Surface properties of poly(vinyl alcohol) films with a fluoroalkyl group at one end

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Surface properties of poly(vinyl alcohol) (PVA) films with a fluoroalkyl group at one end, $H(CF_2)_nCH_2O(CH_2)_3S$–PVA and $F(CF_2)_7CONHCH_2CH_2S$–PVA, were studied by contact angle measurements and X.p.s. analysis. $H(CF_2)_nCH_2O(CH_2)_3S$–PVA and $F(CF_2)_7CONHCH_2CH_2S$–PVA distributed preferentially on the air-side surface, and the surface showed properties corresponding to the characteristics of the fluoroalkyl end groups. Surface free energy, γ_s, was in good agreement with critical surface tension, γ_c, for $F(CF_2)_7CONHCH_2CH_2S$–PVA and n-$C_{12}H_{25}S$–PVA, which had no polar component of γ_s, and with γ_c(max) for a series of $H(CF_2)_nCH_2O(CH_2)_3S$–PVAs which had a polar component. The γ_s of $F(CF_2)_7CONHCH_2CH_2S$–PVA films altered by heat treatment, gave a minimum value at 80°C and increased with a rise in heat treatment temperature above 120°C, which was thought to be caused by distribution changes of the end groups. γ_s was closely related to the distributions of CF_3 and $-CF_2-$ groups in the surface layer estimated by X.p.s. analysis.

(Keywords: poly(vinyl alcohol); fluoroalkylthio end group; critical surface tension; surface free energy; X.p.s.)

INTRODUCTION

We have performed a theoretical investigation on the polymerization of vinyl acetate (VAc) in the presence of thiol compounds as a chain transfer agent and reported a new method of introducing a moiety of the thiol compounds to one end of poly(vinyl acetate) (PVAc) and poly(vinyl alcohol) (PVA)[1]. By this method, PVAs were obtained having various end groups, such as n-alkylthio group and fluoroalkylthio group, at one end. We have studied the surfaces of PVA films prepared by casting aqueous solutions containing conventional PVA and PVA with an n-alkylthio group at one end. The surfaces gave lower critical surface tensions and surface free energies than that of the conventional PVA, depending on the n-alkyl chain length at one end. It was found by X.p.s. analysis that this was caused by concentrations of the n-alkylthio end groups at the air-side surface. However, detailed investigation of the surfaces was not carried out because the C–C bonds of PVAs and those of n-alkyl chains could not be distinguished in X.p.s. measurement[2].

In this study, we focus on the surfaces of PVA films with a fluoroalkylthio group at one end, which can be synthesized by the chain transfer technique to thiols containing fluoroalkyl groups. It is well known that the fluoroalkyl group strongly affects surface properties and is a favourable group for X.p.s. analysis because the C_{1s} level of the C–F bond is higher than that of the C–C or C–H bonds. First, we study the critical surface tensions and surface free energies by contact angle measurements, and secondly investigate the correlation between the composition and configuration of the surface layer estimated by X.p.s. measurements and the surface free energies.

EXPERIMENTAL

VAc monomer (Kuraray Company) was used without further purification. Analytical grade methanol (MeOH) and 2,2′-azobisisobutyronitrile (AIBN) were used without purification.

Thiols containing a fluoroalkyl group were synthesized from the corresponding alcohol or carboxylic acid according to the following scheme[3]:

$$H(CF_2)_nCH_2OH$$

$$\xrightarrow[\text{NaOH, r.t.}]{CH_2{=}CH{-}CH_2Cl} H(CF_2)_nCH_2OCH_2CH{=}CH_2$$

$$\xrightarrow[\text{BPO, r.t.}]{CH_3COSH} H(CF_2)_nCH_2O(CH_2)_3SCOCH_3$$

$$\xrightarrow[N_2,\,50^\circ C]{\text{NaOH/MeOH}} H(CF_2)_nCH_2O(CH_2)_3SH$$

$$F(CF_2)_7COOCH_3$$

$$\xrightarrow{H_2NCH_2CH_2SH} F(CF_2)_7CONHCH_2CH_2SH$$

VAc was polymerized as described previously[1], with uniformly continuous addition of thiol to form PVAc with a thiol moiety at one end. The PVAc was purified by reprecipitation from acetone solution into n-hexane twice. PVA with a thiol moiety at one end was obtained by sodium hydroxide catalysed methanolysis of the PVAcs at 40°C.

The intrinsic viscosity of the PVAc was measured in acetone at 30°C. Since the PVAcs synthesized with continuous addition of thiol were found to have few or

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no branches caused by chain transfer reactions to the polymer[4], the measurement was carried out on the PVAc as polymerized. The viscosity average degree of polymerization of the PVAc ($\bar{P}_{AC}$) was calculated from the intrinsic viscosity [η] using the relation[5]:

$$[\eta] = 7.94 \times 10^{-3} \bar{P}_{AC}^{0.62} \qquad (1)$$

The degree of hydrolysis was more than 99.9 mol% for the end-group-modified PVAs and for the conventional PVA (PVA–HCA) with degree of polymerization of 1750.

