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Synthesis and Surface Characterization of Novel Perfluorooctyl-Functionalized Polymers with Well-Defined Architectures

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Summary: We have successfully synthesized two kinds of novel well-defined chain-end-functionalized polystyrenes with one, two, three, and four perfluorooctyl (C_8F_{17}) groups and structurally analogous block copolymers, poly[styrene-*b*-4-(3-perfluoroocyl)propoxystyrene], by means of living anionic polymerization, followed by the Williamson reaction with $C_8F_{17}(CH_2)_3Br$. The surface properties and compositions of the films prepared from both C_8F_{17}-functionalized polymers have been characterized by contact angles using water and dodecane droplets and angle-dependent XPS measurement. It was observed that C_8F_{17} groups were segregated and preferentially enriched at their topmost surfaces and the extent of the enrichment increased with the number of C_8F_{17} group. The dependence of extent of C_8F_{17} group enrichment on fluorine content however appears to be different between chain-end-functionalized polymer and block copolymer.

Introduction

In general, the surface and interfacial properties of multicomponent polymer systems are different from those of the bulk and may be dominated by chemical species that tend to be preferentially enriched at the surfaces and air-polymer interfaces.[1-4] Among chemical species, perfluoroalkyl (Rf) groups behave especially effectively for preferential enrichment at the surfaces and interfaces because of their low surface free energies. For this reason, surface characterization of homopolymers, random and block copolymers bearing Rf groups and Rf-functionalized segments has widely been investigated so far.[5-11] It is now established that Rf groups are significantly segregated and preferentially enriched at the surfaces and air-polymer interfaces of the films prepared from such Rf-functionalized polymers. As a result, hydrophobic as well as lipophobic surfaces covered with Rf groups are formed. In other words, it is possible to

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intentionally modify the surface properties to the above-mentioned characters by introducing Rf groups into polymers.

Very surprisingly, such segregation and preferential enrichment of Rf group at the film surfaces have also been observed in the films prepared from chain-end-functionalized polymers with Rf group.[12-16] Accordingly, surface properties may possibly be changed by even the minimum amount of Rf group in a polymer chain. However, the influence of the number of Rf group on the surface properties has not been systematically and quantitatively studied. Furthermore, surface characterization studies using structurally analogous chain-end-functionalized polymers with one Rf group and block copolymers having many Rf groups have not yet been realized. Therefore, even at present there seems to be a big gap between both functionalized polymers in understanding how they play roles in surface characterization studies.

Herein, we will synthesize novel chain-end-functionalized polystyrenes with one, two, three, and four perfluorooctyl (C_8F_{17}) groups and a series of structurally analogous block copolymers, poly[styrene-*b*-4-(3-perfluorooctyl)propoxystyrene], by means of living anionic polymerization. The surface properties and compositions of the films prepared from these C_8F_{17}-functionalized polymer will be characterized by contact angle and angle-dependent XPS measurements and discussed with regard to the number of C_8F_{17} groups and polymer structures.

Experimental

Reagents

1-(4-*tert*-Butyldimethylsilyloxyphenyl)-1-phenylethylene (**1**), 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene (**2**), and 4-(*tert*-butyldimethylsilyloxy)styrene was synthesized by the procedure previously reported.[17-18, 19-20] 2-(Perfluorooctyl)ethyl methacrylate (**3**) was purified by distillation over calcium hydride under high vacuum. Styrene and methyl methacrylate (MMA) were washed with 5%NaOH aq., dried with $MgSO_4$, distilled over CaH_2, and then finally distilled from dibutyl magnesium solution or 3 mol-% triethylaluminum solution under high vacuum, respectively. *sec*-Butyllithium (*sec*-BuLi) was used without further purification. 1,1-Diphenylethylene (DPE) was distilled from BuLi solution under vacuum. Lithium chloride (LiCl) was dried under vacuum for 2 days and dissolved in THF. 1,4-Dibromobutane and *N,N*-dimethylformamide (DMF) were distilled over CaH_2. THF was refluxed over Na wire and distilled over lithium aluminum hydride under a nitrogen atmosphere and then distilled from its sodium naphthalene solution on a vacuum line.

Synthesis of 1-bromo-4-*tert*-butyldimethylsilyloxybenzene

tert-Butyldimethylsilylchloride and imidazole (14.5 g, 213 mmol) in DMF (20 mL) was added dropwise to a solution of 1-bromo-4-hydroxybenzene (10.4 g, 69.3 mmol) in DMF (10 mL) at room temperature. The reaction mixture was stirred at rt for 24 h and quenched with a small amount of water. The organic layer was extracted with ether, washed with water, and dried with $MgSO_4$. After removal of ether, distillation under reduced pressure gave pure 1-bromo-4-*tert*-butyldimethylsilyloxybenzene (8.25 g, 30.0 mmol) in 43% yield (bp: 79 °C / 3 mmHg): ^1H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 6H, $SiCH_3$), 0.96 (s, 9H, $SiC(CH_3)_3$), 6.70 and 7.30 (2d, 4H, J=8.7 Hz, Ar); ^{13}C NMR (75 MHz, $CDCl_3$) δ -4.41 ($SiCH_3$), 18.3 ($C(\underline{C}H_3)_3$), 25.7 (SiC), 113.7, 122.0, 132.4, 154.9 (Ar).

