

Synthesis of Block Copolymers Having Perfluoroalkyl and Silicone-Containing Side Chains Using Diazo Macroinitiator and Their Surface Properties

DONG-KWON KIM,¹ SOO-BOK LEE,¹ KAP-SOO DOH,² YOUNG-WOO NAM²

¹ Division of Advanced Chemical Technology, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusong, Taejeon 305-600, South Korea

² Department of Chemical and Environmental Engineering, Soongsil University, Seoul 156-743, South Korea

Received 23 November 1998; accepted 14 January 1999

ABSTRACT: The fluorosilicone block copolymers of poly(perfluoroalkylethyl acrylate)-*b*-poly(3-[tris(trimethylsilyloxy)silyl] propyl methacrylates) (PFA-*b*-PSiMAs) having perfluoroalkyl and silicone-containing side chains were obtained by three-step synthetic approaches. In the first step, hydroxyl-terminated poly(perfluoroalkylethyl acrylate) macromonomer (PFAM) was prepared by the free-radical polymerization of perfluoroalkylethyl acrylate and 2-mercaptoethanol. In the second step, PFAM initiator (PFAMI) was prepared from the condensation reaction of the hydroxyl-terminated PFAM and 4,4'-azobis-4-cyanopentanoic acid chloride (ACPC). ACPC was obtained from the reaction of 4,4'-azobis-4-cyanopentanoic acid and phosphorus pentachloride. In the third step, PFA-*b*-PSiMAs (BPFSs) were synthesized from the reaction of PFAMI macroinitiator and SiMA. Fourier transform infrared spectroscopy and ¹H-NMR analyses verified that the syntheses of ACPC, hydroxyl-terminated PFAM, PFAMI, and BPFS were completed successfully. The intrinsic surface energies of BPFSs and their surface modification effects on poly(vinyl chloride) film were investigated by analyzing the surface free energies and atomic compositions of the outermost layer of the surfaces. BPFSs exhibit extremely low surface free energies of about 9.7–13.0 dynes/cm. It was confirmed that BPFS, having extremely low surface free energy, is preferentially enriched at the outermost layer of the surface of BPFS/poly(vinyl chloride) blend. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1917–1926, 1999

Key words: synthesis of fluorosilicone block copolymer; poly(perfluoroalkylethyl acrylate)-*b*-poly(3-[tris(trimethylsilyloxy)silyl] propyl methacrylate); macroinitiator; surface free energy; surface modification

INTRODUCTION

Various fluoropolymers which have perfluoroalkyl segments in the side chains have attracted particular attention because of the very low surface free energy.^{1–12} Surface property modification using blends of fluoropolymers with hydro-

carbon polymers has been studied.^{1,2,9,12} Most of silicone-containing polymers have low surface energy. Consequently, hybrid fluorosilicone materials containing both fluorine and silicone should be of great interest for surface modifications. Surface properties of several fluorosilicone polymers prepared by adding the fluorocarbon side-chain entities to a preformed siloxane polymer are well reviewed in the literature.¹³ Surface properties of fluorosilicone random copolymers prepared by polymerization of a perfluoroalkyl acrylate (FA)

Correspondence to: S.-B. Lee.

Journal of Applied Polymer Science, Vol. 74, 1917–1926 (1999)

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CCC 0021-8995/99/081917-10

monomer and a silicone-containing acrylate monomer have been investigated.¹⁴

Multiphase polymers such as block and graft copolymers are known to exhibit unique surface properties because of their microphase separation at surface. The bulk and surface structures of multiphase polymers usually differ. The significant surface accumulation of one polymer component at surface is frequently noticed, producing quite different surface structure than expected from that in bulk. The control of the surface structure of polymer materials is an essential requirement for many industrial applications. Nevertheless, the relationship between the bulk and the surface morphology of copolymers is not yet clearly understood. Fluorine-containing graft copolymers were synthesized, and their surface properties were investigated.^{11,15–17} However, block copolymers containing both fluorine and silicone have not been investigated.

In this study, the fluorosilicone block copolymers containing perfluoroalkyl side chains and silicone-containing side chains were synthesized using a macroazobitrile as a biradical initiator. Their intrinsic surface properties and surface modification effects on Poly(vinyl chloride) (PVC) film were investigated. FA as a fluorine-containing monomer and 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate (SiMA) as a silicone-containing comonomer were used to synthesize the fluorosilicone block copolymers having perfluoroalkyl side chains and silicone-containing side chains by free-radical solution polymerization. PVC was chosen as a base polymer in studying the surface modification effects of the fluorosilicone block copolymers, because PVC films are widely utilized for agricultural films.^{18,19} PVC films modified by the fluorosilicone block copolymers were prepared by solvent die-casting method to investigate the surface modification ability of the fluorosilicone block copolymers. The contact angles on the surfaces of both the fluorosilicone block copolymers and the PVC films modified by the fluorosilicone block copolymers were measured, and their surface free energies were calculated from the contact angle data.

