Surface Properties of Perfluoroalkylethyl Acrylate/*n*-Alkyl Acrylate Copolymers

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ABSTRACT: Wetting behavior of perfluoroalkylethyl acrylate (FA)/*n*-alkyl acrylate (AA) copolymers with the various length of side chains of the AAs is discussed from a standpoint of surface molecular mobility. The copolymerization reactivity ratio indicates that these polymers are random copolymers. The surface properties were studied by measuring dynamic contact angle, static contact angle and freeze-dried X-ray photoelectron spectroscopy, and the bulk properties by wide-angle X-ray diffraction and differential scanning calorimetry. The advancing contact angles for water were independent of side-chain length of AAs and were almost constant at 120°. We have attributed this phenomenon to the orientation of perfluoroalkyl groups (R_f groups, C_xF_{2x+1}) in air, which is independent of side-chain length of AAs. On the contrary, the receding contact angles showed small values of about 45° when n numbers below 8 and increased when n numbers above 12. This can be explained as follows. High wettability during the receding process at the n numbers below 8 results from regression of R_f groups at the water–solid interface caused by minimization of the interface free energy. The low wettability during the receding process at the n numbers above 12 shows that R_f groups cannot regress due to its crystallization. This mechanism is also supported by other measurements. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1741–1749, 1999

Key words: perfluoroalkylethyl acrylate/*n*-alkyl acrylate copolymers; dynamic contact angle; freeze-dried X-ray photoelectron spectroscopy; wide-angle X-ray diffraction; differential scanning calorimetry

INTRODUCTION

It has been well known that fluoroalkyl acrylate homopolymers with long side chains have very low critical surface tension (γ_c), which ranges from 10 to 11 mN/m.[1] These values are much lower than the 18 mN/m of polytetrafluoroethylene that is typical fluoropolymer. The γ_c of closely packed —CF$_3$ groups (6 mN/m) is lower than that of —CF$_2$— surfaces (18 mN/m).[2] In fluoroalkyl acrylate homopolymers, the longer the side chain

they have, the tighter the packing of the perfluoroalkyl (R_f) side chains, and consequently the denser the —CF$_3$ terminal groups at surface. Therefore, fluoroalkyl acrylate homopolymer has a very low γ_c.[3] These studies have been obtained from the static surface state where the reorientation does not take place. Recently, the surface reorientation of polar groups in contact with water has been investigated.[4] For example, Maekawa et al. reported that the surface structure of fluoroalkyl acrylate homopolymer with short side chains changes when it is contacted with water.[5] They tried correlating polymer crystallization with dynamic contact angle with regard to the side chain R_f group (—C$_n$F$_{2n+1}$), and

concluded that the surface reorientation in contact with water takes place when n numbers of C_nF_2n+1 are not more than 8, of which polymers are not crystallized.

On the other hand, perfluoroalkyl acrylate copolymers have been scarcely studied in spite of its importance in the practical applications. These copolymers have several important properties for practical application such as film forming and adhesive property. We have been studying the surface properties of perfluoroalkylethyl acrylate (FA)/n-alkyl acrylate (AA) copolymers with the various side-chain length of the AAs. In this paper we discuss the relationship between wetting properties and surface molecular mobility.

EXPERIMENTAL

Materials

The chemical structure of FA is shown below.

$$CH_2 = CHCOOCH_2CH_2(CF_2CF_2)_kCF_2CF_3$$

The distribution of k number is $k = 3$, 64%; $k = 4$, 28%; $k = 5$, 8% (average k number 3.5, FA was synthesized by Daikin Industries Co., Ltd.). The Q and e values were determined by using commercially available Fluowet AC800 ($k = 3$, purity 95%, Hoechst Co., Ltd.).

