

Synthesis of Urethane Graft Copolymers with Perfluoroalkyl and Silicone-Containing Side Chains and their Surface Properties

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ABSTRACT: Dihydroxyl-terminated macromonomers with two groups, a perfluoroalkyl group and a silicone-containing group, were synthesized by free-radical polymerization with perfluoroalkylethyl acrylate (FA), 3-[tris(trimethylsilyloxy)silyl] propyl methacrylate (SiMA), and 1-thioglycerol (TG). Using these macromonomers and toluene-2,4-diisocyanate (TDI), various urethane graft-co-(septadecafluorodecylacrylate)-(tris(trimethylsilyloxy silylpropyl acrylate) copolymers (PUFSGs) with differing FA and SiMA contents were synthesized. The macromonomers and PUFSGs synthesized were characterized and identified by GPC, DSC, (X-ray photoelectron spectroscopy (XPS), FTIR, and ¹H-NMR analysis. The surface free energies of PUFSGs, 9–12 dynes/cm, depend strongly on FA content but not on SiMA content. The glass transition temperature of PUFSG is strongly dependent on SiMA content. The perfluoroalkyl group originating from FA is preferentially arranged to the outermost layer at the air–polymer interface to the silicone-containing group originating from SiMA. The surface free energies of PUFSG/polyvinyl chloride (PVC) blends exhibit extremely low values, 10–14 dynes/cm, indicating that extreme segregation of PUFSG occurs at the air–polymer interface. Most PUFSGs added to PVC are located at the air–polymer interface, and PUFSGs are very effective in lowering the surface free energy. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 2029–2038, 1999

Key words: surface free energy; surface modification; fluorosilicone; macromonomer; urethane graft copolymer

INTRODUCTION

The surface properties of polymers have recently received much attention because of polymers' generic importance in such diverse technological areas as adhesives, biomedical materials, electronic materials, and coatings. Many desirable properties, including compatibility, wettability, adhe-

sion, permeability, solid-state morphology, and so on, can be influenced by polymer surface structure. Polymer surface properties are closely related to the functionality of the materials, such as adhesion, fracture, environmental compatibility, biocompatibility, and electric properties. One of the most popular and successful strategies for lowering the surface tension of a film is to incorporate fluorine into the polymer molecule comprising the coating. The fluorine can be incorporated into the main polymer chain.^{1–13} Various polymers with fluorocarbon segments in the side

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chains have attracted particular attention due to their very low surface free energy.⁵⁻¹⁷

Fluorine- or silicone-containing copolymers have been widely used as surface modification agents because of their good hydrophobic properties.¹⁸⁻²⁰ Surface property modification using blends of fluoropolymers with hydrocarbon polymers has been studied.^{5,6,16,21,22} Most silicone-containing polymers have low surface energies, and many fluoropolymers have much lower surface energies than silicone-containing polymers. Consequently, hybrid fluorosilicone polymers containing both fluorine and silicone should be of great interest for surface modifications. Fluoro-silicone polymer synthesis is achieved by addition of fluorocarbon side-chain entities to a preformed siloxane polymer or by polymerization of suitable monomers. Surface properties of several fluoro-silicone polymers prepared by adding fluorocarbon side-chain entities to a preformed siloxane polymer are well reviewed in the literature.¹⁵ Surface properties of fluorosilicone random copolymers prepared by polymerization of a perfluoroalkyl acrylate monomer and a silicone-containing acrylate monomer also has been investigated.²³

Graft copolymers are an important class of polymers that have the ability to exhibit the physical properties of both components. Generally, the bulk and surface structure of graft copolymers are not consistent with each other. Significant surface accumulation of one polymer component at the surface frequently occurs, producing quite a different surface structure than would be expected

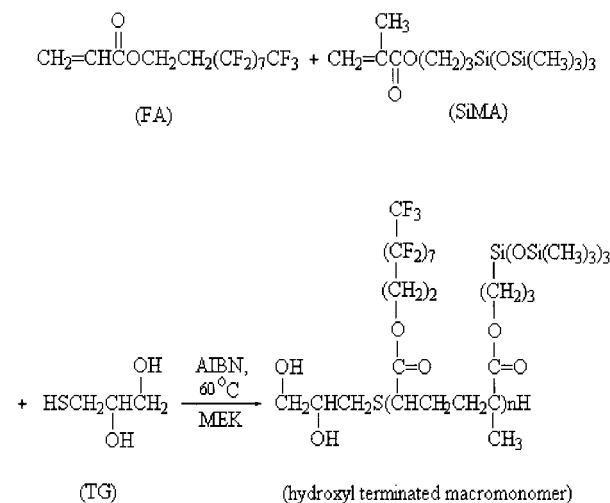


Figure 1 Reaction equation for dihydroxyl-terminated macromonomer synthesis.

