Determination of Low Critical Surface Tensions of Novel Fluorinated Poly(amide urethane) Block Copolymers. 2. Fluorinated Soft-Block Backbone and Side Chains

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Received May 23, 1994; Revised Manuscript Received January 3, 1995®

ABSTRACT: Low critical surface tensions (CST's) of novel copolymers containing a "hard-block" polyurethane and a fluorinated "soft-block" polyamide are reported. The hard segment consists of methylenebis(cyclohexyl isocyanate) (H_{12}MDI) and butanediol. The soft segment contains a fluorinated diacid chloride and a fluorinated diamine. The different diamines studied were *N,N'*-diisopropyl-1,6-diaminohexane, *N,N'*-bis(2,2,3,3,3-pentafluoropropyl)-1,6-diaminohexane, and *N,N'*-bis(1*H*,1*H*-perfluorooctyl)-1,6-diaminohexane. The various diacid chlorides studied were hexafluoroglutaryl chloride and octafluoroadipoyl chloride. The soft-block oligomers were synthesized from different combinations of these diamines and diacid chlorides. Films of the segmented copolymers were examined by contact angle measurements with water, and CST's were determined by Zisman plots. The polymers had relatively high water contact angles but underwent a rapid surface alteration exposing more polar residues. The CST's were low, particularly that of the polymer with pentadecafluorooctyl side chains, which was among the lowest measured for polymers. This latter polymer also retained high contact angles after 2 weeks of exposure to water. Initial studies of biofilm formation by marine bacteria are reported.

Polymers with perfluoroalkyl side chains have been studied because of their attractive surface properties including low surface energies,[1–4] nonstick behavior,[5] and biocompatibility.[6–9] We are preparing poly(amide urethanes) with fluorinated side-chain moieties to combine the favorable coating properties of polyurethanes with the potential for blood compatibility, nonstick behavior, and as a barrier to marine fouling. Such fouling on ships causes performance deterioration and increases fuel consumption and maintenance costs. Current formulations for antifouling coatings are based on the slow leaching of metals, a strategy that is not compatible with current environmental concerns and has been severely restricted by the U.S. Environmental Protection Agency.[10] In our previous paper,[11] we described the synthesis of novel segmented poly(amide urethanes) containing traditional hard blocks and nonself-associating soft-block oligomers prepared from *N,N'*-fluoroalkyl-disubstituted, secondary diamines and adipoyl chloride. These polyamides contain fluoroalkyl substituents as side chain moieties. The block poly(amide urethanes) were spin-cast or dip-coated in films which demonstrated high water advancing contact angles by the Wilhelmy[12] technique and low CST's as measured by contact angles of a series of alkanes[3] using a goniometer. These results demonstrate an organized fluorinated surface with exposed CF_3 groups. The Wilhelmy method also demonstrated large hysteresis between the advancing and receding angles; goniometry on water droplets showed an initial large contact angle which rapidly falls to lower equilibrium values. We proposed that the fluorinated side chains rearrange to expose a more polar entity from the soft-block main chain.

In this paper, we report the determination of low surface tensions of similar poly(amide urethanes) where the soft-block oligomers are prepared from fluorinated diamines as before but with perfluorinated diacid chlorides. This places perfluoromethylene groups in the main chain (Scheme I) as well as perfluoroalkyl groups in the side chains. Specifically, we have chosen to compare similar polymers with either pentafluoropropyl or pentadecafluorooctyl side chains and with main-chain perfluoroadipoyl or perfluoroglutaryl components. It is proposed that the main-chain fluorocarbons will give polymer coatings giving greater equilibrium contact angles with water and smaller CST's. Block poly(amide urea urethanes) were synthesized from the oligomers, butanediol, and 4,4'-dicyclohexylmethane diisocyanate (H_{12}MDI) (Scheme 2). These copolymers were spin-cast into films or dip-coated onto microscope slides. Contact angles and CST's were determined to characterize the interfacial properties of the polymer films.

