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# Determination of Low Critical Surface Tensions of Novel Fluorinated Poly(amide urethane) Block Copolymers. 1. Fluorinated Side Chains

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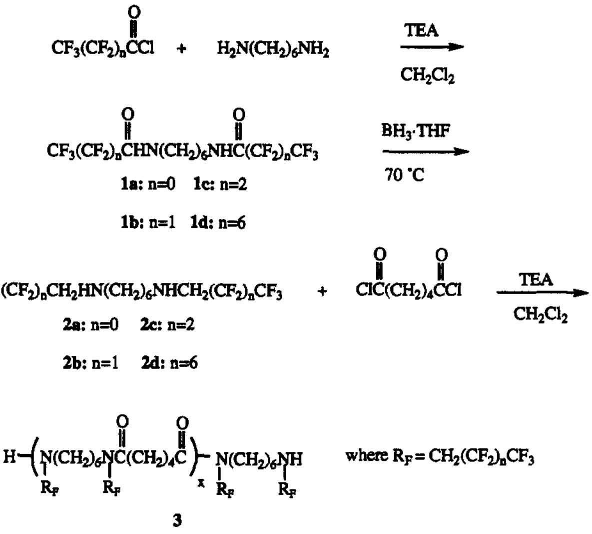
ABSTRACT: Low critical surface energies of novel fluorinated poly(amide urethane) block copolymers were measured. The copolymers contain a "hard block" polyurethane consisting of a diisocyanate and a diol and a "soft block" non-self-associating polyamide consisting of oligomers synthesized from fluorinated secondary diamines and adipoyl chloride. The various diisocyanates studied were methylenebis(phenylene isocyanate) (MDI), isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), and methylenebis(cyclohexane isocyanate) ($H_{12}$MDI). Butanediol and hexanediol were the diols used. The different diamines studied were *N,N'*-diisopropyl-1,6-diaminohexane, *N,N'*-bis(2,2,2-trifluoroethyl)-1,6−diaminohexane-1,6-diaminohexane, *N,N'*-bis(3,3,3,2,2-pentafluoropropyl)-1,6-diaminohexane, *N,N'*-bis(1*H*,1*H*-heptafluorobutyl)-1,6-diaminohexane, and *N,N'*-bis(1*H*,1*H*-perfluorooctyl)-1,6-diaminohexane. The critical surface tensions of the poly(amide urethane) block copolymers were determined with Zisman plots using contact angle goniometry, and water contact angles were obtained by both goniometry and the Wilhelmy method. Intrinsic viscosities and thermal transitions were determined. The large hysteresis seen in the contact angle measurements and the kinetic instability of water drop shapes on polymer films indicate that although the air−polymer interface shows a fluorinated surface, exposure to water can effect a rearrangement allowing exposure of a more polar entity.

## Introduction

Fluorinated polymers have attracted considerable interest due to their low surface energies,[1−3] biocompatibility,[4−6] lubricity, thermal and oxidative stability, and nonsticking behavior.[7] Most studies have been carried out on poly(tetrafluoroethylene), poly(fluoroalkyl acrylates/methacrylates), fluorinated polyethers,[8,9] and polyurethanes[10−15] where the fluorinated components are diisocyanates, chain extenders, and soft block macrodiols. Segmented polyurethane-based elastomers with exceptional hydrolytic and thermooxidative stability have been prepared in our laboratory.[16,17] The non-self-associating soft blocks are tertiary polyamides and polyurethanes derived from bis-secondary diamines. By combining the unique properties of polyfluorocarbons with the ease of preparing fluorinated analogs of these diamines, low surface energy poly(amide urethane) block copolymers have been synthesized.

