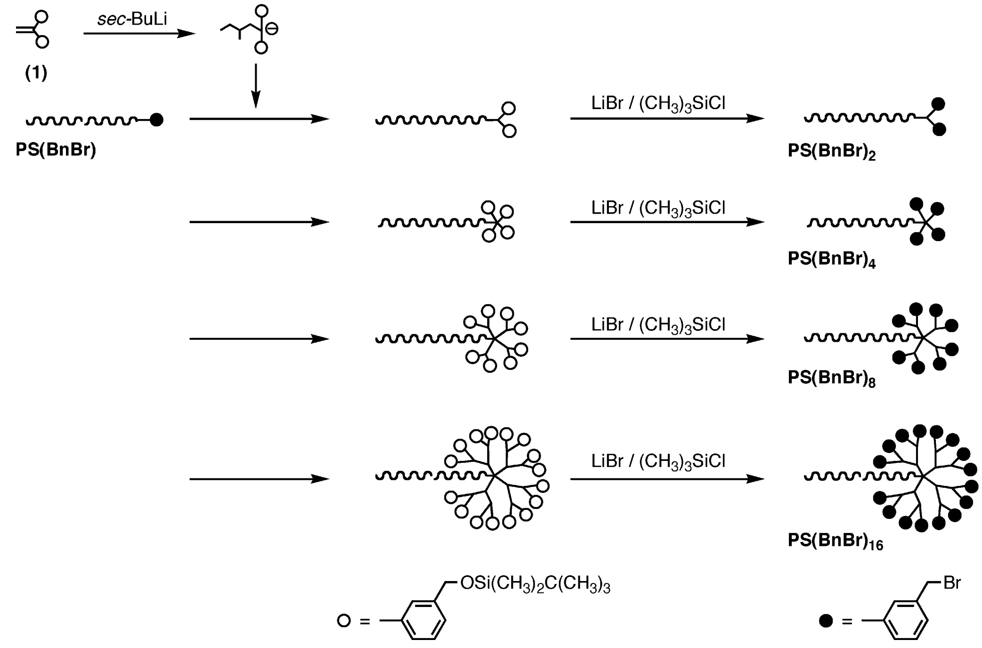
Both polymers were treated with a 5-fold excess of (C$_4$H$_9$)$_4$NF in THF at 25 °C for 12 h. By this treatment, PS′(BnOH)$_6$ and PS′(BnOH)$_{10}$ were obtained quantitatively. They were purified by the same procedures mentioned above and obtained in 90% and 93% yields. The assignments of ^{1}H NMR spectra were shown below. PS′(BnOH)$_6$: δ 0.4−0.8 (br, 6H, CH$_3$), 1.1−2.3 (br, 745H, CH$_2$), 4.4−4.6 (br, 12H, ArCH$_2$), 6.2−7.2 (br, 1210H, Ar). PS′(BnOH)$_{10}$: 0.5−0.8 (br, 6H, CH$_3$), 1.2−2.4 (br, 733H, CH$_2$), 4.4−4.6 (br, 20H, ArCH$_2$), 6.3−7.2 (br, 1230H, Ar).

Introduction of C$_8$F$_{17}$ Groups by the Williamson Reaction. The **DP**, **DB**, **LP**, and **LB** polymer series were synthesized by the Williamson reaction of the corresponding PS(PhOH)$_n$, PS(BnOH)$_n$, PS′(PhOH)$_n$, and PS′(BnOH)$_n$ with C$_8$F$_{17}$(CH$_2$)$_3$Br, respectively. The syntheses of **LP-1**, **LP-2**, **LP-3**, and **LP-4** were reported in our previous paper.[34,35] A typical example is as follows: Under nitrogen, NaH (40.0 mg, 1.67 mmol) was added to PS(PhOH)$_8$ (0.210 g, M_n = 20.4 × 10^3 g/mol, phenol moiety = 0.0824 mmol) dissolved in a mixture of THF (10 mL) and DMF (3 mL) at 0 °C, and the resulting suspension was allowed to stir for 2 h at 25 °C. Then, C$_8$F$_{17}$(CH$_2$)$_3$Br (0.903 g, 1.67 mmol) in THF (3.00 mL) was added slowly to this suspension at 0 °C, and the reaction mixture was stirred at 25 °C for 18 h. Water was cautiously added to quench the excess NaH. The resulting mixture was poured into 1 N HCl methanolic solution to precipitate the polymer. The polymer was purified by reprecipitation with THF/methanol twice. A further purification by column chromatography with benzene followed by freeze-drying from its absolute benzene solution for 24 h gave **DP-8** (0.242 g) in 92% yield. ^{1}H NMR: δ 0.2−0.8 (br, 48H, CH$_3$), 1.2−2.4 (br, 632H, CH$_2$), 3.2−3.6 (br, 14H, ArCH$_2$), 3.9−4.1 (br, 16H, ArOCH$_2$), 6.2−7.2 (br, 1020H, Ar). Similarly, **DP-*n***, **DB-*n***, **LP-*n***, and **LB-*n*** were synthesized under the same conditions. All of the polymers were purified by reprecipitation twice, column chromatography, and freeze-drying from their benzene solutions for 24 h. Yields of polymers isolated were usually around 90%. They were characterized by ^{1}H NMR, SEC, and VPO, respectively. The assignments of ^{1}H NMR spectra of these polymer series were shown below. **DP-2**: δ 0.4−0.8 (br, 12H, CH$_3$), 1.2−2.4 (br, 540H, CH$_2$), 3.2−3.6 (br, 2H, ArCH$_2$), 3.9−4.1 (br, 4H, ArOCH$_2$), 6.3−7.3 (br, 1340H, Ar). **DP-4**: δ 0.4−0.9 (br, 24H, CH$_3$), 1.2−2.5 (br, 388H, CH$_2$), 3.2−3.6 (br, 6H, ArCH$_2$), 3.9−4.1 (br, 8H, ArOCH$_2$), 6.3−7.3 (br, 980H, Ar). **DP-16**: δ 0.4−0.8 (br, 96H, CH$_3$), 1.2−2.5 (br, 382H, CH$_2$), 3.2−3.6 (br, 30H, ArCH$_2$), 3.9−4.1 (br, 32H, ArOCH$_2$), 6.3−7.3 (br, 1000H, Ar). **DP-32**: δ 0.3−0.8 (br, 192H, CH$_3$), 1.1−2.5 (br, 422H, CH$_2$), 3.2−3.6 (br, 62H, ArCH$_2$), 3.9−4.1 (br, 64H, ArOCH$_2$), 6.2−7.3 (br, 1230H, Ar). **DB-2**: δ 0.5−0.8 (br, 12H, CH$_3$), 1.2−2.3 (br, 570H, CH$_2$), 3.2−3.9 (br, 6H, ArCH$_2$), 4.3−4.4 (br, 4H, ArCH$_2$OC*H*$_2$), 6.3−7.2 (br, 942H, Ar). **DB-4**: δ 0.3−0.8 (br, 24H, CH$_3$), 1.2−2.3 (br, 563H, CH$_2$), 3.2−3.9 (br, 14H, ArCH$_2$), 4.3−4.4 (br, 8H, ArCH$_2$OC*H*$_2$), 6.3−7.2 (br, 966H, Ar). **DB-8**: δ 0.2−0.8 (br, 48H, CH$_3$), 1.2−2.4 (br, 649H, CH$_2$), 3.2−3.9 (br, 30H, ArCH$_2$), 4.2−4.4 (br, 16H, ArCH$_2$OC*H*$_2$), 6.1−7.3 (br, 984H, Ar). **DB-16**: δ 0.2−0.8 (br, 96H, CH$_3$), 1.2−2.4 (br, 707H, CH$_2$), 3.2−3.9 (br, 62H, ArCH$_2$), 4.3−4.4 (br, 32H, ArCH$_2$OC*H*$_2$), 6.3−7.2 (br, 1050H, Ar). **DB-32**: δ 0.2−0.9 (br, 192H, CH$_3$), 1.2−2.4 (br, 780H, CH$_2$), 3.2−3.5 (br, 126H, ArCH$_2$), 4.3−4.4 (br, 64H, ArCH$_2$OC*H*$_2$), 6.3−7.2 (br, 1080H, Ar). **LP-8**: δ 0.6−0.8 (br, 12H, CH$_3$), 1.2−2.2 (br, 628H, CH$_2$), 3.8−4.2 (br, 16H, OCH$_2$), 6.2−7.4 (br, 1010H, Ar). **LP-10**: δ 0.4−0.8 (br, 6H, CH$_3$), 1.1−2.5 (br, 488H, CH$_2$), 3.9−4.1 (br, 20H, OCH$_2$), 6.3−7.3 (br, 1050H, Ar). **LB-2**: δ 0.5−0.7 (br, 6H, CH$_3$), 1.2−2.4 (br, 570H, CH$_2$), 3.2−3.5 (br, 4H, ArCH$_2$), 4.3−4.4 (br, 4H, ArCH$_2$OC*H*$_2$), 6.3−7.2 (br, 942H, Ar). **LB-4**: δ 0.3−0.8 (br, 12H, CH$_3$), 1.2−2.3 (br, 597H, CH$_2$), 3.2−3.5 (br, 8H, ArCH$_2$), 4.3−4.4 (br, 8H, ArCH$_2$OC*H*$_2$), 6.3−7.2 (br, 980H, Ar). **LB-6**: δ 0.3−0.8 (br, 6H, CH$_3$), 1.2−2.4 (br, 597H, CH$_2$), 3.2−3.5 (br, 12H, ArCH$_2$), 4.3−4.4 (br, 12H, ArCH$_2$OC*H*$_2$), 6.3−7.3 (br, 979H, Ar). **LB-8**: δ 0.2−0.8 (br, 12H, CH$_3$), 1.2−2.4 (br, 570H, CH$_2$), 3.2−3.5 (br, 16H, ArCH$_2$), 4.3−4.4 (br, 16H, ArCH$_2$OC*H*$_2$), 6.3−7.2 (br, 988H, Ar). **LB-10**: δ 0.5−0.7 (br, 6H, CH$_3$), 1.1−2.3 (br, 761H, CH$_2$), 3.1−3.5 (br, 20H, ArCH$_2$), 4.2−4.5 (br, 20H, ArCH$_2$OC*H*$_2$), 6.2−7.3 (br, 1230H, Ar).