The PVA films were prepared by casting 4% aqueous solutions on a polyethylene terephthalate (PET) sheet or a glass plate, and evaporating water at room temperature to 50 μm or 2–3 μm thickness, respectively. The films were heat treated at 120°C for 10 min and allowed to stand for 7 days at 20°C in 65% r.h. before measurements.

The contact angle measurements were made on the PVA film surfaces at 20°C with a Kyowa contact angle meter CA-DT.

The X.p.s. spectra were taken on a Shimazu ESCA-750 spectrometer using MgKα1,2 exciting radiation with an X-ray source of 8 kV, 30 mA and pressure in the source chamber of 10^{-5} Pa. Under the conditions employed in this investigation, the Ag 3d5/2 line at 368.2 eV binding energy had a full width at half maximum of 1.1 eV. The C_{1s} hydrocarbon level at 285.0 eV binding energy was used for energy calibration. The spectra were recorded at four different take-off angles (15°, 30°, 45° and 90°) defined as the angle between the plane of sample surface and the entrance slit of the analyser. Elemental compositions were calculated by the integrated area ratio of F_{1s} to O_{1s} corrected to the Scofield cross section[6].

RESULTS AND DISCUSSION

Contact angle and critical surface tension

Table 1 lists the PVAs with a fluoroalkyl group at one end. The contact angle (θ) was measured on the air side surface of the PVA films with a fluoroalkyl end group using the liquids listed in *Table 2*[6]. These consist of non-polar liquids (group A), polar liquids (group B-1) and polar liquids forming a hydrogen bond (group B-2); finite values were obtained for all types of liquid. The plots of cos θ against γ_l (Zisman plots) are shown in *Figure 1*; it is seen that the Zisman plots of a series of $H(CF_2)_nCH_2O(CH_2)_3S$–PVAs gave two different lines for group A and group B liquids, in contrast to $F(CF_2)_7CONHCH_2CH_2S$–PVA, which gave only one line for all types of liquid.

Table 3 lists the critical surface tensions, γ_c, which were obtained by extrapolation of the lines of cos θ against γ_l to the cos $\theta = 1$ axis. When two extrapolation values were obtained, the smaller value was taken as γ_c and the other as γ_c(max), according to the established practice[7]. In the case of a series of $H(CF_2)_nCH_2O(CH_2)_3S$–PVAs, γ_c and γ_c(max) were obtained from the plots of group B-1 and group B-2 liquids, respectively, and γ_c decreased with an increase in $-CF_2-$ units. $F(CF_2)_7CONHCH_2CH_2S$–PVA gave the smallest γ_c value in this study. As expected, the PVAs with a fluoroalkyl end group had much smaller γ_c values than n-$C_{12}H_{25}S$–PVA, which was found[1] to have the smallest γ_c value in a series of n-$C_nH_{2n+1}S$–PVAs.

It has been established that wettability is determined by the chemical structure and configuration of the atomic groups comprising the surface and it is known that γ_c of the fluoroalkyl surface changes remarkably depending on the surface composition, especially with the replacement of a single fluorine atom by a hydrogen atom in a terminal $-CF_3$ group[8]. In this study the effect of introducing α-hydrogen, which can interact with the liquids through hydrogen bonding, was observed clearly in the difference between Zisman plots of $H(CF_2)_8CH_2O(CH_2)_3S$–PVA and $F(CF_2)_7CONHCH_2CH_2S$–PVA.

Table 1 RS–PVAs with a fluoroalkyl group at one end

PVA no.	RS–PVA	$\bar{P}_{AC}$
223A	$H(CF_2)_4CH_2O(CH_2)_3S$–PVA	527
236A	$H(CF_2)_6CH_2O(CH_2)_3S$–PVA	516
233A	$H(CF_2)_8CH_2O(CH_2)_3S$–PVA	456
247A	$F(CF_2)_7CONHCH_2CH_2S$–PVA	300
246A	$F(CF_2)_7CONHCH_2CH_2S$–PVA	500
241A	$F(CF_2)_7CONHCH_2CH_2S$–PVA	788
244A	$F(CF_2)_7CONHCH_2CH_2S$–PVA	1809
101A	n-$C_{12}H_{25}S$–PVA	576
PVA–HCA	–	1750

Table 2 Surface tension and its component liquids used in contact angle measurements (20°C)

