

The Effect of Copolymer Composition on the Surface Properties of Perfluoroalkylethyl Acrylates

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ABSTRACT: The surface properties of two perfluoroalkylethyl acrylic copolymers—aqueous, Zonyl[®]329 and solvent-based, Zonyl[®]225—were studied. Zonyl[®]329 is a water-based dispersion and Zonyl[®]225 a solvent-based copolymer solution; both polymers have the same perfluoroalkylethyl side chains [F(CF₂)_nCH₂CH₂—] but have different comonomer compositions. Thin films, prepared by dip coating onto mica and quartz, with and without annealing, were characterized by contact angle and by X-ray photoelectron spectroscopy (XPS). The contact angle measurements showed little variation with polymer and with substrate, consistent with the supposition that the perfluoroalkylethyl chains aggregate on the surface and thus dominate surface properties, irrespective of the composition of the rest of the polymer. XPS revealed only small variations in surface chemistry for studied films. Annealed films showed

improved segregation for solvent-based Zonyl[®]225, which has both hydrocarbon alkyl and perfluoroalkylethyl side chains; the presence of hydrocarbon alkyl chains enables the perfluoroalkylethyl chains to reorganize after annealing. Depending on the external conditions, this thermal treatment can enable more perfluoroalkylethyl chains to reach the film surface (solid/air interface), leading to a reduction in the dispersive-dominant surface and enhancement in perfluoroalkylethyl segregation. This suggested that perfluoroalkylethyl side chains dominate the surface properties, which are thus not dependent on substrate, backbone composition, or formulation. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 4020–4029, 2009

Key words: coatings; ESCA/XPS; contact angle; surfaces; fluoropolymers

INTRODUCTION

Acrylates and similar polymers with polyfluorinated side chain groups, such as perfluoroalkylethyl, F(CF₂)_nCH₂CH₂—, form stabilized ordered phases on drying, preventing reorganization in the presence of water.^{1–5} These stable surfaces have become an important enterprise for coating manufacturers. Such coatings have found their way into a variety of applications in the architectural, industrial, automotive, and aerospace industries.^{6–8} The peculiar properties of perfluoroalkylethyl functionalized polymers are dependent on differing regions within the chemical structure of the polymer. The polymer backbone chemical composition accounts for thermal stability and mechanical characteristics, whereas the surface properties depend on the chemical structures of the

perfluoroalkylethyl side chains and the spatial arrangement they exhibit on drying.^{2,9} Although it is understood that the interfacial characteristics may differ from the properties of the bulk,^{10,11} there is little research in the literature dealing with the role of the comonomer composition on the availability of perfluoroalkylethyl side chains at the surface and ultimately the effect this composition has on surface energy (γ). The surface energy is defined as the energy required to create a new surface, this being proportional to the area of molecules brought to the surface from the bulk, with dimensions of energy per unit area.¹²

Zisman et al.^{13,14} reported that the surface energy of hydrocarbon and fluorocarbon materials decreases in the order $-\text{CH}_2 > -\text{CH}_3 > -\text{CF}_2 > -\text{CF}_3$.

Therefore, to obtain improved repellent properties, a high surface coverage of $-\text{CF}_3$ pendant groups at the air–liquid interface needs to exist.^{15–17} There is an abundance of research in the literature dealing with the ease with which the perfluoroalkyl functionality in polymer systems crystallize at the surface.^{18–20} The way in which pendant perfluoroalkyl-containing side chains organize themselves normal to a surface, allowing the $-\text{CF}_3$ groups to

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position themselves at the air interface, should have a strong dependence not only on the length of the perfluorocarbon chain^{2,4} but also depend on the make-up of the rest of the polymer system.

Surface properties are normally determined by structure and chemical composition of the outermost atomic layer.²¹ Thus, for protective coatings, it is important to ensure that a high proportion of hydrophobic segments—incorporated to reduce the surface energy—are found at the air interface. The inclusion of lower surface tension fluoroalkyl side chains suggests that enthalpically driven migration of fluorinated segments toward the air interface is likely to occur; however, this does not usually consider the complex architectures and compositions of copolymer systems. Studies have looked at controlling and even reversing such segregation.²² Deitzel et al.²³ investigated the segregation of random copolymers of methyl methacrylate and tetrahydroperfluorooctyl acrylate finding that the concentration of fluorine at the surface was two to three times higher than the bulk fluorine content. Xue et al.²⁴ showed that by varying film-forming technique, they were able to regulate and influence the surface properties of copolymers with low-dodecylfluoroheptyl methacrylate. Similarly, Yokoyama et al.²⁵ found that fluoroalkyl segregation could be improved by casting from critical CO₂. Most work, however, has looked at the surface properties as a function of chain length of the fluorinated side chain,^{2,4} or the preparation method,^{20,26} with very little work on effect of comonomer composition on surface properties.

Surface treatment may be performed using solvent- or water-based preparations. Although there are some technical advantages in using solvent-based systems, water-based coatings offer considerable advantages in ease of safe use by an operator and diminished environmental impact from solvents. However, it is important that the performance of a water-based product be about the same, or better, than a solvent-based equivalent. In this work, we examine the effect of comonomer make-up on the ability of the perfluoroalkyl-containing chains to be at the air interface. Data are obtained for two commercially available perfluoroalkylethyl acrylate copolymers from DuPont (Wilmington, DE): Zonyl[®] 329, a water-based dispersion, and Zonyl[®] 225, a solvent-based polymer solution. The polymer in the water-based dispersion incorporates perfluoroalkyl monomers of varying chain lengths containing mostly 2-(perfluorooctyl)ethyl acrylate (Fig. 1; the fluorocarbon chain, F(CF₂)_n— goes up to a maximum length of 14 fluorocarbon units²⁷), an amino-acrylate, vinyl acetate, and silane monomers; in addition, trace amounts of residual solvent from the synthesis stage (<0.5%) may exist. Zonyl[®] 225 includes the same 2-(perfluoroalkyl)ethyl acrylate side chains and hydrophobic

