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A Polyurethane Surface Modifier: Contrasting Amphiphilic and Contraphilic Surfaces Driven by *block* and *random* Soft Blocks having Trifluoroethoxymethyl and PEG Side Chains

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Abstract

A conventional MDI-BD-PTMO polyurethane was modified using 2 wt.% polyurethanes (U) having copolyoxetane soft blocks with hydrophobic 3F, CF₃CH₂OCH₂- and hydrophilic MEn, CH₃O(CH₂CH₂O)_nCH₂-, n = 3, 7) side chains. In contrast to neat 3F-*co*-MEn-U, 2 wt.% 3F-*co*-MEn-U compositions have physically stable morphologies and wetting behavior. Surface composition (XPS) and amphiphilic or contraphilic wetting are controlled by the 3F-*co*-MEn polyoxetane soft block architecture and MEn side chain length. Importantly, γ_{rec} can be tuned for 2 wt.% 3F-*co*-MEn-U compositions independent of swelling, which is controlled by the bulk polyurethane. AFM imaging led to a new morphological model whereby fluororous/PEG-hard block nano-aggregates combine to form near surface features culminating in micron scale texturing.

Keywords

copolyoxetanes; polyurethanes; surface modification; amphiphilic wetting; contraphilic wetting

Introduction

Polymer surface modifiers, PSMs, are used to tailor polymer surfaces via blending. Most commonly, PSMs are employed to change wetting characteristics.^[1] Surfaces are made hydrophobic with poly(dimethylsiloxane) (PDMS) modification.^[2–10] Polydimethylsiloxane PSMs are also important in conferring bio-oxidative stability for biomaterials applications^[11] and for controlling adhesion of fouling.^[12]

Polyethylene glycol (PEG) surface modifiers are extensively employed to impart nonionic hydrophilic character that resists soft fouling such as in membrane applications.^[13, 14] In situ adsorption,^[15] overcoating^[16] or grafting^[17, 18] are alternatives for PEGylating surfaces, but these methods require a separate step compared to blends.

To varying degrees, fluorinated PSMs confer both hydrophobic and oleophobic (omniphobic) wetting behavior.^[19–25] An important consideration tempers studies of fluorinated PSMs with long fluororous CnF side chains, where n is the number of

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perfluorinated carbon atoms. While the omniphobicity of polymers with long fluorinated (C8F₁₇ = -(CF₂)₇CF₃ and C10F₂₁) side chains or end groups has long been known,^[26, 27] degradation under oxidative conditions such as incineration likely leads to bioaccumulative perfluorooctanoic acid (PFOA).^[28, 29] As a result, the challenge of generating omniphobic surfaces is being met by the study of systems with C1F-C4F moieties.^[30, 31]

Another complication can arise under dynamic conditions such as thermal processing/crosslinking, during which fluorinated functionality can be trapped in the bulk.^[32] Similarly, if present in a domain that is above T_g , fluorinated moieties may undergo concentration dependent aggregation such that more fluorinated modifier makes the surface less oleophobic.^[33]

Combining hydrophilic and hydrophobic moieties, amphiphilic surfaces show promise for the development of adhesive and/or biocompatible surfaces. Such surfaces are often comprised of copolymers with PEG and fluorinated (CnF) side chains.^[34, 35] Herein we focus on a PEG/3F combination of weakly hydrogen bonding, hydrophilic PEG with omniphobic trifluoroethoxymethyl, -CH₂OCH₂CF₃, “3F”. As is seen from the work discussed herein, the focus is on “soft” coatings of macroscopic thickness. Soft amphiphilic-fluorinated surfaces have found interesting applications for minimizing adherence of soft fouling^[36–39] and for controlling protein adsorption.^[40, 41] It is thought that a combination of hydrophilic and fluorinated functionality may have application to biocompatible materials.^[35, 42]

In exploring fluorinated-amphiphilic PSMs, we have focused on polyurethanes and have taken a cue from the well known concentration of the low T_g soft block at the air/polymer interface.^[2, 43–48] Given this precedent, our strategy for generating coatings with functional surfaces is directed at novel soft blocks. Neat P[A-*co*-B]-soft block polyurethanes, provide a combination of thermodynamic driving forces that act to surface-concentrate the soft block.^[49, 50] Synergisms include a copolymer effect on wetting behavior^[51] and contraphilic wetting, whereby the dry surface is hydrophilic while the wet surface is hydrophobic.^[52, 53] A fluorinated side chain was shown to act as a “chaperone” for a model functional group^[54] and for oxidative/antimicrobial hydantoin functionality.^[49]

To generate soft blocks with tailored function, P[A-*co*-B]-copolyoxetanes have been prepared with short C1F fluorinated side chains that avoid intrinsic and often ignored problems associated with long CnF side chains.^[28, 29] The soft block fluorinated segment facilitates surface concentration of B functionality and modifies the surface properties of a bulk polyurethane (Figure 1).^[50, 54] For P[A-*co*-B], “P” designates a polymerized copolyoxetane with repeat units having A and B (and sometimes C) side chains that act in concert to achieve a desired function. The designation A or B is used synonymously for the 1,3-propylene oxide repeat that bears the respective side chain.

Employing P[A-*co*-B] copolyoxetane soft blocks has proved to have interesting features for polymer surface modification:

1. Preferential surface concentration results in compositional economy as the P[A-*co*-B]-soft block polyurethane is a minor blend constituent (Figure 1).^[46–48, 55]
2. Multiple A, B side chains act as pseudo-chain ends that entropically enhance surface concentration.^[8, 56–58]
3. Differing solubility parameters for the P[A-*co*-B]-soft block and other blend constituents enhance phase separation and surface concentration.
4. Optimized functionality may be attained by controlling B mole fraction in the P[A-*co*-B] soft block.

5. For random copolymers, propinquity for A and B side chains may facilitate synergistic interactions leading to a new surface property.^[52]
6. Fluorous A repeats may act as “chaperones” to surface-concentrate B groups which, in the absence of A, would not be surface concentrated.^[49]
7. In biomaterials applications, the low P[A-*co*-B]-soft block T_g may enhance B surface function by minimizing energetics of chain reorganization required for conjugation with a target receptor, and
8. A multiplicity of short, environmentally acceptable CnF A side chains are employed resulting in a relatively “green” method for surface concentrating functionality B.

Previously we reported P[A-*co*-B] polyols **3** (Scheme 1) that contain hydrophilic, PEG-like ME3Ox (ME3, $n = 3$) A and omniphobic 3F B side chains.^[59] A novel feature of this work was the discovery of a facile method for preparing random 3F-*r*-MEn and block 3F-*b*-MEn polymer diols. In the present work, the contrasting nano- and microscale surface morphology of polyurethanes containing random and block 3F-*co*-MEn soft blocks is explored further.

The extent to which the surface properties of a conventional linear MDI/BD/PTMO polyurethane is modified by incorporation of 2 wt.% 3F-*co*-MEn soft block polyurethanes is investigated via TM-AFM, XPS, and dynamic contact angle (DCA, Wilhelmy plate) analysis. The practicality of polyurethane surface modification at low weight percents has been recognized by Loontjens.^[60] In the present work, 2 wt.% was chosen on the basis of a previous study that showed a 2 wt.% threshold concentration for introducing oxidative antimicrobial function in a base polyurethane.^[49] Interestingly, in the present survey of 2 wt.% 3F-*co*-MEn-U compositions, more physically stable morphologies and better controlled wetting behavior are observed compared to the neat modifiers themselves.

Based on AFM imaging, a new morphological model is proposed for modified surfaces whereby fluororous/PEG-hard block nano-aggregates combine to form a broad array of near surface features culminating in micron scale texturing. Several features noted above are exhibited by 2 wt.% 3F-*co*-MEn-U compositions, including (1) surface concentration, (2) economy, (3) multiple side chain-ends, (4) differing A/B solubility parameters, and (5) A/B propinquity, synergistic interactions. An unexpected finding from dynamic contact angle analysis was a switch from amphiphilic wetting ($\theta_{adv-1} > \theta_{adv-2}$) for neat 3F-*r*-ME7-U to contraphilic wetting ($\theta_{adv-1} < \theta_{adv-2}$) for 2 wt.% 3F-*r*-ME7-U.

Experimental Section

Notation

Conventional polyurethane notation^[61] leads to designations such as MDI/BD(32)-P[3F-*b*-ME3-3:2 (4200)] where MDI/BD is the hard block composition followed by wt.% (32); “P” indicates polymerized monomer-in-telechelic followed by the repeat unit ratio (x:y) and soft block number average molecular weight (M_n). These designations are cumbersome for the limited number of compositions reported herein. In Table 1, shorter designations are introduced, for example “3F-*r*-ME3” for P[3F-*r*-ME3-1:1 (3100)]. An exception is made for homopolymers P(3F) and P(MEn) to avoid confusion with the respective monomers. For polyurethanes, a similar notation is used by simply adding “-U” to the diol (Table 2). Designations such as P[A-*co*-B] or P[A-*r*-B]-U are used if the composition is clear in context.

Materials

3-Trifluoroethoxymethyl-3-methyloxetane (3F) was prepared as described below or generously provided by OMNOVA Solutions (Akron OH). The oxetane monomers ME3 [3-(2,5,8,11-tetraoxadodecyl)-3-methyloxetane] and ME7 [3-methoxy(polyoxyethylene)oxymethyl-3-methyloxetane] were synthesized from the respective alcohols [2-[2-(2-methoxyethoxy)ethoxy]ethanol (i.e., tri(ethylene glycol) methyl ether) and poly(ethylene glycol) methyl ether (MW = 350), respectively] and 3-bromomethyl-3-methyloxetane (BrOx) by a method previously reported.^[62] Oxetane monomers were distilled under vacuum before use. Boron trifluoride dietherate [BF₃(Et₂O)], tetrabutylammonium bromide (TBAB), poly(tetramethylene oxide) (PTMO), and methylenediphenyl diisocyanate (MDI) were obtained from Sigma-Aldrich and used as received. 1,4-Butanediol (BD) was from Acros. Methylene chloride (CH₂Cl₂), tetrahydrofuran (THF), dimethylformamide (DMF), dimethylacetamide (DMAc) and other organic solvents were used as received or kept over 4Å molecular sieves.

