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Synthesis and Surface Properties of Environmentally Responsive Segmented Polyurethanes

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Polyurethanes, containing well-defined assemblies of perfluoropolyether (PFPE or hexafluoropropene oxide oligomer), polydimethylsiloxane (PDMS), and polyethylene glycol (PEG) segments, exhibit oleophobic, hydrophobic, and hydrophilic properties in response to the polarity of the contacting medium. These polymers were prepared by reacting hydroxy(polyethyleneoxy)-propylether-terminated PDMS block copolymer (HO-PEG-PDMS-PEG-OH) with 4,4′-methylene-bis(phenylene isocyanate) (MDI) in the presence of dibutyltin dilaurate catalyst, followed by reaction with 1,2-diol functional PFPE and chain extension with 2,2,3,3-tetrafluoro-1,4-butanediol (FB). The oleophobic and hydrophobic properties of the segmented polyurethanes (SPU) are due to the segregation of PFPE segments at the polymer–air interface. Wettability studies revealed that the same surface becomes hydrophilic, presumably due to the segregation of the PEG segments at the polymer–water interface. This hydrophobic-to-hydrophilic transformation of the surface prevails not only when the polymer is in contact with liquid water but with water vapor as well. The understanding of the reconstruction mechanism of this novel family of SPU surfaces would furnish valuable information for various applications where dynamic transformation of surface activity is desired.

Key Words: **segmented polyurethane; perfluoropolyether; polyethylene glycol; polydimethylsiloxane; oleophobic; hydrophilic; nonstick coating; fouling release.**

INTRODUCTION

Polymeric materials having low surface energies are widely used for nonstick coatings. These materials are tailored with careful control of their chemical composition (thus surface energy) and mechanical properties. Due to its low surface energy (20 mJ m^{-2}) and high flexibility (1, 2), polydimethylsiloxane and its derivatives (3–8) have traditionally been the materials of choice for the above purpose. Fluorine has also been introduced into coating formulations by cross-linking siloxane with a fluoropolymer (9) or by casting a thin fluorocarbon film onto a silicone-coated substrate (10–12). Polymers containing low-energy perfluoropolyethers (13–22) (PFPE) and perfluoroalkyl groups (23–35) (R_f) have also been explored for low adhesion and solvent repellency applications. While these low-energy polymers facilitate release of materials adhering to them in both air and water, they do not necessarily prevent adhesion of foreign substances, although this adhesion can be minimized in air by choosing surfaces of very low surface energy (8–10 mJ/m^2). However, when a putative nonfouling coating is to be used in aqueous media, it is plausible to design a surface that exhibits negligible interfacial tension with water, thus minimizing the driving force for the adsorption and adhesion of biological entities. Polymers containing polyethylene glycol (PEG) and other water-soluble polymers have, in particular, shown significant promise in these areas (36–38). While the low interfacial energy of polymers is a prerequisite to obtaining easy release in a given environment, recent studies (39) have demonstrated that the mechanical properties of coatings could play crucial roles in the release mechanisms as well. In particular, it has been found that among polymers with a given surface energy, the softer polymers provide better release than the harder polymers.

On the basis of the above considerations, a material exhibiting low interfacial energies in both air and water, along with good flexibility, chemical stability, and mechanical properties, holds the potential for minimizing adhesion and facilitating release of soils and foulants from its surface in both air and water. In achieving the above properties, what is required is a polymer, the surface properties of which would spontaneously adjust by interacting with the environment in order to achieve low interfacial tension in both air and water. Such types of materials with switchable surface properties have been observed with surface-modified polymers (40) and silicones containing segmented polyurethane (41–48). Polymers containing multiblock functional copolymer additives (49, 50), fluorinated coupling agents (51, 52) and fluoro-organo modified polymeric amphiphiles (53–59) also exhibit switchable surface properties.

Previously (11–13, 60, 61), we employed several synthetic strategies to modify the surface of a silicone elastomer in order to impart hydrophilic as well as hydrophobic properties to it. Surface hydrophobicity was achieved either by forming self-assembled monolayers of hydrocarbon and fluorocarbon on the surface of PDMS elastomers (11, 12) or by incorporating a perfluoropolyether (Krytox) functional allylamide (13) into the network. Hydrophilic surface was prepared by incorporating PEG oligomers on the surface of silicone elastomers, which

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was accomplished by first forming a self-assembled monolayer of olefin functional alkylsiloxane on PDMS and then inserting mercapto-functional PEG in to the olefin groups via a free radical process (60, 61). The surfaces prepared in the above manner exhibited a contact angle of water that was as high as 120° (with fluorocarbon) and as low as 54° (with PEG groups).