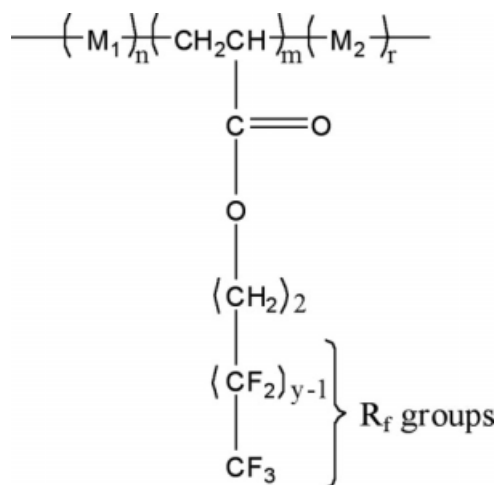


Figure 1 Structure of the 2-(perfluoroalkyl)ethyl acrylate component of the Zonyl[®] products studied; the perfluoroalkylethyl side chains in the polymers used here comprised a mixture of chain lengths, containing mostly 2-(perfluorooctyl)ethyl acrylate.

monomers including hydrocarbon alkyl chains C_nH_{2n+1} randomly positioned between perfluoroalkyl side chains; this polymer is supplied as a solution of the polymer in butyl acetate.

Surface energy cannot be measured directly, but because the surface energies of the various components dictate the contact angle of a drop of fluid on a substrate in air, the surface energy of a solid can be inferred from data for contact angles between the substrate and liquids of differing polarities, using various model hypotheses. There are a number of methods for this in the literature.^{13,28–31} The generic assumptions in these various models are that the surface energy can be broken up into various additive components such as those arising from polar and dispersive effects and that the latter are dominant in very nonpolar fluids. Assuming that the dispersive component is similar with fluids of different polarities, and from knowledge of the surface energies of those fluids, the surface energy of an unknown compound can be inferred. The method adopted here is that of Owens and Wendt,²⁹ with the two fluids of different polarities being water and diiodomethane. Surface energies were determined by measuring contact angles on polymer-coated mica and quartz, dip coated either in a solution of Zonyl[®] 225 or a dispersion of Zonyl[®] 329. If comonomer composition were to affect the location of —CF₃ groups, then it is expected that surface energies would vary with the polymer coating (Zonyl[®] 225 or Zonyl[®] 329).

Two substrates are used: mica and quartz. Mica is an aluminosilicate, and quartz primarily comprised silica. Quartz is microscopically rough with an amorphous structure, whereas mica is atomically smooth

and has a dense crystalline structure.³² This difference in surface roughness suggests that there might exist a difference in films formed on each substrate. We also probe the effect of dry annealing on the conformation of perfluoroalkylethyl tails and ultimately the effect that has on surface energy; annealing has been found to improve the orientation and molecular order of the fluorocarbon (R_f) group³³ and segregation of the component with the lower surface energy, in this case the CF_3 groups.³⁴ This improved packing and segregation due to annealing should lead to lower overall surface energy for the system.

The concentrations of perfluoroalkylethyl groups and other groups at the surface are examined using X-ray photoelectron spectroscopy (XPS). The XPS surface depth sensitivity decreases exponentially into the bulk, thus allowing access to the outermost surface composition.³⁵ This gives information on the difference in surface energies attributed to the three main regions of a perfluoroalkylethyl tail. These three regions, comprising a carbonyl group linked to the polymer backbone followed by a hydrocarbon $-CH_2CH_2-$ spacer and finally the fluorocarbon (R_f) group (Fig. 1), are expected to have a strong effect on the surface energy, depending on the orientation of the side chain. With XPS, it is possible to tell which carbon moieties are concentrated at the surface and, importantly, the density of R_f groups, by accounting for the $-CF_3$ terminal groups.² The information on the concentration of the fluorocarbon moieties at the surface is then compared with surface energies for the corresponding systems; this allows us to determine the mobility of the perfluoroalkylethyl tails for each polymer based on its monomer make-up.

One of the reasons for this study is to understand the behavior of water-borne dispersions against a solvent-based coating; coatings of the latter nature have typically dominated such industry in the past. It is expected that the polymer surface properties are purely governed by the low surface energy of the (perfluoroalkyl)ethyl acrylate segments and that the comonomers, mainly used to enhance substrate interactions, only influence the polymer organization and subsequently the surface properties on annealing. This article aims to test this hypothesis.

EXPERIMENTAL

Materials

Muscovite mica (Proscitech, Australia) was freshly cleaved before use; fused quartz was obtained from Proscitech, Australia. Zonyl[®]225, an impregnating agent of translucent form in butyl acetate solution, containing two unfluorinated acrylic or vinylic monomers, was made up by diluting in commercial

white spirits (Diggers, Australia). Zonyl[®]329, a cationic, cloudy amber-colored aqueous dispersion, was diluted in Milli-Q water. Zonyl[®]329 is synthesized from comparable monomers to Zonyl[®]225, with the major exception being the inclusion of a vinylic silane, used to improve surface adhesion. This product contains no added components to the formulation, although trace amounts of residual solvent from the synthesis stage (<0.5%) may exist. Both polymers incorporate the 2-(perfluoroalkyl)ethyl acrylate side chains, with the solvent-based Zonyl[®]225 also including hydrocarbon alkyl chains C_nH_{2n+1} randomly positioned between perfluoroalkyl side chains. Both polymers were provided by Du Pont de Nemours (Wilmington, DE).

Preparation of films

Freshly cleaved mica, without further cleaning, was dip coated in solutions made up to ~ 3 wt % solids content of Zonyl[®]225 or Zonyl[®]329. Quartz slides were cleaned in Goldie detergent from Elite Chemicals Pty Ltd. (Brisbane, Australia) in an ultrasonicator for 30 min before being further ultrasonicated in acetone for 10 min and then in methanol for 10 min. Coated substrates were then either left to dry under ambient conditions or annealed at 70°C for 24 h. Coated surfaces after having been annealed are referred to as either "mica (annealed)" or "quartz (annealed)."

