Preparation and Surface Properties of Acrylic Polymers Containing Fluorinated Monomers

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ABSTRACT: A series of novel polymers have been prepared by free radical solution polymerization of a variety of hydrocarbon monomers with the (perfluoroalkyl)ethyl methacrylate monomer $H_2C{=}C(CH_3)$-$CO_2(CH_2)_2(CF_2)_nF$, **1** ($\bar{n} \approx 7.7$). Polymers prepared using two different methods of feeding **1** into the reaction mass are discussed. Through a judicious choice of reaction conditions, some control of polymer architecture was exhibited. The resultant (perfluoroalkyl)ethyl methacrylate-containing acrylic polymers were shown to be quite surface active in the solid state. The magnitude of surface activity depends on the monomer **1** feed method. The polymers were formulated into thin films and applied to a variety of surfaces. With levels at 1.5 wt % of **1**, water and oil repellent surfaces were created. Water contact angles (advancing) of ∼80−115° and hexadecane contact angles (advancing) of ∼60−70° were observed routinely. In addition, it was observed that the concentration profile of fluorine in the films exhibited a steep gradient normal to the surface when studied by angle-dependent ESCA and secondary ion mass spectroscopic depth profiling.

Introduction

Organic polymer films have found wide application for coating a diverse array of materials. The surface properties of these films is of paramount importance for such applications where adhesion concerns are present. For example, lowering the surface tension of a film is desirable for formulating nonwettable surfaces. One of the most popular and successful strategies for lowering the surface tension of a film is incorporation of fluorine into the polymer molecule 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 presented. Surface tension reduction has also been studied using blends of fluoropolymers with hydrocarbon polymers.[9,10] Several reports have used the propensity of enthalpically driven chain-end enrichment at surfaces[11,12] in conjunction with fluorination to alter surface tensions.[13−15] Surface tension reduction has also been reported for copolymers prepared by incorporation of fluorinated monomers [16−21] and by grafting perfluoroalkyl groups to polymers chemically.[22]

However, the previous studies have focused mainly on polymers which contain relatively large weight fractions of fluorinated components (∼1−8 atom % F for polyurethanes;[1] ∼0.2−0.6 mole fraction fluoromonomers in acrylates[16−20]). The current work will demonstrate that large weight fractions of fluorinated materials are not necessary to achieve low surface tensions. An example of achieving surface tension reduction by blending small amounts of perfluoroalkyl-ended polyethylenes into polyethylene has been reported.[15] Furthermore, the present systems are cross-linkable, giving high molecular weight, durable films without dealing with viscous solutions or melts. It is the surface activity of these molecules which plays the important role in the magnitude of surface tension reduction. It will also be shown that judicious choices of reaction conditions will allow some control of polymer architecture and molecular weight. The surfaces of these films will be examined using contact angle measurements, X-ray photoelectron spectroscopy (ESCA), time-of-flight static secondary ion mass spectroscopy (ToF-SIMS), and dynamic secondary ion mass spectroscopy (DSIMS).

Results and Discussion

Synthesis of Acrylate Polymer Systems. The conditions used to make the (perfluoroalkyl)ethyl methacrylate-containing acrylic polymers are typical of those used to prepare acrylic polymers. The standard polymer system is prepared by the free radical polymerization (using *tert*-butyl peroxyacetate as initiator) of butyl methacrylate, styrene, butyl acrylate, and hydroxypropyl acrylate in methyl amyl ketone solvent using semibatch, monomer-starved conditions. The composition of this typical acrylic polymer, **2**, is shown in Figure 1. In an effort to make comparisons between standard and fluorine-containing polymers equitable, fluorinated versions of the polymers were prepared by substitution of small amounts of $H_2C{=}C(CH_3)CO_2(CH_2)_2(CF_2)_nF$, **1**, for butyl methacrylate. A variety of fluorinated acrylate monomers have been shown to provide surface active molecules;[23] however, this work will focus on one particular variant, **3**, which incorporates the fluorinated monomer **1**. The pure polymer systems will have a $T_g \approx 0$ °C so cross-linking is necessary to provide the desired mechanical properties. The cross-linker employed in the current study is the isocyanurate trimer of hexamethylene diisocyanate and is shown in Figure 2. Synthetically, the parameters varied included reac-

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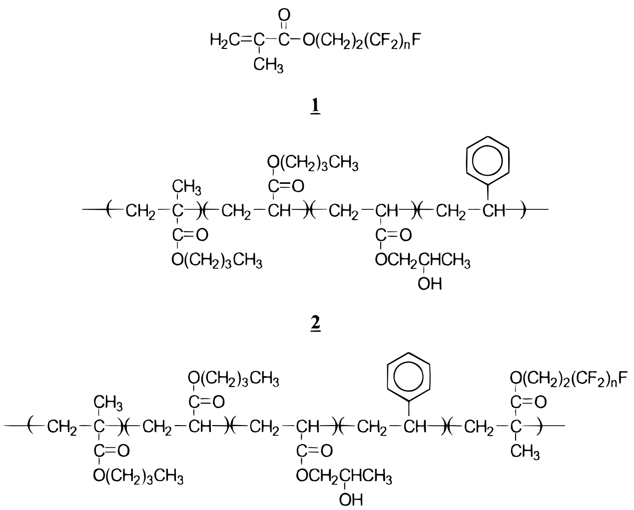

3a 1.5 wt% **1**, shot feed
3b 3.0 wt% **1**, shot feed
3c 6.0 wt% **1**, shot feed
3d 1.5 wt% **1**, continuous feed
3e 3.0 wt% **1**, continuous feed

Figure 1. Types of acrylic monomers and polymers examined.

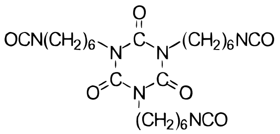

Figure 2. Structure of the isocyanurate trimer of hexamethylene diisocyanate.

tion time, addition method of fluorinated acrylate monomer, and amount of fluorinated methacrylate monomer.

Previous attempts at formulating low surface tension, fluorine-containing acrylate coatings failed because of inefficient and ineffective use of fluorine which necessitated the use of large amounts of fluorinated acrylate or methacrylate monomers. Furthermore, the large amount of added fluorine often decreases valuable bulk properties. From the data, *vide infra*, it can be seen that the amount of fluorinated monomer and especially the method of addition affected the final surface properties of the polymer most. The addition dwell time of the fluorinated monomer (for example, shot vs continuous feed) has provided the single greatest variation in these polymers.