Here we report a new type of polymer (segmented polyurethane) having both fluorocarbon and PEG segments that exhibits an enormous change of hydrophilicity; i.e., the contact angle of water decreases from 120° to 34°, when it comes in contact with water. Furthermore, the surface energy of the polymer is only about 8–10 mJ/m^2 in air. This PFPE-modified segmented polyurethane (SPU) was synthesized by reacting isocyanate-terminated prepolymer (containing polyethylene glycol (PEG) and polydimethylsiloxane (PDMS) segments) with 1,2-diol functional perfluoropolyether (PFPE) followed by chain extension with 2,2,3,3-tetrafluoro-1,4-butanediol (FB) in the presence of dibutyltin dilaurate catalyst (a preliminary account of these studies was previously reported in Refs. (62, 63)). Here the hydrophobic and oleophobic properties of the polymer arise mainly from the perfluoropolyether (PFPE) groups, whereas the hydrophilic property is due to the polyethylene glycol functionalities. The fluorocarbon groups (PFPE) easily segregate at the polymer–air interface because it has the lowest surface energy of all the segments in the polymer. The polyethylene glycol groups, on the other hand, prefer to stay in the bulk of the polymer because of its relatively higher surface energy. However, since the PEG groups are tied to the fluorocarbon groups, they migrate close to the surface along with the fluorocarbon groups (this strategy of pulling a high energy group to the surface by a low energy group was discussed previously by Thanawala and Chaudhury (13)). In contact with water, the PEG segments migrate to the surface, thus lowering its interfacial tension with water. This hydrophobic-to-hydrophilic transformation is reversible; the overall kinetics can be tuned by suitably varying the quantity of different segments present in SPU. In addition to these surface properties, the presence of silicone, PFPE, and urethane linkage impart high flexibility, chemical inertness, and good mechanical strength to the resulting material.

MATERIALS AND METHODS

Materials

3-allyloxy-1,2-propane diol (99%), acetic anhydride (99%), pyridine (99%), and lithium trifluoromethane sulfonate (CF_3SO_3Li, 99.9%) were purchased from Aldrich chemicals and used as received. *m*-Chloroperoxybenzoic acid (MCPBA, 71% active) was purchased from Aldrich chemicals and stored under nitrogen until used. Dichloromethane (99%, Aldrich) was refluxed and distilled over anhydrous $CaCl_2$ before use. Amino terminated PFPE oligomer (molecular weight 1359) and 1,1-dichloro-2-fluoroethane were kindly supplied by Dupont. 4,4′-Methylene bis(phenyl isocyanate) (MDI, 98%), dibutyltin dilaurate (DBDL, 95%), and anhydrous *N*,*N*-dimethyl acetamide (DMAc, 99%) were purchased from Aldrich Chemicals. 2,2,3,3-tetrafluoro-1,4-butanediol (FB, 98%, Aldrich Chemicals) was recrystallized in benzene before use. Hydroxy(polyethyleneoxy)-propylether-terminated poly-(dimethylsiloxane) (HO-PEG-PDMS-PEG-OH) block copolymer and 3-hydroxypropylether terminated PDMS of molecular weight 4000 (Gelest, Inc.) were vacuum-dried before reaction. (Please refer to the MSDSs of the above chemicals.)

Synthetic Procedure

Synthesis of 3-allyloxy-1,2-propane diacetate. A 250-ml three-necked dry round-bottom flask equipped with a magnetic stir bar, a reflux condenser, and a $CaCl_2$ guard tube was charged with 25 g of 3-allyloxy-1,2-propanediol (0.19 moles), 60 g of acetic anhydride (0.58 moles), and 10 g of pyridine (0.126 moles). The reaction mixture was stirred at 70°C for 6 h. The progress of the reaction was monitored using thin-layer chromatography. After completion of the reaction, the crude product was poured into 250 ml of water. The diacetate derivative was extracted in 250 ml of chloroform. The chloroform layer was washed with 250 ml of distilled water until it reached neutral pH and dried over anhydrous sodium sulfate. 3-allyloxy-1,2-propane diacetate was isolated by distilling off chloroform under vacuum. It was characterized using FTIR and NMR.

Product characterization. Clear, colorless liquid; yield 95%; FTIR peaks at 1730 cm^{-1} (acetate C=O stretching); ^1H NMR ($CDCl_3$, ppm) peaks at δ 2.06 (s, 6(H), $-COC\underline{H}_3$), 3.53 (d, 2(H), $-OC\underline{H}_2-CH-$), 3.96 (d, 2(H), $H_2C{=}CH-C\underline{H}_2O-$), 4.12-4.27 (m, 2(H), $-C\underline{H}_2-OCO$), 5.1–5.24 (m, 3(H), $-C\underline{H}-OCO$, $C\underline{H}_2{=}CH$), 5.83 (m, 1(H), $CH_2{=}C\underline{H}$); ^{13}C NMR ($CDCl_3$, ppm) peaks at 20.57 ($-CO\underline{C}H_3$), 62.53 and 67 ($O\underline{C}H_2-$), 70.01($-\underline{C}H_2-OCO$), 71.88 ($-\underline{C}H-OCO$), 116 ($\underline{C}H_2{=}CH$), 134 ($CH_2{=}\underline{C}H$), 170 ($\underline{C}OCH_3$).

Synthesis of 3-glycidyloxy-1,2-propane diacetate. A 500-ml three-necked dry round-bottom flask equipped with a magnetic stir bar, a rubber septum, and a nitrogen balloon was charged with 15 g of 3-allyloxy-1,2-propane diacetate (0.069 moles). Next, 42 g of MCPBA (71% active, 0.173 moles) in 200 ml of dry dichloromethane were charged into it. The reaction mixture was stirred at 25°C for 6 h. The progress of epoxidation reaction was monitored at 25°C, using thin layer chromatography. After 6 h the reaction mixture was filtered off to remove precipitated *m*-chlorobenzoic acid. Organic filtrate was washed with 200 ml of 20% K_2CO_3 solution to remove soluble *m*-chlorobenzoic acid. It was further washed with 200 ml of distilled water until neutral pH and dried over sodium sulfate. The 3-glycidyloxy-1,2-propane diacetate was isolated by distilling off the solvent under vacuum. It was further characterized using FTIR and NMR.

