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Precise Synthesis and Surface Characterization of Well-Defined Chain-End-Functionalized Polystyrenes with Two, Four, Eight, Sixteen and Thirty-Two Perfluorooctyl Groups

Kenji Sugiyama, Shiko Sakai, Ashraf El-Shehawy, Akira Hirao*

Department of Organic and Polymeric Materials, Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro-ku, Tokyo, 152-8552, Japan
Tel: +81-3-5734-2131, Fax: +81-3-5734-2887
E-mail: ksugiyam@polymer.titech.ac.jp

Summary: A series of well-defined chain-end-functionalized polystyrenes with a definite number of two, four, eight, sixteen, and thirty-two C_8F_{17} groups have been successfully synthesized by applying the recently developed methodology based on an iterative divergent approach. These polymers were precisely controlled in chain length and degree of end-functionalization. The surface structures of films cast from these polymers have been characterized by XPS and contact angle measurements. Significant segregation and preferential enrichment of C_8F_{17} group at the surfaces were observed in all films. The surface enrichment estimated from F atomic % measured by XPS increased markedly with increasing the number of C_8F_{17} group from two to four, but almost saturated at the number of four where the F atomic % from top surface to 20 Å depths was 44.2 %. The surface enrichment was enhanced only a small extent by further increasing the number of C_8F_{17} group, although the maximum values (49.8 %) were obtained with chain-end-functionalized polystyrenes with sixteen and thirty-two C_8F_{17} groups.

Keywords: anionic polymerization; dendrimers; ESCA/XPS; fluoropolymers; functionalization of polymers

Introduction

The surface and/or air-polymer interfacial properties of multi-component polymer systems such as random and block copolymers and polymer blends can be quite different from those of bulk and may be dominated by certain chemical species that are enriched preferentially at the surfaces.

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The most typical example of such chemical species is a series of perfluoroalkyl (Rf) groups having low surface free energies. In fact, Rf groups introduced into multi-component polymer systems are segregated and enriched preferentially at the surfaces, resulting in the formation of characteristic hydrophobic and lipophobic surfaces. Thus, the preferential enrichment of Rf group can lead to drastic change of the surface properties. For this reason, many studies on the surface characterization of such polymer systems have so far been reported.[1-8] Furthermore, segregation and surface enrichment phenomena of chain-end-functionalized polymers with Rf group have recently observed.[9-13] Even one terminal Rf group, followed by the enrichment at the surface, can profoundly influence the surface property.

Recently, we have successfully synthesized a series of well-defined chain-end-functionalized polystyrenes with a definite number of one, two, three, and four perfluorooctyl (C_8F_{17}) groups by living anionic polymerization using specially designed 1,1-diphenylethylene (DPE) derivatives and characterized their film surface structures by XPS and contact angle measurements.[14-15] As comparison, we also synthesized and characterized structurally analogous well-defined AB diblock copolymers, polystyrene-*block*-poly[4-(3-perfluorooctylpropoxy)styrene] whose C_8F_{17} groups varied in the range from 7.1 to 31.8 in average number. Structures of these new polymers are shown in Figure 1.

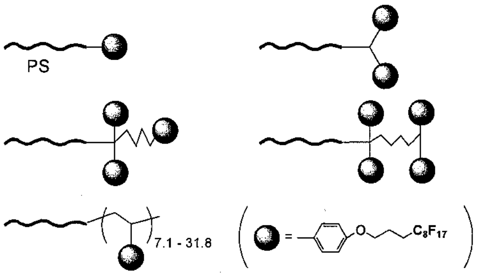

Figure 1. Structures of chain-end-functionalized polystyrenes and block copolymers having C_8F_{17} groups.

It has been observed for the first time that the degree of surface enrichment of C_8F_{17} group estimated from F atomic % from top surface to 20 Å depths increases with increasing the number

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of C_8F_{17} group in both chain-end-functionalized polymers and block copolymers. However, the dependence of number of C_8F_{17} group on F atomic % is quite different between both polymers as shown in Figure 2. Interestingly, the F atomic % of chain-end-functionalized polystyrene with four C_8F_{17} groups reached to the value estimating that the surface was completely covered with C_8F_{17} groups, while fourteen C_8F_{17} groups in the series of the block copolymer was needed to obtain the same value. As can be seen, the two curves are not fitted and discontinuous to each other. In addition, there is no data between them.

