Synthesis of Polyethylene Oxide End-Capped with Perfluoroalkyl Groups/Polystyrene Prototype Brushes

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ABSTRACT: Polystyrene (PS)/poly(ethylene oxide) (PEO) prototype brushes were prepared by alternating free-radical copolymerization of methacryloyl-terminated PS and α-vinylbenzyl-ω-hydroxy or α-vinylbenzyl-ω-perfluoroalkyl (R_f) PEO macromonomers with the addition of Lewis acid ($SnCl_4$). It was found from their dilute-solution properties that PS/PEO end-capped with R_f (PBR$_f$), and PS/PEO having OH groups at terminal ends (PBOH) prototype brushes formed a single molecule in benzene and aggregates in chloroform, respectively. However, the brush PBOH formed a single molecule in *N,N*-dimethylformamide. Such aggregation behaviors seemed to be caused by the interaction between hydroxy groups of PEO chain ends. The brush PBOH was also converted into PBR$_f$-type brush by chemical modification, using corresponding acid chloride. The substitution of R_f groups was ~70% due to slipping of terminal hydroxy groups into PEO internal domains. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 772–778, 2006

Key words: prototype copolymer brush; alternating copolymerization; macromonomer; perfluoroalkyl group; single molecule

INTRODUCTION

Nanostructured polymers are rapidly gaining interest because of their sized-coupled properties. Generally, the branched polymer has a smaller hydrodynamic dimension than a linear polymer with the same molecular weight. The interest in branched polymers arises from their compactness and their enhanced segment density. Recently, a new class of branched architectural polymers, such as nanocylinders, is attracting attention with the expectation that their unique structures may result in unusual properties.[1] Ishizu and coworkers established a novel synthesis of prototype amphiphilic copolymer brushes (see Fig. 1) by alternating free-radical copolymerization of binary macromonomers.[2–4] They have also investigated their dilute-solution properties and aggregation behaviors in aqueous media.[4–9] As a result, such copolymer brushes were molecularly dissolved in a dilute solution and took geometrically anisotropic conformation such as cylinder with increasing aspect ratio. In the self-assembly process in water, hierarchical generation from small rods to large rods was observed, because such copolymer brushes exhibited phase-separated hydrophobic/hydrophilic domains. On the other hand, it is well known that even in chain-end functionalized polymers, the end groups are segregated to enrich at surfaces rather than being randomly distributed through the bulk of the materials.[10–16] Such segregation effects have been accentuated because of low surface free energies, when the chain-end functional groups are perfluoroalkyl (R_f) groups.[17–22] It is interesting to construct the amphiphilic prototype copolymer brushes covered with R_f groups at the peripheral surface of one component.

In this article, polystyrene (PS)/poly(ethylene oxide) (PEO) prototype brushes were synthesized by alternating free-radical copolymerization of methacryloyl-terminated PS and α-vinylbenzyl-ω-hydroxy or α-vinylbenzyl-ω-R_f PEO macromonomers. The brushes having hydroxy groups at terminal PEO ends were also converted into PS/PEO end-capped with R_f groups prototype brushes by chemical modification.

EXPERIMENTAL

Materials

Ethylene oxide (EO; 3*M* Steri-EO Gas, Tokyo), perfluorooctanoyl chloride, 7H-dodeca-fluoroheptanoyl chloride (Daikin Finechemical Laboratory, Tokyo), tetrahydrofuran (THF), and triethyl amine (Et$_3$N; Tokyo Kasei Chemicals, Tokyo) were dried over calcium hydride (CaH$_2$) and then distilled under vacuum. *p*-Chloromethylstyrene (CMS; Seimi Chemicals, Kashima, Japan), dimethyl sulfoxide (DMSO), *N,N*-dimethyl-formamide (DMF), ethanol, methanol, hexane, benzene, toluene, chloroform (CHCl$_3$) naphtha-
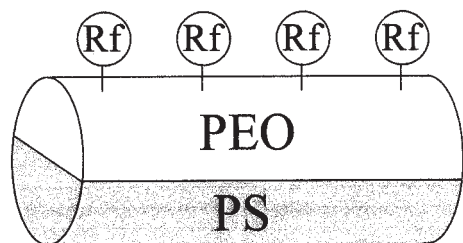
Figure 1 Illustration of amphiphilic PS/PEO having R_f groups prototype brush.

lene (Naph), 2,2-azobis(isobutyronitrile) (AIBN; To-kyo Kasei Chemicals, Tokyo), potassium acetate (CH_3COOK), NaOH, potassium metal, tin tetrachloride ($SnCl_4$), and CaH_2 (Kanto Kagaku Chemicals, Tokyo) were used as received.