All samples were visually inspected using a light microscope for surface defects before analysis. Coated samples were air cleaned using a pressurized air duster from Corporate Express (Sydney, Australia) before contact angle measurements.

Contact angle measurements

The static contact angles (θ_s) of Milli-Q water and diiodomethane (Sigma-Aldrich) on Zonyl[®] films were measured in a temperature-controlled laboratory (20°C) using an OC15 optical contact angle analyzer (Dataphysics Instruments Company, Germany). Final contact angle measurements were the average of five single drops of 5–10 μ L, taken within 5–10 s of applying each drop of liquid, and run in duplicates with an error $< \pm 2^\circ$. Contact angle hysteresis ($\Delta\theta$), defined as the difference between advancing and receding contact angles ($\Delta\theta = \theta_{adv} - \theta_{rec}$) was also determined for both liquids, to qualitatively assess surface roughness. The advancing contact angle was measured as the drop increased in volume, until the three-phase boundary moved over the surface. The receding contact angle was measured as the liquid was withdrawn from the droplet. The geometrical dimensions of all droplets were determined using an elliptical fit.

Surface free energy

The surface free energy of the polymer films on quartz was calculated using the Owens-Wendt-Fowkes model, with water and diiodomethane as the two liquids of different polarities.^{28,29} This assumes the surface energy of a solid can be resolved into polar (water) and dispersive (diiodomethane) components²⁹:

$$\frac{1}{2}(1 + \cos \theta) \frac{\gamma_1}{(d\gamma_1)^{1/2}} = (P\gamma_s)^{1/2} \left(\frac{P\gamma_1}{d\gamma_1} \right)^{1/2} + (d\gamma_s)^{1/2} \quad (1)$$

$$d\gamma_s + P\gamma_s = \gamma_s \quad (2)$$

$$\gamma_1 = d\gamma_1 + P\gamma_1 \quad (3)$$

where θ is the contact angle of the liquid on the polymer surface, γ_1 is the surface free energy of the liquid, whereas $d\gamma_1$ and $P\gamma_1$ are the dispersive and polar components of the surface free energy of the liquid, respectively. The $d\gamma_1$ and $P\gamma_1$ values used for water are 21.8 and 51.0 mN m⁻¹, and those for diiodomethane were 48.5 and 2.3 mN m⁻¹, respectively.²⁹ This method assumes the total surface energy of a solid γ_s is additive, and enables both the dispersive component $d\gamma_s$ of the surface energy and the polar surface component $P\gamma_s$ to be determined.

The dispersive and polar components are evaluated as follows. For each of the two liquids, water and diiodomethane, substituting the observed value of θ and the $d\gamma_1$ and $P\gamma_1$ values into eq. (1), and using eq. (3), gives two linear simultaneous equations for the unknowns $(P\gamma_s)^{1/2}$ and $(d\gamma_s)^{1/2}$, which are trivially solved to yield the desired quantities, $P\gamma_s$ and $d\gamma_s$, from the experimental values of the contact angle for the two solvents, denoted $\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{CH}_2\text{I}_2}$. The uncertainties in these quantities are calculated as follows. Evaluating $P\gamma_s$ and $d\gamma_s$ is a functional relationship, denoted $P\gamma_s = f_p(\theta_{\text{H}_2\text{O}}, \theta_{\text{CH}_2\text{I}_2})$ and $d\gamma_s = f_s(\theta_{\text{H}_2\text{O}}, \theta_{\text{CH}_2\text{I}_2})$. The uncertainty in each quantity is then given by:

$$\Delta P\gamma_s = \Delta\theta_{\text{H}_2\text{O}} \left| \frac{\partial f_p(\theta_{\text{H}_2\text{O}}, \theta_{\text{CH}_2\text{I}_2})}{\partial \theta_{\text{H}_2\text{O}}} \right| + \Delta\theta_{\text{CH}_2\text{I}_2} \left| \frac{\partial f_p(\theta_{\text{H}_2\text{O}}, \theta_{\text{CH}_2\text{I}_2})}{\partial \theta_{\text{CH}_2\text{I}_2}} \right| \quad (4)$$

where $\Delta\theta_{\text{H}_2\text{O}}$ and $\Delta\theta_{\text{CH}_2\text{I}_2}$ are the experimental uncertainties in the corresponding contact angles; there is a corresponding expression for $\Delta d\gamma_s$. The partial derivatives are readily evaluated numerically (from the change in calculated values of $P\gamma_s$ and $d\gamma_s$ with small changes in $\theta_{\text{H}_2\text{O}}$ and $\theta_{\text{CH}_2\text{I}_2}$).

X-ray photoelectron spectroscopy

Data were acquired using a Kratos Axis ULTRA X-ray Photoelectron Spectrometer incorporating a

165 mm hemispherical electron energy analyzer. The incident radiation was Monochromatic Al K α X-rays (1486.6 eV) at 150 W (15 kV, 10 mA) and at 45° to the sample surface. Photoelectron data were collected at a take-off angle of 90°.

Survey (wide) scans were taken at an analyzer pass energy of 160 eV and multiplex (narrow) high-resolution scans at 20 eV for F_{1s}, C_{1s}, and O_{1s}. Survey scans were performed over 1200–0 eV binding energy range with 1.0 eV steps and a dwell time of 100 ms. Narrow high-resolution scans were run with 0.05 eV steps and 250 ms dwell time. Base pressure in the analysis chamber was 1.0 × 10⁻⁹ torr and during sample analysis was 1.0 × 10⁻⁸ torr. All C_{1s} spectra were calibrated for the energy shift corresponding to 284.6 eV.^{36,37} All peaks were fitted with a 30% Lorentzian and a 70% Gaussian function using a least-squares fitting program, CasaXPS (Casa Software, Ltd), version 2.3.12. Peak widths (full width at half maximum) for C_{1s} moieties were kept constant for all samples.