EXPERIMENTAL

Reagents

The macroazobitrile used as a biradical initiator was 4,4'-azobis-4-cyanopentanoic acid chloride

(ACPC) $[\text{ClOC}(\text{CH}_2)_2\text{C}(\text{CH}_3)(\text{CN})\text{N}=\text{NC}(\text{CH}_3)(\text{CN})-(\text{CH}_2)_2\text{COCl}]$, $M_w = 349$. ACPC was prepared from the reaction of ACPA $[\text{HOOC}(\text{CH}_2)_2\text{C}(\text{CH}_3)(\text{CN})\text{N}=\text{NC}(\text{CH}_3)(\text{CN})(\text{CH}_2)_2-\text{COOH}]$, $M_w = 280$ and phosphorus pentachloride $[\text{PCl}_5]$. ACPA of 98% purity Aldrich Co. (USA) was used without purification. Dichloromethane (DCM) and PCl_5 were used as received from Aldrich Co., and their purities were 99.9 and 95%, respectively. FA $[\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_4(\text{CF}_2)_7\text{CF}_3]$, $M_w = 518$ obtained from Hoechst Co. (Frankfurt, Germany), and SiMA $[\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3-\text{Si}[\text{OSi}(\text{CH}_3)_3]_3]$, $M_w = 423$ obtained from Aldrich were used directly as received. The chain transfer agent of 2-mercaptoethanol (MT) $[\text{HSCH}_2\text{CH}_2\text{OH}]$ (Aldrich) was used without further purification. The initiator of 2,2-(azobisisobutyronitrile) (AIBN) (Aldrich) was recrystallized from methanol. Tetrahydrofuran (THF) (Aldrich) was distilled from sodium benzophenone ketyl under N_2 . Anhydrous n-hexane $[\text{C}_6\text{H}_{14}]$, methanol, methyl ethyl ketone (MEK), triethylamine (TEA), dibutyltin diacetate (DBTDA) $[(\text{CH}_3\text{CO}_2)_2\text{Sn}((\text{CH}_2)_3\text{CH}_3)_2]$, and methylene iodide (MI) were used as received from Aldrich. PVC with the degree of polymerization of 1100 (Aldrich) was used as a base polymer. Deionized water was used throughout the experiments.

Analyses

Fourier transform infrared (FTIR) spectra for ACPA, ACPC, hydroxyl-terminated poly(perfluoroalkylethyl acrylate) macromonomer (PFAM), PFAM initiator(macroinimer) (PFAMI) and poly(perfluoroalkylethyl acrylate)-b-poly(3-[tris(trimethylsilyloxy)silyl] propyl methacrylate) (PFA-b-PsiMA or BPFs) were analyzed by a spectrometer (Didilab Division FTS 165, Bio-Rad Co.). The glass-transition temperatures (T_g s) of BPFs and BPFs/PVC blends were determined by differential scanning calorimetry (DSC) (Model Du Pont 2100 system). $^1\text{H-NMR}$ spectra were analyzed by a spectrophotometer (Bruker DRX-500). The molecular weights of hydroxyl-terminated PFAM, PFAMI, and BPFs were measured by a GPC (Waters, R-401 ALC/GPC) using THF as a solvent. The molecular weights were calibrated with polystyrene standards (Shodex, SM-105). Atomic compositions of the BPFs/PVC blend were analyzed with an angle-dependent X-ray photoelectron spectroscopy (XPS) by varying the take-off angle from 5 to 60°. The XPS used was a V.G. Scientific ESCALAB MK II spectrometer with an Al-K α X-ray source and a hemispherical sector analyzer.

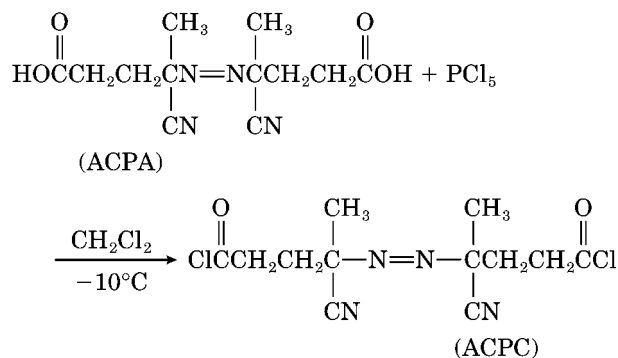


Figure 1 Reaction equation for ACPC synthesis.

Synthesis of ACPC Macroinitiator

ACPC macroinitiator used as a biradical initiator was prepared from the reaction of ACPA suspension [12 g (0.04 mol) of ACPA in 100 mL DCM solvent] and excess PCl_5 suspension [60 g (0.3 mol) of PCl_5 in 200 mL DCM solvent]. PCl_5 suspension was slowly added to ACPA suspension under dry-ice cooling. The reaction was performed for 24 h at below -10°C . The reaction equation for ACPC synthesis from ACPA is shown in Figure 1. After the reaction, about 80 vol % of DCM contained in the reaction mixture was evaporated in a vacuum oven at 20°C and 200 mmHg to promote the crystallization of the unreacted PCl_5 . After the crystallized PCl_5 was filtered off, the resulting reaction mixture was poured drop-wise into anhydrous n-hexane to precipitate ACPC. The precipitated ACPC was recovered by filtration. The ACPC was washed three times with anhydrous n-hexane cooled with dry ice, and dried in a vacuum oven for 3 days at 200 mmHg and 20°C . The yield of ACPC was about 62 wt %.