Synthesis of 1-(4-bromobutyl)-4-*tert*-butyldimethylsilyloxybenzene

In a two-necked pear-shaped flask, was placed magnesium (1.12 g, 46.1 mmol) and THF (40 mL) under nitrogen atmosphere. After activation of magnesium with 1,2-dibromoethane, 1-bromo-4-*tert*-butyldimethylsilyloxybenzene (7.03 g, 25.6 mmol) in THF (10 mL) was added dropwise at rt and the reaction mixture was stirred at rt for 1 h. A solution of 4-*tert*-butyldimethylsilyloxyphenylmagnesium bromide was added to a solution of 1,4-dibromobutane (13.7 g, 63.5 mmol) and Li_2CuCl_4 (0.405 mmol) in THF (3 mL). After stirring at rt for 30 min, the reaction system was quenched with a small amount of water. The organic layer was extracted with ether and dried with $MgSO_4$. After removal of ether, fractional distillation gave 1-(4-bromobutyl)-4-*tert*-butyldimethylsilyloxybenzene (2.72 g, 8.22 mmol) in 32% yield (bp: 123 °C / 1 mmHg): ^1H NMR (300 MHz, $CDCl_3$) δ 0.16 (s, 6H, $SiCH_3$), 0.96 (s, 9H, $SiC(CH_3)_3$), 1.72 (pentad, 2H, J=7.8 Hz, $ArCH_2C\underline{H_2}$), 1.86 (pentad, 2H, J=6.9 Hz, $BrCH_2C\underline{H_2}$), 2.55 (t, 2H, J=7.5 Hz, $ArCH_2$), 3.39 (t, 2H, J=6.6 Hz, $BrCH_2$), 6.75, 6.98 (2d, 4H, J=8.4 Hz, Ar).

Synthesis of 3-perfluorooctylpropyl bromide

Triphenylphosphine (21.1 g, 80.3 mmol) in THF/CH_2Cl_2 (5 mL/10 mL) was added to a mixture of 3-perfluorooctyl-1-propanol (22.5 g, 53.3 mmol) and carbon tetrabromide (27.1 g, 81.7 mmol) in THF/CH_2Cl_2 (12 mL/25 mL) at 0 °C. The reaction mixture was stirred at rt for 20 h and then quenched with a small amount of water. The organic layer was corrected and dried with $MgSO_4$. After evaporating solvents, the residue was poured into a large amount of hexane to precipitate triphenylphosphine oxide and filtrated. This procedure was repeated 3 times and then fractional distillation gave 3-perfluorooctylpropyl bromide (21.9 g, 40.5 mmol) as a colorless liquid in 76% yield (bp: 64 - 65 °C/3 mmHg): ^1H NMR (300MHz, $CDCl_3$) δ 2.10 (2H, t, J = 5.4 Hz, $CH_2C\underline{H_2}CH_2$), 2.21 (2H, m, $CF_2C\underline{H_2}$), 3.48 (2H, t, J = 6.0 Hz, CH_2Br); ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.0 ($CH_2\underline{C}H_2CH_2$), 30.1 ($CF_2\underline{C}H_2$), 32.2 (CH_2Br).

Chain-end-functionalization reactions

All operations were carried out under high vacuum conditions in the all glass apparatus equipped with break-seals. Polystyryllithium was prepared in THF at -78 °C for 20 min with *sec*-BuLi as an initiator. Both reactions of polystyryllithium with **1** and **2** were carried out in THF at -78 °C for 15 min to afford chain end-functionalized polystyrenes with one and two phenol functions after deprotection. Chain-end-functionalized polystyrene with four phenol groups was synthesized as follows: Polystyryllithium was prepared by polymerization of styrene (18.5 mmol) with *sec*-BuLi (0.0959 mmol) in THF at -78 °C for 20 min. The polystyryllithium was reacted with **2** (0.218 mmol) at -78 °C for 15 min followed by treatment with 1,4-dibromobutane (1.30 mmol) in THF at -78 °C for 30 min to afford ω-bromobutylated polystyrene (**P1**). It was purified by reprecipitation and freeze-drying. Then 0.46 g (0.0225 mmol for bromobutyl group) of **P1** was dissolved in 13 ml of THF. **P1** was added to a solution of 1,1-diphenylalkyl anion produced by **2** (0.248 mmol) with *sec*-BuLi (0.177 mmol) at -78 °C and reacted for 2 h to produce the objective functionalized polystyrene with four phenols after deprotection.