Liquid		Surface tension (dyne cm^{-1})		
Group	Name	γ_l	γ_l^d	γ_l^p
A	Transdecarin	29.9	29.9	
	n-Hexadecane	27.6	27.6	
	n-Tetradecane	26.7	26.7	
	n-Dodecane	25.4	25.4	
	n-Decane	23.9	23.9	
	n-Nonane	22.9	22.9	
	n-Octane	21.8	21.8	
	n-Heptane	20.3	20.3	
	n-Hexane	18.4	18.4	
B-1	Methyleneiodide	50.8	46.8	4.0
	1,1,2,2-Tetrabromoethane	47.5	44.3	3.2
	1-Bromonaphthalene	44.6	44.4	0.2
	Tricresylphosphate	40.9	37.4	3.5
	1,1,2,2-Tetrachloroethane	36.3	33.2	3.1
B-2	Water	72.8	29.1	43.7
	Glycerine	63.4	37.4	26.0
	Formamide	58.2	35.1	23.1
	Thiodiglycol	54.0	39.2	14.8
	Ethyleneglycol	47.7	30.1	17.6
	Diethyleneglycol	44.4	31.7	12.7
	Tetraethyleneglycol	43.5	29.9	13.6
	Dipropyleneglycol	33.9	29.4	4.5

The γ_c values of fluorine-containing surfaces have been reported[10] as 15 dyne cm^{-1} for $-CF_2H$ group[8], 18 dyne cm^{-1} for $-CF_2-CF_2-$ group (polymer)[9] and 7.9 dyne cm^{-1} for $F(CF_2)_nCOOH$ (monolayer)*. The film surfaces of $H(CF_2)_8CH_2O(CH_2)_3S$–PVA and $F(CF_2)_7CONHCH_2CH_2S$–PVA have γ_c values of 17 dyne cm^{-1} and 14 dyne cm^{-1}, respectively. The values are not always close to those of the groups comprising the end groups, which suggests that the movement of the fluoroalkyl end groups is restricted due to binding to the long chains of the PVA, and alignment of the end group is not so regular as the low molecular weight compounds. However, it is noteworthy that the value obtained here for $F(CF_2)_7CONHCH_2CH_2S$–PVA ($\gamma_c = 14$ dyne cm^{-1}) is lower than that of poly(tetrafluoroethylene) ($\gamma_c = 18$ dyne cm^{-1}).

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* 1 dyne cm^{-1} = 1×10^{-3} N m^{-1}

