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Strongly amphiphilic wetting behavior for polyurethanes with polyoxetane soft blocks having –CF₂H terminated side chains



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ABSTRACT

Two novel polyoxetanes with $-CF_2CF_2H$ (4F) or $-(CF_2)_3CF_2H$ (8F) terminated side chains were synthesized and characterized by ¹H NMR spectroscopy, DSC and GPC. 4F and 8F diols were incorporated in polyurethanes IPDI-BD(40)/4F-8.2 (U-4F-8.2) and IPDI-BD(40)/8F-5.8 (U-8F-5.8), where isophorone diisocyanate (IPDI) and 1,4-butane diol (BD) comprise the hard block (40 wt%) and 4F-8.2 or 8F-5.8 are soft blocks with M_n in kDa. Surface characteristics were evaluated using TM-AFM, XPS and dynamic contact angle (DCA) measurements. In contrast to U-4F-8.2, TM-AFM reveals an interesting phase separated surface morphology for U-8F-5.8 apparently driven by higher F side chain content. A model is proposed to account for contact angle measurements that show reversible, strongly amphiphilic wetting with $\theta_{adv} > 100^\circ$ and $\theta_{rec} < 40^\circ$. Resistance to surface phase separation and related studies suggest the $-CF_2CF_2H$ moiety is an important candidate for expanding the range of functional groups employed in surface modifiers.

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1. Introduction

Modification of surfaces with fluorous moieties has been widely studied to obtain both hydrophobicity and oleophobicity. Much is known about surfaces with terminal $-CF_3$ groups especially polyacrylates [2–8]. Semifluorinated moieties with eight ($-(CF_2)_7CF_3$, C8F) or more perfluoro-side chain carbons form enthalpically stabilized phases that prevent surface reorganization. Such systems are characterized by low critical surface tensions (ca. 8 mJ/m²) and low contact angle hysteresis ($\theta_{\Delta} = \theta_{adv} - \theta_{rec}$) [3,9–12]. The discovery that C8F and C10F moieties degrade to perfluoroctanoic acid (PFOA) [13,14], which is bioaccumulative, greatly attenuated commercial production [14,15]. This finding stimulated a search for alternatives, such as placing C4F and C6F groups at the end of long alkyl chains [16].

Our interest in $-CF_3$ terminated side chains has focused on copolyoxetane soft blocks. These studies led to novel surface properties including contraphilic wetting, where the dry surface is hydrophilic but the wetted surface is hydrophobic [17,18]. With two identical side chains, polyoxetanes are semicrystalline [19–24]. Poly[bis(trifluoroethoxy)oxetane] is interesting by virtue of cold crystallization that results in spontaneous formation of nanoscale

and microscale roughness and near-superhydrophobic wetting [25,26].

In continuing development of surface modifiers based on fluorous copolyoxetanes [27–30], we sought to expand the palette of side chains beyond those having $-CF_3$ termination so as to tailor further soft block functionality. This led to interest in replacing a – CF_3 terminal fluorine by $-CF_2H$. Sixty years ago, Ellison observed 5° lower contact angles for monolayers of acids having $-CF_2H$ end groups compared to $-CF_3$ analogs [31]. Replacement of terminal – CF_3 by $-CF_2H$ in side chains resulted in substantially increased surface tensions, emphasizing the importance of the terminal group in determining nanosurface (<1 nm) properties [31,32]. Lower contact angles and increased surface tensions were attributed to terminal $C-H\cdots X$ hydrogen bonding due to decreased electron density on the terminal hydrogen creating a partial positive charge.

For polystyrene-*b*-semifluorinated block copolymers, the presence of $-CF_2H$ terminated side chains resulted in 21° lower advancing contact angles (θ_{adv}) compared to $-CF_3$ terminated analogs [33]. Additional studies on liquid crystalline moieties also showed surface energy increases as a result of replacement of $-CF_3$ by $-CF_2H$ end groups [32,34].

Since characteristic hydrophobicity and oleophobicity are reduced, little attention has been paid to systems with $-CF_2H$ terminal groups. An exception is the work of Kunzler, where $-CF_2H$ terminated side chains increased the miscibility of methacrylate







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end-capped dimethyl siloxane intermediates with hydrophilic monomers. This permitted bulk radical polymerization with hydrophilic monomers, such as dimethylacrylamide and resulted in transparent, high water content hydrogels [35].

Extending a preliminary study [36], we report herein polyurethanes containing soft blocks derived from polyoxetane diols 4F and 8F (Fig. 1). Effects of the longer CF₂ sequence are seen clearly by TM-AFM surface morphological studies for a polyurethane with an 8F-based soft block compared to a 4F analog. Dynamic contact angle measurements (DCA, Wilhelmy plate) reveal new details for wetting behavior that contrast with previously investigated $-CF_2H$ systems [31–34]. This wetting behavior is discussed along with a model for high contact angle hysteresis. Other characterization studies expand knowledge of solid state (DSC) and surface science (XPS).