Product characterization. Clear colorless liquid; yield 93%; FTIR peak 1730 cm^{-1} (acetate, C=O stretching); ^1H NMR ($CDCl_3$, ppm) peaks at δ 2.06 (s, 6(H), $-COC\underline{H}_3$), 2.53–2.75 (m, 2(H), epoxy $C\underline{H}_2$), 3.07 (m, 1(H), epoxy $C\underline{H}$), 3.33–3.75 (m, 4(H), $-OC\underline{H}_2CH-$), 4.12–4.27 (m, 2(H), $-C\underline{H}_2-OCO$), 5.1

(m, 1(H), $-\mathrm{C}\underline{\mathrm{H}}-\mathrm{OCO}$); ^{13}C NMR ($\mathrm{CDCl_3}$, ppm) peaks at 20.57 ($-\mathrm{CO}\underline{\mathrm{C}}\mathrm{H_3}$), 43.64 (epoxy $\underline{\mathrm{C}}\mathrm{H_2}$), 50.42 (epoxy $\underline{\mathrm{C}}\mathrm{H}$), 62.41 and 67.2 ($-\mathrm{O}\underline{\mathrm{C}}\mathrm{H_2}-$), 70 ($-\underline{\mathrm{C}}\mathrm{H_2}-\mathrm{OCO}$), 71.82 ($-\underline{\mathrm{C}}\mathrm{H}-\mathrm{OCO}$), 170 ($\underline{\mathrm{C}}\mathrm{OCH_3}$).

Synthesis of aminohydroxy-1,2-diacetate functional PFPE oligomer. A 500-ml three-necked dry round-bottom flask equipped with a magnetic stir bar, a reflux condenser, a rubber septum, and a nitrogen balloon was charged with 3.4 g of 3-glycidyloxy-1,2-propanediacetate (0.0146 moles) and 3 g of lithium trifluoromethane sulfonate (0.0192 moles) in 50 mL of 1,1-dichloro-2-fluoroethane. The mixture was stirred for 10 min at 25°C. A solution of 10 g of amino-terminated PFPE oligomer (0.0074 moles) in 100 ml 1,1-dichloro-2-fluoroethane was charged further. The stirring was continued at 50°C under nitrogen for 12 h. The reaction mixture was filtered off. The crude product was isolated by distilling off the solvent. It was further washed with 25 ml of chilled chloroform to remove unreacted 3-glycidyloxy-1,2-propanediacetate. The undissolved aminohydroxy-1,2-diacetate functional PFPE oligomer was decanted off and further washed twice with 10 ml of chilled chloroform. It was dried under vacuum and characterized using FTIR and NMR.

Product characterization. Viscous, pale yellow liquid; yield 88%; FTIR peak at 1730 cm^{-1} (acetate, C=O stretching), 3400 cm^{-1} (CH–OH group); ^{1}H NMR ($\mathrm{CDCl_3}$, ppm) peaks at δ 2.06 (s, 6(H), $-\mathrm{COC}\underline{\mathrm{H}}_3$), 2.56–2.70 (m, 4(H), $-\mathrm{NHC}\underline{\mathrm{H}}_2$), 3.4–3.80 (m, 5(H), $-\mathrm{OC}\underline{\mathrm{H}}_2\mathrm{CH}-$, $-\mathrm{C}\underline{\mathrm{H}}-\mathrm{OH}$), 4.15–4.25 (m, 2(H), $-\mathrm{C}\underline{\mathrm{H}}_2-\mathrm{OCO}$), 4.97 (m, 1(H), $-\mathrm{C}\underline{\mathrm{H}}-\mathrm{OCO}$); ^{13}C NMR ($\mathrm{CDCl_3}$, ppm) peaks at 20.21 ($-\mathrm{CO}\underline{\mathrm{C}}\mathrm{H_3}$), 53.2 ($-\mathrm{NH}\underline{\mathrm{C}}\mathrm{H_2}$), 61 ($\mathrm{CH_2}\underline{\mathrm{C}}\mathrm{H(OH)}-$), 62.25–66.8 ($-\mathrm{O}\underline{\mathrm{C}}\mathrm{H_2}$, $-\mathrm{CF}\underline{\mathrm{C}}\mathrm{H_2NH}-$); 70.61 ($-\underline{\mathrm{C}}\mathrm{H_2}-\mathrm{OCO}$), 72.12 ($-\underline{\mathrm{C}}\mathrm{H}-\mathrm{OCO}$), 95–125 (fluorinated carbon region); 172 ($\underline{\mathrm{C}}\mathrm{OCH_3}$).

Synthesis of quaternary amino-1,2-diol functional PFPE oligomer. A 250-ml three-necked round-bottom flask equipped with a magnetic stir bar and a reflux condenser was charged with 5 g of aminohydroxy-1,2-diacetate functional PFPE oligomer (0.00367 moles) in 60 ml of an acetone–methanol (2 : 1) mixture. The pH of the reaction mixture was adjusted to 11 using 25% aqueous $\mathrm{K_2CO_3}$ solution (0.02 moles). The hydrolysis was carried out at 50°C for 5 h. The extent of the reaction was monitored by observing the disappearance of the $-\mathrm{OCOC}\underline{\mathrm{H}}_3$ absorption band (1730 cm^{-1}) using an infrared spectrometer. After the completion of hydrolysis, pH was adjusted to 3 by dropwise addition of 15% HCl. The solvent, acetic acid, and water were evaporated under high vacuum (10 mm) at 50°C. The crude product was again dissolved in acetone and the precipitated KCl salt was filtered off. A viscous oil was obtained by distilling off acetone. It was washed twice with 5 ml of chilled chloroform. The quaternary-1,2-diol functional PFPE oligomer was further dried under vacuum and characterized using FTIR and NMR.