The results of this work will focus on two types of polymers prepared using identical amounts of fluorinated monomer **1**. One is prepared by the continuous feed addition of **1** to the reaction mass. The other by the addition of a shot of **1** to the reaction designed to perturb steady-state polymerization conditions. As an example, polymers **3a**−**3c** were prepared by the addition of the entire amount of **1** as rapidly as possible (i.e., as a shot), under current experimental conditions, 10 min prior to the end of the polymerization reaction. Several variations of the shot feed method were examined and the polymers obtained found to be surface active. In addition, the surface properties of polymers similar to **3** were prepared using a variety of fluorinated acrylic monomers and different feed methods. The results are comparable to the series based on **3**.

A comparison of the types of polymers prepared using these two types of synthetic protocols is worth noting. Under the conditions used to prepare **3c** and **3d** (continuous feed of **1**), the fluorinated monomer is added under starved-feed conditions. This results in a steady-state concentration of **1** (and all monomers as well) in the reaction mass. The steady-state concentration condition ensures that all polymer chains will have identical compositions and molecular weights. The shot feed addition of **1** is a perturbation of the steady-state conditions employed in producing **3a**−**3c**. Not only does the shot addition affect the instantaneous composition of the polymer, it alters the molecular weight distribution during addition of **1** by increasing the molecular weight (substitution of lighter hydrocarbon monomers by **1**) and degree of polymerization (addition of monomer without addition of initiator). In essence, the shot feed method resembles blending of a fluorinated system with a nonfluorinated one. Moreover, the preparation, *in situ*, of fluorinated polymer chains seems to ensure the compatibility of the fluorinated polymers with the unmodified one.

The composition of the continuous feed polymers **3d** and **3e** is identical throughout the course of polymerization with each polymer chain containing only a small fraction of **1**. Statistically, this polymer chain will contain a few blocks of (perfluoroalkyl)ethyl methacrylate polymer of any appreciable length and is not expected to result in a particularly effective or efficient surface active species. Contrast this to the type of polymer system prepared when **1** is added as a shot 10 min from the end of the reaction. Until the shot addition of **1**, the polymer chains contain no incorporated (perfluoroalkyl)ethyl methacrylate monomer. As **1** is added, the instantaneous composition of the polymer is richer in fluorocarbon monomer at the expense of the hydrocarbon monomers. Statistically, there is a greater chance of longer blocks of (perfluoroalkyl)ethyl methacrylate in the polymer chain. This should result in a polymer which is a much more effective and efficient surface active species.

Surface Tensions of Acrylate Polymers. As discussed previously, the commercial application of a fluorine-containing acrylate polymer system depends heavily on the effective and efficient use of fluorine. The terms effectiveness and efficiency are borrowed from the language of surfactant science. The term effectiveness refers to the amount that the addition of fluorine lowers the surface tension relative to the parent material. The efficiency term refers to the minimum concentration of fluorine necessary to reach the minimum surface tension. The origin of these effects can be seen from the Gibbs adsorption equation[24]

$$\gamma = f^{\sigma} - \sum_i \Gamma_i \mu_i^{\sigma} \tag{1}$$

where γ is surface tension, Γ is surface excess of i in moles per unit area of surface σ, μ_i^{σ} is the surface chemical tial of the ith species and f^{σ} is the Helmholtz free energy per unit area of surface σ. For a two-component system at constant temperature the equation is stated below.[25]

$$d\gamma = -\Gamma_1 d\mu_1^{\sigma} - \Gamma_2 d\mu_2^{\sigma} \tag{2}$$

The subscripts *1* and *2* refer to the two different species in the mixture. Consider the case of a binary polymer mixture, one of them being a hydrocarbon acrylate polymer and the other a block copolymer of (perfluoroalkyl)ethyl methacrylate and hydrocarbon acrylate. Rearrangement of the Gibbs adsorption equation leads to an expression relating surface excess and surface

Table 1. Contact Angle Data for (Perfluoroalkyl)Ethyl Methacrylate-Modified Acrylic Polymers

			contact angle (deg)			
			water		hexadecane	
polymer[a]	wt % **1**	feed[b]	adv	rec	adv	rec
2[c]	0		75	58	0	0
3a[d]	1.5	S	110	69	63	54
3d[d]	1.5	C	86	58	38	13
3b[e]	3.0	S	112	72	67	58
3e[e]	3.0	C	101	61	51	42
3c[f]	6.0	S	113	69	71	62

[a] 6 h total reaction time. [b] S ≡ single shot addition 10 min from the end of the reaction. C ≡ continuous feed. [c] Styrene/butyl methacrylate/butyl acrylate/hydroxypropyl acrylate (15/30/17/38 wt %). [d] Styrene/butyl methacrylate/butyl acrylate/hydroxypropyl acrylate/**1** (15/28.5/17/38/1.5 wt %). [e] Styrene/butyl methacrylate/butyl acrylate/hydroxypropyl acrylate/**1** (15/27/17/38/3 wt %). [f] Styrene/butyl methacrylate/butyl acrylate/hydroxypropyl acrylate/**1** (15/24/17/38/6 wt %).

tension[25]

$$\Gamma_1 = -\frac{1}{RT}\frac{d\gamma}{d\ln C} \tag{3}$$

where C is the concentration of species *1*, R is the ideal gas constant, and T is temperature. Hence, it can be seen that if the term $d\gamma/d\ln C < 0$, then there will be a surface excess of species 1. Stated differently, if species 1 has a lower surface tension than species 2, there will be an enthalpic driving force for surface segregation of 1 to the air/polymer interface. If the (perfluoroalkyl)ethyl methacrylate/hydrocarbon acrylate copolymer has a lower surface tension than the hydrocarbon acrylate polymer, then it will be in excess at the air/polymer interface.