Methacryloyl-terminated PS (PS-MC) was prepared by coupling of polystyryl anion end-capped with EO with methacryloyl chloride. Details concerning synthesis and characterization have been given elsewhere.[2] Characteristics of PS-MC macromonomers are listed in Table I.

Syntheses of α-vinylbenzyl-ω-hydroxy and α-vinylbenzyl-ω-R_f PEO macromonomers

4-Vinylbenzyl alcohol (VBA) was prepared by acetoxylation of CMS and subsequent hydrolysis of 4-vinylbenzyl acetate.[23,24] In brief, a mixture of CMS, CH_3COOK and DMSO was stirred at 40°C for 48 h and yielded 4-vinylbenzyl acetate. A mixture of 4-vinylbenzyl acetate and NaOH in water/ethanol (1:6, v/v) was refluxed for 1.5 h and yielded VBA. 4-Vinylbenzyl alcohol potassium alkoxide (VBA-K) as anionic initiator was synthesized by the reaction of VBA with potassium naphthalene in THF. PEO anions were prepared by anionic polymerization of EO initiated by VBA-K in THF at 60°C for 100 h (see Scheme 1). After reaction, the resulting solution was poured into a large excess of hexane. The product (α-vinylbenzyl-ω-hydroxy PEO macromonomer: PEO-VB) was purified by reprecipitation from toluene solution with hexane.

The introduction of R_f group on PEO-VB terminal end was carried out as follows. A mixture of PEO-VB and 7H-do-decafluoroheptanoyl chloride (~2.5-fold amount with respect to OH groups of PEO-VB terminal ends) in THF was stirred at 25°C for 24 h, with the addition of Et_3N as an acid acceptor. After reaction, the resulting solution was poured into a large excess of hexane. The product (α-vinylbenzyl-ω-perfluoroalkyl PEO macromonomer: PEO-VBR$_f$) was purified by reprecipitation from toluene solution with hexane.

The number–average molecular weight (M_n) and polydispersity (M_w/M_n) of the PEO macromonomers were determined by gel-permeation chromatography (GPC; Tosho high-speed liquid chromatograph HLC-

8120, Tokyo) equipped with a refractive index, using PEO standard samples, which was operated with DMF as the eluent at 40°C and a flow rate of 1.0 mL/min.

The contents of vinylbenzyl group of PEO-VB and R_f group of PEO-VBR$_f$ were determined by ^{1}H NMR (500 MHz, JEOL GSX-500 NMR spectrometer, Tokyo) in $CDCl_3$.

Synthesis of prototype copolymer brushes and introduction of R_f groups on PEO terminal ends

Free-radical copolymerizations of binary macromonomers (PEO-VB/PS-MC, the brush PBOH having OH groups at PEO ends; and PEO-VBR$_f$/PS-MC, the brush PBR$_f$ having R_f groups at PEO ends) were performed in benzene or toluene with the addition of $SnCl_4$ at 60°C, using AIBN as an initiator (see Fig. 1). It was found from previous results that these copolymerization systems showed strong alternation.[7,8]

The introduction of R_f groups on PEO terminal ends of PBOH was carried out under the same reaction conditions, using perfluorooctanoyl chloride as mentioned in the former section. The introduction of R_f groups on PEO ends was recognized by characteristic absorbance (1130–1350 cm^{-1}) of C—F bond and —CH_2CH_2OH groups (1360 cm^{-1}) for PEO terminal ends on an FTIR spectrometer (Shimadzu FTIR-8500, Tokyo).

Measurements

The M_w of prototype brushes (PBOH and PBR$_f$) was determined by static light scattering (SLS) in DMF and in benzene, respectively, at 25°C in the Zimm plot. The hydrodynamic diameters (D_h) of PBOH and PBR$_f$ were determined by dynamic light scattering (DLS) in THF, $CHCl_3$, DMF, and benzene at 25°C with cumulant method. Details concerning the apparatus and procedure have been given elsewhere.[7]

TABLE I
Characteristics of Methacryloyl-Terminated PS Macromonomer[a]

Code	M_n^b	M_w/M_n	Functionality[c] (number/molecule)
PS-MC1	4200	1.15	0.98
PS-MC2	2300	1.17	0.97

[a] Prepared by coupling between polystyryl lithium end-capped with EO and methacryloyl chloride in a mixture of toluene/THF.
[b] Determined by GPC in THF as eluent at 40°C using PS standard samples.
[c] Determined by ^{1}H NMR in $CDCl_3$.