Product characterization. Viscous orange yellow oil; yield 88%; FTIR peak at 3400–3500 cm^{-1} ($-\mathrm{CH_2}-\mathrm{OH}$ group); ^{1}H NMR ($\mathrm{CD_3COCD_3}$, ppm) peaks at δ 3.49–3.75 (m, 10(H), $-\mathrm{C}\underline{\mathrm{H}}_2-\mathrm{OH}$, $-\mathrm{OC}\underline{\mathrm{H}}_2-\mathrm{CH}-$, $-\mathrm{C}\underline{\mathrm{H}}_2\mathrm{N}^+$), 3.82 (m, 2(H), $-\mathrm{C}\underline{\mathrm{H}}-\mathrm{OH}$); ^{13}C NMR ($\mathrm{CDCl_3}$, ppm) peaks at 60.5 ($\mathrm{CH_2}\underline{\mathrm{C}}\mathrm{H(OH)CH_2}-$), 64.23–66 ($\underline{\mathrm{C}}\mathrm{H_2}-\mathrm{OH}$, $-\underline{\mathrm{C}}\mathrm{H_2N}^+$), 68.5 ($\underline{\mathrm{C}}\mathrm{H_2O}$), 71.2 ($\mathrm{O}\underline{\mathrm{C}}\mathrm{H_2}-\mathrm{CH(OH)}-$), 100–125 (fluorinated carbon region).

Synthesis of SPU-001 and SPU-002. A 250-ml three-necked dry round-bottom flask equipped with a magnetic stir bar, a reflux condenser, a rubber septum, and a nitrogen balloon was charged with a solution of 2 g of MDI (0.008 moles) in 100 ml of anhydrous DMAc. A solution of 4 g of 3-hydroxypropylether-terminated PDMS (0.001 moles in the case of SPU-001) or 4 g of hydroxy(polyethyleneoxy)-propylether-terminated PDMS block copolymer (HO-PEG-PDMS-PEG-OH) (0.001 moles in the case of SPU-002) in 40 ml of DMAc were added (via syringe) to the MDI solution. This was followed by addition of dibutyltin dilaurate catalyst (0.3% by weight of the reactants). The prepolymerization reaction was carried out at 60°C for 1 h, under an inert nitrogen atmosphere. Next, a solution of 1 g of 2,2,3,3-tetrafluoro-1,4-butanediol (0.006 moles, FB) in 20 ml of DMAc was added as the chain extender. The reaction mixture was further stirred at 80°C for 5 h. The extent of the reaction was monitored by observing the disappearance of the isocyanate absorption band (2280 cm^{-1}) using an infrared spectrometer. The SPU polymer was precipitated in water. It was washed with distilled water, dried, and dissolved in acetone. Thin, flexible SPU film of varied thickness (0.2 to 1 mm) was obtained by slow evaporation of acetone, followed by curing the product at 110°C on a glass Petri dish. Surface analysis was carried out using contact angle measurement and X-ray photoelectron spectroscopy.

Synthesis of PFPE modified SPU (SPU003-006). A 250-ml three-necked dry round-bottom flask equipped with a magnetic stir bar, a reflux condenser, a rubber septum, and a nitrogen balloon was charged with a solution of 2 g of MDI (0.008 moles) in 100 ml of anhydrous DMAc. A solution of 4 g of hydroxy(polyethyleneoxy)-propylether-terminated PDMS block copolymer (HO-PEG-PDMS-PEG-OH) (0.001 moles) in 40 ml of anhydrous DMAc were added (via syringe) to the MDI solution. This was followed by the addition of dibutyltin dilaurate catalyst (0.3% by weight of the reactants). The prepolymerization reaction was carried out at 60°C for 1 h under an inert nitrogen atmosphere. A solution of quaternary amino-1,2-diol functional PFPE (0.4 to 10% by weight of reactants; 0.129×10^{-4} to 2.94×10^{-4} moles) in 10 ml of DMAc were added to the reaction mixture and the stirring was continued for 1 h at 60°C. Next, a solution of 1g of 2,2,3,3-tetrafluoro-1,4-butanediol (0.006 moles, FB) in 20 ml of DMAc was added as a chain extender. The reaction mixture was further stirred at 80°C for 5 h. The extent of the reaction was monitored by observing the disappearance of the isocyanate absorption band (2280 cm^{-1}) using an infrared spectrometer. The SPU polymer was precipitated in water. It was washed with distilled water, dried, and dissolved in acetone. Thin, flexible SPU film of varied thickness (0.2 to 1 mm) was obtained by slow evaporation of acetone, followed by curing the product at 110°C on a glass

Petri dish. Surface analysis was carried out using contact angle measurement and X-ray photoelectron spectroscopy.

Methods

FTIR spectroscopy. FTIR spectra were recorded on a Polaris FTIR spectrometer (Mattson instrument) using NaCl crystal in the infrared region 4000–600 cm^{-1}. The reaction mixture was spread on the NaCl crystal and the solvent was removed under high vacuum.

Nuclear magnetic resonance. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker ACP 360 MHz spectrometer using $CDCl_3$, CD_3COCD_3 as the solvent. Chemical shifts of various peaks in the spectra were referenced with respect to $CDCl_3$ and CD_3COCD_3 peaks appearing at δ7.24 and 2.1 respectively.

