# Surface properties of films containing poly(vinyl alcohol) having an n-alkylthio group at one end

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Surface properties of the poly(vinyl alcohol) (PVA) blend films composed of conventional PVA and PVA having an n-alkylthio end group of 4–18 carbon atoms (R*n*-PVA; $n=4$–18) were studied by contact angle measurements and XPS analysis. In the blend films, R*n*-PVA distributed preferentially on the air side surface (but not on the opposite side) depending on the chain length of n-alkylthio end groups. The critical surface tensions, $\gamma_c$, and surface-free energies, $\gamma_s$, of the R12-PVA/PVA-HCA blend were the lowest of all R*n*-PVA/PVA-HCA blends. The polar component of the surface free energy, $\gamma_s^p$, of the blends with R*n*-PVA of $n=8$–16 was substantially zero, from which these film surfaces were deduced to be predominantly covered with n-alkyl chains. The C/O ratio, the ratio of the carbon atoms to the oxygen atoms in the surface layer estimated by XPS analysis, had some correlation with $\gamma_c$ and $\gamma_s$. However, it was suggested that the surface properties were affected not only by the composition of the surface but also by the arrangement of the n-alkyl chains on the surface.

**(Keywords: polyvinyl alcohol; n-alkylthio end-group; critical surface tension; surface-free energy; XPS)**

## INTRODUCTION

A few studies on the solid surface properties of poly(vinyl alcohol) (PVA) and its derivatives have been carried out. Ray *et al.*[1] and Matzunaga and Ikada[2] reported the critical surface tension and surface-free energy of PVA film independently of each other. Shiomi *et al.*[3] showed the surface-free energy of PVA copolymers having various types of alkyl side groups, demonstrating that the free energy changed with the kinds and quantities of the alkyl groups. Nakamae *et al.*[4] reported the surface-free energy of vinyl alcohol-ethylene copolymers, and discussed correlation with the adhesive force.

Okaya and Imai showed that the surfaces of the PVAs polymerized in the presence of higher alcohols such as lauryl alcohol and stearyl alcohol followed by hydrolysis demonstrated more hydrophobic properties than that of the conventional PVA, which was probably based on the hydrophobic group introduced at one end of the PVAs polymerized in the presence of higher alcohol[5]. However, no systematic investigation of PVA solid surfaces containing end-group modified PVA has been carried out.

From the kinetic investigation on the free radical polymerization of vinyl acetate in the presence of chain transfer agent we have proposed a new method to synthesize PVAc and PVA, whose degrees of polymerization, their distributions and the end groups can be controlled[6]. According to the method, we can obtain the PVAc or PVA having a relatively sharp distribution of polymerization degree ($\overline{P_w}/\overline{P_n}\sim 2$) and a specified end group at one end.

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In this work we prepared a series of PVAs having an n-alkylthio group of 4–18 carbon atoms at one end, and studied the surface properties of their blend films with the conventional PVA by contact angle measurements and XPS analysis.

## EXPERIMENTAL

### *Chemicals*

A VAc monomer produced by the Kuraray Company was used without further purification. An analytical grade of methanol (MeOH), n-alkyl thiols of 4–18 carbon atoms, 2-mercaptoethanol (2-ME), and 2,2′-azobisisobutyronitrile (AIBN) were used without purification.

### *Polymerization and hydrolysis*

The polymerization of VAc was carried out in methanol solution at 60°C with incremental additions of an n-alkyl thiol or 2-ME during the course of polymerization, and PVAc having, according to n.m.r. and g.p.c. analyses, an n-alkylthio or a hydroxyethylthio group at one end and a polydispersity index $\overline{P_w}/\overline{P_n}\sim 2$, was obtained.

PVA with an n-alkylthio or 2-hydroxyethylthio group at one end was obtained by the usual methanolysis of the PVAcs catalysed with sodium hydroxide at 40°C. A series of PVAs with a n-alkylthio end group of 4–18 carbon atoms (R*n*-PVA; $n=4$–18) and PVA having a hydroxyethylthio end group were obtained.