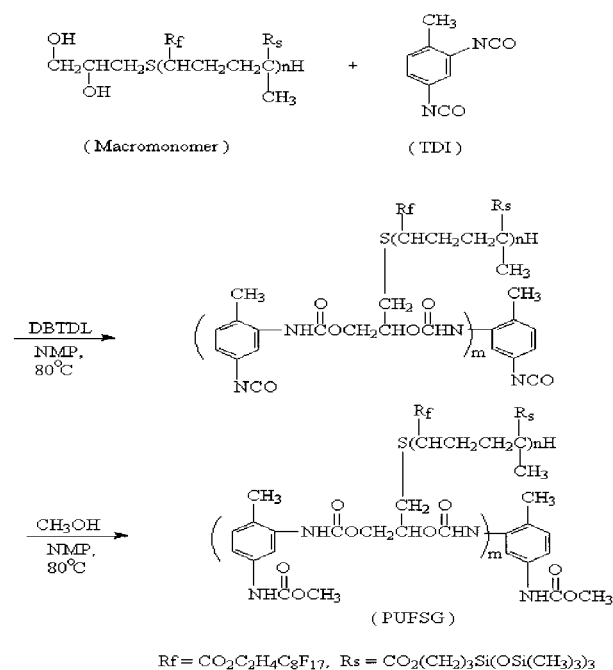


Figure 2 Reaction equation for PUFSG synthesis.

from that in bulk. Controlling the surface structure of polymer materials is an essential requirement in many industrial applications. In an effort to gain more understanding of the relationship between the bulk and surface morphologies of graft copolymers, fluorine-containing graft copolymers have been synthesized and their surface properties investigated.^{17,24-26}

In this study, urethane graft-co-(septadecafluorodecylacrylate)-(tris(trimethylsilyloxy silylpropyl acrylate) copolymers (PUFSGs) with differing perfluoroalkyl groups and silicone-containing groups were synthesized using dihydroxyl-terminated macromonomers and a diisocyanate, and their surface properties were analyzed. The macromonomers with two terminal hydroxyl groups and differing perfluoroalkyl and silicone-containing groups were synthesized using perfluoroalkylethyl acrylate (FA), 3-[tris(trimethylsilyloxy)silyl]propyl methacrylate (SiMA), and 1-thioglycerol (TG) by free-radical copolymerization. The surface modification effects of PUFSGs on polyvinyl chloride (PVC) film were also investigated. FA was chosen as the fluorine-containing main monomer; SiMA, as the silicone-containing comonomer. PVC was chosen as a base polymer to study the surface modification effects of PUFSGs, because it is widely used for agricultural film.^{19,20}

Table I Dihydroxyl-Terminated Macromonomers Prepared and their FA and SiMA Contents

MAC	Mole Ratio (FA/SiMA/TG)	M_n	M_w	PD (M_w/M_n)	FA Content (wt %)	SiMA Content (wt %)	FA + SiMA Content (wt %)
MAC-1	1.0/0.0/1.0	1047	1174	1.12	82.5	0	82.5
MAC-2	0.8/0.2/1.0	1034	1208	1.10	68.0	14.0	82.0
MAC-3	0.6/0.4/1.0	1101	1162	1.06	53.0	28.5	81.5

EXPERIMENTAL

Reagents

FA ($\text{CH}_2=\text{CHCO}_2\text{C}_2\text{H}_4\text{C}_8\text{F}_{17}$; $M_w = 518$), obtained from Hoechst Co., Frankfurt, Germany, was used as received. SiMA [$\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OSi}(\text{CH}_3)_3)_3$; $M_w = 423$], toluene-2,4-diisocyanate (TDI), TG ($\text{HSCH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$, $M_w = 108$), and dibutyltin dilaurate [DBTDL; $(\text{C}_4\text{H}_9)_2\text{Sn}(\text{OCOC}_{10}\text{H}_{20}\text{CH}_3)_2$], obtained from Aldrich Co., USA, were used as received. The initiator of 2,2'-azobisisobutyronitrile (AIBN; Aldrich) was recrystallized from methanol. Tetrahydrofuran (THF; Aldrich) was distilled from sodium benzophenone ketyl under N_2 . *N*-methyl-2-pyrrolidone (NMP; Aldrich) was fractionally distilled under vacuum. Methanol, methyl ethyl ketone (MEK), and methylene iodide (MI) were used as received. PVC with the degree of polymerization of 1100 from Aldrich was used as a base polymer. Deionized water was used throughout the experiments.

Synthesis of Dihydroxyl-Terminated Macromonomers

The dihydroxyl-terminated macromonomers were synthesized using the FA monomer, the SiMA monomer, and TG as a chain transfer agent. AIBN was used as an initiator for free-radical copolymerization. FA and SiMA contents in the dihydroxyl-terminated macromonomers were varied to investigate the effect of the varying contents on surface free energy. AIBN used for dihydroxyl-terminated macromonomer synthesis was 0.5 wt % of the total amount of FA, SiMA, and TG. MEK was used as a reaction solvent, with the content of the total reactant in MEK fixed at 20 wt %. Free-radical copolymerization was done in a 100 mL flask at 60°C for 24 h. The reaction equation for dihydroxyl-terminated macromonomer synthesis is illustrated in Figure 1. The dihydroxyl-terminated macromonomers prepared have two terminated hydroxyl groups and two long side

chains of the perfluoroalkyl group (R_f ; $-\text{CO}_2\text{C}_2\text{H}_4\text{C}_8\text{F}_{17}$) and the silicone group [R_s ; $-\text{CO}_2(\text{CH}_2)_3\text{Si}(\text{OSi}(\text{CH}_3)_3)_3$]. When only FA without SiMA is used for the reaction, the dihydroxyl-terminated macromonomer contains a long side chain of the perfluoroalkyl group. After the reaction was completed, about 80 vol % of MEK in the reaction solution was removed at 20 mmHg and 60°C. The dihydroxyl-terminated macromonomer was recovered by dropwise precipitation of the aforementioned reaction solution in methanol, and purified by recrystallizing three times from methanol. The purified macromonomer was dried in a vacuum oven at 20 mmHg and 40°C for 3 days. The yield of dihydroxyl-terminated macromonomer was about 60–80 wt %.