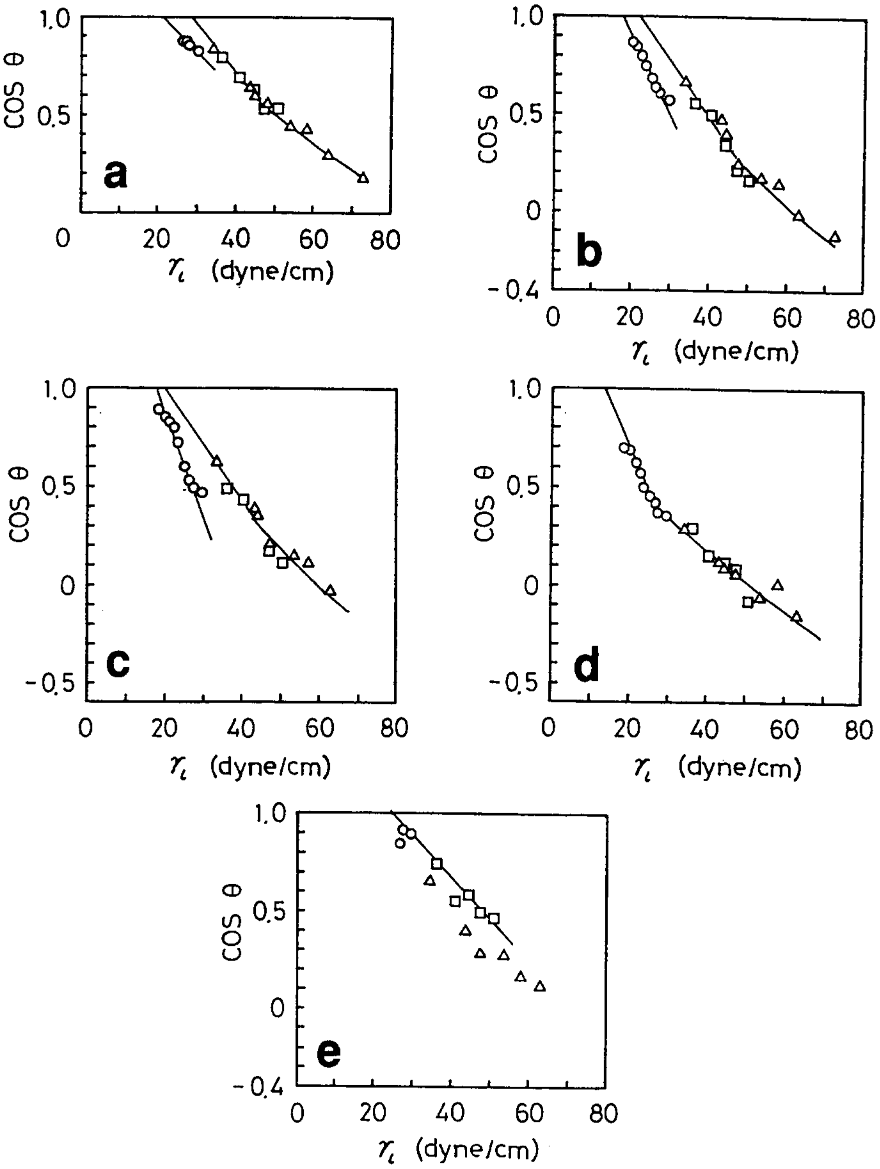

Figure 1 Zisman plots of PVA films with a fluoroalkyl group at one end. ○, Group A; □, group B-1; △, group B-2 liquids. (a) $H(CF_2)_4CH_2O(CH_2)_3S$–PVA; (b) $H(CF_2)_6CH_2O(CH_2)_3S$–PVA; (c) $H(CF_2)_8CH_2O(CH_2)_3S$–PVA; (d) $F(CF_2)_7CONHCH_2CH_2S$–PVA; (e) n-$C_{12}H_{25}S$–PVA

Table 3 Critical surface tensions of PVA films with a fluoroalkyl group at one end

PVA no.	RS–PVA	γ_c (dyne cm^{-1})	γ_c(max) (dyne cm^{-1})
223A	$H(CF_2)_4CH_2O(CH_2)_3S$–PVA	24	29
236A	$H(CF_2)_6CH_2O(CH_2)_3S$–PVA	18	22
233A	$H(CF_2)_8CH_2O(CH_2)_3S$–PVA	17	19
241A	$F(CF_2)_7CONHCH_2CH_2S$–PVA	14	–
101A	n-$C_{12}H_{25}S$–PVA	27	–
PVA–HCA		42	–

Surface free energy

According to Hare *et al.*[11] and Fowkes[12] the interfacial free energy, γ_{12}, is given by:

$$\gamma_{12}=\gamma_1+\gamma_2-2\sqrt{\gamma_1^d\gamma_2^d}-2\sqrt{\gamma_1^p\gamma_2^p} \qquad (2)$$

$$\gamma_1=\gamma_1^d+\gamma_1^p$$

$$\gamma_2=\gamma_2^d+\gamma_2^p$$

where γ_1 and γ_2 denote the surface free energies of phase 1 and phase 2, respectively, and γ_1^d, γ_2^d and γ_1^p, γ_2^p denote the dispersion force component and the polar component of γ_1 or γ_2, respectively.

In the case of the liquid droplet (l)–solid (s) system, the Young–Dupre equation combined with equation (2) for interfacial free energy is given as:

$$\gamma_l(1+\cos\theta)=2\sqrt{\gamma_l^d\gamma_s^d}+2\sqrt{\gamma_l^p\gamma_s^p} \qquad (3)$$

$$\gamma_s=\gamma_s^d+\gamma_s^p$$

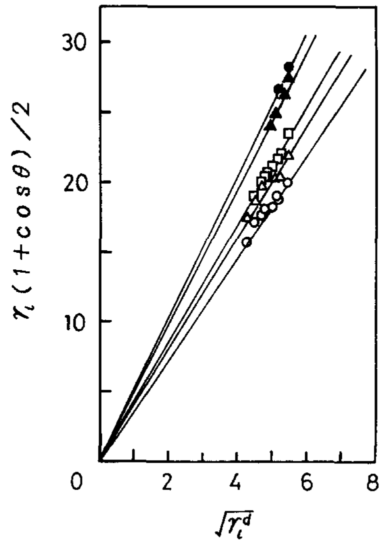

Figure 2 Plots of $\gamma_l(1+\cos\theta)/2$ against $\sqrt{\gamma_l^d}$ of PVA films with a fluoroalkyl group at one end. ▲, $H(CF_2)_4CH_2O(CH_2)_3S$–PVA; □, $H(CF_2)_6CH_2O(CH_2)_3S$–PVA; △, $H(CF_2)_8CH_2O(CH_2)_3S$–PVA; ○, $F(CF_2)_7CONHCH_2S$–PVA; ●, n-$Cl_{12}H_{25}S$–PVA

Table 4 Surface free energies and their components of PVA films with a fluoroalkyl group at one end

PVA no.	RS–PVA	Surface free energy (erg cm^{-2})		
		γ_s	γ_s^d	γ_s^p
223A	$H(CF_2)_4CH_2O(CH_2)_3S$–PVA	29.5	24.5	5.0
236A	$H(CF_2)_6CH_2O(CH_2)_3S$–PVA	20.9	18.0	2.9
233A	$H(CF_2)_8CH_2O(CH_2)_3S$–PVA	19.2	16.5	2.7
241A	$F(CF_2)_7CONHCH_2CH_2S$–PVA	14.3	13.5	0.8
101A	n-$C_{12}H_{25}S$–PVA	27.8	27.1	0.7
PVA–HCA	–	41.4	27.1	14.3

Then we can estimate the surface free energy, γ_s, and its components, γ_s^d and γ_s^p, of the polymer by measurements of contact angle with at least two liquids whose surface tensions and their components are known.