Experimental Section

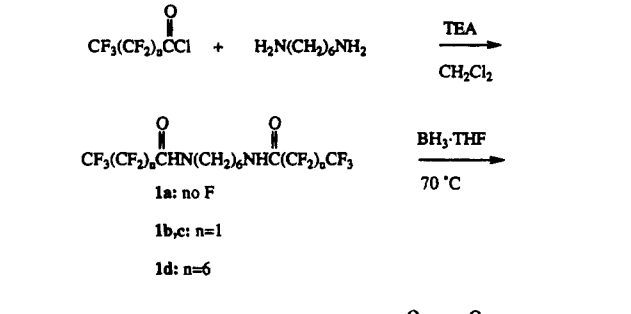
Materials. Hexafluoroglutaryl chloride, pentafluoropropionyl chloride (PCR), H_{12}MDI (Miles), dibutyltin dilaurate (T-12), propionyl chloride, oxalyl chloride, and borane/THF complex (Aldrich) were used as received. Octafluoroadipic acid (PCR) was recrystallized from acetone. Triethylamine (Fisher) 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 and adipoyl chloride (Aldrich) were fractionally distilled under vacuum. Dichloromethane (Mallinckrodt) was distilled from CaH_2 under N_2. The hydrocarbon solvents (*n*-octane, *n*-decane, *n*-dodecane, *n*-tetradecane, and *n*-hexadecane (Aldrich)) were purified by three extractions with concentrated H_2SO_4 and six extractions with water, dried over Na_2SO_4, and then vacuum distilled with a packed (glass helices) column. All other wetting solvents were purified by distillation.

Synthesis of *N,N'*-Bis(pentafluoropropanoyl)-1,6-diaminohexane (1b,c) (General Procedure). 1,6-Diaminohexane (31.866 g, 0.274 mol) and 76.4 mL (0.755 mol) of triethylamine were dissolved in 1 L of THF at 0 °C. To the stirring solution was added 100 g (0.548 mol) of pentafluoropropionyl chloride dropwise. Stirring continued for 2.5 h at room temperature. The precipitate was removed by filtration, washed with water, and recrystallized with hot THF to give **1b** [yield 85.0 g (76%); mp 96.0–102.0 °C; ^{1}H NMR (DMSO-d_5) δ (s, 9.5 NH), (q, 3.15, CH_2), (q, 3.09, CH_2), (t, 1.46, CH_2), (m, 1.20, CH_2); IR (KBr) 3320 (NH), 1701 (C=O), 1171 (CF_2) cm^{-1}; MS *m/z* theoretical 408.0885 g/mol, observed 408.0885 g/mol].

® Abstract published in *Advance ACS Abstracts,* March 1, 1995.

0024-9297/95/2228-2081$09.00/0

Scheme 1. Typical Polyamide Synthesis

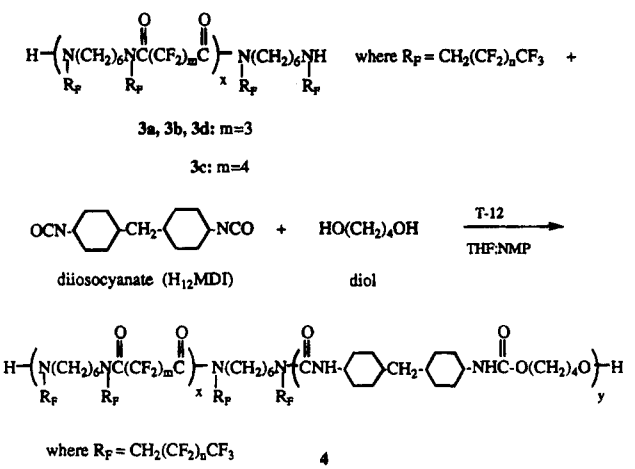


3

	n	Total # Fluorines per side chain	Code name
3a	*a*	0	0F-6F
3b	1	5	5F-6F
3c	1	5	5F-8F
3d	6	15	15F-6F

a: Synthesized with non-fluorinated diamine **2a** and hexafluoroglutaryl chloride.

Scheme 2. Typical Poly(amide urethane) Synthesis



4

	n	Total # Fluorines per side chain	Code name
4a	*a*	0	0F-6F-HB where H=H_{12}MDI, B=Butanediol
4b	1	5	5F-6F-HB
4c	1	5	5F-8F-HB
4d	6	15	15F-6F-HB

a: Synthesized with non fluorinated diamine **2a** and hexafluoroglutaryl chloride.