AAs [$CH_2{=}CHCOOC_nH_{2n+1}$] such as methyl acrylate ($n = 1$, MA), ethyl acrylate ($n = 2$, EA), and n-butyl acrylate ($n = 4$, BA) were obtained from Tokyo Kasei Co., Ltd. (guaranteed grade reagents); n-octyl acrylate ($n = 8$, OA) from Nippon Shokubai Co., Ltd. (ANO); and n-lauryl acrylate ($n = 12$, LA), n-cetyl acrylate ($n = 16$, CA), and n-stearyl acrylate ($n = 18$, StA) from Kyoueisha Co., Ltd.(Lightester series). All these AAs were used without further purification.

FA/AA Copolymerization

The FA/AA copolymers were prepared by radical polymerization in chlorofluorocarbon 316/1,1,1-trichloroethane mixture (weight ratio = 1/1) in a nitrogen atmosphere at 60°C for 6 h, using t-butyl peroxypivarate as initiator. The polymers obtained were precipitated twice in ethyl alcohol and dried under reduced pressure. Unless otherwise specified, the FA/AA copolymers contain 61.5 wt % of FA, which was confirmed by an elemen-

FA content ; 61.5wt%

Figure 1   Chemical structure of FA/AA copolymers.

tary analysis of fluorine. Figure 1 shows their chemical structures.

Molecular Weights

The molecular weights of the polymers were measured in tetrahydrofuran eluent with a Shodex GPC system-11 (Showa Denko Co., Ltd.), equipped with a UV detector. The columns were calibrated with polystyrene standards of known molecular weight. The weight average molecular weights of FA/AA copolymers were 5.0×10^4 for FA/MA and FA/EA, 4.8×10^4 for FA/BA, 4.0×10^4 for FA/OA, 3.0×10^4 for FA/LA, 2.7×10^4 for FA/CA, and 2.5×10^4 for FA/StA.

Copolymerization Reactivity

The copolymerization reactivity of FA and AA was studied by the following methods. Copolymerization of FA (monomer 1) and styrene (monomer 2) were carried out (with the low conversion; 5–25%). The reactivity ratios r_1 (0.21) and r_2 (0.57) were calculated by the Mayo–Lewis method. Using these values, Q (0.55) and e (0.66) were calculated for FA by means of Alfrey and Price's method.[6] The reactivity ratios r_1 (FA, monomer 1) and r_2 (AA, monomer 2) were calculated from Q and e of FA and AA (from the literature[7]).

Preparation of Thin Polymer Coatings

By dipping method, a poly(ethylene terephthalate) film (Tray Co., Ltd., Lumilar film 20 × 50 × 0.25 mm) was coated with the copolymers obtained, which were dissolved in 1,1,1-trichloroethane (concentration; 3 wt %). The dipping speed was 0.5 mm/s.

Measurements

Dynamic Contact Angle

The dynamic contact angles of the polymer films were measured using the sliding method[8] and the Wilhelmy method.[9] In the sliding method, contact

angle meter type CA-A (Kyowa Interface Science Co., Ltd.) was used, and a sample on plate was tilted until a water droplet began to slide down on the sample. Subsequently, an advancing contact angle and a receding contact angle was measured by microscopy. In the Wilhelmy method, the Dynamic contact angle meter type WET-6000 (Rhesca Co., Ltd.) was used, the sample was held in a microbalance and progressively immersed into the water at a constant rate, then, conversely, receded to its original position. The analysis of the wetting force data yielded two contact angles, which were an advancing contact angle and a receding contact angle. The plates were immersed at a speed of 0.5 mm/s into water.

Surface Free Energy

The surface free energy in air and water was calculated from the static contact angle of several liquids. Their surface tensions, dispersion, and polar components are already known, using Owens' equation.[10] The static contact angle were measured by the sessile drop technique with contact angle meter type CA-A.