In this paper, we report the synthesis and characterization of these novel copolymers. The hard block segments consist of a diisocyanate and a diol; diisocyanates studied include methylenebis(phenylene isocyanate) (MDI), isophorone diisocyanate (IPDI), toluene diisocyanate (TDI), and methylenebis(cyclohexane isocyanate) ($H_{12}$MDI). The soft blocks consist of polyamide oligomers synthesized from the fluorinated secondary diamines and diacid chlorides (Scheme 1). Block polyurethanes were synthesized from the oligomers and a diol and diisocyanate (Scheme 2). These copolymers were spin-cast or dip-coated into films and their surface properties determined by contact angle measurements with water and a series of hydrocarbons using goniometry and the Wilhelmy technique.[18]

**Scheme 1. Typical Polyamide Synthesis**



| | n | Total # fluorines per side-chain | Code name[a] |
|---|---|---|---|
| 3a | 0 | 3 | 3F-0F |
| 3b | 1 | 5 | 5F-0F |
| 3c | 2 | 7 | 7F-0F |
| 3d | 6 | 15 | 15F-0F |
| 3e | *b* | 0 | 0F-0F |

a: The first symbol refers to the number of fluorines in the side chains; the second, 0F, indicates there are no fluorines in the main chain.

*b*: Synthesized from N,N-diisopropyl-1,6-hexanediamine and adipoyl chloride.[16]

## Experimental Section

**Materials.** Trifluoroethanoyl chloride, pentafluoropropionyl chloride, heptafluorobutyryl chloride, perfluorooctanoyl chloride (PCR), $H_{12}$MDI, TDI, MDI, IPDI (Miles), dibutyltin dilaurate [T-12], and borane/THF complex (Aldrich) were used as received. Adipoyl chloride (Aldrich) was distilled under vacuum. Triethylamine (Fisher) was dried over $CaSO_4$, distilled, and stored over 4 Å molecular sieves. THF (Fisher) was distilled from sodium benzophenone ketyl under $N_2$. NMP (Aldrich) was fractionally distilled under vacuum. Dichlo-

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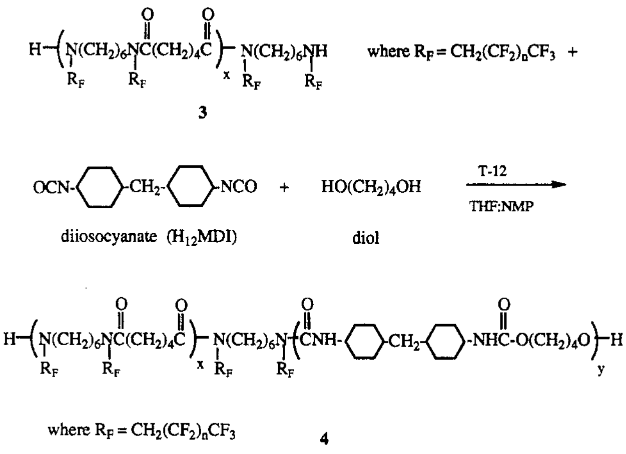
**Scheme 2. Typical Poly(amide urethane) Synthesis**



| | n | Total # fluorines per side chain | Code name |
|---|---|---|---|
| **4a** | 0 | 3 | 3F-0F-IB where I=IPDI, B=Butanediol |
| **4b** | 1 | 5 | 5F-0F-IB where I=IPDI, B=Butanediol |
| **4c** | 2 | 7 | 7F-0F-TB where T=TDI, B=Butanediol |
| **4d** | 6 | 15 | 15F-0F-HB where H=$H_{12}$MDI, B=Butanediol |
| **4e** | *a* | 0 | 0F-0F-MH where M=MDI, H=Hexanediol |

*a*: Synthesized with N,N-diisopropyl-1,6-hexanediamine and adipoyl chloride.[16]

romethane (Mallinckrodt) was distilled from $CaH_2$ under $N_2$. *N,N'*-Diisopropyl-1,6-hexanediamine was distilled.[4] The hydrocarbon solvents used in critical surface tension measurements [*n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, *n*-hexadecane (Aldrich)] were purified by three extractions with concentrated $H_2SO_4$ followed by six extractions with water, drying over $Na_2SO_4$, and then distilling through a packed (glass helices) column.

