Determination of Low Critical Surface Tensions of Novel Fluorinated Poly(amide urethane) Block Copolymers. 3. Siloxane-Containing Side Chains

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ABSTRACT: Low critical surface tensions (CST's) of novel copolymers containing a "hard block" polyurethane and a "soft block" polyamide with siloxane side chains are reported. The hard segment consists of methylenebis(cyclohexyl isocyanate) (H_{12}MDI) and butanediol or a fluorinated analog. The soft segment contains a diacid chloride and secondary siloxane-containing diamines. The different diamines studied were *N*,*N*′-bis[3-(pentamethyldisiloxyl)propyl]-1,6-diaminohexane, *N*,*N*′-bis[3-(heptamethyltrisiloxyl)propyl]-1,6-diaminohexane, and *N*,*N*′-bis[3-(poly(dimethylsiloxyl)propyl]-1,6-diaminohexane. The two diacid chlorides studied were hexafluoroglutaryl chloride and adipoyl chloride. The polyamide 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 from contact angles of water and methylene iodide. Poly(amide urethanes) containing PDMS side chains displayed high advancing *and* high receding water contact angles and maintained this hydrophobicity when exposed to water for 30 days.

Introduction

Siloxane-based polymers are widely studied because of their many desirable properties, including low surface energies,[1−3] high flexibility,[4,5] low glass transition temperatures,[6] high oxygen permeability,[7] biocompatibility,[8,9] and, recently, their ability to act as barriers to marine fouling.[10] Although siloxane-based polymers display low critical surface tensions (CST's) (e.g. PDMS, CST = 21 dyn/cm at 20 °C),[11] polymers containing fluorocarbons display even lower CST's (e.g. poly(tetrafluoroethylene), CST = 18.5 dyn/cm at 20 °C).[12] An advantage of silicones over fluoropolymers, which display similar surface properties, is that silicones are essentially nontoxic.[13,14]

We have previously prepared low surface energy poly(amide urethanes) containing fluorocarbon moieties.[15,16] These copolymers have displayed CST's as low as 10.9 dyn/cm, one of the lowest CST's reported for a polymer.[17] From X-ray photoelectron spectroscopy analysis, we believe the fluorocarbon side chains orient at the surface of the polymer films to create a low energy surface.[18] These polymers display very low receding water contact angles, however, indicating rapid exposure of polar moieties when allowed to equilibrate in water. In this paper, we have prepared poly(amide urethanes) with siloxane side chain moieties with the hope that these side chains would orient and align at the surface as well, resulting in polymer films with hydrophobic surfaces that remain hydrophobic when exposed to water. The soft block polyamide oligomers are prepared from secondary diamines with pentamethyldisiloxane, heptamethyltrisiloxane, and poly(dimethylsiloxane) side chains and from diacid chlorides that were either fluorinated or nonfluorinated. Also, we have placed fluorocarbons in the main chain of the hard block polyurethane as well. These block copolymers were spin-cast or dip-coated into thin films on glass slides. Contact angles were measured using both goniometry and the Wilhelmy technique.[19] CST's were determined using the geometric means approach of Owens and Wendt,[20] with water and methylene iodide as the wetting solvents.

Experimental Section

Characterization. Infrared data were obtained with an IBM FT/IR-32 spectrophotometer. ^{1}H NMR data were obtained with a Bruker AC-300 or an AF-300 spectrometer. High-resolution mass spectra were obtained on a CH-5 double-focusing Varian MAT mass spectrometer or on a VG-70-G mass spectrometer. Thermal transitions were monitored with a Mettler FP90 system in conjunction with a Mettler FP84HT hot stage (rate = 10 °C/min), and also with a TA Instruments, Inc., Model DSC 2910.

Molecular Weight Determination. Gel permeation chromatography was carried out using two narrow-bore Phenogel columns (linear pore size and 500 Å, 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. Viscometry results were obtained with a Cannon Ubbelohde viscometer, no. 1 C304 or no. 1 H206, at 25 °C. The solvent was DMF.

Polymer Film Analysis. Contact angles were measured with a Ramé-Hart Model 100 contact angle goniometer modified with an AST, Inc., VCA2000 camera and also with a KSV Sigma 70 tensiometer (Wilhelmy) using a platinum plate. Samples for goniometry were prepared by spin-casting ∼5 drops of concentrated solutions in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) onto glass slides using a Headway Research, Inc., EC101D photoresist spinner at a spin rate of 3000 rpm and annealing in an Abderhalden pistol for 24 h at 25 or 100 °C. The glass was silanized prior to casting for the PDMS-containing polymers. 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 ∼1 μL from the drop. The average of ten measurements is reported. Samples for Wilhelmy measurements were prepared by dip-coating glass slides into concentrated polymer solutions in HFIP and annealed in a vacuum oven at 25 or 100 °C for 24 h. The slides were immersed at a speed of 5 mm/min into purified water at 20 °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

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test, the immersed slides were periodically removed from water, and contact angles were measured by goniometry or the Wilhelmy technique. Water used in the contact angle measurements and the 30 day water studies was doubly distilled from $KMnO_4$. Sodium azide (~200 ppb) was added to the water during the 30 day water studies.

