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Films Containing Reactive Mixtures of Perfluoroalkylethyl Methacrylate Copolymers and Fluorinated Isocyanates: Synthesis and Surface Properties

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ABSTRACT: The fluorotelomer alcohol $F(CF_2)_n(CH_2)_2OH$ ($n \approx 7.8$), **2**, contains a terminal hydroxyl group that reacts with the isocyanate group of a polyisocyanate cross-linking agent based on the isocyanurate trimer of hexamethylene diisocyanate, **1**. The resulting fluorinated isocyanate, **3**, contains a urethane linkage and a pendant perfluoroalkyl group. The modified isocyanate, **3**, was used to prepare films containing acrylic copolymers with cross-linkable hydroxyl groups. Films were prepared using several varieties of acrylic copolymers with and without the incorporation of small amounts of fluorinated monomers. With regards to surface energy reduction, the initial film properties were excellent. For example, reactive mixtures of **3** with hydrocarbon hydroxyl-containing acrylic copolymers exhibited surfaces enriched with fluorine. Water and hexadecane advancing contact angles were measured to be ~86° and ~40° at ~ 2.3×10^{-2} mole fraction (~1900 ppm by weight F) of $F(CF_2)_n(CH_2)_2O-$, respectively. Hexadecane contact angles on films of copolymer/isocyanate mixtures containing no fluorine were zero. Mixtures of **3** with fluorinated acrylic copolymers gave surfaces that were enriched with fluorine. The source depended on the surface activities of the respective components. Using mixtures of **3** with the various acrylic copolymers, a variety of surfaces can be constructed. The prepared films were examined by contact angle measurements, electron spectroscopy for chemical analysis and dynamic secondary ion mass spectroscopic depth profiling.

Introduction

Organic polymer films have found wide application for coating many materials. The surface properties of these films are of paramount importance for such applications where adhesion concerns are present. For example, lowering the surface energy of a film is desirable for formulating repellent coatings. One of the most popular and successful strategies for lowering the surface energy of a film is incorporation of fluorine into the polymer comprising the coating. The fluorine can be incorporated into the main polymer chain. Examples using fluorinated diols[1−7] and fluorinated alcohols[8] to prepare polyurethanes have been reported. Surface energy reduction has also been studied using blends of fluoropolymers with hydrocarbon polymers.[9,10] Several reports have used the propensity of chain-end enrichment at surfaces[11,12] in conjunction with fluorination to alter surface energies.[13−15] Surface tension reduction has also been reported for copolymers prepared by the incorporation of fluorinated monomers[16−21] and by chemically grafting perfluoroalkyl groups to polymers.[22] In an earlier report, the results of work on acrylic copolymer films containing small amounts of copolymerized fluorinated monomers using pure hydrocarbon isocyanate cross-linking chemistry were described.[23] Polymer surfaces obtained were enriched highly in fluorine. This indicated that the polymer molecules prepared by the incorporation of small amounts of fluorinated monomers were quite surface-active. The films used isocyanate cross-linking to impart the necessary mechanical properties to the low T_g resins.

The possibility arose of modifying the isocyanate chemically by reaction with fluorinated alcohols and utilizing this modified material as a source of surface-active fluorine. Mixtures of fluorinated materials may have properties that are enhanced compared to the individual components. Such a strategy is used extensively for many commercially important polymer blends.

Isocyanate cross-linking is a reaction that is ubiquitous in the coatings industry. The preparation and application of low surface energy, fluorinated versions of isocyanates allow for the formation of low surface energy films. Fluorinated isocyanates can be prepared easily in high yield. The fluorinated isocyanate used in the current study is based on the reaction product of $F(CF_2)_n(CH_2)_2OH$, **2**, ($n = 6-12$; average $n = 7.8$) with the iscyanurate trimer of hexamethylene diisocyanate, **1**. The reaction scheme is shown in Figure 1. Low surface energy acrylic copolymer-based films can be prepared using these fluorine-modified isocyanates. The fluorinated iso cyanate can be used alone, as the reactive cross-linker with hydroxyl-containing acrylic copolymers, or in tandem with a fluorinated version of the acrylic copolymer. Depending on the type of fluorinated intermediate used, low surface energy coatings can be obtained with ~$10^{-2}-10^{-4}$ mole fraction of $F(CF_2)_n(CH_2)_2O-$ in the final film. This work has focused on the use of one particular variant of fluorinated isocyanate **3**; however, this scheme has been demonstrated

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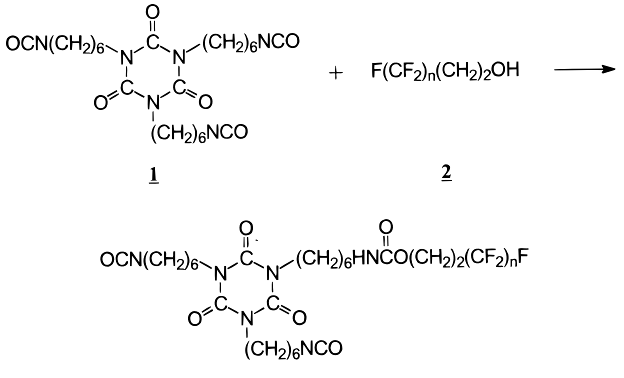

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Figure 1. Reaction scheme for perfluoroalkylethyl alcohol with isocyanate.

with other hydroxyl-terminated fluorinated intermediates to modify the isocyanate **2**.[24-26] Contact angle measurements have demonstrated the variety of surfaces attainable with reactive mixtures of acrylic copolymers and fluorinated isocyanate. Although only one system has been reported in this study, it is anticipated that these fluorine-modified isocyanates can find use, generically, as cross-linkers in a variety of coatings. Fluorinated isocyanates compete effectively, in certain instances, with the fluorinated acrylic copolymer for the surface before cross-linking, gelation, and vitrification prevent diffusion to the film surface.

The surfaces of films prepared with reactive mixtures of the fluorinated isocyanate **3** (Figure 1) and various hydrocarbon and fluorine-modified hydrocarbon acrylic copolymers (Figure 2) have been examined by contact angle, dynamic secondary ion mass spectroscopic (DSIMS), and ESCA measurements.

Results and Discussion

Fluorinated Acrylic Copolymers. The incorporation of the perfluoroalkylethyl methacrylate, $H_2C{=}C(CH_3)CO_2(CH_2)_2(CF_2)_nF$, **4**, ($n = 6-12$) into an acrylic copolymer, **5**, to form a copolymer that is fluorinated, **6**, has been shown to result in the formation of a low free energy surface.[23] Representative structures are shown in Figure 2. This surface behaves in a fashion typical of a fluorochemical repellent.[27] Two acrylic copolymers were chosen for study due to their differences in preparation. Both were synthesized by the incorporation of 1.5 wt % of **4** into a copolymer consisting of styrene/butyl methacrylate/butyl acrylate/hydroxypropyl acrylate/**4** ($0.19/0.26/0.17/0.38/4.0 \times 10^{-3}$ mole fraction). The difference in preparation resided in the addition method of **4**. One copolymer, **6a**, was prepared by a one-time addition of the fluorinated monomer near the end of the reaction. The other, **6b**, was prepared by continuous addition of the fluorinated monomer throughout the course of polymerization. Copolymer **6a** was much more surface-active than **6b**.[23]

The explanation for this behavior was based on kinetics during copolymer formation. The copolymer, **6a**, prepared by a one-time addition of **4** would have, on average, a smaller number of chains containing a greater amount of a fluorinated monomer than a copolymer, **6b**, prepared by the continuous feed method. While the quantity of fluorine added by the two preparation methods remains equal, copolymer **6a** exists in small proportion with unmodified copolymer **5**. The surface excess on films of low surface energy "blocky" copolymers versus statistical copolymers has been observed previously.[28] Surface tensions and excesses have been measured on solutions of statistical and block polyethers.[29] These authors reported no observable surface excess for the statistical copolymers but an appreciable excess for similar composition block copolymers. For block copolymers, surface excesses were related to the block length of monomer sequences. The synthetic protocol used to prepare **6b** guarantees an equitable distribution of a fluorinated monomer between a larger number of chains. Therefore, it is expected that copolymer **6a** will be more "blocky" than copolymer **6b**. As a result, films prepared using **6a** exhibited much higher water and hexadecane contact angles than those using copolymer **6b** at the same relative concentration of $F(CF_2)_n(CH_2)_2O-$. This can be seen clearly from the data in Table 1. In addition to surface energy reduction, dynamic mechanical property differences and benefits of copolymers prepared using a variable monomer feed method (vs continuous monomer feed) have been reported by others.[30] The behavior of the fluorine-modified isocyanate will be examined with both of these types of copolymers.