RESULTS

Contact angles

Stable Zonyl[®] films were obtained by dip coating on a quartz surface; however, applying either polymer to freshly cleaved mica led to poor film-forming properties resulted in a patchy coating. In particular, it was not possible to obtain a stable annealed Zonyl[®]225 film on the mica surface, and this is indicated by dashes (–) in Table I.

Water and diiodomethane static contact angles on the various films are reported in Table I. All polymers showed strong hydrophobic properties, with contact angles for water ranging $\theta_{\text{water}} = 109\text{--}123^\circ$; water hysteresis values were all relatively low for such polymers and were the same within experimental error. The dispersive contact angles of diiodomethane all showed values $\geq 89^\circ$, with the largest contact angle of 100°, obtained for Zonyl[®]225 film on mica; the hysteresis values for diiodomethane were all the same within experimental error. Annealing the polymer film seemed to have little effect on the water contact angle for quartz. This was not the case with Zonyl[®]329 on mica, which saw a 14° drop on annealing. The diiodomethane contact angles for all samples were within range of one another, except Zonyl[®]225 on mica, which showed a relatively high contact angle of 100°.

Table I also shows the surface free energy (γ) of all polymers as determined by the Owens-Wendt-Fowkes method [eqs. (1) and (2)]. Surface energies ranged between 8.9 ± 0.6 and 13.5 ± 0.6 mN m⁻¹, with the lowest surface energies seen for Zonyl[®]225/mica at 8.9 ± 0.6 mN m⁻¹. The

TABLE I
Static Contact Angles θ_s , Hysteresis $\Delta\theta$ and Surface Free Energies γ , with Standard deviations σ , of Water and Diiodomethane on Polymers Dip Coated onto Quartz and Mica

Sample	Contact angles ($^\circ$)								Surface energy (mN m^{-1}) diiodomethane					
	Water				Diiodomethane				γ	σ	γ^d	σ	γ^p	σ
	θ_s	σ	$\Delta\theta$	σ	θ_s	σ	$\Delta\theta$	σ						
Zonyl [®] 329/Quartz	116	1	14	3	90	2	17	2	12.5	1.1	12.2	1.1	0.4	0.2
Zonyl [®] 329/Quartz (annealed)	116	1	16	2	94	2	17	2	11.1	1.0	10.6	1.0	0.5	0.2
Zonyl [®] 225/Quartz	120	1	15	2	92	1	20	3	12.1	0.5	12.0	0.5	0.06	0.07
Zonyl [®] 225/Quartz (annealed)	121	2	14	1	94	2	17	1	11.1	0.5	11.0	0.5	0.1	0.1
Zonyl [®] 329/Mica	123	2	14	2	91	2	19	3	12.6	0.6	12.6	0.6	0.001	0.02
Zonyl [®] 329/Mica (annealed)	109	2	14	2	89	1	19	2	13.5	0.6	12.1	0.5	1.4	0.4
Zonyl [®] 225/Mica	120	1	14	1	100	1	18	2	8.90	0.6	8.40	0.5	0.4	0.2
Zonyl [®] 225/Mica (annealed)	–	–	–	–	–	–	–	–	–	–	–	–	–	–

dispersive energy component dominated the overall surface free energy of all the polymer films considered, with Zonyl[®]329/quartz and Zonyl[®]329/mica showing the highest dispersive component values at $12.2 \pm 1.1 \text{ mN m}^{-1}$ and $12.6 \pm 0.6 \text{ mN m}^{-1}$, respectively. All the films had very small polar components relative to the total surface free energy. The effects of annealing, however, were most prominent on the polar component of the surface free energy. In particular, when Zonyl[®]329/Mica was annealed, the polar surface free energy contribution was observed to increase from essentially 0 to $1.4 \pm 0.4 \text{ mN m}^{-1}$, with this being the highest polar surface free energy contribution observed for all of the films. Table I also shows the effects of annealing on the surface energy for thin films formed. All annealed surfaces with the exception of Zonyl[®]329 on mica showed a reduction in total surface energy, but this decrease was statistically significant only for Zonyl[®]225 on quartz.

X-ray photoelectron spectroscopy

Figure 2 gives typical photoelectronic peaks for fluorine (singlet) at $\sim 688.3 \text{ eV}$ and oxygen (doublet)

corresponding to the two different oxygen atoms of the ester functional group, with $-\text{O}-\text{C}=\text{O}$ at $\sim 532.4 \text{ eV}$ and $\text{C}-\text{O}$ at $\sim 533.8 \text{ eV}$.

Figure 3 shows the XPS results for the standard and annealed Zonyl[®]225 and Zonyl[®]329 films on a quartz surface. Carbon was observed between 282 and 298 eV and was resolved into five distinct (Gaussian-Lorentzian) peaks: $-\text{CF}_3$ at $\sim 293.5 \text{ eV}$, $-\text{CF}_2-$ at ~ 291.3 , $-\text{O}-\text{C}=\text{O}$ at $\sim 288.8 \text{ eV}$, $-\text{CH}_2-\text{O}-$ at ~ 286.2 and hydrocarbon $-\text{CH}_n$ at $\sim 284.6 \text{ eV}$. All four carbon spectra in Figure 3 are qualitatively similar; there is little difference between the Zonyl[®]225 and Zonyl[®]329 films, although the relative intensities of the $-\text{CF}_3$ and $-\text{CH}_n$ peaks varied. The $-\text{CH}_n$ and $-\text{CH}_2-\text{O}-$ peaks showed a broader combined peak when the Zonyl[®]329 film was not annealed.