In this report, we analysed the contact angle data as follows: first, according to equation (3), γ_s^d was determined from the slope of the plot of $\gamma_l(1+\cos\theta)/2$ against $(\gamma_l^d)^{1/2}$ for group A liquids that have no γ_l^p component; and secondly, γ_s^p from each group B liquid was calculated using equation (3) and the average value was adopted for γ_s^p.

Figure 2 shows the plot of $\gamma_l(1+\cos\theta)/2$ against $(\gamma_l^d)^{1/2}$ for group A liquids, giving a good straight line for all samples. The γ_s^d, γ_s^p and γ_s values are summarized in *Table 4*. $F(CF_2)_7CONHCH_2CH_2S$–PVA had the lowest γ_s and γ_s^d values in this study and had no polar component, γ_s^p, as well as n-$C_{12}H_{25}S$–PVA. In a series of $H(CF_2)_nCH_2O(CH_2)_3S$–PVAs, the γ_s and γ_s^d values decreased with an increase in $-CF_2-$ units; however, the γ_s value of $H(CF_2)_8CH_2O(CH_2)_3S$–PVA was higher than that of $F(CF_2)_7CONHCH_2CH_2S$–PVA in spite of containing longer $-CF_2-$ units. The γ_s^d value decreased with the introduction of fluorine atoms to the alkyl end group; even $H(CF_2)_4CH_2O(CH_2)_3S$–PVA, which had the shortest $-CF_2-$ units, showed a much lower value of γ_s^d than n-$C_{12}H_{25}S$–PVA, which was found[1] to have the lowest γ_s^d in a series of n-$C_nH_{2n+1}S$–PVAs. The γ_s^p value of $H(CF_2)_nCH_2O(CH_2)_3S$–PVAs also decreased with an increase in $-CF_2-$ units; however, it reached a constant value of 2.9–2.7 dyne cm^{-1}, not zero, at more than six $-CF_2-$ units. This clearly indicates that the γ_s^p originates with α-hydrogen of the CF_2–H group as well as hydroxy groups of the PVA. Then the γ_s^p of $H(CF_2)_4CH_2O(CH_2)_3S$–PVA is based on both the α-hydrogen and the hydroxy groups, in contrast to those of $H(CF_2)_6CH_2O(CH_2)_3S$–PVA and $H(CF_2)_8CH_2O(CH_2)_3S$–PVA which depend on the α-hydrogen alone. From the comparison with $F(CF_2)_7CONHCH_2CH_2S$–PVA and $H(CF_2)_8CH_2O(CH_2)_3S$–PVA, it is obvious that the replacement of the CF_2H group by CF_3 group contributes effectively to the decline of γ_s^p and γ_s. As far as the surface free energy is concerned, the surfaces of $F(CF_2)_7CONHCH_2CH_2S$–PVA, $H(CF_2)_8CH_2O(CH_2)_3S$–PVA and $H(CF_2)_6CH_2O(CH_2)_3S$–PVA films seem to be essentially covered with fluoroalkyl chains; that is, no hydroxy groups exist in the surface layer for liquids to penetrate and interact with.

In this study, the relationship between surface free energy and critical surface tension was found to be as follows: the γ_s was substantially identical with γ_c for $F(CF_2)_7CONHCH_2CH_2S$–PVA and n-$C_{12}H_{25}S$–PVA, which had no polar component, and with γ_c(max) for a series of $H(CF_2)_nCH_2O(CH_2)_3S$–PVAs, which had a polar component. These results agree well with those of Kitazaki and Hata[7].

Next we examined the surfaces of the blend films composed of PVA–HCA and $F(CF_2)_7CONHCH_2CH_2S$–PVA, which was found to have the lowest surface free energy as described above. *Figure 3* shows the plots of contact angle against $F(CF_2)_7CONHCH_2CH_2S$–PVA content in the blend films for n-hexadecane (group A), 1,1,2,2-tetrabromethane (group B-1) and diethylene glycol (group B-2), indicating that the contact angles with any liquids increased rapidly by adding small amounts of $F(CF_2)_7CONHCH_2CH_2S$–PVA to PVA–HCA. *Figure 4* shows γ_s, γ_s^d and γ_s^p calculated from equation (3), indicating that the surface free energy and its components decreased rapidly with an increase in