Synthesis of PUFSGs

The PUFSGs were synthesized using the macromonomers prepared by the method just de-

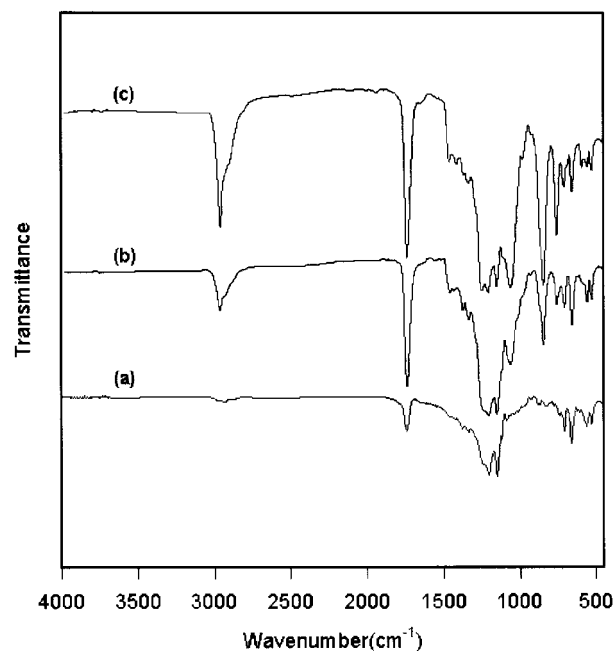


Figure 3 FTIR spectra of dihydroxyl-terminated macromonomers (a) MAC-1, (b) MAC-2, and (c) MAC-3.

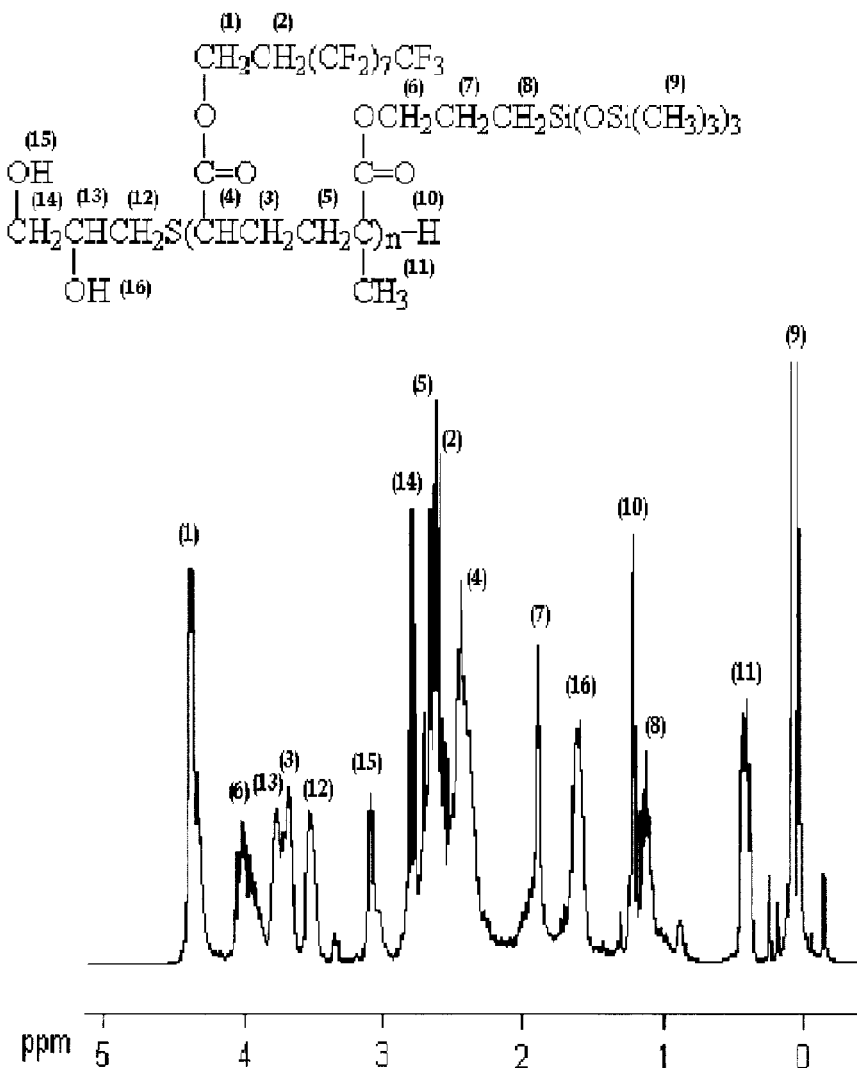


Figure 4 ¹H-NMR spectrum of MAC-3.