Surface Free Energy in Air. The surface free energy in air was obtained by modified Owens' method.[11] Equation (3) was obtained from Owens' eq. (1) extended Fowkes' concept and Young's eq. (2).

$$\gamma_{sl} = \gamma_s + \gamma_l - 2(\gamma_s^d \gamma_l^d)^{1/2} - 2(\gamma_s^p \gamma_l^p)^{1/2} \quad (1)$$

$$\gamma_s = \gamma_{sl} + \gamma_l \cos\theta \quad (2)$$

$$1 + \cos\theta = 2[(\gamma_s^d \gamma_l^d)^{1/2}/\gamma_l + (\gamma_s^p \gamma_l^p)^{1/2}/\gamma_l] \quad (3)$$

where γ_s, γ_l, and γ_{sl} are the surface free energy of the solid, liquid, and the interfacial free energy between the solid and liquid, respectively. The superscripts d and p are to the dispersive force and polar force components.

Equations (4) and (5) were obtained by deformation of eq. (3):

$$\gamma_l(1 + \cos\theta)/2(\gamma_l^p)^{1/2}$$
$$= (\gamma_s^d)^{1/2}[(\gamma_l^d)^{1/2}/(\gamma_l^p)^{1/2}] + (\gamma_s^p)^{1/2} \quad (4)$$

$$\gamma_l(1 + \cos\theta)/2(\gamma_l^d)^{1/2}$$
$$= (\gamma_s^p)^{1/2}[(\gamma_l^p)^{1/2}/(\gamma_l^d)^{1/2}] (\gamma_s^d)^{1/2} \quad (5)$$

For the purpose of the data analysis, if X, X', Y, Y' are taken as follows:

$$X = (\gamma_l^d)^{1/2}/(\gamma_l^p)^{1/2}, Y = \gamma_l(1 + \cos\theta)/2(\gamma_l^p)^{1/2}$$

$$X' = (\gamma_l^p)^{1/2}/(\gamma_l^d)^{1/2}, Y' = \gamma_l(1 + \cos\theta)/2(\gamma_l^d)^{1/2}$$

eqs. (6) and (7) result:

$$Y = (\gamma_s^d)^{1/2}X + (\gamma_s^p)^{1/2} \quad (6)$$

$$Y' = (\gamma_s^p)^{1/2}X' + (\gamma_s^d)^{1/2} \quad (7)$$

When the static contact angles of water (γ_l = 72.8, γ_l^d = 21.8), ethylene glycol (γ_l = 48.0, γ_l^d = 32.8), glycerin (γ_l = 63.3, γ_l^d = 39.7), diethylene glycol (γ_l = 44.8, γ_l^d = 38.1), ethanol amine (γ_l = 48.3, γ_l^d = 34.4), α-bromonaphthalene (γ_l = 44.6, γ_l^d = 44.6), and methylene iodide (γ_l = 50.8, γ_l^d = 49.5) in air and γ_l, γ_l^d, and γ_l^p are substituted in eqs. (4) and (5), X-Y,X'-Y' were plotted, and γ_s^d and γ_s^p were obtained from the slope and the intercept by extrapolating the straight line. In this method, two values of γ_s^d and γ_s^p were obtained, so the average value was used as the result. The values of surface tension γ_l and its dispersion force component γ_l^d used for this study are quoted from ref. 11.

Surface Free Energy in Water. The static contact angles of methylene iodide and bubble on polymer films in water were measured by the Nakamae's method.[12] The surface free energy in water was calculated from the static contact angles using Owens' equation.

For the dynamic and static contact angles, the average of the five readings was used as the contact angle.

X-ray Photoelectron Spectroscopy

The X-ray photoelectron spectroscopy (XPS) were carried out on a ESCA 750 (Shimadzu Manufacturing Co., Ltd.) with a Mg Kα X-ray source. The X-ray gun was operated at 8 kV and 30 mW and the analyzer chamber pressure was 10^{-6}–10^{-7} Pa. Take-off angles were kept constant at 90°. To characterize the surface chemical composition in water, the freeze-dried XPS method was applied using the modified ESCA 750.[13] Following is our procedure in the hydrated state. First, a sample (polymer films) was hydrated by mounting with a