Materials. Hexafluoroglutaryl chloride, pentamethyldisiloxane, heptamethyltrisiloxane (PCR), H_{12}MDI (Bayer), dibutyltin dilaurate [T-12], 1,6-dibromohexane, butanediol, 2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol, chlorodimethylsilane (Aldrich), and Pt:DVDS (United Chemical) were used as received. Hexamethylcyclotrisiloxane (Aldrich) was dried over CaH_2 overnight and then sublimed under vacuum. Allylamine (Aldrich) was fractionally distilled from $CaCl_2$ and stored over 4 Å molecular sieves. Cyclohexane (J. T. Baker) was extracted with concentrated H_2SO_4, H_2O, Na_2CO_3, and H_2O, distilled from P_2O_5, and stored over 4 Å molecular sieves. 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.

Synthesis of *N,N′*-Diallylhexamethylenediamine (1).[21] 1,6-Dibromohexane (30 mL, 0.1950 mol) was slowly added to allylamine (73 mL, 0.9746 mol). Room temperature was maintained with an ice bath and stirring was continued for 1 h. The reaction mixture was poured into 100 mL of 1 M HCl and then extracted with Et_2O. The Et_2O layer was discarded, and the aqueous layer was neutralized with 1 M NaOH. The organic layer was distilled at reduced pressure to give **1** [yield 9.8396 g (26%); bp 105 °C (15 Torr); ^{1}H NMR ($CDCl_3$; δ) (m, 5.88, 2H), (t, 5.10, 4H), (d, 3.22, 4H), (m, 2.58, 4H), (m, 1.48, 4H), (m, 1.33, 4H), (m, 1.00, 2H); IR (NaCl) 3266, 3075, 3025, 3000, 2925, 2850, 2800 cm^{-1}; LRMS *m/z* theoretical 196 g/mol, observed 197 g/mol; HRMS calcd for [$CH_2CHCH_2NH(CH_2)_6$-NH] 155.1548 g/mol, observed 155.1552 g/mol].

Synthesis of *N,N′*-Bis[3-(pentamethylsiloxyl)propyl]-1,6-hexamethylenediamine (2a) [General Procedure]. A few drops of Pt:DVDS in xylenes was added to a solution of pentamethyldisiloxane (1.5253 g, 0.0103 mol) and **1** (1.0063 g, 0.0051 mol) in 10 mL of $CDCl_3$. After an immediate increase in temperature, the reaction was stirred at room temperature and was monitored by ^{1}H NMR. After 22.5 h, the solvent was removed *in vacuo* and the crude product was vacuum distilled to give **2a** [yield 1.0448 g (41%); ^{1}H NMR ($CDCl_3$; δ) (m, 2.71, 4H), (m, 2.54, 4H), (t, 1.47, 4H), (m, 1.31, 4H), (m, 1.04, 4H), (m, 0.91, 4H), (m, 0.50, 2H), (m, 0.04, 30H); IR (NaCl) 2960, 2940, 2860, 2815, 1250, 1060 cm^{-1}; HRMS *m/z* theoretical 492.3419 g/mol, observed 492.3443 g/mol].

2b: 73%; ^{1}H NMR ($CDCl_3$; δ) (m, 2.75, 4H), (m, 2.55, 4H), (t, 1.50, 4H), (m, 1.32, 4H), (m, 1.07, 4H), (m, 0.93, 4H), (m, 0.54, 2H), (m, 0.03, 42H); IR (NaCl) 2920, 2850, 2780, 1246, 1042 cm^{-1}.

2c: 82%; ^{1}H NMR ($CDCl_3$; δ) (m, 2.75, 4H), (m, 2.50, 4H), (t, 1.50, 4H), (m, 1.33, 4H), (m, 1.20, 4H), (m, 0.91, 4H), (m, 0.55, 2H), (m, 0.05, 42H); IR (NaCl) 2963, 1261, 1026, 800 cm^{-1}; molecular weight determined by GPC, $\bar{M}_n$ = 1940 g/mol, PDI = 1.19.