Synthesis of Hydroxyl-Terminated PFAM

The hydroxyl-terminated PFAM was prepared from the reaction of FA and MT using AIBN as an initiator by free-radical polymerization. The reaction was performed for 10 h at 60°C . The amounts of FA and MT used for the reaction were 20 g (0.04 mol) and 3.0 g (0.04 mol), respectively. The solvent used was MEK. The mol ratio of FA/MT was 1 : 1 and AIBN was 0.5 wt % of the total monomers. The content of the monomer mixture in the reaction solution was maintained at 20 wt %. The equation of polymerization reaction between FA and MT is shown in Figure 2. After the reaction was completed, about 80 vol % of MEK contained in the reaction mixture was evaporated

in a vacuum oven at 20 mmHg and 60°C . The resulting reaction mixture was poured into methanol by drop-wise precipitation. The hydroxyl-terminated PFAM was precipitated and recovered by filtration. The hydroxyl-terminated PFAM was washed three times with methanol. The purified PFAM was dried in a vacuum oven for 3 days at 50°C and 20 mmHg. The yield of PFAM was approximately 94 wt %.

Synthesis of PFAMI

The macroinimer of PFAMI was prepared from the reaction of the hydroxyl-terminated PFAM as a macromonomer and ACPC as a macroinitiator in the presence of a small amount of TEA as a catalyst using the solvent of THF/DCM mixture. THF and DCM are good solvents for PFAM and ACPC, respectively. The ratio of THF/DCM in the solvent mixture was 3 : 1. The amounts of the hydroxyl-terminated PFAM ($M_n = 1796$) and ACPC used were 10 g and 1.0 g, respectively. The concentration of TEA was 0.5 wt % of PFAM and ACPC. The content of PFAM and ACPC in the reaction mixture was maintained at 10 wt %. The reaction was homogeneously performed for 24 h at 10°C . A small amount of hydrogen chloride [HCl] is produced in the reaction, which combines with TEA to form triethylamine HCl salt [$\text{C}_2\text{H}_5\text{N}\cdot\text{HCl}$]. The equation of condensation reaction between the hydroxyl terminated PFAM and ACPC is shown in Figure 3.

After the condensation reaction, about 80 vol % of THF contained in the reaction mixture was removed in a vacuum oven at 20 mmHg and 20°C . The resulting reaction mixture was poured drop-wise into anhydrous n-hexane cooled by dry ice to precipitate PFAMI. The PFAMI was recovered by filtration, and washed three times with cold anhydrous n-hexane to remove triethylamine hydrogen chloride salt. The purified PFAMI was dried

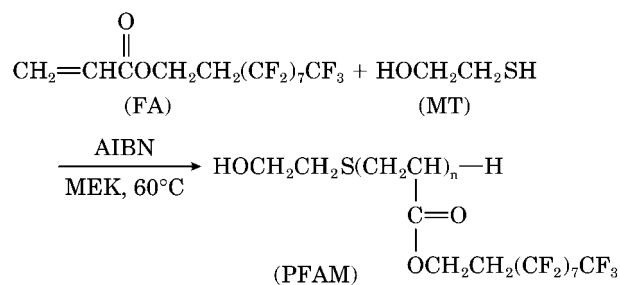


Figure 2 Reaction equation for hydroxyl-terminated PFAM synthesis.

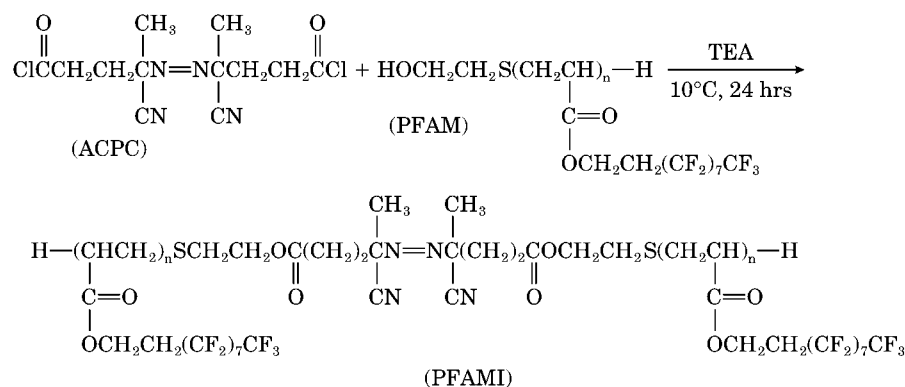


Figure 3 Reaction equation for PFAMI synthesis.

in a vacuum oven for 2 days at 20°C and 20 mmHg. The yield of PFAMI was about 85 wt %.

Synthesis of BPFS

The fluorosilicone block copolymers of BPFSs were synthesized from the reaction of PFAMI and SiMA in the presence of a small amount of DBTDA as a catalyst by varying the concentration of SiMA within the range of 18.4–44.4 wt %. For the reaction, 4.0 g of PFAMI ($M_n = 3821$) and 0.9–3.2 g of SiMA were reacted in THF solvent. The concentration of DBTDA was 0.5 wt % of PFAMI and SiMA. Four BPFSs were prepared by varying the mol ratios of SiMA/PFAMI as 2.0 : 1.0, 3.6 : 1.0, 5.4 : 1.0, and 7.2 : 1.0, respectively, as shown in Table I. The content of PFAMI and SiMA in the reaction mixture was maintained at 10 wt %. The reaction was performed for 24 h at 60°C. After the reaction, THF in the reaction mixture was completely evaporated in a vacuum oven for 3 days at 20 mmHg and 60°C to recover BPFS. The equation of reaction between PFAMI and SiMA is shown in Figure 4. The yields of BPFSs were about 73–82 wt % as shown in Table I.