Introduction of C$_8$F$_{17}$ Groups by Esterification. The polymers of **D′B** and **L′B** series were synthesized by the reaction of the corresponding PS(BnOH)$_n$ and PS′(BnOH)$_n$ with C$_8$F$_{17}$COCl, respectively. A typical example is as follows: Under nitrogen, C$_8$F$_{17}$COCl (0.700 g, 1.45 mmol) in dry CH$_2$Cl$_2$ (5 mL) was added to PS(BnOH)$_8$ (0.200 g, M_n = 22.2 × 10^3 g/mol, benzyl alcohol moiety = 0.0721 mmol) and pyridine (0.115 g, 1.45 mmol) dissolved in CH$_2$Cl$_2$ (10 mL) at 0 °C for 10 min. The reaction mixture was allowed to stir at 25 °C for 24 h. After evaporation, the residue was dissolved in a small amount of THF and poured into methanol to precipitate the polymer. After reprecipitation with THF/methanol twice and freeze-drying from its benzene solution, **D′B-8** (0.223 g) was obtained in 96% yield. ^{1}H NMR: δ 0.2−0.8 (br, 48H, CH$_3$), 1.2−2.4 (br, 627H, CH$_2$), 3.1−3.5 (br, 14H, ArCH$_2$), 5.0−5.2 (br, 16H, ArCH$_2$OCO), 6.1−7.2 (br, 1030H, Ar). Similarly, **D′B-*n*** and **L′B-*n*** were synthesized under the same conditions. The resulting polymers were purified in a similar way mentioned in the case of **D′B-8** and usually isolated in around 95%. The assignments of ^{1}H NMR spectra of **D′B-*n*** and **L′B-*n*** were summarized below: **D′B-2**: δ 0.5−0.8 (br, 12 H, CH$_3$), 1.2−2.3 (br, 556H, CH$_2$), 3.2−3.5 (br, 2H, ArCH$_2$C), 5.2−5.3 (br, 4H, ArCH$_2$OCO), 6.3−7.2 (br, 913H, Ar). **D′B-4**: δ 0.3−0.8 (br, 24H, CH$_3$), 1.2−2.3 (br, 578H, CH$_2$), 3.2−3.5 (br, 6H, ArCH$_2$C), 5.2−5.3 (br, 8H, ArCH$_2$OCO), 6.3−7.2 (br, 1000H, Ar). **D′B-16**: δ 0.2−0.8 (br, 96H, CH$_3$), 1.2−2.3 (br, 664H, CH$_2$), 3.2−3.5 (br, 30H, ArCH$_2$C), 5.2−5.3 (br, 32H, ArCH$_2$OCO), 6.3−7.2 (br, 1100H, Ar). **D′B-32**: δ 0.1−0.9 (br, 192H, CH$_3$), 1.1−2.3 (br, 720H, CH$_2$), 3.2−3.5 (br, 62H, ArCH$_2$C), 5.1−5.3 (br, 64H, ArCH$_2$OCO), 6.3−7.2 (br, 1180H, Ar). **L′B-2**: δ 0.5−0.7 (br, 6H, CH$_3$), 1.1−2.3 (br, 556H, CH$_2$), 3.3−3.5 (br, 4H, ArCH$_2$), 5.2−5.4 (br, 4H, ArCH$_2$OCO), 6.3−7.4 (br, 913H, Ar). **L′B-4**: δ 0.3−0.8 (br, 12H, CH$_3$), 1.1−2.3 (br, 689H, CH$_2$), 3.3−3.5 (br, 8H, ArCH$_2$), 5.2−5.4 (br, 8H, ArCH$_2$OCO), 6.3−7.4 (br, 1120H, Ar). **L′B-6**: δ 0.3−0.8 (br, 6H, CH$_3$), 1.1−2.3 (br, 689H, CH$_2$), 3.3−3.5 (br, 12H, ArCH$_2$), 5.2−5.4 (br, 12H, ArCH$_2$OCO), 6.2−7.4 (br, 1110H, Ar). **L′B-8**: δ 0.3−0.7 (br, 12H, CH$_3$), 1.1−2.3 (br, 681H, CH$_2$), 3.3−3.5 (br, 16H, ArCH$_2$), 5.2−5.4 (br, 16H, ArCH$_2$OCO), 6.2−7.4 (br, 1130H, Ar). **L′B-10**: δ 0.5−0.8 (br, 6H, CH$_3$), 1.1−2.3 (br, 757H, CH$_2$), 3.3−3.5 (br, 20H, ArCH$_2$), 5.2−5.4 (br, 20H, ArCH$_2$OCO), 6.3−7.4 (br, 1230H, Ar).

Characterization of Polymers. In all **L** type polymers and their precursory polymers as well as the **D** type polymers and their precursory polymers with fewer than four functional groups, their calculated M_n values were always agreed with those estimated by SEC relative to standard polystyrene. On the other hand, it was observed that the estimated M_n values

Scheme 1. Synthesis of PS(BnBr)n by the Iterative Methodology



by SEC were relatively smaller than those calculated in the **D** type polymers with more than eight functional groups. In such polymer samples, their M_n values were determined by the above-mentioned ^{1}H NMR analysis and VPO measurement, respectively. These values thus determined were usually very close to each other. Therefore, the M_n values listed in the tables are those determined by ^{1}H NMR. The molecular weights (M_n values) of the polymers were determined by ^{1}H NMR as follows: The molecular weight of polystyrene part was first determined by comparing the ^{1}H NMR signal area ratio of aromatic protons of the main chain (6.1−7.4 ppm) with methyl protons of the initiator fragment (0.2−0.8 ppm) (as well as SEC relative to standard polystyrene). The degree of C_8F_{17} functionalization was determined by ^{1}H NMR signal area ratio of methyl protons of the initiator fragment (0.2−0.8 ppm) to methylene protons of $OCH_2CH_2CH_2C_8F_{17}$ (3.8−4.5 ppm for ether linkage) or benzyl protons of $ArCH_2COOC_8F_{17}$ (5.0−5.4 ppm for ester linkage). Then, the total molecular weight of the polymer was obtained by adding the molecular weight of C_8F_{17} part to that of the polystyrene part.

Film Preparation. The film samples for both contact angle and XPS measurements were prepared by spin-coating (4000 rpm, 20 s) onto cover glasses from 3 to 5.0 wt % THF solutions of the polymers. The samples were dried at 25 °C for 24 h and annealed at 110 °C for 2 h under vacuum to allow the polymer chains to reach their equilibrium configurations.

Measurements. Both ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX300 (300 MHz for ^{1}H and 75 MHz for ^{13}C) in $CDCl_3$ for all polymers. Chemical shifts were recorded in ppm relative to tetramethylsilane (δ 0) for ^{1}H NMR or $CDCl_3$ (δ 77.1) for ^{13}C NMR. 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 at 40 °C. Three polystyrene gel columns (pore size (bead size): 650 Å (9 μm), 200 Å (5 μm), and 75 Å (5 μm)) were used. Measurable molecular weight ranges are 10^3−4×10^5 (g/mol). Calibration curve was made with standard polystyrene samples for determining both M_n and M_w/M_n values. Vapor pressure osmometry (VPO) measurements were made with a Corona 117 instrument in benzene at 40 °C with a highly sensitive thermoelectric couple (TM-32K: sensitivity; 35 000 μV ± 10%/1 M) and with equipment of very exact temperature control. Angle-dependent X-ray photoelectron spectroscopy (XPS) was performed on Perkin-Elmer 5500MT with a monochromatic Al Kα X-ray source. Contact angles using water and dodecane droplets were measured with Kyowa Interface Science CA-A.

Results

Synthesis of Chain-End-Functionalized Polystyrenes with a Definite Number of C_8F_{17} Groups Dendritically Distributed (D Type Polymers). Recently, we have been developing a novel promising methodology based on iterative divergent approach, by which a series of chain-end-functionalized polystyrenes with a definite number of benzyl bromide (BnBr) moieties, PS(BnBr)$_n$, can be synthesized. Since the detailed methodology has been reported elsewhere, it is herein described briefly.[71,72] As illustrated in Scheme 1, basically only two sets of the reactions are needed in each iterative reaction sequence: a coupling reaction of the BnBr functionalities with the 1,1-diphenylalkyl anion generated from 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**) and *sec*-BuLi and a transformation reaction of the introduced 3-*tert*-butyldimethylsilyloxymethylphenyl groups into BnBr functionalities by treatment with LiBr−$(CH_3)_3SiCl$.