Block copolymerizations

Block copolymerization of 4-(*trert*-butyldimethylsilyloxy)styrene with styrene was carried out in THF at -78 °C for 30 min according to the previous method.[19] Poly(styrene-*b*-**3**) was synthesized by the polymerization of styrene with *sec*-BuLi, end-capping with DPE, followed by the polymerization of **3** in the presence of lithium chloride in THF at -78 °C. Similarly, poly(MMA-*b*-**3**) was synthesized by the sequential polymerization of **3** and MMA with *sec*-BuLi/DPE/LiCl system. The polymers were precipitated by pouring the polymerization mixtures into large amounts of methanol. The precipitated polymers were collected by filtration and purified by reprecipitation from THF solution to methanol and freeze-dried from their benzene solutions.

Deprotection

tert-Butyldimethylsilyl group of the resulting polymer was completely removed by treating the polymer with a 5-fold excess of $(C_4H_9)_4NF$ in THF at rt for 2 h. For instance, $(C_4H_9)_4NF$ (0.30 mmol) in THF (1.2 mL) was added to a solution of four-functionalized polystyrene (0.30 g, 0.054 mmol) in THF (20 mL) at rt for 2 h. The reaction mixture was poured into methanol to precipitate the polymer. The collected polymer was purified by reprecipitation two times using THF/methanol and freeze-dried from its benzene solution. Poly[styrene-*b*-4-(*tert*-butyldimethylsilyloxy)styrene] was similarlly deprotected.

Introduction of perfluoroalkyl groups

The phenol functions introduced in the resulting polymers were quantitatively transferred into perfluoroalkyl group by Williamson reaction as follows: NaH (5.0 mg, 0.21 mmol) was added to a solution of polystyrene with four hydroxyphenyl groups (0.21 g, 0.038 mmol) in DMF (10 mL) and stirred at rt for 1 h to generate the corresponding sodium phenoxides. Perfluorooctylpropyl bromide (0.41 g, 0.76mmol) in DMF (2 mL) was added dropwise into the solution at 0 °C and stirred at rt for 12 h. The reaction mixture was poured into water to quench the residual NaH. The organic layer was corrected, poured into large amount of methanol to precipitate the polymer. It was finally purified by column chromatography with benzene as eluent and freeze-dried. Poly[styrene-*b*-4-(perfluorooctyl)propoxystyrene] was similarly synthesized.

Measurement

^{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 tetramethylsilane (δ 0) for ^{1}H NMR and relative to chloroform-*d* (δ 77.1) for ^{13}C NMR as standards. Size-exclusion chromatograms (SEC) were obtained 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. The molecular weights and the molecular weight distributions of polymers were determined by SEC using the calibration of polystyrene standard. TLC-FID was performed by IATRON IATROSCAN NEW MK-5. Contact angle of the polymer film was measured with a Kyowa Interface Science CA-A. 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 measurement were prepared by spin coating (4000 rpm, 20 seconds) onto cover glasses from 5 wt% polymer solution of benzene. The sample was dried at room temperature one night and annealed for 2 h at 80 °C under vacuum.

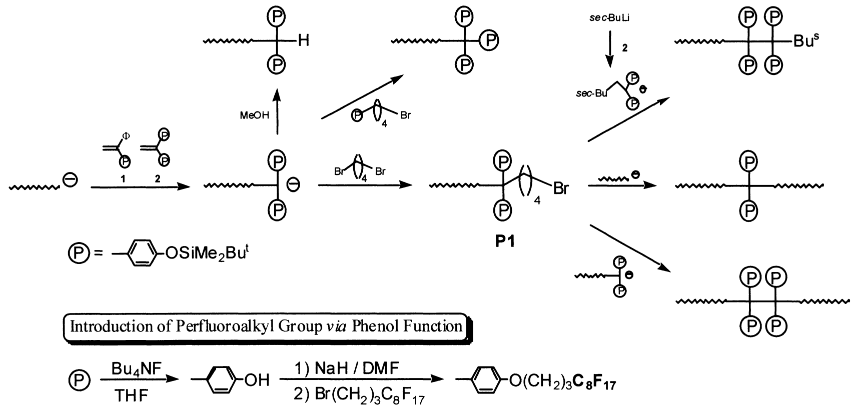
Results and Discussion

Synthesis of chain-end-functionalized with one, two, three, and four C_8F_{17} groups with well-defined architectures

For the synthesis of chain-functionalized polymers with a definite number of functional groups, we have recently been developing a new general, versatile methodology, which involves diverse modes of addition and coupling reactions of living anionic polymers with functionalized DPE derivatives. By developing this methodology, novel chain-end- and in-chain-functionalized polymers with plural benzyl halide moieties,[21-24] monosaccharide residues,[25] α-methylstyryl, 1,3-butadienyl, [26] and anhydride[27] groups have successfully been synthesized. These polymers were quantitatively functionalized in desired numbers as well as precisely controlled with respect to chain length. The numbers of the introduced functional groups are usually among one and four but reached to more than ten and sixteen in a certain case.