1)

VBA-K

PEO-VB

2)

PEO-VB   PS-MC   Prototype copolymer brush
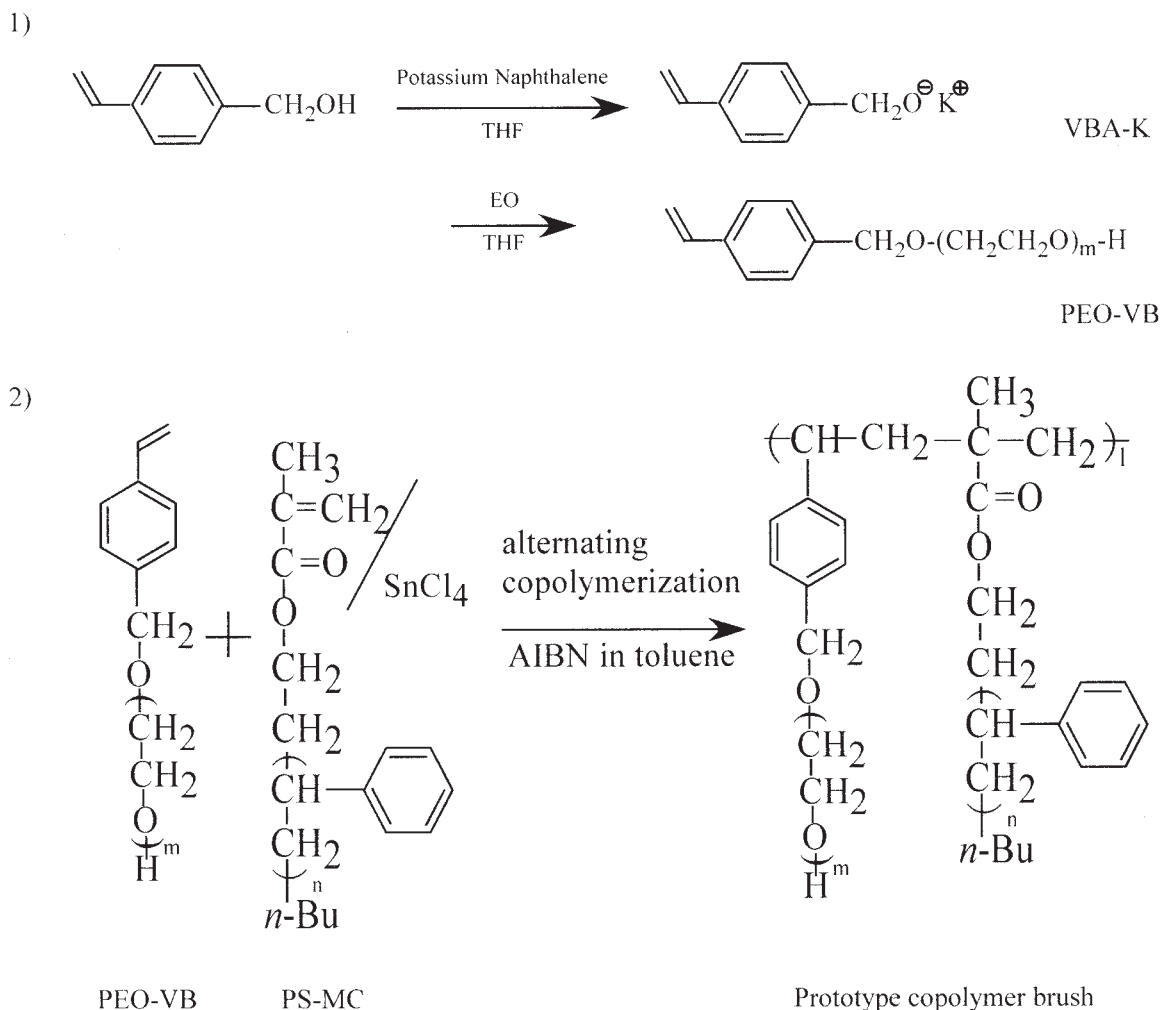
Scheme 1