Synthesis of Polyamide Oligomer. *N,N′*-Bis[3-(pentamethylsiloxyl)propyl]-1,6-hexamethylenediamine + Hexafluoroglutaryl Chloride (4a) [General Procedure]. Hexafluoroglutaryl chloride (0.1357 g, 0.49 mmol) was slowly added dropwise to 0.261 g (0.53 mmol) of **2b** and 0.14 mL (0.9 mmol) of TEA in 10 mL of dichloromethane at 0 °C. The reaction was stirred at room temperature for 43 h. The TEA salts were removed by filtration, and the filtrate was 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 **4a** [yield 0.3523 g (89%); IR (NaCl) 2910, 1654, 1248, 1050 cm^{-1}; molecular weight determined by GPC, $\bar{M}_n$ = 4470 g/mol, PDI = 1.27; intrinsic viscosity = 0.063 dL/g; T_g = −13.9 °C].

3a: 59%; IR (NaCl) 2928, 1719, 1632, 1244 cm^{-1}; molecular weight determined by GPC, $\bar{M}_n$ = 5783 g/mol, PDI = 1.47; intrinsic viscosity = 0.365 dL/g; T_g = −19.8 °C.

3b: 27% IR (NaCl) 2936, 1651, 1248, 1042 cm^{-1}; molecular weight determined by GPC, $\bar{M}_n$ = 7775 g/mol, PDI = 1.64; intrinsic viscosity = 0.068 dL/g; T_g = −1.0 °C.

3c: 95%; IR (NaCl) 2965, 1633, 1257 cm^{-1}; molecular weight determined by GPC, $\bar{M}_n$ = 3749 g/mol, PDI = 1.43; intrinsic viscosity = 0.591 dL/g; T_g = −106.9 °C.

4b: 76% IR (NaCl) 2930, 1665, 1248, 1040 cm^{-1}; molecular weight determined by GPC, $\bar{M}_n$ = 4776 g/mol, PDI = 1.75; intrinsic viscosity = 0.197 dL/g; T_g = −16.9 °C.

4c: 87%; IR (NaCl) 2959, 1676, 1254 cm^{-1}; molecular weight determined by GPC, $\bar{M}_n$ = 6522 g/mol, PDI = 1.29; intrinsic viscosity = 0.111 dL/g; T_g = −49.4 °C.

Synthesis of Poly(amide urethane) (7a). *N,N′*-Bis[3-(pentamethylsiloxyl)propyl]-1,6-hexamethylenediamine/Hexafluoroglutaryl Polyamide (4a) + H_{12}MDI + Butanediol [General Procedure]. H_{12}MDI (0.07 g, 0.27 mmol) was dissolved in 0.5 mL of NMP:THF (1:1) and added to 0.10 g of oligomer **4a** dissolved in 5.0 mL of the same. The reaction was stirred at room temperature for 1.5 h. Butanediol (0.03 g, 3.3 mmol) and 2 drops of T-12 were added, and the reaction was monitored by IR. The reaction was stirred for 21.5 h, and then an additional 0.04 g (0.15 mmol) of H_{12}MDI was added. After 72 h the polymer solution was precipitated in water. The white solid was collected to give the block poly(amide urethane) **7a** [yield 0.1324 g (50%); IR (NaCl/film) 3405, 2921, 2851, 1651, 1559, 1179 cm^{-1}; intrinsic viscosity = 0.310 dL/g; T_g = −4.6 °C].

5a: 29%; IR (NaCl/film) 3405, 2921, 2851, 1651, 1559, 1179 cm^{-1}; intrinsic viscosity = 0.086 dL/g; T_g = −2.2 °C.

5b: 25%; IR (NaCl/film) 3359, 2924, 2859, 1684, 1559, 1217 cm^{-1}; intrinsic viscosity = 0.374 dL/g; T_g = −4.6 °C.

5c: 27%; IR (NaCl/film) 3351, 2923, 2853, 1630, 1555, 1181 cm^{-1}; intrinsic viscosity = 0.202 dL/g; T_g = −95 and −84 °C.

6a: 77%; IR (NaCl/film) 3345, 2921, 2861, 1660, 1651, 1565, 1181 cm^{-1}; intrinsic viscosity = 0.250 dL/g; T_g = −3.2 °C.

6b: 39%; IR (NaCl/film) 3359, 2923, 2860, 1651, 1557, 1219 cm^{-1}; intrinsic viscosity = 0.099 dL/g; T_g = 4.8 °C.

7b: 73%; IR (NaCl/film) 3339, 2924, 2860, 1674, 1559, 1181 cm^{-1}; intrinsic viscosity = 0.090 dL/g; T_g = −13.2 °C.

7c: 28%; IR (NaCl/film) 3349, 2921, 2851, 1647, 1553, 1100 cm^{-1}; intrinsic viscosity = 0.100 dL/g; T_g = −50.1 °C.

8a: 64%; IR (NaCl/film) 3320, 2923, 2860, 1710, 1607, 1574, 1177 cm^{-1}; intrinsic viscosity = 0.233 dL/g; T_g = −10.6 °C.