scribed and TDI ($M_w = 174$). The reaction was performed in two steps, as shown in Figure 2. In the first step, the dihydroxyl-terminated macromonomer and TDI were reacted with the excess mole ratio of TDI to dihydroxyl-terminated macromonomer (mole ratio in the range of 1.2–2.0) to obtain polyurethane with two terminal isocyanate groups (-NCO). In the second step, the polyurethane with two terminal isocyanate groups was reacted with methanol to block the terminal isocyanate groups. The amount of DBTDL used as a catalyst for polyurethane reaction was 0.5 wt % of the reactant of dihydroxyl-terminated macromonomer and TDI. NMP was used as reaction solvent, and the content of reactant in NMP was adjusted at 20 wt %. The reaction was performed

in a 100 mL flask at 80°C for 6 h. After the polyurethane reaction was finished, 20 wt % excess of methanol was rapidly added to the reaction solution obtained in the first step, and the reaction solution was further reacted for 3 h to block the terminal isocyanate groups. After the reaction, about 80 vol % of NMP contained in the reaction solution was removed at 20 mmHg and 60°C. PUFSG was recovered by dropwise precipitation of the reaction product in methanol and purified by recrystallizing three times from methanol. The purified PUFSG was dried in a vacuum oven at 20 mmHg and 40°C for 3 days. The yield of PUFSG was about 40–50 wt %. The FA content in the PUFSG was varied within the range of 40–70 wt %.

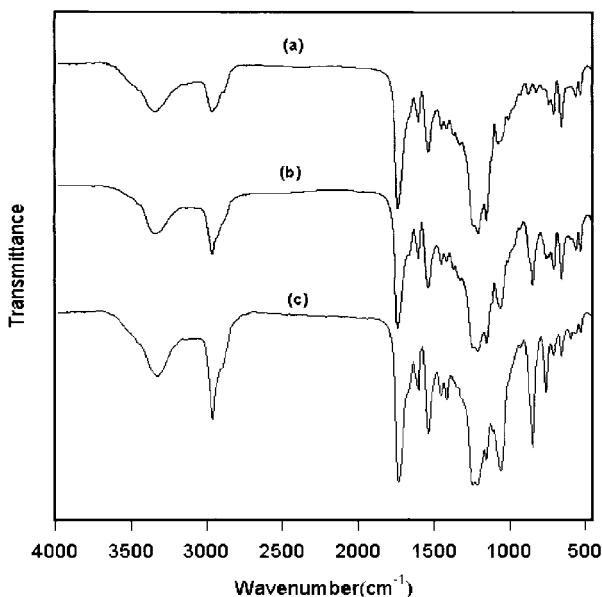


Figure 5 Comparison of FTIR spectra for PUFSGs prepared using (a) MAC-1, (b) MAC-2, and (c) MAC-3 with a TDI/macromonomer mole ratio of 2.0.

Instrumentation

FTIR spectra for the dihydroxyl-terminated macromonomers and PUFSGs were analyzed with a Didilab Division FTS 165 spectrometer (Bio-Rad Co.). The glass transition temperatures (T_g) of the PUFSGs and PUFSG/PVC blends were determined with a DuPont model 2100 DSC system. $^1\text{H-NMR}$ spectra for the PUFSGs were analyzed with a Bruker DRX-300 spectrophotometer. The molecular weights of the dihydroxyl-terminated macromonomers and PUFSGs were measured with a 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 surface of PUFSG/PVC blend were analyzed by angle-dependent XPS, using a V.G. Scientific ESCALAB MK II spectrometer with an $\text{AlK}\alpha$ X-ray source and a hemispherical sector analyzer by changing the take-off angle from 5° to 90° .

Contact Angle Measurements and Surface Free Energy Estimation

The specimens for contact angle measurements were prepared by solvent die-casting with the solutions containing 1.0 wt % of polymer in THF. Smooth polymer surfaces were obtained with a uniform thickness of about $100\ \mu\text{m}$ on a glass plate by slow evaporation of the die-casting sol-

vent. Contact angles on the surfaces of the PUFSGs and PUFSG/PVC blends were measured by the sessile-drop method with an Rame-Hart 100 series optical goniometer at $20\text{--}25^\circ\text{C}$. Water and methylene iodide were the wetting liquids used for contact angle measurements.²⁷ The surface free energies were estimated by Fowkes's theory using the contact angle data.^{10,27}

RESULTS AND DISCUSSION

Synthesis of Dihydroxyl-Terminated Macromonomers

The macromonomers containing two hydroxyl groups, which can be used to prepare PUFSGs with a diisocyanate compound, were obtained from the FA monomer, the SiMA monomer, TG as a chain transfer agent, and AIBN as an initiator by free-radical copolymerization. The reaction equation for the dihydroxyl-terminated macromonomer synthesis is shown in Figure 1. The molecular weight of the dihydroxyl-terminated macromonomer can be controlled by varying the amount of TG, but in this study the TG amount was maintained constant with respect to the amounts of FA and SiMA to obtain nearly the same molecular weight. The reaction mole ratios of FA/SiMA/TG used for the synthesis of three dihydroxyl-terminated macromonomers designated MAC-1, MAC-2, and MAC-3 were 1.0/0.0/1.0, 0.8/0.2/1.0, and 0.6/0.4/1.0, respectively. These dihydroxyl-terminated macromonomers were used to prepare PUFSGs with various FA and SiMA contents. In Table I, FA and SiMA content are calculated from the reactant mole ratio introduced initially to the reaction. The dihydroxyl-terminated macromonomers prepared in this study and their FA and SiMA contents are summarized. The molecular weights of the dihydroxyl-terminated macromonomers are nearly the same, in the range of $1000\text{--}1100\ M_n$, and their polydispersities are very narrow. The FA and SiMA contents were varied in the range of 82.5–53.0 wt % and 0–28.5 wt %, respectively. But the sum of FA and SiMA contents was nearly constant, at 81.5–82.5 wt %.