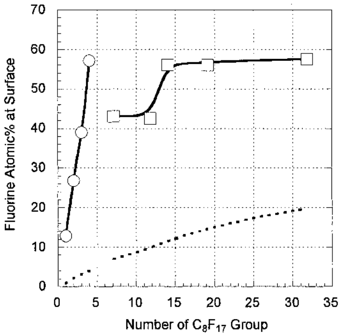

Figure 2. Fluorine atomic % at surface as a function of number of C_8F_{17} group. ○: Chain-end-functionalized polystyrene, □: block copolymer, and calculated value in bulk (dashed line).

Very recently, we have developed a novel methodology based on an iterative divergent approach, by which benzyl bromide moiety can be greatly increased in number with 2^n by repeating the iterative reaction sequence.[16-17] By applying this methodology to the synthesis of C_8F_{17}-chain-end-functionalized polystyrenes, we have been successful in synthesizing chain-end-functionalized polystyrenes with a definite number of many C_8F_{17} groups up to thirty-two. Herein, we report on the successful synthesis of such new C_8F_{17}-chain-end-functionalized polystyrenes and their film surface characterization by XPS and contact angle measurements in order to bridge the gap between the two curves mentioned above and further elucidate the relationships of number of C_8F_{17} groups on surface structure.

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Experimental

Materials

Tetrahydrofran (THF) was refluxed over sodium wire, distilled over $LiAlH_4$ under nitrogen and finally distilled from its sodium naphthalene under high vacuum (10^{-6} torr). *sec*-Butyllithium (*sec*-BuLi) (Nakarai Chemicals, Japan) was used without further purification. Styrene (Tokyo Kasei, Japan) was washed with 5% NaOH, dried over $MgSO_4$, and distilled over CaH_2 under reduced pressure. After adding Bu_2Mg (3 mol-%), styrene was finally distilled under high vacuum (10^{-6} torr). 1,1-Bis(4-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**) and 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl) ethylene (**2**) were synthesized according to the procedure previously reported.[18-19] Chain-end-functionalized polystyrenes with two, four, eight, and sixteen benzyl bromide moieties (**PS(BnBr)$_2$**, **PS(BnBr)$_4$**, **PS(BnBr)$_8$**, **PS(BnBr)$_{16}$**) were synthesized according to the method reported previously.[16-17] The polymerizations and reactions were carried out under high vacuum conditions using break seal technique, reported elsewhere.[17]

Synthesis of chain-end-functionalized polystyrenes with phenol groups

The phenol-functionalized polystyrenes were synthesized by the reaction of polystyrenes having benzyl bromide moieties with the functionalized 1,1-diphenylalkylanion prepared from *sec*-BuLi and **2**, followed by deprotection of the silyl groups with $(C_4H_9)_4NF$ in THF. A typical experiment was as follows: A THF solution (4.5 mL) containing **PS(BnBr)$_2$** (0.39 g, 0.0396 mmol for benzyl bromide moiety) was added to the 1,1-diphenylalkylanion prepared from *sec*-BuLi (0.0667 mmol) and **2** (0.0936 mmol) in THF (6.5 mL) at –78 °C and the reaction mixture was allowed to stand for additional 4 h at –78 °C. After quenching with degassed methanol, the reaction mixture was evaporated to *ca.* 2 mL and poured into methanol to precipitate the polymer. The polymer was reprecipitated twice from THF to methanol and freeze-dried from its absolute benzene for 24 h. It was characterized by ^1H and ^{13}C NMR, IR, and SEC, respectively.

The deprotection was carried out by treating the polymer with a 5-fold excess of $(C_4H_9)_4NF$ in THF. The polymer (0.29 g) dissolved in THF (5.0 mL) was mixed with a THF solution (1.5 mL) containing $(C_4H_9)_4NF$ (1.5 mmol) and the reaction mixture was stirred at 25 °C for 2 h under an

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atmosphere of nitrogen. After evaporation to *ca.* 2 mL of solution, the solution was poured into methanol to precipitate the polymer. It was reprecipitated twice from THF to methanol, freeze-dried from its absolute benzene solution for 24 h, and used for the next Williamson reaction.