At first, the PS(BnBr) synthesized in a separate experiment[73] was coupled with the above-mentioned 1,1-diphenylalkyl anion from **1** and *sec*-BuLi to introduce two 3-*tert*-butyldimethylsilyloxymethylphenyl groups. They were subsequently transformed into two BnBr functionalities by treatment with LiBr−$(CH_3)_3SiCl$. Since the resulting PS(BnBr)$_2$ had the same BnBr functionalities at the chain end as the starting polymer, the same process could be repeated. Iteration of this sequence doubled the number of BnBr functionality to afford PS(BnBr)$_4$ and so on to PS(BnBr)$_8$.

In our previous paper,[71,72] the PS(BnBr)$_n$ thus synthesized were employed as precursory polymers for the synthesis of chain-end-functionalized polystyrenes with C_8F_{17} groups. As illustrated in Scheme 2, the functionalized polystyrenes having 4, 8, and 16 C_8F_{17} termini could be synthesized by the reaction of PS(BnBr)$_n$ with the 1,1-diphenylalkyl anion generated from 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene (**2**) and *sec*-BuLi, followed by the reacting of $C_8F_{17}(CH_2)_3Br$ after deprotection of the silyl groups.

To further examine the effect of number of C_8F_{17} group on surface enrichment in this study, a new chain-

Scheme 2. Synthesis of Chain-End-Functionalized Polystyrenes with a Definite Number of C_8F_{17} Groups (DP, DB, and D′B Series): (a) 1,1-Diphenylalkylanion Prepared from *sec*-BuLi with 1,1-Diphenylethylene Derivatives, (b) $(C_4H_9)_4NF$, (c) $C_8F_{17}(CH_2)_3Br$/NaH, and (d) $C_8F_{17}COCl$/Pyridine

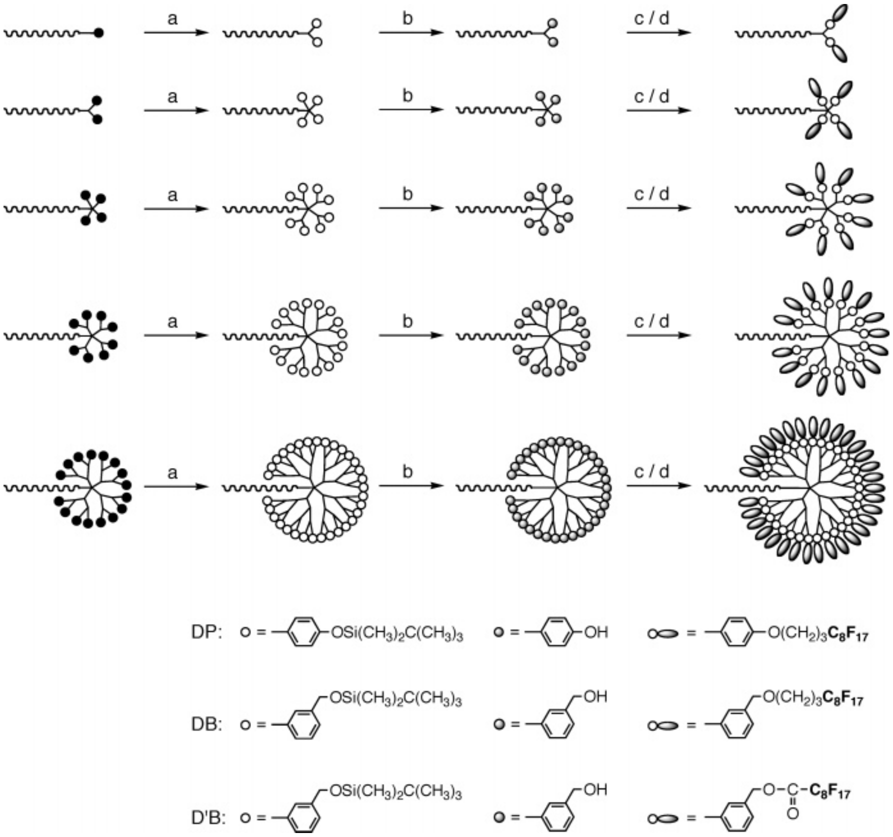


Table 1. Synthesis of Chain-End-Functionalized Polystyrenes with C_8F_{17} Groups (DP-*n*) and Their Precursory Polymers

polymer	code	M_n (kg/mol) calcd	M_n (kg/mol) obsd[a]	M_w/M_n[b]	functionality calcd	functionality obsd[a]
C_8F_{17}-functionalized polystyrene	**DP-2**	26.4	28.9	1.03	2	2.00
	DP-4	21.3	22.4	1.07	4	3.80
	DP-8	24.1	25.5	1.06	8	7.72
	DP-16	29.8	29.6	1.05	16	15.7
	DP-32	41.6	42.0	1.05	32	32.2
PhOH-functionalized polystyrene	$PS(PhOH)_2$	25.5	25.5	1.03	2	2.00
	$PS(PhOH)_4$	19.6	19.5	1.02	4	3.80
	$PS(PhOH)_8$	20.4	20.4	1.02	8	7.72
	$PS(PhOH)_{16}$	22.4	22.4	1.03	16	15.7
	$PS(PhOH)_{32}$	27.0	26.9	1.03	32	32.2
BnBr-functionalized polystyrene	PS(BnBr)	25.3	25.3	1.02	1	1.00
	$PS(BnBr)_2$	19.1	19.2	1.02	2	1.92
	$PS(BnBr)_4$	19.7	20.0	1.02	4	3.96
	$PS(BnBr)_8$	20.8	20.7	1.02	8	7.91
	$PS(BnBr)_{16}$	23.9	23.6	1.03	16	15.8

[a] Determined by ^1H NMR. [b] Determined by SEC.

end-functionalized polystyrene with 32 C_8F_{17} groups was synthesized by using $PS(BnBr)_{16}$ in a manner similar to that as shown in Scheme 2. In a series of these polymers, C_8F_{17} groups are connected via phenyl ether linkage to the main chains. Table 1 summarizes the characterization results of the resulting polymers. In addition, the results of their precursory polymers having BnBr and phenol functionalities introduced at the chain ends are also listed in this table.

Figure 1 shows SEC profiles of chain-end-functionalized polystyrenes with 8 BnBr moieties, with 16 3-*tert*-butyldimethylsilyloxyphenyl groups, with 16 phenol functions, and with 16 C_8F_{17} groups.

As can be seen, all of these polymers exhibit sharp, symmetrical monomodal SEC distributions, indicating that all reactions proceed cleanly without any side reactions leading to chain coupling and degradation. However, small high molecular weight shoulders (<5%), which double the molecular weight of the parent polymers, were sometimes formed during the course of the Williamson reaction. In such cases, they were completely removed by fractional precipitation using a mixture of cyclohexane and hexane.

Herein, we have further synthesized two more different series of chain-end-functionalized polystyrenes with C_8F_{17} groups by modifying the introduction stage of C_8F_{17} group in the same iterative methodology as illustrated in Scheme 2.

As can be seen, the 3-*tert*-butyldimethylsilyloxymethylphenyl groups introduced at the chain ends are

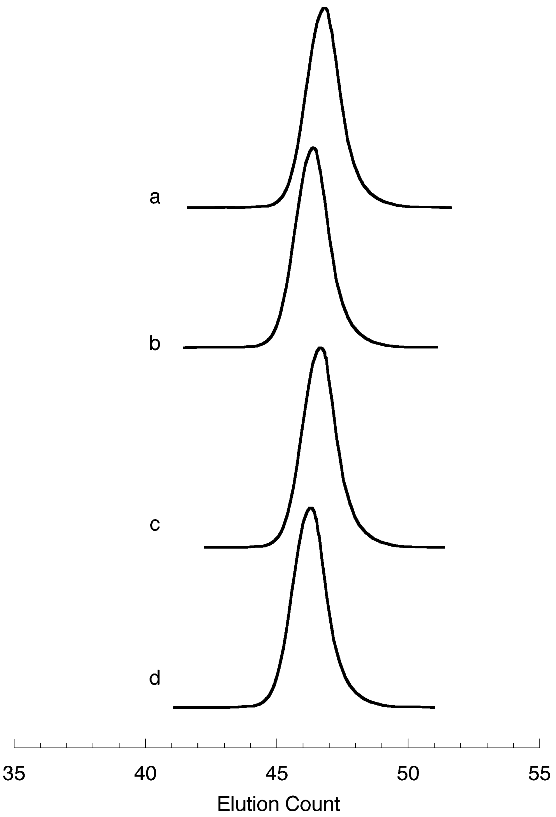


Figure 1. SEC curves for (a) chain-end-functionalized polystyrenes with 8 BnBr moieties, (b) with 16 3-*tert*-butyldimethylsilyoxyphenyl groups, (c) with 16 phenol functions, and (d) with 16 perfluorooctylpropyl ether functions.

treated with $(C_4H_9)_4NF$ instead of LiBr$-(CH_3)_3$SiCl. Benzyl alcohol functions are regenerated by this treatment. The same numbers of C_8F_{17} group are then introduced via the resulting benzyl alcohol functions by reacting not only with $C_8F_{17}(CH_2)_3Br$ in a manner similar to that mentioned above but also with C_8F_{17}-COCl, as illustrated in Scheme 2. Fortunately, either of both reactions proceeded efficiently to quantitatively introduce C_8F_{17} groups.

The objective C_8F_{17}-chain-end-functionalized polystyrenes as well as their precursory chain-end-functionalized polymers synthesized in all iteration processes possess predictable molecular weights and narrow molecular weight distributions, as summarized in Tables 2 and 3.