FTIR spectra of the dihydroxyl-terminated macromonomers are compared in Figure 3. The characteristic stretching band due to the C–F groups (CF_2 , CF_3) originating from the FA monomer are strongly shown at the wave number of $1100\text{--}1200\ \text{cm}^{-1}$ for all of the macromonomers.

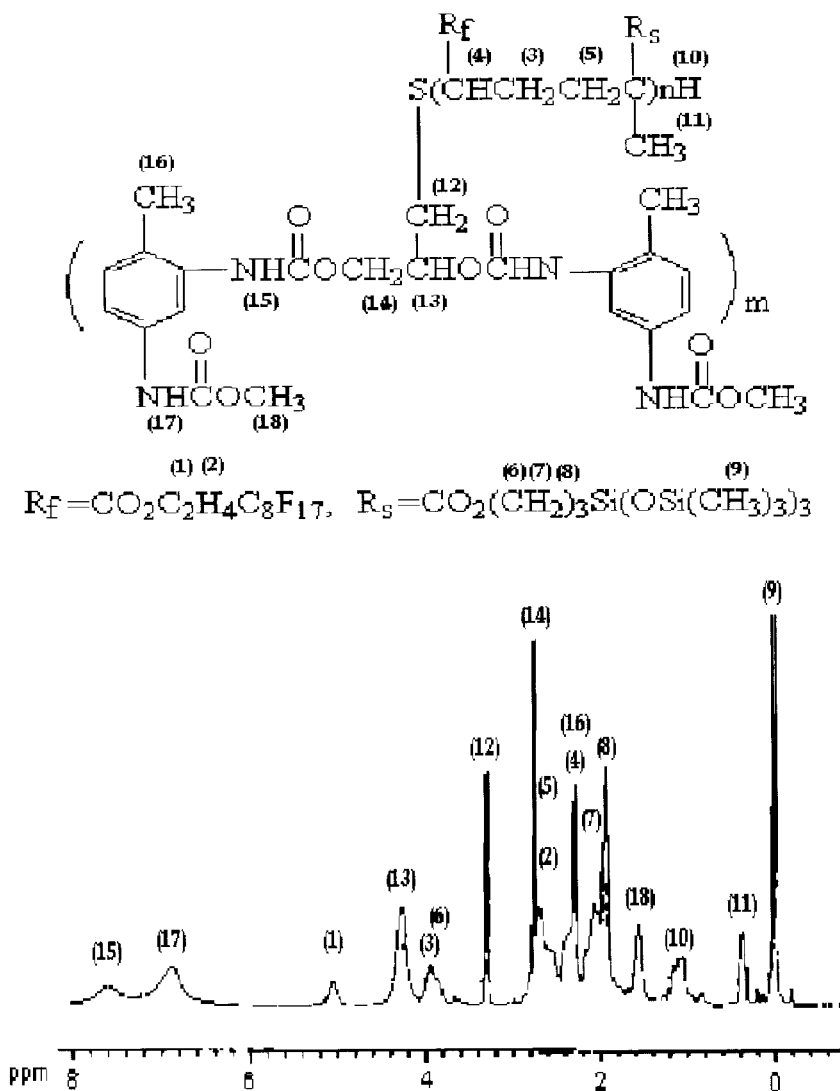


Figure 6 ^1H -NMR spectrum of PUFSG prepared using MAC-3 with a TDI/macromonomer mole ratio of 2.0.

The stretching bands due to the C–H groups (CH_2 , CH_3) and Si–C groups originating from the SiMA monomer are shown at $2850\text{--}2960\text{ cm}^{-1}$ and $800\text{--}850\text{ cm}^{-1}$, respectively, for the MAC-2 and MAC-3 dihydroxyl-terminated macromonomers. However, the stretching bands due to the C–H groups (CH_2 , CH_3) and Si–C groups for the MAC-1 dihydroxyl-terminated macromonomer, which was prepared from the FA monomer only without SiMA, are not shown. A carboxyl (COO) stretching band is shown at 1740 cm^{-1} for all three dihydroxyl-terminated macromonomers. Figure 3 also shows that both the C–H and carboxyl stretching bands become stronger with increasing SiMA content of the dihydroxyl-ter-

nated macromonomers. The hydroxyl stretching band originating from TG is not shown, because of its very small content in the dihydroxyl-terminated macromonomers. These results confirm that the desired dihydroxyl-terminated macromonomers were well synthesized.