The atomic peaks in the XPS spectra were integrated to obtain the relative atomic compositions for fluorine, carbon, and oxygen; this is given in Table II. This shows that the atomic composition of each film does not change on annealing. Zonyl[®]225 showed a higher fluorine content than Zonyl[®]329 for both untreated and annealed surfaces: 43.7 ± 4.1 atom % for Zonyl[®]225/quartz compared with $41.4 \pm$

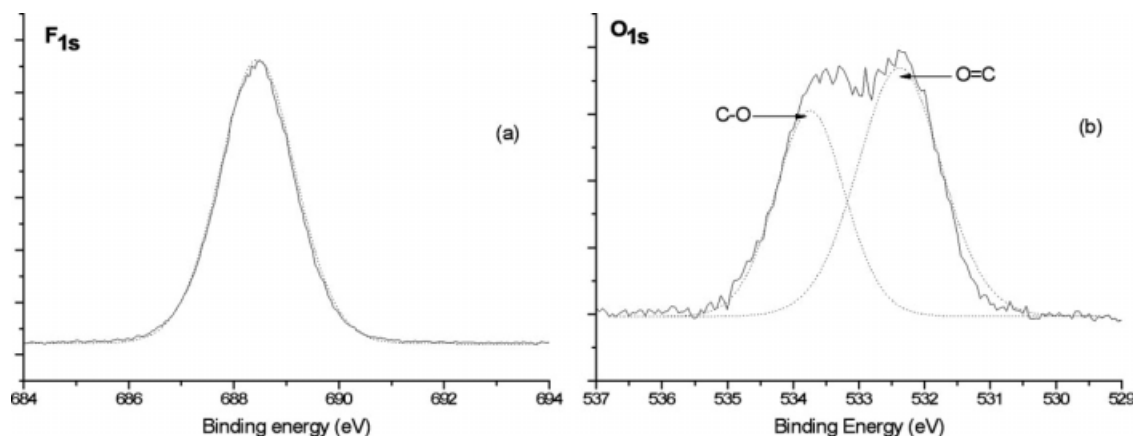


Figure 2 Typical XPS high-resolution F_{1s} and O_{1s} spectra for polymers used.

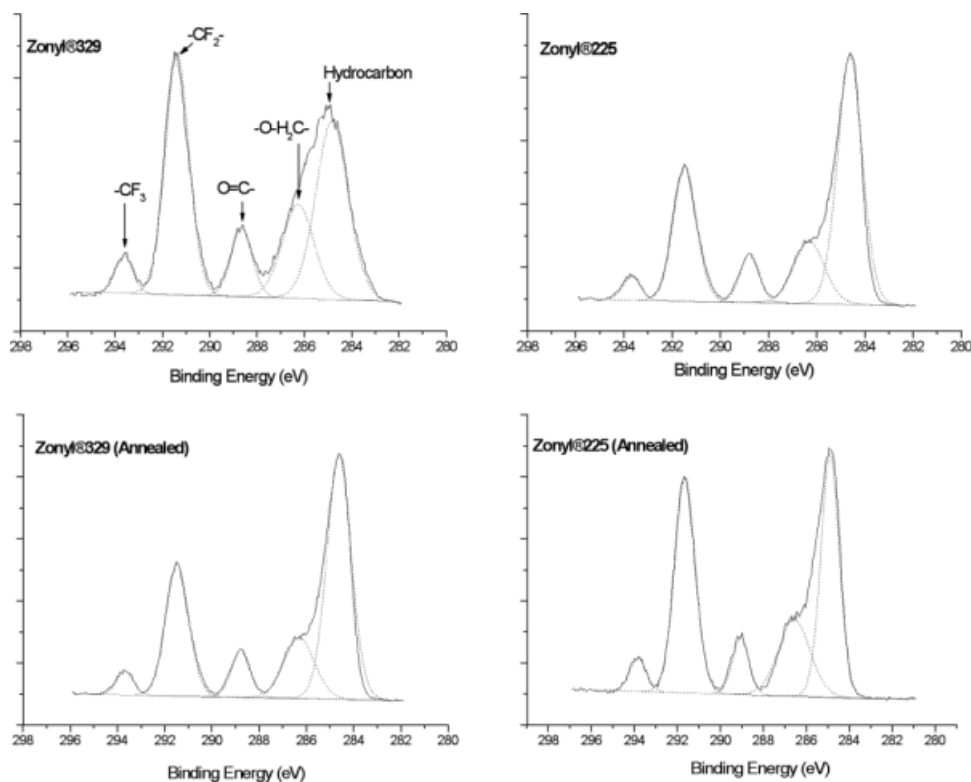


Figure 3 XPS C_{1s} core-level spectra of all polyfluorinated acrylate thin films on quartz, as indicated, at a take-off angle of $\theta = 90^\circ$ (~ 9 nm sampling depth).

0.010 atom % for Zonyl[®]329/quartz and 47.5 ± 1.9 atom % for Zonyl[®]225/quartz (annealed) compared with 40.7 ± 4.7 atom % for Zonyl[®]329/quartz (annealed). Fluorine to carbon ratios (F/C) were found to be the same for all substrates and polymers within experimental error: 0.9 ± 0.003 atom % for Zonyl[®]329/quartz, 0.9 ± 0.2 atom % for Zonyl[®]225/quartz, 0.8 ± 0.2 atom % for Zonyl[®]329/quartz (annealed), and 1.1 ± 0.1 atom % for Zonyl[®]225/quartz (annealed). Because these purely show the monomer compositions, no inference could be made to either support or contradict the hypothesis.

The XPS spectra in Figure 3 were also integrated to obtain the $-CF_3$, $-CF_2-$, $-COO$, $-OCH_2$, and hydrocarbon ($-CH_n$) composition of the various films. These values are reported in Table III, together with the CF_2/CF_3 ratio. Table III indicates that the CF_2/CF_3 ratios were very similar for all four films,

at approximately 8, i.e., one $-CF_3$ moiety for every eight $-CF_2$ groups. The percentage of hydrocarbon ($-CH_n$) at the surface of the nonannealed Zonyl[®]225 film was found to be significantly larger than that of nonannealed Zonyl[®]329. This value for Zonyl[®]225 dropped from $49.3 \pm 0.4\%$ to $41.5 \pm 3.9\%$ on annealing. Annealing resulted in a 25.7% increase in $-CF_2$ values of Zonyl[®]225, from $24.5 \pm 0.7\%$ to $30.8 \pm 2.2\%$; as expected, this resulted in an equivalent enhancement of 22.6% in $-CF_3$ values.