1a: mp 134.5–136.0 °C; ^{1}H NMR ($CDCl_3$) δ (m, 5.61, NH), (q, 3.26, CH_2), (m, 2.22, CH_2), (m, 1.50, CH_2), (m, 1.35, CH_2), (t, 1.15, CH_3); IR (KBr) 3308 (NH), 1638 (C=O) cm^{-1}; MS *m/z* theoretical 228.184 g/mol, observed 228.185 g/mol.

1d: mp 126.0–127.0 °C; ^{1}H NMR (TFA-*d*) δ (m, 7.53, NH), (t, 3.56, CH_2), (m, 1.74, CH_2), (m, 1.50, CH_2); IR (KBr) 3320 (NH), 1680 (C=O), 1202 (CF_2) cm^{-1}; MS *m/z* theoretical 908 g/mol, observed 908 g/mol; calcd for [$CF_3(CF_2)_6CONH(CH_2)_6$-NH] 511.0879 g/mol, observed 511.0888 g/mol.

Synthesis of *N,N'*-Bis(1*H*,1*H*-pentafluoropropyl)-1,6-diaminohexane (2b,c) (General Procedure). The BH_3·THF complex (500 mL) was added through a canula to 30.0 g (0.074 mol) of pentafluorinated diamide **1b** at 0 °C; the molar ratio was 3 mol of borane: 1 mol of diamide. After the addition was complete, 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 60.7 mL (1.50 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 off, 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 **1b** [yield 21.0 g (70%); bp 90 °C (4.5 Torr); ^{1}H NMR ($CDCl_3$) δ (t, 3.21, CH_2), (m, 2.15, CH_2), (m, 1.38, CH_2), (m, 1.28, CH_2), (m, 1.06, NH); ^{19}F NMR ($CFCl_3$) δ (t, −115.0, CF_3), (m, −122.3, CF_2); IR (NaCl) 3330 (NH), 2930, 2820 (CH_2), 1201 (CF_2) cm^{-1}; MS *m/z* theoretical 380 g/mol, observed 380 g/mol, calcd for [$CF_3CF_2CH_2NH(CH_2)_6$-$NHCH_2$] 261.1384 g/mol, observed 261.1384 g/mol].

2a: bp 109 °C (3 Torr); ^{1}H NMR ($CDCl_3$) δ (m, 2.55, CH_2), (m, 1.47, CH_2), (m, 1.33, CH_2), (m, 0.91, CH_3); IR (NaCl) 3237 (NH), 2923, 2870, 2806 (CH_2) cm^{-1}; MS *m/z* theoretical 200.370 g/mol, observed 200.224 g/mol.

2d: bp 56 °C (2 Torr); ^{1}H NMR ($CDCl_3$) δ (s, 1.16, NH), (m, 1.35, CH_2), (m, 1.50, CH_2), (t, 2.74, CH_2), (t, 3.26, CH_2); ^{19}F NMR ($CFCl_3$) δ (t, −81.40, CF_3), (m, −118 to −126, CF_2); IR (NaCl) 3370 (NH) cm^{-1}; MS *m/z* theoretical 880 g/mol, observed 878 g/mol, 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.

Synthesis of Oligomer. Bis(pentafluoropropyl)diamine + Hexafluoroglutaryl Chloride (3b) (General Procedure). Hexafluoroglutaryl chloride (6.20 g, 0.022 mol) was slowly added dropwise (2–3 h) with a syringe pump to 10.0 g (0.0263 mol) of **2b** and 7.0 mL (0.050 mol) of TEA in 50 mL of dichloromethane at 0 °C. The reaction mixture was stirred at room temperature for 23 h. The TEA salts were removed by filtration, and the dichloromethane was evaporated at reduced pressure. The oligomer residue was a thick, viscous 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 anhydrous $MgSO_4$. The solvent was removed *in vacuo* to give the oligomer **3b** [yield 11.03 g (68.1%); IR (NaCl) 2950, 2840 (CH_2), 1696 (C=O), 1200 (CF_2) cm^{-1}; $\bar{M}_n$(GPC) = 5337 g/mol, PDI = 1.53, $\bar{M}_n$(VPO) = 4140 g/mol; intrinsic viscosity = 0.087 dL/g; T_g = 119.4 °C].