Amphiphilic polyoxetanes

Cationic ring opening polymerization of MEn and 3F utilized BF₃(Et₂O) and 1,4-butane diol co-catalysts (Scheme S1).^[20, 62] The synthesis and characterization of 3F-*r*-ME3-1:1 (3100), “3F-*r*-ME3”, and 3F-*b*-ME3-3:2 (4200), “3F-*b*-ME3” and the ME7Ox analogs are described in detail in Supplemental Information. ¹H-NMR spectra were used to confirm stoichiometry. Figure S1 provides ¹H-NMR spectra for P(ME3) and P(3F) homopolymer diols and 3F-*r*-ME3, 3F-*b*-ME3 copolymer diols. Figure S2 has ¹H-NMR spectra for P(ME7) and P(3F) homopolymer diols and 3F-*r*-ME7, 3F-*b*-ME7 copolymer diols.

Polyurethanes

Polyurethanes were synthesized by modification of the two step, soft block first method described previously.^[63] As shown in Scheme 1, MDI and BD were used for the hard segment with P[3F-*co*-MEn] copolyoxetanes as the soft segment. Different solvents or solvent combinations were used depending on component reactivity and polyurethane solubility: (1) THF for MDI/BD(37)-P(ME3-3000), “ME3-U”, (2) THF / DMF for MDI/BD(29)-(3F-7100), “3F-U”, and MDI/BD(27)-3F-*r*-ME3-1:1 (3100), “3F-*r*-ME3-U” and (3) DMAc for other polyurethanes. To avoid water contamination commonly observed for commercially obtained linear polyurethanes in dynamic contact angle measurements, a conventional base polyurethane was also prepared by the soft block first method. The composition MDI/BD(36)-PTMO(2200), “base-U” was confirmed by ¹H-NMR spectroscopy. Tables 1, 2, and 3 contain characterization data.

The P[3F-*co*-MEn]-U and 2 wt.% compositions were dip coated from 10 wt.% solutions in THF. Previously coatings that were “dried” at 60 °C for 24 hr were described as “as cast”.^[59] This seemed like a mild solvent removal process. We now find that 60 °C for 24 hr is an annealing condition. As described in the AFM section, morphological and topological changes occur compared to coatings from which solvent was removed in vacuum at ambient temperature (25 °C). In the present discussion, “as cast” coatings were drip- or dip-coated and solvent was removed at room temperature (24 hr) and then under reduced pressure (24 hr). Subsequent heat treatment at 60 °C is considered annealing.

Instrumentation

¹⁹F-NMR (Varian Mercury 300, 283 MHz) spectra were used to qualitatively distinguish between random and block copolyoxetanes diols^[59] and respective polyurethanes. ¹⁹F-NMR spectra were obtained in chloroform-*d* for polyoxetanes or in DMSO-*d*₆ for polyurethanes using trifluoroacetic acid as an internal reference.

Polyurethane molecular weights were determined using a Viscotek TriSEC triple detector GPC system (THF) with sample concentrations of 10–15 mg/ml and a flow rate of 1 ml/min. Universal calibration by polystyrene standards was used for calculation of molecular weight (M_n , M_w) and polydispersity.

Differential Scanning Calorimetry (DSC) was performed with a TA-Q 1000 Series™ instrument (TA Instruments). Temperature modulated DSC (MDSC) from –95 °C employed a modulation amplitude of ± 0.5 °C, a modulation period of 30 seconds, and a heating rate of 3 °C/min. T_g 's were determined from reversing heat flow curves. Standard DSC experiments (without temperature modulations) with heating rate 10 °C/min were also conducted from –95 to 250 °C (Figure S7). Thermogravimetric analyses (10 °C/min) employed a TA-Q5000 TGA (TA Instruments-Waters, LLC) with platinum pans. Nitrogen was used as an inert balance gas (10 mL/min). Initial thermal degradation (2% weight loss) was marked on each curve. Polyurethanes for DSC and TGA were specially purified and dried after preparation or were from solution cast “25 °C” samples as described above.

A Dimension Nanoscope V (Veeco, CA) atomic force microscope was used for morphological analysis of polyurethane film surfaces in air. Images were obtained in tapping mode using silicon crystal cantilevers (40 N/m). The tapping force was increased from soft to hard by decreasing the setpoint ratio r_q or A_{exp}/A_o , where A_o is free oscillation amplitude and A_{exp} is the experimental oscillation amplitude.

Dynamic Contact Angle (DCA) analysis was carried out with a Cahn Model 312 Analyzer (Cerritos, CA) based on the Wilhelmy plate method. The surface tension quantification limit of the instrument is 0.1 dyne/cm. The probe liquid was ~ 18 M Ω /cm deionized water from a Barnstead (Dubuque, IA) Nanopure system. The surface tension of the probe liquid was checked daily (72.6 ± 0.5 dynes/cm). Containers used for DCA analysis were cleaned by soaking in an isopropanol/potassium hydroxide base bath for at least 24 hr, rinsed for 30 sec with hot tap water and then rinsed another 30 sec with Nanopure water. In a typical determination, a coated slide was attached to the electrobalance via a clip and the stage with the beaker of water was automatically raised and lowered to allow the water to impinge upon the slide. By analyzing the resulting force versus distance curves (fdc), advancing (θ_{adv}) and receding (θ_{rec}) contact angles were obtained.^[64] Unless otherwise noted, the stage speed was 100 μ m/sec and dwell times between advancing and receding test segments was 10 sec.

Molecular Dynamics

ChemBio3D, (version 12.0), CambridgeSoft, Cambridge MA was used for molecular modeling. To simulate copolyoxetanes, 16-mers for 3F-*b*-ME3-1:1 and exactly alternating 3F-*r*-ME3-1:1 were created conventionally using ChemBioDraw Ultra v. 12.0.2.1076. Terminal –OH were replaced with –OCH₃. The 3F-ME3-1:1 molecular weight for 16-mers is ~ 3.5 kDa, which is in the range of the experimentally determined P[AB] soft block molecular weights. These structures were imported into ChemBio3D and the MM2 force field calculation method for molecular simulations was performed. Energy minimization calculations were performed after molecular dynamics simulation using the same force field method. Even though the global minimum is still unknown, multiple independent calculations were run and similar results were obtained. Several display modes are available in this program. Space filling models were thought to convey most clearly the relative positions of –CF₃ groups.

Results and Discussion

The synthesis of 3F-*co*-MEn copolyoxetane diols by ring opening polymerization (ROP) is discussed briefly. This is followed by results on incorporation of the polyoxetane diols into polyurethanes. The contrasting surface morphology (TM-AFM) and dynamic wetting behavior (DCA) for 3F-*r*-MEn-U and 3F-*b*-MEn-U is presented. AFM, XPS, and DCA analyses for base-U, MDI/BD(36)-PTMO(2200), 3F-*co*-MEn-U and 2 wt.% modified base-U compositions are discussed.

Homopolyoxetane and copolyoxetane diols

Synthesis and NMR Characterization

3,3-Bromomethylmethyloxetane (BrOx) was used as the starting material for the preparation of 3F, ME3, and ME7 monomers utilizing the respective alcohols and phase transfer catalysis.^[51, 59, 62] ME3 and ME7 homopolyoxetane diols were prepared by ROP as described previously. Details are provided in Supplementary Information.

Cyclics are formed in oxetane ring opening polymerizations.^[20, 65] Cyclics interfere with accurate determination of contact angles by diffusing from the coating to the water surface and thereby reducing surface tension.^[66] Cyclics can be removed from the 3F diol by thermal treatment.^[23] To estimate cyclic content in the crude product, 3FOx cyclics were separated by sublimation at 160 °C/0.1 mmHg. Under these conditions, a white viscous liquid formed on the cold finger. After a week at ambient temperature, the liquid turned to a semi-solid. From ¹H- and ¹⁹F- NMR and GPC analyses, this product was identified as the cyclic tetramer [3FOx]₄, (MW = 736 g/mol). Figure S3-b shows these results and the NMR analysis for a 3F diol and P[3FOx]₄ cyclic mixture from a typical reaction. GPC (Figure S3-a) showed complete separation was obtained for 3F diol and P[3FOx]₄. The proton coupled ¹⁹F spectrum (blue) in Figure S3-b has a 1:2:1 triplet (*J*_{1H-19F} = 8.2 Hz) for purified 3F diol. The spectrum of cyclic tetramer consists of overlapping triplets in intensity pattern 1:4:6:4:1. This pattern is explained by the presence of three geometric isomers with overlapping peaks. One of the three possible isomers is shown in Figure S3. Only 3F monomer purified by distillation was used for polymerization reactions.

We reported that the order of addition of 3F and ME3 monomers provides control of the P[A-*co*-B] sequence (Scheme 1).^[59] The same control of P[A-*co*-B] sequence is found for 3F-*co*-ME7. Adding 3F and ME7 monomers simultaneously yields random copolyoxetanes (Scheme 1, Eq 1). Block copolyoxetanes are obtained as transparent, viscous liquids by first adding ME7 monomer followed by the slow addition of 3F monomer (Scheme 1, Eq 2). Adding 3F monomer first and ME7 monomer second gave a mixture of P[3F] and P[MEn] diols (Scheme 1, Eq 3). This was evidenced by the formation of two separate layers after evaporation of CH₂Cl₂ solvent.