2. Experimental section

2.1. Materials

2,2,3,3-Tetrafluoropropan-1-ol and 2,2,3,3,4,4,5,5-octafluoro-1ol were generously provided by Daikin Industries, Yodogawa, Japan. 3-Bromomethyl-3-methyl oxetane (BrOx) was a gift from OMNOVA Solutions, Akron, OH. Isophorone diisocyanate (IPDI), tetrabutylammonium bromide (TBAB), boron trifluoride dietherate (BF₃·Et₂O), dibutyltin dilaurate catalyst (T-12) and trifluorotoluene (TFT, 99+%) were from Aldrich. Butane diol (BD), tetrahydrofuran (THF) and dimethylformamide (DMF) were obtained from Across Organics (99+%). BrOx was vacuum distilled at 85 °C/5 mmHg. IPDI, BD, fluorinated alcohols, catalysts and organic solvents were used as received.

2.2. Monomers

3-Methyl-3-(2.2.3.3.-tetrafluoropropoxymethyl)oxetane and 3-methyl-3-(2.2.3.3.4.4.5.5-octafluoropentyloxymethyl)-oxetane are designated 4F and 8F monomers (Fig. 1). Their preparation was carried out by nucleophilic substitution using phase transfer catalysis (TBAB) [37-39]. Scheme S1 illustrates the reaction of BrOx with fluorinated alcohols. As a specific example for 4F monomer, BrOx (41.25 g, 250 mmol), 4F alcohol (46.2 g, 350 mmol) and TBAB (5 g, 0.0125 mmol) were heated to 60 °C in 20 mL water. Aqueous KOH (15.8 g, 87%) in water (20 mL) was added drop wise over 1 h. The solution was heated to 75 °C with stirring for 72 h. 4F monomer was extracted with dichloromethane, the solution dried with MgSO₄, and the product freed of solvent with a rotovap. GC-MS showed the presence of a small amount of BrOx. Short path distillation gave >99% 4F monomer (b.p. 85 °C/3.3 mmHg). ¹H NMR (300 MHz, CDCl₃, δ: ppm): 6.09– 6.06, 5.91-5.88, 5.74-5.70 (-CF₂H, 1H, t), 4.48-4.34 (oxetane ring, -CH2-, 4H, d), 3.92-3.91, 3.87-3.87, 3.83-3.82 (-CH2CF2-, 2H, t), 3.63 (-CH₂O-, 2H, s), 1.30 (-CH₃, 3H, s). 8F monomer was prepared and purified in an analogous manner (b.p. 65 °C/ 0.8 mmHg).



Fig. 1. 4F (x = 1) and 8F (x = 3) monomers and polyoxetane diols.

2.3. Polyoxetane diols

4F and 8F polyols were prepared by cationic ring opening polymerization method described previously [22,37]. An example follows for the synthesis of 4F. A three necked round bottom flask was placed in a cooling bath and a nitrogen purge (45 min) CH_2Cl_2 (5–7 mL) was added. Butane diol (0.23 g. 2.54 mmol) and BF₃·Et₂O (0.73 g, 5.13 mmol) were injected sequentially via syringe. A refrigeration system (PolyScience Model 912) was used to cool the solution (-9 °C). 4F monomer (5.54 g, 25.7 mmol) in 7.02 g CH₂Cl₂ was added. After stirring overnight (13 h), the solution was warmed to ambient temperature and washed sequentially with aqueous 3% HCl and 3% NaCl. The CH₂Cl₂ solution containing 4F polyoxetane was added drop wise to MEOH: $H_2O(3:1, v:v)$ for precipitation. The fluorous diol layer was separated and placed in a vacuum oven for solvent evaporation (40 °C, 36 h). ¹H NMR (300 MHz, CDCl₃, δ : ppm): 6.09-6.06, 5.91-5.88, 5.74-5.70 (-CF₂H, 1H, t), 3.81, 3.75, 3.72 (-CH₂CF₂-, 2H, t), 3.42 (-CH₂O-, 2H, s), 3.22-3.14 (main chain -CH2-C-CH2-, 4H, d), 0.91 (-CH3, 3H, s).

A number of 4F polyoxetane diol preparations were carried out with monomer-catalyst ratios of 10:1, 20:1 and 100:1 (Table S1). 8F polyoxetane diols were prepared following the same procedure using only a 10:1 monomer–catalyst ratio (Table S1). 4F-8.2 and 8F-5.8 (designated by approximate M_n in kDa) were chosen for polyurethane synthesis.

2.4. Polyurethanes

Polyurethanes with 40 wt% hard block were made by the conventional soft block first procedure [1]. Designations are IPDI-BD(40)/4F-8.2 and IPDI-BD(40)/8F-5.8, where IPDI-BD hard block content is indicated in parenthesis followed by the soft block with the M_n in kDa. Shortened designations are U-4F-8.2 and U-8F-5.8, respectively. An example for U-4F-8.2 synthesis follows.