**Synthesis of *N,N'*-Bis(pentadecafluorooctanoyl)-1,6-diaminohexane (1d) (General Procedure).** 1,6-Diaminohexane (2.687 g, 0.023 mol) and 6.50 mL (0.047 mol) triethylamine were dissolved in 20 mL THF at 0 °C. To the stirring solution was added 20.0 g (0.046 mol) of perfluorooctanoyl chloride dropwise. Stirring was continued for 48 hours at room temperature. The precipitate was removed by filtration, washed with water, and recrystallized with hot THF to give **1d** [yield 11.56 g (55%); mp 126.0–127.0 °C; $^1$H NMR (TFA-*d*) $\delta$ (m, 7.53, NH), (t, 3.56, $CH_2$), (m, 1.74, $CH_2$), (m, 1.50, $CH_2$) ppm; IR (KBr) 3320 (NH), 1680 (C=O), 1202 ($CF_2$) cm$^{-1}$; MS *m/z* theoretical 908 g/mol, observed 908 g/mol; and calcd for [$CF_3(CF_2)_6CONH(CH_2)_6NH$] 511.0879 g/mol, observed 511.0888 g/mol].

**1a:** Mp 130.0–135.0 °C; IR (KBr) 3300 (NH), 1650 (C=O), 1170 ($CF_2$); MS *m/z* theoretical 308.0971 g/mol, observed 308.0951 g/mol.

**1b:** Mp 96.0–102.0 °C; $^1$H NMR (DMSO-$d_6$) $\delta$ (s, 9.5, NH), (q, 3.15, $CH_2$), (q, 3.09, $CH_2$), (t, 1.46, $CH_2$), (m, 1.20, $CH_2$) ppm; IR (KBr) 3310 (NH), 1700 (C=O), 1171 ($CF_2$) cm$^{-1}$; MS *m/z* theoretical 408.0885 g/mol, observed 408.0885 g/mol.

**1c:** Mp 185.0–186.0 °C; IR (KBr) 3337 (NH), 1655 (C=O), 1171 ($CF_2$) cm$^{-1}$; MS *m/z* theoretical 508 g/mol, observed 508 g/mol; and calcd for [$NHCOCF_2CF_2CF_3$] 212 g/mol, observed 212 g/mol.

**Synthesis of *N,N'*-Bis(1*H*,1*H*-perfluorooctyl)-1,6-diaminohexane (2d) (General Procedure).** The $BH_3$·THF complex (300 mL) was added through a cannula to 11.45 g (0.013 mol) pentadecafluorinated diamide **1d** at 0 °C; the molar ratio was 3 mol borane/1 mol diamide. After the addition was complete, the reaction was heated to 70 °C. The reaction was heated under reflux for 72 h until the complete disappearance of the IR carbonyl peak was noted. The reaction was quenched with 36.4 mL (0.889 mol) of MeOH, heated under reflux for 1 h, and then cooled to room temperature. The solution was placed in an ice bath and then saturated with HCl gas to form the diamine hydrochloride salt. The dried solid salt was suction filtered, suspended in 15% NaOH solution, and extracted three times with dichloromethane. The extract was dried over anhydrous $MgSO_4$. The solvent was removed *in vacuo* and the crude product was distilled at reduced pressure to give **2d** [yield 6.52 g (56.9%); bp 56 °C (2 Torr); $^1$H NMR ($CDCl_3$) $\delta$ (s, 1.16 NH), (m, 1.35, $CH_2$), (m, 1.50, $CH_2$), (t, 2.74, $CH_2$), (t, 3.26, $CH_2$) ppm; $^{19}$F NMR ($CFCl_3$) $\delta$ (t, −81.40, $CF_3$), (m, −118 to −126, $CF_2$) ppm; IR (NaCl) 3370 (NH), 2932, 2859 ($CH_2$), 1169($CF_2$) cm$^{-1}$; MS *m/z* theoretical 880 g/mol, observed 878 g/mol; and calcd for [$CF_3(CF_2)_6CH_2NHCH_2$] 412.0183 g/mol, observed 412.0202 g/mol. Anal. Calcd for $C_{22}H_{14}F_{30}N_2$ C, 30.02; H, 2.06; F, 64.74; N, 3.18; found C, 30.24; H, 2.13; F, 64.23; N, 3.26.