Synthesis of Poly(amide urethane) (4b). Bis(pentafluoropropyl)diamine–Hexafluoroglutaryl Polyamide (3b) + H_{12}MDI + Butanediol (General Procedure). H_{12}-MDI (1.57 g, 0.006 mol) was dissolved in 5.0 mL of NMP:THF (1:1) and added to 2.00 g of oligomer **3b** dissolved in 10.0 mL of the same. The reaction mixture was stirred at room temperature for 2.2 h. Butanediol (0.49 g, 0.011 mol) and 2 drops of T-12 were added, and the reaction mixture was stirred for 19.75 h. More butanediol (0.37 g, 0.004 mol) was added, and the reaction mixture was stirred for 71 h. The polymer solution was precipitated in water. The white solid was collected to give the block poly(amide urethane) **4b** [yield 3.46 g (77.8%); IR (KBr) 3333 (NH), 2940, 2850 (CH_2), 1700 (C=O), 1226 (CF_2) cm^{-1}; intrinsic viscosity = 0.29 dL/g; T_g = 118.6 °C].

Synthesis of Octafluoroadipoyl Chloride. Oxalyl chloride (1.80 mL, 0.021 mol) was added to 1.358 g (0.0047 mol) of octafluoroadipic acid under nitrogen at 0 °C. The reaction mixture was stirred for 72 h at room temperature and was gravity filtered to give octafluoroadipoyl chloride [yield 0.599 g (39.2%); ^{19}F NMR ($CFCl_3$) δ (m, −113.4, CF_2), (m, −121.1, CF_2); IR (NaCl) 1801 (C=O), 1208 (CF_2) cm^{-1}; MS *m/z* theoretical 326.9540 g/mol, observed 235 g/mol [$(CF_2)_3CF_2Cl^+$];

Table 1. Molecular Weights, Intrinsic Viscosities, and Glass Transition Temperatures of the Polyamides

oligomer	GPC $\bar{M}_n$	VPO $\bar{M}_n$	$[\eta]$ (dL/g)	DSC T_g (°C)
0F–6F	10653	2065	0.101	142.5
5F–6F	5337	4140	0.087	119.4
5F–8F	3155	3823	0.043	174.0
15F–6F	1273	5249	0.022	187.5

calcd for $[ClCO(CF_2)_4^+]$ 262.9509 g/mol, observed 262.9543 g/mol].

Instrumentation. Infrared data were obtained with an IBM FT/IR-32 spectrophotometer. ^1H, ^{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 columns (100, 10^3, 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, a Waters 410 differential refractometer maintained at 40 °C, and a Waters 745 Data Module. Molecular weights are relative to monodisperse polystyrene standards (Waters). The solvent used was THF. Vapor pressure osmometry data were obtained with a Gonotec OSMOMAT 070-SA vapor pressure osmometer 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 or THF.

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 of the previous paper of this series.[11] The reported 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 DCA-312 dynamic contact angle analyzer. 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. The average of 10 measurements is reported. Samples for Wilhelmy measurements were dip-coated onto glass slides and annealed 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. During the 30 day water exposure test the immersed slides were periodically removed from water, excess water was shaken off, and the film was air-dried for 5 min before contact angles were measured by goniometry.

Results and Discussion

A series of poly(amide urethanes) were prepared in which the non-self-associating tertiary polyamide blocks contained fluorinated side chains as well as perfluoromethylenes in the main chain of the soft segments. The fluorinated side chains are 1*H*,1*H*-perfluoropropyl (5F) and 1*H*,1*H*-perfluorooctyl (15F); the diacid residues of the soft block come from perfluoroglutaryl chloride (6F) or perfluorodipoyl chloride (8F). The oligomers were characterized by GPC, VPO, intrinsic viscosity measurements, and DSC (Table 1). They were then incorporated into poly(urethane/urea) hard blocks (Scheme 2), and the copolymers were characterized by intrinsic viscosity and DSC measurements (Table 2). The T_g's of the fluorinated backbone polymers are significantly higher than those determined for the hydrogen-containing analogs and generally followed the T_g of the corresponding polyamide oligomer. The inordinately low intrinsic viscosities of the 15F–6F oligomer and its corresponding copolymer are due, most likely, to the large weight fraction of matter in the side chains giving these the solution properties of dense branched polymers. Their hydrodynamic equivalent sphere would be small, showing low viscosities[13] and low retention volumes in GPC.