The polystyrene main chains were designed to be around 20 kg/mol in all polymer samples to compare the previous results. The M_n values determined by SEC were generally in good agreement with the calculated values in the polymers with two and four functional groups at the chain ends, but somewhat smaller than those calculated in the polymers having 8, 16, and 32 functional termini because of smaller hydrodynamic volumes of their dendritic branched structures. The M_n values of these samples were therefore determined by end-group analysis with ^{1}H NMR and VPO and found to agree well with those calculated. SEC profiles of the polymers exhibit sharp symmetrical monomodal distributions. Neither shoulder nor tailing is observed in each polymer sample.

Thus, two new series of chain-end-functionalized polystyrenes with 2, 4, 8, 16, and 32 C_8F_{17} groups could be successfully synthesized by using the same chain-end-functionalized polystyrenes with a definite number of benzyl alcohol moieties. Their C_8F_{17} groups are connected via the benzyl ether or benzyl ester linkages to the main chains and dendritically distributed as illustrated in Scheme 2. As mentioned in the Experimental Section, these polymer series are referred to as **DB-*n*** and **D′B-*n***, respectively. The “*n*” indicates the number of C_8F_{17} groups. Accordingly, **DB-4** and **D′B-4** correspond to the chain-end-functionalized polystyrenes with four C_8F_{17} groups connected via benzyl ether and benzyl ester linkages. The above-mentioned chain-end-functionalized polystyrenes with C_8F_{17} groups connected via phenyl ether linkages are referred to as **DP-*n***.

When both **DB-16** and **DB-32** samples were measured by SEC using THF as an eluent, the difficulty was encountered, presumably due to the micelle formation by aggregating C_8F_{17} termini of such polymers in THF. The expected sharp monomodal distributions could not be obtained. No peak was observed at usual ranges of the concentration (SEC) in each case, and at higher concentrations, broad multimodal peaks were always eluted at lower molecular weight sides than those expected. On the other hand, their precursory polymers all exhibited symmetrically sharp monomodal SEC distributions and possessed the expected structures and chain architectures as confirmed by ^{1}H NMR and VPO. The two reactions with $C_8F_{17}(CH_2)_3Br$ and $C_8F_{17}COCl$ employed for the introduction of C_8F_{17} groups proceeded cleanly and quantitatively in each case. The degrees of C_8F_{17} group determined by ^{1}H NMR agreed quite well with those predicted in the two polymer samples. Accordingly, it may be concluded that both **DB-16** and **DB-32** are the expected chain-end-functionalized polystyrenes with 16 and 32 C_8F_{17} groups.

Synthesis of Chain-End-Functionalized Polystyrenes with a Definite Number of C_8F_{17} Groups Linearly Aligned in a Double Line (L Type Polymers). As mentioned above, the C_8F_{17} groups of chain-end-functionalized polystyrenes synthesized in the preceding section are dendritically distributed in spherical branched structures. In this section, we have synthesized another type of C_8F_{17}-chain-end-functionalized polystyrenes, whose C_8F_{17} groups are linearly aligned in a double line. The synthetic methodology herein proposed is based on our methodology previously reported.[71,74−76]

In the first polymer series of this type, the C_8F_{17} groups are connected via phenyl ether linkages to the main chain. We previously reported the synthesis of well-defined chain-end-functionalized polystyrenes with a definite number of 1, 2, 3, and 4 C_8F_{17} groups by the addition reactions of PSLi to either 1-(4-*tert*-butyldimethylsilyloxyphenyl)-1-phenylethylene or **2** and the subsequent Williamson reaction with $C_8F_{17}(CH_2)_3Br$ after deprotection of the introduced silyl groups.[59] In this synthesis, chain-end-functionalized polystyrenes with a definite number of phenol moieties, PS′(PhOH)$_n$, were always used as precursory polymers. Herein, we have further synthesized the same series of chain-end-functionalized polystyrenes with 8 and 10 C_8F_{17} groups, as illustrated in Scheme 3.

New functionalized dianion, **3**, and dibromide, **4**, were needed for the synthesis. The dianion, **3**, was quantitatively obtained by the radical coupling reaction of **2** with potassium naphthalenide and in situ used in the next reaction. The dibromide, **4**, was synthesized in more than 70% yield by the reacting of **3** with a 10-fold

Table 2. Synthesis of Chain-End-Functionalized Polystyrenes with C_8F_{17} Groups (DB-*n*) and Their Precursory Polymers

		M_n (kg/mol)			functionality	
polymer	code	calcd	obsd[a]	M_w/M_n[b]	calcd	obsd[a]
C_8F_{17}-functionalized polystyrene	**DB-2**	20.5	20.7	1.05	2	1.96
	DB-4	22.0	22.3	1.05	4	3.94
	DB-8	24.9	25.0	1.06	8	7.77
	DB-16	30.9	32.8		16	15.9
	DB-32	42.7	42.8		32	31.8
BnOH-functionalized polystyrene	PS(BnOH)$_2$	19.6	19.8	1.03	2	1.99
	PS(BnOH)$_4$	20.1	20.4	1.02	4	4.00
	PS(BnOH)$_8$	21.2	21.2	1.03	8	8.00
	PS(BnOH)$_{16}$	23.5	23.5	1.03	16	15.9
	PS(BnOH)$_{32}$	28.0	28.0	1.03	32	31.9
BnBr-functionalized polystyrene	PS(BnBr)	19.4	19.4	1.02	1	1.00
	PS(BnBr)$_2$	19.7	19.7	1.02	2	1.98
	PS(BnBr)$_4$	20.4	20.4	1.03	4	3.99
	PS(BnBr)$_8$	21.7	21.7	1.03	8	8.00
	PS(BnBr)$_{16}$	24.5	24.4	1.03	16	16.0

[a] Determined by ^{1}H NMR. [b] Determined by SEC.

Table 3. Synthesis of Chain-End-Functionalized Polystyrenes with C_8F_{17} Groups (D′B-*n*) and Their Precursory Polymers

		M_n (kg/mol)			functionality	
polymer	code	calcd	obsd[a]	M_w/M_n[b]	calcd	obsd[a]
C_8F_{17}-functionalized polystyrene	**D′B-2**	20.0	20.0	1.02	2	1.99
	D′B-4	22.8	23.1	1.03	4	3.96
	D′B-8	25.7	25.8	1.03	8	7.91
	D′B-16	31.5	31.7	1.03	16	15.9
	D′B-32	42.2	42.3	1.02	32	31.9
BnOH-functionalized polystyrene	PS(BnOH)$_2$	19.1	19.3	1.04	2	1.99
	PS(BnOH)$_4$	21.0	21.4	1.04	4	3.96
	PS(BnOH)$_8$	22.6	22.0	1.03	8	7.94
	PS(BnOH)$_{16}$	24.4	24.6	1.03	16	15.8
	PS(BnOH)$_{32}$	28.0	28.0	1.03	32	31.9
BnBr-functionalized polystyrene	PS(BnBr)	18.9	18.9	1.02	1	1.00
	PS(BnBr)$_2$	20.6	20.6	1.02	2	2.00
	PS(BnBr)$_4$	21.3	21.4	1.03	4	3.95
	PS(BnBr)$_8$	22.7	22.8	1.03	8	7.91
	PS(BnBr)$_{16}$	24.4	24.4	1.03	16	16.0

[a] Determined by ^{1}H NMR. [b] Determined by SEC.

excess of 1,4-dibromobutane. PSLi was reacted with **2**, followed by treatment with a 8-fold excess of **4** to afford a chain-end-functionalized polystyrene with six protected phenol functionalities and 4-bromobutyl terminus. The resulting polymer was then reacted with the functionalized 1,1-diphenylalkyl anion, **7**, generated from **2** and *sec*-BuLi to afford PS(PhOH)$_8$ after deprotection. Similarly, PS(PhOH)$_{10}$ was prepared by the reaction of the same functionalized polymer with **3**, followed by deprotection. In this case, the expected polymer was quantitatively obtained by using a 6-fold excess of **3** in the reaction and no dimeric product between **3** and 2 equiv of the functionalized polystyrene was produced. Eight and 10 C_8F_{17} groups were introduced via phenol functions by the reacting of PS(PhOH)$_n$ (n = 8 or 10) with NaH, followed by treatment with $C_8F_{17}(CH_2)_3Br$. Thus, it is possible to introduce a definite number of C_8F_{17} groups from 1 to 10 into the polymer chain ends via phenol moieties by various modes of stepwise addition reactions of PSLi with 1-(4-*tert*-butyldimethylsilyloxyphenyl)-1-phenylethylene, **2**, **3**, and/or **4**. Table 4 summarizes the results of C_8F_{17}-chain-end-functionalized polystyrenes and their precursory polymers. As can be seen, the objective chain-end-functionalized polymers are well-defined in number of C_8F_{17} group and precisely controlled in chain length.