**2a:** Bp 90 °C (0.5 Torr); $^1$H NMR ($CDCl_3$) $\delta$ (s, 1.1, NH), (m, 1.3, $CH_2$), (t, 1.4, $CH_2$), (t, 2.7, $CH_2$), (q, 3.2, $CH_2$) ppm; IR (KBr) 3350 (NH), 2940, 2850 ($CH_2$), 1170 ($CF_2$) cm$^{-1}$; MS *m/z* theoretical 280 g/mol, observed 280 g/mol; and calcd for [$CF_3$-$CH_2NH(CH_2)_6NHCHCF_2$] 260.1312 g/mol, observed 260.1295 g/mol.

**2b:** Bp 90 °C (4.5 Torr); $^1$H NMR ($CDCl_3$) $\delta$ (t, 3.21, $CH_2$), (m, 2.15, $CH_2$), (m, 1.38, $CH_2$), (m, 1.28, $CH_2$), (m, 1.06 NH) ppm; $^{13}$C NMR ($CDCl_3$) $\delta$ (s, 38, $CH_2$), (s, 42, $CH_2$), (s, 61, $CH_2$), (t, 62, $CH_2$), (m, 136–142, $CF_2CF_3$) ppm; IR (KBr) 3300 (NH), 2930, 2820 ($CH_2$), 1201 ($CF_2$) cm$^{-1}$; MS *m/z* theoretical 380 g/mol, observed 380 g/mol; and calcd for [$CF_3CF_2CH_2NH(CH_2)_6$-$NHCH_2$] 261.1384 g/mol, observed 261.1384 g/mol.

**2c:** Bp 84 °C (0.5 Torr); $^1$H NMR ($CDCl_3$) $\delta$ (s, 1.1, NH), (t, 1.3, $CH_2$), (t, 1.4, $CH_2$), (t, 2.7 $CH_2$), (q, 3.2, $CH_2$) ppm; $^{13}$C NMR ($CDCl_3$) $\delta$ (s, 22, $CH_2$), (s, 24, $CH_2$), (t, 43, $CH_2$), (s, 44, $CH_2$), (m, 100–120, $CF_2CF_2CF_3$) ppm; IR (KBr) 3300 (NH), 2940, 2830 ($CH_2$), 1200 ($CF_2$) cm$^{-1}$; MS *m/z* theoretical 480 g/mol, observed 481 g/mol; and calcd for [$CF_3(CF_2)_2CH_2NH(CH_2)_5C$] 280.0936 g/mol, observed 280.0937 g/mol.

**Synthesis of Oligomer. Bis(pentadecafluorooctyl)-diamine + Adipoyl Chloride (3d) (General procedure).** Adipoyl chloride (0.80 mL, 0.005 mol) was dissolved in 10.0 mL dichloromethane and slowly added dropwise (2–3 h) with a syringe pump to 1.00 g (0.0014 mol) of **2d** and 0.34 mL (0.002 mol) of TEA in 25 mL of dichloromethane. The TEA salts were removed by filtration and the dichloromethane was evaporated at reduced pressure. The oligomer residue was a brown oil which was dissolved in ethyl acetate and extracted three times each with water, 1 M HCl, 1 M NaOH, and water again. The extract was dried over $MgSO_4$. The solvent was removed *in vacuo* to give the light brown viscous oligomer **3d** [yield 0.02992 g (14.9%); IR (NaCl) 2938, 2864 ($CH_2$), 1736 (C=O), 1205 ($CF_2$) cm$^{-1}$; molecular weight determined by GPC $\bar{M}_n$ = 1548 g/mol, $\bar{M}_w/\bar{M}_n$ = 1.41 and VPO $\bar{M}_n$ = 2678 g/mol; $T_g$ = 129.7 °C].