In this section, novel well-defined chain-end-functionalized polystyrenes with one, two, three, and four perfluorooctyl (C_8F_{17}) groups have been synthesized by utilizing the above-mentioned methodology. Although the direct use of C_8F_{17}-functionalized DPE derivative would be the most effective for such polymer syntheses, it may be difficult because Rf groups are generally not compatible with living anionic polymer of styrene and highly reactive anionic initiators like organolithium compounds. Therefore, a definite number of phenol functions have been first introduced at polystyrene chain-ends followed by introduction of C_8F_{17} groups *via* the phenol functions by means of

Williamson reaction. Both 1-(4-*tert*-butyldimethylsilyloxyphenyl)-1-phenylethylene (**1**) and 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene (**2**) were used as phenol-functionalized agents. The synthetic procedure is illustrated in Scheme 1.



Scheme 1. Synthetic route of end-functionalized polystyrenes with one, two, three, and four perfluorooctyl groups.

Chain-end-functionalized polystyrenes with one and two phenols were synthesized by the addition reaction of polystyryllithium to **1** and **2**, respectively. The silyl group was quantitatively deprotected to regenerate phenol function by treatment with $(C_4H_9)_4NF$ in THF. Chain-end-functionalized polystyrene with three phenols was synthesized by the addition reaction of polystyryllithium to **2** and the subsequent *in-situ* reaction with 1-(4-bromobutyl)-4-*tert*-butyldimethylsilyloxybenzene. In order to synthesize chain-end-functionalized polystyrene with four phenols, a prepolymer (**P1**) was first prepared by the reaction of polystyryllithium with **2**, followed by treatment with a 10-fold excess of 1,4-dibromobutane. The objective polystyrene with four phenol termini was obtained by the reaction of the prepolymer with the anion prepared from **2** and *sec*-BuLi. Since phenol-functionalized polystyrenes are not stable in the air because of oxidation of the phenol functionalities, they were characterized prior to deprotection step. The results are summarized in Tab. 1.

Table 1. Synthesis of end-functionalized polystyrenes with one, two, three, and four *tert*-butyldimethylsilyloxy groups[a), b)]

code	*sec*-BuLi	styrene	DPE deriv.	R-Br	*Mn* X 10^{-3}		*Mw/Mn*	functionality	
	mmol	mmol	type, mmol	mmol	calc	obs[c)]		calc	obs[d)]
E-1	0.0429	9.86	**1**, 0.0677	-	24.6	26.8	1.02	1	1.0_0
E-2	0.0851	16.8	**2**, 0.107	-	21.7	19.6	1.04	2	2.0_0
E-3	0.0762	14.5	**2**, 0.116	**3**, 0.171	21.2	19.3	1.03	3	2.8_8
E-4	0.177	-	**2**, 0.248	**P1**, 0.0225	21.1	22.1	1.02	4	4.0_2

a) in THF at -78 °C for 30 min.
b) Yields of polymers were quantitative in all cases.
c) Determined by SEC.
d) Determined by ^{1}H NMR.

All of the polymers showed symmetrical monomodal SEC peaks with narrow molecular weight distributions. The observed M_n values by SEC agreed well with those calculated from [M]/[I]. The degrees of end-functionality were determined by ^{1}H NMR using two resonances at 0.24 ppm (silylmethyl protons) and at 0.70 ppm (methyl protons of the initiator fragment). The observed values are very close to those predicted as expected.

As mentioned before, the silyl groups were deprotected with $(C_4H_9)_4NF$ in THF. Quantitative deprotection was confirmed by the observation that two resonances at 1.0 and 0.24 ppm characteristic to the *tert*-butyldimethylsilyl group completely disappeared in each ^{1}H NMR spectrum of all polymer samples. In order to introduce C_8F_{17} groups *via* phenol functions, the phenols thus regenerated were first reacted with a 5-fold excess of NaH in DMF at 25 °C for 1 h, followed by *in-situ* reaction with a 20-fold excess of $C_8F_{17}(CH_2)_3Br$ at 25 °C for 12 h. The results are summarized in Tab. 2. The resulting polymers all showed symmetrically monomodal SEC peaks with remaining their molecular weight distributions narrow. Typical examples, E-2 and E-4, were shown in Fig. 1. The M_n values observed by SEC were in good agreement with those calculated. The degrees of C_8F_{17}-end-functionalization were determined by ^{1}H NMR using two resonances at 4.0 ppm (methylene protons attached to phenoxy group) and 0.70 ppm (methyl protons of the initiator fragment). Agreement between observed and predicted values is quite satisfactory in each sample. Thus, the resulting polymers all were quantitatively end-functionalized within analytical errors and well controlled with respect to chain length. The objective chain-end-functionalized polystyrenes with one, two, three, and four C_8F_{17} groups were successfully synthesized. The results also confirmed that both the reactions to introduce phenol and C_8F_{17} groups proceeded satisfactorily as desired. For comparison with other polymer samples, molecular weights of chain-end-functionalized polystyrenes were designed to be *ca* 20 kg/mol order.