The difference in surface tension between the components and interaction parameter between the segments of two polymers will determine the magnitude of surface excess.[26] Obviously, the present system is much more complicated than a simple binary; however, the aforementioned principles still apply. Shown in Table 1 are water and hexadecane advancing, θ_{adv}, and receding, θ_{rec}, contact angles on surfaces of a variety of polymer formulations. Of importance to note is a comparison of data for formulations containing differing amounts of (perfluoroalkyl)ethyl methacrylate and different feed conditions. The data for varying amounts of fluorine in the polymer (1.5−6 wt %) do not show any obvious advantage upon increasing the weight percent of **1** beyond 6 in the formulation. The different feed conditions exhibit the largest effects on contact angles. At a given weight percent of (perfluoroalkyl)ethyl methacrylate in the polymer, the single shot feed produces the higher water and hexadecane contact angles. This can be explained by examination of the types of polymers expected from the two systems. The copolymer which results from the single shot addition will have statistically-longer contiguous blocks of (perfluoroalkyl)ethyl methacrylate than that copolymer produced by continuous feed. The high hexadecane θ_{adv} and low hysteresis obtained on the surfaces of **3c**, for example, would argue for close-packing of $-CF_3$ groups, *vide infra*, from the perfluoroalkyl chains. From eq 3, it can be seen that,

$$d\gamma/d\ln C_{\text{single shot}} < d\gamma/d\ln C_{\text{continuous}}$$

and $\Gamma_{\text{single shot}} > \Gamma_{\text{continous shot}}$. The perfluoroalkyl groups from several polymer chains are then able to form domains of appreciable surface area fractions. Since the polymer is not fluorinated completely, this implies that domains of hydrocarbon-rich species (higher surface free energy) will also be present on the surface. In contrast, consider the polymer made by continuous feed of **1**. On average, each polymer chain will have less fluorine than the single shot feed-produced polymer.

Any fluorine-rich domains present at the surface will be smaller and more interspersed with regions which are rich in hydrocarbon moieties. The presence of domains or chemical heterogeneity results in a phenomenon known as contact angle hysteresis (equal to the difference between advancing and receding contact angles; $\theta_{adv} - \theta_{rec}$).[27] Other explanations for hysteresis are possible (surface roughness), but they are not thought to be applicable in the present case.[28,29] Films of **3a** were spin coated on silicon wafers and examined by atomic force microscopy. Surface roughness was on a scale smaller than that which would produce substantial hysteresis, yet those samples did show appreciable hysteresis when subjected to contact angle measurements (Figure 7). Size of domains and spatial orientation will determine the magnitude of hysteresis observed. All polymers prepared (Table 1) exhibited varying degrees of hysteresis, indicating chemical heterogeneity. Care must be taken in the interpretation of advancing contact angles alone. Dettre and Johnson calculated advancing and receding contact angles on model surfaces containing various degrees of chemical heterogeneities.[27] They concluded that relatively small domains of low surface free energy species will yield relatively large advancing contact angles accompanied by relatively low receding contact angles. The value of the receding contact angle does not approach the advancing angle until large area fractions of the surface are occupied by the low surface free energy species.

At present, insufficient data exist to make any firm estimation of polymer architecture and orientation at the air/polymer interface based on contact angle or hysteresis data. However, the data do suggest that the perfluoroalkyl chains are oriented with the $-CF_3$ groups at the outermost surface. On the basis of contact angle measurements, it can be estimated that the surface tensions of polymers **3a**−**3c** are lower than that of PTFE (~24 mN/m).[30] Water and hexadecane advancing contact angles measured on self-assembled perfluoroalkyl acid monolayers (a close-packed $-CF_3$ surface) are ≈110−120° [31,32] and 80°,[33] respectively, with little hysteresis. Water and hexadecane advancing contact angles on PTFE surfaces have been measured to be 109° and 46°, respectively.[15] The relatively low surface tensions afforded by polymers of the type **3** serve to demonstrate the fact that a surface dominated by $-CF_3$ groups will have a lower surface tension than one dominated by $-CF_2-$.[33,34] The parent hydrocarbon acrylic copolymer, **2**, surface shows little repellency to water ($\theta < 90°$) and no repellency to hexadecane ($\theta = 0°$).

ESCA Spectroscopy of Polymer Surfaces. The surfaces of the acrylate polymers were examined by ESCA. In this surface spectroscopic experiment, the sample of interest is irradiated with Mg Kα X-rays as the kinetic energy of the emitted photoelectron is recorded. Since the mean free path of the ejected photoelectron controls analysis depth, a nondestructive depth profile analysis of the outer ~100 Å of the polymeric surface can be obtained by changing the angle of the sample surface relative to the collection aperture of the spectrometer. Several fluoro methacrylate poly-

Table 2. ESCA Data for Various Acrylate Polymer Formulations

				atom %							
				experimental				theory			
polymer[a]	wt % **1**	feed[b]	exit angle (deg)	F	C	O	N	F	C	O	N
2[c]	0		30	0.8	76	17	6.2	0	74.8	23.1	4.2
3a[d]	1.5	S	30	39	49	11	1.8	0.58	74.9	20.2	4.3
			90	24	57	15	3.4				
3d[d]	1.5	C	30	22	59	16	3.0	0.58	74.9	20.2	4.3
			90	13	64	18	4.5				
3b[e]	3.0	S	30	27	56	14	3.0	1.00	74.6	20.1	4.3
			90	16	63	17	4.6				
3e[e]	3.0	C	30	33	51	13	2.6	1.00	74.6	20.1	4.3
			90	19	61	16	4.1				

[a] 6 h total reaction time. [b] S ≡ single shot addition 10 min from end of reaction. C ≡ continuous addition. [c] Styrene/butyl methacrylate/butyl acrylate/hydroxypropyl acrylate (15/30/17/38 wt %). [d] Styrene/butyl methacrylate/butyl acrylate/hydroxypropyl acrylate/**1** (15/28.5/17/38/1.5 wt %). [e] Styrene/butyl methacrylate/butyl acrylate/hydroxypropyl acrylate/**1** (15/27/17/38/3 wt %).

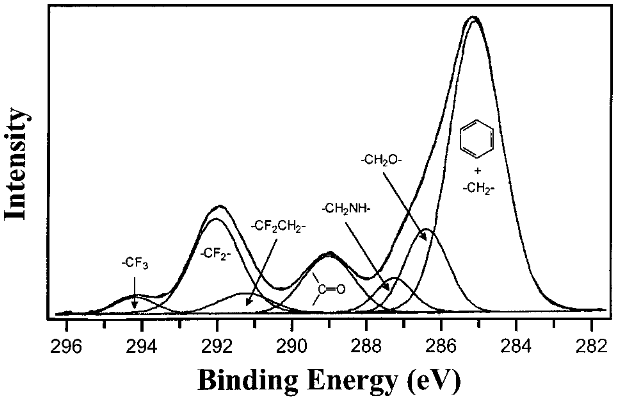

Figure 3. High-resolution ESCA spectrum of the C 1s region of an acrylic polymer, **3a**, prepared using 1.5 wt % of **1** added via the shot feed conditions.