During one preparation of 3F-*b*-ME3, *M*_n was determined after addition of each monomer. After the polymerization of ME3, *M*_n was 2.6 kg mol⁻¹ by end group analysis.^[59] Subsequently, after slow (dropwise, 24 h) addition of 3F, a block cotelechelic was obtained with *M*_n = 4.2 kg mol⁻¹. In contrast, if 3F monomer was added rapidly, a two-phase mixture of homo-telechelics was obtained. Thus there is competition for monomer addition to the P(ME3) chain end from 3F homopolymerization. Keeping the concentration of 3F monomer low favors addition to the block chain end (Scheme 1, Eq 2).

Homopolyoxetane and P[3F-*co*-MEn] diol compositions are shown in Table 1 together with molar feed ratios and P[3F-*co*-MEn] molar ratios found by ¹H-NMR spectroscopy. With reference to Figures S1 and S2, mole ratios of 3F and MEn in the P[3F-*co*-MEn] diols are

obtained from integrals of methylene peaks **f** (3F) and **d** (MEn). 3F tends to have less than calculated incorporation under the conditions employed for block P[3F-*co*-MEn] diol synthesis. For example, with a 3F to ME3 monomer feed ratio of 2:1, a composition 3F-*b*-ME3-3:2 results (Table S1). Number average molecular weights determined by ¹H-NMR end group analysis^[59] are in Table S1. Aggregation of 3F-*co*-MEn diols precluded accurate GPC determination of molecular weights.

Examination of the ¹H-NMR spectra for ME3, 3F-*r*-ME3, 3F-*b*-ME3, and 3F diols (Figure S1) shows that the “fingerprint” for main chain -CH₂- at 3.2 ppm has a different pattern for block and random structures. The pattern has sharper peaks for 3F-*b*-ME3 compared to 3F-*r*-ME3. This peak pattern for 3F-*b*-ME3 is characteristic of the 3F homopolymer main chain -CH₂- protons and provides evidence for repeating 3F sequences in 3F-*b*-ME3. However, the splitting pattern for the -CH₂- protons for 3F-*b*-ME3 is not as well defined as for 3F diol suggesting varying block lengths for 3F-*b*-ME3.

The ¹H-NMR spectra for ME7, 3F-*r*-ME7, 3F-*b*-ME7, and 3F diols and assignments are shown in Figure S2. A similar differentiation between block and random sequences is observed for main chain -CH₂- protons. The sharpness of the peaks for the 3F-*b*-ME7 -CH₂- protons is less pronounced compared to 3F-*co*-ME3 diols. This may reflect interference from ¹H-¹⁹F spin-spin coupling by the longer PEG-like side chain.

¹⁹F-NMR spectra for 3F-*r*-ME3, 3F-*b*-ME3 and P[3F] were previously reported.^[59] P(3F) and 3F-*b*-ME3 showed a series of well-resolved CF₃- peaks with *J*_{H-19F} = 8 Hz. In contrast, the corresponding 3F-*r*-ME3 peak was broad with little resolvable structure. A similar result is found for the 3F-*co*-ME7 diols.

M_n was determined via ¹H-NMR end group analysis. *M_n* ranged from 3 kDa for P(ME3) to 7.1 kDa for P(3F) diols. P(ME7) and 3F-*co*-ME7 diols had intermediate molecular weights (Table S1). This molecular weight range is convenient for use as polyurethane soft blocks.

Calorimetry

Modulated-DSC was used to determine telechelic *T_g*s. Table S1 lists *T_g*s for homo- and copolyoxetanes; thermograms for the ME3 series are provided in Figure S6. P(3F) and P(ME3) diols have *T_g*s at -47 and -74 °C, respectively. A physical mixture of P(3F) and P(ME3) diols has two *T_g*s (-70, -58 °C).^[59] Some solubility of P(ME3) and P(3F) must account for >10 °C decrease in the P(3F) *T_g* and the increase in the P(ME3) *T_g*. The 3F-*r*-ME3 *T_g* is -62 °C and 3F-*b*-ME3 *T_g* is 60 °C; each is close to the weighted average of the homo-polyoxetanes. P(ME7) also has a low *T_g* (-72 °C) similar to P(ME3). 3F-*r*-ME7 and 3F-*b*-ME7 also have intermediate *T_g*s, but these are a few degrees closer to P(ME7), presumably due to the influence of the longer PEG-like side chain.

Each *block*-copolyoxetane also has only *one* *T_g* that approximates the expected weight average. The results for 3F-*co*-MEn copolyoxetanes may be compared with results of DeSimone for fluorous / PEG mixtures and networks having low molecular weight blocks.^[67] When the perfluoropolyether (PFPE) and PEG blocks had very low molecular weights, precursor mixtures and networks showed microscale miscibility (optical transparency) but nanoscale phase separation (AFM). Separate *T_g*'s were not observed in DSC for combinations of low molecular weight PFPE and lowest weight fraction PEG but two *T_g*'s were observed for other compositions and for networks derived from higher molecular weight components.^[67]

By DSC, P(3F) and P(MEn) are slightly miscible, which parallels observations for certain molecular weight ranges of perfluoropolyether (PFPE) and PEG blocks. Both random and

block P[3F-*co*-MEn] diols are transparent, viscous liquids with one T_g . This is similar to the result for combinations of low molecular weight PFPE and lowest weight fraction PEG. Nanoscale phase separation is different for P[3F-*r*-MEn]-U vs. P[3F-*b*-MEn]-U and prompted a further comparison with the PFPE / PEG results^[67] in the section on polyurethane thermal transitions below.

Polyurethanes

Synthesis and characterization

Polyurethanes were prepared from the P[3F-*co*-MEn] diols (Table 1) by the conventional “soft block first” method. The feed molar ratio was targeted for 65~70 wt.% soft block, which was close to the experimentally observed range of 58 to 73 wt.% determined by ¹H-NMR spectra. GPC molecular weights have a wide range (M_w 10 – 43 KDa). The molecular weights of polyurethanes with ME3-containing soft blocks were generally higher than those for ME7. This may be due to increased steric hindrance of terminal hydroxyl groups for telechelics containing longer PEG side chains. All P[3F-*co*-MEn]-U form optically transparent coatings when dip coated from solvents similar to those used in synthesis (THF or THF/DMAC).

¹H- and ¹⁹F NMR

Figure S4 shows ¹H-NMR spectra and assignments for representative P[3F-*co*-MEn]-U from which the soft block and hard block ratios were calculated. Integration of aromatic protons **j**, chain extender methylene protons **k**, **l** and protons for the 3-methyl moieties **a/e** were among the peaks used. Similar spectra were observed for the other P[3F-*co*-MEn]-U. ¹⁹F NMR spectra for 3F-U and 3F-*co*-MEn-U are shown in Figure S5. 3F-*b*-MEn-U displayed sharper and better resolved patterns than 3F-*r*-MEn-U. 3F-*co*-MEn-U displayed a broad absorption on the high field side of the sharp peaks, the origin of which is not known.

Thermal transitions

Figure 2 shows the MDSC curves while Table 2 lists thermal properties of 3F-*co*-MEn-U as well as base-U. Base-U and 3F-U have soft block T_g 's close to the precursor diols. Previously, a T_g of –37 °C was found for IPDI/BD(40)-P(3F-3400).^[63] This led to an estimated 84% soft block in the pure soft block domain (Fox equation). Somewhat increased phase separation is suggested by the 40 °C T_g for 3F-U. Several factors contribute to improved phase separation in polyurethanes including the shape and symmetry of the hard block, which influences the extent of hydrogen bonding.^[68, 69] Considering the 3F soft block T_g 's for the MDI/BD and IPDI/BD polyurethanes and the different symmetries of the hard block, immiscibility appears to be driven by a synergistic combination of MDI hard block crystallization ($T_m \sim 186$ °C) and the lack of phase mixing of the fluororous soft block.

Soft block T_g s for 3F-*co*-ME3-U and 3F-*co*-ME7-U are about –38 and –48 °C, respectively (Table 2). Thermograms for 3F-*co*-ME3-U in Figure S7-**e/f** and 3F-*co*-ME7-U Figure S7-**h/i** are identical. Conventionally, diblock copolymers comprised of segments that form amorphous domains have two T_g s,^[70] but a growing body of evidence indicates that nanoscale phase separation does not result in separate T_g 's. Even for conventional, high molecular weight glassy polymers, when the scale of phase separation is reduced to a few tens of nanometers, separate T_g s for each phase is not observed.^[71]

The results for the 3F-*co*-MEn-U may be compared with the results of DeSimone for fluororous / PEG mixtures and networks having low molecular weight blocks.^[67] When the perfluoropolyether (PFPE) and PEG blocks had very low molecular weights, precursor mixtures and networks showed microscale miscibility (optical transparency) but nanoscale

phase separation (AFM). Separate T_g 's were not observed in DSC thermograms for combinations of low molecular weight PFPE and lowest weight fraction PEG but two T_g 's were clearly observed for other compositions and for networks derived from higher molecular weight components.^[67] The block cotelecholics provide another example wherein separate T_g s are not observed for nanoscale domains.

A mixed soft block composition (3F + ME3)-U was prepared to compare thermal behavior with the 3F-*co*-ME3n-U. Two T_g 's occur at -47 (ME3) and -34 °C (3F). At the modulation rate employed (± 0.50 °C/20 sec) a relaxation process almost obscures these T_g s. Figure S7-**d**' presents a conventional DSC thermogram that clearly shows the two T_g 's. In contrast to 3F-*co*-MEN-U, the scale of phase separation for (3F + ME3)-U is large enough to observe two T_g 's.