Table 2. End-functionalized polystyrenes with one, two, three, and four Rf groups

code	Mn X 10^{-3}		Mw/Mn	functionality	
	calc	obs[a)]		calc	obs[b)]
E-1	27.7	27.6	1.02	1	1.0_0
E-2	20.0	20.2	1.02	2	2.0_5
E-3	20.5	20.4	1.02	3	3.1_9
E-4	24.8	23.8	1.06	4	4.0_0

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

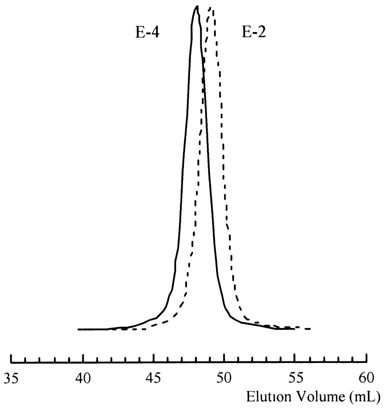
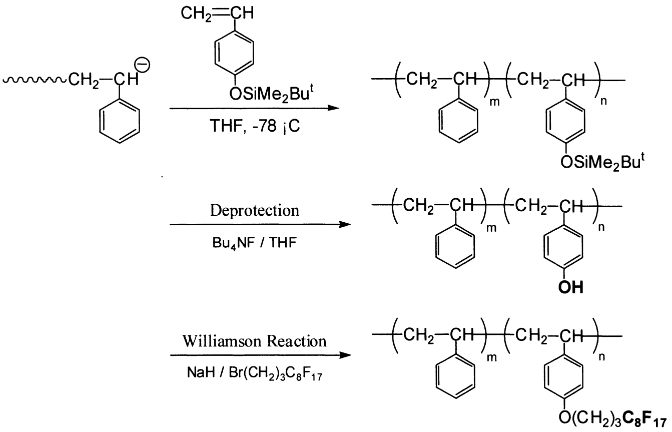


Figure 1. SEC curves of end-functionalized polystyrene with two (E-2) and four (E-4) perfluorooctyl groups.

Synthesis of well-defined block copolymers, poly[styrene-*b*-4-(3-perfluorooctyl)propoxystyrene], poly[styrene-*b*-2-(perfluorooctyl) ethyl methacrylate], and poly[MMA-*b*-2-(perfluorooctyl)ethyl methacrylate]

In the preceding section, we successfully synthesized well-defined chain-end-functionalized polystyrenes with one, two, three, and four C_8F_{17} groups. As will be mentioned later, the number of the C_8F_{17} group introduced is significantly affected on the surface structure. Accordingly, chain-end-functionalized polystyrenes with more than five C_8F_{17} groups are of particularly interest in this regard. Although it is potentially possible to introduce even sixteen functional groups at chain-end by the methodology developed by our group, the synthetic route is relatively complicated and involves time-consuming process. Instead, herein we have synthesized a series of structurally analogous new block copolymers, poly[styrene-*b*-4-(3-perfluorooctyl)propoxystyrene] by means of living anionic polymerization. Very fortunately, we were previously successful in achieving the living anionic polymerization of 4-vinylphenol by the protection of phenol function with *tert*-butyldimethylsilyl group during the polymerization.[17-18] Therefore, block copolymers of styrene with 4-vinylphenol with any desired compositions can readily be synthesized. As illustrated in Scheme 2, new block copolymers containing functionalized segments with C_8F_{17} groups have been synthesized by living anionic block copolymerization of styrene with silyl-protected 4-vinylphenol, followed by deprotection, and the subsequent Williamson reaction of the resulting block copolymer, poly(styrene-*b*-4-vinylphenol), with $C_8F_{17}(CH_2)_3Br$ under the same conditions as mentioned before. The results are summarized in Tab. 3. The resulting block copolymers showed sharp monomodal SEC peaks without any shoulders and tailings. The M_n values observed by SEC coupled with ^{1}H NMR were always in good agreement with those predicted. Their molecular weight distributions remained very narrow after two steps of deprotection and the Williamson reaction. All M_w/M_n values were observed to be less than 1.05. These results strongly indicate that the resulting block copolymers are the expected block copolymers with well-defined architectures. Typical SEC trace of the block copolymer is shown in Fig. 2. The fluorine contents of the block copolymers were in the range from 11.2 to 29.1 wt-

% that corresponded to six to eighteen C_8F_{17} groups at the chain-ends. They were always higher than those of chain-end-functionalized polystyrenes with C_8F_{17} groups. The numbers of C_8F_{17} group introduced in such block copolymers are, needless to say, not exactly definite but average values.



Scheme 2. Synthetic route of poly[styrene-*b*-4-(3-perfluorooctyl)propoxystyrene].

Table 3. Synthesis of poly[styrene-*b*-4-(perfluorooctylpropoxy)styrene]

code	*Mn* X 10^{-3}		*Mw/Mn*	number of	fluorine content
	calc	obs[a)]		Rf groups[b)]	wt-%
B-11	22.2	21.3	1.02	7.4	11.2
B-16	12.8	12.5	1.02	6.3	16.3
B-17	22.8	23.2	1.03	12.4	17.3
B-19	30.5	29.4	1.04	17.6	19.3
B-21	17.5	16.4	1.05	15.3	20.9
B-29	16.1	17.0	1.03	10.6	29.1
Ba-13[c)]	24.7	21.9	1.03	9.2	13.0
Bb-13[d)]	29.2	29.2	1.02	23.0	13.3

[a)] Determined by SEC.
[b)] Degree of polymerizatin of poly[4-(perfluorooctylpropoxy)styrene] segment.
[c)] poly[styrene-*b*-2-(perfluorooctyl)ethyl methacrylate].
[d)] poly[MMA-*b*-2-(perfluorooctyl)ethyl methacrylate].