Synthesis of chain-end-functionalized polystyrenes with C_8F_{17} groups

The plural number of C_8F_{17} groups was introduced *via* the phenol functions by a Williamson reaction with $C_8F_{17}(CH_2)_3Br$ in DMF under an atmosphere of nitrogen. Sodium hydride (9.7 mg, 0.40 mmol) was added to a DMF solution (8.0 mL) containing chain-end-functionalized polystyrene with four phenols (0.28 g, 0.0571 mmol for phenol) and the reaction mixture was stirred at 25 °C for an additional 1 h. Then, 3-perfluorooctylpropyl bromide (0.29 g, 0.54 mmol) dissolved in DMF (3.0 mL) was added dropwise to the solution at 0 °C for 0.5 h and the mixture was allowed to stir at 25 °C for 24 h. Water was cautiously added to destroy the residual NaH. The organic layer was collected and poured into methanol to precipitate the polymer. The polymer was purified by column chromatography using benzene and freeze-dried from its absolute benzene solution for 24 h. The resulting polymers were characterized by ^{1}H, ^{13}C, and ^{19}F NMR, IR, SEC, and TLC coupled with flame ionization detector (FID), respectively.

Film preparation

The polymer films for contact angle and XPS measurements were prepared by spin coating (4000 rpm, 20 seconds) onto cover glasses from 3.0 - 5.0 wt-% benzene solution of the polymer. The film sample was dried at 25 °C for 24 h and annealed for 2 h at 110 °C under vacuum to allow the chains to reach their equilibrium configurations.

Measurements

^{1}H and ^{13}C NMR spectra were measured on a BRUKER DPX300 in $CDCl_3$. Chemical shifts were recorded in ppm downfield relative to $(CH_3)_4Si$ (δ 0 ppm) for ^{1}H NMR and relative to $CDCl_3$ (δ 77.1 ppm) for ^{13}C NMR as standards. Size-exclusion chromatograms (SEC) were measured with a TOSOH HLC-8020 at 40 °C equipped with ultraviolet (254 nm) and refractive index detections. THF was a carrier solvent at a flow rate of 1.0 mL/min. Calibration curves were made with standard polystyrene to determine M_n and M_w/M_n values. TLC coupled with flame ionization detector (FID) was performed by IATRON IATROSCAN NEW MK-5

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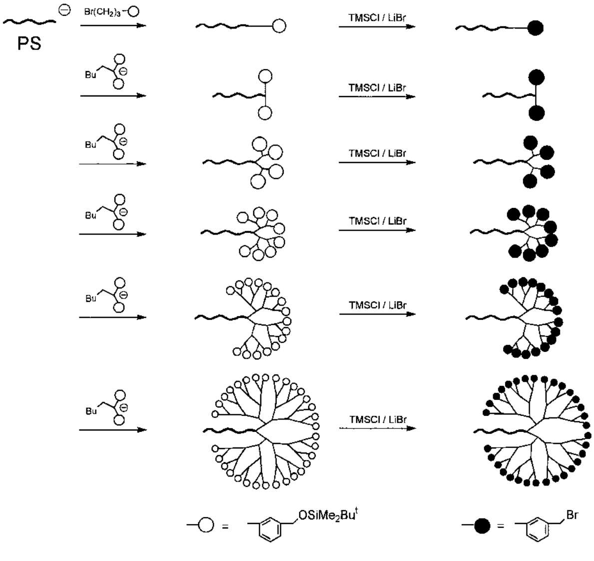
equipped with IATROCORDER TC-21 from Iatron Co., Ltd. Specially designed quartz rods (150 mm x 2.0 mm) were used on which silica gel was sintered. Contact angles of the polymer films were measured with a Kyowa Interface Science CA-A using water and dodecane droplets. Angle-dependent X-ray photoelectron spectroscopy (XPS) was performed on Perkin-Elmer 5500MT with a monochromatic Al Kα X-ray source.

Results and Discussion

Synthesis of well-defined chain-end-functionalized polystyrenes with a definite number of C_8F_{17} groups

As mentioned in introduction, we have recently developed a novel iterative methodology effective for the synthesis of chain-end-functionalized polystyrenes with a definite number of many benzyl bromide moieties (**PS(BnBr)$_n$**). This methodology involves only two reactions in each iterative reaction sequence as illustrated in Scheme 1.



Scheme 1. Iterative methodology for synthesis of chain-end-functionalized polystyrenes with a definite number of two, four, eight, sixteen, and thirty-two benzyl bromide moieties.