The present system (acrylic copolymer + isocyanate) is multicomponent. From the equation for the Gibbs adsorption isotherm, it can be seen that a differential in surface tension will result in a surface enrichment of the lower surface tension species.[31]

$$d\gamma = \sum_i \Gamma_i \mu_i \qquad (1)$$

where Γ is the surface excess and μ is the chemical potential of species i. The electron spectroscopy for chemical analysis (ESCA) data collected previously indicated that the surface excess of fluorine observed in films made with the fluorinated acrylic copolymers is large (≈25−75; atom % F at surface/atom % in bulk). However, the surface excess of fluorine observed poses an interesting problem in interfacial mixing. The fluorinated acrylic copolymer chains are surface-active enough to exclude almost everything else from the surface region including the isocyanate required for cross-linking to occur. This can be seen clearly in Figure 3 in the dynamic secondary ion mass spectroscopic (DSIMS) data for the reactive mixture of fluorinated acrylic copolymer **6b** with isocyanate **1**. An excess of fluorine is observed at the air−polymer interface even though this copolymer is less surface active than the fluorinated acrylic copolymer **6a**. The excess of fluorine (from the fluorinated acrylic copolymer **6b**) at the film/air interface is large enough that a signal attributable to nitrogen (from the isocyanate **1**) is not observed until ~50 Å of the surface has been sputtered away.

With no cross-linker present near the surface, the surface-active fluorinated copolymer chains near the surface would not be linked chemically to the rest of the film. A surface active, fluorinated isocyanate, such as **3**, might be able to compete for the surface region and react with the most surface-active fluorinated polymer chains of fluorinated acrylic copolymers **6**. It is the purpose of this work to explore the effect of fluorinated isocyanate cross-linking on acrylic copolymer surface properties. Additionally, a search for potential synergistic effects of mixtures of fluorinated acrylic copolymers and fluorinated isocyanates was made. Surface energy synergism is not uncommon in mixed surfactant systems[32] and has been observed with mix-

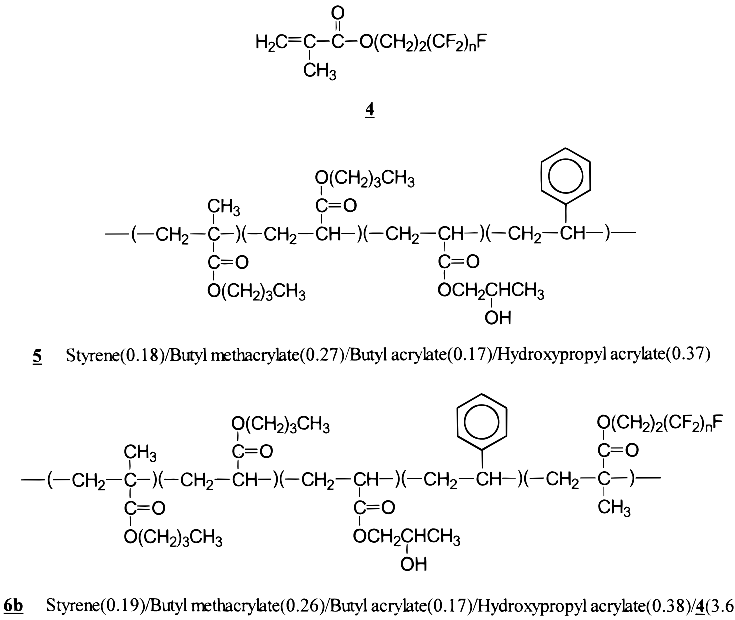

Figure 2. Structures of fluorinated monomer and acrylic copolymers. Monomer mole fractions in parentheses.

Table 1. Contact Angle Data for Perfluoroalkylethyl Methacrylate-Modified Copolymer and Isocyanate Films

sample	mole fraction $F(CF_2)_n(CH_2)_2O-$ [a]	feed[b]	contact angle water (°)		contact angle hexadecane (°)		ppm F (wt)
			adv	rec	adv	rec	
5[c]	0		75	58	0	0	0
6a[d]	2.4×10^{-4}	SF	110	69	63	54	5800
6b[d]	2.4×10^{-4}	CF	86	58	38	13	5800
3[e]	8.0×10^{-3}		81	60	29	0	950
3[e]	2.3×10^{-2}		86	61	40	12	1900
3[f]	2.7×10^{-2}		117	107	79	79	17 000

[a] In final film (copolymer + isocyanate) and based on acrylic copolymer $M_n \approx 5000$ g/mol for copolymers and added **2** for isocyanate ($M_n \approx 504$ g/mol, based on isocyanurate trimer). For the film of pure cured **3**, the mole fraction of fluorochemical is based on fluorinated alcohol **2** added to the reaction mass. [b] SF ≡ single shot addition of **4**, 10 min from the end of the reaction. CF ≡ continuous feed of **4**. [c] Styrene/butyl methacrylate/butyl acrylate/hydroxypropyl acrylate (0.18/0.27/0.17/0.37 mole fraction). [d] Styrene/butyl methacrylate/butyl acrylate/hydroxypropyl acrylate/**4** (0.19/0.26/0.17/0.38/4.0×10^{-3} mole fraction). [e] Mixed reactively with hydrocarbon acrylic copolymer **5** to prepare film. [f] Cured film prepared from pure fluorinated isocyanate **3**.

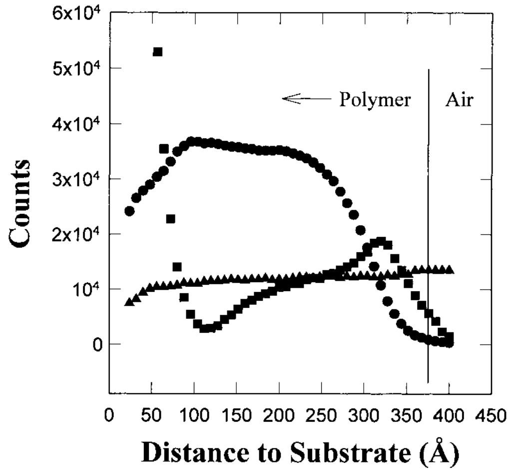

Figure 3. DSIMS data for fluorinated acrylic polymer **6b** using hydrocarbon isocyanate, **1**, crosslinking chemistry. Shown are F (■), N × 5 (●) and C (▲) as a function of depth. The film is ≈370 Å thick on a silicon wafer covered with native oxide.

tures of surfactants containing the perfluoroalkyl group $F(CF_2)_n(CH_2)_2O-$.[33]