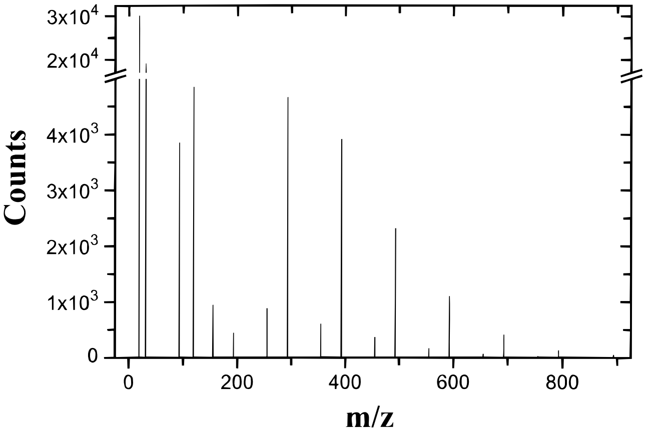

Figure 4. ToF-SIMS negative ion spectrum of acrylic polymer **3a** prepared using 1.5 wt % of **1** via shot feed addition.

mer systems were examined using this approach and compared to the parent acrylic copolymer. The results are shown in Table 2. For typical polymer systems, a 90° exit angle corresponds to an integrated depth sensitivity of ~100 Å. There exists a *sin* φ (where φ is the exit angle) relation to sensitivity; so a 30° exit angle samples to about one-half the depth or ~50 Å. High-resolution spectra were collected in each atomic region to identify unique functional groups that describe the surface chemistry. The theoretical atomic compositions were calculated from a knowledge of the acrylic polymer recipe and composition-corrected for the amount of isocyanate cross-linker added. The parent acrylic copolymer, cross-linked with isocyanate, exhibits a spectrum which is typical of most organic polymers having a relative atomic composition: 76% C, 17% O, and 6.2% N. The polymers containing **1** all show a remarkable excess of fluorine at the surface. A high-resolution carbon 1s spectrum, typical of one of the fluorine-containing polymers, **3a**, is shown in Figure 3. Discrete peaks assignable to CF_3 and CF_2 functional groups show clearly the fluorotelomer end group, $-(CF_2)_nF$, at the air/polymer interface.

Semiquantitative measurements of the surface fluorine for these particular samples showed the surface excess of fluorine ranges ~20−70-fold above bulk levels. For a polymer system, this magnitude of surface excess is relatively rare. Grazing angle (exit angle <12°) data hints at even higher (≈55 atom %) concentrations of fluorine at the surface. The angle-dependent ESCA data do indicate, as anticipated, that the concentration of fluorine begins to decrease deeper into the film.

ToF-SIMS Spectroscopy of Polymer Surfaces. In order to elucidate the structure of the polymer at the air/polymer interface, ToF-SIMS was employed. In the static mode, the primary beam flux is maintained at a value $<10^{12}$ ions/cm^2. In this fashion, the very top surface of the polymer can be examined. Cursory investigations of the acrylic copolymers modified by addition of **1** revealed that the primary fragmentation pathway is quite different from typical hydrocarbon acrylate polymers.[35] Unlike hydrocarbon acrylate polymers, the positive ion spectra of the (perfluoroalkyl)ethyl methacrylate-modified polymers contained no information about the fluorotelomer end groups. Therefore, the discussion will concentrate on negative ion spectra. A mass spectrum obtained from a polymer with 1.5 wt % **1** (shot addition) is shown in Figure 4. The low-mass region displayed in Figure 4 shows those peaks typical of all highly fluorinated polymers (m/z 19 (F)), 31 (CF), 69 (CF_3), and 93 (C_3F_3). The high-mass region has a large peak at m/z 119 (CF_2CF_3) and a series of peaks at $m/z = 93 + 100n$ ($n = 1, 2\ 3, ..., 8$) which are clearly due to the fluorotelomer end group. These fragment ions have the general structure $-C{\equiv}C\text{-}(CF_2CF_2)_nCF_3$. A lower intensity series at $m/z = 55 + 100n$ is also discernible and has the general structure $-C{\equiv}CCF{=}CF(CF_2CF_2)_{n-1}CF_3$. The chain length distribution of the fluorotelomer end group can be inferred from the fragment ion distribution if a common fragmentation mechanism is assumed. Shown below is the general structure of the fluorotelomer attached to the polymer via an ester linkage.

$$-C(O{=})OC^1H_2C^2H_2C^3F_2C^4F_2...C^xF_2F$$

The synthetic path used to produce this particular

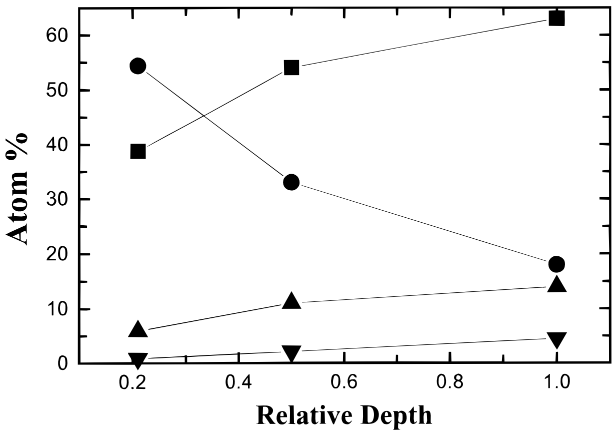

Figure 5. Integrated angle-dependent ESCA atom percent values for acrylic polymer **3a** incorporating 1.5 wt % **1** via single shot feed. Data for carbon (■), fluorine (●), oxygen (▲), and nitrogen (▼) are shown.