Polyol 4F-8.2 (3.6 g, 0.36 mmol) in 1.23 g THF was added to a three-necked round bottom flask containing IPDI (1.75 g, 7.58 mmol). Dibutyltin dilaurate catalyst (4 drops, 10 wt% in THF) was added and the solution was heated to 70 °C under nitrogen purge. The progress of the reaction was followed by FT-IR, i.e., the growing carbonyl peak at 1716 cm⁻¹. After 4 h, the carbonyl peak remained unchanged indicating completion of prepolymer formation. 1,4-Butane diol (0.65 g, 7.21 mmol) in 5.4 g THF was added drop wise followed by heating at 70 °C until complete disappearance of -NCO peak at 2267 cm⁻¹ (ca. 3 h). The mixture was cooled to room temperature and added drop wise to methanol/water (1:3) to affect polyurethane precipitation. Residual solvent was evaporated under vacuum at 60 °C for 48 h. Polyurethane U-8F-5.8 wad prepared similarly using trifluorotoluene (TFT) as solvent. IPDI-BD(40)-3F-3.4 designated U-3F-3.4 was reported previously [1].

2.5. Molecular weights

Fluorous diol molecular weights (M_n) were determined by reaction with trifluoroacetic anhydride (TFAA) for end group analysis. ¹H NMR spectra for 4F monomer, 4F-8.2 polyol and post-TFAA are shown in Fig. 2. GPC was also used for polyol molecular weight determinations (Table 1).

2.6. DSC

A TA-Q 1000 (TA instruments) temperature Modulated Differential Scanning Calorimetry (MDSC) was used for determination of thermal transitions at a heating rate of 3 °C/min. and ± 0.5 °C modulation at 60 s.



Fig. 2. ¹H NMR spectra and assignments: A, 4F monomer; B, polyoxetane 4F-8.2; C, 4F-8.2 polyol-TFAA.

Table 1	
Molecular weight data for 4F-8.2 and 8F-5.8 ¹ H NMR peak assignments for α β and γ are in Fig.	2

	-			-	-				-							
Sample	Peak	$-CF_2H$	α	β	α/β	λ2	λ1	DP ^a			M _n (kD	a) ^a		M_n^{b} (kDa)	$M_{\rm w}{}^{\rm b}({\rm kDa})$	PDI ^b
								$\alpha + \beta$	λ1	λ2	$\alpha + \beta$	λ2	λ1			
4F-8.2	Shift/ppm	6.1-5.7	4.28	4.38	-	1.03	0.85	-	-	-	-	_ 0 0	_ 7 7	4.8	8.5	1.8
8F-5.8	Shift/ppm	6.1–5.7	4.28	4.38	-	1.03	0.16	40 	-	-	- -	0.2 —	-	5.0	8.7	1.7
	Integral area	1.0	0.21	0.06	3.5	0.39	0.35	15	16	17	5.5	5.8	6.2			

^a DP: degree of polymerization by ¹H NMR end group analysis; The integral area of reference peak **d** in main chain for: 4F-8.2, 3.08; for 8F-5.8, 2.81. ^b GPC.

2.7. Coatings

For contact angle measurements, cover slips (Corning, $24 \times 40 \times 0.5$ mm) were dip coated from 10 wt% polyurethane solutions in THF and manipulated to give an even distribution during solvent evaporation. Slides were stored at room temperature for 4 h and then at 60 °C overnight under reduced pressure.

2.8. X-ray photoelectron spectroscopy (XPS)

Spectra were obtained using a Thermo Fisher Scientific ESCALAB 250 X-ray photoelectron spectrometer having monochromatized Al K α X-rays and low energy electron flood gun charge neutralization. X-ray spot size for these acquisitions (90° TOA) was on the order of 500 mm. Pressure in the analytical chamber during spectral acquisition was less than 2 \times 10⁻⁸ Torr; pass energy for survey spectra was 150 eV. The data were analyzed with the Thermo Avantage software (v4.40). Calibration of C_{1s} binding energies to correct for the energy shift caused by charging was done by assuming that the lowest energy peak (285.0 eV) was for aliphatic carbon moieties. For peak fitting, the program PeakFit, version 4.12, was used for C_{1s} spectra assuming 100% Gaussian peaks.

2.9. Atomic force microscopy (AFM)

Topological and morphological analyses were carried out using a Dimension-3100 (Digital Instruments, CA) atomic force microscope with a NanoScope V controller. Tapping mode imaging was performed in air using microfabricated silicon cantilevers (40 N/m, Veeco, Santa Barbara, CA). A tapping force corresponding to a setpoint ratio $r_{\rm sp}$ of 0.8 was used; $r_{\rm sp} = A_{\rm exp}/A_{\rm o}$, where $A_{\rm o}$ is free oscillation amplitude and $A_{\rm exp}$ is the experimental oscillation amplitude. Images were analyzed by using NanoScope v710r1 software.

2.10. Wetting behavior

Dynamic contact angles (DCA) were obtained using a Cahn Model 312 Analyzer (Cerritos, CA). The surface tension of the probe liquid (Nanopure water) was checked before each measurement and was typically 72.6 \pm 1 dyn/cm. Beakers used for DCA analysis were cleaned by soaking in an isopropanol/potassium hydroxide base bath for at least 24 h, rinsing with Nanopure water and treatment with a gas/oxygen flame.

DCA measurements were based on the Wilhelmy plate method [40]. A coated slide is attached to the electrobalance via a clip. The stage speed was 150 μ m/s and dwell time between advancing and receding test segments was 10 s. Resulting force versus distance curves (fdc's) were used to calculate advancing (θ_{adv}) and receding (θ_{rec}) contact angles. Five cycles (~3 min/cycle) in succession were obtained to study any change in wetting behavior on exposure to water. The surface tension of the test water was also determined

after DCA analysis to assess whether water contamination had occurred [41].