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The first reaction is a coupling reaction of the terminal benzyl bromide moiety[20] with 1,1-diphenylalkyl anion prepared from *sec*-BuLi and 1,1-bis(3-*tert*-butyldimethylsilyloxymethylphenyl)ethylene (**1**) to introduce two 3-*tert*-butyldimethylsilyloxymethylphenyl groups at the chain-end. In the second reaction, the two 3-*tert*-butyldimethylsilyloxymethylphenyl groups thus introduced are transformed into two benzyl bromide moieties by treatment with a 1:1 mixture of LiBr and $(CH_3)_3SiCl$. Very fortunately, these two reactions quantitatively proceeded and the number of benzyl bromide moiety doubled. Since the resulting polystyrene had the same benzyl bromide moieties as the starting polymer, this reaction sequence could be repeated. Thus, chain-end-functionalized polystyrene with four benzyl bromide moieties, **PS(BnBr)$_4$**, was quantitatively obtained. Furthermore, **PS(BnBr)$_8$**, and the following **PS(BnBr)$_{16}$** were successively synthesized by repeating the reaction sequence two more times. The results are summarized in Table 1. As can be seen, the resulting polymers are well controlled in molecular weight and molecular weight distribution. A definite number of two, four, eight, and sixteen benzyl bromide moieties were introduced at the polymer chain-ends within experimental errors.

Table 1. Synthesis of chain-end-functionalized polystyrenes with a definite number of benzyl bromide moieties.

Polymer	M_n x 10^{-3}		M_w/M_n b)	Functionality	
	calcd	obsd a)		calcd	obsd c)
PS(BnBr)$_2$	19.1	19.1	1.02	2	1.9_2
PS(BnBr)$_4$	19.8	19.6	1.02	4	3.9_6
PS(BnBr)$_8$	21.2	23.3	1.02	8	7.9_1
PS(BnBr)$_{16}$	23.9	24.3	1.03	16	$15._8$

a) Determined by ^{1}H NMR and SEC.
b) Determined by SEC.
c) Determined by ^{1}H NMR.

The introduction of C_8F_{17} group via the terminal benzyl bromide moiety is outlined in Scheme 2. At first, a new functionalized 1,1-diphenylalkyl anion was prepared from *sec*-BuLi and 1,1-bis(4-*tert*-butyldimethylsilyloxyphenyl)ethylene (**2**) instead of **1** and reacted with each of the **PS(BnBr)$_n$** to introduce the silyl-protected phenol functions. Similar to the reaction of the

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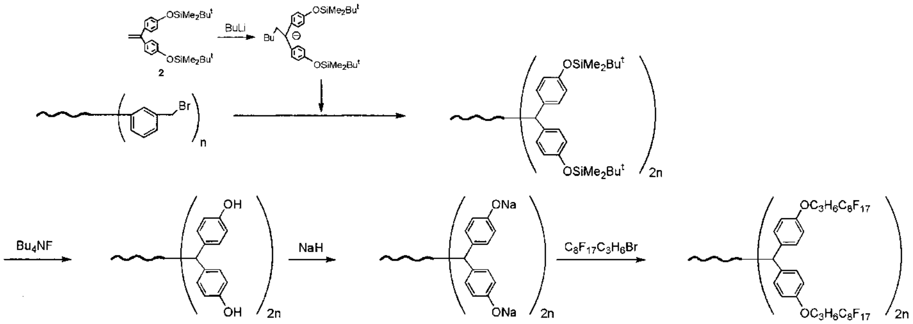
terminal benzyl bromide moiety with the 1,1-diphenylalkylanion derived from **1** illustrated in Scheme 1, this reaction using the new 1,1-diphenylalkyl anion derived from **2** proceeded cleanly and quantitatively. Two silyl-protected phenol functions were introduced into each benzyl bromide moiety. The *tert*-butyldimethylsilyl protecting group was completely removed by treatment with $(C_4H_9)_4NF$. Finally, C_8F_{17} group was introduced into each phenol function by treatment of the phenol-functionalized polymer with NaH, followed by reacting with $C_8F_{17}(CH_2)_3Br$. This Williamson reaction was also virtually quantitative in each case. Thus, we were successful in synthesizing chain-end-functionalized polystyrenes with two, four, eight, sixteen, and even thirty-two C_8F_{17} groups.