Similar to **DB-*n*** and **D′B-*n*** polymer series whose C_8F_{17} groups are connected by benzyl ether and ester linkages, chain-end-functionalized polystyrenes with a definite number of benzyl alcohol moieties (PS′(BnOH)$_n$) linearly aligned in a double line were prepared as precursory polymers for the introduction of C_8F_{17} groups. The synthetic outlines of such functionalized polystyrenes are illustrated in Scheme 3. PS′(BnOH)$_2$ was prepared simply by the reacting of PSLi with **1**, followed by deprotection. To prepare both PS′(BnOH)$_4$ and PS′(BnOH)$_6$, a new chain-end-functionalized polystyrene having two silyl-protected benzyl alcohol functionalities and 4-bromobutyl terminus was first prepared by the reaction of PSLi with **1**, followed by treatment with a 10-fold excess of 1,4-dibromobutane. The resulting chain-end-functionalized polymer was then reacted with the functionalized 1,1-diphenylalkyl anion, **8**, generated from **1** and *sec*-BuLi to afford PS′(BnOH)$_4$. PS′(BnOH)$_6$ was prepared by the reaction of the same polymer with a 6-fold excess of the functionalized dianion, **5**, generated from **1** and potassium naphthalenide. For the preparation of PS′(BnOH)$_8$ and PS′(BnOH)$_{10}$, the procedures similar to those used for the preparation of PS′(PhOH)$_8$ and PS′(PhOH)$_{10}$ were employed. In these procedures, **1** was used instead of **2**.

The C_8F_{17} groups ranging from 2 to 10 in number were introduced at the polymer chain ends by the reacting of the benzyl alcohol moieties of PS′(BnOH)$_n$ with either $C_8F_{17}(CH_2)_3Br$ or $C_8F_{17}COCl$ in the similar manners mentioned above, as illustrated in Scheme 3. Table 5 summarizes the results of all the polymer samples.

The M_n values observed by SEC and ^{1}H NMR agreed quite well with those calculated in all cases. SEC

Scheme 3. Synthesis of Chain-End-Functionalized Polystyrenes with a Definite Number of C_8F_{17} Groups (LP, LB, and L′B Series): (a) *sec*-BuLi, (b) $(C_4H_9)_4NF$, (c) $C_8F_{17}(CH_2)_3Br$/NaH, (d) $C_8F_{17}COCl$/Pyridine, (e) Potassium Naphthalenide, and (f) 1,4-Dibromobutane

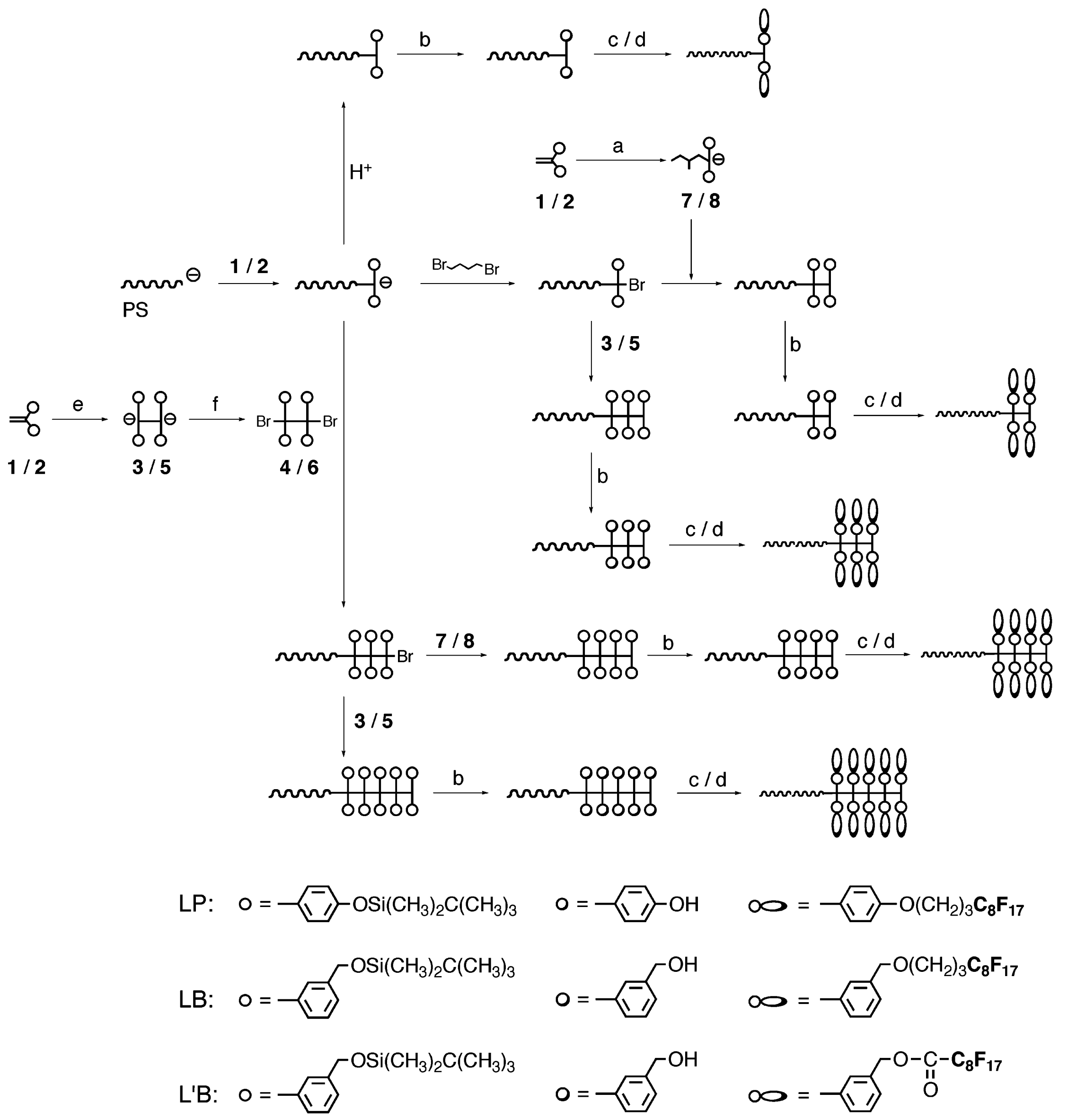


Table 4. Synthesis of Chain-End-Functionalized Polystyrenes with C_8F_{17} Groups (LP-*n*) and Their Precursory Polymers

	C_8F_{17}-functionalized polystyrene					PhOH-functionalized polystyrene				
	M_n (kg/mol)			functionality		M_n (kg/mol)			functionality	
code	calcd	obsd[a]	M_w/M_n	calcd	obsd[a]	calcd	obsd[a]	M_w/M_n	calcd	obsd[a]
LP-1[c]	27.7	27.6	1.02	1	1.00	27.2	27.2	1.02	1	1.00
LP-2[c]	19.9	20.0	1.02	2	2.05	19.0	19.0	1.04	2	2.00
LP-3[c]	20.5	20.4	1.02	3	3.19	19.1	19.1	1.02	3	3.00
LP-4[c]	21.2	23.8	1.06	4	3.90	20.1	19.5	1.03	4	4.02
LP-8	24.5	25.1	1.02	8	7.87	20.9	21.5	1.02	8	8.00
LP-10	25.7	26.5	1.02	10	9.95	21.1	21.9	1.02	10	10.0

[a] Determined by ^1H NMR. [b] Determined by SEC. [c] These data were reported in our previous study.[59]

profiles of the polymer samples exhibited symmetrical monomodal distributions, and narrow molecular weight distributions were always attained. The degrees of C_8F_{17} end-functionalization measured by ^1H NMR analysis were in good agreement with those expected in all cases within error limits. As described in experimental part, such polymer series are abbreviated as **LB-*n*** and **L′B-*n***. Chain-end-functionalized polystyrenes with C_8F_{17} groups connected via phenol ether linkages are referred to as **LP-*n***. In all polymer samples, the main polystyrene chains were also adjusted to be around 20 kg/mol in M_n value.

In summary, we are successful in synthesizing two different **D** and **L** types of well-defined chain-end-functionalized polystyrenes with a definite number of C_8F_{17} groups. The C_8F_{17} groups are dendritically distributed in the **D** type polymers, while they are linearly aligned in a double line in the **L** type polymers. Two to 32 and 1 to 10 C_8F_{17} groups in number were introduced at chain ends of the **D** and **L** type polymers, respec-

Table 5. Synthesis of Chain-End-Functionalized Polystyrenes with C_8F_{17} Groups (LB-*n* and L′B-*n*) and Their Precursory Polymers

	C_8F_{17}-functionalized polystyrene					BnOH-functionalized polystyrene				
	M_n (kg/mol)			functionality		M_n (kg/mol)			functionality	
code	calcd	obsd[a]	M_w/M_n	calc	obsd[a]	calcd	obsd[a]	M_w/M_n	calcd	obsd[a]
LB-2	20.5	20.7	1.05	2	1.96	19.6	19.8	1.03	2	1.99
LB-4	21.4	22.6	1.03	4	3.98	19.6	20.8	1.04	4	3.99
LB-6	22.4	23.5	1.04	6	5.98	19.6	20.8	1.03	6	5.96
LB-8	23.5	24.7	1.03	8	7.99	19.8	21.1	1.04	8	7.96
LB-10	29.6	30.8	1.04	10	9.94	25.0	26.1	1.05	10	9.95
L′B-2	19.9	20.0	1.02	2	1.99	19.1	19.3	1.04	2	1.99
L′B-4	25.0	25.3	1.04	4	3.96	23.2	23.6	1.05	4	3.90
L′B-6	26.0	26.3	1.03	6	5.87	23.3	23.6	1.04	6	5.87
L′B-8	27.0	27.4	1.03	8	7.80	23.5	23.9	1.04	8	7.91
L′B-10	29.0	30.6	1.05	10	10.0	25.0	26.1	1.05	10	9.95

[a] Determined by ^1H NMR. [b] Determined by SEC.

tively. In each polymer type, there are three polymer series, whose C_8F_{17} groups are connected to polystyrene main chains by phenyl and benzyl ethers and benzyl ester linkages. Thus, we have established the synthetic routes for total six different series of well-defined chain-end-functionalized polystyrenes with a definite number of C_8F_{17} groups: **DP-*n***, **DB-*n***, **D′B-*n***, **LP-*n***, **LB-*n***, and **L′B-*n***.