To support the FTIR results of dihydroxyl-terminated macromonomer synthesis, the ^1H -NMR spectrum (CDCl_3 , δ in ppm) of MAC-3 was measured, as shown in Figure 4. This analysis confirmed that MAC-3 contains the main proton groups of COOCH_2 (4.3–4.5 ppm), $\text{CH}_2(\text{CF}_2)_7\text{CF}_3$ (2.4–2.6 ppm), SCHCOO (2.3–2.4 ppm), CHCH_2 (3.7–3.9 ppm), and CH_2COO (2.6–2.7 ppm) originating from FA; COOCH_2 (3.9–4.1 ppm),

Table II PUFSGs Prepared and their Molecular Weights

PUFSG	MAC	TDI/MAC Mole Ratio	M_n	M_w	PD (M_w/M_n)
PUFSG-1-1	MAC-1	1.2	6826	7236	1.06
PUFSG-1-2	MAC-1	1.5	3759	4323	1.15
PUFSG-1-3	MAC-1	2.0	1203	1745	1.45
PUFSG-2-1	MAC-2	1.2	6074	7046	1.16
PUFSG-2-2	MAC-2	1.5	3713	4567	1.23
PUFSG-2-3	MAC-2	2.0	1124	1989	1.77
PUFSG-3-1	MAC-3	1.2	5848	6959	1.19
PUFSG-3-2	MAC-3	1.5	3927	4438	1.13
PUFSG-3-3	MAC-3	2.0	1272	1615	1.27

CH₂CH₂ (1.9–2.0 ppm), CH₂CH (1.7–1.8 ppm), CHCOO (1.0–1.2 ppm), CH₂Si (1.0–1.2 ppm), and Si (OSi(CH₃)₃)₃ originating from SiMA; and CH₂OH (2.7–2.9 ppm), HOCH₂ (3.0–3.1 ppm), CHOH (2.7–2.8 ppm), and CH₂S (3.5–3.6 ppm) originating from TG. From the results of the FTIR and ¹H-NMR analyses, it can be concluded that the dihydroxyl-terminated macromonomers were successfully synthesized.

Synthesis of PUFSGs

PUFSGs were synthesized by solution polymerization using the three dihydroxyl-terminated macromonomers prepared as discussed earlier and TDI with a DBTDL catalyst. The reaction equation for the PUFSG synthesis is shown in Figure 2. The reactant mole ratio of TDI/macromonomer was varied at 1.2/1.0, 1.5/1.0, and 2.0/1.0 for MAC-1, MAC-2, and MAC-3, respectively.

The PUFSGs prepared were characterized by FTIR and ¹H-NMR analysis. Figure 5 compares the FTIR spectra for three PUFSGs prepared using the dihydroxyl-terminated macromonomers shown in Table I. The stretching bands of the C–H groups (CH₂, CH₃), carboxyl group (COO), C–F groups (CF₂, CF₃), and Si–C group originated from the dihydroxyl-terminated macromonomers appear at wave numbers 2850–2960, 1740, 1100–1200, and 800–850 cm⁻¹, respectively. The urethane group (NHCO) produced from the reaction between the hydroxyl group of the dihydroxyl-terminated macromonomers and isocyanate group of TDI is shown at wave number 3300–3400 cm⁻¹. The strengths of both the C–H and Si–C stretching bands become stronger as the SiMA content of the dihydroxyl-terminated macromonomer used for the synthesis of PUFSG increases. The Si–C stretching band of the PUFSG prepared using the MAC-1 dihydroxyl-terminated

Table III Contact Angles of Both Water and Methylene Iodide (MI) on the Surfaces of PUFSGs and PUFSG/PVC Blends

PUFSG	FA Content (%)	SiMA Content (%)	FA + SiMA Content (%)	Contact Angle on PUFSG (deg.)		Contact Angle on PUFSG (1.0 wt %)/PVC (deg.)	
				Water	MI	Water	MI
PUFSG-1-1	69.4	0	69.4	117.5	97.5	116.5	96.4
PUFSG-1-2	67.9	0	67.9	116.8	97.3	115.0	95.0
PUFSG-1-3	61.1	0	61.1	116.0	96.1	114.6	90.0
PUFSG-2-1	57.5	11.8	69.3	116.0	97.5	115.7	96.3
PUFSG-2-2	56.2	11.6	67.8	115.2	95.7	115.0	95.3
PUFSG-2-3	50.7	10.4	61.1	115.0	95.1	114.0	94.1
PUFSG-3-1	44.5	23.9	68.4	115.1	95.4	110.8	93.6
PUFSG-3-2	43.5	23.4	66.9	111.1	95.4	109.4	93.3
PUFSG-3-3	39.1	21.0	60.1	110.2	93.2	111.0	90.2