Hard block T_g s and T_m s were observed for 3F-U and all 3F-*co*-MEN-U (Table 2, figure 2). Hard block T_g 's are ~ 110 °C while T_m s are in the range $180 - 210$ °C. However, DSC's showed exotherms near or slightly above T_m s indicating 3F-*co*-MEN-U decomposition temperatures are ~ 200 °C. TGA thermograms are provided in Figure S8 along with 2% weight loss temperatures ($T_{d2\%}$) that range from 192 °C for 3F-*b*-ME7-U to 265 °C for (3F + ME3)-U.

Models for random and block soft blocks

Before considering morphological studies via AFM and dynamic wetting behavior, a model for the structure of block and random soft blocks is considered briefly. The 3F-*co*-MEN soft blocks are comprised of segments that are largely immiscible, but both segments have low T_g s. Immiscibility is evidenced by the formation of two layers in a mixture of P(3F) and P(MEN) diols and by the observation of separate T_g s for the polyurethane comprised of mixed soft blocks (Figure S7). On the other hand, the shifted T_g s for the mixture of P(3F) and P(MEN) diols reflect slight miscibility, perhaps of lower molecular weight components.

The space filling models in Figure 3 were generated using ChemBio3D as described in the Experimental section. The models consist of eight 3F and ME3 repeats and facilitate visualization of structures for block and random soft blocks (Figure 3a and b, respectively). The 16-mers have a molecular weight of 3.5 kDa that approximates the M_n range of the 3F-*co*-ME3 diols.

The copolymer model in Figure 3a was generated with an exactly alternating structure so as to visualize the limit for dispersal of 3F repeats in the main chain. Clustering of 3F side chains is apparent in the 3F-*b*-ME3 copolymer. While this is intuitive, the models provide insight into a pathway for intermolecular soft block aggregation through association of 3F-rich clusters. This association is favored for 3F-*b*-MEN but is restricted by the dispersal of 3F side chains in the random copolymer. This model is discussed in considering results from AFM imaging and other characterization studies of neat 3F-*co*-MEN polyurethanes in the next section and in modified base polyurethane compositions.

Surface morphology by TM-AFM

The effect of changing the length of the methoxy-terminated PEG side chain from 12 (ME3) to 24 (ME7) atoms is examined in two sections.

3F-*co*-ME3 polyurethanes—Previously, the contrasting nanoscale surface morphology of 3F-*r*-MEN-U and 3F-*b*-MEN-U was reported.^[59] Below, we describe further studies of nanoscale surface morphology as well as microscale morphology. TM-AFM imaging reported previously was on coatings that were “dried” at 60 °C for 24 hr and were described

as “as cast”.[59] At the time, this seemed like a mild solvent removal process. We now find that 60 °C is actually an annealing condition because morphological changes occur compared to coatings from which solvent was removed in vacuum at ambient temperature (25 °C). In the present discussion, “as cast” coatings were drip- or dip-coated and solvent was removed at room temperature under reduced pressure. Heat treatment at 60 °C is now considered an annealing process.

AFM imaging ($2 \times 2 \mu\text{m}$) for 3F-*co*-ME3-U confirms prior results but demonstrates subtle effects of annealing at 60 °C (Figure 4). Images were obtained at a setpoint ratio of 0.8, a moderate tapping force that reveals near surface hard block domains. Phase contrast images for as cast and annealed (60 °C, 24 h) 3F-*b*-ME3-U coatings show nanodomains with distinct phase contrast and dimensions (~ 20 –50 nm). Even though the size scale of these domains did not change with 60 °C annealing, contrast for the phase images increased. These phase images for 60 °C annealing parallel those previously reported.[59] The more clearly resolved phase images after 60 °C is explained by enhanced phase separation of fluorous and PEG-like domains. A model for these domains is proposed below.

The surface morphology for 3F-*r*-ME3-U is shown in Figure 4, Right set. With similar imaging conditions, the phase image for the as cast random copolyoxetane polyurethane shows less distinct features compared that for the block analog (Left set). R_q (~ 1 nm) for the as cast 3F-*r*-ME3-U coating is lower than that for the 3F-*b*-ME3-U analog (~ 8 nm). Annealing 3F-*r*-ME3-U coatings follow the same trend as that observed for the block analog with an enhanced nanoscale phase separation in the phase image. The phase image for 3F-*r*-ME3-U after annealing resembles that for 3F-*b*-ME3-U before annealing.

The size for the well defined nanoscale phase separated domains for 3F-*b*-ME3 soft blocks is at least 10 times higher than chain dimensions estimated by a valence angle random coil calculation (2 nm). In addition, the T_g for the soft block is ~ 60 °C lower than ambient temperature. Thus, we propose that enhanced nanoscale phase separation for 3F-*b*-ME3 soft blocks imaged in phase contrast is due to synergism with hard block organization.

A model for the phase separated nanodomains is proposed in Figure 5. Individual 3F-*b*-ME3 soft blocks are represented as a Janus-like nanostructures generated by self association of 3F side chains. Individual clusters of 3F side chains (Figure 4b) are represented by dark gray shading on one end of the oval soft block representation while the PEG enriched side chain aggregates are light gray. As such, the depiction is for the surface in air. Aggregation to fluorous nanodomains is proposed that in turn results in synergistic organization of near surface hard blocks (Figure 5, striped rectangles). The choice of 8 associated soft block / hard blocks is arbitrary; the depiction leaves space for clarity. Merging domains after 60 °C annealing is proposed to account for the growth in phase image feature size.

Self aggregation for 3F-*r*-ME3 soft blocks is less favored entropically compared to the block analog due to the more disperse arrangement of 3F side chains (Figure 3a). As a result, the phase image for 3F-*r*-ME3-U is devoid of features (Figure 4C, phase image). However, after 60 °C annealing, aggregated features appear (Figure 5D-phase image) that are attributed to the formation of soft block/hard block domains depicted in Figure 5.

The above results confirm that soft block sequence distribution has an effect on the nanoscale morphology.[59] We now find that microscale surface morphology also differs. Figure 6 shows $100 \times 100 \mu\text{m}$ TM-AFM images of as cast and annealed 3F-*b*-ME3-U. In comparing $2 \times 2 \mu\text{m}$ with $100 \times 100 \mu\text{m}$ images, the trend of increasing R_q with increasing scan area is observed. The as-cast film has a relatively low R_q (21 nm). Some height and phase contrast features are evident from solvent evaporation and the initial stage of phase separation. Striking morphological and topological changes are found for 3F-*b*-ME3-U after

60 °C annealing. R_q increases from 21 nm to 178 nm due to 10 to 40 μm globular and larger crater-like features that are best seen in the 3D image. The coating imaged in Figure 6A was exposed to vacuum overnight so it is unlikely that solvent evaporation is a primary contributor to 3D topological complexity. Rather, we propose that densification due to enhanced phase separation drives roughening observed in the 3D height image (Figure 6B). The phase image, Figure 6B enlarged in Figure S9, brings into focus a coarsened microscale topology for 3F-*b*-ME3-U compared to 3F-*r*-ME3-U that is attributed to growth of 3F-*b*-ME3 / hard block clusters illustrated in Figure 5.

Compared to the block analog, the topology of 3F-*r*-ME3-U coatings is relatively smooth and featureless (Figure 6C, D and Figure S9). Surface roughness increases moderately after 60 °C annealing (5 to 23 nm). These topological changes are minimal compared to those for the block analog. The finer scale near surface morphology is ascribed to the more dispersed arrangement of 3F side chains (Figure 5a) and attendant less favored clustering.

3FOx/ME7Ox polyurethanes—Figures 7 ($100 \times 100 \mu\text{m}$) shows AFM images for polyurethanes containing block and random 3F-*co*-ME7 soft blocks. The morphology and morphological development are quite different compared to the 3F-*co*-ME3 analogs with complexities that will require more work to develop understanding.

Morphologies for as cast and post-60 °C 3F-*b*-ME7-U are shown in $100 \times 100 \mu\text{m}$ images in Figure 7A and 7B, respectively. For both 3F-*b*-ME7-U and 3F-*r*-ME7-U a decrease of about half in surface roughness (R_q) is found after 60 °C annealing. This “smoothing” trend is commonly observed for coatings, but is opposite that for the ME3 analogs. We attribute the conventional decrease in surface roughness for 3F-*co*-ME7-U to dilution of 3F-functionality by larger ME7 side chains that diminishes 3F intra- and intermolecular association.

At the smallest resolvable scale, scattered nanopikes are observed in 3D height images. Nanopikes are common for block and random copolymers but more prominent for 3F-*b*-ME7-U. These features may be associated with higher orders of fluororous / PEG self aggregation as observed for cross-linked amphiphilic fluororous / pyrrolidinone networks.^[72] Higher order aggregated structures would be facilitated for 3F-*b*-ME7-U compared to the random analog. Nano- and micropeaks were attributed to phase separation of higher MW components during coating deposition for HMDI-BD(30)-3F polyurethanes.^[73] A similar origin for 3F-*co*-ME7-U is possible, despite relatively low molecular weights (Table 2).

A remarkable $100 \times 100 \mu\text{m}$ phase image for 3F-*b*-ME7-U is observed after 60 °C annealing (Figure 7B, Figure S10). This pattern is not seen for the random analog (Figure 7D) suggesting that the phase image for the block analog is not due to an artifact. The lighter portions of the phase image are tentatively assigned to a 3F-rich phase. Micropeaks (1 – 5 μm laterally) rather than nanopikes are prominent in the 3D height image (Figure 7B, $z = 1000 \text{ nm}$, Figure 8 C, $z = 500 \text{ nm}$). The surprisingly high micropeaks (several are $\sim 1 \mu\text{m}$) may result from vertical shrinkage during 60 °C annealing. Annealing would have less effect on pre-formed fluororous near-surface domains resulting from association of nanostructures depicted in Figure 5. Coating thickness is typically 50–100 μm so that a vertical shrinkage of $\sim 1 \%$ would account for the appearance of the micropeaks.