RESULTS AND DISCUSSION

Synthesis of α-vinylbenzyl-ω-hydroxy PEO macromonomers

Since simple potassium alkoxides are well known to initiate the living polymerization of EO with a reason-able rate and good functionality,[25–28] we synthesized α,ω-functionalized PEO macromonomers initiated by VBA-K as an initiator. Reaction conditions and result are listed in Table II. The conversion of EO achieved 82–100% under these reaction conditions. Figure 2 shows typical GPC profile of PEO-VB1. GPC distribu-

TABLE II
Reaction Conditions and Results for α-Vinylbenzyl-ω-hydroxyl PEO Macromonomers[a]

Code	Feed			Conversion[c] (%)	M_n^d	M_w/M_n^d	Functionality[e] (number/molecule)
	EO (mol)	VBA (mmol)	K-Naph[b] (mmol)				
PEO-VB1	0.2	3.07	3.07	100	3000	1.06	0.86
PEO-VB2	0.2	2.80	2.80	100	3600	1.08	0.88
PEO-VB3	0.17	2.16	1.50	82	2800	1.05	1.0

[a] Polymerized in THF (100 mL) at 60°C for 100 h.
[b] Potassium naphthalene.
[c] Determined by gravimetric method.
[d] Determined by GPC in DMF as eluent at 40°C using PEO standard samples.
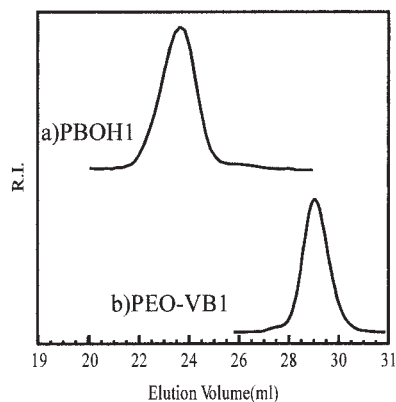[e] Determined by ^{1}H NMR in CDCl$_3$.

Figure 2 GPC profiles of PEO-VB1 macromonomer and PBOH1 brush in DMF as eluent at 40°C.

tion is unimodal and shows narrow molecular weight distribution (M_w/M_n = 1.06). ^{1}H NMR spectrum of PEO-VB1 in CDCl$_3$ is shown in Figure 3(a). In addition to the signals of the ethylene protons (f: —CH$_2$CH$_2$—; δ 3.62 ppm) of the PEO, the spectrum exhibits the

expected resonances assignable to the methylene protons (e: —CH$_2$—; 4.60 ppm) and aromatic protons (c and d: 6.7–7.4 ppm) of the vinylbenzyl group, and the methylene protons (a: =CH$_2$; 5.8 and 5.3 ppm) of the double bond. The content of vinylbenzyl group was evaluated to be 0.86 from the integration ratio of the methylene protons (a) of the double bond to ethylene protons (f) of the PEO chains. Characteristics of PEO-VB are also listed in Table II.