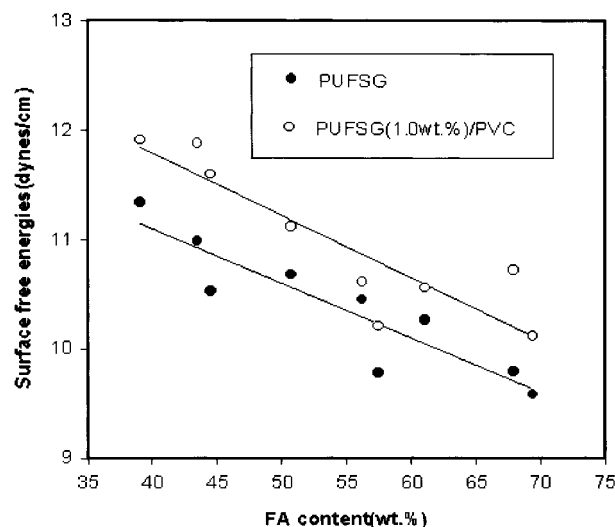


Figure 7 Variation of surface free energies of PUFSGs and PUFSG (1.0 wt %)/PVC blends with FA content.

macromonomer, which does not contain SiMA, is not shown. Figure 6 shows the $^1\text{H-NMR}$ spectrum (CDCl_3 , in ppm) of the PUFSG prepared using MAC-3 with a TDI/macromonomer mole ratio of 2.0. The main proton groups of the PUFSG are the urethane group ($\text{NHC}_6\text{H}_3\text{NH}$; 6.9, 7.5–7.8 ppm), fluorine-containing group [$-\text{CH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3$; 2.3–2.5, 4.9–5.2 ppm], and silicone-containing group ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{SiO}-$; 0.0, 1.9–2.1 ppm). From the results of FTIR and $^1\text{H-NMR}$ analysis, it can be concluded that the desired PUFSGs were well synthesized.

The molecular weights and polydispersities of the PUFSGs prepared by varying the dihydroxyl-terminated macromonomers and the mole ratio of TDI/macromonomer are summarized in Table II. The molecular weight (M_n) varies from 1100 to 7000 and increases as the mole ratio of TDI/mac-

romonomer decreases, which shows that the molecular weight can be controlled as expected. The polydispersities of the PUFSGs prepared are in the range of 1.06–1.77, showing that the molecular weight distributions are relatively narrow.

Surface Properties of PUFSGs

To investigate the surface properties of the PUFSGs prepared in this study, the contact angles of both water and methylene iodide on the surfaces of the PUFSGs and PUFSGs/PVC blends were measured. The FA and SiMA contents in the PUFSGs are calculated from the dihydroxyl-terminated macromonomer content introduced initially to the reaction, and are summarized in Table III. From these contact angle data, the surface free energy can be estimated by Fowkes's theory.^{10,27} Figure 7 shows the variation of surface free energies of PUFSGs and PUFSG (1.0 wt %)/PVC blends with FA content. The surface free energies of PUFSGs, 9–12 dynes/cm, depend strongly on FA content. The surface free energies of both the PUFSGs and PUFSG (1.0 wt %)/PVC blends increase linearly as FA content decreases, even though the sum of FA and SiMA contents is nearly constant. The perfluoroalkyl group (R_f) originating from FA may be preferentially enriched to the outermost layer at the air–polymer interface against the silicone-containing group (R_s) originating from SiMA, because the surface free energy of the perfluoroalkyl group (~ 6 dynes/cm) is much lower than that of the silicone-containing group (~ 20 dynes/cm). Therefore, the surface free energy of PUFSG is not influenced by increasing SiMA content when the perfluoroalkyl group exists together. These results can be also confirmed by XPS analysis of the PUFSG-2-3 (1.0 wt %)/PVC blend, as shown in Table IV. The preferential segregation of PUFSG at the air–polymer interface can

Table IV Atomic Compositions of the Surface of PUFSG-2-3 (1.0 wt %)/PVC Blend as a Function of Take-Off Angle

Atoms	Take-Off Angles (deg.)					
	5	10	20	40	60	90
F _{1s}	48.01	46.29	45.19	43.82	38.58	32.93
O _{1s}	6.88	6.97	7.03	6.66	6.64	6.36
N _{1s}	0.84	0.66	0.48	0.33	1.69	1.47
C _{1s}	39.50	39.94	40.92	42.83	45.48	49.33
Cl _{2p}	2.44	3.46	3.92	5.18	7.03	9.41
Si _{2p}	2.33	2.68	2.46	1.18	0.58	0.50

be justified by high atomic concentration of F_{1s} . The atomic composition of F_{1s} in the surface of the PUFSG/PVC blend decreases almost linearly with take-off angle, and the atomic composition of C_{1s} increases almost linearly with take-off angle. (The take-off angle corresponds to the depth of the polymer surface at the air-polymer interface.) However, the atomic composition of Si_{2p} is nearly independent of the take-off angle. In other words, the composition of R_f at the air-polymer interface is higher than it is in the bulk phase, but the composition of R_s is nearly independent on the distance from the air-polymer interface. This confirms that R_f is more preferentially oriented to the outermost layer than R_s , and that R_f dominates the surface free energy of PUFSG.

The content of SiMA in PUFSG does not significantly influence the surface free energy of PUFSG; however, it can modify some physical properties of PUFSG. For example, the T_g can be significantly affected by the addition of SiMA.

