Surface Characterization of Poly(styrene-*co*fluoroalkylfumarate): XPS and Contact Angle Measurement Study

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ABSTRACT: We studied styrene and fluoroalkylfumarate (FAF) copolymers and their surfaces by means of contact angle measurement and X-ray photoelectron spectroscopy (XPS). The surfaces of the copolymers were very hydrophobic (even with a small amount of FAF) because of the concentration of FAF segments at the surface. The hydrolyzed surfaces of the copolymers became slightly hydrophilic compared to the as cast. The XPS data suggested that the fluoroalkyl groups seemed to be primarily hydrolyzed. The surfaces with a large amount of FAF changed their characteristics to hydrophobic again under atmospheric conditions. This phenomenon was due to the inversion of the carboxyl and the fluoroalkyl groups. These hydrolyzed surfaces seemed to be useful for modifying polymer surfaces by attaching to other functional molecules. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 1049–1054, 1999

Key words: fluoroalkylfumarate; copolymer; surface analysis; X-ray photoelectron spectroscopy; contact angle

INTRODUCTION

Recently, poly(dialkylfumarate)s, which are prepared by the radical polymerization of fumaric acid derivatives, have been evaluated as novel polymeric materials that have potential practical applications.¹ Otsu et al. analyzed the radical homopolymerization of various dialkylfumarates and the characterization of the polymers.^{2,3} They reported that the physical properties of these polymers could be drastically changed by selecting the bulky ester substrates of fumarate monomers. Fluoroalkylfumarates (FAFs) can be easily polymerized to poly(fluoroalkylfumarate)s^{4,5} [poly-(FAF)]; some of them are used as membranes for oxygen permeation⁶ and pervaporation.⁷ Even though they have no crystalline phase, these polymers have excellent heat stability because of the high rigidity of their backbone chain.⁶

Poly(FAF)'s use as a surface modifier is of interest. When it is mixed with other polymers, the strong surface enrichment of poly(FAF) and the effective water repellency occur even at low concentrations because of the very low surface energy of the fluoroalkyl side chain of FAF. Other researchers have noted that the surface properties of poly(FAF)s are very hydrophobic.^{1,8} However, because of their poor solubility and incompatibility with common organic solvents and syn-

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thetic polymers, it is difficult to use the FAF homopolymer as an additive. One possible strategy that can solve this problem is the copolymerization of FAF with other monomers. FAF can copolymerize with various kinds of vinyl monomers.^{9,10} Researchers have analyzed the copolymers of various FAFs and vinyl monomers as gas-separation membranes^{9,10}; in addition, other researchers have found that poly(diisopropyl fumarate-*co*-styrene) has liquid crystallinity.¹¹ To date, there has been no extensive research on the FAF copolymer.

As a basic study of the FAF copolymer, we analyzed the copolymerization of FAF with styrene and the surface properties of the copolymers. The surfaces of the copolymers and the FAF homopolymer have high hydrophobicity. The surface enrichment of the FAF group may provide a functional surface. In other words, the hydrolysis of FAF copolymers may generate carboxyl groups on their surfaces. We studied the original and the hydrolyzed surfaces in detail by means of X-ray photoelectron spectroscopy (XPS) and contact angle measurement.

MATERIALS AND METHODS

Materials

The FAF monomer used in this study is 1H, 1H, 2H, 2H-heptadecafluorodecyl-isopropylfumarate [(iP-F₁₇)F]. Styrene, benzoyl peroxide (BPO), and 1,1,2-trichloro-1,2,2-trifluoroethane (Cl₂FCCClF₂) were purchased from Wako Pure Chemicals (Osaka, Japan). Toluene, trifluoroacetic acid-D (CF₃COOD), and tetramethylsilane (TMS) were purchased from Nacalai Tesque Inc. (Kyoto, Japan). Methylene iodide and 1-bromonaphthalene were purchased from Tokyo Kasei (Tokyo). Styrene was purified by distillation. The $(iP-F_{17})F$ and other chemicals were used as obtained.