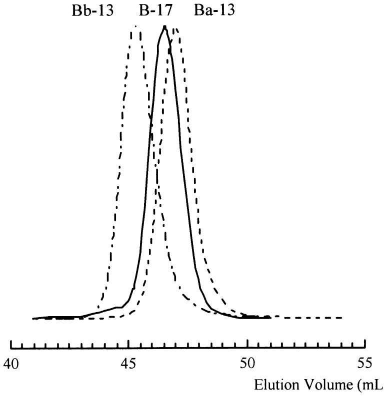


Figure 2. SEC curves of poly[styrene-*b*-4-(3-perfluorooctyl)propoxystyrene] (B-19), poly[styrene-*b*-2-(perfluorooctyl)ethyl methacrylate] (Ba-13), and poly[MMA-*b*-2-(perfluorooctyl)ethyl methacrylate] (Bb-13)

In order to compare the chemical composition of block copolymer, new two block copolymers were also synthesized in this study. In these polymer syntheses, 2-(perfluorooctyl)ethyl methacrylate (**3**) was used for preparing the functionalized segment with C_8F_{17} group. The block copolymer, poly(styrene-*b*-**3**) (Ba-13), was synthesized by living anionic polymerization with sequential addition of two monomers, styrene and **3** in this order. Similarly, poly(MMA-*b*-**3**) (Bb-13) was synthesized by the sequential polymerization of MMA and **3** in this order. The results are also summarized in Tab. 3. The resulting two block copolymers were observed to possess well-controlled structures with respect to chain length and composition. Their SEC traces are also shown in Fig. 2. Since architectural parameters of chain-end-functionalized polystyrenes and functionalized block copolymers are thus defined as much as possible, these Rf-functionalized polymers are considered to be suitable model polymers for elucidating fundamental understanding regarding the effect of the number of Rf group on surface structure and property.

Surface Characterization of Chain-End-Functionalized Polystyrene with C_8F_{17} Groups

At first, the surfaces of the annealed films prepared from chain-end-functionalized polystyrenes with C_8F_{17} groups were characterized by contact angle measurements using water and dodecane droplets. The results are summarized in Tab. 4. The contact angle of water droplet increased with the number of C_8F_{17} group and was always higher than 91.3°, the value of the film prepared from polystyrene end-capped with DPE (M_n = 23 kg/mol) used as a reference polymer. A similar result was obtained by contact angle measurement using dodecane droplet. All the polystyrenes end-functionalized with C_8F_{17} groups showed measurable contact angles, while the film surface of the polystyrene covered with dodecane. Thus, the surfaces exhibited more hydrophobic as well as lipophobic characters, strongly indicating that the C_8F_{17} group was preferentially enriched at the surface of each film. It was also observed that the values increased with the number of C_8F_{17} group. It should be mentioned that the contact angle value using dodecane droplet gradually decreased with time and reached to 10 ~ 25° after 20 seconds. Therefore, the value after 1 min was listed herein in each sample and discussed. Dodecane may possibly be soaked into the film surface and dissolve the polystyrene layer under the first layer covered with C_8F_{17} groups.

Table 4. Surface characterization of end-functionalized polystyrenes with Rf groups

code	Fluorine content [wt-%]	contact angle [°]		XPS atomic-% (F / C)		
		water	dodecane	10 ° TOA[a]	80 ° TOA	bulk
E-1	1.43	95.4	15.7	12.9 / 86.1	3.66 / 96.2	0.80 / 99.2
E-2	3.06	99.4	32.8	26.9 / 71.5	10.3 / 87.4	2.2 / 97.8
E-3	4.50	105	40.4	39.0 / 59.3	13.9 / 84.7	3.2 / 97.8
E-4	5.19	111	47.8	57.1 / 40.5	32.3 / 65.6	3.6 / 96.2
PS[b)]	0	91.3	ND[c)]	-	-	-
$C_8F_{17}(CH_2)_3O$	-	-	-	-	-	58.6 / 37.9

[a)] Take-off Angle; the values of 10 ° and 80 ° correspond 20 Å and 100 Å depths, respectively.
[b)] Polystyrene end-capped with 1,1-diphenylethylene (*Mn* = 24 kg/mol, *Mw/Mn* = 1.03).
[c)] Not detecable. The film surface was covered with dodecane.