Contact Angle Measurements and Surface Free Energy Estimation

The specimens for contact angle measurements were prepared by the solvent die-casting method from solutions containing BPFSs and BPFS/PVC blends in THF. A smooth polymer surface was obtained with a uniform thickness about 100 μm on a glass plate by slow evaporation of die-casting solvent. Contact angles on the surface of BPFSs and BPFS/PVC blends were measured by the sessile-drop method with an optical goniometer (Rame-Hart, 100-series) at 20–25°C. Wetting liquids used for contact angle measurements were water and MI. The surface free energies were estimated by the Fowkes' theory using the contact angle data.¹

RESULTS AND DISCUSSION

Synthesis of ACPC Macroinitiator

The ACPC prepared from ACPA was analyzed by FTIR and ¹H-NMR. Figure 5 shows the compari-

Table I The Experimental Results of BPFS Synthesis

BPFS	PFAMI (g)	SiMA (g)	Mol Ratio of SiMA/PFAMI	Molecular Weight			Yield (wt %)
				M_n	M_w	M_w/M_n	
BPFS-1	4.0	0.9	2.0	4298	4958	1.15	82.2
BPFS-2	4.0	1.6	3.6	4633	5233	1.13	73.4
BPFS-3	4.0	2.4	5.4	4910	5881	1.20	79.3
BPFS-4	4.0	3.2	7.2	5388	6230	1.16	75.5

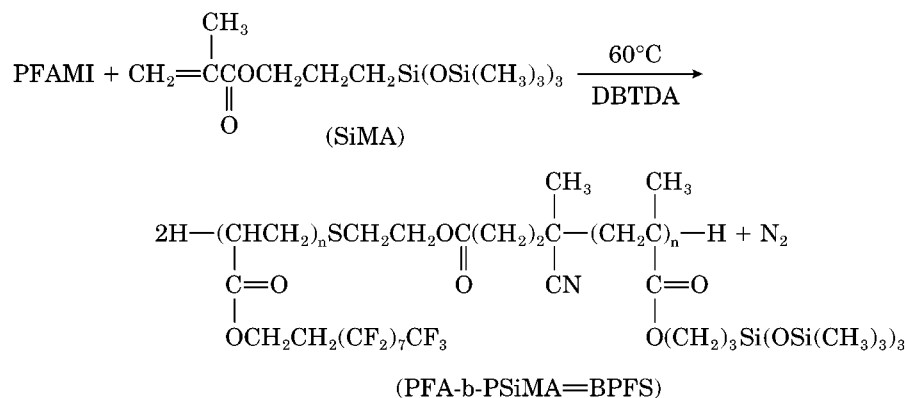


Figure 4 Reaction equation for BPFS synthesis.

son of FTIR spectra of ACPA and ACPC. It can be seen that the stretching band of the COOH group appears at the wavenumbers of 3000 cm^{-1} and 1700 cm^{-1} in the FTIR spectrum of ACPA. On the other hand, it can be seen from the FTIR spectrum of ACPC that the stretching band of the COOH group disappears, but the stretching band of the C=O group is shown at the wavenumber of 1790 cm^{-1} . The stretching bands of CH₂ and CH₃ groups are shown at the wavenumbers of $3000\text{--}2900\text{ cm}^{-1}$, and the stretching band of the CN group is shown at the wavenumber of 2220 cm^{-1} . These results indicate that ACPC was successfully synthesized from ACPA. The main proton groups of the ACPC were analyzed from ¹H-NMR (acetone-d₆, δ in ppm). Their proton groups were shown in CCH₂ (m, 4H, 3.1–3.4), CH₂CO (m, 4H, 2.4–2.7), CCH₃ (m, 6H, 1.7–1.8). The ¹H-NMR analysis supports the FTIR results of ACPC synthesis.

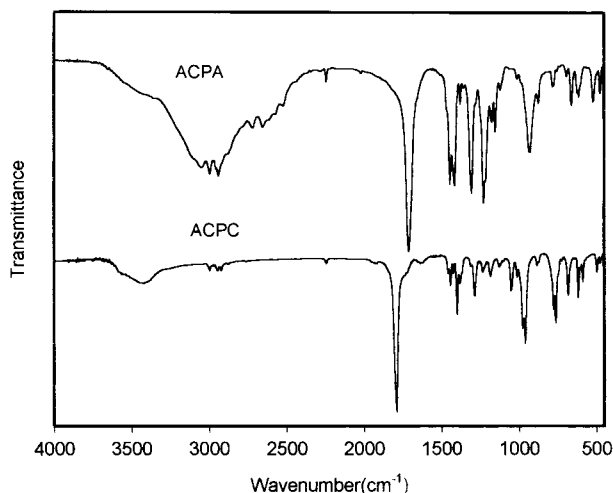


Figure 5 FTIR spectra of ACPA and ACPC.

Synthesis of PFAMs

The molecular weights of the hydroxyl-terminated PFAM prepared by the method described above were analyzed to be 1796 (M_n) and 2220 (M_w), respectively. The polydispersity of the hydroxyl-terminated PFAM is 1.18, which means that the molecular weight distribution of the hydroxyl-terminated PFAM is very narrow. This hydroxyl-terminated PFAM was used to synthesis PFAMI.