Copolymerization

The copolymers were prepared by bulk polymerization as follows: the total monomers (10 mmol) and 0.01 g of BPO as an initiator were poured into a glass tube, degassed, and polymerization was performed at 60°C for 18 h (Scheme 1). After the polymerization, the resulting copolymers (PSFF) and the (iP- F_{17})F homopolymer (PFF) were dissolved in Cl₂FCCClF₂ and poly(styrene) (PS) was dissolved in toluene. The polymer solutions were poured into a large amount of methanol to remove the unreacted monomers, and the isolated homopolymers and the resulting copolymers were dried under a vacuum.

Characterization

The polymer yields were calculated from gravimetry and are summarized in Table I. ¹H-NMR spectra were recorded on a JNM-EX270 FT NMR System (Jeol, Tokyo). The copolymers were dissolved in CF₃COOD, and TMS was used as a reference. The (iP-F₁₇)F contents in the copolymer in bulk were calculated from the CH₃/aromatic H ratio in the ¹H-NMR spectra. The intrinsic viscosity of PSFF and PFF were measured using Ostowald's viscometer in Cl₂FCCClF₂ at 30°C and that of PS was measured in toluene at 30°C.

Preparation of Polymer Membranes and Hydrolysis

PSFF and PFF were dissolved in $Cl_2FCCClF_2$ and PS was dissolved in toluene at a concentration of 10 wt %. These solutions were poured into a 6-cm diameter glass dish and were dried at atmospheric pressure overnight. Membrane hydrolysis

	(iP-I	$(iP-F_{17})F(\%)$		Intrinsic
Sample	Feed	Polymer ^a	(%)	(dL/g)
PS	0	0.0	47.2	0.84^{b}
PSFF-10	5	10.4	36.0	
PSFF-16	10	15.5	53.2	
PSFF-30	15	29.5	52.7	
PSFF-41	25	41.3	76.0	$0.25^{ m c}$
PSFF-60	50	60.0	89.4	0.36°
PSFF-72	75	72.0	48.1	$0.21^{ m c}$
PFF	100	100.0	79.6	0.23°

Table I Radical Copolymerization of Styrene and $(iP-F_{17})F$

^a Calculated by ¹H-NMR.

 $^{\rm b}$ Measured at concentrations of 0.1, 0.2, and 0.3 g/dL in toluene at 30°C.

 $^{\rm c}$ Measured at concentrations of 0.1, 0.2, and 0.3 g/dL in $\rm Cl_2FCCClF_2$ at 30°C.

was carried out in a 4N NaOH solution at 60° C for 48 h.

Contact Angle Measurement

The static contact angle of the water, the methylene iodide, and the 1-bromo-naphthalene on the membrane surfaces were measured with a Gonio meter type G-1 (Erma Co., Tokyo) using the sessile drop method at 25°C and 65% relative humidity. This procedure was repeated 6 times at various locations on the surface of the film surface, and all values were averaged. The level of agreement was generally within $\pm 2^{\circ}$. The total surface free energy (γ_s) of the polymers was estimated from the contact angles of the water and the methylene iodide on the solid surfaces using Young's equation¹² and Fowkes' equation.¹³ γ_s^{d} and γ_s^p are the contributions from the dispersion forces component and the polar forces component. The amount of $(iP-F_{17})F$ on the copolymer surfaces were calculated using Cassie's equation^{14,15}:

$$\cos \theta = f_1 \cos \theta_1 + f_2 \cos \theta_2 (f_1 + f_2 = 1)$$

where f_1 and f_2 represent the fractional surface areas of regions 1 (PS) and 2 [(iP-F₁₇)F] and θ_1 and θ_2 are the water contact angle values on the pure homogeneous surfaces of 1 (PS) and 2 [(iP-F₁₇)F], respectively.