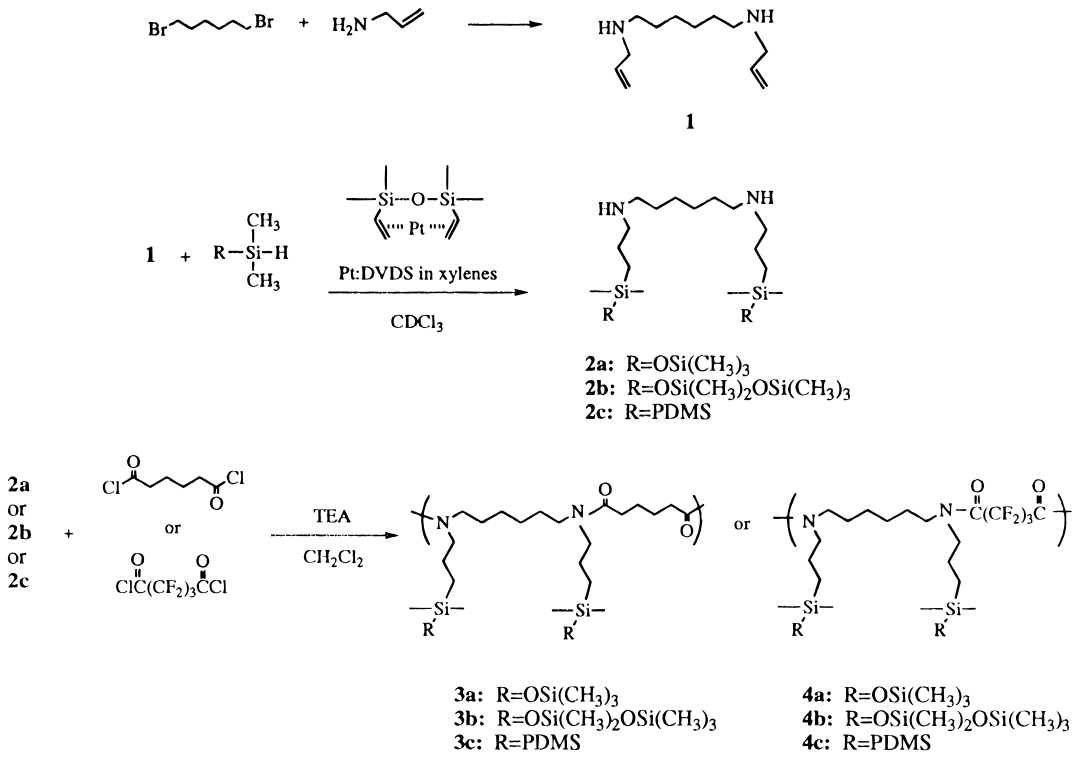
8b: 18%; IR (NaCl/film) 3340, 2923, 2850, 1730, 1646, 1557, 1196 cm^{-1}; intrinsic viscosity = 0.110 dL/g; T_g = −1.3 °C.

Synthesis of SiH-Terminated Poly(dimethylsiloxane) (PDMS).[22] Hexamethylcyclotrisiloxane (D_3) was dried over CaH_2 in a 70 °C oven for 15 h and sublimed onto a preweighed cold finger. Purified D_3 (17.9 g, 0.08 mol, 0.24 equiv of Si) was dissolved in 100 mL of cyclohexane, and polymerization was initiated with 13.8 mL (0.018 mol) of *sec*-butyllithium (1.3 M in cyclohexane). The mixture was stirred for 2 h, 10 mL of THF was added, and stirring was continued for another 48 h. Chlorodimethylsilane (1.9 mL, 0.018 mol) was added to terminate the reaction and cap the polymer. The reaction mixture was filtered, and the solvent was removed *in vacuo*. A viscous liquid remained that was washed with methanol to give **PDMS** [yield 12.68 g (71%); ^{1}H NMR ($CDCl_3$; δ) (br, 4.7, 1H), (s, 0.05−0.08, 127H); IR (NaCl) 2953, 2907, 2857, 2128, 1945, 1413, 1260, 1028, 913, 801 cm^{-1}; molecular weight determined by GPC, $\bar{M}_n$ = 1444 g/mol, PDI = 1.10; VPO $\bar{M}_n$ = 1783 g/mol; ^{1}H NMR $\bar{M}_n$ = 1570 g/mol (CH_3:SiH ratio)]. The average degree of polymerization is 21 ± 1.5.