The introduction of R$_f$ group on PEO-VB3 terminal end was carried out using 7H-do-decafluoroheptanoyl chloride. ^{1}H NMR spectrum of PEO-VB3R$_f$ in CDCl$_3$ is shown in Figure 3(b). In addition to the signals of the terminal vinylbenzyl group of PEO, the spectrum exhibits the expected resonance assignable to —(CF$_2$)$_7$H protons (g: δ 5.9–6.2 ppm) of R$_f$. The content of the R$_f$ group was evaluated to be 1.0 from the integration ratio of the —(CF$_2$)$_7$H protons (g) to methylene protons (a: =CH$_2$) of the double bond. R$_f$ group was introduced quantitatively into the terminal OH group of the PEO chain.
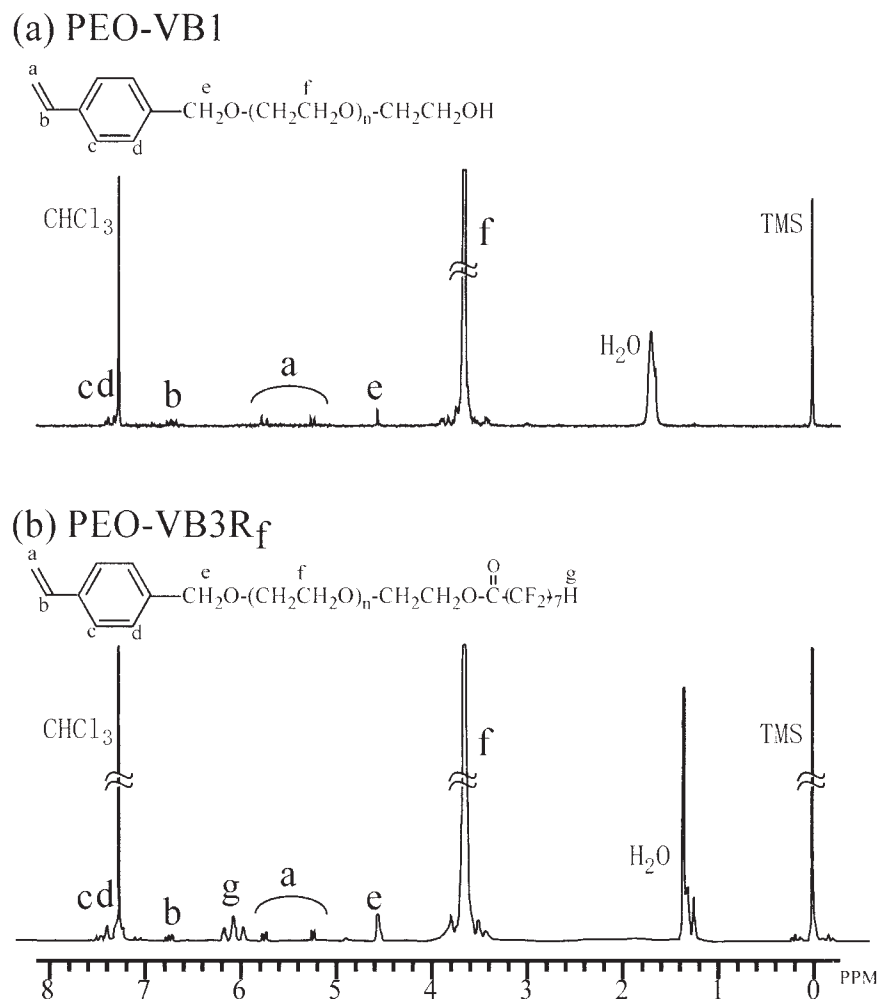

Figure 3 ^{1}H NMR spectra of PEO-VB1 (a) and PEO-VB3R$_f$ (b) macromonomers in CDCl$_3$.

TABLE III
Copolymerization Conditions and Results for Prototype Copolymer Brushes[a]

Code	Feed concentration (mmol/L)				Copolymer brush			
	[PEO-VB]	[PS-MC]	[AIBN]	[SnCl$_4$]	Conv[b] (%)	M_w/M_n^c (10^{-6})	M_w/M_n^b	F^d (mol %)
PBR$_f$1	PEO-VB3R$_f$ 150	PS-MC2 150	15	300	80.1	9.51	1.68	32.0
PBOH1	PEO-VB1 400	PS-MC1 400	20	400	96.0	1.50	1.31	28.6

[a] Polymerized in benzene (PBR$_f$1) and in toluene (PBOH1) at 60°C for 100 h.
[b] Determined by GPC in DMF as eluent at 40°C.
[c] Determined by SLS with Zimm plot in benzene (PBR$_f$1) and in DMF (PBOH1) at 25°C.
[d] F, PEO mole fraction in the brush was determined by ^{1}H NMR in CDCl$_3$.