DISCUSSION

Effect of comonomer composition on surface energies

Perfluoroalkylethyl side chains, common to both polymers, are expected to dominate surface energies due to the presence of the perfluorocarbon groups,

TABLE II
XPS Data for Quartz Showing Atomic Percentages and Standard Deviation

Polymer	Atom %							
	F	σ	C	σ	O	σ	F/C	σ
Zonyl [®] 329/quartz	41.4	0.010	47.3	0.116	11.3	0.13	0.9	0.003
Zonyl [®] 225/quartz	43.7	4.1	46.7	5.23	9.6	1.1	0.9	0.2
Zonyl [®] 329/quartz (annealed)	40.7	4.7	49.2	3.10	10.1	1.6	0.8	0.2
Zonyl [®] 225/quartz (annealed)	47.5	1.9	44	1.17	8.5	0.75	1.1	0.1

TABLE III
Surface Concentration of C_{1s} Polymer Moieties for Quartz- Treated Surfaces

Polymer	Area percentage/total area of C _{1s}											
	CF ₃	σ	CF ₂	σ	COO	σ	OCH ₂	σ	CH _n	σ	CF ₂ /CF ₃	σ
Zonyl [®] 329/quartz	4	0.1	34.4	0.1	8.9	0.4	18.3	0.3	34.6	0.6	8.6	0.03
Zonyl [®] 225/quartz	3.1	0.3	24.5	0.7	7.3	0.1	15.9	0.8	49.3	0.4	7.9	0.1
Zonyl [®] 329/quartz (annealed)	4	1.1	31.6	8.3	8.1	1	19.2	9.9	37.2	0.4	7.9	0.5
Zonyl [®] 225/quartz (annealed)	3.8	0.3	30.8	2.2	6.7	0.1	17.5	1.3	41.5	3.9	8.1	0.2

which are absent from the polymer backbone. Considering this postulate, contact angles are expected to be the same for the two polymers studied. It was shown in Table I that for Zonyl[®]329 and Zonyl[®]225 on quartz, there was a minimum contact angle difference of 2°; this did not change on annealing. The largest contact angle difference was seen for diiodomethane on mica, which showed a maximum of 12° difference between Zonyl[®]225 and Zonyl[®]329. Such relatively small differences are likely due to subtle differences in the final film-forming properties due to the formulation, rather than being inherent to the comonomer compositions.

Surface energies of the two polymer coatings were determined from contact angles of water and diiodomethane, as described in eqs. (1) and (2). Implicit in these equations is that the polymer films are uniform. This was not always the case, however, with the polymer solution, Zonyl[®]225, showing poor film formation on the mica substrate. This may be explained by the presence of adsorbed potassium ions which are exposed on cleavage of the mica. This cationic layer will limit the availability of binding sites (Si, Al, and O atoms), thus leading to poor film formation of the solvent-based Zonyl[®]225.³⁸ This is not a problem with the cationic aqueous dispersion of Zonyl[®]329, as the weakly bound potassium ions move into solution, the positively charged polymer is attracted to the resulting negatively charged mica surface. At pH 4–5, we expect both mica and quartz surfaces to have a negative surface charge.³⁹ Indeed, the Zonyl[®]225 film on mica degraded further on annealing, and no results were able to be obtained in this case.

The contact angle of the dispersive component of the surface energy, Table I, saw little variation for both Zonyls[®] on surfaces of mica and quartz or thermal treatment; an exception to this was Zonyl[®]225 on mica, which showed values higher than the average at 100° ± 1°. All surfaces gave a nonwetting angle greater than 90° for CH₂I₂. The maximum contact angle found for water was larger than the contact angle for CH₂I₂; all the surfaces were strongly hydrophobic. The largest contact angle obtained for water was 123° ± 2° on the Zonyl[®]329 on mica; 120° is the maximum static contact angle possible on a flat hydrophobic surface.⁴⁰ This static contact angle

above 120° is attributed to surface roughness.⁴⁰ Mica, however, is atomically flat and any surface roughness must be intrinsic to the polymer film. Table I indicates that the contact angle for Zonyl[®]329 on mica is reduced on annealing, from 123° ± 2° to 109° ± 2°, thus increasing surface energy in Table I, from 12.6 ± 0.6 to 13.5 ± 0.6 mN m⁻¹. Thus, annealing in this case either reduced the surface roughness or changed the surface composition of the film.

Contact angle values greater than 90° on a flat surface are known to be amplified by surface roughness.⁴¹ In most cases, the hysteresis value gives a qualitative assessment of surface roughness. The hysteresis values here are relatively high and might be construed as suggesting significant surface roughness. However, in the case of Zonyl[®]329 and Zonyl[®]225, other possible causes for a high Δθ must also be considered, such as surface rearrangement on exposure to contact angle liquids, i.e., kinetic hysteresis.⁴² Péés et al.⁴³ showed through hysteresis data that perfluorooctyl-alkyl polyacrylates had varying degrees of surface mobility that depended on the alkyl (spacer) chain length. In the case of perfluorooctyl acrylates with ethyl spacers, as found in both Zonyl[®] coatings studied here, the hysteresis value for water was found to be 19°,⁴³ as large or larger than all values measured here. Many other polymer systems incorporating perfluorinated side chains exhibit similar hysteresis values for both water and diiodomethane.^{44–46} Kim et al.⁴⁶ showed experimentally that these values corresponded to negligible surface roughness values, ranging between 0.7 and 1.4 nm. Based on this evidence, it is unlikely that surface energy values for the Zonyl[®] products are influenced by surface roughness, and the hysteresis values are most likely the result of surface rearrangement of the perfluoroalkyl segments.