3. Results and discussion

3.1. Polyoxetane monomers and diols

4F and 8F monomers (Fig. 1) were prepared by nucleophilic substitution (Williamson synthesis) using bromomethyl(methyl) oxetane (Scheme S1) [42]. The ¹H NMR spectrum of 4F monomer with assignments is shown in Fig. 2A. The characteristic peaks for – CF₂H consist of a triplet of triplets centered at 6.08, 5.90, 5.72 ppm. This set of peaks was noted by Kunzler for –CF₂H terminated siloxane side chains [35]. The high field shift for the terminal proton reflects a strongly acidic nature. The ¹H NMR spectrum of 8F monomer with assignments is shown in Fig. S1A.

Ring opening polymerization (ROP) was carried out using $BF_3 \cdot Et_2O$ catalyst and BD as co-catalyst to give 4F polyoxetane diols as transparent, viscous liquids (Scheme S1) [43,44]. Information on monomer to catalyst ratios and resulting molecular weights is provided in Table S1. Monomer/catalyst ratios of 100/1 gave relatively high molecular weight 4F polyoxetanes ($M_n > 15$ kDa) while lower ratios resulted in $M_n < 10$ kDa. This catalyst/co-catalyst method followed Desai [45], Malik [43], Fujiwara [37] and Jutier [46]. Alternatively, Kawakami [47a] and more recently Moller [47b,48] used BF₃ alone for ROP. From the results reported below, it is apparent that the latter method is advantageous for control of end group chemistry.

A low molecular weight polyol was sought for polyurethanes. This influenced the choice of 4F-8.2 and 8F-5.8 polyoxetane diols for polyurethanes reported herein. The designations are based on the number of fluorines in the side chains (Fig. 1) and approximate number average molecular weights in kDa (Table 1). ¹H NMR spectra and peak assignments for 4F-8.2 polyoxetane are shown in Fig. 2B. The peaks for monomer ring methylene groups **e** and 3-methyl groups **d** shift to high field (**f**) in the 4F-8.2 polyoxetane.

8F monomer and 8F polyoxetanes were prepared in a similar manner. A 10/1 ratio of $BF_3 \cdot Et_2O/BD$ co-catalyst was used to obtain a relatively low molecular weight copolyoxetane suitable for a soft block (Table S1). The ¹H NMR spectra of 8F monomer and 8F-5.8 polyoxetane (selected for polyurethane synthesis) are shown with assignments in Figs. S2A and B, respectively.

End group analysis followed a previously reported procedure [37,49]. Fig. 2C shows structures for end group trifluoromethyl esters. One analysis provides M_n based on methylene peaks associated with oxetane (α) and butoxy (β) end groups (Fig. 2C, insert). The α : β integral ratio is 1.1 indicating the BD co-catalyst competes for end group sites.

A second end group analysis is based on γ^1 , the methyl end group peak upfield from the main chain methyl peak **d** for 4F-8.2 (Fig. 2B, γ^1). This peak shifts downfield (γ^2 , 0.85 ppm) from the main chain methyl peak **d** after TFAA addition (Fig. 2C). Comparison of integrals for ($\alpha + \beta$) and γ^2 peaks to main chain peaks gives number average molecular weights of 8.6 and 8.2 kDa, respectively (Table 1), while γ^1 gives 7.7 kDa.

Molecular weight determinations were also obtained by GPC for several 4F polyols (Table S1). Table 1 shows molecular weights by end group analysis and GPC for 4F-8.2 and 8F-5.8. Fair agreement is found between the two methods, although M_n is systematically lower for GPC measurements.

Thermal analysis by modulated DSC gave glass transition temperatures of -46 °C for 4F-8.2 and -56 °C for 8F-5.8 (Fig. 3). The 10 °C lower $T_{\rm g}$ for 8F-5.8 was surprising considering the longer fluorous side chain. No thermal transitions were observed at higher temperatures confirming the amorphous state above $T_{\rm g}$ of these viscous liquid diols.

3.2. Polyurethanes

IPDI/BD(40)-(4F-8.2), where 40 is the IPDI/BD wt% and 4F M_n is in kDa, was prepared in THF/DMF while trifluorotoluene was used for IPDI/BD(40)-(8F-5.8). The two polyurethanes are designated U-4F-8.2 and U-8F-5.8 (Fig. 4). GPC for U-4F-8.2 gave M_w = 36.1 kDa and M_n = 21.2 (PDI = 1.7). U-8F-5.8 was not be characterized by GPC due to poor solubility in THF.