Fluorinated Isocyanates. Film properties of isocyanate-cross-linked acrylic copolymer films are the sum of both components (copolymer and isocyanate). The use of a surface energy reduction scheme based on the isocyanate instead of the copolymer was explored. The isocyanate used in the current study is a mixture of several different oligomers of hexamethylene diisocyanate ($M_n \approx 691 \pm 54$ g/mol by vapor pressure osmometry) and dominated by the cyclic isocyanurate trimer, **1**. Representative structures are shown in Figure 4. The hypothesis was that modification of isocyanate by perfluoroalkyl chains might lead to surface activity and add synergistically to the repellent properties imparted by the fluorinated acrylic copolymers. Furthermore, the fluorinated isocyanates might be surface-active enough to replace the fluorinated acrylic copolymers in certain coatings. This was explored by the preparation of fluorine-functionalized isocyanates by reaction of isocyanate **1** with the fluorotelomer alcohol, **2**. The reaction products of **1** and **2** are shown in Figure 1. Since only a small amount of perfluoroalkyl ethyl alcohol **2** is added (~2.6 mol %), the major reaction product is the fluorinated isocyanate **3**, with a majority of the isocyanate remaining unmodified. Due to the small amount of added perfluoroalkyl ethyl alcohol **2**, characterization of the fluorinated isocyanate **3** was limited. Cast as a pure film, **3** would react with water and lose CO_2 with the formation of an amine that would react rapidly with another isocyanate to form, inter alia, a polyurea. Attempts at preparing fluorinated

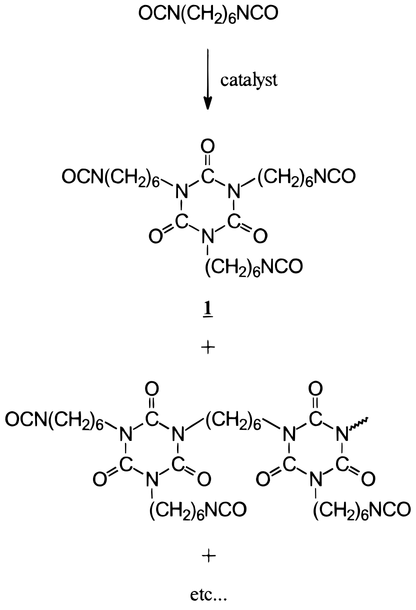

Figure 4. Polyisocyanate structures.

isocyanate **3** containing larger mole fractions (>0.1) of fluorinated alcohol **2** resulted in a gel.

The system chosen for study was based on a matrix of experiments in which the source of fluorine is varied incrementally between the two reactive components. At one extreme, all of the fluorine originates from the acrylic copolymers **6a** or **6b**. This is denoted on a mole fraction of a $F(CF_2)_n(CH_2)_2O-$ basis as "$\chi_{F(CF_2)_n(CH_2)_2O^-}$ from Polymer" in Figures 5−16. This value of "$\chi_{F(CF_2)_n(CH_2)_2O-}$ from Polymer" approaches unity when all of the fluorine originates from one of the fluorinated copolymers. On the other extreme, all of the fluorine is derived from the fluorinated isocyanate **3**. For this case, "$\chi_{F(CF_2)_n(CH_2)_2O-}$ from Polymer" approaches zero. On the other axis of Figures 5−16 is the total mole fraction of $F(CF_2)_n(CH_2)_2O-$, $\chi_{F(CF_2)_n(CH_2)_2O-}$, used in the film.

The efficiency of fluorinated isocyanate **3** alone in reducing surface energy was examined using reactive mixtures with hydrocarbon acrylic copolymer **5**. Contact angle data for such a mixture are shown in Table 1 for two levels of $F(CF_2)_n(CH_2)_2O-$ in the final film. On a mole fraction basis, the surface excess using fluorinated isocyanate **3** as the only source of fluorine was not as large as that seen using reactive mixtures of either fluorinated acrylic copolymer **6a** or **6b** as the sole source of fluorine. It is difficult to compare surface excesses on a ppm fluorine basis (Table 1) due to discrepancies in molecular weight between the two copolymers and isocyanate. Although, for comparable wt % fluorine, acrylic copolymers **6a** and **6b** were still found to be more surface-active than fluorinated isocyanate **3** when each was used as the only source of fluorine in a reactive mixture. The effects of perfluoroalkyl chain-loading levels on films prepared from reactive mixtures of fluorinated isocyanate **3** and hydrocarbon acrylic copolymer **5** can be seen in Figures 5−8 along the "$\chi_{F(CF_2)_n(CH_2)_2O-}$ from Polymer = 0" isotherm (fluorinate isocyanate **3** as the only source of fluorine in mixture).

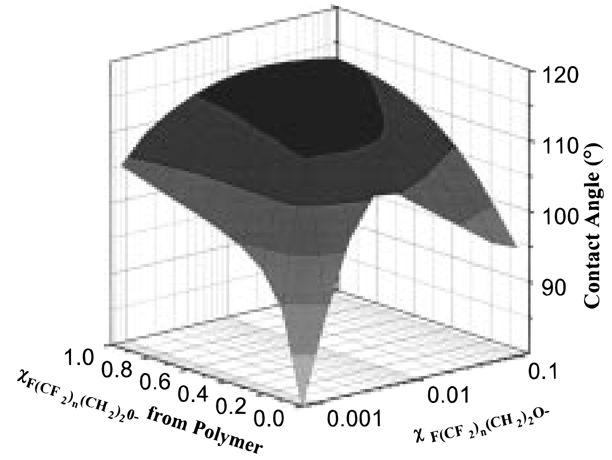

Figure 5. Advancing water contact angles as a function of fluorine source and mole fraction for fluorinated acrylic copolymer **6a** and fluorinated isocyanate **3** mixtures.

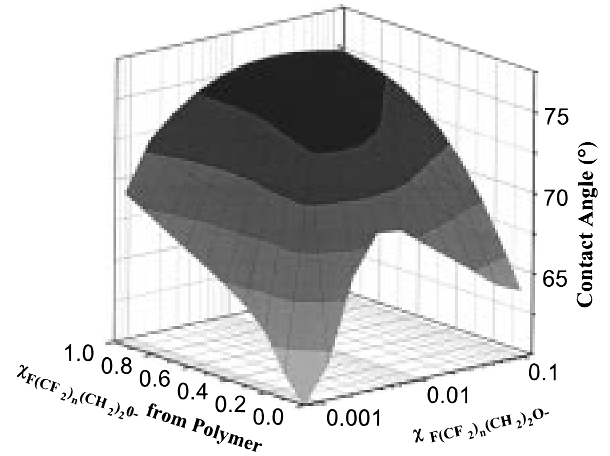

Figure 6. Receding water contact angles as a function of fluorine source and mole fraction for fluorinated acrylic copolymer **6a** and fluorinated isocyanate **3** mixtures.

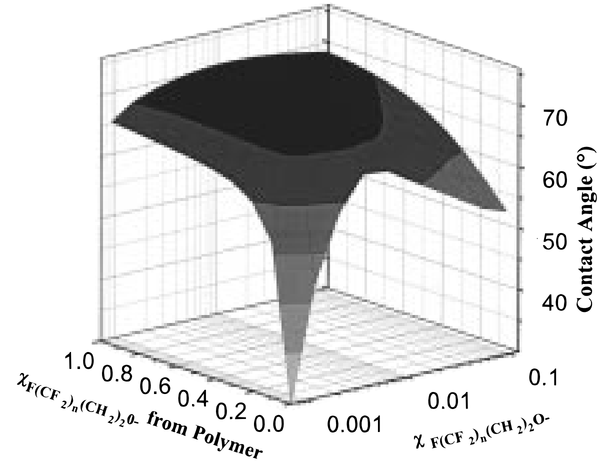

Figure 7. Advancing hexadecane contact angles as a function of fluorine source and mole fraction for fluorinated acrylic copolymer **6a** and fluorinated isocyanate **3** mixtures.