Scheme 2. Introduction of C_8F_{17} groups via benzyl bromide moieties

The characterization results are summarized in Table 2. As can be seen, all of the chain-end-functionalized polystyrenes with C_8F_{17} groups are precisely controlled in chain length as well as degree of C_8F_{17}-end-functionalization. As typical examples, SEC profiles of the starting **PS(BnBr)$_4$**, the polymer obtained by the reaction of **PS(BnBr)$_4$** with the 1,1-diphenylalkylanion from **2** and *sec*-BuLi, and the resulting chain-end-functionalized polystyrene with eight C_8F_{17} groups are shown in Figure 3. All polymers exhibit sharp monomodal SEC distributions. Neither shoulder nor tailing was observed at all in each sample.

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Table 2. Chain-end-functionalized polystyrenes with C_8F_{17} groups.

Polymer	M_n x 10^{-3}		M_w/M_n [b)]	Functionarity	
	calcd	obsd [a)]		calcd	obsd[c)]
D-2	19.9	19.9	1.03	2	2.0_0
D-4	21.3	22.4	1.07	4	3.8_0
D-8	24.2	25.5	1.06	8	7.7_2
D-16	30.0	29.6	1.05	16	$15._7$
D-32	41.6	42.0	1.05	32	$32._2$

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

These polymers are termed D polymer series in this study and abbreviated to D-(number of C_8F_{17} group), D-2, D-4, D-8, D-16, and D-32, respectively. In this series, the molecular weight of the polystyrene main chain remained unchanged (M_n = 19 kg/mol) because the same starting polystyrene was used in the synthesis, while the dendritic terminal C_8F_{17} groups increased in size and molecular weight going from D-2 to D-32.

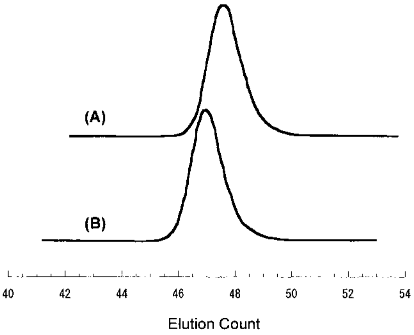

Figure 3. SEC profiles of chain-end-functionalized polystyrenes with four benzyl bromide moieties (A) and eight C_8F_{17} groups (B).

Surface characterization of C_8F_{17}-chain-end-functionalized polystyrene films by XPS measurement

The surface composition as a function of depth was measured by angle-dependent XPS at take-off angles of 10 ° and 80 ° on each of the annealed films of D series. The results are summarized

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in Table 3. Take-off angles (TOA) of 10 ° and 80 ° approximately correspond to 20 Å and 100 Å depths from outmost top surface, respectively. As expected, it was observed that the atomic percent ratios of F/C measured at 10 °TOA were much higher than they were in the bulk in all polymer films. Moreover, F/C values at 10° TOA were always higher than those at 80 °TOA. These results confirm the preferential enrichment of the terminal C_8F_{17} groups of all polymers at the firm surfaces.

Table 3. XPS atomic % of the film surfaces of D-2 – D-32.

Polymer	XPS atomic% (F/C)		
	10 °TOA[a)]	80 °TOA[a)]	Bulk[c)]
D-2	22.4 / 76.2	8.4 / 90.7	2.3 / 97.6
D-4	44.2 / 54.0	19.3 / 79.2	4.3 / 95.5
D-8	44.0 / 54.5	20.7 / 78.2	7.6 / 91.9
D-16	49.8 / 48.8	27.3 / 71.4	12.6 / 86.7
D-32	49.8 / 48.5	34.7 / 63.1	18.6 / 80.3

[a)] 10 ° and 80 °TOA (Take-off angle) correspond to approximately 20 Å and 100 Å depths, respectively.

[b)] Calculated value from chemical composition of the polymer.

Let us focus on the relationship between F atomic % at 10 °TOA and number of C_8F_{17} group in each sample. The F atomic % increased dramatically with increasing the number of C_8F_{17} group from two to four. Curiously, no increase in F atomic % was seen with increasing the number of C_8F_{17} group from four to eight. Then, a slight increase was observed by increasing the number of C_8F_{17} group from 8 to 16, but no more increase was attained between D-16 and D-32. These were plotted in Figure 4. In addition, the previous data using another type chain-end-functionalized polymers and structurally analogous block copolymers shown in Figure 2 were also plotted in the same figure. Herein, both polymers are abbreviated to E-(number of C_8F_{17} group) and B-(number of C_8F_{17} group), respectively. For example, E-4 and B-31.8 indicate chain-end-functionalized polystyrene with four C_8F_{17} groups and the block copolymer having 31.8 C_8F_{17} groups in average number, respectively. The polystyrene chains of E and B series were also ca. 20 kg/mol in molecular weight similar to D series, the number of C_8F_{17} group can be directly compared for the discussion of surface enrichment using F atomic %.