Thermograms for the two polyurethanes are shown in Fig. 4. The T_g for the soft block shifts upward by 21 °C in U-4F-8.2 while the shift in T_g for P-8F-5.8 diol to U-8F-5.8 is 10 °C. Based on the difference in T_g 's, the Fox equation (Eq. (1)) may be used to estimate the percent soft block in the pure soft block domain (Table 2).

$$(T_{\rm g})^{-1} = w_{\rm SOFT} (T_{\rm g \ SOFT})^{-1} + w_{\rm HARD} (T_{\rm g \ HARD})^{-1}$$
 (1)

Calculations were based on the T_g of pure hard block as 85 °C [1]. Based on % soft block in the pure soft block domain obtained from the Fox equation there is more phase mixing for U-4F-8.2 than for U-8F-5.8. Less phase mixing for U-8F-5.8 is attributed to minimal intermolecular interactions and low solubility parameter for the – $(CF_2)_4$ – sequence counteracting terminal –CF₂H hydrogen bonding. Phase mixing is also greater for U-4F-8.2 than for U-3F-3.4, which has trifluoroethoxymethyl side chains [1]. Phase mixing is ascribed to a gain in enthalpy due to terminal –CF₂H hydrogen bonding and the smaller influence of the short –(CF₂)₂– group.

Because of low molecular symmetry, hard block endotherms for IPDI polyurethanes are not always observed or have low enthalpies [50,51]. Endotherms for hard block melting are not seen at <100 °C for U-4F-8.2 or U-8F-5.8 (Fig. 3).

3.3. Surface morphology

Tapping Mode Atomic Force Microscopy, TM-AFM, revealed a complex surface morphology at the microscale and nanoscale. Fig. 5 shows phase images for U-4F-8.2 and U-8F-5.8. Columns A and B



Fig. 3. DSC for polyols and polyurethanes: A, 4F-8.2; B, 8F-5.8; C, U-4F-8.2; D, U-8F-5.8.



Fig. 4. Polyurethanes U-4F-8.2 (x = 1) and U-8F-5.8 (x = 3), highlighting $-CH_2-A$, B, and C assigned to XPS binding energies in Table S2.

Table 2

Molecular weight, thermal transitions, and calculation of phase mixing in U-3F-3.4, U-4F-8.2 and U-8F-5.8.

Polyurethane	Mw ^a	Soft block	Polyol	Soft block in
	(kDa)	T _g (°C)	T _g (°C)	pure soft block (%)
U-3F-3.4 ^b	37.5	-37	-51	84
U-4F-8.2	36.1	-25	-46	77
U-8F-5.8 ^c	nd	-46	-56	89

^a GPC.

^b Previously published [1].

^c Not determined due to insolubility in THF.

contain images for U-8F-5.8 at two setpoint ratios. Columns C and D have images for U-4F-8.2 at the same two setpoint ratios. Rows 1, 2, and 3 present images for increasing areas.

A 1 × 1 µm phase image for U-8F-5.8 at relatively hard tapping (r_{sp} 0.7, Fig. 5-B1) shows nano-domains ranging in size from the lower limit of TM-AFM (~20 nm) to ~80 nm. By the conventional interpretation of phase imaging, the lighter color (yellow in the web version) domains are assigned to hard block aggregates [52,53]. A phase image for U-8F-5.8 at somewhat lighter tapping (r_{sp} 8.0, Fig. 5-A1) barely resolves near surface phase separation suggesting a steep morphological gradient at the nanosurface.

The 10 \times 10 μ m phase image for U-8F-5.8 (Fig. 5-B2, r_{sp} 0.7) reveals interesting fringed circular microdomains surrounded by a field of nanodomains. The corresponding image at r_{sp} 0.8, Fig. 5-A2, shows that the microdomains are comprised of clusters of nanodomains as only the near surface nano-components are imaged. Imaging at 50 μ m (Fig. 5-B3) shows that the microdomains are fairly uniform in size (\sim 3 μ m) and evenly distributed. Some groups of these domains form chain-like rows. The corresponding images



Fig. 5. TM-AFM phase images: Left (columns A, B), U-8F-5.8; Right (columns C, D), U-4F-8.2.

at r_{sp} 0.8, Fig. 5-A3, again reflect a gradient for these microscale domains with fainter features.

Surface phase separation for U-8F-5.8 is reminiscent of microscale phase separation in a polyurethane having a *block*-copolyoxetane soft block with trifluoroethoxymethyl (3F) and PEG-like side chains [30]. A model for synergistic 3F/urethane hard block selfaggregation to form Janus-like nanostructures was proposed by Zhang [30]. An analogous version of the model for U-8F-5.8 is shown in Fig. 6. Synergistic nanoscale demixing driven by fluorous 8F-5.8 soft block and hard block phase separation is proposed to account for the nanoscale features that aggregate to form micron scale domains (Fig. 5).

Fig. 5 shows AFM images for U-4F-8.2 at the same acquisition conditions used for U-8F-5.8. In contrast to the latter, images for U-4F-8.2 are largely devoid of morphological features. At hard tapping ($r_{\rm sp}$ 0.7) dispersed dot-like 20–50 nm features signal phase separated domains. These features remain isolated without aggregation seen for U-8F-5.8. A 500 × 500 nm image for U-4F-8.2 was taken on a different sample (Fig. S2). Nanoscale phase separation was found similar to that for U-8F-5.8 (Fig. 5-B1). At the nanoscale, the phase separated features (20–50 nm) are quite similar to polyurethanes with fluorous [27,54] and conventional polyether [55,56] soft blocks.