Surface Analysis by XPS

An XPS 1000 spectrometer (Shimadzu Co., Kyoto, Japan) was employed to carry out the XPS mea-

surements of the polymer membranes using a MgK α X-ray source at 8 kV and 20 mA. All of the binding energy at the emission angle of the photoelectron at 90° was referenced by setting the CH_x peak at the maximum in the resolved C1s spectra to 285.0 eV. The F/C and O/C ratios were calculated from the peak areas of the F1s, O1s, and C1s spectra. The level of agreement was generally within ± 0.01 .

RESULTS AND DISCUSSION

Copolymerization of Styrene and (iP-F₁₇)F

In this study the free radical polymerization was carried out in bulk according to the method described previously.¹⁶ The results are shown in Table I. The $(iP-F_{17})F$ contents of the PSFFs increased with an increase in the $(iP-F_{17})F$ in the feed. From this result it is clear that various PSFFs that contain $(iP-F_{17})F$ can be prepared by changing the feed. We could not determine the molecular weight of the PSFFs by using gel permeation chromatography (GPC), because these polymers generally did not dissolve in the solvents used in the GPC analysis. Thus, we attempted to evaluate the molecular weight of the polymers by intrinsic viscosity. The intrinsic viscosities of these PSFFs varied from 0.21 to 0.36. Because the PSFFs with a small amount of (iP- F_{17})F did not homogeneously dissolve into either the toluene or the Cl₂FCCClF₂, the viscosity measurement was not attempted. This was ascribed to the complexity of the dissolving properties of the FAF content. Every PSFF seemed to have enough molecular weight to give a cast film, which had a thickness of $80-100 \ \mu m$.

Evaluation of Poly(styrene-*co*-(iP-F₁₇)F) by Contact Angle Measurement

Table II summarizes the results of the contact angle measurements. It is apparent that the hydrophobicity of the surfaces increases with an increase in the (iP-F₁₇)F content. The PSFF surfaces were very hydrophobic as compared to PS, even at low amounts of (iP-F₁₇)F. The surface energy of the PSFFs was drastically reduced. This reduction was due to a decrease in γ_s^d , but the γ_s^p did not change. This indicates that the PSFF surfaces were covered with fluorocarbon groups and there were no other groups on the surfaces. These results show that the surface of the PSFFs have a

	Contact Angle (°)		Surface Energy ^a (dyn/cm)		
Sample	Water	Methylene Iodide	γ_s	γ^d_s	γ^p_s
PS	87.2	31.4	43.8	42.7	1.1
PSFF-10	104.4	86.8	14.7	12.4	2.2
PSFF-16	104.9	86.7	14.6	12.6	2.1
PSFF-30	104.1	86.5	14.8	12.5	2.3
PSFF-41	106.4	88.2	13.9	12.0	1.9
PSFF-60	108.2	91.0	12.6	10.9	1.8
PSFF-72	110.0	91.8	12.1	10.7	1.4
PFF	111.3	92.0	11.9	10.8	1.2

Table IISurface Characterization of
Poly(styrene-co-(iP-F17)F)Surfaces

^a Calculated by water and methylene iodide.

high level of hydrophobicity as do the concentrated FAF segments; this was comparable to poly(tetrafluoroethylene) (published data¹⁶ are γ_s = 19.1, γ_s^d = 18.6, and γ_s^p = 0.5 dyn/cm), even at low amounts of FAF.

Evaluation of Poly(styrene-*co*-fumarate) by XPS Measurement

A surface chemical analysis of the polymers was carried out by XPS. Figure 1(a) shows the C1s spectra for the surfaces of the polymers. The C1s peak (which corresponds to the hydrocarbon) was observed at a binding energy of 285 eV. The PFF spectrum had a C-O peak at 286.5 eV and a C=O peak at 289 eV. The C1s peak of $-CF_2$ and $-CF_3$ were observed at 292 and 294 eV, respectively. The PS spectrum had a large hydrocarbon peak at 285 eV. The PSFF spectra were typically a mixture of both components. Table III shows the F/C and O/C of the polymer surfaces. The calculated F/C and O/C ratios were estimated from the chemical structures of the monomers and their contents. The F/C ratios observed were larger than the calculated ones. This means that the fluorocarbon chains were concentrated at the surface. Figure 2 shows the $(iP-F_{17})F$ content of the PSFF that was calculated by using the C1s peak areas of $-CF_2$ (292 eV) and $-CH_x$ (285 eV) and by using Cassie's equation (water contact angles were used). It is clear that the surface



Figure 1 XPS spectra of poly(styrene-co-(iP- F_{17})F) surfaces: (a) as cast and (b) after hydrolysis.