Surface Characterization of C_8F_{17}-Chain-End-Functionalized Polystyrene Films by XPS Measurement. The polymer films were prepared by spin-coating onto cover glasses from their benzene solutions. They were dried at 25 °C for 24 h and annealed at 110 °C for 2 h. The surface composition as a function of depth can be quantitatively 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° correspond to approximately 20 and 100 Å depths from the top surface, respectively.

(1) Chain-End-Functionalized Polystyrenes with C_8F_{17} Groups Dendritically Distributed (D Type Polymers). It was previously observed that the atomic percent ratios of F/C measured at 10° TOA were much higher than they were in the bulk in all films cast from **DP** polymer series having 2, 4, 8, and 16 C_8F_{17} termini (**DP-2** to **DP-16**).[62] This result clearly confirms the large segregation phenomena and enrichment of C_8F_{17} groups to the film surfaces of all polymer samples. Furthermore, the F/C values at 10° TOA were always higher than those at 80° TOA, strongly indicating that their C_8F_{17} groups are especially enriched at outmost top surfaces. These results are summarized in Table 6.

Interestingly, F atomic % values at 10° TOA were found to greatly increase with increasing the number of C_8F_{17} group from two to four, but no increase was observed from **DP-4** to **DP-8**. Moreover, **DP-16** showed only a little bit increase in value with increasing the number of C_8F_{17} group to 16. To further examine the effect of F atomic % on number of C_8F_{17} group, the annealed film of the newly synthesized polymer having 32 C_8F_{17} termini, **DP-32**, was measured by XPS. Unexpectedly, the value was almost the same as that of **DP-16**. Thus, F atomic % increased discontinuously with increasing the number of C_8F_{17} group and appeared to be saturated at the number of 16. The extent of increase was however relatively small from 4 to even 32. On the other hand, it was observed that the value of F atomic % at 80° TOA gradually increased with the number of C_8F_{17} group. This trend nearly corresponds to the increase of F content in bulk, suggesting that the value of F atomic % at 80° TOA reflects only to a small extent the surface atomic composition. Therefore, we have used the value of F atomic % at 10° TOA to examine the surface composition in the present study.

Table 6. Atomic Percent Ratios of F/C for DP, DB, and D′B Polymer Series by XPS Measurement at 10° and 80° TOA

	atomic % (F/C)		
code	10° TOA[a]	80° TOA[b]	bulk[c]
DP-2	22.4/76.2	8.4/90.7	1.6/98.4
DP-4	44.2/54.0	19.3/79.2	4.3/95.5
DP-8	44.0/54.5	20.7/78.2	7.6/91.9
DP-16	49.8/48.8	27.3/71.4	12.6/86.7
DP-32	49.8/48.5	34.7/63.1	18.6/80.3
DB-2	34.1/63.7	15.0/83.5	2.2/97.7
DB-4	45.1/53.2	22.7/75.9	4.1/95.7
DB-8	48.7/49.6	24.9/83.9	7.3/92.2
DB-16	48.6/49.7	24.1/74.1	11.3/88.0
DB-32	51.2/46.5	30.8/67.0	17.8/81.2
D′B-2	20.2/77.9	10.8/87.8	2.3/97.5
D′B-4	29.8/67.9	15.5/82.4	4.0/95.6
D′B-8	29.0/69.5	16.6/81.9	7.1/92.1
D′B-16	51.8/45.7	25.8/72.4	11.9/86.8
D′B-32	48.8/48.5	32.9/64.1	17.8/80.2

[a] Corresponding to 20 Å depth. [b] Corresponding to 100 Å depth. [c] Calculated value from the chemical composition of polymer.

The F atomic % values of the film surfaces cast from **DB** and **D′B** polymer series were also measured by XPS under the same conditions. The results are also summarized in Table 6. In the **DB** series, the value increased with increasing number of C_8F_{17} groups but appeared to be saturated at the number of eight. Interestingly, **DB-2** is much higher than **DP-2** in F atomic % value. Thus, the dependence of F % atomic percent on number of C_8F_{17} group obtained by **DB** series is somewhat different from that obtained by **DP** series.

In the case of **D′B** polymer series whose C_8F_{17} groups are connected to the main chains via benzyl ester, the F atomic % increased slightly with increasing the number of C_8F_{17} group from 2 to 4 or even 8. Therefore, the degrees of surface enrichment of **D′B-4** and **D′B-8** were much less effective than those of **DP-4**, **DP-8** and **DB-4**, **DB-8**. However, the F atomic % dramatically increased when the number was 16, but again no more increase was attained with increasing up to 32. The value appeared to be saturated at the number of C_8F_{17} group of 16 and was comparable to those of **DP-16**, **DP-32**, **DB-8**, **DB-16**, and **DB-32**. The F atomic % values are plotted versus number of C_8F_{17} group in all samples to visually compare the relationship as shown in Figure 2.

(2) Chain-End-Functionalized Polystyrenes with C_8F_{17} Groups Linearly Aligned in a Double Line

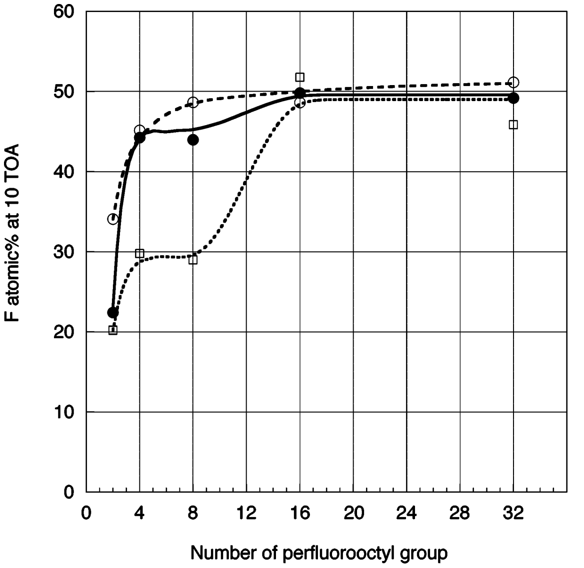


Figure 2. F atomic % at 10° TOA vs number of C_8F_{17} group in **DP-*n*** (filled circle), **DB-*n*** (circle), and **D′B-*n*** (square) polymer series. As can be seen, the trend is different in either case and the F atomic % is saturated at the number between 8 and 16, 4 and 8, or 8 and 16 in **DP**, **DB**, or **D′B** series. Importantly, the saturated F atomic % values of all three polymer series are comparable and close to 50%. The significant meaning of this value will be discussed later.

Table 7. Atomic Percent Ratios of F/C for LP, LB, and L′B Polymer Series by XPS Measurement at 10° and 80° TOA

	atomic% (F/C)		
code	10° TOA[a]	80° TOA[b]	bulk[c]
LP-1	12.9/86.1	3.7/96.2	0.8/99.2
LP-2	26.9/71.5	10.3/87.4	2.2/97.6
LP-3	39.0/59.3	13.9/84.7	3.1/96.7
LP-4	49.6/48.0	27.7/70.5	4.0/95.8
LP-8	47.2/50.1	27.6/69.9	7.3/92.3
LP-10	48.2/46.5	21.3/76.6	8.7/90.8
LB-2	34.1/63.7	15.0/83.5	2.2/97.7
LB-4	45.2/51.8	29.1/68.1	4.0/95.8
LB-6	50.1/47.3	25.0/73.2	5.8/93.9
LB-8	51.2/47.4	25.9/72.6	7.4/92.1
LB-10	51.7/46.2	25.3/72.7	8.4/91.1
L′B-2	20.2/77.9	10.8/87.8	2.2/97.5
L′B-4	37.9/59.4	21.3/77.1	3.6/96.0
L′B-6	46.7/50.5	26.5/71.5	5.2/94.2
L′B-8	48.0/49.3	28.2/69.5	7.7/91.5
L′B-10	48.2/49.0	26.9/70.9	8.5/90.6

[a] Corresponding to 20 Å depth. [b] Corresponding to 100 Å depth. [c] Calculated value from the chemical composition of polymer.

(L Type Polymers). The F atomic percents at 10° and 80° (TOA)s were also measured in all cast films of **L** type polymer series by XPS under the same conditions. Table 7 summarizes all data.

As reported previously, the value rapidly increased with increasing the number of C_8F_{17} group from one to four in **LP** polymer series. In this study, two more samples, **LP-8** and **LP-10**, having 8 and 10 C_8F_{17} termini, were newly synthesized to elucidate the dependence of F atomic % value on number of C_8F_{17} group. Contrary to the expectation, an increase was not observed by increasing the number from 4 to 8 followed by 10, but there appeared even a small decrease in either case. Thus, the surface enrichment of C_8F_{17} group was apparently saturated at the number of four in this **LP** polymer series.