The absence of aggregated microscale features for U-4F-8.2 reinforces the conclusion from DSC that demixing is driven more strongly for U-8F-5.8 by the higher fluorous content of the 8F-side chain. Furthermore, the surface features for U-8F-5.8 result in a higher root mean square roughness. For comparable 50 \times 50 µm scans, Rq is 30.4 nm for U-8F-5.8 compared to 8.7 nm for U-4F-8.2.

3.4. X-ray photoelectron spectroscopy

Atomic percentages of carbon, fluorine, nitrogen and oxygen were analyzed by XPS at a 90° TOA (Table 3). Previous studies have shown that the soft blocks in polyurethanes tend to be concentrated in the nanosurface, that is, the outermost 1–2 nm [57–60]. This trend is also observed for polyoxetane soft blocks containing side chains terminated by $-CF_3$, viz., U-3F-3.4 [27]. For U-3F-3.4 at a takeoff angle of 55°, 18.1 at% F was found compared to the bulk value of 15.4 at% and to the 3F soft block 25.1 at%. The moderate F at % nanosurface enrichment is consistent with phase mixing noted above (Table 2).

At a 90° TOA, the 19.4 at% F for U-4F-8.2 may be compared with the bulk value (16.7) and that calculated for the soft block (28.6). As



Fig. 6. Model for surface nanoscale phase separation. Phase image Fig. 5-B1.

Tab	le 3	

Atomic percentages of elements in	U-4F-8.2 and U-8F-5.8.
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Atom	U-4F-8.2			U-8F-5.8			
	Calc. U (at%)	Calc. soft block (at%)	Obs. (at%)	Calc. U (at%)	Calc. soft block (at%)	Obs. (at%)	
F _{1s}	16.7	28.6	19.40	23.1	40	24.30	
0 _{1s}	15.8	14.3	15.96	13.4	10	15.31	
C _{1s}	63.4	57.1	59.34	59.6	50	57.4	
N _{1s}	3.8	-	2.71	3.9		2.02	

for U-3F-3.4, a moderate nanosurface enrichment of F at% is found. The nitrogen at% (2.71) indicates the presence of near surface hard block but supports soft block surface concentration, as the bulk N at % (3.8) is attenuated by ~30%.

Unexpectedly, at% F for U-8F-5.8 is only slightly higher than the bulk (Table 3). On the other hand, the N at% is 2.02 at% while 3.9 at% is calculated for the bulk. Surface concentration of the soft block is indicated, but a complex interplay of soft block molecular weight difference and nanosurface structure and morphology precludes a simple interpretation.

Fig. 7 shows high resolution C_{1s} XPS spectra for U-4F-8.2 and U-8F-5.8. The U-8F-5.8 hydrocarbon C–C–C peak at 285 eV [61,62] is used as a reference for binding energies. The C_{1s} binding energies assignments given in Table S2 are guided by literature values for carbon in similar chemical environments [32,63–66].

The peak at 293.1 eV is unique for U-8F-5.8 and is assigned to the $-CF_2CF_2-$ unit in the side chain. Binding energies for urethane carbonyl -C(O)-N-, $-CH_2-CF_2-CF_2-$ and $-CF_2H$ are superposed in a broad peak at 290.6 eV. Previously, it was shown that -C-C-O- binding energies depend on the nature of the polyether [61]. Assignments for -C-C-O-A, B, and C environments (Fig. 2) are made based on this previous study and studies on fluorinated polyethers [66].

Curve fitting was used to facilitate binding energy assignments (Experimental section). The insert in Fig. 7 shows a six peak fit for U-8F-5.8. Peak areas are provided in Table S2. Phase mixing and superposition of binding energies precludes an accurate analysis of contributions.

3.5. Dynamic contact angles (Wilhelmy plate)

Contact angles for U-4F-8.2 and U-8F-5.8 were obtained for comparison with previously studied longer, rigid rod analogs having $-CF_3$ and CF_2H termini [32–34] and with U-3F-3.4 [27]. As



Fig. 7. C_{1s} XPS spectra for U-4F-8.2 and U-8F-5.8. Assignments are shown for U-8F-5.8.

described previously, dynamic contact angles θ_{adv} and θ_{rec} are obtained from force distance curves (fdc's) via Eq. (2) [41].

$$F = m/g = P\gamma\cos\theta \tag{2}$$

Where *F* is the force derived from respective mass (*m*) changes on immersion and emersion, *g* is the gravitational constant, γ is the liquid surface tension, and θ is the contact angle. Extrapolating an fdc to the point of maximum (or minimum) initial mass upon immersion eliminates the need for a buoyancy correction to F.

An important step after dynamic contact angle (DCA) analysis comprises measuring post-test water surface tension. Diffusion and surface migration of water immiscible contaminants such as cyclics or surfactants changes water surface tension and hence contact angles. This simple test provides important information that differentiates whether changes for contact angles after repeated immersion are due to surface reorganization or water contamination [41].

Unlike polysiloxane coatings reported earlier [41] minimal contamination was observed for polyurethanes with 3F-3.4, 4F-8.2, and 8F-5.8 soft blocks. Thus, except for slight water contamination by U-3F-3.4, contact angles are used with confidence to assess relative wetting behavior and extent of surface reorganization during immersion.