These observations can be quantitatively followed by angle-dependent XPS measurement. The surface compositions as a function of depth were measured at take-off angles (TOA) of 10° and 80°, which approximately corresponded to 20 Å and 100 Å depths from topmost surface, respectively. The results are also listed in Tab. 4. It was observed in all the films that both F/C atomic percent ratios measured at 10° and 80° TOAs were much higher than they were in bulk. Moreover, the F/C values at 10° TOA were always higher than those at 80° TOA. Thus, the film topmost surface shows a marked enhancement of C_8F_{17} group in each case. As could be expected from the results of contact angle, the F/C value increased with the number of C_8F_{17} group. It is thus evident that the number of the C_8F_{17} group introduced at the chain-end significantly affects the surface structure. This is, to the best of our knowledge, the first clear and quantitative demonstration on the effect of the number of C_8F_{17} group on the surface structure.

The maximum F/C value measured at 10° TOA was 57.1/40.5 in the film of E-4. Very interestingly, this value is very closed to 58.6/37.9 of the value calculated from $C_8F_{17}(CH_2)_3O$ group of a part of functionalized moiety. The length of the moiety is estimated to be around 15 ~ 18 Å based on the simple molecular model. As mentioned before, the analyzable depth from topmost surface at 10° TOA is about 20 Å. It is therefore indicated that the surface of the film is completely covered with $C_8F_{17}(CH_2)_3O$ moiety if this moiety would be highly ordered and oriented with the chain axis perpendicularly to the surface.

Surface Characterization of Block Copolymers Containing C_8F_{17}-Functionalized Segments

In this section, the surfaces of the annealed films prepared from the block copolymers containing C_8F_{17}-functionalized segments were similarly characterized by using contact angle and angle-dependent XPS measurements. At first, a series of poly[styrene-*b*-4-(3-perfluorooctyl)propoxystyrene] were examined. As mentioned before, these block copolymers are analogous in structure to the chain-end-functionalized polystyrenes and possess more numbers of C_8F_{17} group. In the case of the block copolymer, however, the number of C_8F_{17} group is not exactly proportional to the fluorine wt-% in some case, since the molecular weight of the polystyrene block is not equal to each other. In addition, their total molecular weights range from 12.5 to 29.4 kg/mol. Therefore, the fluorine wt-% is used instead of the number of C_8F_{17} group in the series of block copolymers. The analytical results are summarized in Tab. 5.

Table 5. Surface characterization of poly[styrene-*b*-4-(perfluorooctylpropoxy)styrene]

code	fluorine content [wt-%]	contact angle [°]		XPS Atomic-% (F / C)		
		water	dodecane	10 ° TOA[a]	80 ° TOA	bulk
B-11	11.2	107	48.7	43.1 / 54.3	24.0 / 74.2	7.89 / 92.0
B-16	16.3	108	53.4	45.9 / 48.1	19.2 / 78.8	11.2 / 88.2
B-17	17.3	111	58.4	46.7 / 51.9	33.9 / 55.3	12.5 / 86.7
B-19	19.3	112	67.3	56.0 / 42.1	40.2 / 57.1	13.5 / 85.7
B-21	20.9	104	67.2	55.6 / 40.4	41.6 / 53.4	13.4 / 85.9
B-29	29.1	115	67.4	54.9 / 42.6	38.1 / 56.4	20.9 / 77.9
Ba-13[b]	13.0	105	43.5	33.3 / 62.6	15.4 / 83.0	9.27 / 89.6
Bb-13[c]	13.3	92.4	31.8	16.7 / 61.9	5.54 / 67.8	10.2 / 65.7

[a] Take-off Angle; 10 ° ~ 20 Å, 80 ° ~ 100 Å.
[b] poly[styrene-*b*-2-(perfluorooctyl)ethyl methacrylate].
[c] poly[MMA-*b*-2-(perfluorooctyl)ethyl methacrylate].

The values of contact angle using water droplet showed similar values in all the films, although the fluorine wt-% increased from 11.2 to 29.1 %. They were comparable to those of E-3 and E-4. In contrast, all values of contact angle with dodecane droplet were higher than that of E-4. The value measured by dodecane droplet increased by 19.3 % of the fluorine wt-% and saturated to *ca.* 67° in the range of 19.3 ~ 29.1 fluorine wt-%. These values were unchanged even after 30 min. This may be reasonable because of higher fluorine percents of the block copolymers. This also indicates that the use of dodecane is more sensitive and effective than that of water to elucidate the surface structure of this kind of block copolymer.

The surface compositions at 10 Å and 80 Å TOAs of all films were determined by angle-dependent XPS measurement. The results are also summarized in Tab. 4. Again as expected, all films of the block copolymers show marked surface segregation and preferential enrichment of the C_8F_{17}-functionalized segments. The tendencies that were observed in the block copolymers are similar to those in chain-end-functionalized polystyrenes, i.e., F/C values at 10° TOA > 80° TOA > bulk. The F/C value was observed to increase by 19.3 % of fluorine wt-% and became constant in the range of 19.3 ~ 29.1 fluorine wt-%. This is quite consistent with the result by contact angle measurement with dodecane droplet.