FTIR spectrum of the hydroxyl-terminated PFAM is shown in Figure 6. The characteristic stretching bands of the C-F groups (CF₂ and CF₃) and the C=O group originated from FA monomer are strongly shown at the wavenumbers of $1100\text{--}1200\text{ cm}^{-1}$ and 1700 cm^{-1} , respectively. The stretching band of the OH group originated from MT is shown at the wavenumber of 3400 cm^{-1} .

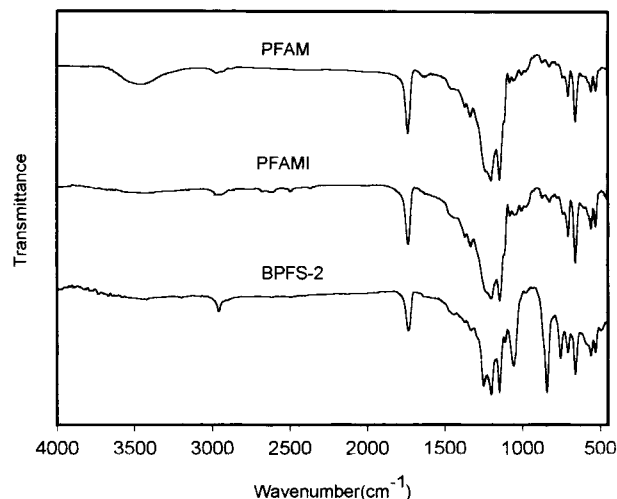


Figure 6 FTIR spectra of hydroxyl-terminated PFAM, PFAMI, and BPFS-2.

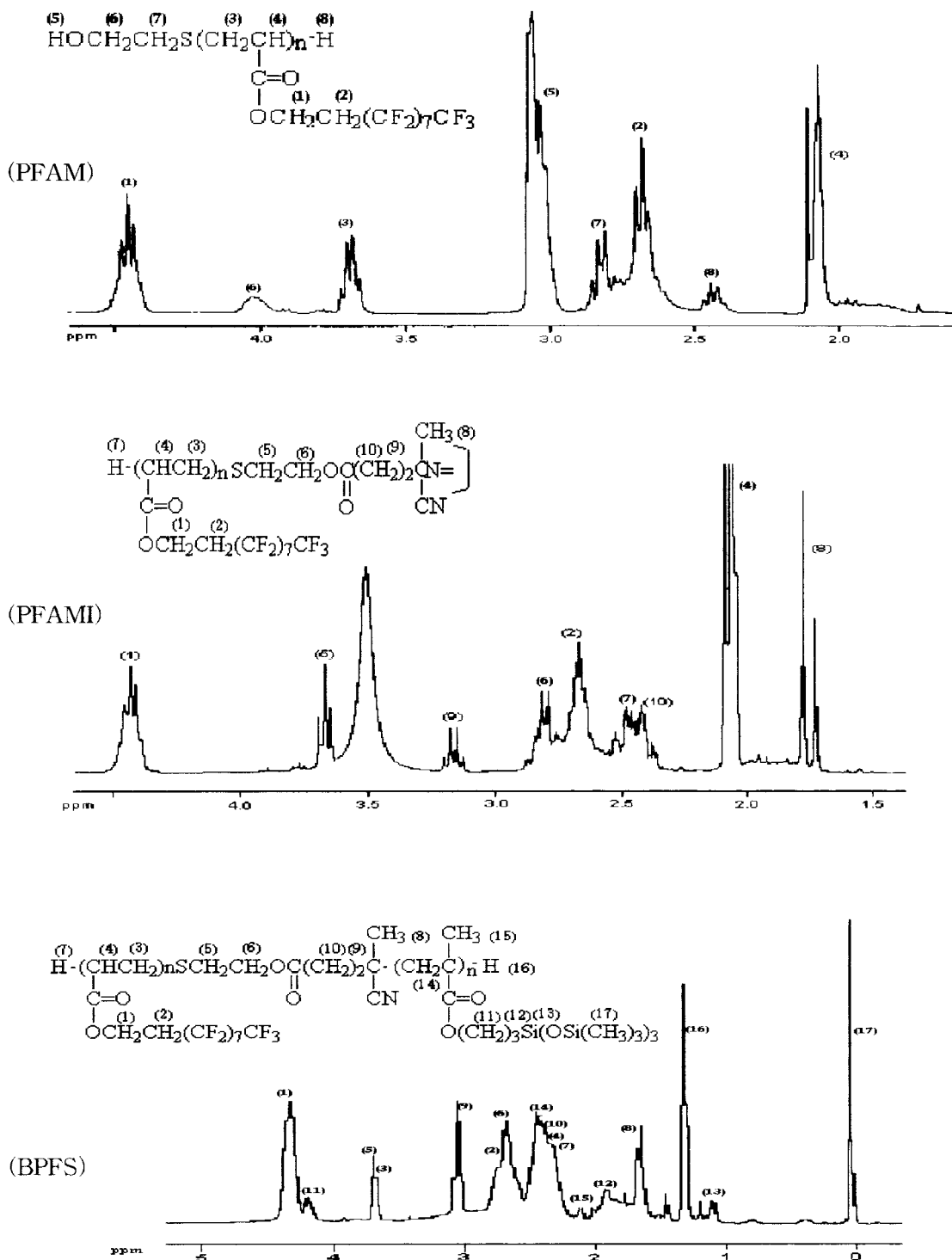


Figure 7 ^1H -NMR spectra of hydroxyl-terminated PFAM, PFAMI, and BPFS-2.