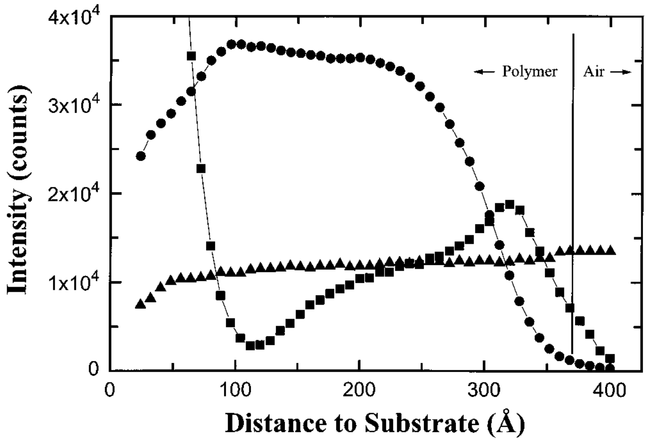

Figure 6. DSIMS depth profile for fluorine-modified acrylic polymer **3a** (1.5 wt % **1**; single shot). The polymer film was measured to be 370 Å thick on a silicon wafer. Shown are data for fluorine (■), carbon (▲), and nitrogen (×5; ●).

fluorotelomer moiety dictates that x must be an even number. In order to form the acetylide-type fragment ions which are observed, bond cleavage must be followed by the loss of two molecules of (i) H_2 if cleavage is between O and C^1, (ii) HF if cleavage occurs between C^1 and C^2, (iii) F_2 if cleavage is between C^2 and C^3, and (iv) F_2 if cleavage occurs between C^x and C^{x+1} ($x > 2$). The fourth possibility is not unique; it should produce a fragment ion distribution with a 50 amu $-(CF_2)-$ repeat interval rather than the 100 amu $-(CF_2CF_2)-$ interval which was observed. The first and third options would produce a distribution with a 100 amu repeat interval but offset from the observed distribution by 50 amu (i.e., peaks at $m/z = 43 + 100n$ rather than the observed $m/z = 93 + 100n$). Only the second fragmentation mechanism (cleavage between C^1 and C^2 followed by the loss of two HF molecules) can produce the observed fragment ion distributions.

DSIMS and ESCA Depth Profiling. Surface analysis of the acrylate polymers containing **1** demonstrates clearly that the surface is enriched in fluorine well above bulk levels. This fact implies that a gradient of fluorine must exist normal to the surface into the bulk of the polymer film. The magnitude of this gradient and its spatial dependence will have important effects on coating properties such as repellency and durability. The fluorine distribution was examined by a variety of spectroscopic techniques. Shown in Figure 5 are the angle-dependent ESCA atomic percent data for one of the fluorinated acrylate films, **3a**. Note that the data are plotted with relative depth on the abscissa. The absolute depth depends on the mean free path of the ejected photoelectron and varies between samples. The relative depth of 1, however, can be estimated at several hundred angstroms. The atomic percentage of fluorine drops from its high level at the surface to bulk concentration with a rather sharp profile that extends only over a small distance normal to the surface. Work is in progress to look at the effects of different feed conditions on this distribution. The distribution determined by this type of experiment is only approximate since the signal is an integrated one.

In an effort to obtain more quantitative data, DSIMS depth profiling was performed. Shown in Figure 6 are the DSIMS depth profiling data for an acrylic polymer film, **3a**, containing 1.5 wt % **1** added via a single shot feed for a film which is 370 Å thick. The data indicate that the fluorine level at the surface of the film is increased by a factor ≈10 compared to bulk levels. The data also indicate that a gradient of fluorine exists normal to the surface and extends down ~100−200 Å from the air/polymer interface (neglecting any instrumental broadening). Similar spectra have been observed with other polymer compositions. Such a step profile has been observed and predicted during other surface segregation studies on miscible polymer mixtures.[22−39]

It is the magnitude (excess) of fluorine at the surface and gradient normal to the surface which will determine the ultimate repellency and durability properties of these (perfluoroalkyl)ethyl methacrylate-modified polymers. It is important to note the differences in fluorine atom concentration differences provided by the ESCA data (~20−70-fold excess) compared to the DSIMS depth profiling data (~10-fold excess). The apparent difference can have its origin from two sources. One is instrumental, whereby the fluorine signal is distributed over an interfacial width which is broadened artificially. If the total integrated fluorine signal was summed into a narrower interfacial depth profile, the excess of fluorine would appear larger. The other is due to the sample geometry. The Gibbs adsorption equation (eq 1) has been used to explain the surface excess of the fluorine-rich component to the air/polymer interface. This formalism is based on a model which is used to describe a surface state and has several underlying assumptions. One of these is that the surface layer is infinitely thin and a dividing surface can be fixed accurately between the surface and the two bulk phases. Another is that the composition of the bulk phases is homogeneous up to the surface layer. The present case is not so simple and may not follow this model exactly. The surface region in the current study can be portrayed as one rich in fluorinated polymer chains, but may not exist as a phase separate from the bulk.

The surface tension term in eq 1 is derived from consideration of the chemical potential of species i, μ_i^σ, on the interface alone. In reality, the situation is more complex. The Helmholtz free energy per unit area of surface σ, f^σ, depends on variables which determine the surface state as well as those which determine the state of the bulk phases. The total differential for f^σ can be written as follows.[24]

$$\mathrm{d}f^\sigma = -S^\sigma \mathrm{d}T + \sum_i \mu_i^\sigma \mathrm{d}\Gamma_i + \sum_i \epsilon_i' \mathrm{d}c_i' + \sum_i \epsilon_i'' \mathrm{d}c_i'' \quad (4)$$

Therefore, it follows that the total differential for surface tension can be written as

$$\mathrm{d}\gamma = -S^{\sigma}\mathrm{d}T - \sum_i \Gamma_i \mathrm{d}\mu_i^{\sigma} + \sum_i \epsilon_i' \mathrm{d}c_i' + \sum_i \epsilon_i'' \mathrm{d}c_i'' \quad (5)$$

where S^{σ} is the surface entropy per unit area, ϵ_i is the cross chemical potential of the ith species, T is temperature, and c_i is the concentration of the ith species. The superscripts $'$ and $''$ refer to the two phases bordering the interface. In the present case, let the $'$ phase be the air phase. Since polymer molecules are not expected in this phase, $\mathrm{d}c_i' = 0$ and all $'$ phase terms disappear. The cross chemical potential terms reflect the influence on surface free energy of species i in the bulk phases $'$ and $''$. Rearranging eq 4, the cross chemical potentials can be defined.[24]

$$\epsilon_i' = \frac{\partial f^{\sigma}}{\partial c_i'} \quad \text{and} \quad \epsilon_i'' = \frac{\partial f^{\sigma}}{\partial c_i''} \quad (6)$$