The F/C values of B1-4, B1-5, and B1-6 were 56.0/42.1, 55.6/40.4, and 54.9/42.6, respectively, and close to 58.6/37.9 calculated from $C_8F_{17}(CH_2)_3O$ moiety. These values are also comparable to that of E-4, indicating that the imagined surface structures from topmost to 20 Å depth are very similar to that of E-4 as mentioned before. Rather surprisingly, the block copolymers with fluorine contents less than 17.3 wt-% showed lower F/C values, although their fluorine contents were still much higher than 5.19 wt-% of E-4.

On the other hand, the contact angle values using dodecane droplet of the block copolymers were higher than that of E-4. Furthermore, their values were unchanged even after 1 h. This is in a marked contrast to the observation that the contact angles of the chain-end-functionalized polystyrenes decrease with time as mentioned in the preceding section. Since F/C values at 80° TOA and total fluorine contents of the block copolymers are much higher than those of chain-end-functionalized polymers, the C_8F_{17}-functionalized segments may be existed to some extents in lower layers under the first layers from topmost to 20 Å depth. Therefore, soaking of dodecane into the film surfaces may be prevented from these layers.

Fig. 3 shows the relationship between F/C value measured at 10° TOA and fluorine wt-%. As can be seen, the F/C value abruptly increases with the fluorine wt-% in chain-end-functionalized polystyrenes, whereas it gradually increases by 19.3 % of the fluorine wt-% and then saturated with higher fluorine wt-% of 19.3 ~ 29.1 % in the series of block copolymers. Both curves are not fitted, although it can be observed how the fluorine percent affects the surface composition. Higher F/C values were observed in E-3 and especially E-4 taking their fluorine percents into consideration. Obviously, the dependence of F/C value with fluorine wt-% appears to be different between chain-end-functionalized polystyrene and the block copolymer. At present there is no clear explanation for this. Since the C_8F_{17}-functionalized segments of the block copolymers are analogous to but somewhat different in microstructure from those of the chain-end-functionalized polymers, it would be necessary to introduce more C_8F_{17} groups at the chain-end by using our methodology previously reported and compare their data in the future surface studies. In addition, the molecular weight of the polystyrene part may also be influenced on the surface structure to a certain extent. In the case of chain-end-functionalized polystyrenes, their polystyrenes were similar in molecular weight, whereas molecular weights of the polystyrene blocks relatively varied in the series of the block copolymers. Therefore, we are now considering that the molecular weight of polystyrene block should be controlled to be equal and again characterized.

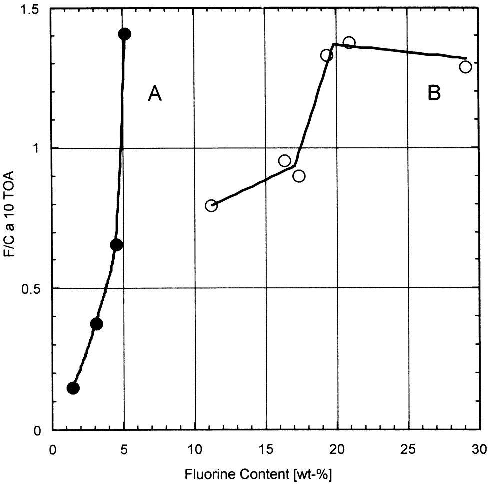


Figure 3. F/C values at 10 ° TOA of (A) end-functionalized polymer and (B) block copolymer as a function of fluorine content.

The surface characterization studies have also been carried out with use of two different functionalized block copolymers, poly(styrene-*b*-**3**) and poly(MMA-*b*-**3**). Both polymer films were studied under the same conditions to examine any possible effects due to the difference by chemical compositions of both non-functionalized block and C_8F_{17}-functionalized segment. The results are also summarized in Tab. 5. The first block copolymer also showed a preferential enrichment of the C_8F_{17}-functionalized segment. The extent was however somewhat lower than that of poly[styrene-*b*-4-(3-perfluorooctyl)propoxystyrene] with comparable parameters (B-11). Very surprisingly, the C_8F_{17}-functionalized segment of the poly(MMA-*b*-**3**) was not found preferentially at the surface by considering the results of XPS measurement as well as contact angle using water droplet. Thus, there appears to be some dependence of surface enrichment of C_8F_{17}-functionalized segment on the chemical composition of block copolymer. The influence of the number of C_8F_{17} group (or fluorine wt-%), the microstructure of the C_8F_{17}-functionalized segment, and chemical composition of block copolymer on the surface structure is now under investigation.

Conclusion

We have herein synthesized two kinds of novel well-defined C_8F_{17}-functionalized polymers, chain-end-functionalized polystyrenes with C_8F_{17} groups and structurally analogous block copolymers. Their annealed films were characterized by contact angles using water and dodecane droplets and angle-dependent XPS. It has been observed in all the film that C_8F_{17} group is segregated and preferentially enriched at the topmost surface in each of all cases. As expected, the extent of the surface enrichment is observed to be significant affected by the number of C_8F_{17} group. Different dependence is however observed between chain-end-functionalized polystyrenes with C_8F_{17} groups and structurally analogous block copolymers.

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