It does not appear that the fluorinated isocyanate **3** is completely dominating the surface in a film prepared by cross-linking the hydrocarbon copolymer **5**. If the surface of a mixture of fluorinated isocyanate **3** and hydrocarbon acrylic copolymer **5** was saturated with the former, much higher contact angles would be expected. A wetting layer of fluorinated isocyanate **3** on the film should be transformed by reaction with atmospheric moisture to a polyurea. Polyurea films prepared from pure fluorinated isocyanate **3** show large water and hexadecane contact angles (Table 1) with low contact angle hysteresis, indicating a surface that is at near saturation levels with perfluoroalkyl groups.[27,34,35] The

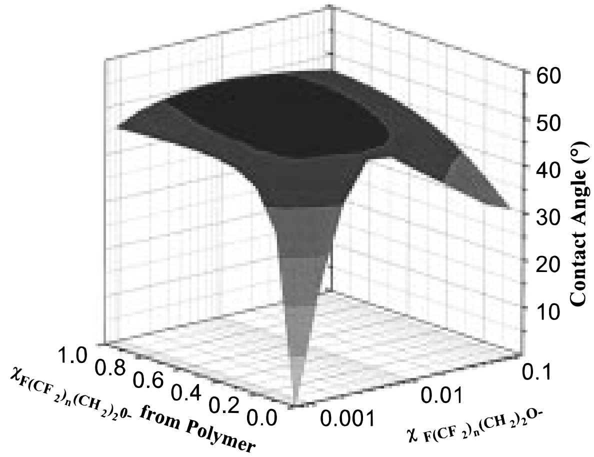

Figure 8. Receding hexadecane contact angles as a function of fluorine source and mole fraction for fluorinated acrylic copolymer **6a** and fluorinated isocyanate **3** mixtures.

relationship between surface energies of the pure components and their behavior in mixed fluorine source experiments is examined in the next sections.

Mixtures of Fluorinated Isocyanate with Fluorinated Copolymer 6a. Shown in Figures 5−8 are the contact angle data collected on systems where the only source of fluorine is either the fluorine-modified isocyanate **3** or the fluorinated acrylic copolymer, **6a**, prepared by the shot feed method of fluorinated monomer **4**. The mole fraction fluorochemical ($F(CF_2)_n(CH_2)_2O-$) values are final film estimates based on calculations assuming a copolymer molecular weight ≈5000 g/mol and an isocyanate molecular weight ≈504 g/mol. On an equal mole fraction of a $F(CF_2)_n(CH_2)_2O-$ basis, the fluorinated acrylic copolymer is much more efficient at lowering the surface energy, vide infra, of the film than is the fluorinated isocyanate. This is observed in higher contact angle values observed for both water and hexadecane using fluorinated acrylic copolymer **6a** + hydrocarbon cross-linker **1** when compared to fluorinated isocyanate **3** + hydrocarbon copolymer **5** at lower mole fractions of $F(CF_2)_n(CH_2)_2O-$ (Table 1). This suggests that fluorinated acrylic copolymer **6a** has a lower surface energy relative to fluorinated isocyanate **3** and that it should dominate the surface in a mixture of the two. A comparison of the relative surface energies of films prepared with the two materials as the sole source of fluorine in a mixture can be seen in Table 1. This effect can be observed dramatically as the source of fluorine is varied between fluorinated acrylic copolymer **6a** and fluorinated isocyanate **3** in Figures 5−8 for both advancing and receding contact angles using water and hexadecane, respectively.

A feature that is common to the data exhibited in Figures 5−8 is the decrease in the values of all contact angles as the concentration of fluorine is reduced to zero. This is a direct consequence of the Gibbs adsorption equation and will be seen in the data for all systems examined.[31]

$$\Gamma_i = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln C_i}\right)_T \qquad (2)$$

where Γ_i is the surface excess of species i, C_i is the concentration of species i, R is the ideal gas constant, T is the temperature, and γ is the surface tension. However, the relative decrease in contact angles is less when a majority of fluorine originates from the fluorinated acrylic copolymer **6a**. This effect is pronounced at low fluorochemical mole fractions ($\chi_{F(CF_2)_n(CH_2)_2O-}$), and is thought to be a consequence of the surface being at less than saturation levels of fluorinated material at low $\chi_{F(CF_2)_n(CH_2)_2O-}$. Therefore, with equal mixtures of fluorinated copolymer **6a** and fluorinated isocyanate **3**, **6a** should be in excess at the surface. This excess can be observed by the low N/F ratios in the angle-dependent ESCA data discussed later.

It has been shown that relatively small (≈2 mN/m) surface free energy differences can lead to surface volume fractions ≈1 of the lower surface free energy component.[36] This can be seen in the asymmetrical nature of the contact angle curves near the equal composition mark. If the surface energies of fluorinated acrylic copolymer **6a** and fluorinated isocyanate **3** were comparable, the contact angle values would be more symmetrical about the mixture midpoint. This hypothesis is made on the assumption of a relationship between contact angle and surface tension[37] and based on an analogy to regular solution theory of mixtures[38] extended to the solid state. Regular solution theory would predict a smooth isotherm between the two contact angle (surface energy) extremes based on mole fractions of components. The shape of the curve would be determined by thermodynamics of mixing and configurational energy for molecules of different sizes.[38] A direct correspondence between solid state and solution behavior is yet to be established. On the basis of preliminary curing studies, vide infra, the final film is estimated to be at thermodynamic equilibrium and the analogy is thought to be reasonable. Figures 5−8 indicate clearly that the largest contact angle values are obtained at high fluorine mole fraction levels when the fluorine source is biased toward fluorinated copolymer **6a**. There is a substantial penalty to be paid (based on the mole fraction) by substituting the fluorinated acrylic copolymer for the fluorinated isocyanate in a reactive mixture. On the basis of contact angle measurements, the surfaces of films prepared with a majority of fluorine from fluorinated copolymer **6a** are dominated by $-CF_3$ from the pendant $F(CF_2)_n(CH_2)_2O-$ groups oriented toward the air interface[27,34,35] with an estimated surface energy less than that of polytetrafluoroethylene.[39] The enhanced surface activity of fluorinated copolymer **6a** versus fluorinated isocyanate **3** can be seen more dramatically in the hexadecane contact angle response surfaces or isotherms (Figures 7 and 8). Hexadecane contact angles on cured films of reactive mixtures containing no fluorinated components are zero. This accounts for the much larger contact angle differences when comparing fluorinated copolymer **6a** and fluorinated isocyanate **3**.

There appears to be an interesting feature which is evident in all the contact angle data for this reactive mixture (Figures 5−8). The contact angle data seem to have a relative maximum at $\chi_{F(CF_2)_n(CH_2)_2O-}$, smaller than the largest amount of fluorochemical used as the response surface is followed along the isotherm of the majority of fluorine ($\chi_{F(CF_2)_n(CH_2)_2O-}$ from Polymer → 0) coming from fluorinated isocyanate **3**. This would seem to violate eq 2 unless the activity of fluorinated isocyanate **3** was being reduced somehow. At present, not enough information is available to comment on the solution thermodynamics of fluorinated isocyanate **3**.

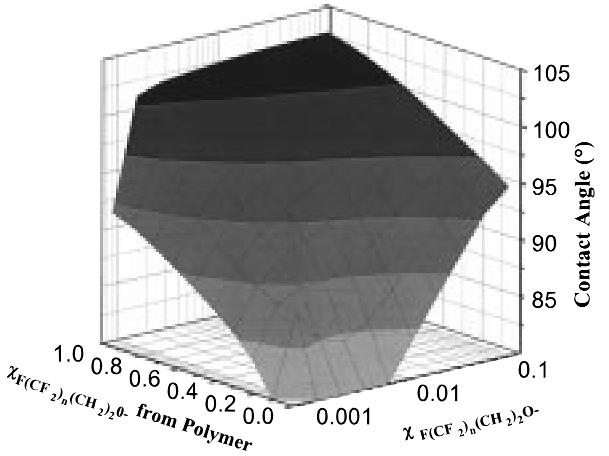

Figure 9. Advancing water contact angles as a function of fluorine source and mole fraction for fluorinated acrylic copolymer **6b** and fluorinated isocyanate **3** mixtures.