The T_g 's of some PUFSGs (PUFSG-1-1, PUFSG-2-1, and PUFSG-3-1), the PUFSG-2-1 (2.0 wt %)/PVC blend, and PVC were measured by DSC and compared in Table V. The T_g 's of PVC can be found in the literature.^{28,29} PUFSG-1-1, which does not contain SiMA, has a T_g of 49.2°C. PUFSG-2-1 and PUFSG-3-1, containing 11.8 and 23.9 wt % of SiMA, respectively (see Table III), exhibit T_g 's of 29.0 and -4.0°C, respectively. The T_g of PUFSGs is strongly dependent on SiMA content. The softness or flexibility of PUFSGs may be easily modified by adjusting the SiMA content.

Compatibility of polymers in a polymer blend has been defined in various ways.³⁰ The widely used definition of polymer blend compatibility involves the T_g 's of the polymers and the blend measured by DSC. Compatible blends must exhibit a single T_g between the 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 PUFSG-2-1 and PVC was exam-

Table V Comparison of T_g 's of Some PUFSGs, PUFSG (2.0 wt %)/PVC Blend, and PVC

Polymer	T_g (°C)
PUFSG-1-1	49.2
PUFSG-2-1	29.0
PUFSG-3-1	-4.0
PUFSG-2-1 (2.0 wt %)/PVC blend	51.3
PVC	97.0

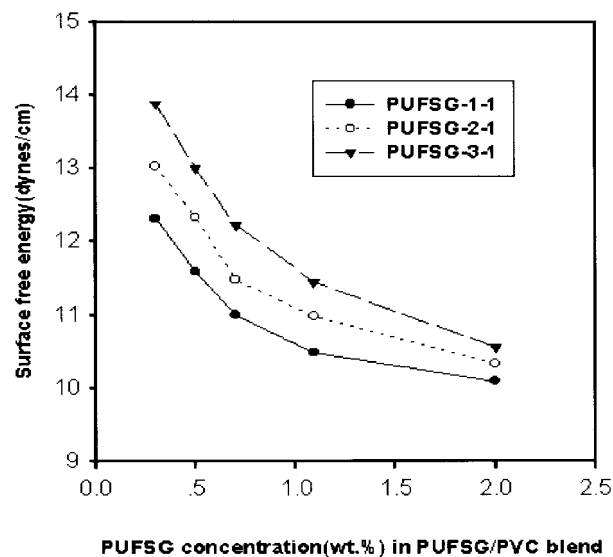


Figure 8 Surface modification effect of PUFSG on PVC film.

ined by measuring their T_g 's, which are compared in Table V. The PUFSG-2-1 (2.0 wt %)/PVC blend shows a single T_g of 51.3°C, between the T_g 's of PUFSG-2-1 (29.0°C) and T_g 's of PVC (97.0°C). This indicates that the PUFSG prepared in this study may be compatible with PVC when the PUFSG concentration in the PUFSG/PVC blend is less than 2.0 wt %.

Surface Modification Effect of PUFSG on PVC Film

To investigate the surface modification effect of PUFSG, PUFSG/PVC blends were prepared by varying the concentration of PUFSG with three PUFSGs PUFSG-1-1, PUFSG-2-1, and PUFSG-3-1 and measuring the surface free energies of these PUFSG/PVC blends. Figure 8 illustrates the variation of surface free energy of the three PUFSG/PVC blends as a function of PUFSG concentration. Even though the concentrations of PUFSGs added to PVC are relatively low, the surface free energies of the PUFSG/PVC blends show extremely low values of 10–14 dynes/cm, indicating extreme segregation of PUFSG at the air-polymer interface. Most PUFSGs added to PVC are located at the air-polymer interface, and PUFSGs are very effective in lowering the surface free energy. The surface free energy of PUFSG/PVC blends decreases rapidly with increasing PUFSG concentration up to about 1.0 wt %, but diminishes gradually above 1.0 wt %. The minimum concentration of PUFSG for the suf-

efficient modification of surface free energy of PUFSG/PVC blends seems to be about 1.0 wt %.

CONCLUSIONS

Dihydroxyl-terminated macromonomers with two terminal hydroxyl groups, perfluoroalkyl and silicone-containing side chains, were synthesized by free-radical copolymerization using FA, SiMA, and TG. PUFSGs were synthesized by solution copolymerization using the dihydroxyl-terminated macromonomers and TDI. The perfluoroalkyl and silicone-containing side chain contents of the PUFSGs were varied in the range of 39–70 and 11–24 wt %, respectively, by adjusting the FA and SiMA contents of the dihydroxyl-terminated macromonomers. The dihydroxyl-terminated macromonomers and PUFSGs synthesized were characterized and identified by FTIR and ¹HNMR analysis. The surface free energies of the PUFSGs and PUFSG/PVC blends were estimated from the contact-angle data measured by the sessile-drop method.

The results of our experiments show that surface free energies of PUFSGs with differing FA and SiMA contents, 9–12 dynes/cm, depend strongly on FA content, but not on SiMA content. The perfluoroalkyl group is preferentially arranged in the outermost layer at the air–polymer interface against the silicone-containing group. The preferential segregation of PUFSG at the air–polymer interface could be also confirmed by XPS analysis. Even though the concentrations of PUFSGs added to PVC are relatively low, the surface free energies of the PUFSG/PVC blends exhibit extremely low values, 10–14 dynes/cm, indicating extreme segregation of PUFSG at the air–polymer interface. Most of the PUFSGs added to PVC are located at the air–polymer interface, and PUFSGs are very effective in lowering the surface free energy.

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