2342 *Macromolecules* **1994,** *27,* 2342–2344

Surface Property of Polymer Films with Fluoroalkyl Side Chains

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Received November 19, 1993
Revised Manuscript Received January 25, 1994

Introduction

Fluorocarbon polymers have been widely studied in recent years as useful materials in the field of biomaterials and coating engineering due to their unique surface property.[1–4] For example, the polymers have a hydrophobic and lipophobic property, while hydrocarbon polymers have a hydrophobic and lipophilic property.[5] Both the strong electronegativity of the fluorine atoms and the helical chain structure of the fluorocarbon[6] affect this unique property. In addition, as mentioned in numerous reports, the surface morphology of the polymers also affects the surface property.[7,8] The factors determining the surface property of fluorocarbon polymers are complicated and have not been clarified yet.

It is important to study the surface structure that affects the surface property. In particular, we investigated the environmental effect on the surface structure in the process of generating a solid surface of the polymer films when the melted polymers are cooled either in air or in liquid. We chose poly(fluoroalkyl acrylate)s (PFAAs) and poly(fluoroalkyl methacrylate)s (PFAMAs) as the samples.

Recently, we have found that the wettability of the films of some PFAAs and PFAMAs increases considerably when they are heated in air and then cooled in a liquid such as water. This change in the wettability is not anticipated based on the general point of view that the surface is usually stable and hydrophobic. Moreover, we have found that, when the polymers previously treated as described above are heated again and cooled gradually in air, the surface recovers its original character. These reversible characteristics of the wettability of PFAAs and PFAMAs have not been reported previously and are useful in the field of industrial applications.

In this study, we discuss the mechanism of the surface property of the polymer films with fluoroalkyl side chains based on the results of X-ray diffraction and surface energy measurements.

Experimental Method

Sample Preparation. The monomers (Osaka Organic Chemical Ltd.) listed in Table 1 were polymerized at 70 °C in 1,1,1-trichloroethane by a radical polymerization technique. The polymers were precipitated twice in methanol and then dried under reduced pressure.

By a dipping method, a microscope glass plate (20 × 30 × 0.2 mm) was coated with the polymer which was dissolved in 1,1,1,3,3,3-hexafluoro-2-propanol at 0.2 wt %. The dipping speed was 10 mm/s.

Procedure of Heating and Cooling. A schematic diagram of the procedure of heating and cooling samples is shown in Figure 1. The surface of the polymer films is generated in liquid by procedure A: the polymer is heated in air to a range from 25 to 150 °C for 1 min and cooled to room temperature at a rate of 10 °C/s by immersing it into a liquid. Purified water was used as the liquid in this study. The surface of the polymer films is generated in air by procedure B: the polymer is heated to the same temperature for 1 min and gradually cooled in air to room temperature.

Measurements. Dynamic contact angles of the polymer film were measured using the Wilhelmy plate technique.[9] The plates were immersed at a speed of 10 mm/min into purified water. The temperature of the water was maintained at 22 °C.

The surface free energy of the polymers was calculated using measured receding contact angles for various liquids on the polymer films by eqs 1 and 2[10]

$$\gamma_{\mathrm{solid}} = \gamma^{\mathrm{d}}_{\mathrm{solid}} + \gamma^{\mathrm{p}}_{\mathrm{solid}} \qquad (1)$$

$$\gamma_{\mathrm{liquid}}(\cos\theta + 1) = 2(\gamma^{\mathrm{d}}_{\mathrm{solid}}\gamma^{\mathrm{d}}_{\mathrm{liquid}})^{1/2} + 2(\gamma^{\mathrm{p}}_{\mathrm{solid}}\gamma^{\mathrm{p}}_{\mathrm{liquid}})^{1/2} \qquad (2)$$

where γ is the surface free energy and the superscripts d and p correspond to dispersion and polar components of the surface free energy, respectively.

X-ray diffraction experiments were carried out in the reflection mode with a standard-focus copper tube using a Max Science Model MXP-3 instrument.

Melting points of the polymers were measured by differential scanning calorimetry (DSC) using a thermal analyzer (Seiko-Denshi Model SSC-5000) over a range from 30 to 300 °C at a heating rate of 1 °C/min.