Results and Discussion

A series of poly(amide urethanes) were prepared in which the polyamide segments contained pendant siloxyl groups emanating from tertiary polyamide nitrogen atoms. The polyamide soft blocks were prepared from siloxane-containing diamines and diacid chlorides as shown in Scheme 1. The diamines were prepared by the hydrosilation of *N,N′*-diallylhexamethylenediamine with a platinum catalyst, Pt:DVDS. The siloxane side chains are pentamethyldisiloxyl (2Si), heptameth-

Scheme 1. Synthesis of Polyamides



yltrisiloxyl (3Si), and poly(dimethylsiloxyl) (PDMS). The preparation of the monofunctional PDMS followed a recent procedure by Peters *et al.*[22] to obtain a low molecular weight, monodisperse, hydrosilane-terminated PDMS. The PDMS chains contain an average of 20−23 monomer units. The polyamides are made by elaboration of the diamine with hexafluoroglutaryl chloride (F) or adipoyl chloride (noF). Excess diamine is used to control molecular weight and confirm amine end groups. The poly(amide urethanes) are fashioned from the amine-terminated polyamides, methylenebis(cyclohexyl isocyanate) (H_{12}MDI), and a nonfluorinated (butanediol) or fluorinated (2,2,3,3,4,4,5,5-octafluoro-1,6-hexanediol) chain extender (Scheme 2). These copolymers were characterized by intrinsic viscosity and DSC measurements (Table 1). The T_g's of the copolymers generally correspond to the T_g's of the starting polyamides but are significantly lower for the PDMS-containing copolymers. The copolymers are white powdery solids at room temperature.

Siloxane polymers, known to have low surface energy by themselves or in block copolymers, have been extensively studied.[1−3,23,24] The synthesis of polymers with poly(dimethylsiloxane) side chains has recently been published by Sakakibara *et al.*, in which they prepared aromatic poly(benzobisoxazoles) containing PDMS side chains for the purpose of dispersing rigid-rod molecules in silicone matrices for molecular reinforcement.[25] Tezuka *et al.* have prepared polyurethanes from MDI, butanediol, and a macromonomer diol with PDMS side chains ranging from 31 to 93 residues in length and siloxane contents from 5.8 to 64 wt %.[26] They demonstrated that water contact angles changed over a 3 h period with the surfaces becoming more polar in nature. Samples with over 50% siloxane showed minimal change. The authors concluded that a surface with a siloxane layer greater than 100 Å will remain hydrophobic in water. Allcock *et al.* studied poly(organophosphazenes) with heptamethyltrisiloxane side chains. Contact angles taken quickly after droplet application on spin-cast films demonstrated very high water contact angles. There was no attempt to measure surface changes or hysteresis. An interesting finding was that perfluoroalkanes dominated the surface even if a polysiloxane alternative was available.[27]

Surface analysis of thin films of our block copolymers was carried out using both goniometry and the Wilhelmy procedure. Water contact angles and critical surface tensions were studied as a function of side chain siloxane length and of the presence of fluorine in the polyurethane and/or polyamide segments. The influence of annealing temperature was also studied (Tables 2 and 3). Although goniometry and the Wilhelmy plate technique both measure contact angle, it is clear that a number of samples do not give consistent results. In general, the advancing angles were greater and the receding angles much lower in the Wilhelmy measurement. The same observation has been made in several recent studies. A self-assembled monolayer (SAM) of hexadecyl groups on silicon and on glass demonstrated significantly greater hysteresis by the Wilhelmy plate as compared to goniometry on syringe-deposited droplets.[28] Recently, it was reported that a low surface energy cross-linked coating with perfluoroalkyl groups also demonstrated higher advancing contact angles and lower receding angles by the Wilhelmy method relative to tilt-stage goniometry.[29] Bruil *et al.*[30] found that a polyurethane made hydrophobic by treatment with a CF_4 plasma shows significantly higher advancing contact angles by the Wilhelmy plate method (128°) than by sessile drop and captive bubble measurements (104 and 89°, respectively). Although the initial receding angle (Wilhelmy) is fairly high (83°), it goes to almost zero after 100 s. The large differences in receding angle were also a feature of our earlier studies on poly(amide urethanes) with perfluoroalkyl side chains.[15,16] The difference in receding angles is not uncommon since the time the sample is exposed to water is significantly longer during the Wilhelmy immersion. The differences in advancing angles may be due in part to the instan-

Scheme 2. Synthesis of Poly(amide urethanes)