^1H -NMR spectrum (tetrahydrofuran- d_8 , δ in ppm) of the hydroxyl-terminated PFAM is shown in Figure 7. It can be seen that the hydroxyl-terminated PFAM contains the main proton groups of

COOCH_2 (4.4–4.5 ppm), OH (4.0 ppm), OCH_2 (3.6–3.7 ppm), CH (2.0–2.1 ppm), CH_2S (2.4–2.5 ppm), $\text{CH}_2(\text{CF}_2)_7\text{CF}_3$ (2.6–2.7 ppm), SCH_2 (3.0–3.1 ppm), and CH_2 (2.8 ppm). From the results of

FTIR and $^1\text{H-NMR}$ analyses, it can be concluded that the hydroxyl-terminated PFAM desired was well synthesized.

Synthesis of PFAMI

The molecular weights of the PFAMI prepared are 3281 (Mn) and 5780 (Mw), respectively, and the polydispersity is about 1.8. The PFAMI has a fairly narrow molecular weight distribution. This PFAMI was used to synthesize BPFs.

FTIR spectrum of the PFAMI is compared with those of the hydroxyl-terminated PFAM and BPFs in Figure 6. The characteristic stretching bands of the C-F groups (CF_2 and CF_3) and the C=O group originated from FA monomer are strongly shown at the wavenumbers of 1100–1200 cm^{-1} and 1700 cm^{-1} , respectively, which are the same as in the FTIR spectrum of the hydroxyl-terminated PFAM. However, the stretching band of the OH group, which appears in the FTIR spectrum of the hydroxyl-terminated PFAM at the wavenumber of 3400 cm^{-1} , is not shown in the FTIR spectrum of the PFAMI. It can be confirmed that the OH group that existed in the hydroxyl-terminated PFAM has disappeared and does not exist in the PFAMI because of the reaction between PFAM and ACPC. The weak stretching bands of the C-H groups (CH_2 and CH_3), originated from ACPC macroinitiator, appear at the wavenumbers of 2800–2950 cm^{-1} .

To support the FTIR results of PFAMI synthesis, $^1\text{H-NMR}$ spectrum of the PFAMI was measured and is shown in Figure 7. It can be seen that the PFAMI synthesized contains the main proton groups of COOCH_2 (4.4–4.5 ppm), CH_2 (CF_2) $_7\text{CF}_3$ (2.6–2.7 ppm), CHCOO (2.0–2.1 ppm), CH_2S (3.4–3.6 ppm), CH_2CH (2.7–2.8 ppm), SCH_2 (2.4 ppm) and CH_2COO (3.6 ppm) originated from the PFAM, and COCH_2 (2.4–2.5 ppm), CH_2CN (3.2–3.3 ppm) and CNCH_3 (1.7–1.8 ppm) originated from ACPC macroinitiator, respectively. From the results of both FTIR and $^1\text{H-NMR}$ analyses, it can be concluded that the PFAMI was successfully synthesized.

Synthesis of BPFs

As summarized in Table I, four BPFs were synthesized with the variation of SiMA/PFAMI mol ratio. The molecular weights of BPFs were analyzed to be in the range of 4300–5400 (Mn) and 5000–6300 (Mw), respectively. Their polydispersities vary within the range of 1.13–1.20. The

BPFs prepared have fairly narrow molecular weight distribution. The molecular weight tends to increase linearly with the increase of SiMA content in BPFs.

FTIR spectrum of the BPFs-2 is compared with those of the hydroxyl-terminated PFAM and PFAMI in Figure 6. The characteristic stretching bands of the C-F groups (CF_2 and CF_3) and the C=O group originated from FA monomer are strongly shown at the wavenumbers of 1100–1200 cm^{-1} and 1700 cm^{-1} , respectively, which are the same as the FTIR spectra of the hydroxyl-terminated PFAM and PFAMI. However, the stretching bands of the Si-C groups and Si-O groups originated from SiMA monomer, which are not shown in the FTIR spectra of the hydroxyl-terminated PFAM and PFAMI, appear at the wavenumbers of 1050–1100 cm^{-1} and 800–850 cm^{-1} , respectively. Therefore, it can be said that the BPFs, having both perfluoroalkyl group and silicone-containing groups, was well synthesized.

The $^1\text{H-NMR}$ spectrum of the BPFs-2 is shown in Figure 7. The BPFs-2 contains the main proton groups of COOCH_2 (4.3–4.4 ppm), CH_2 (CF_2) $_7\text{CF}_3$ (2.7–2.8 ppm), CHCOO (2.3–2.4 ppm), CH_2S (3.7–3.8 ppm), CH_2CH (2.8 ppm), SCH_2 (2.3–2.4 ppm), CH_2O (3.8 ppm), COCH_2 (2.3–2.4 ppm), CH_2C (3.0–3.1 ppm), CCH_3 (2.6–2.7 ppm) originated from PFAMI, and COOCH_2 (4.2 ppm), CH_2CH_2 (1.9–2.0 ppm), CH_2Si (1.1–1.2 ppm), CCH_3 (2.0–2.1 ppm), CH_2C (2.3–2.4 ppm), CH_2CH_2 (1.2–1.3 ppm), CCH_3 (2.1 ppm), and $\text{Si}[\text{OSi}(\text{CH}_3)_3]_3$ (0.0 ppm) originated from SiMA, respectively. This $^1\text{H-NMR}$ analysis confirms that the BPFs desired were well synthesized.