Table I Q and e values[7] for AA (Monomer 2) and Calculated Reactivity Ratios of FA (Monomer 1) with AA (Monomer 2)

n	n-Arkyl Acrylate	Q	e	r_1	r_2	$r_1 r_2$
1	Methylacrylate	0.45	0.64	1.20	0.83	1.00
2	Ethylacrylate	0.41	0.55	1.25	0.79	0.99
4	Butylacrylate	0.38	0.85	1.64	0.59	0.97
8	Octylacrylate	0.63	2.01	2.13	0.08	0.16
12	Laurylacrylate	—	—	—	—	—
16	Cetylacrylate	—	—	—	—	—
18	Stearylacrylate	0.33	1.26	2.48	0.28	0.70

droplet of water on the surface at room temperature in air, frozen at $-50°C$ in an entry chamber under a nitrogen gas purge, then freeze dried until completed, and finally transferred to the analysis chamber and the XPS was measured at $-50°C$ in the water-equilibrated surface. Using the surface in a dry state as a reference, we define rearrangement as a change from a hydrated surface composition to a dry one. In a dry state, same procedure was used without hydration.

Crystallinity

The crystallinity of FA/AA copolymers was measured by X-ray diffractometry with a CuKα X-ray source [Rotaflex RAD-rA (Rigaku Denki Co., Ltd.)] for powdered polymers. Diffractograms were collected over $3°–30°$ (as 2Θ). Differential scanning calorimetry (DSC) data were obtained from DSC-50 (Shimadzu Manufacturing Co., Ltd.). Heating rate of $20°C/min$ was used for a sample of 10 mg. Before the DSC measurements, the samples were preheated up to $120°C$ in order to eliminate the effect of thermohistory. Subsequently, they were cooled down to $-80°C$, and measured from -80 to $120°C$.

Unless otherwise specified, the samples were measured at $25°C$ except DSC.

RESULTS AND DISCUSSION

Copolymerization Reactivity

Table I shows Q and e values of AA and calculated reactivity ratios of FA with AA. As $r_1 r_2$ were from 0 to 1.0 for all AA, it can be presumed that FA/AA copolymers are random copolymers.[14]

Dynamic Contact Angle

Figure 2 shows the effect of dynamic contact an-

gles of FA/AA copolymers for water measured by the sliding method, altering the number of carbon atoms in side chains of the AAs. The advancing contact angles were independent of side-chain length of AAs and were almost constant at $120°$. However, the receding contact angles showed small values of about $45°$ for n numbers below 8 and increased suddenly as n numbers increased. The similar result was also obtained from the Wilhelmy method. The contact angle hysteresis, which is expressed as $\theta a - \theta r$, with movement of the liquid front is often a result of surface roughness, heterogeneity, reorientation, mobility, etc.[15] In this case, reorientation and mobility could be foreseen. This phenomenon indicates that the surface structures in water differs from those in air; that is, it changes that orientation of side chain with mobility of main chain as the conversion air into water.

The following investigations were carried out to prove the above assumption.

Figure 2   Dynamic contact angles of FA/AA copolymers for water.

Figure 3 X-ray diffractograms (a) and DSC thermograms (b) of FA/AA copolymers and FA homopolymer.

Crystallinity

Figure 3 shows X-ray diffractograms (a) and DSC thermograms (b) of FA/AA copolymers and FA homopolymer. In X-ray diffractograms, the FA/AA copolymers with short side chains of the AAs where n numbers are below 8 had no steep peak. When n number was 12, the FA/AA copolymer had 1 peak at $2\theta = 18°$ and When n numbers were 16 and 18, the FA/AA copolymers had two peaks at $2\theta = 18°$ and $22°$, respectively. These peaks were caused by the side-chain R_f groups[16] and alkyl groups packing,[17] respectively. Thus, when n numbers were below 8, the FA/AA copolymers were in the rubbery state and had high mobility; however, when n numbers were above 12, they were in the crystalline state and had low mobility. A similar result in regard to crystallinity was also obtained by the DSC. The FA/AA copolymers with short side chains of the AAs where n numbers were 1, 2, and 4 had T_g's at 14, -4, and $-22°C$, respectively. When n number was 8, the FA copolymer had a T_m at $12°C$. These FA/AA copolymers had a T_g or T_m below $25°C$, at which dynamic contact angles were measured. On the contrary, the FA/AA copolymers with long side chains of the AAs where n numbers were 12,

16, and 18 had a T_m at 36, 41, and $48°C$, respectively. It can be concluded that the mobility of the polymer chain was hindered when n numbers are above 12 at measurements of dynamic contact angle.