Results and Discussion

Dynamic Wettability Change. The dynamic contact angles of 17F in Table 1 are shown in Figure 2; parts a and b correspond to the samples treated by procedures A and B, respectively. The receding contact angle θ_r of the prepared sample is 110°, and the polymer surface repels liquid. We call this surface state the "low wetting state" (Figure 1). In Figure 2a, θ_r shows a sharp decrease near the temperature T_c and is constant ($\theta_r = 60°$) beyond T_c, where T_c is defined as the temperature at which θ_r reaches a constant value in procedure A. Water adheres strongly to the surface of the sample treated beyond T_c. We call this surface state the "high wetting state" (Figure 1). Wettability changes in organic films were reported in the case of stearic acid cooled in water[11] and poly(tetrafluoroethylene) cooled in contact with gold.[12] However, in our present results, the contact angle change is extremely large compared with those mentioned above.

In procedure B, as seen in Figure 2b, θ_r increases with temperature and is constant beyond T_c', where T_c' is defined as the temperature at which θ_r reaches a constant value. θ_r of the sample treated beyond T_c' in procedure B is in good agreement with that of the prepared sample. Thus we conclude that the final state of procedure B is the same as the initial state of procedure A. The value of T_c is nearly equal to that of T_c' as shown in Figure 2. This shows that the reversible change between the *low wetting state* and the *high wetting state* occurs beyond the same temperature. Repeatability of this wettability change was confirmed over 100 times.

The reversible change is also observed when the film is treated with various liquids other than water, such as glycerol, ethanol, poly(ethylene glycol), octane, and benzene. This indicates that the dynamic contact angle change in 17F is independent of the polarity of the contacting liquid.

The dynamic contact angles of the other polymers are also listed in Table 1. The results indicate that the wettability change is observed for the polymers with long side chains.

The temperature T_c values and the melting points of the polymers are listed in Table 1. T_c is observed only for the polymers with long side chains and is nearly equal to the melting point. Therefore, the reversible change in the wettability is observed when the polymers have long side chains and are heated to a temperature above the melting point.

0024-9297/94/2227-2342$04.50/0

Table 1. Wettability and Structural Data for the Polymers

chemical structure of monomers	sample code	no. of C atoms in a fluoroalkyl side chain	contact angle/deg				T_c/°C	melting point/°C	side-chain length/Å	layer spacing/Å	surface energy/(dyn·cm^{-1})			
			as prepared		after procedure A						as prepared		after procedure A	
			θ_a	θ_r	θ_a	θ_r					γ_d	γ_p	γ_d	γ_p
CH_2=$CHCOOCH_2CF_3$	3F	1	130	22	133	17	n	n	7	n	—	—	—	—
CH_2=$CHCOO(CH_2)_2(CF_2)_4F$	9F	4	130	20	130	20	n	n	11	n	—	—	—	—
CH_2=$CHCOO(CH_2)_2(CF_2)_6F$	13F	6	135	47	137	40	n	n	14	n	—	—	—	—
CH_2=$CHCOO(CH_2)_2(CF_2)_8F$	17F	8	117	110	124	58	86	75	16	32	14	0.3	17	12
CH_2=$CHCOO(CH_2)_2(CF_2)_{10}F$	21F	10	120	99	113	67	135	128	19	37	—	—	—	—
CH_2=$C(CH_3)COOCH_2CF_3$	3FM	1	88	83	88	81	n	n	7	n	22	5.0	24	6
CH_2=$C(CH_3)COO(CH_2)_2(CF_2)_4F$	9FM	4	110	80	109	75	n	n	11	n	—	—	—	—
CH_2=$C(CH_3)COO(CH_2)_2(CF_2)_8F$	17FM	8	115	110	120	64	93	87	16	32	14	0.1	15	8
CH_2=$C(CH_3)COO(CH_2)_2(CF_2)_{10}F$	21FM	10	120	94	115	72	132	133	19	36	—	—	—	—

[a] n, not observed. —, cannot be done.

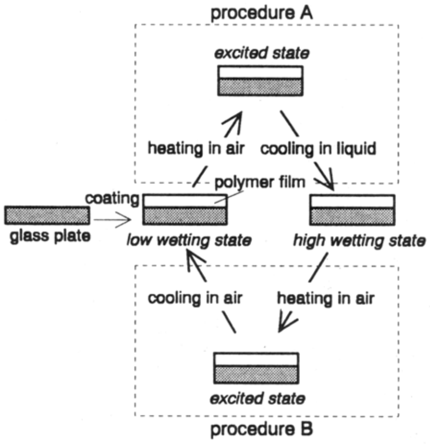

Figure 1. Schematic diagram of the procedure of heating and cooling polymer films.