### *Measurements*

The intrinsic viscosities ($[\eta]_{AC}$) of PVAc were measured in acetone at 30°C. The PVAcs synthesized in this manner have been confirmed to have no or little branches caused by the chain transfer reactions to the polymer[7].

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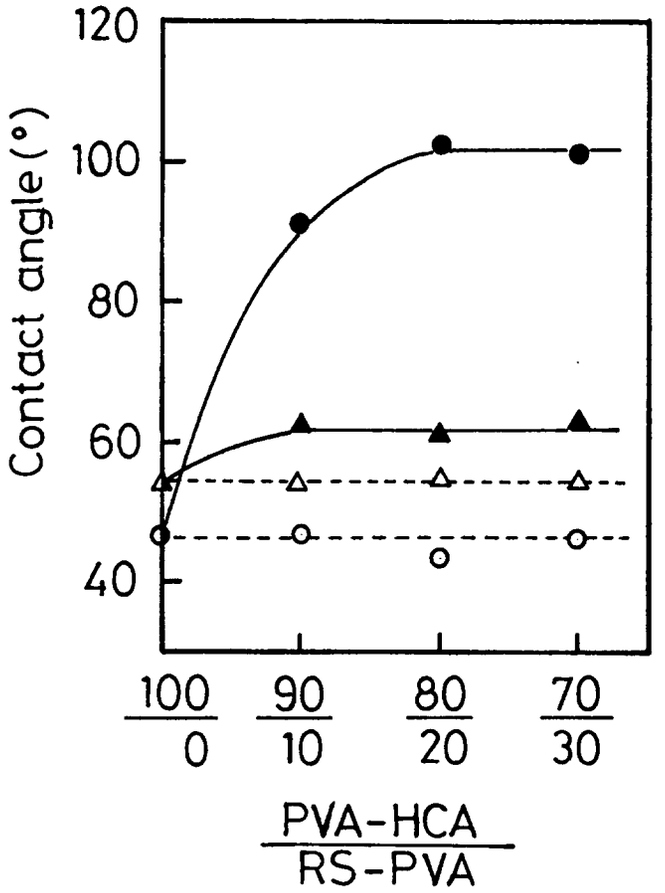


**Figure 1** Plots of contact angle of water against the blend ratio for the blend films composed of PVA-HCA and end group modified PVA. (●) measured on the air side surface of the film containing R12-PVA, (○) measured on the air side surface of the film containing HO-PVA, (▲) measured on the PET side surface of the film containing R12-PVA, (△) measured on the PET side surface of the film containing HO-PVA

The degree of hydrolysis (DH) of the end group modified PVAs and the conventional PVA (PVA-HCA: degree of polymerization 1750) were more than 99.9 mol% in all cases.

The PVA films were prepared by placing 4% aqueous solutions of PVAs on a polyethyleneterephthalate (PET) film or a glass plate and evaporating water at room temperature to 50 $\mu$m or 2–3 $\mu$m of film thickness. 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 films at 20°C with a Kyowa CA-DT contact angle meter. The XPS spectra were taken on a Shimadzu ESCA-750 spectrometer by using $MgK_{\alpha_{1,2}}$ exciting radiation with an X-ray source of 8 kV–30 mA and a 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 of binding energy had a full width at a half-maximum of 1.1 eV. The $C_{1s}$ hydrocarbon level at 285.0 eV of binding energy was used for energy calibration. The spectra were recorded at two 'take-off' angles of 30° and 90° which is the angle between the plane of sample surface and the entrance slit of the analyser. Elemental compositions were calculated by using the integrated area ratio of $C_{1s}$ to $O_{1s}$ corrected to Scofield's cross-sections[8].