Thin-layer chromatography (TLC). TLC was performed on silica gel (particle size 2–25 μm, layer thickness 200 μm, pore size 60 Å; Aldrich–Sigma) coated on aluminum plates. Hexane : ether (80 : 20 or 90 : 10) was used as the solvent system, with a drop of acetic acid (80 : 20). The TLC plates were further developed in an iodine chamber.

Wettability method. SPU film (1 cm^2 area and 0.2 mm thickness) was heated to 80°C under vacuum for 1 h before wettability measurements were made. Contact angles were measured at room temperature with a contact angle goniometer obtained from Rame–Hart Inc., U.S.A. Contact angle measurements of water on the SPU surface were carried out using both sessile drop and captive bubble techniques (64). The SPU film was attached to a glass plate and the glass plate was immersed in water. A small air bubble was released from a microsyringe beneath the film surface. The contact angle of water with the film was measured using a telescope fitted with a video camera. Contact angle measurements with hexadecane were carried out using the sessile drop method.

X-ray photoelectron spectroscopy (XPS). The surface composition of the films was determined using X-ray photoelectron spectroscopy (XPS) with a Scienta ESCA-300. X-rays are generated using a water-cooled high-intensity rotating AlK anode source at a power of 4.5 kW. A thin film of thickness 0.2 mm was used for XPS analysis. The pass energy of 300 eV was used for survey spectra. For the high-resolution spectra, silicon $2p$ (102 eV), carbon $1s$ (285 eV), nitrogen $1s$ (400 eV), oxygen $1s$ (533 eV), and fluorine $1s$ (690 ev) regions were acquired with a pass energy of 150 eV at 15° and 90° take off angles. Spectra were interpreted by referring to the Scienta ESCA300 data base (65). Curve-fitting analysis was performed using the Scienta ESCA 300 data system software.

Dynamic mechanical properties. Dynamic mechanical analysis (DMA) was performed using a mechanical property analyzer in torsion mode. For these tests, SPU films having a thickness of $\sim$1 mm were synthesized by following the same procedure described in the experimental section. Slabs (1×3 cm) were cut to fit the DMA apparatus. Each sample was first cooled to -150°C, after which storage and loss modulus were determined at regular temperature intervals from -150 to 25°C.

RESULTS AND DISCUSSION

Synthesis of PFPE-Modified Segmented Polyurethane (SPU)

Figure 1 describes the preparation of PFPE-modified SPU. Isocyanate-terminated prepolymer (3) was first synthesized by reacting hydroxy(polyethyleneoxy)-propylether-terminated PDMS block copolymer (1) (HO-PEG-PDMS-PEG-OH) with 4,4′-methylene-bis(phenyl isocyanate) (2) in the presence of dibutyltin dilaurate catalyst. Next, 1,2-diol functional PFPE (4) (0.129×10^{-4} to 2.94×10^{-4} moles) was reacted with isocyanate-terminated prepolymer (3) (and also with unreacted MDI) to give several PFPE-modified isocyanate intermediate products (such as 5,5′ or 5″). These intermediate products (5,5′, or 5″) and unreacted (2) and (3) further undergo chain extension with 2,2,3,3-tetrafluoro-1,4-butanediol (6) (FB) to give segmented polyurethanes (SPU) and other chain-extended polyurethanes. The progress of the reaction was monitored by observing the disappearance of the isocyanate absorption band (2280 cm^{-1}) using an infrared spectrometer. During the reaction cross-linking occurs to a very low extent, due to the presence of 1,2-diol functional PFPE, which is present at a low concentration. The SPU was precipitated in excess water as a sticky mass. It was further washed with distilled water and dissolved in acetone. Thin, flexible SPU film was obtained by slow evaporation of acetone followed by curing the product at 110°C on a glass Petri dish.

The presence of PDMS and urethane linkage imparts high flexibility and good mechanical strength to the SPU. Dynamic mechanical analysis (indicated in Fig. 2) showed two low glass transitions at -102°C and -28°C, which are due to the PDMS and PEG segments respectively. Similar glass transitions were previously observed with polysiloxane-modified segmented polyurethanes (66).

Synthesis of 1,2-diol functional PFPE (4) is described in Fig. 3. Reaction of amino functional PFPE (Dupont Krytox) with isocyanate-terminated prepolymer (3) was sluggish, due to the insolubility PFPE in most of the common organic solvents. We therefore incorporated polar quaternary amino-1,2-diol functionality onto PFPE (Dupont Krytox). Detailed synthetic procedures are described in the experimental section. As indicated in Fig. 3, 3-glycidyloxy-1,2-propane diacetate was first prepared by epoxidation of 3-allyloxy-1,2-propane diacetate using MCPBA. Quaternary amino-1,2-diol functional PFPEs were synthesized by reacting amino functional PFPE with 3-glycidyloxy-1,2-propane diacetate in the presence of lithium triflate catalyst, followed by base hydrolysis and quaternization. Triflates (for example, lithium trifluoromethanesulfonate, CF_3SO_3Li, and copper (II) trifluoromethanesulfonate, $(CF_3SO_3)_2Cu$) are the effective catalysts used for epoxy–amines reactions (67, 68). Detailed synthetic procedures of SPU films containing varied amounts of PFPE are described in the