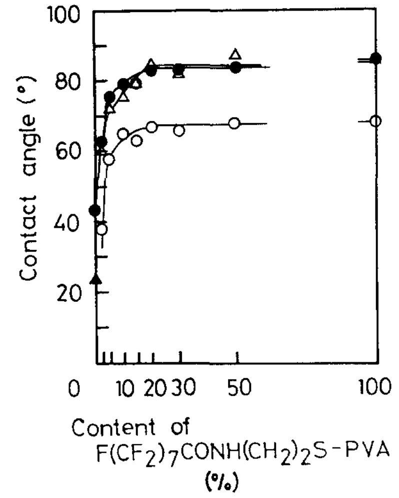

Figure 3 Plots of contact angle against $F(CF_2)_7CONHCH_2CH_2S$–PVA content for the blend films composed of $F(CF_2)_7CONHCH_2$-CH_2S–PVA and PVA–HCA. ○, n-Hexadecane; ●, 1,1,2,2-tetrabromethane; △, diethylene glycol

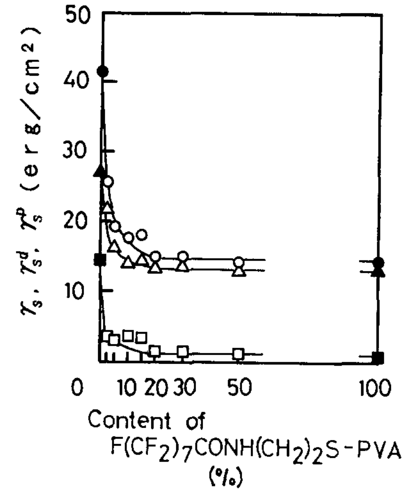

Figure 4 Plots of surface free energy and its components against $\mathrm{F(CF_2)_7CONHCH_2CH_2S}$–PVA content for the blend films composed of $\mathrm{F(CF_2)_7CONHCH_2CH_2S}$–PVA and PVA–HCA. ○, γ_s; △, γ_s^d; □, γ_s^p

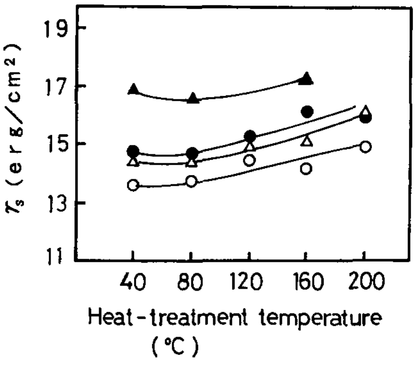

Figure 5 Plots of γ_s against heat treatment temperature for films of $\mathrm{F(CF_2)_7CONHCH_2CH_2S}$–PVA with various degrees of polymerization ($\bar{P}_{AC}$): ○, 300; △, 500; ●, 788; ▲, 1809

$\mathrm{F(CF_2)_7CONHCH_2CH_2S}$–PVA content, and gave constant values almost the same as those of $\mathrm{F(CF_2)_7CONHCH_2CH_2S}$–PVA itself at contents of $\mathrm{F(CF_2)_7CONHCH_2CH_2S}$–PVA over 20 wt%.

Surface composition

In order to investigate the relationship between the surface free energy and the composition of the surface layer or the configuration of the fluoroalkyl chains in the surface layer, we made contact angle measurements and X.p.s. analysis on the films of a series of $\mathrm{F(CF_2)_7CONHCH_2CH_2S}$–PVAs.

Figure 5 shows plots of γ_s against the heat treatment temperature with varying degrees of polymerization ($\bar{P}_{AC}$). γ_s increased with an increase in $\bar{P}_{AC}$ under the same heat treatment temperature. This may be caused by an increase in the cross section occupied by one fluoroalkyl end group, which is supposed to be proportional to the mean square end-to-end length of the PVA. The minimum value of γ_s was at 80°C and increased with an increase in heat treatment temperature above 120°C, irrespective of $\bar{P}_{AC}$. With heat treatment of the films, a change of γ_s was expected to occur by rearrangement of the fluoroalkyl end groups and migration of the end groups in the bulk to the surface layer; however, the behaviour was complicated. This issue will be discussed later.

Figure 6 shows the X.p.s. spectra of F_{1s} on the air-side surface and the opposite surface of $\mathrm{F(CF_2)_7}$–$\mathrm{CONHCH_2CH_2S}$–PVA (246A) film formed on PET sheet, clearly indicating that fluorine atoms are present in the air-side surface in preference to the PET-side surface.

Thus the ratio of fluorine atoms in the surface layer seems to relate to the critical surface tension and the surface free energy. *Figure 7* shows the plots of area ratio of F_{1s} peak to O_{1s} (F/O ratio) against heat treatment temperature of the films with varying $\bar{P}_{AC}$. It is seen that the F/O ratio reached a maximum at 80°C and decreased with an increase in heat treatment temperature above 120°C irrespective of $\bar{P}_{AC}$, and decreased with an increase in $\bar{P}_{AC}$ under the same heat treatment temperature. These facts are in good agreement with the changes of γ_s with