Fig. 8 shows the first cycle fdc's for U-4F-8.2, U-8F-5.8, and U-3F-3.4. Contact angles are summarized in Table 4 for first and fifth cycles and in Table S3 for all five cycles. The total immersion time after five cycles is ~ 15 min. For U-3F-3.4 θ_{adv} is 102° (Fig. 8, curve C) which is in the >100° range expected for a fluorous polymer at the air–liquid– solid interface [27]. A 4° decrease in θ_{adv} was observed after several fdc cycles (Table 4). Part of this decrease (~1-2°) is due to slight water contamination that was not entirely eliminated despite several reprecipitations. The receding contact angle is 46° thereby giving a contact angle hysteresis of 52° ($\theta_{\Delta} = \theta_{adv} - \theta_{rec}$). Sources that account for high contact angle hysteresis are considered below.

3.5.1. Roughness

Effects of uniform rugosity on contact angles are well understood [10,67,68]. Increasing roughness generally increases θ_{adv} . Receding contact angles (θ_{rec}) determine contact angle hysteresis and are important in determining both hydrophobic and lyophobic character. TM-AFM 50 × 50 µm images for U-4F-8.2 in Fig. 5 show Rq is 8.7 nm. This low level of nanoscale roughness is unlikely to influence contact angles.

3.5.2. Static heterogeneity

Johnson and Dettre showed that for smooth, rigid surfaces, hydrophilic and hydrophobic area fractions changed contact angles at



Fig. 8. Dynamic contact angle force distance curves: A. U-4F-8.2 (− − −); B, U-8F-5.8 (• • •); C, U-3F-3.4 (−−).

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Polyurethane	Cycle	$\theta_{\rm adv}$	$\theta_{\rm rec}$
U-3F-3.4	1	102	45
	5	98	46
U-4F-8.2	1	108	40
	5	103	40
U-8F-5.8	1	108	31
	5	106	30

low respective coverages [69,70]. For example, on a hydrophobic surface, a low area fraction of homogeneously distributed polar moieties "pins" water at the three phase contact line and disproportionately decreases $\theta_{\rm rec}$.

3.5.3. Dynamic heterogeneity

Unlike rigid, heterogeneous surfaces, "soft surfaces" comprised of flexible chains can display high contact angle hysteresis due to rapid surface reorganization during immersion. Enthalpic interactions of polar groups with water drive interfacial chain reorganization at the nanosurface [71–74]. At longer immersion times contact angles can change as polar groups slowly diffuse to the surface [75]. Both slow and rapid processes are driven by minimization of interfacial free energy.

XPS showed that the 3F soft block is surface concentrated, while DSC points to a low soft block T_g and a significant degree of hard block/soft block phase mixing. Contact angle hysteresis for U-3F-3.4 reflects "dynamic heterogeneity" due to the presence of a nanosurface soft block that rapidly undergoes enthalpically driven reorganization. Water hydrogen bonding to the $-CH_2-$ group adjacent to $-CF_3$ was proposed to account for this observation [18,63]. Water H-bonding to ether oxygen (side chain, and main chain) as well as to near surface hard block amide oxygen is also likely.

In contrast to prior studies for $-(CF_2)_7CF_2H$ systems where θ_{adv} *decreases* 10–20° compared to $-CF_3$ analogs [32–34], U-4F-8.2 has a 6° *higher* initial θ_{adv} (108°) and a 6° lower θ_{rec} (40°) than U-3F-3.4 (Fig. 8, curve A, Table 4). U-4F-8.2 has an initial contact angle hysteresis (θ_{Δ}) of 68°. After five cycles, θ_{Δ} was 63° due mainly to a decrease in θ_{adv} . This decrease is ascribed to water adsorption driven by hydrogen bonding. After drying, initial force distance curves are obtained.

U-8F-5.8 also has a 6° *higher* initial θ_{adv} of 108° with force distance curve B closely paralleling that for U-4F-8.2. The receding contact angle is uniquely low (θ_{rec} 31°) compared to U-3F-3.4 and U-4F-8.2 (Fig. 8, Table 4), which results in the highest θ_{Δ} of 76°. Over five immersion/emersion cycles, contact angle hysteresis for U-8F-5.8 is more stable than U-4F-8.2, perhaps due to better phase separation.

For both U-4F-8.2 and U-8F-5.8, dynamic heterogeneity facilitated by a low T_g and driven by enthalpically favored hydrogen bonding accounts for high contact angle hysteresis. In contrast, for block copolymers with $-(CF_2)_7CF_2H$ and similar side chain termini θ_{Δ} of 7–19° were reported [32,33]. Microscale roughness may contribute to the uniquely low θ_{rec} for U-8F-5.8 (31°). Further studies including angle resolved XPS or ATR-IR spectroscopy may clarify the origin of the high θ_{Δ} .

Models for wetting behavior of surfaces having A, longer – $(CF_2)_nCF_3$ terminated side chains and B, analogous – $(CF_2)_nCF_2H$ side chains are shown in Fig. 9. Fig. 9A is applicable to long side chain fluorous methacrylates investigated by Katano [2] and Takahara [3] and poly(styrene-*b*-semifluorinated isoprene) block copolymers reported by Ober [33]. Surfaces with – $(CF_2)_7CF_3$ (and longer) terminated side chains are characterized by high contact angles and

low θ_{Δ} (Fig. 9A). Such systems are enthalpically stabilized by the formation of ordered phases driven by side chain crystallization.