An unexpected feature of the phase images for both post-annealed block and random soft block polyurethanes is the “switch” in appearance of the nano- and micropeaks from a light color for as cast coatings (Figures 7A, block; 7C for random analog) to dark roughly circular features on a lighter background (Figures 7B, block; 7D for random analog). These are well defined for 3F-*b*-ME7-U in the $10 \times 10 \mu\text{m}$ shown in Figure 8, appearing as dark irregular-

shaped features superposed on light gray domains. The latter are assigned to association of nano-aggregates depicted in Figure 5.

Apparently, an unforeseen consequence of topological complexity resulting from the nano- and micropeaks while using conventional AFM settings produced a phase image where the “harder” nanopeaks appear dark gray while the matrix is light gray (Figures 7, 8B, or medium gray (Figures 7, 8D). The color/representation is opposite phase images for the as cast coatings (Figure 7A and C). It is also opposite to AFM images for polyurethanes where near surface hard block domains appear as light gray while soft block domains are black.^[47, 48, 50, 51]

In general, contrast in phase images reflects the surface modulus and viscoelasticity, from which physical form or compositional differences are deduced. However, phase contrast images can be altered by different amplitude setpoint ratios, driving frequency or tip-surface distance.^[74–78] In the present case, the amplitude setpoint ratio was not changed intentionally, but the setpoint ratios are not very accurate. This is because the A_0 (free amplitude) varies across the area and an average is usually taken. Unless the imaged area is fairly flat, the real distance from the surface to the tip varies within the scanned area. In addition, the interactions of the AFM tip with associated domains (Figure 5) can affect the traditional interpretation of surface modulus and viscoelasticity from phase images.

Why the nanopeak features are imaged conventionally in Figure 7A and C but not in Figure 7B and D is not clear. The origin of the reversing phase images for post-annealing nanopeaks is apparently related to sudden changes in topography that affects tip-sample interactions from repulsive to attractive mode or vice versa. Another peculiar aspect to the phase image for 3F-*b*-ME7-U, Figure 7B (enlarged in Figure S10) is a band near the top of the image where the nanopeaks appear “conventionally” as light gray. There is another such band at the bottom of the image. AFM is a mechanical imaging method dependent on tip-sample interactions. Perhaps a bit of contamination on the tip changed this interaction and switched the image temporarily.

In summary, topological and morphological complexity is found for 3F-*co*-ME_n-U. The above results are not amenable to easy explanation but display a range from fine topology and morphology (Figure 6D) to surprising topological and morphologic complexity (Figure 6B and Figure 7B). At the least, it is important to be aware of these complexities before discussing wetting behavior.

Wetting behavior

3F-*co*-ME3-U. DCA advancing (θ_{adv}) and receding (θ_{rec}) contact angles for post-60 °C 3F-*co*-ME3-U are summarized in Table 2. These are derived from force distance curves (fdc's) shown in Figure 9. Contact angles for three immersion / immersion cycles were obtained to determine the effect of immersion (~ 10 min). The different wetting behavior of 3F-*b*-ME3-U and 3F-*r*-ME3-U reveals macroscopic consequences of differing nano- and microscale soft block sequence distribution on polyurethane surface morphology.^[59]

DCA facilitates examining repeated fdc's for systematic changes after immersion in water.^[39, 52, 66, 79] For 3F-*co*-ME3-U, θ_{adv} decreases by a few degrees over the three DCA cycles, which is expected due to the presence of near surface hydrophilic ME3Ox side chains. A clear trend is the increase of θ_{rec} (11°) for 3F-*r*-ME3-U compared to the constant receding contact angle for the block analog. These observations indicate that near surface rearrangement due to water adsorption / absorption is more pronounced for 3F-*r*-ME3-U. Over the time scale of three force distance curves (10 min) phase separation for 3F-*b*-ME3-U inhibits near surface rearrangement resulting in a stable θ_{rec} . As a result of changes in θ_{rec} ,

3F-*r*-ME3-U exhibits a large initial contact angle hysteresis: $\theta_{adv} (104^\circ) - \theta_{rec} (39^\circ) = 65^\circ$, while θ_{adv} is lower (50°) for 3F-*b*-ME3-U. The relatively stable wetting behavior for 3F-*b*-ME3-U is more like 3F-U ($\theta_{adv}, 110^\circ$; $\theta_{rec}, 70^\circ$, Figure S12) than the random soft block analog.

3F-co/ME7-U—The initial estimated contact angles from the first fdc's are listed in Table 2, while force distance curves are shown in Figure 10. Wetting behavior is quite different for 3F-co-ME7-U compared to ME3 analogs. For 3F-*r*-ME7-U (Figure 10A), the first fdc (fdc_{adv-1}) is horizontal, rather than displaying a downward slope due to buoyancy. The horizontal fdc is characteristic of mass increase due to hydration canceling decreased mass due to buoyancy. 3F-*b*-ME7-U also absorbs water, but at a slow enough rate to permit accurate contact angle analysis.

To confirm absorption of water for 3F-*r*-ME7-U, mass gain was studied by noting the mass at the end of successive DCA cycles (Figure S13). The presence of the longer ME7 side chain results in substantial water absorption. Mass gain could be measured after only two fdc's because of partial detachment of the coating after two cycles. The effect of absorbed water for 3F-*r*-ME7-U is seen in fdc_{adv-2} that reflects hydrophilic behavior with a θ_{adv} of approximately 73° .

From un-tared mass measurements, Figure S13 shows that 3F-*b*-ME7-U absorbs about 5 mg water for each cycle. The successive fdc's in Figure 10B are tared at the beginning of a given cycle so that cumulative mass increase does not influence θ_{adv} for a given cycle. Despite absorption of water during fdc_1 , which might be expected to lower θ_{adv-2} , a decrease in apparent mass is evident for fdc_2 reflective of increased θ_{adv-2} . θ_{adv-1} is 85° for 3F-*b*-ME7-U coating (Figure 13B) while θ_{adv-2} is 89° . Such wetting behavior whereby contact with liquid water results in the surface becoming more hydrophobic has been designated "contraphilic" because of an opposite result compared to usual amphiphilic wetting (seen for 3F-*r*-ME7-U).^[52] Another example where the presence of fluorinated and PEG-like groups leads to contraphilic wetting has been reported.^[80] A proposed model for contraphilic behavior includes hydrogen bonding of the electron poor $-OCH_2CF_3$ hydrogens to ether oxygens in the dry solid (Figure 11). This enthalpically driven hydrogen bonding "submerges" some fraction of fluororous groups. On immersion in water, fluororous groups are "released" due to preferential H-bonding of ether oxygens to water resulting in increased hydrophobicity. The contraphilic effect is reversible on dehydration for 3F-*b*-ME7-U.

Inspection of Figure 10B for the 3F-*b*-ME7-U coating shows normal slopes due to buoyancy for cycle 2 and 3 fdc's. These results are consistent with the amplified presence of 3F and microscale phase separation that results in less "response" compared to 3F-*r*-ME7-U. Also, the 3F content is higher in 3F-*b*-ME7-U (3:2) compared to 3F-*r*-ME7-U (1:1).

Base-U with 3F-co-MEn-U as 2 wt.% surface modifiers

The prospects for surface modification using 3F-co-MEn-U appeared dim given the complex surface morphology and wetting behavior for neat coatings. As noted in the Introduction, low weight percents of fluororous modifiers are typically employed for surface modification.^[49, 50, 60, 81] Here, a survey of 2 wt.% 3F-co-MEn-U modified base polyurethane reveals much less complicated morphologies and wetting behavior compared to the parent modifier. Importantly, negligible water absorption occurs during DCA analysis. Surface modification is clearly differentiated for random and block 2 wt.% 3F-co-MEn-U compositions with regard to XPS and wetting behavior.

To achieve P[3F-*co*-MEn] surface concentration using dip coating from an initially homogeneous solution, microscale surface concentration must occur as well as nanoscale surface concentration of the functional soft block (Figure 1). A balance of thermodynamic forces determines near surface composition. At one extreme, P[3F-*co*-MEn]-U / base polymer immiscibility would result in phase separation with attendant visible light scattering, i.e., a white “product”. For the 2 wt.% P[A]-U and P[3F-*co*-MEn]-U surface modified base polyurethane compositions, transparent homogeneous coatings were obtained from THF solutions. The coatings remained transparent after solvent was removed at 60 °C. It follows from these qualitative observations that phase separation must be on a scale smaller than the wavelength of visible light. TM-AFM, XPS, and DCA studies were carried out to compare morphology, chemical composition, and wetting behavior with neat 3F-*co*-MEn-U, with the base-U, and with base-U modified by P[3F] or P[ME3].

Atomic force microscopy

Figure 12 shows 100 × 100 μm TM-AFM images for 2 wt.% 3F-*co*-MEn-U compositions. In contrast to the often complex images for 3F-*co*-ME3-U (Figure 6) and 3F-*co*-ME7-U (Figures 7–8), 2D height and phase images for 2 wt.% 3F-*co*-MEn-U reveal fairly uniform topologies and morphologies.