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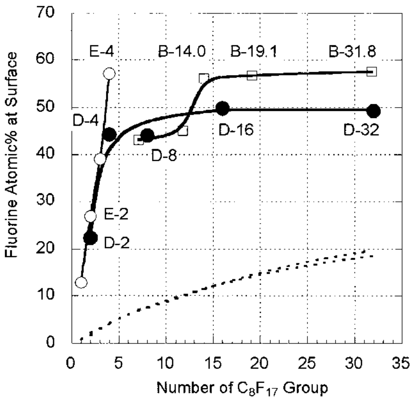

Figure 4. Fluorine atomic % at surface as a function of number of C_8F_{17} group. ●: D-series, ○: Chain-end-functionalized polystyrene, □: block copolymer, and calculated value in bulk (dashed line).

The XPS data strongly suggests that the surface enrichment of C_8F_{17} group seems to be almost saturated at D-4 and would not have been enhanced with further increasing the number of C_8F_{17} group. Only a small increase in the F atomic % was observed in between D-8 and D-16. The dependence of F atomic % on number of C_8F_{17} group observed in D series is different from those observed in not only E series but also B polymer series. Furthermore, the maximum saturated value of 49.8 % obtained by D-16 and D-32 was much lower than those obtained by E-4 as well as B-14.0, B-19.1, and B-31.8.

As mentioned in our previous paper, we proposed the following surface structure covered with C_8F_{17} group based on the saturated F atomic % of ca. 59 % and the F atomic % analyzable at 10 ^{o}TOA of 20 Å depths from top surface. As illustrated in Figure 5, the $C_8F_{17}(CH_2)_3O$ moieties are highly ordered and oriented with the chain axis perpendicularly to the surface and completely cover the surface. The molecular length of the moiety is approximately 15 ~ 20 Å from the molecular model and consistent with 20 Å depths analyzable by XPS. Based on the proposed surface structure, the F atomic % can be calculated from the $C_8F_{17}(CH_2)_3O$ moiety to be 58.6%. This value is closed to either of those of E-4, B-14.0, E-19.1, and B-31.8.

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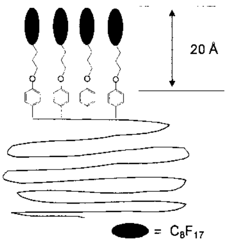

Figure 5. Possible surface structure for E-series.

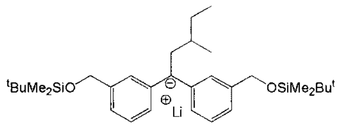

Figure 6. Reaction product of *sec*-BuLi with **1**.

In the case of D series where terminal C_8F_{17} groups are branched in dendritic shape, it seems relatively difficult for the terminal groups to be highly ordered and oriented by their rigid conformation and steric hindrance. In addition, 3-methylpentyl group was always introduced into each dendritic unit by the addition reaction of *sec*-BuLi to the vinyl group of **1** in the synthesis of the terminal group as shown in Figure 6. When $C_8F_{17}(CH_2)_3O$ moieties are enriched at the surfaces, the 3-methylpentyl group may also segregate at the surface because this group is consisted of dendritic unit with two $C_8F_{17}(CH_2)_3O$ moieties. Koberstein and his coworkers previously reported that the surface structure of *sec*-BuLi-initiated polystyrene is dominated by the terminal 3-methylpentyl group of the initiator fragment having a lower surface free energy than that of the polystyrene main chain.[11] This is an additional reason for the surface segregation of the 3-methylpentyl group. Accordingly, the 3-methylpentyl group may possibly be segregated at the surface in addition to two $C_8F_{17}(CH_2)_3O$ moieties. In this case, the F atomic % can be calculated to be 53.1 % based on the following equation: F atomic % = number of F atom (17 + 17)/(number of F (17+17) + number of C (11+11+6) + number of O (1+1)) = 34/64. This value is closed to the F atomic % values of D-16 and D-32. The lower saturated value of 49.8 % would thus be explained by insufficient ordering and orientation of the terminal dendritic group and the enrichment of 3-methylpentyl group together with the $C_8F_{17}(CH_2)_3O$ moieties at the surface (see Figure 7). By taking into consideration in these regards, we should redesign and synthesize chain-end-functionalized polymers with perfluoroalkyl groups.