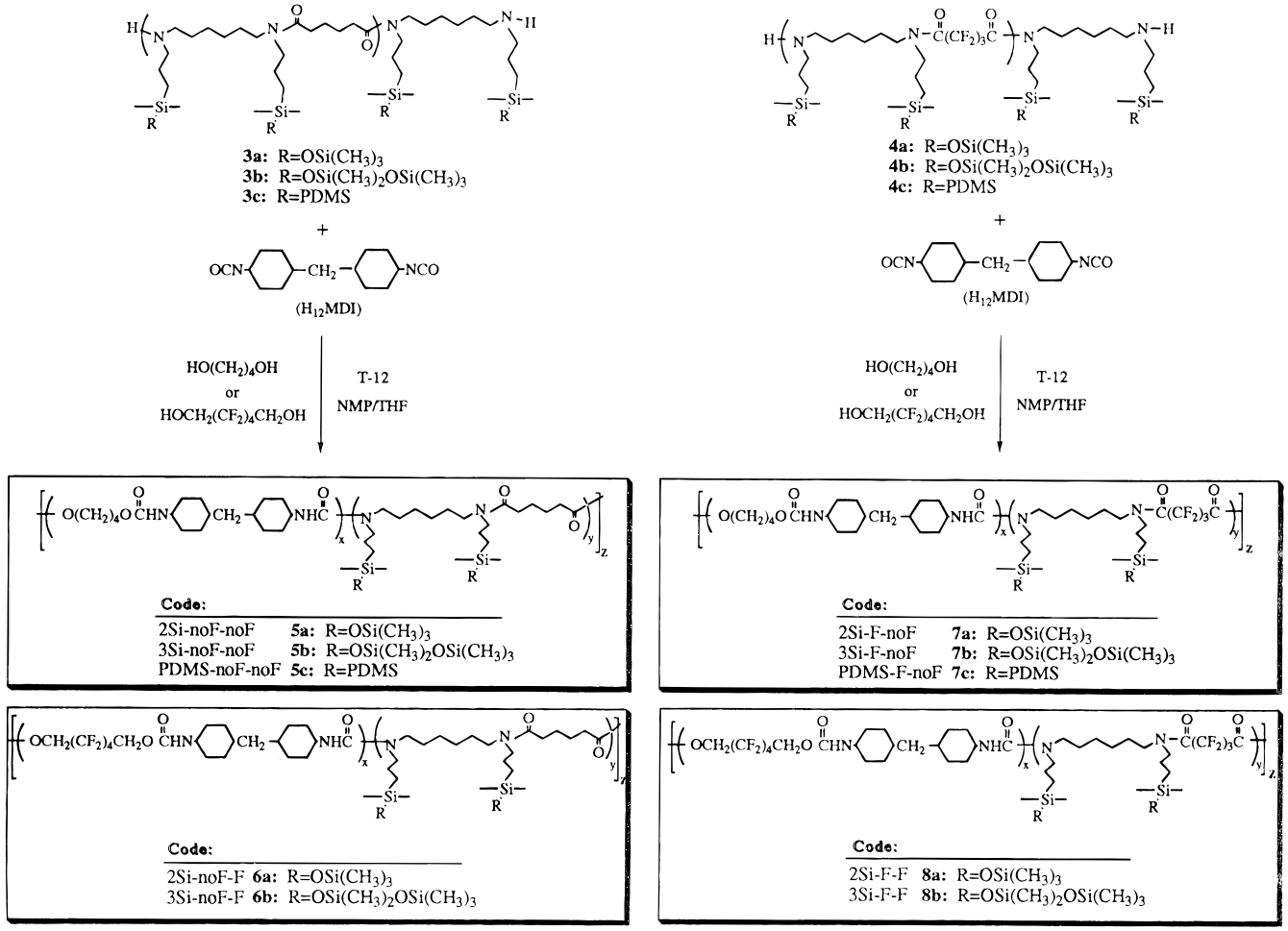


Table 1. Intrinsic Viscosities, Glass Transition Temperatures, and Percent Composition of Poly(amide urethanes)

polymer	[η] (dL/g)	*Tg* (°C)[a]	% siloxane	% soft block/ % hard block
2Si-noF-noF[b] (**5a**)	0.09	−2.2/−19.8	23	42/58
3Si-noF-noF (**5b**)	0.37	−4.6/−1.0	25	36/64
PDMS-noF-noF (**5c**)	0.20	−95.0/−106.9	42	45/55
2Si-F-noF (**7a**)	0.31	−4.6/−13.9	15	38/62
3Si-F-noF (**7b**)	0.09	−13.2/−16.9	26	44/56
PDMS-F-noF (**7c**)	0.10	−50.1/−49.4	43	47/53
2Si-noF-F (**6a**)	0.25	−3.2/−19.8	19	35/65
3Si-noF-F (**6b**)	0.10	4.8/−1.0	29	43/57
2Si-F-F (**8a**)	0.23	−10.6/−13.9	9	23/77
3Si-F-F (**8b**)	0.11	−1.3/−16.9	27	46/54

[a] The first glass transition temperature is the *Tg* of the poly(amide urethane), and the second temperature is the *Tg* of the polyamide. [b] *2Si-noF* indicates the length of the siloxane (disiloxane) and no fluorine in the adipoyl residue, whereas the second *noF* indicates the polyurethane fluorine content.

taneous nature of the Wilhelmy method as the three-phase boundary advances onto the dry surface; the time lag between addition of liquid to the droplet and making the measurement in goniometry can allow for significant surface reorientation. Tretinnikov and Ikada[31] have determined that in the Wilhelmy method, the advancing angles are relatively insensitive to immersion speed whereas the receding angles are a function of exposure time.