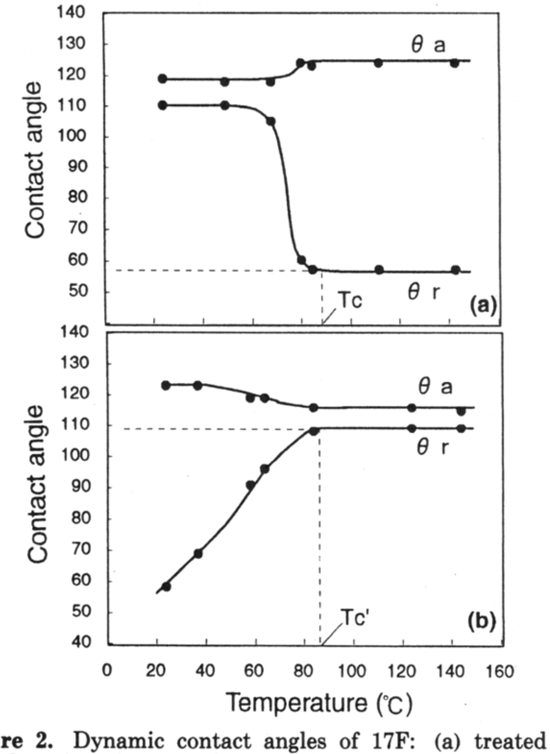

Figure 2. Dynamic contact angles of 17F: (a) treated by procedure A with purified water; (b) treated by procedure B after treatment by procedure A up to 130 °C.

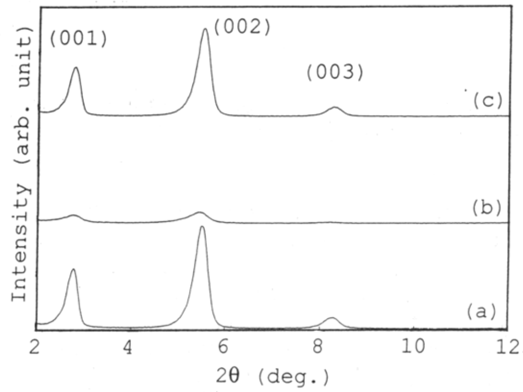

Figure 3. X-ray diffraction patterns from 17F: (a) as prepared; (b) after treatment by procedure A up to 130 °C; (c) after treatment by procedure B up to 130 °C.

X-ray Diffraction and Surface Energy Measurement. The X-ray diffraction patterns from 17F are shown in Figure 3. In this figure, part a shows the pattern for the prepared sample, part b that for the sample treated by procedure A up to 130 °C, and part c that for the sample treated by procedure B up to 130 °C. In the prepared sample, the (00*l*) plane diffraction pattern shows a lamellar structure.[13-15] In the case treated by procedure A, the intensity of the diffraction peaks decreases without a peak shift; the orientation of the molecular chains is shown to be disturbed by procedure A. However, in the case treated by procedure B, its pattern is similar to that of the prepared sample. These results also support the observation that the surface structure of the sample treated by procedure B returns to that of the prepared sample. The X-ray diffraction patterns of 21F, 17FM, and 21FM show features similar to those of 17F. The other polymers in Table 1 show no X-ray diffraction peak. The side-chain lengths and the layer spacings calculated from the X-ray diffraction patterns are listed in Table 1. The layer spacings are approximately twice as long as the side-chain lengths as shown in Table 1. These results suggest that the neighboring side chains of the polymers are oriented in opposite directions from each other.

The values of surface free energy of the polymers are listed in Table 1. In the *low wetting state* of 17F and 17FM, the polar component γ_p of the surface free energy is extremely smaller than the dispersion component γ_d of the surface free energy. After treatment by procedure A, γ_p increases remarkably, although the change in γ_d is small. In the case of 3FM, both γ_d and γ_p do not change after procedure A. These results suggest that the polar groups (carbonyl groups) of the polymers electrically affect the wettability as a result of procedure A.