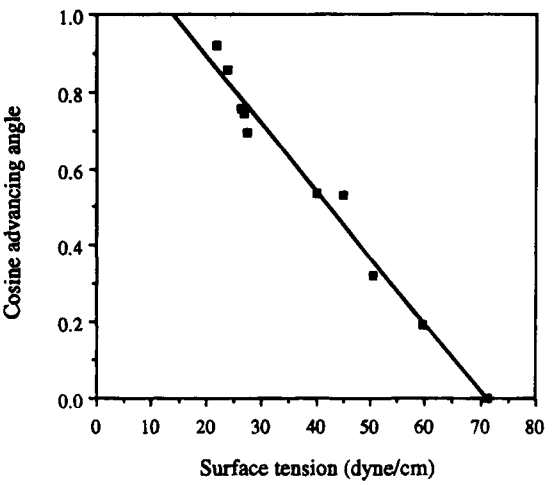


Figure 1. Zisman plot of poly(amide urethane) 5F–6F–HB with liquids 1–7, 9, and 11 in Table 1 in ref 11.

Table 2. Intrinsic Viscosities, Glass Transition Temperatures, and Percent Composition of Poly(amide urethanes)

polymer	$[\eta]$ (dL/g)	T_g (°C)	% soft block/ % hard block
0F–6F–HB	0.25	166.6	44/56
5F–6F–HB	0.29	118.6	45/55
5F–8F–HB	0.30	165.7	30/70
15F–6F–HB	0.19	182.8	37/63

We previously determined that similar polymers lacking the main-chain fluorocarbons show high initial contact angles with water, indicating a highly fluorinated interface which rearranges so as to give equilibrium contact angles of smaller magnitude. Similarly, there is a large hysteresis between the advancing and receding contact angles in water measured by the Wilhelmy method, which we attributed to this exposure of a more polar entity to the water. A Zisman plot is shown in Figure 1 for a variety of wetting liquids[11] on the polymer 5F–6F–HB. Critical surface tension determinations based on contact angles with a series of *n*-alkanes are shown in Figure 2, and the results for all the polymers are recorded in Table 3. The low CST's and high water contact angles of the fluorinated block poly(amide urethanes) demonstrate surfaces that are significantly nonpolar, reflecting an overlay of the fluorinated side chains. The Wilhelmy water contact angle increases as the fluorine content increases and is particularly large for the polymer containing pentadecafluorooctyl side chains, this in spite of being only 37% by weight fluorinated polyamide. The hexadecane contact angle of these latter materials (goniometer) also reflects the total fluorine content (Table 3); moreover, polymers 5F–6F–HB and 15F–6F–HB have contact

Table 3. Contact Angles and Critical Surface Tensions of Poly(amide urethanes)

polymer	H_2O contact angle (goniometry) [advancing/receding]	H_2O contact angle (Wilhelmy) [advancing/receding]	hexadecane contact angle (goniometry) [advancing]	critical surface tension (dyn/cm)
0F–6F–HB	97.8/73.8	92.5/30.3	26.0	28.44
5F–6F–HB	92.4/69.4	94.9/52.2	46.1	19.89
5F–8F–HB	92.4/71.5	101.7/54.8	48.5	19.72
15F–6F–HB	102.9/72.6	110.8/48.6	68.0	10.87