Many of the polymers described in Tables 2 and 3, even with short siloxyl appendages, display remarkably high Wilhelmy advancing contact angles and correspondingly large hysteresis values. Annealing at 100 °C generally increases the advancing contact angles with water and leads to generally lower critical surface tensions, and indeed significantly lower with the PDMS side chains. The effect of annealing on contact angles measured by goniometry is minimal for most samples.

Table 2. Contact Angles and Critical Surface Tensions of Poly(amide urethanes) Annealed at 100 °C for 24 h

polymer	H_2O contact angle (advancing/receding) goniometry	H_2O contact angle (advancing/receding) Wilhelmy	CST (dyn/cm)
2Si-noF-noF	86/64	126/30	31.0
3Si-noF-noF	77/48	100/16	33.9
PDMS-noF-noF	107/93	105/82	18.4
2Si-F-noF	82/64	136/18	35.8
3Si-F-noF	96/76	118/53	26.3
PDMS-F-noF	111/97	115/65	12.2
2Si-noF-F	95/49	105/<10	31.0
3Si-noF-F	74/35	99/<10	33.3
2Si-F-F	85/67	122/70	32.3
3Si-F-F	100/67	96/65	30.9
silicone A[a]	103/96	110/89	23.4
silicone B	107/91	117/86	20.5
polyurethane[b]	80/58	81/32	30.0

[a] For comparison, the contact angles and CST's of a film prepared by cross-linking silanol-terminated PDMS with AIBN and no added filler (silicone A) and a film prepared by cross-linking silanol-terminated PDMS, trimethylsiloxy-terminated PDMS, and methyltriacetoxysilane with a tin catalyst (silicone B) are included. [b] The contact angles and CST of a homopolyurethane prepared from H_{12}MDI and butanediol are included for comparison.

By goniometry, the copolymers with the disiloxyl and trisiloxyl side chains display unremarkable water contact angles, well below those of cross-linked dimethyl-

Table 3. Contact Angles and Critical Surface Tensions of Poly(amide urethanes) Annealed at 25 °C for 24 h

	H_2O contact angle (advancing/receding)		
polymer	goniometry	Wilhelmy	CST (dyn/cm)
2Si-noF-noF	76/52	115/32	34.2
3Si-noF-noF	76/55	94/34	31.8
PDMS-noF-noF	92/87	90/79	26.9
2Si-F-noF	81/56	113/32	37.4
3Si-F-noF	95/66	105/57	29.6
PDMS-F-noF	111/93	122/71	26.6
2Si-noF-F	88/47	78/41	32.1
3Si-noF-F	71/44	90/41	34.5
2Si-F-F	85/63	89/18	33.3
3Si-F-F	94/73	105/41	28.5

Table 4. Contact Angles of Poly(amide urethanes) after Being Exposed to Water for 28 days (Initially Annealed at 100 °C for 24 h) Measured by Goniometry

polymer	H_2O advancing contact angle	H_2O receding contact angle	hysteresis
2Si-noF-noF	69	40	29
3Si-noF-noF	69	54	15
PDMS-noF-noF	100	84	16
2Si-F-noF	78	51	27
3Si-F-noF	67	49	18
PDMS-F-noF	112	90	22
2Si-noF-F	74	58	16
3Si-noF-F	69	49	20
2Si-F-F	73	53	20
3Si-F-F	63	48	15

silicones prepared by us.[32] These polymers showed virtually no dependence of contact angle or critical surface tension on siloxane content (weight percent). In contrast, the two copolymers containing PDMS side chains display extremely hydrophobic surfaces, even before annealing, as demonstrated by the water advancing contact angles of 111° (goniometry) and 115° (Wilhelmy) for PDMS-F-noF. It is noted as well that for these materials containing the PDMS side chains, hysteresis is minimized, there is reasonable agreement between the two measuring techniques, and the results are in confluence with those of the pure silicones.