The complete chemical potential for such a system is, therefore, not entirely intensive since $f^{\sigma} = F^{\sigma}/A$, where F^{σ} is the surface free energy and A represents the surface area of contact between the different phases. For simplification, only one species, i, of fluorine-modified acrylate polymer molecule is discussed. This is clearly an oversimplification, but the mathematical arguments are still valid. The presence of polymer species i in the interface is already tabulated in eqs 1, 4, and 5 in the term μ_i^{σ}. This reduces the problem to the determination of the following equation[24]

$$\frac{\partial F^{\sigma}}{\partial n_i''} = \frac{A}{V''}\epsilon_i'' \quad (7)$$

where F^{σ} is the surface free energy, V'' is the volume of phase $''$, ϵ_i'' is the cross chemical potential of the ith species from the $''$ phase on surface free energy, and n_i'' is the number of moles of i in the $''$ phase. Therefore, the surface free energy and surface tension values depend on the area-to-volume ratio of the interface with phase $''$. As the ratio A/V'' increases, so should $\partial F^{\sigma}/\partial n_i''$, and hence the value of the surface tension should rise. The ESCA experiments were performed on films of thickness ≈2.2 mils and the DSIMS experiments on films of thickness ranging from ~1000 to 2000 Å. A calculation of A/V'' for the ESCA sample yields a value $\approx 10^2$ cm^{-1}, while that for the DSIMS sample gives a value $\approx 10^5$ cm^{-1}. Advancing and receding hexadecane contact angles on a variety of polymer formulations, **3a**, **3b**, and **3c**, as a function of film thickness are shown in Figure 7. As film thickness increases (and A/V'' decreases), the surface tension reaches lower values, as predicted by eqs 5 and 7. This is manifested in the higher contact angle values. Such behavior with other surface active fluoropolymers has been observed previously.[40] Substantial differences are observed when polymers prepared under identical conditions are compared, except for the amount of **1** added to the polymer. As the weight percent of the (perfluoroalkyl)ethyl methacrylate is increased, there is less of an effect on contact angles, especially receding. This indicates that a change in A/V'' does not alter the surface tension and that $\partial F^{\sigma}/\partial n_i'' \rightarrow 0$. This can only occur if the surface is saturated with species i molecules and is less so at lower weight percent **1** in the other compositions. Surface saturation of fluorinated material for composition **3c** is corroborated by contact angle measurements (Table 1) and ESCA data (Table 2) when compared to data from **3a** and **3b**. The effect of A/V'' is most noticeable in θ_{rec}. This results from the chemical heterogeneity of the surface and the fact that θ_{rec} is most sensitive to this phenomenon at surface coverages of less than 90% of low surface energy material.[27]

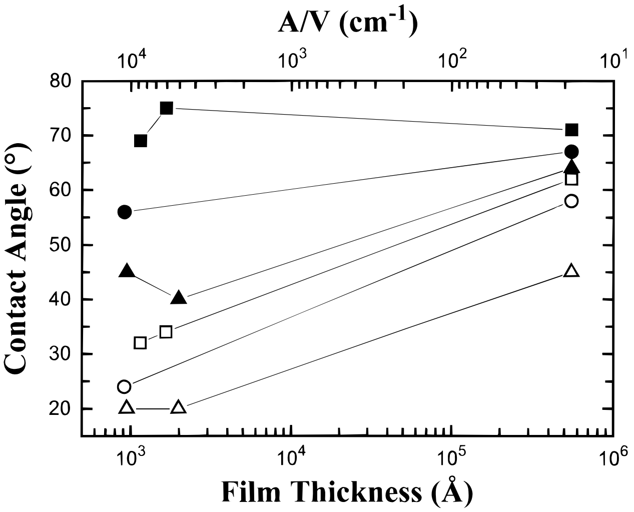

Figure 7. Effect of film thickness on contact angles for several modified acrylate polymers, **3a**−**3c**. The preparation of all polymers was identical except that the amount of **1** was varied (**3a**, advancing (▲) and receding (△); **3b**, advancing (●) and receding (○); **3c**, advancing (■) and receding (□)).

The distribution of the fluorinated component is important. In reality, an actual system is composed of several phases, each of which has a free energy term[24]

$$F = F' + F'' + F^{\sigma} \quad (8)$$

where F is the total free energy of the system, F' is the free energy of the $'$ phase, F'' is the free energy of the $''$ phase, and F^{σ} is the free energy of the interface. The free energy of the interface has been explored in some detail. The additional free energy terms will also contribute to the distribution of material in the film. These terms contain contributions by mixing terms. Unfortunately, at present, not much information has been collected in this regard. See Figure 6 for example. Previous work has suggested that polymer compatibility can play a substantial role in surface enrichment.[41−43] This is where the mixing terms, and hence compatibility, become important. Early discussions focused on the surface enrichment of fluorine in the acrylic polymer modified by addition of **1** were simplistic. It was assumed that only one species of modified polymer molecule was prepared during synthesis. This is obviously not the case in the single shot monomer feed method. The kinetics of solution free radical polymerization would predict that a variety of fluorine-containing polymer chains are being formed. If this model is correct, then a wide variety of material is being made. Each of these molecules will have a different propensity (chemical potential) to enrich the surface.

Conclusions

A series of novel polymers have been prepared by free radical solution polymerization of a variety of hydrocarbon monomers with the (perfluoroalkyl)ethyl methacrylate monomer, **1**. Through a judicious choice of reaction conditions, some control of polymer architecture was exhibited. The resultant (perfluoroalkyl)ethyl methacrylate-containing acrylic polymers were shown to be quite surface active in solution and, even more importantly, in the solid state. The polymers were formulated into films and applied to a variety of surfaces. With incorporation of 1.5 wt% **1** into an acrylic polymer, water and oil repellent surfaces were created. Water contact angles (advancing) of ~80−115° and hexadecane contact angles (advancing) of ~60−70° were observed routinely. With the low levels of **1** incorporated into the polymers, bulk properties are unaffected. In addition, these acrylic polymers can be formulated into coatings which offer unique repellency properties. Two factors, thermodynamics and kinetics, were crucial in the successful preparation of this type of polymer. The placement of fluorine along the polymer chain during copolymerization was critical in determining the propensity for fluorine enrichment at the air/polymer interface. The synthetic methodology employed permitted the control of polymer molecular weight and dispersity. This will have a substantial effect on the ability of the polymer chains to segregate to the air/polymer interface (kinetics). The diffusion of a polymer chain in an unentangled polymer matrix or viscous polymeric medium (as is the case in the present work) scales as $M^{-(0.5-0.6)}P^{-1}$, where M is the molecular weight of the diffusing species and $P \sim$ viscosity, η.[44,45] The nonlinear scaling behavior of the diffusion coefficient on molecular weight will have a great negative impact on the ability of the (perfluoroalkyl)ethyl methacrylate-modified polymer chains to diffuse to the air/polymer interface. In the present system, molecular weights ($M_n \approx 3000$) and dispersity ($M_w/M_n \approx 2$) of the polymers are kept quite low. This allows the fluorine-modified chains to diffuse to the surface before the onset of substantial cross-linking. Once cross-linking and, eventually, vitrification have occurred, a film having the bulk properties of the parent material is prepared while having the unique repellent properties of a fluorochemical-rich surface.