The total surface energy range of 8.9 ± 0.6 – 13.5 ± 0.6 mN m⁻¹ found for the semicrystalline Zonyl[®] films (Table I) was similar to the surface energy of the homopolymer of poly-2-(perfluorooctyl) ethyl acrylate, reported as 9.4 mN m⁻¹.⁴⁷ The comparison with poly-2-(perfluorooctyl)ethyl acrylate, which has the same side chain as Zonyl[®]225 and Zonyl[®]329 but is a homo- rather than a copolymer, suggests that the added bulk of the copolymer does not have a large effect on the surface energy. Interestingly, it was also

considerably lower than that of poly(tetrafluoroethylene) (PTFE) at 18.5 mN m^{-1} , which is also partly crystalline, or poly(methyl methacrylate) at 39 mN m^{-1} .^{48,49} The $-\text{CF}_3$ dominated air-vapor interface of both Zonyl[®] products, as opposed to the $-\text{CF}_2-$ rich PTFE, is expected to result in a lower surface free energy.⁵⁰ The critical surface tension component (γ_c) of the surface free energy for closely packed $-\text{CF}_3$ groups has been reported to be as low as 6 mN m^{-1} , significantly lower than that of $-\text{CF}_2-$ surfaces (18 mN m^{-1}).⁵¹ This is partly the result of bulky fluorine groups reducing the availability of attractive centers at the air-vapor interface.^{13,42} The surface free energy will further drop if an organized crystalline array of $-\text{CF}_3$ groups exists at the surface.⁵² Eastoe et al.⁵³ illustrated this phenomenon of drop in surface energy with increasing fluorine content, by comparing the surface energies of two surfactants whose hydrophobic terminal groups comprised $\text{F}-\text{CF}_2$ and $\text{H}-\text{CF}_2$. It was found that by substituting a fluorine atom on the fluoromethyl group with a hydrogen atom, the surface tension increased by 9 mN m^{-1} . Poly(methyl methacrylate) is a model for the acrylic backbone of the Zonyl[®] polymers. Its large surface energy, compared with Zonyl[®]225 and Zonyl[®]329, highlights the importance of perfluoroalkylethyl groups in obtaining low surface energies.

PTFE has larger fluorine content and a much larger surface energy than the polymers considered here. Thus, these results show that it is possible to obtain lower surface energies while reducing fluorine content: an economic goal. The data suggest that it is not the fluorine content, but the surface structure/packing, that determines the surface energy. Genzer et al.⁵² showed this by creating a tightly packed, uniformly organized array of perfluorolauric acid groups; this yielded the lowest recorded critical surface energy of 6 mN m^{-1} . Therefore, it is important to characterize the surface properties of the polymer films.

In all the systems considered, the dispersive surface energy dominates the total surface energy. Polar effects on the surface energy are small as seen in Table I, suggesting very few ester groups (Fig. 1) or other strong hydrogen-bonding species are present at the air interface to interact with polar wetting liquids. This also suggests that the surface energy is dominated by the concentration and ordering of $-\text{CF}_3$ groups at the surface. The similarities between the Zonyl[®]225 and the Zonyl[®]329 surface energies further suggest that the surface energy is effectively independent of comonomer composition.

Surface composition by XPS

The surface composition of the polymer films on the quartz substrates was characterized using XPS; mica-treated surfaces were not analyzed by XPS due

to their poor film-forming properties. It should be noted that although XPS analyzes the top $\sim 9 \text{ nm}$, the XPS signal will fall off exponentially with depth with the majority of signal coming from the top $\sim 3 \text{ nm}$. Therefore, atoms found at the upper surface will contribute proportionally more to the signal than those found in the bulk.⁵⁴ Figures 2 and 3 show electron binding energies in agreement with literature values for similar polymers.^{2,20,21,36} The spectra in Figure 3 show prominent $-\text{CF}_2$ and $-\text{CF}_3$ peaks, consistent with segregation of the perfluoroalkylethyl tails near the surface.

The XPS peaks were integrated to obtain atom composition, as given in Table II. This shows that there was a higher content of surface fluorine for Zonyl[®]225 than Zonyl[®]329, which was maintained after annealing; this is consistent with the average polymer compositions of both polymers. Surface energy is determined not only by this surface fluorine content but also by the form of the fluorine: whether as $-\text{CF}_2$ or $-\text{CF}_3$. The surface $-\text{CF}_2$ and $-\text{CF}_3$ concentrations were determined by integrating the $-\text{CF}_2$ and $-\text{CF}_3$ XPS peaks in Table III. The CF_2/CF_3 ratios show the monomer composition of the side chain; here, all polymers show an average of eight $-\text{CF}_2$ groups for every $-\text{CF}_3$ moiety at the surface. This is consistent with the side chains being predominantly of 2-(perfluorooctyl)ethyl acrylate origin. From CH_n , it is also evident that there is a substantial amount of the backbone present in the top layer. Importantly, Table III shows a similar segregation of side chains at the surface, when compared with the variation in CH_n values ($34.6 \pm 0.6 - 49.3 \pm 0.4$), despite differences in side chain distribution along the backbone. Table III also shows that there are ~ 2 ester groups per $-\text{CF}_3$, which is twice that expected from the fluorinated side chain in Figure 1. It seems that this excess represents the backbone esters present at the surface; these did not segregate for either coating even on annealing.

The preferential organization of the perfluoroalkylethyl side chains is clear in the surface compositions as seen by XPS. There is little evidence suggesting that the organization of such side chains is backbone dependent, with all polymers exhibiting similar concentrations of $-\text{CF}_3$ pendant groups. This is consistent with surface properties being dominated by side chain segregation.