Mechanism. Van Damme et al. have shown that the wettability change in the polymers with hydrocarbon side chains is due to tumbling of the side chains.[16] If the wettability change in 17F and 17FM is due to the tumbling of the side chains, their surface energy should be equal to that of poly(tetrafluoroethylene) (PTFE) because the

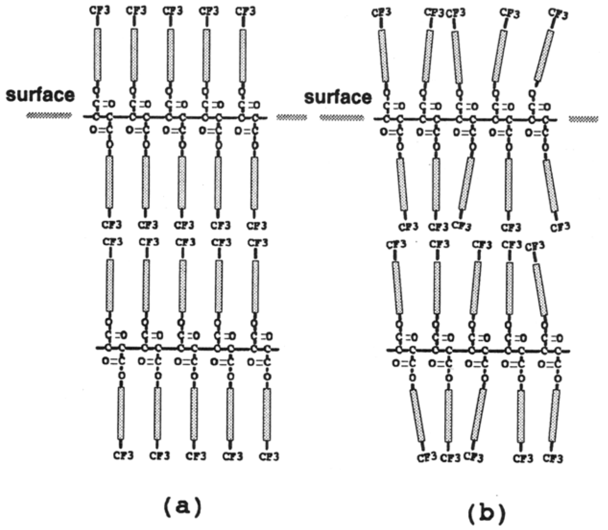

Figure 4. Schematic diagram of the orientation of fluorocarbon side chains on a surface: (a) in the *low wetting state*; (b) in the *high wetting state*.

tumbled structure of these polymers is similar to the structure of PTFE. As a result of our surface energy measurements, γ_d of PTFE is 25 dyn/cm. According to the tumbled model, γ_d of the *high wetting state* should be larger than that of the *low wetting state* by a factor of 1.8. Based on our measurement, the factor is determined to be 1.2. This indicates that the side chains of 17F or 17FM tilt, and the tilt angle is small. So the wettability change in 17F and 17FM cannot be explained by the tumbled model. The model of this reversible change in the wettability is considered as follows. In the *low wetting state*, the side chains of the polymers are oriented normal to the surface as illustrated in Figure 4a, and the fluoroalkyl groups screen the electrical effect of the polar groups, resulting in the small surface energy. In the *high wetting state*, the tilt of the side chains increases at a small angle as illustrated in Figure 4b. Because the electrical screening effect of the fluoroalkyl groups decreases, γ_p of either 17F or 17FM increases but the increase in γ_d is small. Therefore, the wettability of these polymers increases.

According to our model, not only PFAAs or PFAMAs but also other polymers having long fluoroalkyl side chains with polar groups may have this dynamic surface property.

References and Notes

(1) Rabolt, J. F.; Russell, T. P.; Tweig, R. J. *Macromolecules* **1984**, *17*, 2786.
(2) Iwatsuki, S.; Kondo, A.; Sakai, Y. *Nippon Kagaku Gakkaishi* **1985**, *10*, 1884.
(3) Ishiwari, K.; Ohmori, A.; Koizumi, S. *Nippon Kagaku Gakkaishi* **1985**, *10*, 1924.
(4) Schineider, J.; Erdelen, C.; Ringsdorf, H.; Rabolt, J. T. *Macromolecules* **1989**, *22*, 3475.
(5) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; Wiley-Interscience: New York, 1975.
(6) Bunn, C. W.; Howells, E. R. *Nature* **1954**, *174*, 549.
(7) Schonhorn, H. *Polym. Lett.* **1967**, *5*, 919.
(8) Schonhorn, H. *Macromolecules* **1968**, *1*, 145.
(9) Hogt, A. H.; Gregonis, D. F.; Andrade, J. D. *J. Colloid Interface Sci.* **1985**, *106*, 289.
(10) Dynes, P. J.; Kaeble, D. H. *J. Adhes.* **1974**, *6*, 195.
(11) Nietz, A. *J. Phys. Chem.* **1928**, *32*, 255.
(12) Schonhorn, H.; Ryan, F. *J. Adhes.* **1969**, *1*, 43.
(13) Barisova, T. I.; *et al. Vysokomel. Soedin.* **1980**, *22*, 2672.
(14) Stepanova, T. P.; *et al. Zh. Fiz. Khim.* **1984**, *58*, 1949.
(15) Okawara, A.; Maekawa, T.; Ishida, Y.; Matsuo, M. *Polym. Prepr. Jpn.* **1991**, *10*, 389.
(16) Van Damme, H.; Hogt, A.; Feijen, J. *J. Colloid Interface Sci.* **1986**, 167.