Synthesis and dilute-solution properties of PBOH and PBR$_f$ prototype brushes

The copolymerization conditions and results of PBOH and PBR$_f$ are listed in Table III. In the copolymerization of PBR$_f$1, SnCl$_4$ was added twofold amount with respect to each molecule of PEO-V3R$_f$ and PS-MC2, because both macromonomers exhibited the carbonyl groups at terminal ends. After polymerization, the solution was poured into an excess of hexane. Unreacted PEO-VB3R$_f$ was removed from the copolymerization product with water. Subsequently, unreacted PS-MC2 was removed from the mixture of PS-MC2 and copolymer brush by precipitation fractionation with a toluene–methanol system. The resulting prototype brush (PBR$_f$1, conversion = 80.1%) exhibited a unimodal pattern (M_w/M_n = 1.68) on the GPC profile. Examination of the [1]H NMR (in CDCl$_3$) of PBR$_f$1 showed the expected resonances for the aromatic protons of PS (δ 6.2–7.3 ppm) and the ethylene protons (3.62 ppm) of PEO chains. The composition ratio of PS to PEO was 8.5:4 from the integration ratio of these signals. The PEO mole fraction in the brush (F = 32.0 mol %) extremely deviated from the previous results.[1–4] It seemed in this copolymerization system that the vinylbenzyl group of PEO-VB3R$_f$ formed 1:1 complex with not only PS-MC2 but also —C(=O)(CF$_2$)$_7$H of PEO-VB3R$_f$ terminal end. As mentioned in the previous results on DLS,[4–7] the brush PBR$_f$1 also showed strong angular dependence ($\Gamma_e q^{-2}$ versus q^2; $qR_h < 1$, where Γ_e and q are the first cumulant and scattering, respectively) in benzene and the translational diffusion coefficient $D(C)$ had a constant value against polymer concentration. These facts suggested that the brush PBR$_f$1 with wormlike shape was molecularly dissolved in the dilute benzene solution. The M_w (9.51 × 10^6) of PBR$_f$1 was determined by SLS with Zimm plot in benzene. Then, the degree of polymerization (DP_n) was 1150.

Then, we carried out the copolymerization (PBOH1) of binary macromonomers PEO-VB1 and PS-MC1. The copolymer brush was purified by a similar method as mentioned in the PBR$_f$1 brush. The resulting brush exhibited a unimodal pattern on the GPC profile (see

Fig. 2) and relatively narrow polydispersity (M_w/M_n = 1.31). The PEO mole fraction F was evaluated to be 28.6 mol %. A result which supports our expectation was not obtained from NMR data. Therefore, DLS measurements of PBOH1 were carried out with the cumulant method in CHCl$_3$, THF, and DMF at 25°C. Figure 4 shows typical size distribution profiles of PBOH1 in CHCl$_3$ [Fig. 4(a)] and in DMF [Fig. 4(b)]. The hydrodynamic radius (R_h) is defined by the Stokes–Einstein equation, $R_h = kT/6\pi\eta_0 D_0$, where k, T, η_0, and D_0 indicate the Boltzmann constant, the absolute
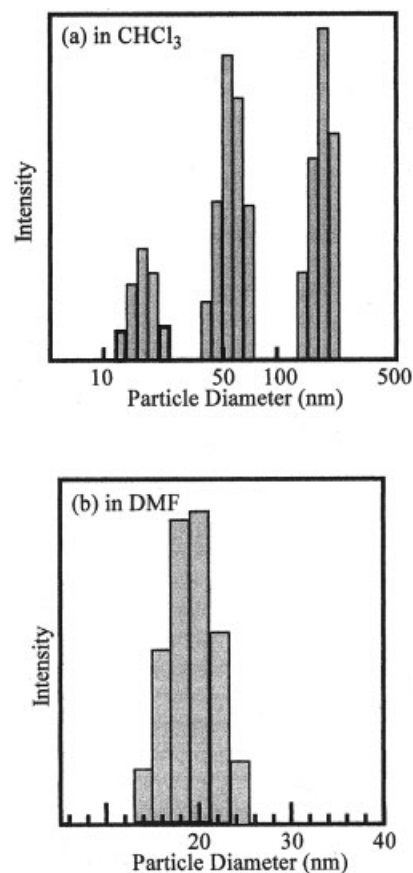

Figure 4 Size distribution profiles of PBOH1 brush (C = 0.001 mg/mL) in CHCl$_3$ (a) and in DMF (b) by DLS with cumulant method.
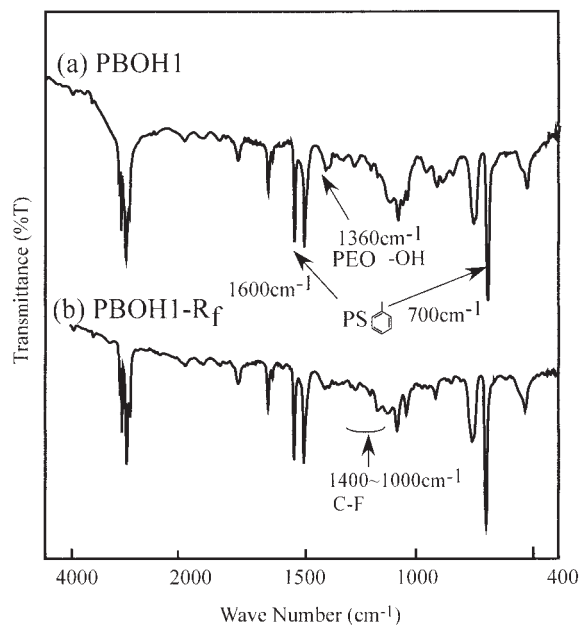
Figure 5 FTIR spectra of PBOH1 (a) and PBOH1-R$_f$ brushes (b).