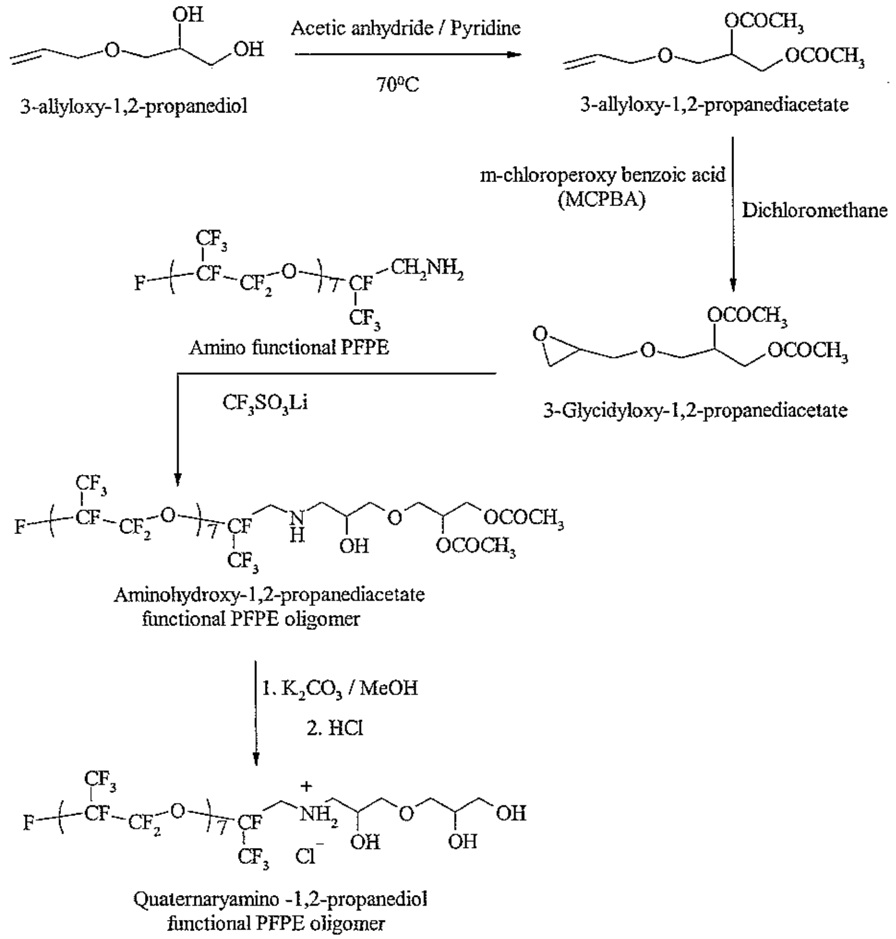

FIG. 1. Synthesis of PFPE modified segmented polyurethane (SPU).

Experimental section. Characterization data regarding molecular weights and compositions of the SPU films are shown in Table 1.

Evidence of Enrichment of PFPE on SPU Surface

Surface compositions of PFPE-modified SPU films were determined using X-ray photoelectron spectroscopy. The pass energy of 300 eV was used for survey spectra, which indicated peaks at 690, 535, 400, 285, and 102 eV due to fluorine (1*s*), oxygen (1*s*), nitrogen (1*s*), carbon (1*s*), and silicon (2*p*), respectively. For the high-resolution spectra, Si_{2p} (102 eV), C_{1s} (285 eV), N_{1s} (400 eV), O_{1s} (535 eV), and F_{1s} (690 eV) regions were acquired with a pass energy of 150 eV.

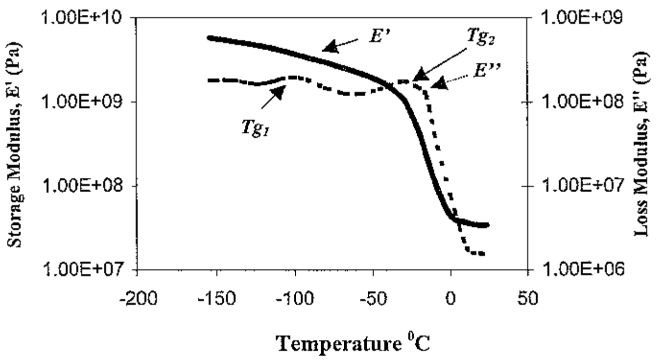

FIG. 2. The storage (E′) and loss (E″) moduli for the PFPE-modified SPU.

TABLE 1
Characterization of SPU

Code	HO–PEG–PDMS–PEG–OH (1) (g) M.Wt. = 4000	MDI (2) (g)	PFPE (g) (% by weight) M.Wt. = 1359 g	FB(6) (g)	Mole ratio of (1)/(2)/(6)
SPU-001	[a]	2	—	1	1 : 8 : 6
SPU-002	4	2	—	1	1 : 8 : 6
SPU-003	4	2	0.0176 (0.44%)	1	1 : 8 : 6
SPU-004	4	2	0.0344 (0.86%)	1	1 : 8 : 6
SPU-005	4	2	0.1 (2.5%)	1	1 : 8 : 6
SPU-006	4	2	0.4 (10%)	1	1 : 8 : 6

[a] In the case of SPU-001, 4 g of 3-hydroxypropyl terminated PDMS was used instead of HO–PEG–PDMS–PEG–OH.