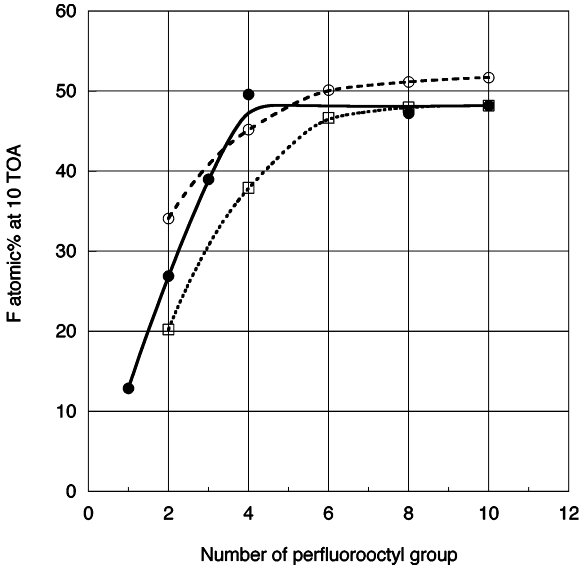


Figure 3. F atomic % at 10° TOA vs number of C_8F_{17} group in **LP-*n*** (filled circle), **LB-*n*** (circle), and **L′B-*n*** (square).

In **LB** polymer series whose C_8F_{17} groups are connected via benzyl ether linkage, the F % value of **LB-2** was exceptionally large, compared to other samples having two C_8F_{17} termini, and increased with increasing the number of C_8F_{17} group from two to six. The saturated value of around 50% was obtained in **LB-6**, and no more increase in value was observed in **LB-8** and **LB-10**. In **L′B** series, the value increased rapidly at first and then gradually by going from **L′B-2**, **-4**, to **-6** and was saturated at **L′B-6**. The F atomic % vs number of C_8F_{17} group is plotted in each **L** polymer series as shown in Figure 3. As can be seen, the value is clearly saturated at the number of four in **LP** polymer series, while it appears to level off at the number between four and six in **LB** and **LB′** series, respectively. Again, the saturated value was close to 50% in each of **L** type polymers.

Contact Angle Measurements with Water and Dodecane Droplets. Contact angle measurements with water and organic solvent droplets are also convenient and useful methods for obtaining information on the surface character of the annealed films. Hydrophobic nature of the surface can be estimated by the contact angle value with water droplet. On the other hand, certain organic solvents are useful to elucidate the extent of surface lipophobicity due to the C_8F_{17} group segregated to the surface. Herein, dodecane was used as the organic solvent of choice for this purpose.

Contact angles using water droplet showed values in the range 95.4°−115° for all films examined herein. These values are always higher than 91.3° of the film of DPE-end-capped polystyrene with a comparable molecular weight (M_n = 23.0 kg/mol), as summarized in Table 8.

This clearly indicates that C_8F_{17} groups preferentially segregated to form more hydrophobic surfaces. In **DP** polymer series, for example, the value of contact angle increased progressively with increasing the number of C_8F_{17} group from 2 to 16, but no more increase was observed even by greatly increasing the number up to 32. Actually, **DP-16** showed a comparable value to **DP-32**. Thus, the surface segregation of C_8F_{17} group was enhanced with increasing the number of C_8F_{17} group, reached to maximum, and no more segregation was

Table 8. Contact Angles Using Water and Dodecane Droplets in DP, DB, D′B, LP, LB, and L′B Polymer Series

	contact angle (deg)			contact angle (deg)			contact angle (deg)	
code	water	dodecane	code	water	dodecane	code	water	dodecane
DP-2	99.7	23.3	**DB-2**	104	40.9	**D′B-2**	101	29.4
DP-4	105	47.7	**DB-4**	109	50.6	**D′B-4**	104	40.2
DP-8	107	48.7	**DB-8**	112	54.8	**D′B-8**	105	41.4
DP-16	113	55.6	**DB-16**	110	54.8	**D′B-16**	111	53.9
DP-32	111	51.7	**DB-32**	111	55.5	**D′B-32**	111	53.8
LP-1	95.4	15.7						
LP-2	99.4	32.8	**LB-2**	104	40.9	**L′B-2**	101	29.4
LP-3	105	40.4						
LP-4	111	47.8	**LB-4**	113	54.5	**L′B-4**	100	50.0
			LB-6	114	55.8	**L′B-6**	111	55.6
LP-8	112	53.3	**LB-8**	115	56.2	**L′B-8**	112	56.2
LP-10	112	53.0	**LB-10**	115	56.4	**L′B-10**	110	55.1
PS	91.3	—[a]						

[a] Contact angle could not be measured by getting wet the surface with dodecane.

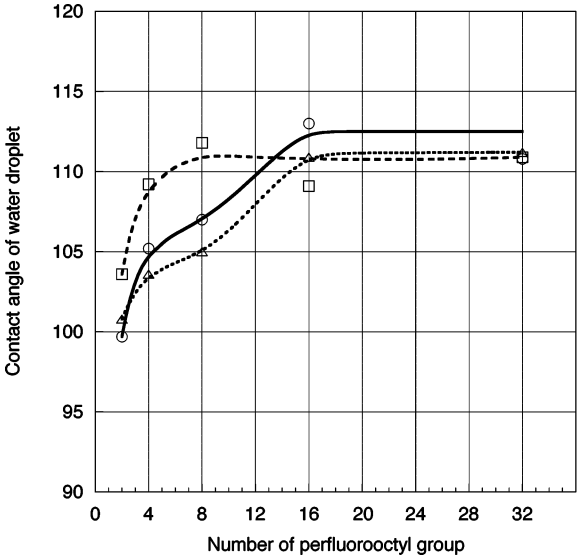


Figure 4. Contact angle using water droplet vs number of C_8F_{17} group in ***DP-n*** (circle), ***DB-n*** (square), and ***D′B-n*** (triangle).

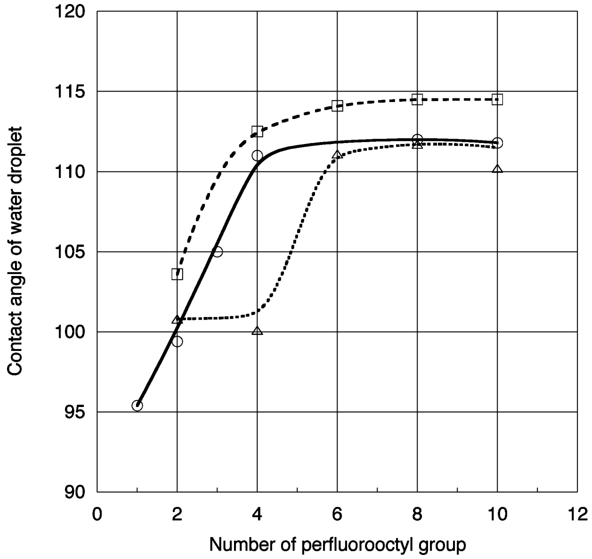


Figure 5. Contact angle using water droplet vs number of C_8F_{17} group in ***LP-n*** (circle), ***LB-n*** (square), and ***L′B-n*** (triangle).

observed. This result is in fair accord with that obtained by the values of F atomic % at 10° TOA as mentioned above.

The results of other polymer series are also summarized in Table 8. In each polymer series, the value of contact angle increased with increasing the number of C_8F_{17} group and was saturated at the appropriate number. It can be seen in this table that these values almost correspond to those of F atomic % in most cases. As mentioned before, the F atomic % appeared to be saturated at around 50%. The contact angle corresponding to ca. 50% was within the range from 110° to 115° in value.

The contact angle values are plotted versus number of C_8F_{17} groups in Figures 4 and 5. As you can see, 4, 2−4, and 4−6 C_8F_{17} groups are enough to reach a plateau in **LP**, **LB**, and **L′B** series, respectively, while **DP**, **DB**, and **D′B** series require more C_8F_{17} groups of 8−16, 4−8, and 8−16 in number. Thus, the resulting graph of each polymer series is always very similar to the graph plotting F atomic % vs C_8F_{17} group observed in the preceding section.

The extent of the surface enrichment of C_8F_{17} group is also observable by measuring the film surface with contact angle using dodecane droplet. The results are also summarized in Table 8. The contact angle of DPE-end-capped polystyrene with a M_n value of 23.0 kg/mol could not be measured by getting wet the surface with dodecane, whereas all of the C_8F_{17}-chain-end-functionalized polymer samples used herein showed measurable values. This clearly indicates that the lipophobic surfaces covered with C_8F_{17} groups apparently formed in all cases as expected. The values of contact angle with dodecane droplet were plotted versus number of C_8F_{17} group in Figures 6 and 7.

The maximum saturated value is around 55° in each case. Again, the resulting graphs look similar to those observed in Figures 4 and 5 as well as Figures 2 and 3. Accordingly, the contact angle measurement with dodecane droplet is also effective analytical method to estimate the extent of surface enrichment of C_8F_{17} groups.