Polymer compatibility can play a substantial role in determining the distribution of material (specifically fluorine) in the film. Not only will the different types of polymer chains synthesized have a different chemical potential, but also they will have different polymer−polymer interaction parameters which will determine the extent of their compatibility. Both of these factors become important in determining the distribution of material at the interface.[26] Considering the number of types of polymer molecules prepared and, hence, possible interaction parameters possible, makes the mixing term an exceedingly difficult problem to solve. No evidence exists for phase separation in any of the polymers prepared (at least not in a macroscopic sense). In addition, the low molecular weights would not favor phase separation. Therefore, it is assumed that all of the polymer chains synthesized are mutually compatible to various extents and the behavior of the system will resemble a typical polymeric surfactant. In any event, there are data on simple binary blends of homopolymers that the concentration profile of the surface-enriched homopolymer exhibits, approximately, an exponential decay into the bulk.[41−43,46] Furthermore, the decay profile can be influenced through the control of polymer−polymer compatibility.

Experimental Section

Materials. The (perfluoroalkyl)ethyl methacrylate monomer $H_2C{=}C(CH_3)CO_2(CH_2)_2(CF_2)_nF$, **1**, is obtained from E. I. du Pont de Nemours and Co. as sold under the tradename ZONYL TM. The average value for n is 7.7. Methyl amyl ketone (MAK) (Eastman Chemical Co., 99%) was used as received. Styrene (S) (99.6+%, Sterling Chemical Co.), butyl methacrylate (BMA) (99.2+%, ICI Acrylics, Inc.), butyl acrylate (BA) (99.5+%, Union Carbide Corp.), and hydroxypropyl acrylate (HPA) (96.5+%, Dow Chemical Co.) were used as received. *tert*-Butyl peroxy acetate (TBPAC) was from Aztec Catalyst Co. and obtained as 76 wt % in mineral spirits. The isocyanate cross-linking agent (99.8+%) was obtained from Miles, Inc. and sold under the tradename Desmodur N3300. It is composed of the isocyanurate trimer of hexamethylene diisocyanate.

Film Preparation. In all additions of isocyanate, the −OH (from hydroxypropyl acrylate)/NCO ratio was maintained at 1. This was done to ensure that no free isocyanate remained. The films were cast onto a variety of substrates and dried in an ~80° convection oven for 30 min.

Preparation of Acrylic Polymer 2. An acrylic polymer, **2**, solution was prepared by charging a vessel with 699.2 g of MAK and blanketing with nitrogen. The solvent was heated to reflux, and a solution consisting of 614.5 g of BMA, 31 g of S, 34 g of BA, and 78 g of HPA in 4.2 g of MAK was added over a period of 6 h. To this was added a solution of 69.0 g of TBPAC in 114.59 g of MAK over a period of 375 min. This was done to ensure complete conversion of monomer. An additional 33 g of MAK was added and the reaction mass kept at reflux for another hour. The resulting polymer solution was then allowed to cool to room temperature before decanting. The resulting acrylic polymer solution had a weight percent solids content of 70 and a composition of BMA/S/BA/HPA in the following weight percentages, 30, 15.0, 16.75, and 38.25, respectively. The polymer had a weight average molecular weight ≈6000 and a dispersity ≈2 (by GPC vs polystyrene standards).

Preparation of Acrylic Polymer 3a. An acrylic polymer, **3a**, solution was prepared by charging a vessel with 699.2 g of MAK and blanketing with nitrogen. The solvent was heated to reflux and a solution consisting of 583.8 g of BMA, 307.3 g of S, 343.2 g of BA, and 783.6 g of HPA in 4.2 g of MAK was added over 6 h. Another solution containing 69.0 g of TBPAC in 114.59 g of MAK was added over a period of 375 min while reflux was maintained to ensure complete conversion of monomer. Ten minutes before the end of the reaction, a solution composed of 30.7 g of **1** in 30 g of MAK is added as a shot. An additional 33.3 g of MAK was added and the reaction mass kept at reflux for another hour. The resulting polymer solution was then allowed to cool to room temperature. The resulting acrylic polymer solution had a weight percent solids content of 70 and a composition of BMA/S/BA/HPA/**1** in the following weight percentages, 28.5, 15.0, 16.75, 38.25, and 1.5, respectively.

Preparation of Acrylic Polymers 3b and 3c. The preparation of these polymers was identical to that of **3a** except the required portion of **1** was substituted for BMA.

Preparation of Acrylic Polymer 3d. Polymer **3d** was prepared using the identical amounts and proportions of monomers as **3b** and **3c**, respectively. However, the monomer solution containing BMA, S, BA, HPA, and **1** was added continuously over a period of 6 h at reflux.

Contact Angle Measurements. Methodology. A Ramé-Hart optical bench is used to hold the substrate in the horizontal position. The contact angle is measured with a telescoping goniometer from the same manufacturer. Distilled water was passed through a SYBRON/Barnstead purification unit (ion exchange) to >16 MΩ cm resistivity. Hexadecane was of the highest purity possible from Aldrich Chemical Co. An "Agla" micrometer syringe (Burroughs Wellcome & Co.) was used with a 27 gauge stainless steel needle. The data were collected according to published protocol.[47] Four advancing angle and four receding angle measurements were made and the data averaged. Typically, the standard deviations were ~ 1−2°.

ESCA Experiments. ESCA data were collected in both survey and high-resolution mode on a Phi LS5000 and 5400 system equipped with a Mg anode. Typical analysis areas were 2 × 8 mm. Data were recorded at both 30° and 90° collection angles, resulting in analysis depths of ~50 and 100

Å, respectively. The element-specific detection limit was on the order of 0.5 atom %.

ToF-SIMS Experiments. Static secondary ion mass spectra were obtained from the surface of the modified polymer using a Phi 7200 ToF-SIMS spectrometer. The surfaces were bombarded at an incident angle of 45° with a pulsed (1 ns), 8 keV cesium ion beam. The surface analysis area was ≈200 × 200 μm. The accumulated ion dose never exceeded 10^{12} ions/cm^2; therefore, all of the results are representative of an undamaged surface (static mode). Although both positive and negative ion spectra were obtained from all samples, the positive ion spectra contained no discernible information regarding the perfluoroalkyl end groups. Consequently, the discussion pertains only to the negative ion mass spectra.