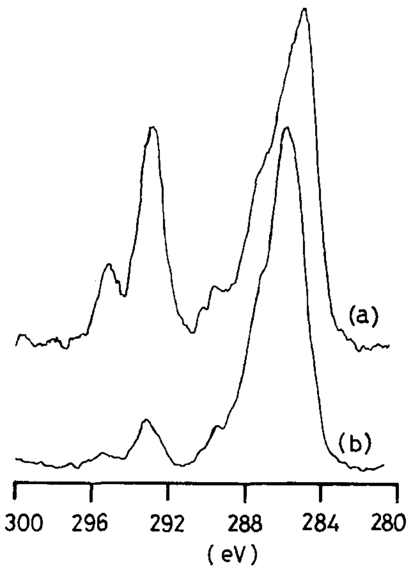

Figure 6 X.p.s. spectra of C_{1s} on (a) air-side surface and (b) the opposite surface of $\mathrm{F(CF_2)_7CONHCH_2CH_2S}$–PVA film with $\bar{P}_{AC}=500$

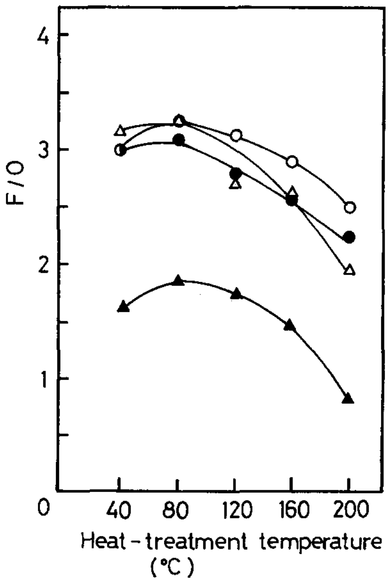

Figure 7 Plots of F/O ratio against heat treatment temperature for films of $\mathrm{F(CF_2)_7CONHCH_2CH_2S}$–PVA with various degrees of polymerization ($\bar{P}_{AC}$): ○, 300; △, 500; ●, 788; ▲, 1809

degree of polymerization and heat treatment temperatures as shown in *Figure 5*, and it suggests that γ_s is closely related to the composition of the surface layer. A more detailed investigation into the surface compositions was carried out.

Figure 8 shows the deconvolution of C_{1s} spectrum of $F(CF_2)_7CONHCH_2CH_2S$-PVA (246A, $\bar{P}_{AC}=500$). It shows the existence of many kinds of carbon atoms having different chemical shifts — the carbon atoms of CF_3 at 294.4 eV, of $-CF_2-$ at 292 eV, of C=O at 288.8 eV, of C–O (PVA) at 286.6 eV and of C–C at 284.4 eV — from which the surface composition of the carbon atoms can be determined.

Figure 9 shows the distributions of these carbon atoms in the depth direction of the surface layer on $F(CF_2)_7CONHCH_2CH_2S$-PVA films, heat treated at 40°C and 160°C, where each ratio measured at various escape angles (ϕ_e) was plotted against $\sin\phi_e$. ϕ_e relates to the detectable depth (d) and the electron mean free path (λ) in the equation, $d=3\lambda\sin\phi_e$. In the case of $\lambda=23$ Å, taken in this study[13], the values of d obtained from measurements at 15°, 30°, 60° and 90° are estimated to be 18 Å, 34.5 Å, 59.7 Å and 69 Å, respectively. The ratios of the carbon atoms in CF_3, $-CF_2-$ and C=O decreased with an increase in $\sin\phi_e$, that is, in the depth. On the contrary, the ratio of C–O in PVA increased rapidly with an increase in $\sin\phi_e$, while that of C–C, which contains two kinds of C–C originating from the end group and PVA, showed no dependence on $\sin\phi_e$. The results clearly prove that the fluoroalkyl end groups distribute in the air-side surface in preference to the bulk. These phenomena were observed in the films heat treated at both 40°C and 160°C; however, the compositions in 18 Å and 34.5 Å depth, which seem to decide the surface free energy, clearly changed by increasing the heat treatment temperature from 40°C to 160°C, that is, the ratios of CF_3 group and $-CF_2-$ group decreased and that of C–O group increased. This is in good agreement with the fact that the γ_s of the film surface heat treated at 160°C was higher than that heat treated at 40°C, as shown in *Figure 5*. From a comparison with the distributions of CF_3 group and $-CF_2-$ group on the films heat treated at 40°C and 160°C, heat treatment at 160°C seems to bring about some disorder in the arrangement or the configuration of the fluoroalkyl end group in the surface layer. This disorder is believed to be caused by the migration and rearrangement of the end group, which seems to occur readily above the glass transition temperature of PVA (80°C); however, further investigation is needed to clarify this issue.