	XPS ^a		Calculated ^b	
Sample	F/C	O/C	F/C	O/C
PS	0.01	0.06	0.00	0.00
PSFF-10	0.69	0.15	0.20	0.05
PSFF-16	0.68	0.13	0.28	0.07
PSFF-30	0.72	0.13	0.47	0.11
PSFF-41	0.97	0.18	0.60	0.14
PSFF-60	1.01	0.19	0.76	0.18
PSFF-72	0.92	0.19	0.85	0.20
PFF	1.14	0.22	1.00	0.24

Table III Composition of Poly(styrene-co-(iP- F_{17})F) Surface Estimated by XPS Spectra

^a Calculated by XPS spectra.

 $^{\rm b}$ Calculated by the bulk content from the chemical structures of the monomers.

(iP- F_{17})F amounts were larger than the calculated values. However, there were differences between them at a low amount of (iP- F_{17})F. This was ascribed to the differences in the analytical depth from the surface of both measuring methods. The analytical depth of the XPS for a synthetic polymer is about 100 nm. The contact angle, however, gives the outermost surface characteristic. The PSFF surfaces with a small (iP- F_{17})F content seemed to have very thin fluorinated layers, which are related to their (iP- F_{17})F content.



Figure 2 (iP-F₁₇)F content of PSFF surface estimated by water contact angle measurement and XPS spectra: (\bigcirc) contact angle and (\triangle) XPS.



Figure 3 Contact angles of poly(styrene-*co*-(iP- F_{17})F) surfaces after hydrolysis: (\bigcirc) PFF, (\triangle) PSFF-41, and (\Box) PSFF-60.

The outermost surfaces of the copolymers in all the ranges with $(iP-F_{17})F$ content were almost completely covered with FAF units.

Evaluation of Surface as Cast and After Hydrolysis

We expected that the carboxyl groups would be generated by surface hydrolysis, because the (iP- F_{17})F group was concentrated at the surface of the copolymer. Figure 1(b) shows the C1s spectra of the hydrolyzed polymer surfaces. After hydrolysis, the peaks at 292 and 294 eV (which were assigned to the fluoroalkyl side chain) were drastically decreased as compared with those as cast. Hydrolysis therefore was performed at the surface and carboxyl groups may have been generated on the surface by hydrolysis. The XPS spectra indicated that the fluoroalkyl chains were primarily hydrolyzed.

Figure 3 shows the changes in the contact angle after hydrolysis. The hydrolyzed surface became slightly more hydrophilic than that before hydrolysis; however, there was no significant difference among the wettability of the PSFFs. PSFF-10, 16, and 30 showed almost the same values as PSFF-41. The carboxyl group, which contributes to the hydrophilicity, was degenerated by the hydrolysis of FAF. Because the outermost content of the FAF was almost the same in all the samples, the resulting hydrolyzed surface of the PSFFs showed the same wettability. The PSFF-60 and PFF surface became hydrophobic again under atmospheric conditions. This phenomenon was attributed to the inversion of the generated carboxyl and fluoroalkyl groups.¹⁷

CONCLUSION

The results of the surface analysis of the PSFFs showed that the surfaces of the PSFFs were very hydrophobic because of the concentration of (iP- F_{17})F segments at the surface. The hydrolyzed surfaces became more hydrophilic than before hydrolysis; however, the surfaces with a large amount of (iP- F_{17})F were relatively unstable. The modification of PSFF surfaces (e.g., the immobilization of biomolecules) may be possible by using the generated carboxyl groups. The use of PSFF as an additive for surface modifiers appears likely; however, further research is needed in regard to the solubility and miscibility of the polymers that are to be modified.

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