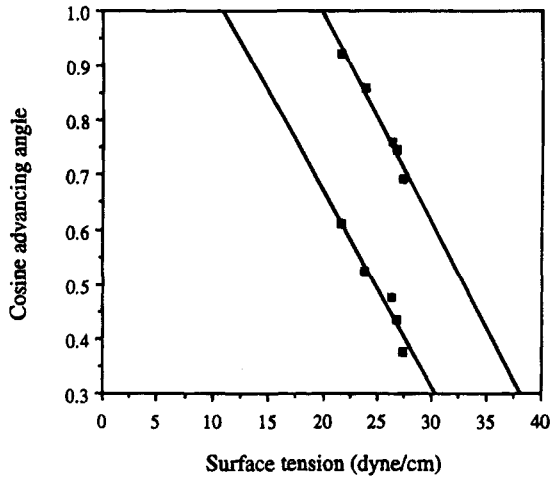


Figure 2. Zisman plot of poly(amide urethanes) 15F–6F–HB and 5F–6F–HB (with liquid hydrocarbon numbers 1–5 in Table 1 in ref 11) demonstrating critical surface tensions of 10.87 and 19.89 dyn/cm, respectively.

angles greater than those of the analogs without main-chain fluorine (Table 4, ref 11). It is noteworthy that the fluorinated side chain polymers in Table 3 have hexadecane contact angles comparable to or greater than the 46° reported for poly(tetrafluoroethylene);[3] that with the 15F side chains is particularly large and begins to approach the 71° angle for a fluorinated thiol on gold monolayer.[14] A film of the oligomer 15F–6F shows a hexadecane contact angle of 70.5°; however, it is completely wetted by water, perhaps a result of its low degree of polymerization. A comparison of water contact angles between the polymers with and without fluorine in the backbone shows differences to be small (see Table 4, ref 11); however, there is the increase in the hexadecane contact angle and a significant lowering of the CST with main-chain fluorine. The CST of 15F–6F–HB (10.87 dyn/cm) is close to those of 1*H*,1*H*-perfluorooctyl acrylate (10.4 dyn/cm)[2] and methacrylate (10.6 dyn/cm);[1] these are among the lowest measured surface tensions found in bulk polymers to this point. The acrylate polymer is 62.8% fluorine b weight; polymer 15F–6F–HB is only 21.3% fluorine. It is clear that the air–polymer interface shows a high concentration of CF_3 groups that does not reflect the total bulk concentration. Indeed, XPS measurements demonstrate a striking segregation of fluoroalkyl moieties to the polymer surface.[16]

There is a large hysteresis in the measurements with striking differences between the advancing and receding angles, particularly in the Wilhelmy experiments. The hysteresis in not as great as seen with the corresponding nonfluorinated backbone polymers.[11] Unlike the nonfluorinated backbone polymers, there is a reasonable agreement between the advancing angles, independent of method. It is observed as in the previous paper 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. Considering the high T_g's of the polymers, we do not believe the hysteresis to be due to rapid diffusion of the polyurethane segments to the surface. We believe this reflects a rearrangement of the side chains allowing some penetration by the water to the more polar polyamide backbone. This is hardly a new concept. Yasuda *et al.* demonstrated that hydrophobic polymers treated with oxygen plasma are able to bury the hydrophilic extensions with aging and that the magnitude of hysteresis is a function of aging time.[17] The hysteresis is minimized by a high degree of crosslinking. By studying the kinetics of F_{1s}/C_{1s} ratio changes upon exposure to water of a series of common polymers that had been surface fluorinated by a CF_4 plasma, they determined that fluorines are submerged at rates and activation energies commensurate with simple chain motion instead of large segmental reorientation.[18] Most recently, such changes have been determined by dynamic contact angle studies in ethylene–vinyl alcohol copolymers[19] and for various plasma polymers.[20] Ratner has shown the poly(2-hydroxyethyl methacrylate) has surface methyls in the dry state but surface hydroxyls in water.[21] Finally, Trettinnikov and Ikdada have examined the question of contact angle hysteresis and demonstrated the importance of time-dependent surface reorientation for poly(ethylene terephthalate), nylon 6, and a poly(ether urethane).[22] For the poly(amide urethanes) described here and in our previous work,[11] we have pictured the nonpolar surface as layered with fluorinated polyamide segments which are bent so as to allow the gathering of perfluoroalkyl chains into a dense layer. Wilson and Griffin have postulated a similar "hairpin" structure for their fluoroalkyl appended polyesters.[4] Upon exposure to water we believe that these segments flatten as to expose surface carbonyl groups. This can occur at temperatures well below the T_g's we have determined for these materials. The hysteresis is diminished by retention of nonpolar fluoroalkyl groups in the main chain of the polyamide. The hysteresis is particularly great when the polymer lacks the fluorinated side chain as in the 0F–6F–HB material with a simple propyl appendage, and the surface tension reflects the polar amide groups.