As a control, Figure S14 contains height and phase images (100 × 100 μm) for base-U. Base-U is featureless at this scale with an R_q of 2 nm. In contrast, Figure 12 shows 2D images for 2 wt.% 3F-*co*-MEn-U compositions that have textured morphologies with R_q ranging from 33–57 nm. Modified surfaces are replete with height features ranging up to several hundred nanometers. For a better comparison of surface texture, 3D images are shown in Figure 12E for 3F-*r*-ME3 and Figure 12F for 3F-*r*-ME7. Careful scrutiny of these images reveals that 3F-*r*-ME3 has courser nanopeaks than 3F-*r*-ME7, which correlates with the strong influence of fluororous content in determining phase separation during coating formation. The nanopeak features are attributed to surface phase separation of the fluororous modifier driven by immiscibility of the 3F-*co*-MEn soft block.

While only subtle morphological and topological differences are observed for 100 × 100 μm images there are systematic trends for nanoscale morphology. Figure 13 shows AFM phase images (500 × 500 nm) for 2 wt.% P[3F-*co*-MEn]-U coatings. At this scale, 2D images (not presented) showed that all coatings are topologically smooth ($R_q < 1.3$ nm). The base-U phase image Figure 13A reveals modest contrast at $r_{sp} = 0.87$ and clearer contrast at hard tapping ($r_{sp} = 0.60$). This result is typical for a polyurethane (or polyurethane urea) that has moderately good near surface phase separation with soft blocks preferentially surface concentrated.^[23, 48, 82]

Images for 2 wt.% P[3F-*r*-MEn]-U (Figure 13B and D) have a similar pattern of faint features at soft tapping but clear near surface morphological features at hard tapping. Nanoscale phase separation is attributed to a combination of near surface hard block domains from the respective P[3F-*r*-MEn]-U surface modifier (Figure 5) and from the bulk polyurethane.

In comparison, Figures 13C and E for the 2 wt.% P[3F-*b*-MEn]-U compositions have similar patterns of clear morphological features even at moderate tapping ($r_{sp} = 0.83$ – 0.86). Many aggregates have a characteristic circular shape, which is particularly noticeable for 3F-*b*-ME7. Again, nanoscale phase separation driven by synergistic 3F-hard block aggregates (Figure 5) is proposed to account for the observed features. We assign the lighter color portions of the modulus-sensitive phase images at light tapping to these domains.^[Uilk, 2002 #533] The contribution of base polyurethane hard block to near surface morphology must be low based on wetting behavior discussed below. The average domain size is about 20 nm in

diameter, somewhat larger than the hard- and soft-segment segregation observed in base-PU (Figure 13A). The proposed phase separated model in Figure 5 reflects the immiscibility of the 3F and MEnOx block segments and the synergistic association of near surface hard blocks.

X-ray photoelectron spectroscopy

XPS analysis was obtained for 2 wt.% 3F-*co*-MEn-U compositions (Table 3). Related compositions include 2 wt.% 3F-U, ME3-U, and 3F + ME3. As a negative control for F, XPS analysis for the base-U was obtained. A background of ~2 atom% F and Si was detected for the base polyurethane and for 2 wt.% ME3-U. The 2 wt.% 3F-U and 3F-*co*-MEn-U samples had less than half or no detectable Si contamination. In view of these low levels, F, N, O, and C atom percents have not been normalized.

The 2 wt.% 3F-*b*-MEn-U samples both have high F atom percents (~21 at.%). This value approaches that obtained for 2 wt.% 3F-PU (24.2 at.%). The atom percent F for the 3F-*b*-MEn-U modified compositions is closer to that calculated for the P(3F) soft block (alone, 25 at.%) than to the respective 3F-*b*-MEn soft blocks (3F-*b*-ME3-U, 12.9 at.%; 3F-*b*-ME7-U, 9.4 at.%). The high F atom percent for the block soft block modified compositions is consistent with the model in Figure 1 and the supposition that the intermolecular clustering of 3F side chains leads to the phase separated nanostructures (Figure 5) that coalesce as suggested by AFM images described above. In the dry state, the outermost atom layers are comprised largely (but not solely) of 3F side chains.

Compared to the block 2 wt.% 3F-*b*-MEn-U compositions, the 2 wt.% 3F-*r*-MEn-U samples have lower atom %F (~14). These values are above the calculated %F for the soft blocks alone (3F-*r*-ME3-U, 10.3 atom% F; 3F-*r*-ME7-U, 9.4 at.%). The relatively low F at % for the 2 wt.% 3F-*r*-MEn-U samples stems from the dispersed nature of the 3F side chains in the model presented in Figure 5. The latter model for an exactly alternating structure maximizes 3F side chain dispersion. Qualitatively, the ¹⁹F-NMR spectrum of 3F-*r*-MEn copolyoxetanes suggests diads and perhaps higher groups of 3F repeat units are present. The higher than calculated values for atom% F may stem in part from near surface clustering of these smaller units.

Interestingly, the mixed soft block composition 2wt.% (3F + ME3)-U has virtually the same C, O, and F atom percents as the 2wt.% 3F-PU composition. The observed atom percents are close to the calculated values for the P(3F) soft block alone. This analysis testifies to the surface concentration of the P(3F) soft block. Low or negligible N at % also is consistent with this view.

As a reference, 2 wt.% ME3-U was examined to investigate a polyurethane surface modifier without the 3F “chaperone”. The relatively high 1.5 at.% N and low 21 at.% O is consistent with the presence of near surface hard block. However, coatings with 3F copolyoxetane surface modifiers also have detectable N and relatively low O at.%. The RMS end-to-end distance of the soft blocks is on the order of 2–3 nm, while the majority of photoejected electrons at a 55° TOA results in a detection depth of 4–5 nm. Thus, the presence of N, at diminished levels is still consistent with P[3F-*co*-MEn] surface concentration.

In summary, XPS analysis gives evidence for nanoscale surface concentration of 3F-*co*-MEn-U soft blocks. The surface concentration of the fluorous component is moderated by the soft block architecture. The outermost surface at.% F for 2 wt.% 3F-*b*-MEn-U compositions is much higher than random analogs.

Wetting behavior

Dynamic contact angle (DCA) analysis provides contact angles and information on the stability of wetting behavior over the course of three cycles that constitutes ~10 min coating immersion. Table 2 contains DCA contact angle for base-U, neat and modified base-U compositions. As one reference, the 2 wt.% 3F-U coating resulted in average contact angles of $\theta_{adv} = 107^\circ$ and $\theta_{rec} = 68^\circ$ (Table 2, Figure S12). Wetting behavior is similar to the corresponding neat modifier ($\theta_{adv} = 110^\circ$, $\theta_{rec} = 70^\circ$). Compared to base-U, the modifier confers expected hydrophobic character to the coating. The wetting behavior confirms surface concentration of P(3F-7100) observed via XPS and emphasizes the importance of soft block concentration at the outermost surface.

As another reference, contact angles for 2 wt.% ME3-U were $\theta_{adv} = 91^\circ$ and $\theta_{rec} = 44^\circ$. The advancing contact angle is similar to the neat modifier ($\theta_{adv} = 93^\circ$, Table 2) but base-U has a similar θ_{adv} (92°). The receding contact angle for 2 wt.% ME3-U is 12° higher than neat ME3-U (32°) and 7° lower than base-U. The intermediate wetting behavior is consistent with near surface phase mixing indicated by XPS analysis.

(3F + ME3)-U is an interesting reference modifier having mixed soft blocks. The DCA wetting behavior of 2 wt.% (3F + ME3)-U gives $\theta_{adv} = 108^\circ$ and $\theta_{rec} = 52^\circ$ (Table 3). Contact angles for the neat modifier were $\theta_{adv} = 102^\circ$ and $\theta_{rec} = 48^\circ$. The character of the modified surface based on $\theta_{adv} = 108^\circ$ is 3F-like, which is in agreement with the high F at.% from XPS analysis. However, $\theta_{rec} = 52^\circ$ is 17° lower than that for neat or 2 wt.% (3F + ME3)-U and relatively close to $\theta_{rec} = 44^\circ$ for 2 wt.% ME3-U. The reversible air / water wetting behavior is explained by assuming a reorganization of near surface soft blocks similar to the hydrophobic-to-hydrophilic transformation of mixed soft block polyurethanes reported by Chaudhury.^[83] Of note are the long and gradual portions of the three superposable fdc's shown in Figure S15. This will be a matter of future study but may be associated with slow kinetics for reorganization of near surface soft blocks.

2 wt.% 3F-co-ME3-U—Figure 9 shows force distance curves (3 cycles) for 2 wt.% 3F-*r*-ME3-U (C) and 2 wt.% 3F-*b*-ME3-U (D) as well as the previously discussed neat 3F-*r*-ME3-U (A) and 3F-*b*-ME3-U (B) coatings. In contrast to the neat 3F-*co*-ME3-U coatings, the wetting behavior for the 2 wt.% modified base-U coatings is stable over the course of three immersions. It is likely that the time dependent wetting behavior for neat 3F-*co*-ME3-U coatings is influenced by complex morphology observed in AFM imaging. On the other hand, the stable wetting behavior of the 2 wt.% 3F-*co*-ME3-U modified coatings is consistent with the fairly uniform topologies and morphologies for the modified coatings (Figure 12). Interestingly, microscale roughness (R_q , $100 \times 100 \mu\text{m}$) that ranges from 33–57 nm (Figure 12) does not significantly affect contact angles.

Figure 14 summarizes contact angle data for the 2 wt.% 3F, ME3, (3F + M3), and 3F-*co*-ME3 coatings. Contact angles for the first fdc's are chosen but there are no significant differences for contact angles over three cycles. There is a gradual decrease of $\sim 15^\circ$ in θ_{adv} with the order being $3F \sim (3F + ME3) > 3F\text{-}b\text{-}ME3 > 3F\text{-}r\text{-}ME3 > ME3$; even ME3 has $\theta_{adv} > 90^\circ$. The receding contact angle shows a drop of 17° from 3F to (3F + ME3) followed by a more gradual drop to ME3 for a total decrease of 25° .