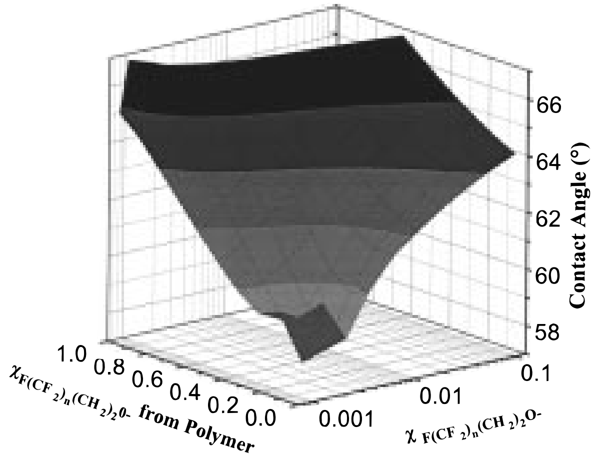

Figure 10. Receding water contact angles as a function of fluorine source and mole fraction for fluorinated acrylic copolymer **6b** and fluorinated isocyanate **3** mixtures.

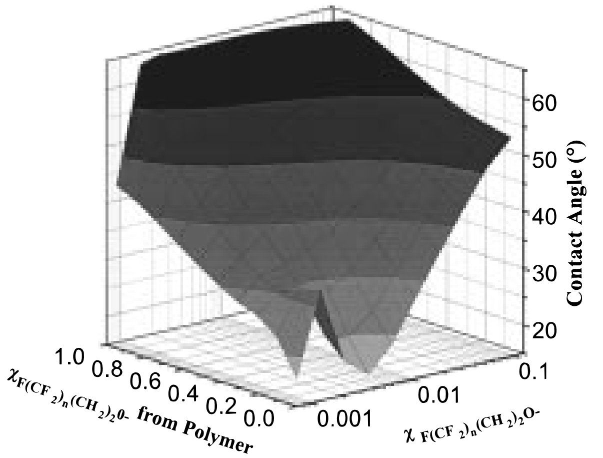

Figure 11. Advancing hexadecane contact angles as a function of fluorine source and mole fraction for fluorinated acrylic copolymer **6b** and fluorinated isocyanate **3** mixtures.

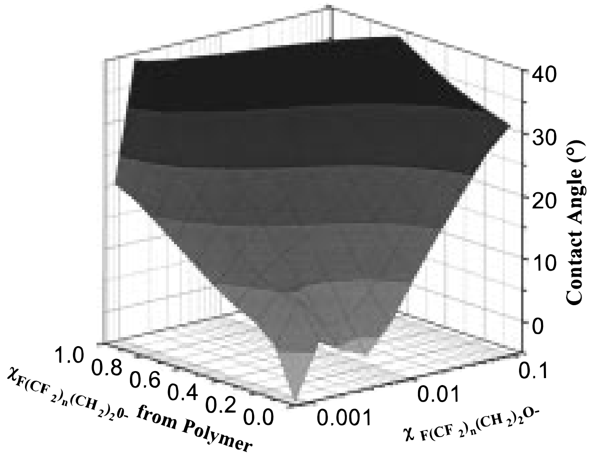

Figure 12. Receding hexadecane contact angles as a function of fluorine source and mole fraction for fluorinated acrylic copolymer **6b** and fluorinated isocyanate **3** mixtures.

Mixtures of Fluorinated Isocyanate with Fluorinated Copolymer 6b. Surface properties of a series of mixed fluorine-source coatings prepared from the continuous feed fluorinated acrylic copolymer **6b** and fluorinated isocyanate **3** were examined. The contact angle data obtained from this system are markedly different from that obtained using the fluorinated acrylic copolymer **6a**. The reduced fluorine effectiveness and efficiency of the fluorinated copolymer **6b** are evident when compared to that of fluorinated copolymer **6a** (compare Figures 5−8 with 9−12) using comparable cross-linking chemistries. Overall, the contact angles obtained on surfaces of the reactive mixture of fluorinated copolymer **6b** with fluorinated isocyanate **3** are less than those obtained for the fluorinated copolymer **6a** + fluorinated isocyanate **3** at comparable $\chi_{F(CF_2)_n(CH_2)_2O-}$. This is suggested by the comparison of the relative surface energies that can be estimated from Table 1. The data indicate that fluorinated copolymer **6b** and fluorinated isocyanate, **3**, might be able to compete effectively for the surface of the coating. The contact angle versus fluorine source data are more symmetrical about the equal mixture mark. This can be observed in the contact angle isotherms exhibited in Figures 9−12 that are much more planar than those for reactive mixtures of fluorinated copolymer **6a** and fluorinated isocyanate **3**. The water and hexadecane advancing contact angle isotherms slope downward to the lower fluorine levels, as anticipated from eq 2. Further evidence substantiating the fact that fluorinated copolymer **6b** and fluorinated isocyanate **3** are mixing at the air/polymer interface is given by comparing the contact angle data obtained on reactive mixtures of the two compared to the film of pure cured **3** (Table 1). If the surface was dominated completely by fluorinated isocyanate **3** upon mixing, contact angles comparable to those measured for the film of pure fluorinated isocyanate **3** would be expected. This hypothesis is based on the assumption of the eventual formation of a wetting layer of polyurea on the film surface.

ESCA Depth Profiling of Mixtures of Fluorinated Isocyanate 3 with Fluorinated Acrylic Copolymer 6a. The mixing of fluorinated acrylic copolymer and fluorinated isocyanate in the surface region was probed by angle-dependent ESCA examination. The nitrogen/fluorine atomic ratio (N/F) was measured, as a function of incident X-ray angle, for several of the fluorinated acrylic copolymer/fluorinated isocyanate mixtures. It is important to mention that the acrylic copolymers contain no nitrogen, so that the nitrogen signal will arise only from the presence of isocyanate at the surface (∼0−100 Å). The calculated N/F ratio for both cross-linked acrylic fluorinated copolymers, **6a** or **6b**, is ≈ 14 based on no surface excess of the fluorinated copolymer and the use of unmodified isocyanate **1**. The calculated N/F ratio for the cross-linking

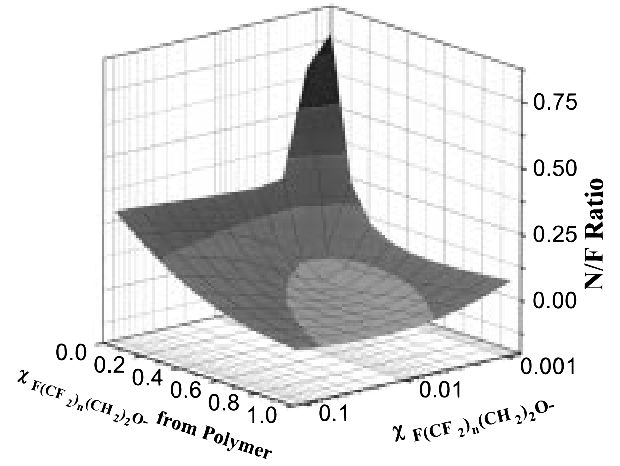

Figure 13. ESCA N/F atomic ratios for fluorinated acrylic copolymer **6a**/fluorinated isocyanate **3** mixtures (30° take-off angle) as a function of composition.