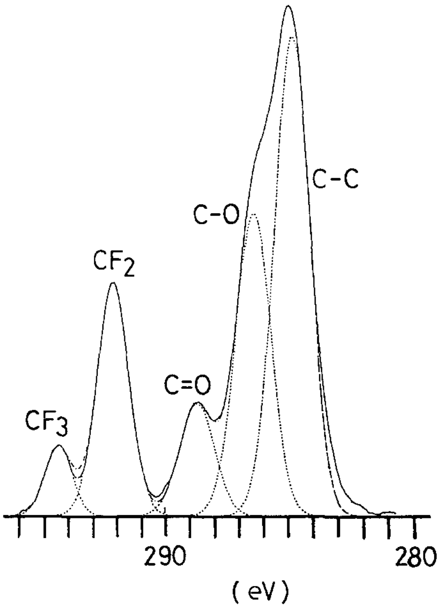

Figure 8 Peak resolution of C_{1s} spectrum of $F(CF_2)_7CONHCH_2CH_2S$-PVA film with $\bar{P}_{AC}=500$

CONCLUSION

Surface properties of PVA films with a fluoroalkyl group at one end, $H(CF_2)_nCH_2O(CH_2)_3S$-PVA and $F(CF_2)_7CONHCH_2CH_2S$-PVA, were studied.

It was confirmed by contact angle measurements and X.p.s. analysis that $H(CF_2)_nCH_2O(CH_2)_3S$-PVA and $F(CF_2)_7CONHCH_2CH_2S$-PVA distributed preferentially in the air-side surface, and the surface showed properties corresponding to the characteristics of the fluoroalkyl end groups. The surface of $F(CF_2)_7CONHCH_2CH_2S$-PVA films gave the smallest values for γ_c, and γ_s in this study. The γ_c of 241A ($\bar{P}_{AC}=788$)

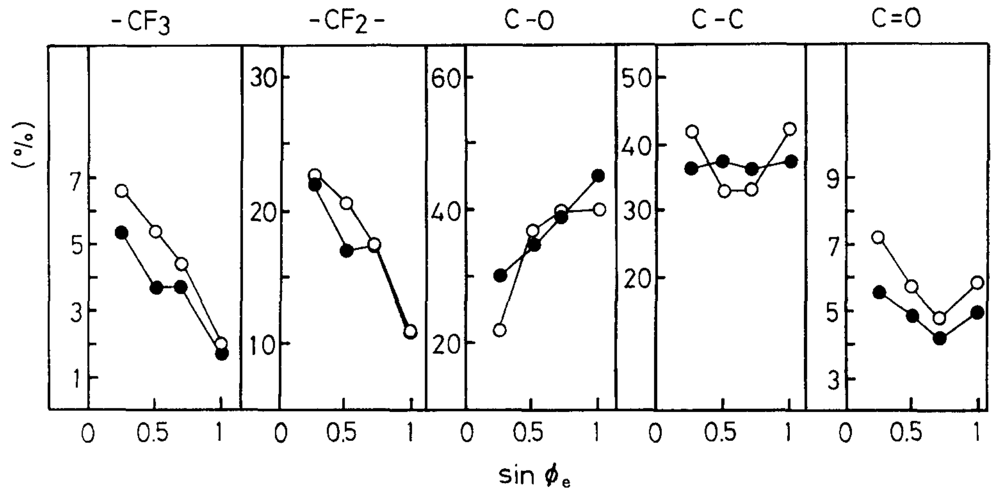

Figure 9 Change of the surface composition with $\sin\phi_e$ of $F(CF_2)_7CONHCH_2CH_2S$-PVA film with $\bar{P}_{AC}=500$. Heat treatment temperature: ○, 40°C; ●, 160°C

was 14 dyne cm^{-1}, which is lower than that of poly(tetrafluoroethylene) (18 dyne cm^{-1}). It is noteworthy that such a low free surface energy can be embodied by introducing a small amount of fluoroalkyl groups as the polymer end group. The γ_s of a series of $H(CF_2)_nCH_2O(CH_2)_3S$–PVA film surfaces decreased with an increase in $-CF_2-$ units, but γ_s^p remained steady in $H(CF_2)_8CH_2O(CH_2)_3S$–PVA because of the α-hydrogen.

In the case of PVA film surfaces with no polar component, such as the $F(CF_2)_7CONHCH_2CH_2S$–PVA and the n-$C_{12}H_{25}S$–PVA, the γ_s values were in good agreement with the γ_c values. On the other hand, for surfaces with a polar component, such as a series of $H(CF_2)_nCH_2O(CH_2)_3S$–PVAs, the γ_s values were in good agreement with γ_c(max) rather than γ_c.

There were rather complicated changes in the γ_s values of $F(CF_2)_7CONHCH_2CH_2S$–PVA with heat treatment. With increasing the heat treatment temperature, γ_s had a minimum value at 80°C and increased above 120°C, which was thought to be caused by the distribution changes of the end groups. The F/O ratio and the distributions of the atoms constituting the end group in the surface layer of $F(CF_2)_7CONHCH_2CH_2S$–PVA films, estimated by X.p.s. analysis, were found to be closely associated with γ_s.

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