2 wt.% 3F-co-ME7-U—The DCA fdc's for neat and 2 wt.% 3F-*co*-ME7-U are shown in Figure 10. In contrast to the nonlinear wetting behavior of neat 3F-*co*-ME7-U, fdc's for 2 wt.% coatings are “well behaved”. As noted above, the amphiphilic behavior for 3F-*r*-ME7-U ($\theta_{adv-1} > \theta_{adv-2}$) is attributed to water uptake by this composition. Unexpectedly, and in contrast to both 3F-*r*-ME7-U and 2 wt.% 3F-*r*-ME3-U discussed above, 2 wt.% 3F-*r*-ME7-U exhibits contraphilic wetting behavior ($\theta_{adv-1} < \theta_{adv-2}$).^[52] That is, fdc_{adv-1}, marked in

Figure 10C, gives $\theta_{adv-1} = 76^\circ$ while θ_{adv-2} , which parallels θ_{adv-1} but at a lower apparent mass, which signals a higher contact angle, gives $\theta_{adv-2} = 80^\circ$. Receding force distance curves for the wetted coating and θ_{adv-2} and θ_{adv-3} are superposable indicating stable wetting behavior once the coating is wet. The magnitude of contraphilic wetting is given by $\theta_C = \theta_{adv-2} - \theta_{adv-1} = 4^\circ$.^[53] As a result of contraphilic wetting, contact angle hysteresis increases from 41° for the first DCA cycle to 46° for the second and succeeding cycles. Once the coating was dried, the identical sequence of θ_{adv} 's shown in Figure 10C was reproduced.

A general mechanism for contraphilic wetting, which parallels that suggested earlier^[52, 53] is proposed in Figure 11. Figure 11A depicts hydrogen bonding of $-\text{CH}_2$ adjacent to $-\text{CF}_3$ to an ether oxygen. This enthalpically driven secondary bonding results in the displacement of some area fraction of $-\text{CF}_3$ groups away from the air-polymer interface. The surface is less hydrophobic due to that area fraction being replaced with less hydrophobic moieties. When the surface is immersed, water replaces $-\text{CH}_2$ and the trifluoroethoxy group is "released" resulting in a higher area fraction of $-\text{CF}_3$ groups and enhanced hydrophobic character. There are many variations on structures proposed in Figure 11A and B. Unlike an example where the presence of fluorinated and higher molecular weight PEG groups leads to contraphilic wetting, the proposed mechanism shown in Figure 11 does not involve PEG side chain crystallization.^[80] The ME7 side chain is too short to crystallize.

The switch from amphiphilic behavior for 3F-*r*-ME7-U to contraphilic wetting for 2 wt.% 3F-*r*-ME7-U is quite remarkable. Apparently, sorption of water for neat 3F-*r*-ME7-U masks this behavior. Swelling is minimal for 2 wt.% 3F-*r*-ME7-U as base-U, which constitutes 98 wt.% of the coating, sorbs at most a few percent water.

The θ_{adv} 's for 2 wt.% 3F-*b*-ME7 are shown in Figure 10D. This coating also has contraphilic wetting, but interestingly the effect is more pronounced than for both neat 3F-*b*-ME7 (Figure 10B) and the random analog (Figure 10C). The magnitude of contraphilic wetting for 2 wt.% 3F-*b*-ME7-U is $\theta_C = 8^\circ$. Once wet, 2 wt.% 3F-*b*-ME7 has θ_{adv-2} that is 3F-like (97°) while θ_{rec} is low ($\sim 45^\circ$). After immersion, the contact angles for 2 wt.% 3F-*b*-ME7 resemble those for 2 wt.% 3F-*r*-ME3-U. Unlike the latter, when the 3F-*b*-ME7 coating is dried, contraphilic wetting is once again observed. It is not clear why 2 wt.% 3F-*b*-ME7 displays contraphilic wetting. Additional donor ether oxygens presumably promote hydrogen bonding as shown in Figure 12A, but the combination of factors that leads to this result requires additional investigation.

Conclusions

This research is part of a broader program that seeks facile polymer surface modification that is processing compatible (solution, melt) and results in robust functionality. To explore amphiphilic surface modification, solution deposited base polyurethane coatings were modified by including 2 wt.% P[3F-*co*-ME_n] polyurethane having a low T_g soft block with hydrophobic 3F side chains and short PEG-like ME3, ME7 side chains.

Neat P[3F-*co*-ME_n] polyurethanes displayed complex surface morphologies (Figures 7, 8) and wetting behavior (Figures 9, 10). In contrast, by using 2 wt.% 3F-*co*-ME_n-U as surface modifiers for a conventional linear MDI-BD-PTMO polyurethane, surface morphologies had consistent multiscale phase separated features (Figures 12, 13). Compared to base-U with $R_q \sim 2$ nm ($100 \times 100 \mu\text{m}$ area), the microscale morphology of 2 wt.% 3F-*co*-ME_n-U modified base-U coatings is textured with R_q ranging from 33–57 nm depending on the modifier (Figure 12).

2 wt.% 3F-*co*-MEn-U modified base-U coatings have properties that are consistent with soft block surface concentration depicted in Figure 1. However, the model in Figure 1, which is a modification of conventional polyurethane morphology, does not take into account self aggregation of soft blocks driven by association of fluorous soft block side chains. Multiscale texturing is attributed to phase separation driven by clustering of nano-aggregates depicted in Figure 5. In so doing, larger micron scale features acquire curvature leading to texturing noted above (Figure 12). Aggregate formation during coating deposition results from a synergistic combination of insolubility due to 3F inter- and intramolecular interactions and hard block phase separation. The latter is especially favored for the MDI-BD due to symmetry that favors H-bonding and hard block crystallization.^[61, 84–86] Evidence for the latter comes from DSC for neat 3F-*co*-MEn-U, where melting endotherms are observed at 200 °C.

The nano-aggregate model depicted in Figure 5 features soft block surface concentration consistent with results from XPS and DCA analysis. Trends in outermost surface composition (XPS, Table 3) correlated well with soft block chain architecture. Thus 2 wt.% 3F-*b*-MEn-U has a higher atom% F compared to 2 wt.% 3F-*r*-MEn-U. That being said, χ_{adv-1} for 2 wt.% 3F-*co*-MEn-U were similar, but χ_{rec-1} was higher for block modifiers (like 3F-U).

Several features enumerated in the Introduction are reflected in 2 wt.% 3F-*co*-MEn-U compositions, including surface concentration (1), economy (2), multiple side chain-ends (3), differing 3F/MEn solubility parameters (4), and 3F/MEn propinquity leading to synergistic interactions (6). Illustrating the latter, neat 3F-*r*-ME7-U had amphiphilic wetting behavior with $\chi_{adv-1} > \chi_{adv-2}$ but a modest contraphilic effect is found for 2 wt.% 3F-*r*-ME7-U with $\chi_{adv-1} < \chi_{adv-2}$. The switch is attributed to water sorption masking the contraphilic effect for neat 3F-*r*-ME7-U. Interestingly, both 3F-*b*-ME7-U and 2 wt.% 3F-*b*-ME7-U exhibited contraphilic wetting with χ_c for 2 wt.% 3F-*b*-ME7-U (8°) being the highest of all 3F-*co*-MEn-U coatings.

Observations on amphiphilic wetting for 2 wt.% P[3F-*co*-MEn] show that χ_{rec} , which is a measure of the strength of water-substrate interaction, can be independently controlled without significant swelling. The range of χ_{rec} was 35° for 2 wt.% 3F-*r*-ME7-U to 68° for 2 wt.% P(3F)-U. This observation is important for coating applications where retention of bulk mechanical properties and adhesion to substrate are desired while independently tuning interactions of the surface with the environment.

While nanoscale to microscale phase separation and surface texturing seem rather benign for 2 wt.% 3F-*co*-MEn-U coatings, phase separation can be problematical for 3F based surface modification. We previously reported time dependent phase separation of a P[A-*co*-B]-U modifier with A = 3F and B = dodecylammonium-butoxy (C12). Within a day or two after coating, the PSM modified base polyurethane conferred high contact antimicrobial efficiency against bacterial spray challenges.^[50] However, measurement of near surface charge density via streaming potentials (SP) showed rapid charge attenuation for 1 wt % P[3F-*co*-C12]-U over the course of a few minutes. Aging in air resulted in diminution of antimicrobial effectiveness after two weeks.^[87] Studies are not complete, but it appears that fluorous phase separation sequesters near-surface quaternary charge and accounts for temporal instability of function.

To circumvent phase separation new PSMs are being developed that do not have a trifluoromethyl-based “chaperone” for surface concentrating durable functionality. This work is underway and will be reported in due course.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Figure 1.
Schematic of a conventional polyurethane (soft block, solid line) modified with a P[A-co-B]-U having a copolymer soft block (dashed line) with A and B side chains.

Figure 2. MDSC (reversing curves) for, **a**, 3F-U, **b**, 3F-*r*-ME3-U, **c**, 3F-*b*-ME3-U, **d**, 3F-*r*-ME7-U, **e**, 3F-*b*-ME7-U.

Figure 3. Models for a 6-mer polyoxetane with equal numbers of repeat units: **a**, 3F-*alt*-ME3 and **b**, 3F-*b*-ME3

Figure 4.

AFM ($2 \times 2 \mu\text{m}$, $r_{sp} = 0.8$) for: **Left set**, 3F-*b*-ME3-U; **A**, as cast, **B**, annealed 60 °C, 24 hr; left, 2D height ($z = 200$ nm); middle, phase ($z = 80^\circ$); right, 3D height ($z = 50$ nm). **Right set**, 3F-*r*-ME3-U; **C**, as cast, **D**, annealed 60 °C, 24 hr; left, 2D height ($z = 200$ nm); middle, phase ($z = 80^\circ$); right, 3D height ($z = 50$ nm).