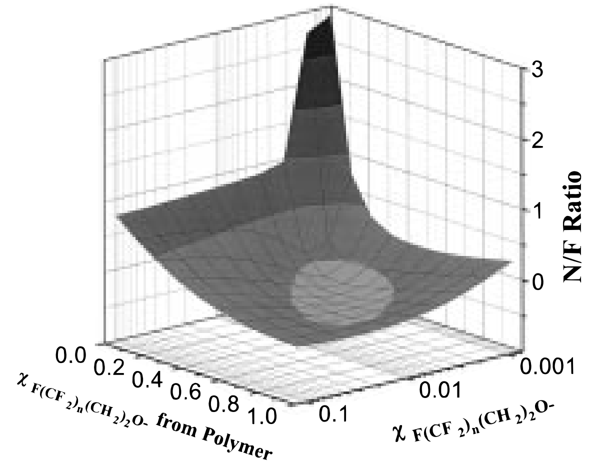

Figure 14. ESCA N/F atomic ratios for fluorinated acrylic copolymer **6a**/fluorinated isocyanate **3** mixtures (90° take-off angle) as a function of composition.

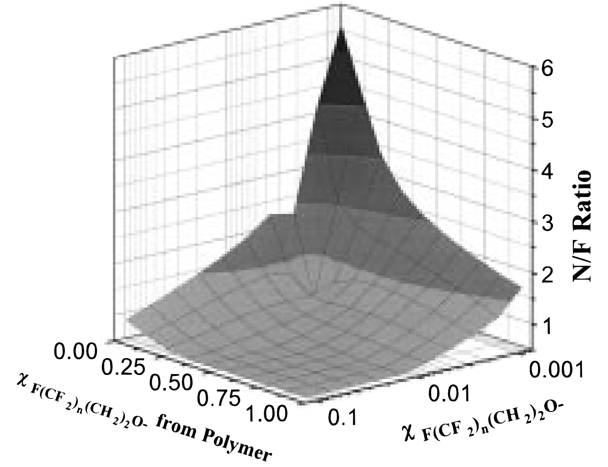

Figure 15. ESCA N/F atomic ratios for fluorinated acrylic copolymer **6b**/fluorinated isocyanate **3** mixtures (30° take-off angle) as a function of composition.

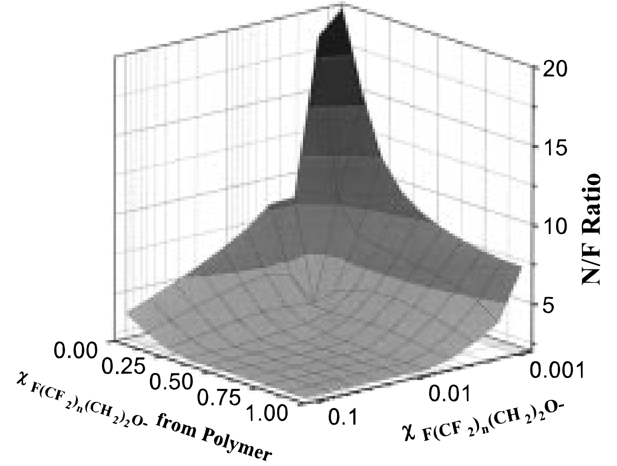

Figure 16. ESCA N/F atomic ratios for fluorinated acrylic copolymer **6b**/fluorinated isocyanate **3** mixtures (90° take-off angle) as a function of composition.

of nonfluorinated acrylic copolymer, **5**, with fluorinated isocyanate **3** is ≈13, again, assuming no surface excess of fluorinated material. The N/F ratio of the unmodified copolymer **5** with unmodified isocyanate **1** is undefined since there is no fluorine present in this case. Previous work has shown that the N/F ratios observed experimentally to be ≈4.6×10^{-2} at a 30° takeoff angle and ≈ 0.14 at a 90° takeoff angle.[23] The surface-tension-driven excess of fluorinated acrylic copolymer **6a** at the surface clearly precludes isocyanate **1** from entering the sampling depth of the ESCA measurement (∼0−100 Å, depending on the takeoff angle).

Shown in Figures 13 and 14 are the ESCA N/F atomic ratios as a function of the $\mathrm{F(CF_2)}_n\mathrm{(CH_2)_2O-}$ mole fraction, $\chi_{\mathrm{F(CF_2)}_n\mathrm{(CH_2)_2O-}}$, and source using the fluorinated acrylic copolymer **6a**, prepared by shot feeding of monomer **4** and fluorinated isocyanate **3** at 30° and 90°, respectively. Common to both figures are relatively low N/F ratios, not exceeding 6 in either example. At high fluorinated acrylic copolymer-to-fluorinated isocyanate ratios until the mole fraction of fluorochemical drops to very low levels, the N/F ratio is low, indicating that the fluorinated acrylic copolymer **6a** is very effective in screening the fluorinated isocyanate **3** away from the surface. Only when the source of fluorine is almost exclusively from the fluorinated isocyanate **3** and $\chi_{\mathrm{F(CF_2)}_n\mathrm{(CH_2)_2O-}}$ approaches zero do the N/F ratios exceed 1.

Another feature of interest is the difference in N/F ratios at the two takeoff angles as the mixture is enriched in fluorinated isocyanate **3** (N/F ≈ 1.5 at 30° and N/F ≈ 6 at 90°). This can occur only if there is a surface tension gradient normal to the surface (excluding phase separation or insolubility). The exclusion of fluorinated isocyanate **3** from the surface in the presence of the lower surface energy fluorinated acrylic copolymer **6a** implies that an excess (gradient) of isocyanate must exist elsewhere. The greater sampling depth at a 90° takeoff angle (∼100 Å at 90° vs ∼50 Å at 30°) exposes the concentration gradient of fluorinated isocyanate lying normal to the surface.

ESCA Depth Profiling of Mixtures of Fluorinated Isocyanate 3 with Fluorinated Acrylic Copolymer 6b. Shown in Figures 15 and 16 are 30° and 90° ESCA N/F ratios, respectively, for reactive mixtures of fluorinated acrylic copolymer **6b**, prepared by continuous feeding of monomer **4** and fluorinated isocyanate **3**. The N/F response surfaces are similar to those obtained with mixtures of fluorinated copolymer **6a** and fluorinated isocyanate **3**, but the magnitude of the N/F ratio is larger. The N/F values again increase as $\chi_{\mathrm{F(CF_2)}_n\mathrm{(CH_2)_2O-}}$ decreases and as the fluorine source is biased toward the fluorinated isocyanate **3**. However, N/F ratios reach much larger values of ~3.5−4.5 (30° takeoff angle) and ~12−16 (90° takeoff angle). The increased N/F ratio indicates that the mixture surface is becoming enriched in fluorine with fluorinated isocyanate **3** as the source. With a reactive mixture consisting of fluorinated copolymer **6b** and fluorinated isocyanate **3**, the effect of a surface free energy gradient is lessened. In essence, the entire system is becoming more homogeneous in component distribution.

Discussion

Through a judicious choice of fluorinated components, it is possible to control the surface energy of a final film. This has been demonstrated on reactive mixtures of various acrylic copolymers and isocyanates. By varying not only the fluorinated component but its amount as well, a variety of low surface energy films can be fabricated. Contact angles on cured films obtained from reactive mixtures of fluorinated acrylic copolymers **6a** and **6b**, hydrocarbon acrylic copolymer **5**, fluorinated isocyanate **3**, and hydrocarbon isocyanate **1** in various proportions have been used to demonstrate the concept. The surface composition implied from contact angle measurements of these films is corroborated by angle-dependent ESCA data. In reactive mixtures, the surface energy of the final cured film is dominated by the component with the lower surface energy. The ESCA data on these same films substantiate the observation that the surface region is dominated by the lower surface energy component. This observation neglects any solution thermodynamic effects, such as mixing, that can play an important role in determining the composition of a mixture surface.