## RESULTS AND DISCUSSION

### *Contact angle and critical surface tension*

*Figure 1* shows the contact angles of water on the PVA blend films composed of the conventional PVA (PVA-HCA) and the end group modified PVA. In the case of the PVA having a hydroxyethylthio group at one end (HO-PVA) no detectable changes were observed on either the air side surface or the PET side surfaces. On the contrary, the contact angle on the air side surface increased sharply with addition of a small amount of the PVA having an n-dodecylthio group at one end (R12-PVA) and reached a constant value over 20 wt% of R12-PVA, although the increase in the contact angle on the opposite side was small. This is assumed to be caused by the concentration of R12-PVA on the air side surface during film formation, because the R12-PVA adsorbed at the air–water interface and formed some kind of micelle in its aqueous solution, as described elsewhere[9].

In order to investigate the blend film surfaces more closely we synthesized a series of the PVAs having an n-alkylthio end group of 4–18 carbon atoms (R*n*-PVA; $n=4$–18) and $[\eta]_{AC}$ value of around 0.1 (*Table 1*), and blended them with PVA-HCA in a ratio of 80/20 by weight. All the films were transparent and all measurements were performed on the air side surface.

The contact angle ($\theta$) measurements were carried out on the PVA blend films using liquids (*Table 2*)[10]. Those liquids included non-polar liquids (group A), polar liquids (group B-1) and polar liquids forming a hydrogen bonding (group B-2). Finite values of $\theta$ were obtained by group B liquids. The $\theta$ increased with a rise in the number of carbon atoms, $n$, of the n-alkylthio end group and showed a maximum at $n=10$ or 12 and then decreased for all groups of liquids.

The plots of $\cos\theta$ against $\gamma_l$ (Zisman plot) for PVA-HCA and R6-PVA/PVA-HCA, R12-PVA/PVA-HCA and R18-PVA/PVA-HCA blends are shown in *Figure 2*. The Zisman plot with group B-1 liquids gave a good straight line for all samples. However, the plot with group B-2 liquids, which have the ability of hydrogen bonding, gave a non-linear curve, showing complicated behaviour that depends on the n-alkyl chain length.

*Figure 3* shows the relationship between critical surface tension ($\gamma_c$) and $n$. The $\gamma_c$ values were obtained from the intercept by extrapolation of the plot of $\cos\theta$ against $\gamma_l$ to the $\cos\theta=1$ axis with B group liquids. The plot for group B-1 liquids gave a well-defined value of $\gamma_c$ for each polymer. However, $\gamma_c$ for group B-2 liquids was not obtained due to too large an error in the extrapolation. $\gamma_c$ first decreased with an increase in $n$, and, passing through a minimum at $n=10$–12, it increased. This result is very similar to the relation between the surface tension

**Table 1** Values of intrinsic viscosity of the PVAs having a thioether group at one end

| R*n*-PVA | $[\eta]_{AC}$ (dl g$^{-1}$) |
|---|---|
| HO-PVA | 0.127 |
| R4-PVA | 0.119 |
| R6-PVA | 0.132 |
| R8-PVA | 0.137 |
| R10-PVA | 0.147 |
| R12-PVA | 0.126 |
| R16-PVA | 0.146 |
| R18-PVA | 0.145 |

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

| Liquid | | Surface tension (dyn cm$^{-1}$) | | |
|---|---|---|---|---|
| Group | Name | $\gamma_l$ | $\gamma_l^d$ | $\gamma_l^p$ |
| 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 |

of aqueous R*n*-PVA solutions and $n$ as reported elsewhere[9]. This means that the film surfaces strongly reflected the characteristics of the surface structure of the slowly evaporated polymer solutions.