temperature, the viscosity of solvent, and the translational diffusion coefficient, respectively. The size distribution profile in CHCl$_3$ [see Fig. 4(a)] clearly shows three scattering peaks (hydrodynamic diameter D_h = 17.2, 55.2, and 190.5 nm). It seems that the brush PBOH1 forms the aggregates in CHCl$_3$. The size distribution profile in THF also showed almost the same result. On the other hand, the size distribution profile in DMF [see Fig. 4(b)] shows a unimodal pattern (D_h = 19.6 nm). The brush PBOH1 also showed strong angular dependence ($\Gamma_e q^{-2}$ versus q^2; $qR_h < 1$) in DMF and the translational diffusion coefficient $D(C)$ had a constant value against polymer concentration. These facts also suggested that the brush PBOH1 with wormlike shape was molecularly dissolved in the dilute DMF solution. It can be speculated from the above results that the relaxation rate of PEO chains of PBOH1 in CDCl$_3$ was very slow than that of PS chains as shown in the ^{1}H NMR spectrum because of the interaction of OH groups of PEO chain ends.

Therefore, the composition of the brush PBOH1 was determined again by FTIR as the most reasonable method. The spectrum of the brush PBOH1 is shown in Figure 5. This spectrum shows the expected absorbance for the aromatic ring (1600 and 700 cm^{-1}) and characteristic absorbance for —CH$_2$OH groups (1360 cm^{-1}) for PEO chains. To determine the composition of the brush, a calibration curve was constructed using a mixture of PS and PEO homopolymers (aromatic ring at 700 cm^{-1} and —CH$_2$OH groups at 1360 cm^{-1}). As a result, the PEO mole fraction F of the brush was evaluated to be 50.6 mol %. This copolymerization system showed strong alternation and formed the pro-

totype brush structure. The M_w (1.50×10^6) of PBOH1 was also determined by SLS with Zimm plot in DMF. The DP_n was 318. One can easily control the aspect ratio of prototype copolymer brushes by alternating copolymerization.

The introduction of R$_f$ groups on PEO terminal ends of PBOH1 was performed using perfluorooctanoyl chloride. FTIR spectrum of the product (PBOH1-R$_f$) is shown in Figure 5(b). It can be seen that the characteristic absorbance for C—F bonds (1300–1200 cm^{-1}) appears in this spectrum and the absorbance for —CH$_2$OH groups (1360 cm^{-1}) of PEO terminal ends decreases compared with the starting brush PBOH1. The introduction of R$_f$ groups was evaluated to be 66.7% from the absorbance ratio of —CH$_2$OH to aromatic ring (700 cm^{-1}) moieties. The substitution of R$_f$ groups did not proceed quantitatively because of slipping of terminal hydroxy groups into PEO internal domains. We are investigating the solution properties and surface characterization of two types of prototype brushes having R$_f$ groups on PEO terminal ends. The results obtained will be reported in the near future.

CONCLUSIONS

We have explored the scope of the synthetic approach to prototype copolymer brushes having R$_f$ groups. It was found from free-radical copolymerization of PS-MC2/PEO-VB3R$_f$ with the addition of SnCl$_4$ that the vinylbenzyl group of PEO-VB3R$_f$ formed 1:1 complex with not only PS-MC2 but also —C(=O)(CF$_2$)H of PEO-VB3R$_f$. As a result, the PEO mole fraction F was 32.0 mol %. On the other hand, free-radical copolymerization of PEO-VB1/PS-MC1 showed strong alternation with the addition of SnCl$_4$. However, the subsequent substitution of R$_f$ groups was ∼70% because of slipping of terminal hydroxy groups into PEO internal domains. Both brushes PBR$_f$1 (in benzene) and PBOH1 (in DMF) with wormlike shape were molecularly dissolved in the dilute solution.

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