It should be mentioned that dodecane droplets on the film surfaces of **LP-1−4** were not stable, and the contact angle values gradually decreased with time during measuring and reached to 10−20° after 20 min in all samples. Therefore, the reproducible values after 1 min are listed in Table 8. The reason is that dodecane may gradually soak into the films inside from the surfaces and dissolve the second layers mainly comprised of polystyrene segments under the surface layers covered with C_8F_{17} groups. In contrast, dodecane droplets on the film surfaces of **LP-8** and **LP-10** were very stable and remained unchanged. Similarly, the droplets were also

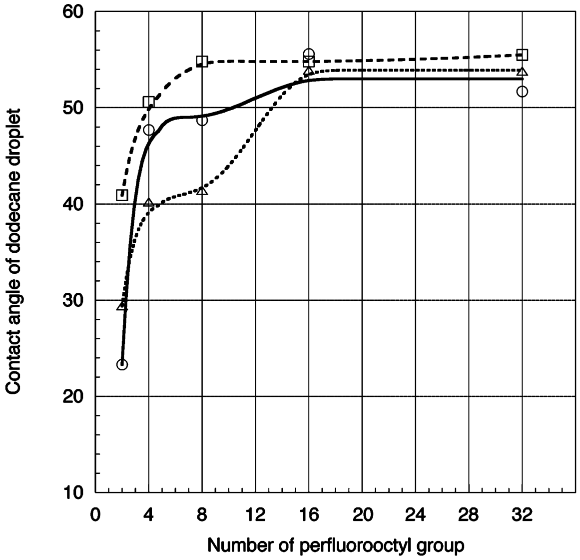


Figure 6. Contact angle using dodecane droplet vs number of C_8F_{17} group in **DP-*n*** (circle), **DB-*n*** (square), and **D′B-*n*** (triangle).

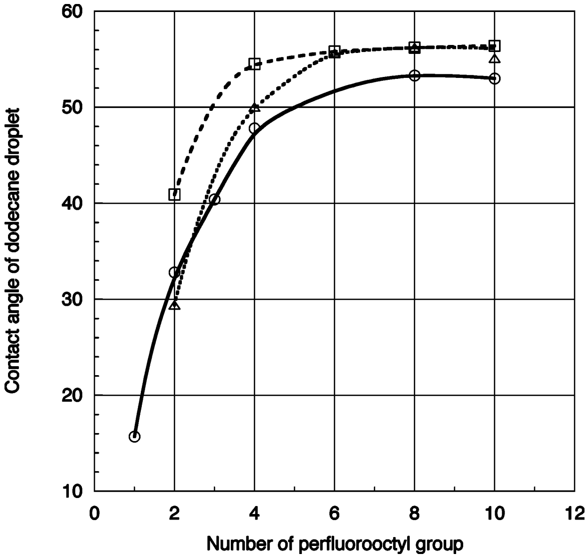


Figure 7. Contact angle using dodecane droplet vs number of C_8F_{17} group in **LP-*n*** (circle), **LB-*n*** (square), and **L′B-*n*** (triangle).

stable on the film surfaces of other polymer series having six or more C_8F_{17} termini. In these annealed films, enough amounts of C_8F_{17} group may be present even in the second layer to prevent the soaking of dodecane.

Discussion

In this study, we have successfully established the synthetic routes for two different types (**D** and **L**) of well-defined chain-end-functionalized polystyrenes with a definite number of C_8F_{17} groups. The first **D** type polymers were synthesized by applying the recently developed methodology based on an iterative divergent approach. The introduced C_8F_{17} termini were 2, 4, 8, 16, and 32 in number and highly branched in dendritic distribution. The other chain-end-functionalized polymers (**L** type) were synthesized by developing the stepwise methodology based on diverse array of addition reactions of PSLi with **1**, **2**, and/or their derivatized agents. In these polymers, 2, 4, 6, 8, and 10 C_8F_{17} groups linearly aligned in a double line were introduced at the chain ends. In each of the two polymer types, phenyl ether, benzyl ether, and benzyl ester linkages were employed for connecting C_8F_{17} termini to the main polystyrene chains. Totally, six different polymer series could be systematically synthesized herein: **DP-*n***, **DB-*n***, **D′B-*n***, **LP-*n***, **LB-*n***, and **L′B-*n***.

The resulting polymers all were well-defined in number of C_8F_{17} groups and precisely controlled in chain length. Their main polystyrene chains were adjusted to be around 20 kg/mol in M_n value in order to minimize the influence of main chain length. Therefore, the effect of number of C_8F_{17} group on surface segregation of C_8F_{17} group was directly compared. It should be mentioned that the intermediate polymers synthesized herein are also novel well-defined chain-end-multifunctionalized polymers with a definite number of reactive PhOH, BnOH, and BnBr moieties, via which useful other functional groups and molecules can be introduced.

In some chain-end-functionalized polymers with large numbers of C_8F_{17} groups, the difficulty was encountered in SEC measurements using THF as an eluent, presumably due to the micelle formation among polymer chains by the aggregating of terminal C_8F_{17} groups in THF. A detailed study on the micelle formation vs number of C_8F_{17} group in selected solvents is now in progress.

All of the analytical results by XPS and contact angle measurements using water and dodecane droplets clearly indicate fairly large segregation and surface enrichment of C_8F_{17} group in all the chain-end-functionalized polystyrenes with C_8F_{17} groups herein synthesized. The extent of enrichment always increased with increasing the number of terminal C_8F_{17} group and then saturated at a certain number of C_8F_{17} group in each case. After the saturation, no more increase was attained even by increasing the number of C_8F_{17} group. The saturated values of F atomic % at 10° TOA and contact angle using water or dodecane droplet were generally around 50%, 110−115°, and 55°, respectively. Very importantly, the surface analytical results obtained by XPS and contact angle measurements are similar to each other and the minimum numbers of C_8F_{17} group necessary for the saturation can be estimated from such analytical results. They were approximately between 4 and 8, 4 and 6, and 6 and 8 for **LP**, **LB**, and **L′B** polymer series and 8 and 16, 4 and 8, and 8 and 16 for **DP**, **DB**, and **D′B** polymer series, respectively. More than 8 and 16 C_8F_{17} groups in **L** and **D** type polymers seem not to be required for saturating the surface enrichment.

It has been reported that C_8F_{17} group aligns parallel one another to form a smectic layer structure at the surface because of the liquid crystal character of C_8F_{17} group and CF_3 group having the least surface energy.[77] As mentioned above, the saturated values of F atomic % at 10° TOA were ca. 50% and very close to the values of 49, 47, and 49% calculated from $C_8F_{17}(CH_2)_3{-}O{-}C_6H_4{-}$, $C_8F_{17}(CH_2)_3{-}O{-}CH_2C_6H_4{-}$, and $C_8F_{17}CO{-}O{-}CH_2C_6H_4{-}$ moieties, respectively. These moieties are ~18−21 Å in molecular length based on simple molecular models. The depth from outmost surface analyzable at 10° TOA by XPS is about 20 Å. Therefore, it can be reasonably speculated that the film surfaces are completely covered with the above-mentioned C_8F_{17}-functionalized moieties on the assumption that they are highly ordered and oriented with the chain axis perpendicularly to the surface or even with somewhat leaning angles to the surface in the smectic layer structure. Additional evidence for this speculation is provided by the agreement between oxygen atomic percents observed (2−5%) and calculated (3−6%) and the presence of peaks arising from aromatic carbon.

Since the main chains employed are limited only to polystyrenes having M_{n} values of ca. 20 kg/mol, the influence of the alignment of C_8F_{17} group and the linkage between C_8F_{17} group and main chain on surface structure can be compared. For example, the numbers of C_8F_{17} group required for the saturation in the **D** type polymers were generally more than those in the **L** type polymers. This may possibly be attributed to the highly branched structures and dendritic shapes of C_8F_{17} groups that seem relatively difficult to closely pack on the surfaces. In other words, the dendritic architecture may prevent the packing of C_8F_{17} group in a smectic layered planar domain due to its nonlinear spreading shape, while the ladder architecture of C_8F_{17} group in the **L** type polymers is rather compatible with the smectic layered structure.

It is observed that the phenyl and benzyl ether linkages are more effective than the benzyl ester linkage in surface enrichment irrespective of the architecture of C_8F_{17} group. This can be explained by the presence of the carbonyl group that prevents to some extents the close packing and orientation of C_8F_{17} group on the surface due to the polarity and conformation. In addition, there is no flexible alkyl ether spacer in the ester linkage and therefore the C_8F_{17} group may be restricted to align in the smectic surface layer more than that connected via phenyl or benzyl ether linkage having C_3H_6O spacer. This restriction is especially enhanced in the case of the dendritic architecture.

Conclusions

We have synthesized a variety of novel well-defined chain-end-functionalized polystyrenes with a definite number of C_8F_{17} groups ranging from 2 to 32 in number and examined their surface segregation behaviors of C_8F_{17} group by XPS and contact angle measurements. As expected, all of the C_8F_{17}-functionalized polymers examined herein show fairly large segregation and surface enrichment of C_8F_{17} group. Furthermore, the influence of surface enrichment of C_8F_{17} group on number of C_8F_{17} group could be quantitatively elucidated in each polymer series. Very surprisingly and importantly, the surface analytical results obtained by XPS are similar to or, in some cases, even almost consistent with those by the contact angle measurements using water and dodecane droplets. Accordingly, the extent of the surface enrichment can be readily estimated by the more ready-operated contact angle measurement.

In the present study, the main chains were used only to polystyrenes having M_{n} values of around 20 kg/mol to minimize the effects of composition and molecular weight. Therefore, the information on segregation and surface enrichment herein obtained is also limited in terms of polystyrene main chain and molecular weight. Synthesis and surface characterization studies on C_8F_{17}-chain-end-functionalized polystyrenes with M_{n} values of both lower and higher than 20 kg/mol and other C_8F_{17}-functionalized polymers, whose main chains are polyisoprene (low T_{g}) and water-soluble poly(ethylene oxide), are now in progress in order to elucidate the influence of molecular weight and character of main chain polymer on surface structure. In addition, the uses of other perfluoroalkyl ($(CF_3)_2CFCF_2$, C_4F_9, and C_6F_{13}) moieties are now under investigation.

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