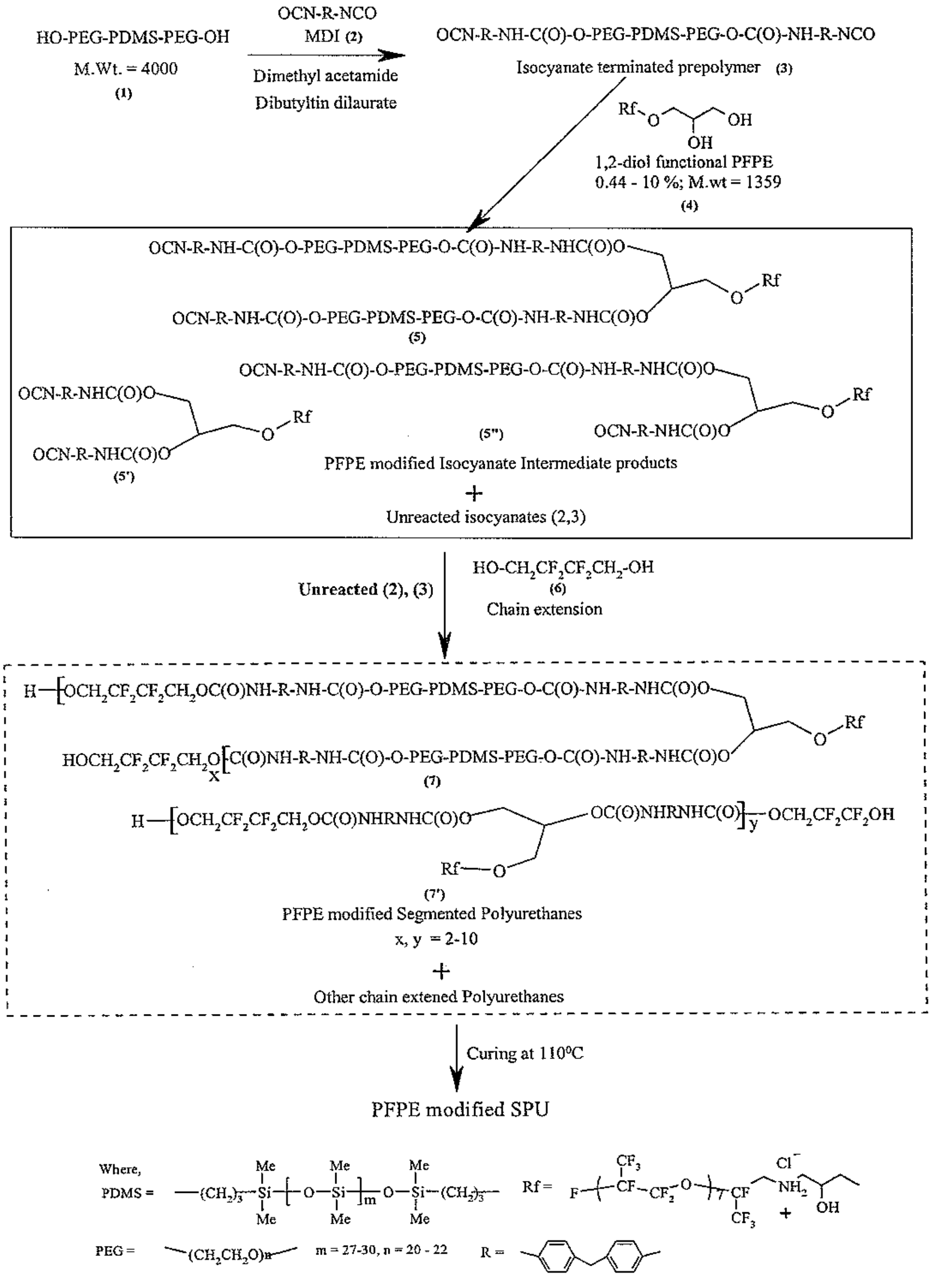

FIG. 3. Synthesis of quaternary amino-1,2-diol functional PFPE.

Figure 4A shows the carbon (1*s*) region at a 90° takeoff angle in SPU-004 film. The peak corresponding to carbon atoms bound to hydrogen, specifically the signals due to the C–H groups present in the aromatic ring and in the PDMS segments, appear at 284.7 eV. Another peak due to the C–O bonding present in PEG segments appears at 286.5 eV. The peaks corresponding to carbon atoms bonded to fluorine, specifically $OCF(CF_3)$, OCF_2CF, and CF_3–CFO– carbon signals, appear at 291.4, 293.2, and 293.8 eV respectively. Spectra were also taken at a 15° takeoff angle in order to maximize the signal obtained from the surface-enriched segments. The spectra taken at 15° takeoff angle (Fig. 4B) show that the intensity of CF peaks increases and the relative intensity of the CO peak decreases, compared to those taken at a 90° takeoff angle. This indicates that the