Figure 5.
Model for surface nanoscale phase separation in 3F-*b*-ME3-U

Figure 6.

AFM ($100 \times 100 \mu\text{m}$, $r_{sp} = 0.8$) for: **Left set (LS)**, 3F-*b*-ME3-U; **A**, as cast, **B**, annealed 60 °C, 24 hr; 15 min; LS left, 2D height ($z = 1000 \text{ nm}$); LS middle, phase ($z = 80^\circ$), LS right, 3D height ($z = 1000 \text{ nm}$). **Right set (RS)**, 3F-*r*-ME3-U; **C**, as cast, **D**, annealed 60 °C, 24 hr; RS left, 2D height ($z = 1000 \text{ nm}$); RS middle, phase ($z = 80^\circ$); RS right, 3D height ($z = 1000 \text{ nm}$).

Figure 7.

AFM ($100 \times 100 \mu\text{m}$, $r_{sp} = 0.8$) for: **Left set (LS)**, 3F-*b*-ME7-U **A**, as cast, **B**, annealed 60 °C, 24 hr; LS left, 2D height ($z = 1000$ nm); LS middle, phase ($z = 80^\circ$), LS right, 3D height ($z = 1000$ nm). **Right set (RS)**, 3F-*r*-ME7-U, **C**, as cast, **D**, annealed 60 °C, 24 hr; RS left, 2D height ($z = 1000$ nm); RS middle, phase ($z = 80^\circ$); RS right, 3D height ($z = 1000$ nm).

Figure 8. TM-AFM ($10 \times 10 \mu\text{m}$, $r_{sp} = 0.8$) for post-60°C annealed 3F-*b*-ME7-U: **A**, 2D height ($z = 500 \text{ nm}$); **B**, phase ($z = 80^\circ$); **C**, 3D height ($z = 500 \text{ nm}$).

Figure 9.
DCA force distance curves for: **A.** 3F-*r*-ME3-U; **B.** 3F-*b*-ME3-U; **C.** 2 wt.% 3F-*r*-ME3-U;
D. 2 wt.% 3F-*b*-ME3-U.

Figure 10.

DCA force distance curves: **A.** 3F-*r*-ME7-U; **B.** 3F-*b*-ME7-U; **C.** 2 wt.% 3F-*r*-ME7-U; and **D.** 2 wt.% 3F-*b*-ME7-U.

Figure 11.
Proposed mechanism for contraphilic wetting in 3F-co-ME7-U

Figure 12. TM-AFM 100 × 100 μm 2D height ($r_{sp}=0.8$, $z = 1000$ nm) and phase ($z = 60^\circ$) images for 2 wt.% P[3F-co-MEn]-U: **A**, 3F-*b*-ME3; **B**, 3F-*r*-ME3; **C** 3F-*b*-ME7; **D**, 3F-*r*-ME7; For comparison of surface texture, 3D images are shown in **E**, 3F-*r*-ME3 and **F**, 3F-*r*-ME7 ($z = 1000$ nm). Samples were annealed at 60 °C for 24 hr.

Figure 13.
AFM phase images (500×500 nm) for 2 wt.% P[A-*co*-B]-U

Figure 14.

Contact angles for 2 wt.% P[A-co-B]-U: grey bar, θ_{adv-1} , white bar θ_{rec-1} ; designations follow those in Table 3.

Scheme 1.

Synthesis of 3F-co-MEn-U, $n = 3$ or 7 . x , y , and z refer to mole fractions delineated in Table 1.

Table 1

Designations, compositions, and characterization data for P[A] and P[AB] polyurethanes.

Polyurethanes (PU)	Designations	Molar feed ratio ^a	Observed molar ratio ^b	Soft block wt. % ^b	MW (kDa) ^c		
					M_n	M_w	M_w/M_n
Hard segment(wt. %)-soft segment(M_n)							
MDI/BD(36)-PTMO(2200)	Base-U	3/2/1	4.5/3.9/1	64	38.1	122.4	3.2
MDI/BD(29)-P(3FOx-7100)	3F-U	9/8/1	8.8/7.1/1	71	13.4	43.1	3.2
MDI/BD(37)-P(ME3Ox-3000)	ME3-U	4/3/1	5.4/3.1/1	63	7.8	14.1	1.8
MDI/BD(30)-[P(3FOx) + P(ME3Ox)-3:2] ^d	(3F + ME3)-U	6/5/1	7.7/4.0/1	70	7.9	16.0	2.0
MDI/BD(27)-P[(3FOx)- <i>r</i> -(ME3Ox)-1:1 (3100)]	3F- <i>r</i> -ME3-U	4/3/1	4.0/2.1/1	73	9.1	24.3	2.7
MDI/BD(32)-P[(3FOx)- <i>b</i> -(ME3Ox)-3:2 (4200)]	3F- <i>b</i> -ME3-U	6/5/1	6.3/4.1/1	68	7.4	15.2	2.1
MDI/BD(31)-P(ME7Ox-3200)	ME7-U	4.5/3.5/1	4.6/2.8/1	69	6.5	10.0	1.6
MDI/BD(42)-P[(3FOx)- <i>r</i> -(ME7Ox)-1:1 (5800)]	3F- <i>r</i> -ME7-U	6.5/5.5/1	12/8.2/1	58	6.0	10.1	1.7
MDI/BD(34)-P[(3FOx)- <i>b</i> -(ME7Ox)-2:3 (5200)]	3F- <i>b</i> -ME7-U	7/6/1	8.6/5.4/1	66	6.3	12.3	2.0

^a Feed molar ratio was calculated based on the molecular weight of soft segment for targeted wt. % 65–70% in polyurethane.

^b Molar ratios of MDI/BD/soft block and soft block weight% were calculated from integration of ¹H-NMR spectra. Values correspond to subscripts x, y, and z in Scheme 1.

^c Molecular weights and polydispersities (M_w/M_n) were obtained by GPC in THF using universal calibration.

^d Mixed soft block polyurethane.

Table 2
Thermal properties and DCA contact angle data for 3F-co-MEn polyurethanes and modified base polyurethane.

Polyurethanes	MDSC (°C) ^a			Dynamic Contact Angles (°)									
	T_g^b ()	T_g^{hb} ^d	T_m	Neat					2 wt. %				
				Adv	Rec	Adv	Rec	Adv	Rec	Adv	Rec	Adv	Rec
Base-U	-70 (8)	102	156	93	49	92	49	92	49	-	-	-	-
3F-U	-40 (7)	111	186	110	70	109	71	109	72	106	69	107	67
ME3-U	-37 (37)	nd ^d	nt ^d	93	32	93	40	87	45	91	44	91	44
(3F + ME3)-U ^e	-43 (27/15)	nd	nd	102	48	96	48	96	48	108	52	108	52
3F- <i>h</i> -ME3-U	-37 (25)	108	207	104	39	105	44	101	50	99	46	98	45
3F- <i>h</i> -ME3-U	-38 (21)	109	180	106	56	101	57	99	57	101	53	100	52
ME7-U	-74 (-2)	nd	nt	f									
3F- <i>h</i> -ME7-U	-49 (18)	111	204/213	87	54	73	60	70	61	76	35	80	34
3F- <i>h</i> -ME7-U	-47 (18)	112	204	85	59	89	59	90	58	89	49	97	44

^aMDSC: modulation amplitude $\pm 0.5^\circ\text{C}$, modulation period 30 sec, and heating rate $3^\circ\text{C}/\text{min}$. All T_g 's were recorded at the midpoint of on-set and off-set heat flow.

^bSB = soft block; diol = polyoxetane diol, = $T_{g\text{sb}}-T_{g\text{diol}}$

^c T_g or lower temperature phase transition for hard block (hb).

^dNot detected = nd; Not tested = nt.

^eMixed soft block polyurethane

^fME7-U swelling and detachment from the substrate precluded study.

Table 3

X-ray photoelectron spectroscopy analysis for neat base polyurethane and 2 wt.% P[A]-U and 2 wt.% P[A-co-B]-U.

2 wt.% modified	Calc. atom% P[A] or P[AcoB] soft block				Calc. atom% P[A] or P[AcoB]-U				XPS atom% ^{a, b}				
	C	O	F		C	O	N	F	C	O	N	F ^c	Si ^c
Base_U ^d	80.0	20.0	0		78.6	18.3	3.2	0	74.8	19.5	1.6	(1.9)	(2.3)
3F-U	58.3	16.7	25.0		64.0	16.2	2.6	17.2	58.3	17.5	0.2	24.2	nd ^e
ME3U	70.6	29.4	0		73.2	23.3	3.5	0	71.4	21.3	1.6	(2.5)	(2.4)
3F + ME3	64.3	22.9	12.9		68.4	19.9	2.9	8.9	57.9	18.0	nd	24.0	nd
3F- <i>r</i> -ME3	65.5	24.1	10.3		69.0	21.0	2.7	7.3	62.4	21.8	1.3	13.8	(0.8)
3F- <i>p</i> -ME3	64.3	22.9	12.9		68.6	19.9	3.0	8.5	59.4	18.8	0.8	21.1	nd
3F- <i>r</i> -ME7	65.9	26.9	7.2		70.8	21.3	3.9	4.0	65.6	18.2	0.9	14.6	(0.7)
3F- <i>p</i> -ME7	64.9	25.6	9.4		69.2	21.5	3.2	6.0	58.9	18.7	1.0	21.2	nd

^aTake off angle 55°.

^bAtom percents are the average of two determinations.

^cF and Si contamination values in parenthesis.

^dNeat base polyurethane MDI-BD(36)-PTMO(2200).

^end: not detected.