Effect of annealing

Annealing polymeric materials above their glass transition temperature, T_g , allows all components of the system to reach a thermodynamic equilibrium; the polymer may undergo chain relaxation, migration, or reorganization.⁵⁵

The generally poor film-forming on mica as a substrate were exacerbated by annealing, resulting in the lower contact angle for water on Zonyl[®]329 (annealed) and an immeasurable contact angle for Zonyl[®]225. Heating a nonbound thin film exposes weaknesses in the hydrophobic film, which can then be easily penetrated by water, as was the case with Zonyl[®]225 on mica. Quartz-treated surfaces are unlikely to undergo such effect, as small defects present on quartz are expected to increase polymer-substrate interactions.

On the other hand, contact angles for Zonyl[®]329 (Table I) on mica showed a contact angle that decreased by 14° when annealed. It was found that annealing Zonyl[®]329 coatings on mica led to a heterogeneous coating of the surface, which led to a reduction in the surface hydrophobicity.

Annealing of Zonyl[®]329 on quartz at temperatures above its T_g of 47°C²⁷ resolved the single broad peak XPS peak at ~ 285 eV in Figure 3 into two well-defined peaks, for the $-\text{CH}_2-\text{O}-$ and hydrocarbon $-\text{CH}_n$. This suggests that annealing ordered the surface layer of the Zonyl[®]329 film. This assertion is supported by the calculated surface energies: the surface energy of Zonyl[®]329 on quartz is reduced on annealing.

Small changes in surface composition on annealing of Zonyl[®]225 above its T_g 's of -9°C and 37°C²⁷ were also observed. The increase in $-\text{CF}_3$ surface concentration and the drop in CH_n values from 49.3 ± 0.4 to 41.5 ± 3.9 suggests sections of the side chains aligned toward the surface are replaced by perfluoroalkylethyl chains. This reduction in the surface $-\text{CH}_n$ concentration (both main chain and side chain hydrocarbons) on annealing equated to an increase in the $-\text{CF}_3$ and $-\text{CF}_2$ concentrations, as more $-\text{CF}_n$ groups orient toward the surface. This surface ordering on annealing also led to a reduced surface energy for the annealed Zonyl[®]225 and Zonyl[®]329 films on quartz, as seen in Table I, and a decrease in the polar $-\text{COO}$ concentration.

The effects of annealing on the Zonyl[®]329 XPS spectra were not as pronounced as those seen for Zonyl[®]225. The inclusion of two types of pendant groups (additional alkyl chains) in the solvent-based Zonyl[®]225 explains the significant effect annealing has on the perfluoroalkylethyl chains of Zonyl[®]225 and the absence of any statistically significant annealing effects for the aqueous Zonyl[®]329. This has been elegantly demonstrated by De Crevoisier et al.⁵⁶ who found that copolymers bearing perfluoroalkyl-containing and long alkyl chains, i.e., differing pendant groups, imparted an additional degree of freedom to the side chains. Perfluoroalkyl-containing side chains found in systems comprising two pendant groups—compared with homo-polymers of each monomer—are better suited to rotate around

the main chain, leading to extra organizational possibilities. This partially crystallized lamellar phase allows both pendant groups to crystallize independently in two different lattices.⁵⁶ The effect of this is most pronounced after thermal treatment, where side chain reorganization from the isotropic to smectic phase is further driven by the incompatibility of the hydrocarbon alkyl and the perfluoroalkyl-containing side chains, thus enabling more perfluoroalkyl-containing chains to reach the solid/air interface. De Crevoisier et al.⁵⁶ showed that a system comprising a fluorinated monomer (AC8n) and an alkyl monomer mixture of both stearyl and palmityl methacrylates exhibited a phase diagram consisting of two phases below 90°C at 20% and 80% mole fraction.

CONCLUSION

The surface properties of two perfluoroalkylethyl acrylate copolymers (Zonyl[®]329, an aqueous dispersion, and Zonyl[®]225, a copolymer solution) sharing a common perfluoroalkylethyl side chain were studied by dip coating onto both surfaces of mica and quartz. Surface properties were examined by measuring the contact angles with a polar and nonpolar liquid (water and diiodomethane) and with XPS. Mica-treated surfaces showed poor film-forming properties and were therefore not analyzed further with XPS. The effect of the comonomer composition on the perfluoroalkylethyl segregation was studied by calculating the surface energies, concentration of fluorine and carbon moieties, and testing the effect of annealing on the segregation. The surface energies were determined from the contact angle data by adding the polar and dispersive surface energies using the Owens-Wendt-Fowkes model.^{28,29} All films exhibited a strong hydrophobic surface with surface energies in the range of $8.9 \pm 0.6 - 13.5 \pm 0.6 \text{ mN m}^{-1}$, this being in the range of the surface energy of the homopolymer of the perfluoroalkylethyl side chain. There was a statistically significant reduction in surface energies on annealing for Zonyl[®]225 on quartz (the other systems also showed a decrease, although below the level of statistical significance).

The postulated cause of the low surface energies, surface concentration of side chains, was determined by XPS measurements. Preferential organization was evident through high $-\text{CF}_2$ and $-\text{CF}_3$ concentrations for both polymers, with higher values recorded on annealing for Zonyl[®]225. Annealing Zonyl[®]225 led to statistically significant improvements in surface properties due to the increase in $-\text{CF}_2-$ and $-\text{CF}_3$ values and the concurrent reduction in the more polar $-\text{COO}$ groups. Annealing Zonyl[®]225 led to improved surface properties, it was suggested that this is the result of additional hydrocarbon alkyl

side chains, absent from Zonyl[®]329. The incompatibility of the additional hydrocarbon alkyl side chains drives reorganization of the perfluoroalkylethyl side chains, thus enabling more perfluoroalkylethyl chains to reach the solid/air interface, thereby improving the surface properties.

This work indicates that distinct fluorinated polymers with varying comonomer compositions and formulations will produce similar surface properties, as long as the dominant side chains are kept constant; such properties are likely to be altered on annealing. This might have applications in the coatings industry where it is important to improve substrate–polymer interactions depending on the intended substrate and its end use.

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