DSC spectra of BPFs to analyze their T_g s are shown in Figure 8. T_g of BPFs decreases very slightly from 50.3 to 49.3°C as the content of SiMA in BPFs increases from 18.4 wt % to 44.4 wt %. It seems that T_g s of BPFs is nearly independent on the content of SiMA.

Intrinsic Surface Free Energies of BPFs

The contents of FA and SiMA of four BPFs prepared as above are summarized in Table II. FA and SiMA contents of BPFs vary in the range of 42.1–61.8 wt % and in the range of 44.4–18.4 wt %, respectively. Contact angles measured with water and MI on the surfaces of BPFs are listed in Table II. The contact angles on the surfaces of BPFs show 115.7–117.6° for water and 89.4–95.5° for MI, indicating that BPFs are very hy-

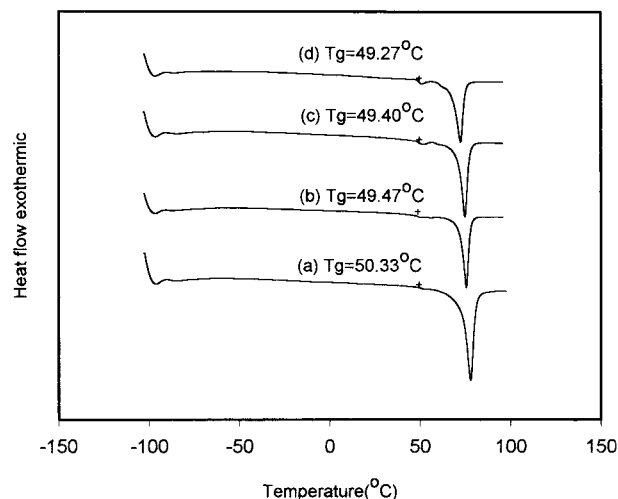


Figure 8 DSC spectra of BPFSSs [(a) BPFSS-1, (b) BPFSS-2, (c) BPFSS-3, and (d) BPFSS-4].

drophobic. The contact angles for both water and MI increase with increasing FA content, which means that the content of perfluoroalkyl side chain determines the hydrophobicity of BPFSS.

Table III shows the inherent surface free energies of BPFSSs calculated from the contact angles. As expected, BPFSSs exhibit extremely low surface free energies of about 9.7–13.0 dynes/cm mainly dependent on the FA content. As the content of FA increases, the surface free energy decreases. The surface free energy is closely related to the FA content. The surface free energy of BPFSS-1 containing the highest FA content of 61.8 wt % is found to be the lowest. The surface free energy of BPFSS-1 is about 9.7 dynes/cm, which is nearly the same as that of PFA homopolymer,¹ even though BPFSS-1 contains much lower FA content compared with PFA homopolymer. From the results, it can be deduced that most of the perfluoroalkyl groups in BPFSS may arrange preferentially at the air-polymer interface.

Table III Inherent Surface Free Energies of BPFSSs

BPFSS	Surface Free Energy (dynes/cm)
BPFSS-1	9.7
BPFSS-2	10.6
BPFSS-3	11.5
BPFSS-4	13.0

Surface Modification Effect of BPFSSs on PVC Film

The contact angles on the surfaces of BPFSS/PVC blends, containing 1.0 wt % of BPFSS, were measured to be 113.9–115.2° for water and 83.2–92.2° for MI as shown in Table II. Even though the content of BPFSS in BPFSS/PVC blend is only 1.0 wt %, the contact angles on BPFSS/PVC blends are almost the same as those on BPFSS. It seems that most of BPFSS added to PVC may migrate to the outermost layer at the air-polymer interface. BPFSS is expected to be very effective to modify the surface properties of PVC.

The surface free energies of BPFSS/PVC blends modified by BPFSS were calculated from the contact angle data. The surface free energies of BPFSS/PVC blends are shown in Figure 9 as a function of BPFSS concentration. The surface free energies of BPFSS/PVC blends decrease almost linearly as the concentration of BPFSS added to PVC increases within the range of 0.3–2.0 wt %. The surface free energies of BPFSS/PVC blends containing 2.0 wt % of BPFSS were estimated to be approximately 10.8–14.0 dynes/cm, which are very slightly less than those of BPFSSs. The inherent surface free energy of PVC film is known to be about 39.0 dyne/cm.²⁰ It can be confirmed again that BPFSS is very effective to lower the surface

Table II Contact Angles Measured with Water and MI on the Surfaces of BPFSSs and BPFSS/PVC Blends

BPFSS	FA Content (wt %)	SiMA Content (wt %)	FA + SiMA Content (wt %)	Contact Angle on BPFSS (deg.)		Contact Angle on BPFSS (1.0 wt %)/PVC (deg.)	
				Water	MI	Water	MI
BPFSS-1	61.8	18.4	81.5	117.6	95.5	115.2	92.2
BPFSS-2	54.1	28.6	82.7	117.1	93.1	114.5	90.6
BPFSS-3	47.3	37.5	84.8	116.0	91.0	114.2	85.3
BPFSS-4	42.1	44.4	86.5	115.7	89.4	113.9	83.2