Surface Free Energy

Figure 4(a,b) shows the effect of side-chain length of the AAs on surface free energy of FA/AA copolymers. The surface free energies in air were independent of side-chain length of the AAs, which is similar to the result of advancing contact angles. However, the surface free energy in water decreased with increasing n numbers in contrast to the result of receding contact angles. Since the surface free energies in air were close to 10.4 mN/m of the FA homopolymer and the polar components were close to zero, it is concluded that the R_f groups orient to the air–solid interface. On the contrary, in water, when n numbers are below 8, both dispersion force and polar component were larger than those in air. Therefore, R_f groups regress and main-chain, spacer ($—CH_2CH_2—$), side-chain alkyl groups of AA ($—C_nH_{2n+1}$), and carbonyl groups ($—COO—$) reorient to the water–solid interface in order to minimize interface free

Figure 4 Effect of side-chain length of AAs on surface free energy of FA/AA copolymers in air (a) and in water (b).

energy. When n numbers are above 12, the both components are almost equal to that in air. Therefore, R_f groups do not regress even in water.

Freeze-Dried XPS

Freeze-dried XPS was conducted to obtain direct evidence of surface reorientation during environmental change. Since ordinary XPS is measured under a high-vacuum condition, the surface structure may be different from that in water. To characterize the surface chemical composition in water, it is necessary to examine hydrated specimens in a frozen state.[18] The surface structures of FA/AA copolymers in the dry state and in the hydrated state were measured using freeze-dried XPS. Figure 5 shows the result of F1s/C1s values of FA copolymer in the dry state and in the hydrated state at $-50°C$ using freeze-dried XPS. The F_{1s}/C_{1s} values represent the relative magnitude of fluorine concentration at the surface. F_{1s}/C_{1s} values in the dry state were independent of side-chain length of the AAs, similar to the result of advancing contact angles. We attributed this phenomenon to the orientation of R_f groups in air, which is independent of side-chain length of the AAs. On the other hand, F_{1s}/C_{1s} values in the hydrated state increased with increasing n numbers, similar to the result of receding contact angles. The change of chemical composition in the

surface area indicates the molecular reorientation. Low values of F_{1s}/C_{1s} for n numbers below 8 are probably derived from the R_f groups regressing at water-solid interface, and the high value for n numbers above 12 are derived from the R_f groups not regressing due to crystallization of the side chains.

Mechanism for Water Repellency of FA/AA Copolymers

From the above description, the mechanism for water repellency of FA/AA copolymers is explica-

Figure 5 F_{1s}/C_{1s} values of FA/AA copolymers.

Figure 6   Models for water repellency of FA/AA copolymers.

ble from the standpoint of surface molecular mobility. We suggest the models for water repellency of FA/AA copolymers shown in Figure 6. The FA/BA copolymer is representative of the FA/AA copolymers with the short side chain of the AAs (C_nH_{2n+1}; $n \leq 8$). These FA/AA copolymers were not crystalline at 25°C. The FA/StA copolymer is representative of the FA/AA copolymers with long side chains of the AAs (C_nH_{2n+1}; $n \geq 12$). These FA/AA copolymers were crystalline at 25°C. The advancing contact angles for water were independent of side-chain length of AAs and were almost constant at 120° ($\theta a \approx 120°$). We attributed this behavior to the orientation of R_f groups in air, which is independent of side-chain length of AAs. On the contrary, the receding contact angles showed small values of about 45° for n numbers below 8 and increased suddenly with increasing n numbers. This behavior was explained as follows. High wettability during the receding process at the n numbers below 8 is derived from the R_f groups regressing at the water–solid interface in order to minimize the interface free energy. In these copolymers, microbrownian motion easily takes place because of its noncrystallinity [Fig. 3(b)] at 25°C at which dynamic contact angles were measured. The regression of R_f groups is apparent from increase in the surface free energy in water [Fig. 4(b)] and F_{1s}/C_{1s} in hydrated state (Fig. 5). Then, low wettability during the receding process at the n numbers above 12 is caused by the result that the R_f groups cannot regress at the water–solid interface. Since these copolymers were restrained due to its crystallinity at 25°C, it is difficult to occur the reorientation in contact