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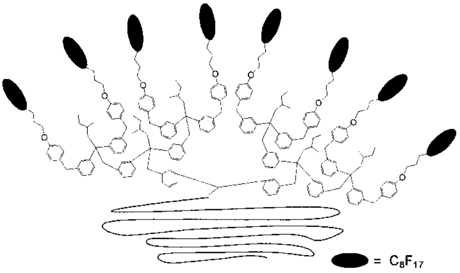

Figure 7. Possible surface structure for D-series.

Contact Angle Measurements Using Water and Dodecane Droplets

Contact angle measurements using both water and dodecane droplets were carried out to elucidate the surface characters of cast films. The results are summarized in Table 4. Contact angles using water droplet showed values in the range of 99 ° ~ 113 ° for all films cast from D-2 ~ D-32. As expected, these values are definitely higher than 91.3 ° of the film of polystyrene end-capped with DPE (M_n = 23 kg/mol) under the same conditions. This clearly indicates that C_8F_{17} groups are preferentially enriched at the surfaces to change more hydrophobic characters in all cases. The value of contact angle increased gradually with the number of C_8F_{17} group and saturated at the number of sixteen.

Table 4. Contact angle values of the film surfaces of D-2 ~ D-32.

Polymer	Contact angle [°]	
	Water	Dodecane
D-2	99.7	23.3
D-4	105	47.7
D-8	107	48.7
D-16	113	55.6
D-32	111	51.7

When used dodecane droplet, the contact angle of DPE-end-capped polystyrene (M_n = 23 kg/mol) could not be measured at all by getting wet with dodecane, whereas D-2 showed a measurable value of 23.3 °, indicating that the lipophobic surface covered with C_8F_{17} groups was

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apparently formed. The contact angle value markedly increased with increasing the number of C_8F_{17} group from two to four but a slight increase in the value was observed with increasing from four to eight. It increased again with increasing the number to sixteen, while D-32 showed the value close to D-16.

The contact angle values of D-2 ~ D-32 were plotted vs. the number of C_8F_{17} group in Figure 8. The contact angle values of E and B series previously reported were also added to the figure. Very surprisingly, both figures (Figures 4 and 8) resemble very closely in dependence.

It should be mentioned that the contact angle of D-2 gradually decreases with time, while the values of D-4 ~ D-32 are stable and remain unchanged. In the film cast from D-2, dodecane may gradually soak into the film inside from the surface and dissolve the polystyrene layer under the layer covered with C_8F_{17} groups. Four C_8F_{17} groups were therefore needed to form stable lipophobic surfaces toward organic solvents dissolving polystyrene like dodecane.

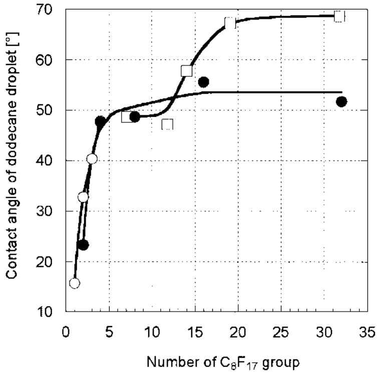

Figure 8. Contact angle of dodecane droplet as a function of number of C_8F_{17} group. ●: D-series, ○: Chain-end-functionalized polystyrene, and □: block copolymer.

Conclusions

We have successfully synthesized new chain-end-functionalized polystyrenes with a definite number of two, four, eight, sixteen, and thirty-two C_8F_{17} groups branched in dendritic shapes by utilizing the recently developed methodology based on iterative divergent approach. All films

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cast from these polymers show significant segregation and preferential enrichment of C_8F_{17} group at the surfaces as evidenced by the analytical results with XPS and contact angle measurements.

The dependence of surface enrichment on number of C_8F_{17} group has been quantitatively investigated by F atomic % from top surface to 20 Å depths and observed to be different from that using either E or B polymer series previously reported, possibly due to the characteristic dendritic shapes of the terminal end groups.

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