Solution thermodynamics may play an important role in the current investigation. The difference in surface energy estimated using films prepared with fluorinated acrylic copolymers **6a** or **6b** with hydrocarbon isocyanate **1** has been explained due to differences in synthetic procedure. It is difficult to understand why the fluorinated isocyanate **3** is not very surface-active. According to the principle of Braun and Le Chatelier, it is know that a decrease in surface energy in a mixture is caused by an increase in adsorption of the component with the smaller molecular area demand.[40] On the basis of this fact alone, it can be argued that the partial molar area demand increases as fluorinated acrylic copolymer **6a** < fluorinated acrylic copolymer **6b** ≤ fluorinated isocyanate **3**. The increase in area demand for fluorinated acrylic copolymer **6b** relative to that of fluorinated acrylic copolymer **6a** is easy to understand. The fluorinated copolymer **6b** is estimated to contain less of the fluorinated monomer **4** along each chain. Attempting to bring all the perfluoroalkyl chains to the surface would, necessarily, drag other nonfluorinated, hydrocarbon monomers incorporated into the polymer chain into the interface. This would result in a significant increase in molecular area demand compared to fluorinated copolymer **6b** which should be more efficient at packing the surface with perfluoroalkyl chains. The lower relative surface activity of fluorinated isocyanate **3** is more difficult to explain simply based on molecular architecture and area demand. The fluorinated acrylic copolymers **6a** and **6b** ($M_n \approx 6000$ g/mol, $M_w \approx 5000$ g/mol) are larger than the oligomeric fluorinated isocyanate **3** ($M_n \approx 691 \pm 54$ g/mol), yet are more surface-active. On a mole fraction basis, the fluorinated isocyanate **3** contains much more $F(CF_2)_n(CH_2)_2O-$ (2.7×10^{-2}) than do the fluorinated acrylic copolymers **6a** or **6b** (2.4×10^{-4}). A molecule of fluorinated isocyanate **3** should be more surface-active than one chain of the fluorinated copolymers **6a** or **6b**. This is demonstrated by the large contact angles obtained from films of pure-cured fluorinated isocyanate **3** (without acrylic copolymers **6a**, **6b**, or **5**).

The molecular area demand discrepancy between fluorinated acrylic copolymers **6a** or **6b** and fluorinated isocyanate **1** appears to be one of thermodynamics not kinetics. Torsional braid rheological measurements suggest a gel time ≈60 min and a vitrification time ≈4 days at 30 °C for these systems.[41] This time should be sufficient to allow relatively small molecules to diffuse to and saturate the surface. Therefore, it is doubtful that the fluorinated acrylic copolymers **6a** or **6b** or fluorinated isocyanate **3** have increased their molecular area demand by reaction prior to migration to the film surface. A possible explanation is that there are interaction parameters (copolymer/isocyanate and/or isocyanate/isocyanate) that would favor bulk-mixing thermodynamics versus surface segregation. Such phenomena have been noted previously in compatible mixtures[36,42] and used to explain the diminished surface excess predicted by surface tension differences alone compared to those obtained experimentally.[43] In addition, aggregation phenomena would not be unexpected, particularly, in systems containing relatively large amounts of fluorine such as that found in the fluorinated isocyanate **3**.[44]

The ultimate low surface energy attainable by a mixture of surface-active components can be lower than that afforded by any of the components and is termed synergy. The physical conditions leading to synergism have been detailed previously.[45] In the present case, synergism would be very attractive. From the data presented in Figures 5−8, it can be seen that mixtures of the fluorinated acrylic copolymer **6a** with the fluorinated isocyanate **3** produce initial surface energies (estimated by contact angle measurements) that are intermediate between the two materials. If surface energy synergy was present, contact angles larger (or surface energy lower) for mixtures than the pure components would be exhibited. Relative maxima in the contact angle versus fluorine source curves (Figures 5−12) are absent, substantiating a lack of synergism. No relative maxima are observed when examining the contact angle data (Figures 9−12) for mixtures of fluorinated copolymer **6b** and fluorinated isocyanate **3**. In the present investigation, no evidence is seen for synergism between the two fluorinated components concerning surface tension reduction.

Conclusions

A surface-active fluorinated isocyanate, **3**, can be prepared easily by the reaction of hydroxyl-terminated perfluoroalkyl precursors, such as **2**, with an isocyanate such as the isocyanurate trimer of hexamethylene diisocyanate **1**. When used as a cross-linker with hydrocarbon acrylate copolymers containing a reactive hydroxyl monomer, surface segregation of the resulting fluorinated material occurs, resulting in surface energy lowering of films. Initial surface properties of these fluorinated systems are excellent. For example, water and hexadecane advancing contact angles ≈86° and 40°, respectively, can be obtained on films containing ~ 2.3×10^{-2} mole fraction of $F(CF_2)_n(CH_2)_2O-$ (~1900 ppm

F by weight). By comparison, the reactive mixture of hydrocarbon acrylic copolymer **5** with hydrocarbon isocyanate **1** formed films with water and hexadecane advancing angles ≈75° and 0°, respectively. When fluorinated isocyanate **3** is used to cross-link a more surface-active fluorinated acrylic copolymer, **6a**, surface energy lowering is observed but the surface is dominated with fluorine arising from **6a**. Angle-dependent ESCA data on this mixture suggests that there is not a great deal of interfacial mixing of the two fluorinated materials. When fluorinated isocyanate **3** is used to cross-link a less surface-active fluorinated acrylic copolymer, **6b**, surface energy lowering is observed. Angle-dependent ESCA data indicate that there is now substantial mixing of the two fluorinated materials at the air/polymer interface. For both mixed fluorine source reactive systems, fluorinated acrylic copolymers **6a** or **6b** with fluorinated isocyanate **3**, no evidence exists for either surface energy synergy or agonistic interactions between the two components.

Experimental Section

General. The preparation of acrylic copolymers **5**, **6a**, and **6b**, contact angle measurement and DSIMS protocol, materials, analytical methods, and sample preparation have been described in a previous report and will be mentioned here briefly.[23] The perfluoroalkylethyl alcohol, $F(CF_2)_n(CH_2)_2OH$, **2**, was obtained from E. I. du Pont de Nemours and Co. and is sold under the tradename ZONYL BA. The value of *n* ranges from 6−12; the average ≈ 7.8. The polyisocyanate cross-linker was Desmodur N3300 (Miles, Inc.) and based on the isocyanurate trimer of hexamethylene diisocyanate.

Film Preparation. (1) Contact Angles and ESCA. After appropriate mixing of isocyanate and acrylic copolymer, films were applied on steel panels by spraying, using a Devilbiss gun. The samples were then dried for 30 min in a 90 °C convection oven for 30 min. The nominal film thickness was 2.2 mil. For all mixtures, the ratio of isocyanate-to-acrylic copolymer was kept constant to ensure a mole ratio of acrylic copolymer hydroxyl/isocyanate NCO = 3

(2) DSIMS. After of the isocyanate and acrylic copolymer were appropriately mixed and diluted, samples were cast by spin coating. The samples were then dried for 30 min in a 90 °C convection oven for 30 min. Sample thicknesses were checked by ellipsometry.

(3) Vapor Pressure Osmometry. Measurements were performed using a Wescan model 233 vapor-pressure osmometer (Jupiter Instrument Co.). The instrument was calibrated using PMMA ($M_n = 8338$ g/mol, PD = 1.55; Aldrich, secondary standard) in CH_2Cl_2 (spectral grade) for polymers and squalene (Eastman; purified by fractional crystallization) in *n*-butyl acetate (Acros Organic Chemicals; 99+%). Several batches of **5** were analyzed in CH_2Cl_2, yielding $M_n \approx 4500-5000$ g/mol. The molecular weight (M_n) for Desmodur N3300 was determined to be 691 ± 54 g/mol.