We have studied the effects of water exposure over a 30 day period, submerging the films and monitoring the contact angles. Earlier we had shown that for the polymers lacking main-chain fluorine, the advancing and receding angles had dropped within 2 days to ≈70 and 40°, respectively, and remained constant for the remaining time.[11] The advancing angles are less than those reported for nylon 6 and poly(ethylene terephthalate) but greater than that of poly(vinyl alcohol). Polymer 5F–6F–HB demontrated a similar decline in contact angle, decreasing from 92° to 71° within 72 h, and remained ≈71° for the rest of the time; however, 15F–6F–HB retained a contact angle above 90° for 2 weeks and reached an equilibrium value of 71° after 21 days. There was no significant decline in receding

contact angle for either polymer during the 30 day period.

A recent study of fluorinated polyurethanes with hexamethylene diisocyanate and a family of fluorinated diols having main-chain fluorines as well as a number of trifluoromethyl side groups has shown materials of excellent mechanical properties and CST's as low as 25.5 dyn/cm.[23] It is concluded that the surface composition of these polymers reflects their bulk composition. There are many intervening hydrocarbon and polar functional groups between the fluorocarbon moieties, but without the longer perfluorinated side chains of our materials.

There have been preliminary studies on fouling of the fluorinated poly(amide urethanes) by marine bacteria. Goodman and Dalton[24] have studied the binding of SW5 to 15F–0F–HB and 15F–6F–HB. The organism, originally found in surfboard wax that had been exposed to sea water, adheres strongly to hydrophobic surfaces and serves as an indicator of hydrophobiicity.[25] Indeed, it forms a biofilm on both fluorinated polymers under flow conditons indicating they are homogeneously hydrophobic even after the films had been aged in sea water. It also binds to a cross-linked silicone lacking filler we prepared. White and Arrage[26] have studied the binding of *V. harveyi* to metal coupons coated with 15F–6F–HB and a nonfluorinated analog with isopropyl side chains, 0F–0F–HB. The fluorinated polymer shows a definite inhibition to biofilm development and a corresponding loss of metabolic activity. The nonfluorinated analog showed essentially no such activity.

Conclusions

Poly(urethane/ureas) with tertiary polyamide soft blocks containing fluorinated side chains phase segregate, giving a surface coating of exposed fluorocarbons. This is demonstrated by the low CST's and relatively large water contact angles, well beyond what would be expected from the bulk fluorine content. The existence of fluorine in the main chain does not appear to have significant influence on the interfacial properties in water if there are fluorinated side chains. Main-chain fluorine does lower the CST's, and in one case the material has a value among the lowest measured for a bulk polymer; the low-energy interface is not stable in water and rearranges to expose more polar residues. In this aspect the materials suffer by the relatively low fluorine content. With the longer fluorinated alkyl side chain there is an enhanced stability, diminishing the contact angle hysteresis and allowing for retention of nonpolar properties on longer term exposure to water. The fluorinated polymers show inhibition of biofilm formation by one marine bacterium, but are bound by a bacterium that selectively develops on hydrophobic surfaces.

Continuing studies include polyamide blocks with increasing fluorocarbon length and materials with siloxane side chains. We are also continuing ESCA studies to further characterize the polymer surfaces. Future studies will determine the utility of these polymers in marine fouling prevention and biocompatibility potential.

Acknowledgment. This research was supported by the Office of Naval Research, Grant No. N00014-92-J-1316. We would like to thank Susana Steppan and Marilyn Kwiatkowski at Miles, Inc., for their technical assistance with the Cahn dynamic contact angle analyzer. We also acknowledge Navy support of A. E. Goodman, H. Dalton, D. C. White, and A. A. Arrage, who graciously carried out the biofilm studies as part of the Molecular Interactions at Marine Interfaces program.

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MA945073F