DSIMS Depth Profiling. Sample Preparation. The DSIMS depth profiling experiment requires thin films due to charging during the sputtering process. This necessitated dilution of the polymer solutions from their nominal 70 wt % concentration down to the 1−6 wt % level. After dilution of the polymer solutions in MAK, the appropriate (see **Film Preparation**) amount of isocyanate was added. The films were prepared by spin coating (Headway Research) on 4 in. diameter silicon wafers and dried at ~80 °C for 30 min. Using these conditions, film thicknesses in the range 500−2000 Å could be prepared.

Ellipsometry. Spectroscopic ellipsometry was performed using a Sopra ellipsometer at an incident angle of 60° for films on silicon wafers. Thicknesses and refractive indices were determined experimentally.

Equipment and Measurement. The depth profiling data were collected courtesy of Profs. J. Sokolov and M. Rafailovich at the State University of New York at Stony Brook. The details of the measurement have been published elsewhere.[48]

References and Notes

(1) Yoon, S. C.; Ratner, B. D. *Macromolecules* **1986**, *19*, 1068.
(2) Yoon, S. C.; Ratner, B. D. *Macromolecules* **1988**, *21*, 2392.
(3) Yoon, S. C.; Ratner, B. D. *Macromolecules* **1988**, *21*, 2401.
(4) Yoon, S. C.; Sung, Y. K.; Ratner, B. D. *Macromolecules* **1990**, *23*, 4351.
(5) Honeychuck, R. V.; Ho, T.; Wynne, K. J.; Nissan, R. A. *Chem. Mater.* **1993**, *5*, 1299.
(6) Yoon, S. C.; Ratner, B. D.; Iván, B.; Kennedy, J. P. *Macromolecules* **1994**, *27*, 1548.
(7) Chapman, T. M.; Marra, K. G. *Macromolecules* **1995**, *28*, 2081.
(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.*, in press.
(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. M*acromolecules* **1996**, *29*, 8211.
(16) DeSimone, J. M.; Guan, Z.; Elsbernd, C. S. *Science* **1992**, *257*, 945.
(17) Schmidt, D. L.; Coburn, C. E.; DeKoven, B. M.; Potter, G. E.; Meyers, G. F.; Fischer, D. A. *Nature* **1994**, *368*, 39.
(18) Van Der Grinten, M. G. D.; Clough, A. S.; Shearmur, T. E.; Bongiovanni, R.; Priola, A. *J. Colloid Interface Sci.* **1996**, *182*, 511.
(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) Park, I. J.; Lee, S.-O.; Choi, C. K.; Kim, K.-J. *J. Colloid Interface Sci.* **1996**, *181*, 284.
(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) Anton, D. R.; Darmon, M. J.; Graham, W. F.; Thomas, R. R. U.S. Patent Application No. 08/543,770, filed Oct. 16, 1995.
(24) Defay, R.; Prigogine, I.; Bellemans, A.; Everett, D. H. *Surface Tension and Adsorption;* Wiley: New York, 1966; Chapter V.
(25) Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; Interscience Publishers: New York, 1990; Chapter III.
(26) Jones, R. A. L.; Kramer, E. J. *Polymer* **1993**, *34*, 115.
(27) Johnson, R. E., Jr.; Dettre, R. H. *J. Phys. Chem.* **1964**, *68*, 1744.
(28) Bayramli, E.; van den Ven, T. G. M.; Mason, S. G. *Can. J. Chem.* **1981**, *59*, 1954.
(29) Bayramli, E.; Mason, S. G. *Can. J. Chem.* **1981**, *59*, 1962.
(30) Wu, S. *Polymer Interface and Adhesion*; Marcel Dekker: New York: 1982; Chapter 3.
(31) Schönherr, H.; Ringsdorf, H. *Langmuir* **1996**, *12*, 3891.
(32) Schönherr, H.; Ringsdorf, H.; Jaschke, M.; Butt, H.-J.; Bamberg, E.; Allinson, H.; Evans, S. D. *Langmuir* **1996**, *12*, 3898.
(33) Johnson, R. E., Jr.; Dettre, R. H. in *Wettability;* Berg, J. C., Ed.; Marcel Dekker: New York, 1993; pp 39−44.
(34) Hoernschemeyer, D. *J. Phys. Chem.* **1966**, *70*, 2628.
(35) Gardella, J. A., Jr.; Hercules, D. M. *Anal. Chem.* **1981**, *23*, 1879.
(36) Zhao, X.; Zhao, W.; Sokolov, J.; Rafailovich, M. H.; Schwarz, S. A.; Wilkens, B. J.; Jones, R. A. L.; Kramer, E. J. *Macromolecules* **1991**, *24*, 5991.
(37) Norton, L. J.; Kramer, E. J.; Bates, F. S.; Gehlsen, M. D.; Jones, R. A. L.; Karim, A.; Felcher, G. P.; Kleb, R. *Macromolecules* **1995**, *28*, 8621.
(38) Budkowski, A.; Steiner, U.; Klein, J. *J. Chem. Phys.* **1992**, *97*, 5229.
(39) Genzer, J.; Faldi, A.; Oslanee, R.; Composto, R. J. *Macromolecules* **1996**, *29*, 5438.
(40) Phillips, R. W.; Dettre, R. H. *J. Colloid Interface Sci.* **1976**, *56*, 251.
(41) Schmidt, I.; Binder, K. *J. Phys.* **1985**, *46*, 1631.
(42) Nakanishi, H.; Pincus, P. *J. Chem. Phys.* **1983**, *79*, 997.
(43) Sakellariou, P. *Polymer* **1993**, *34*, 3408.
(44) Green, P. F.; Kramer, E. J. *Macromolecules* **1986**, *19*, 1108.
(45) Whitlow, S. J.; Wool, R. P. *Macromolecules* **1991**, *24*, 5926.
(46) Binder, K.; Firsch, H. L. *Macromolecules* **1984**, *17*, 2928.
(47) Reference 33, pp 45−50.
(48) Zheng, X.; Rafailovich, M. H.; Sokolov, J.; Briber, R. M.; Schwartz, S. A. *Macromolecules* **1993**, *26*, 6431.

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