with water. These results obtained in this study indicated that the surface crystallinity reflects the bulk crystallinity.

By the way, Damme et al. studied a similar polymer system, poly(n-alkyl methacrylates) —[CH—C(CH₃)COOC$_n$H$_{2n+1}$]—.[9] They suggested that receding contact angle of poly(n-alkyl methacrylates) decreased suddenly when n increased from 8 to 12. They attributed this phenomenon to the increased mobility of surface groups with decrease in T_g. This mobility is seriously influenced by internal plasticization due to increase of side-chain length. On the other hand, for the FA/AA copolymer mobility is influenced by crystallization of the side chain. In this manner, the effect of side-chain length on receding contact angle varies with the structure of polymer.

Temperature Dependency on Surface Properties

The data stated above shows R_f groups of the FA/StA ($n = 18$) copolymer do not regress even in water due to its crystallization at 25°C. In this section, surface properties at temperature above T_m were investigated. Figure 7 shows temperature dependency of receding contact angles and F_{1s}/C_{1s} of FA/StA copolymer. Receding contact angles were measured by Wilhelmy method, and F_{1s}/C_{1s} were measured by ordinary XPS technique. The used sample for XPS was quenched until 25°C after immersing in water at temperature that receding contact angle was measured. It can be presumed that the surface condition in contact with water was kept and surface mobility was frozen during this measurement. The reced-

Figure 7 Temperature dependency on contact angles and F_{1s}/C_{1s} of FA/StA copolymer.

ing contact angles decrease at temperature above T_m. This result shows that R_f groups regress due to increase of surface mobility of copolymer. Since F_{1s}/C_{1s} values are also similar to receding contact angles, the above idea is supported from the standpoint of surface chemical composition.

Katano et al. reported wettability of the film poly(perfluorooctyl acrylates) increases considerably when it is heated above T_m in air and then cooled down to room temperature in water.[19] They explained the decrease of screening effect of

polar groups due to tilting of R_f groups causes high wettability. Our result of Figure 7 supports the view of Katano et al.

Effect of FA Content on Dynamic Contact Angle

Regarding FA/StA ($n = 18$) and FA/BA ($n = 4$) copolymer, the effect of FA content on dynamic contact angles [Fig. 8(a,b)] was investigated. The dynamic contact angles of the polymers whose FA content is below 60 mol % were similar to the result described in Figure 2, where tendency of the weight ratio is constant. The receding contact angles of FA/StA copolymer were larger than those of FA/BA copolymer. On the other hand, above 80 mol % even FA/BA copolymer had the high values, which are equal to those of FA/StA copolymer, due to crystallization of R_f groups. This fact was confirmed by X-ray diffraction measurement (not described in this paper).

CONCLUSIONS

The relationship between wetting behavior and surface molecular mobility was studied. The main conclusions from this study are summarized as follows:

1. Physical properties of FA/AA copolymers depend on side-chain length of the AAs.

Figure 8 Dynamic contact angles of FA/StA (a) and FA/BA (b) copolymer as a function of FA content.

2. Wetting behavior depends on surface reorientation in contact with water.
3. The surface molecular mobility reflects the bulk molecular mobility
4. Direct evidence of surface reorientation of environmental change was observed by freeze-dried XPS.

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