**Synthesis of Poly(amide urethane) (4d). Bis(pentadecafluorooctyl)diamine–Adipoyl Polyamide (3d) + $H_{12}$-MDI + Butanediol (General Procedure).** $H_{12}$MDI (0.19 g, 0.0007 mol) was dissolved in 6.0 mL of NMP/THF (1:1) and added to 0.24 g of oligomer **3d** dissolved in the same. The reaction stirred at room temperature for 1 h. Butanediol (0.06 g, 0.0007 mol) and 2 drops of T-12 were added, and the reaction was stirred for 119 h. The polymer solution was precipitated in 950 mL of water. The white solid was collected to give the block poly(amide urethane) **4d** [yield 0.32 g (65.0%); IR (KBr) 3345 (NH), 2926, 2853 ($CH_2$), 1703, 1694, 1667 (C=O), 1242 ($CF_2$) cm$^{-1}$; intrinsic viscosity = 0.23 dL/g; $T_g$ = 131.0 °C].

**Instrumentation.** Infrared data were obtained with the use of an IBM FT/IR-32 spectrophotometer. $^1$H, $^{13}$C, and $^{19}$F NMR data were obtained with a Bruker AC-300 or an AF-300 spectrophotometer. High resolution mass spectra were obtained on a CH-5 double focusing Varian MaT mass spectrometer or on a VG-70-G mass spectrometer. Melting points were determined with a Thomas Hoover Unimelt Capillary melting point apparatus. Thermal transitions were monitored with a Mettler FP90 system in conjunction with a Mettler FP84HT hot stage, rate = 5 °C/min. Elemental analysis results were obtained from Oneida Research Services, Inc.

**Molecular Weight Determination.** Gel permeation chromatography was carried out using three Waters Ultrastyragel

**Table 1. Measured Surface Tensions (dyn/cm) of Various Wetting Liquids at 23.0 °C**

| liquid no. | liquid | surface tension |
|---|---|---|
| 1 | *n*-octane | 21.7 |
| 2 | *n*-decane | 23.8 |
| 3 | *n*-dodecane | 26.3 |
| 4 | *n*-tetradecane | 26.8 |
| 5 | *n*-hexadecane | 27.4 |
| 6 | 1-methylnaphthalene | 40.1 |
| 7 | 1-bromonaphthalene | 45.1 |
| 8 | methylene iodide | 50.5 |
| 9 | formamide | 59.6 |
| 10 | glycerol | 63.0 |
| 11 | water | 71.4 |

**Table 2. Molecular Weights and Glass Transition Temperatures of the Polyamides**

| | $\bar{M}_n$ (g/mol) | | |
|---|---|---|---|
| oligomer | GPC | VPO | $T_g$ (°C) |
| 0F−0F | 2000 | 1268 | <20 |
| 3F−0F | 1000 | 4425 | 40.0 |
| 5F−0F | 5200 | 2115 | 59.4 |
| 7F−0F | 4000 | 3890 | 97.4 |
| 15F−0F | 1548 | 2678 | 129.7 |

columns (100, $10^3$, and $10^5$ Å) or two narrow bore Phenogel columns (linear pore size, Phenomenex) in series maintained at 35 °C, equipped with a Waters 590 Programmable HPLC pump, Waters 410 differential refractometer maintained at 40 °C, and Waters 745 Data Module. Molecular weights are relative to monodisperse polystyrene standards (Waters). The solvent used was THF. Vapor pressure osmometry data was obtained with use of a Gonotec vapor pressure osmometer: OSMOMAT 070-SA in THF or DMF. Viscometry results were obtained with a Cannon Ubbelohde viscometer, no. 1 C304 or no. 1 H206 in a constant temperature Neslab water bath (25 °C). The solvent was DMF.