Surfaces having $-(CF_2)_7CF_2H$ and similar side chain termini have lower θ_{adv} but retain low θ_{Δ} in the 7–19° range [32,33]. The lower θ_{adv} was ascribed to the dipolar nature of the $-CF_2H$ end group that enhances hydrogen bonding depicted in Fig. 9B-i [33]. The formation of ordered phases stabilizes the $-CF_2H$ surface against reorganization on short time scales, but over the course of weeks contact angles decrease [33].

A model for surfaces with a single –CF₃ terminal group as in U-3F-3.4 is shown in Fig. 9C. These surfaces have fairly high θ_{adv} (~106°), though not as high as well ordered surfaces having, longer –(CF₂)₇CF₃ terminated side chains (Fig. 9A). The amorphous nature of the soft blocks, which are too short to form ordered side chain phases results in low θ_{rec} and high contact angle hysteresis ($\theta_{\Delta} = 52^{\circ}$).

Fig. 9D shows a model for the wetting behavior of U-4F-8.2. Upon immersion, hydrogen bonding of $-CF_2CF_2H$ to the side chain ether oxygen (depicted) and ether and other polar moieties (e.g., carbonyl) is proposed (Fig. 9D-i). The latter is consistent with thermal analysis that suggests only moderate soft block-hard block phase separation.

A model paralleling that for U-4F-8.2 (Fig. 9D) is suggested for U-8F-5.8. Due to the longer $-(CF_2)_4-$ unit in the side chain, this model might imply that U-8F-5.8 would have a higher θ_{adv} but this is not observed. Neither does this nanoscale model explain the low

 θ_{adv} . Thus, we return to the conclusion suggested above that a combination of phase separated morphology and microscale roughness accounts for low θ_{rec} . With a longer $-CF_2CF_2CF_2-CF_2$ unit in the side chain, it seems counter intuitive that a wet state for U-8F-5.8 similar to that depicted by Fig. 9D-i would result in a lower receding contact angle. Apparently, surface microscale surface roughness increases dynamic heterogeneity and amplifies θ_{rec} . Further work is required to elucidate this interesting result.

4. Conclusion

In continuing development of surface modifiers based on fluorous copolyoxetanes [27–30], we sought to expand the palette of side chains to include copolyoxetanes with $-CF_2H$ terminal groups. Extending a preliminary study [36], U-4F-8.2 and U-8F-5.8 polyurethanes containing soft blocks with $-CF_2H$ terminated side chains are reported (Fig. 3). Effects of the longer CF₂ sequence for U-8F-5.8 are seen by TM-AFM that reveals "blooming" of chrysanthemum-shaped phase separated microfeatures. In contrast, U-4F-8.2 surface structure is minimal at the micron scale, while typical polyurethane hard block/soft block domains are seen at the nanoscale.

Low T_{g} 's for the 4F and 8F soft blocks mean that side chains are not constrained by ordered domains previously described for – (CF₂)_nCF₂H systems (Fig. 9B) [32,33]. Dynamic contact angle measurements show reversible amphiphilic wetting with in $\theta_{adv} > 100^{\circ}$



Fig. 9. Wetting models for dry (d) and immersed (i) surfaces for side chains terminated with: A rigid –CF₃; B, rigid –CF₂H; C, flexible –CF₃ and D, flexible –CF₂CF₂H. H-bonding interactions are depicted; terminal –CF₂H hydrogen bonding is highlighted and circled; For D-d, 4F-ether H-bonding is designated with an arrow while shaded semicircles highlight –CF₂CF₂– surface concentration driven by –CF₂H hydrogen bonding to side chain oxygen.

and $\theta_{rec} < 40^{\circ}$. A model for the strongly amphiphilic nature of U-4F-8.2 and U-8F-5.8 is proposed (Fig. 9D). In the dry state, $-(CF_2)_n$ moieties are projected to the surface by virtue of enthalpically favored inward-directed H-bonding of $-CF_2H$ with resultant high θ_{adv} . In contrast, in the wet state, strong hydrogen bonding of - CF_2H to water "submerges" hydrophobic $-(CF_2)_n$ moieties. Strongly amphiphilic character is shown by high contact angle hysteresis ($>60^{\circ}$). Importantly, amphiphilic behavior is reversible.

The AFM morphological study discussed above, which revealed minimal microscale phase separation for U-4F-8.2 (Fig. 5), inspired replacement of -CF₃ by -CF₂CF₂H to generate copolyoxetane soft blocks with 4F and quaternary side chains, as described in a preliminary report [76]. Phase separation that resulted in sequestration of quaternary charge for the $-CF_3$ analog was avoided but surface concentrated guaternary function was retained. Thus, the -CF₂CF₂H moiety is an important candidate for expanding the range of functional groups employed in surface modifiers. This adds a new layer of interest to Kunzler's finding that -CF₂CF₂H side chains are useful in compatibilizing methacrylate/silicones [35].

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.polymer.2014.03.011.

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