(5) Contact Angle Goniometry. Sessile drop contact angle measurements were performed using a Ramé-Hart model 100 contact angle goniometer. Four drops of the appropriate liquid were used to measure contact angles with standard deviations ≈2°.

(6) Preparation of Fluorinated Isocyanate, 3. Into a 5-L flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and thermocouple is added (under positive nitrogen pressure) 4.835 kg (~9.58 mol) of isocyanate **1**. To this mixture are added 116 g (0.255 mol) of perfluorolalkylethyl alcohol, **2**, and 0.50 g (0.158 mmol) of catalyst. The catalyst is comprised of ethyl acetate (98 wt %) and di-*n*-butyl tin dilaurate (2 wt %). The mixture is heated to 75−80 °C for 2 h. The reaction product was kept in a sealed container while not in use to prevent reaction with atmospheric moisture.

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References and Notes

(1) Honeychuck, R. V.; Ho, T.; Wynne, K. J.; Nissan, R. A. *Chem. Mater.* **1993**, *5*, 1299.
(2) Chapman, T. M.; Marra, K. G. *Macromolecules* **1995**, *28*, 2081.
(3) Yoon, S. C.; Ratner, B. D. *Macromolecules* **1986**, *19*, 1068.
(4) Yoon, S. C.; Ratner, B. D. *Macromolecules* **1988**, *21*, 2392.
(5) Yoon, S. C.; Ratner, B. D. *Macromolecules* **1988**, *21*, 2401.
(6) Yoon, S. C.; Sung, Y. K.; Ratner, B. D. *Macromolecules* **1990**, *23*, 4351.
(7) Yoon, S. C.; Ratner, B. D.; Iván, B.; Kennedy, J. P. *Macromolecules* **1994**, *27*, 1548.
(8) Tang, Y. W.; Santerre, J. P.; Labow, R. S.; Taylor, D. G. *J. Appl. Polym. Sci.* **1996**, *62*, 1133.
(9) Park, I. J.; Lee, S.-B.; Choi, C. K. *J. Appl. Polym. Sci.* **1994**, *54*, 1449.
(10) Kano, Y.; Akiyama, S. *Polymer* **1996**, *37*, 4497.
(11) Elman, J. F.; Johs, B. D.; Long, T. E.; Koberstein, J. T. *Macromolecules* **1994**, *27*, 5341.
(12) Dee, G. T.; Sauer, B. B. *Adv. Phys.* **1998**, *47*, 161.
(13) Affrossman, S.; Bertrand, P.; Hartshorne, M.; Kiff, T.; Leonard, D.; Pethrick, R. A.; Richards, R. W. *Macromolecules* **1996**, *29*, 5432.
(14) Schaub, T. F.; Kellog, G. J.; Mayes, A. M.; Kulasekere, R.; Ankner, J. F.; Kaiser, H. *Macromolecules* **1996**, *29*, 3982.
(15) McLain, S. J.; Sauer, B. B.; Firment, L. E. *Macromolecules* **1996**, *29*, 8211.
(16) van der Grinten, M. G. D.; Clough, A. S.; Shearmur, T. E.; Bongiovanni, R.; Priola, A. *J. Colloid Interface Sci.* **1996**, *182*, 511.
(17) Park, I. J.; Lee, S.-B.; Choi, C. K.; Kim, K.-J. *J. Colloid Interface Sci.* **1996**, *181*, 284.
(18) DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *257*, 945.
(19) Kassis, C. M.; Steehler, J. K.; Betts, D. E.; Guan, Z.; Romack, T. J.; DeSimone, J. M.; Linton, R. W. *Macromolecules* **1996**, *29*, 3247.
(20) Schmidt, D. L.; Coburn, C. E.; DeKoven, B. M.; Potter, G. E.; Meyers, G. F.; Fischer, D. A. *Nature* **1994**, *368*, 39.
(21) Schmidt, D. L.; DeKoven, B. M.; Coburn, C. E.; Potter, G. E.; Meyers, G. F.; Fischer, D. A. *Langmuir* **1996**, *12*, 518.
(22) Iyengar, D. R.; Perutz, S. M.; Dai, C.-A.; Ober, C. K.; Kramer, E. J. *Macromolecules* **1996**, *29*, 1229.
(23) Thomas, R. R.; Anton, D. R.; Graham, W. F.; Darmon, M. J.; Sauer, B. B.; Stika, K. M.; Swartzfager, D. G. *Macromolecules* **1997**, *30*, 2883.
(24) Anton, D. R.; Darmon, M. J.; Graham, W. F.; Thomas, R. R. U.S. Patent 5,597,874, 1997; *Chem. Abstr.* **1997**, *126*, 200709.
(25) Anton, D. R.; Darmon, M. J.; Graham, W. F.; Thomas, R. R. U.S. Patent 5,605,956, 1997; *Chem. Abstr.* **1997**, *126*, 239675.
(26) Anton, D. R.; Darmon, M. J.; Graham, W. F.; Thomas, R. R. U.S. Patent 5,629,372, 1997; *Chem. Abstr.* **1997**, *127*, 52290.
(27) Johnson, R. E., Jr.; Dettre, R. H. In *Wettability*; Berg, J. C., Ed.; Marcel Dekker: New York, 1993; Chapter 1.
(28) Kumler, P. L.; Matteson, H. L.; Gardella, J. A., Jr. *Langmuir* **1991**, *7*, 2479.
(29) Rastogi, A. K.; St. Pierre, L. E. *J. Colloid Interface Sci.* **1969**, *31*, 168.
(30) Takemura, A.; Shimizu, Y.; Tomita, B.; Mizumachi, H. *J. Adhes.* **1992**, *37*, 161.
(31) Defay, R.; Prigogine, I.; Bellemans, A.; Everett, D. H. *Surface Tension and Adsorption*; Wiley: New York, 1966; Chapter 7.
(32) Rosen, M. J. In *Phenomena in Mixed Surfactant Systems*; Scamehorn, J. F., Ed.; American Chemical Society: Washington, DC, 1986; p 144.
(33) Thomas, R. R.; Taylor, C. K.; Hoffman, M., unpublished results.
(34) Schönherr, H.; Ringsdorf, H.; Jaschke, M.; Butt, H.-J.; Bamburg, E.; Allinson, H.; Evans, S. D. *Langmuir* **1996**, *12*, 3898.

(35) Schönherr, H.; Ringsdorf, H. *Langmuir* **1996**, *12*, 3891.
(36) Jones, R. A. L.; Kramer, E. J. *Polymer* **1993**, *34*, 115.
(37) ref 31, Chapter 1.
(38) ref 31, Chapters 12 and 13.
(39) Wu, S. *Polymer Interface and Adhesion*; Marcell Dekker: New York, 1982; Chapter 3.
(40) Fainerman, V. B.; Miller, R. *Langmuir* **1997**, *13*, 409.
(41) Thomas, R. R.; Graham, W. F.; Kevrekidis, I. G.; Gillham, J. K.; Achilleos, E., unpublished results.
(42) Sakellariou, P. *Polymer* **1993**, *34*, 3408.
(43) Cowie, J. M. G.; Devlin, B. G.; McEwen, I. J. *Polymer* **1993**, *34*, 4130.
(44) Petit, F.; Iliopoulos, I.; Audebert, R.; Szönyi, S. *Langmuir* **1997**, *13*, 4229.
(45) Rosen, M. J. *Surfactants and Interfacial Phenomena*, 2nd ed.; Wiley: New York, 1989; p 393.

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