**Surface Tension Measurements.** Surface tensions of the liquids used to probe the surface energies of the fluorinated polymers were determined using a CSC DuNoüy interfacial tensiometer. They are listed in Table 1. The values are an average of 12 measurements.

**Polymer Film Analysis.** Contact angles were measured with a Ramé-Hart contact angle goniometer model 100, and also with a Cahn Dynamic Contact Angle Analyzer DCA-312. Polymer films were prepared by spin-casting 4−8 drops of concentrated solutions in 90% DMAc/10% PM acetate on a Headway Research, Inc. EC101D photoresist spinner at a spin rate of 4000 rpm and annealing in an Abderhalden pistol for a minimum of 48 h at several degrees above $T_g$. Stationary angles were measured on 3 μL of wetting solvent. Advancing angles were measured by adding 1 μL to the stationary drop. Receding angles were measured by removing 2 μL from the drop. Samples for Wilhelmy measurements were dip-coated onto slides and annealed above the measured $T_g$'s in a vacuum oven. The slides were immersed at a speed of 110.18 μm/s into purified water at 22 °C. All films were examined under a light microscope (1000× magnification) and were discarded if they showed any surface roughness or heterogeneity.

## Results and Discussion

A series of poly(amide urethanes) were prepared in which the non-self-associating tertiary polyamide blocks contained fluorinated side chains. The fluorinated amines found in the various polyamide blocks differ in the length of the appended 1*H*,1*H*-perfluoroalkyl group. The oligomer molecular weights were determined by VPO and GPC vs polystyrene standards (Table 2). From the molecular weight of the oligomers, the amount of diisocyanate and diol were adjusted so as to give a 50% soft block content; small amounts of diol or diisocyanate were added to complete the polymerization reaction as demanded by analysis of the infrared spectrum. Various diisocyanates were studied with the goal that one would give a free film that could be peeled or soaked from a glass substrate; this has not been realized. Intrinsic viscosities, glass transition temperatures, and final % compositions by weight are given in Table 3.

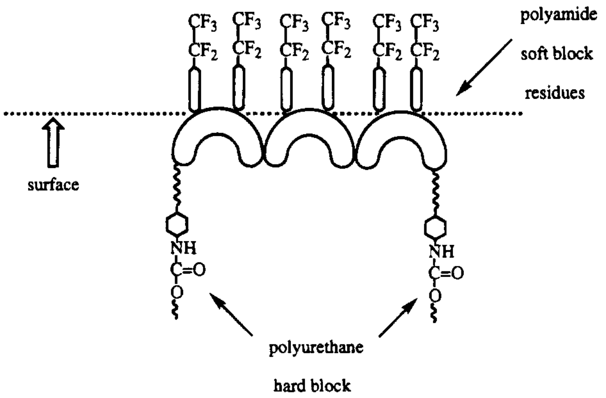


**Figure 1.** Schematic diagram of the poly(amide urethane) surface.

**Table 3. Intrinsic Viscosities, Glass Transition Temperatures, and % Composition of Poly(amide urethanes)**

| polymer | [η] (dL/g) | $T_g$ (°C) | % soft block/% hard block |
|---|---|---|---|
| 0F−0F−MH | 0.21 | 121.7 | 50/50 |
| 3F−0F−1B | 0.40 | 142.3 | 45/55 |
| 5F−0F−IB | 0.18 | 140.3 | 43/57 |
| 7F−0F−TB | 0.27 | 133.5 | 40/60 |
| 15F−0F−HB | 0.23 | 131.0 | 49/51 |