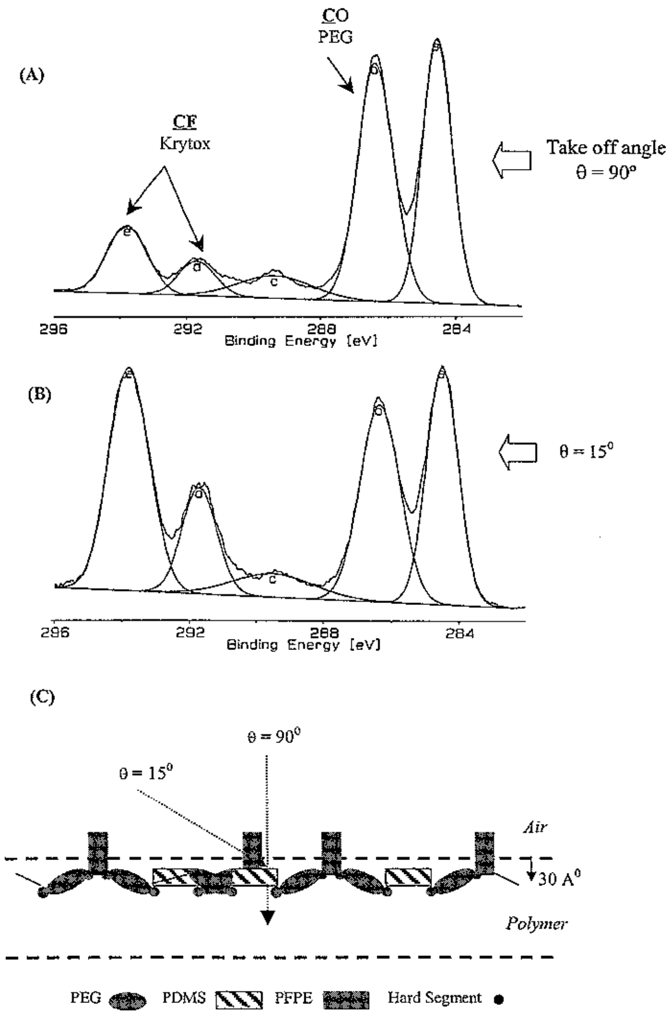

FIG. 4. High-resolution C(1*s*) regions at takeoff angles (A) 90° and (B) 15° in the case of SPU-004; (C) Schematics of the structure of PFPE-modified SPU at polymer–air interface.

SPU surface is enriched with PFPE segments, whereas the PEG segments are present close to the surface. Similar observations were made with other SPU films as well. SPU-001 (having absence of PFPE) shows a peak due to C–H bonding, specifically PDMS groups, at 284 eV and a peak due to C–F bonding, specifically $-CF_2CF_2-$, at 293 eV. This indicated that SPU-01 is enriched with PDMS and $-CF_2CF_2-$.

Contact angle measurements of hexadecane and water on SPU films also suggest enrichment of PFPE segments ($-CF_2CF_2-$ groups in the case of SPU-001) at the polymer–air interface. As shown in Figure 5, the contact angle of hexadecane (θ_{HX}) increases with increased PFPE concentration in SPU, ultimately reaching a plateau value of 74°. The dispersion component of the surface energy (γ^{d}_{SA}) of SPU as estimated using θ_{HX} and the Good–Girifalco equation (69, 70),

$$\cos\theta_{HX} = -1 + 2\left(\gamma^{d}_{SA}/\gamma_{Hx}\right)^{1/2}, \qquad [1]$$

where γ_{Hx} (27 mJ/m^2) is the surface tension of hexadecane, are summarized in Fig. 5. The reduction in γ^{d}_{SA} (from 23 to 10 mJ m^{-2}) with the increase in PFPE concentration in SPU indicates that the SPU surface is enriched with low-energy CF_3 groups.

The lowest surface energy (10 mJ m^{-2}) of the SPU film is similar to that of self-assembled monolayers (71) of perfluoroalkanes having close-packed CF_3 groups. The contact angle of water (θ_W) on SPU surfaces also increases with increased PFPE concentration. However, these surfaces exhibit significant reconstruction when they come in contact with water as discussed below. Our preliminary experiments and the earlier literature (72) show that the contact angle of water and the surface energy of nonfluorinated SPUs (absence of PFPE and $-CF_2CF_2-$ units) were ~85°–75° and ~30 mJ m^{-2}, respectively.

Surface Rearrangement of PFPE-Modified SPU Surface

When a water drop is placed on these SPU surfaces, it initially exhibits a high advancing contact angle, which varies from 120° to 135°, as the PFPE concentration increases from 0% to 10%. Over the same range of PFPE concentrations, the initial receding angle varies from 35° to 75°. When these surfaces are kept in contact with water, they all become progressively hydrophilic. This was confirmed by measuring the contact angle as a function of time using a captive bubble method, which ensures that observed changes are not due to the evaporation of water as could happen in sessile drop measurements. We note, however, that the contact angles measured by captive bubbles agree with those measured using sessile drops, when the measurements are carried out at 100% relative humidity. All the SPU surfaces (SPU-001 to 005; compositions are explained in Table 1) exhibited surface rearrangement in water. The SPU that is free of PEG functionality (i.e., the PDMS-containing SPU surface, SPU-001) exhibited a minimum amount of reconstruction, where the advancing contact angle of water decreases from 106°

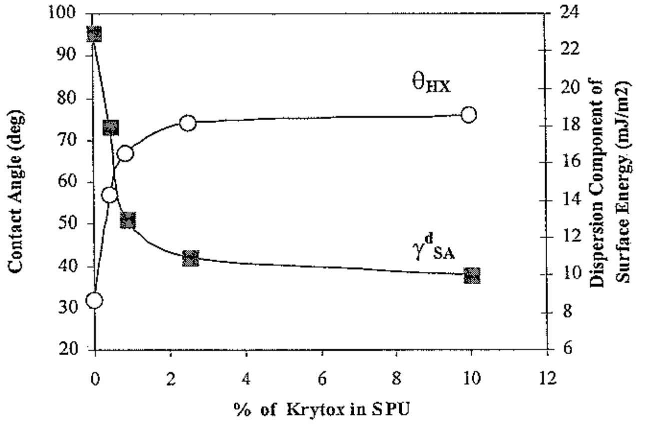

FIG. 5. Contact angles (○) of hexadecane (θ_{HX}) on SPU surface as a function of the PFPE concentration. The dispersion component of surface energy (γ^{d}_{SA}) of SPU (mJ m^{-2}) (■) decreases with PFPE and reaches a plateau value of 10 mJ/m^2.

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