Receding water contact angles are a good indication of the surface hydrophilicity after water exposure. The receding angles are lower in the Wilhelmy method, but this is to be expected. The film is exposed to water for ~3 min during the measurement of the advancing angle, hence giving the surface ample time to reorient and expose a more hydrophilic facade. In comparison, a goniometry measurement only requires about 10 s. A study of the effects of long-term exposure to water was carried out using the heat-annealed polymers to give them every opportunity to adjust and expose underlying polar moieties. The advancing and receding water contact angles were measured for all the polymers over a 30 day period. The results for the heat-annealed polymers are shown in Table 4. In general, the influence of the water exposure on the polymers with short siloxane sequences is manifest in the uniformly lower advancing contact angles and they are typically lower receding angles. Indeed, the figures are all similar for these materials and close to the values of the model polyurethane. This indicates significant reordering of the polymer morphology. Remarkably, the effect on the PDMS-containing polymers is nearly negligible. The polymer with PDMS and perfluoroglutaryl polyamide moieties demonstrated the highest contact angles before and after treatment and negligible change. Indeed, the two polymers with PDMS side chains retain advancing contact angles above 100 °C. The critical surface tension of the heat-annealed polymer containing the fluorinated polyamide (Table 5) is initially low, and long-term water exposure has negligible effect. The CST is so low as to demand that fluoroalkyl groups have come to the surface, even through the PDMS layer. The low energy surface the of PDMS side chain polymers is more stable than that of our previous perfluoroalkyl-appended polymers.[16] This reflects the thick layer of low energy segments at the surface which is penetrated by water only with difficulty. The low surface energy is stabilized by the perfluoroglutaryl component of the polyamide. ESCA studies in air and also in water are currently being conducted.[33]

Table 5. Critical Surface Tensions of PDMS-noF-noF and PDMS-F-noF before and after 30 day Water Exposure

	annealed at 25 °C		annealed at 100 °C	
polymer	pre-H_2O CST (dyn/cm)	post-H_2O CST (dyn/cm)	pre-H_2O CST (dyn/cm)	post-H_2O CST (dyn/cm)
PDMS-noF-noF	26.9	24.5	18.4	23.8
PDMS-F-noF	26.6	17.5	12.2	13.4

Contact angle hysteresis of various polymer surfaces is being widely studied. Bruil *et al.*[30] reported extraordinarily high advancing and unusually low receding water contact angles for modified polyurethane surfaces. Scanning electron microscopy indicated surface roughness, which contributes to the large hysteresis. Yasuda *et al.*[34] have attempted to explain the high advancing water contact angles for moderately hydrophobic polymers as a result of the cumulative effects of both the attractive forces and the repulsive forces of the polymer surface with water. The extent of surface change is a function of the differential surface tension between the polymer and surrounding medium. The authors point out that an accurate measure of the surface energy of the initial polymer surface can be made from the advancing angle if the phase boundary line moves faster than the rate of the surface structure change. Tretinnikov and Ikada have studied both the thermodynamic and kinetic reasons for hysteresis.[31] Thermodynamic sources include surface roughness and surface heterogeneity; kinetic sources include swelling, penetration of the liquid into the surface, and surface reorientation of functional groups. They studied the latter by varying the immersion rates during Wilhelmy measurements. For example, nylon 6 fibers have receding contact angles that are a function of immersion rate if the total contact time is short. There are many causes for hysteresis; however, surface reorientation appears to be the most likely cause of our short siloxyl side chain polymer hysteresis. The T_g's of these copolymers are below room temperature and thus the polymers are able to freely reorient. Varying the immersion rate from 1 to 10 mm/min had no influence on contact angles. Preliminary ESCA results indicate that the PDMS-containing polymers have a surface enriched with siloxanes, whereas the short siloxyl side chains' surfaces indicate a polyurethane/siloxane surface.[33]

Comparison of the CST's of the polymers annealed at room temperature vs annealed at 100 °C for 24 h shows the greatest difference with the PDMS-containing polymers. Although the films cast at room temperature display low energy surfaces, annealing the PDMS-F-noF polymer at 100 °C greatly reduces the CST (26.6 dyn/cm vs 12.2 dyn/cm, respectively). In spite of the length of the PDMS side chains, there must be a fluorinated surface from the glutaryl residues to explain the low

CST; the PDMS must somehow stabilize this surface and shield the glutaryl amide residues since the influence of the fluorine is negligible with the short siloxane. This low CST is comparable to that of the poly(amide urethanes) previously prepared by this group in which there are pendant fluorocarbon groups in lieu of siloxane side chains.[15,16] These fluoropolymers, however, do not show a stable morphology on long-term water exposure. The CST of the nonfluorinated PDMS side chain polymer is also low, comparable to that of the pure silicones.

Conclusions

Poly(amide urethanes) with tertiary polyamide soft blocks with PDMS-containing side chains phase segregate to expose the low-energy siloxanes at the surface. This is demonstrated by high water contact angles and low critical surface tensions. Receding water contact angles are low for the polymers with short siloxyl side chains, but our goal of increasing the receding water contact angles was achieved with the PDMS-containing polymers. The prolonged water exposure studies have demonstrated a somewhat stable surface morphology for the PDMS-containing polymers, particularly the polymer with backbone fluorine in the polyamide blocks.

Future studies will determine the biocompatibility potential of these polymers and their utility in marine fouling prevention.

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