**Table 4. Contact Angles and Critical Surface Tensions of Poly(amide urethanes)**

| | contact angle (deg) | | | |
|---|---|---|---|---|
| polymer | $H_2O$ (goniometry) [advancing] | $H_2O$ (Wilhelmy) [advancing/ receding] | hexadecane (goniometry) [advancing] | critical surface tension (dyn/cm) |
| 0F−0F−MH | 68.0 | 83.8/42.2 | <10 | 48.1 |
| 3F−0F−IB | 70.0 | 87.6/46.3 | 14.8 | 32.2 |
| 5F−0F−IB | 90.0 | 102.2/53.8 | 36.3 | 24.6 |
| 7F−0F−TB | 91.0 | 100.6/44.5 | 42.6 | 20.0 |
| 15F−0F−HB | 86.8 | 116.9/37.2 | 64.5 | 14.1 |

Just as the polyether soft segments in the block poly(ether urethanes) coat the air interface,[19] we deduced that polyamide blocks would line the surface as well with the fluorinated side chains acting as the pile of a carpet (Figure 1). If so, this would be manifest in high contact angles with water and low critical surface tensions. Goniometry and Wilhelmy techniques were applied to obtain the requisite contact angles (Table 4). Zisman plots[1−3] of the cosine of advancing contact angles (goniometer) vs surface tensions of the solvents in Table 1 (Figure 2) show significant scatter and may reflect partial solubility of the films in some of the solvents as well as reflecting the fact that contact angle is a function of solvent type.[1] It is standard to determine critical surface tensions of low energy surfaces from the contact angles with a series of *n*-alkanes (Figure 3). Our results using the alkanes listed in Table 1 are given in Table 4. The nature of the diisocyanate does not appear to significantly affect the contact angle; similar results obtained for 0F−0F−HB (67°), 5F−0F−HB (86°), and 7F−0F−HB (90°)[20] to those of the corresponding materials in Table 4. The low critical surface energies and high water contact angles of the more highly fluorinated block poly(amide urethanes) demonstrate surfaces that

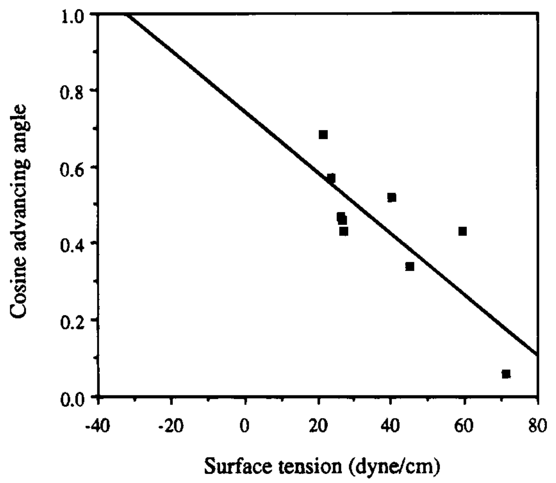


**Figure 2.** Zisman plot of poly(amide urethane) 15F–0F–HB with liquid numbers 1–7, 9, and 11 in Table 1.

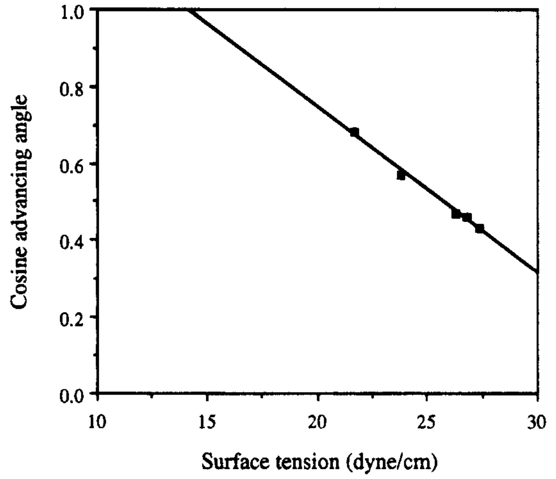


**Figure 3.** Zisman plot of poly(amide urethane) 15F–0F–HB with hydrocarbon liquid numbers 1–5 in Table 1. The critical surface tension is the intercept at $y = 1$, where $\theta = 0^\circ$.