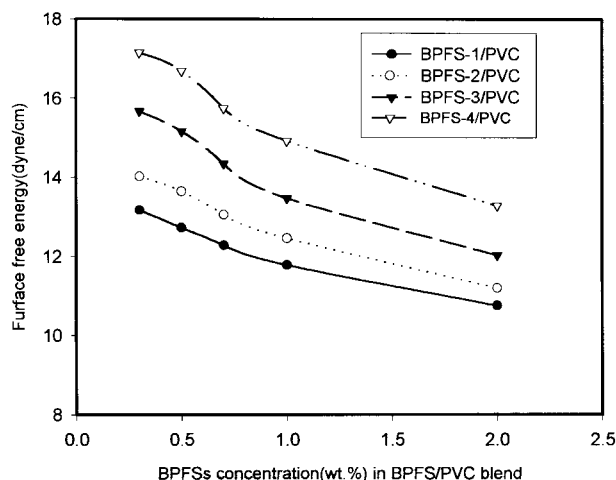


Figure 9 Surface free energies of BPFSS/PVC blends.

free energy of PVC even though a small amount of BPFSS is added. This indicates that most of BPFSS added to PVC might arrange to the outermost layer at the PVC-air interface. The surface enrichment of BPFSS-2 in the BPFSS-2/PVC blend containing 2.0 wt % of BPFSS-2 could be observed and confirmed by XPS measurement. The atomic compositions of the surface of BPFSS-2/PVC blend measured by XPS as a function of take-off angle are shown in Table IV. The take-off angle corresponds to the depth of a surface from the air-polymer interface. Both fluorine and silicone contents decrease rapidly with an increase in the take-off angle from 5 to 10°, and then fluorine content decreases gradually but silicone content does not vary with an increase in the take-off angle from 10 to 60°. On the other hand, both carbon and oxygen contents increase gradually with the take-off angle. These results indicate the preferential surface enrichment of BPFSS having extremely low surface free energy to the outermost layer of the surface of BPFSS/PVC blend. The

Table IV Atomic Compositions of the Surface of BPFSS-2/PVC Blend Containing 2.0 wt % of BPFSS-2 as a Function of Take-Off Angle

Take-Off Angles (deg.)	F _{1s}	C _{1s}	Si _{2p}	O _{1s}
5	49.4	42.8	1.9	5.9
10	45.8	46.1	1.4	6.7
20	43.9	47.5	1.4	7.2
40	39.4	51.7	1.4	7.5
60	35.8	54.9	1.4	7.9

Table V T_g s of BPFSS-2, PVC, and BPFSS-2 (2.0 wt %)/PVC Blend

Polymer	BPFSS-2	BPFSS-2/PVC Blend	PVC
T_g (°C)	49.5	56.4	97.0

outermost layer corresponds to the take-off angle below 5°. These results confirm again the enrichment of fluoropolymer having lower surface energy in polymer blends at the polymer-air interface, which is reported in the literature.^{1,21}

The T_g of BPFSS-2, PVC, and BPFSS-2/PVC blend were analyzed by DSC. Compatibility of polymers in a polymer blend has been defined in a number of ways.²² The widely used definition of polymer blend for compatibility involves T_g s of polymers and the blend measured by DSC. Compatible blends must exhibit a single T_g between T_g s of the polymers, whereas incompatible blends will have two T_g s that correspond to those of the polymers. The compatibility of BPFSS-2 and PVC were examined by measuring T_g s. As shown in Table V, the BPFSS-2/PVC blend containing 2.0 wt % of BPFSS-2 shows a single T_g of 56.4°C between T_g s of BPFSS-2 (49.5°C) and PVC (97.0°C). DSC spectrum of BPFSS-2 to measure T_g is shown in Figure 8. T_g of PVC in Table V can be found in the literature.²³ From the results, it can be deduced that BPFSSs prepared in this study are compatible with PVC if the concentration of BPFSS in BPFSS/PVC blend is less than 2.0 wt %. Because the BPFSSs prepared in this study have an excellent ability for lowering the surface free energy and good compatibility as described above, they may be very useful as surface modification additives.

CONCLUSIONS

The fluorosilicone block copolymers of PFA-b-PSiMAs, having perfluoroalkyl side chains and silicone-containing side chains, were synthesized by the free radical polymerization of PFAMI macroinimer and SiMA monomer. PFAMI was synthesized from the reaction of the hydroxyl-terminated PFAM and ACPC. The hydroxyl-terminated PFAM was prepared by the free radical polymerization of FA and MT using AIBN. ACPC was prepared from the reaction of ACPA and PCl_5 . It was confirmed by FTIR and ¹H-NMR analyses that the syntheses of ACPC, hydroxyl-terminated PFAM, PFAMI, and BPFSS were completed successfully. The molecular

weights of BPFs were analyzed to be in the range of 4300–5400 (Mn) and 5000–6300 (Mw), respectively. Their polydispersities vary within the range of 1.13–1.20. The intrinsic surface properties of BPFs and their surface modification effects on PVC film were investigated by analyzing the surface free energies and atomic compositions of the outermost layer of the surfaces. BPFs exhibit extremely low surface free energies of about 9.7–13.0 dynes/cm mainly dependent on the FA content. The surface free energies of BPF/PVC blends containing 2.0 wt % of BPF were estimated to be approximately 10.3–14.0 dynes/cm. It was confirmed that BPF having extremely low surface free energy is preferentially enriched to the outermost layer of the surface of BPF/PVC blend. Because BPF has an excellent ability for lowering surface free energy and good compatibility it may be very useful as a surface modification additive.

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