are significantly nonpolar, reflecting an overlay of the fluorinated side chains. To give some perspective, poly(tetrafluoroethylene) has a critical surface tension (CST) of 18.5 dyn/cm;[3] poly(1*H*,1*H*-perfluorooctyl acrylate) has a CST of 10.4 dyn/cm.[21] A monomolecular film of perfluorododecanoic acid on platinum has a CST of 5.6 dyn/cm.[22] The water contact angle determined on the Wilhelmy apparatus increases as the fluorine content increases and is particularly large with the pentadecafluorooctyl side chains. Also noteworthy, the hexadecane contact angle of these latter materials (Table 4) is significantly greater than the 46° reported for poly(tetrafluoroethylene)[1] but less than the 78° on the perfluorododecanoic acid monolayer. A tightly packed monolayer made from 1*H*,1*H*,2*H*,2*H*-perfluorooctanethiol on gold has an advancing contact angle of 71°.[23] A remarkably high hexadecane contact angle of 77° has been reported for a polyethylene tipped at both ends with perfluorodecyl groups.[24] Relative to poly(tetrafluoroethylene), the lower critical surface tensions and higher hexadecane contact angles of many fluorinated surfaces reflects the concentration of $CF_3$ groups.[22] Our polymer with the pentadecafluorooctyl side chains must have a limiting surface featuring a reasonably close packing of $CF_3$ residues, in spite of a low bulk density of such residues.

Our polymers show a large hysteresis in the measurements with striking differences between the advancing and receding angles in the Wilhelmy experiments in water. This is also reflected in the differences between the goniometer and Wilhelmy measurements of advancing angles. It is observed that when a water droplet is placed onto the films, there is an initial beading with a high contact angle followed by a rapid (seconds) spreading to some lower constant reading. Indeed this is most likely an equilibrium contact angle. As we have striven to minimize the effects of surface roughness. We believe this reflects a rearrangement of the side chains allowing some penetration by the water to the more polar polyamide backbone. This may be exacerbated by the many intervening atoms in the main chain between fluorinated side-chain moieties. Wynne and Ho[25] have conducted experiments whereby a siloxane-*b*-urethane segmented copolymer is exposed to water over an extended period of time with advancing and receding contact angles monitored regularly (Wilhelmy). We have carried out similar experiments for 30 days (goniometer) with 15F–0F–HB and find that there is a drop in the advancing angle within 2 days to the 70–80° range and then a constant value of approximately 70° for the remaining time. The receding angle begins at 60° but remains between 45–50° from days 2 to 30. We conclude that any structural changes upon exposure to water occur rapidly leading to a stable morphology.

In general, the polyamide segments have high glass transition temperatures, well above room temperature. Although the surface exposed to water may be partially plasticized we do not believe the chains would have mobility to allow for exposure of the polyurethane segments. Only local motions would be sufficient to expose the amide carbonyl groups. Preliminary XPS measurements indicate excellent segregation of the fluorine to the surface.[26] The hysteresis appears to be less when the backbone has some fluorine content and is the subject of the next paper.

## Conclusions

Poly(amide urethanes) with tertiary polyamide soft blocks containing fluorinated side chains can phase segregate giving a surface coating of exposed fluorocarbons. This was demonstrated by the decrease in critical surface tension and increases in water contact angles with increasing fluorine content. From the high hysteresis demonstrated by the differences in advancing and receding contact angles with water and the kinetic instability of a water droplet shape when first applied to a film surface, it is concluded that the chains may rearrange allowing water to penetrate to the more polar polyamide backbone. Continuing studies include polyamide blocks with increasing fluorocarbon length and materials with siloxane side chains. Future studies will determine the utility of these polymers in marine fouling prevention and biocompatibility potential.

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