It has been established that wettability is determined by the chemical structure and configuration of the atomic groups comprising the surface[11]. The $\gamma_c$ values of about 26 dyn cm$^{-1}$ observed for the R10-PVA/PVA-HCA and R12-PVA/PVA-HCA blend films are closer to the values of about 20–24 dyn cm$^{-1}$ reported for the crystals[11] and monolayers[12] of saturated higher fatty acids, whose surfaces consist of $-CH_3$ groups, than to that of polyethylene (31 dyn cm$^{-1}$)[11], whose surface consists of $-CH_2-$ groups. This suggests that the n-alkyl chains of 10–12 carbon atoms may lie fairly perpendicularly on the film surface rather than lie flat on it.

*Surface-free energy*

According to Fowkes[13] and Owens[14] the interfacial free energy $\gamma_{12}$ is given by

$$\gamma_{12}=\gamma_1+\gamma_2-2\sqrt{\gamma_1^d\cdot\gamma_2^d}-2\sqrt{\gamma_1^p\cdot\gamma_2^p} \quad (1)$$

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

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

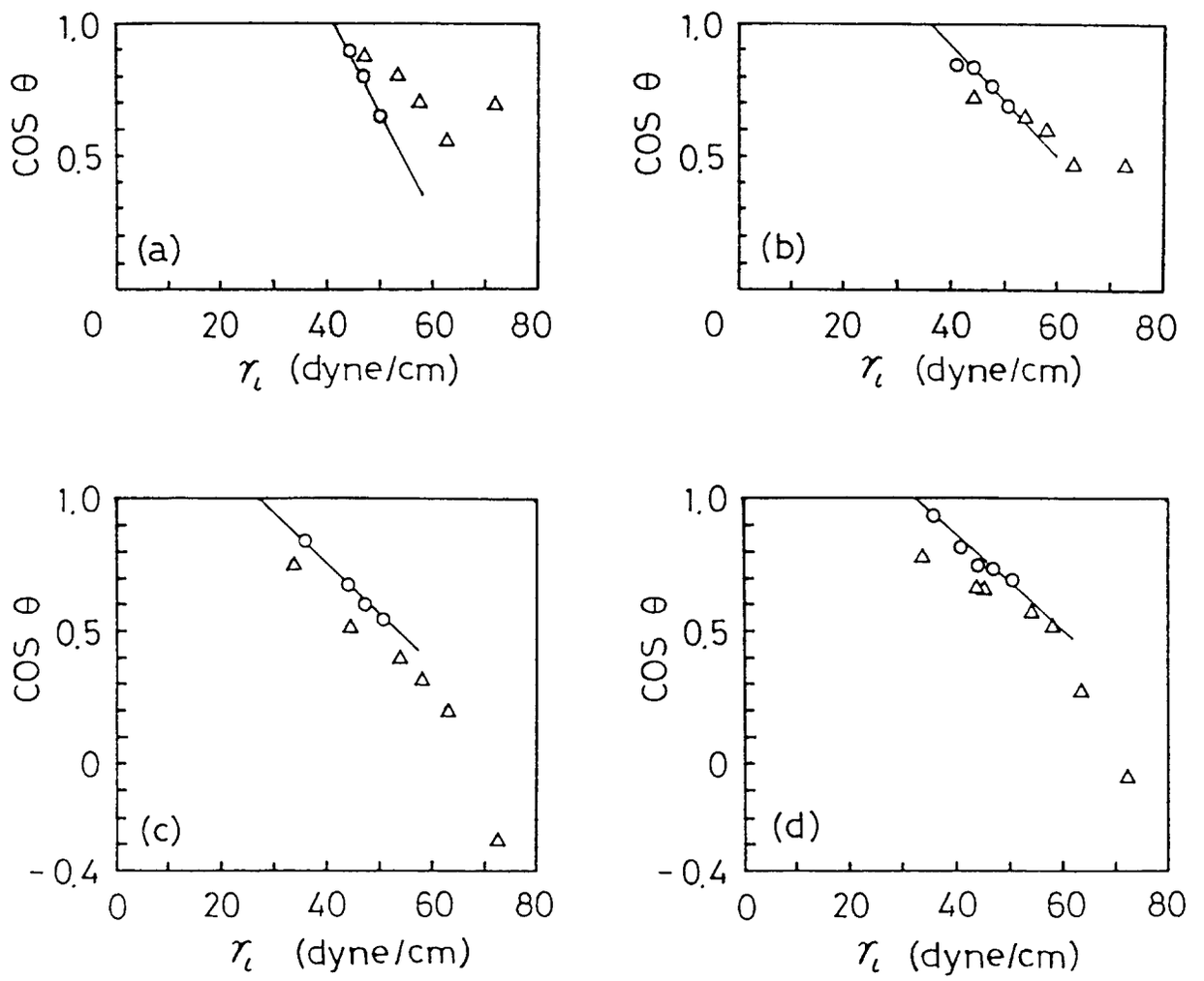


**Figure 2** Zisman plots for the blend films composed of 80 wt% PVA-HCA and 20 wt% R*n*-PVA. (a) PVA-HCA; (b) R6-PVA/PVA-HCA; (c) R12-PVA/PVA-HCA; (d) R18-PVA/PVA-HCA

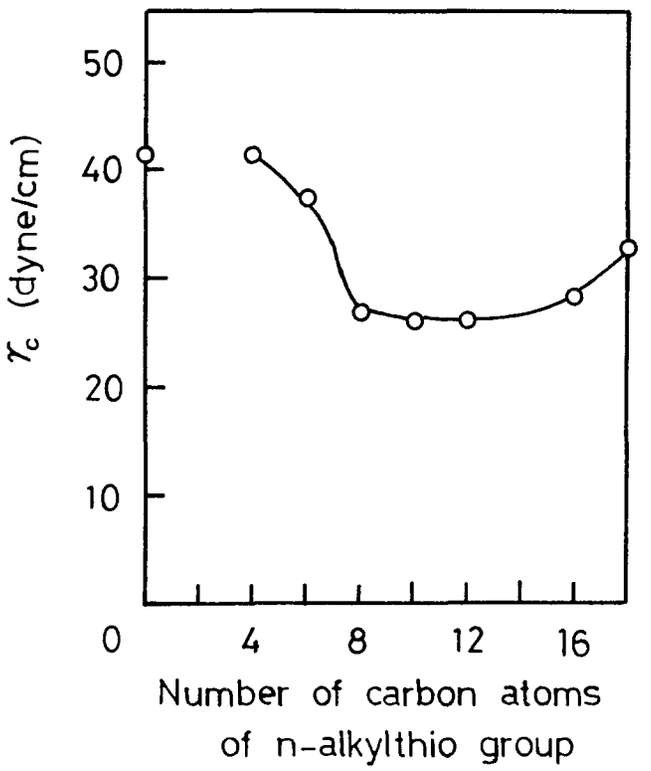


**Figure 3** Relationships between $\gamma_c$ and the number of carbon atoms of the n-alkylthio end group for the blend films composed of 80 wt% PVA-HCA and 20 wt% R*n*-PVA

where $\gamma_1$ and $\gamma_2$ denote the surface-free energy of phase 1 and phase 2, respectively, and $\gamma_1^d$, $\gamma_2^d$ and $\gamma_1^p$, $\gamma_2^p$ the dispersion force and polar components of $\gamma_1$ and $\gamma_2$, respectively.

In the case of liquid droplet (l)–solid (s) system, the Young–Dupré equation combined with equation (1) is given by

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

We can then estimate the surface-free energy and its components of a polymer by measurements of contact angles with at least two liquids whose surface tension and components are known.

In this study, we analysed the data according to the method proposed by Ikada *et al.*[15] as follows. The values of $\gamma_s^d$ and $\gamma_s^p$ are determined by the plot of $\gamma_l(1+\cos\theta)/2\sqrt{\gamma_l^d}$ against $\sqrt{\gamma_l^p}/\sqrt{\gamma_l^d}$ according to equation (3), which is equivalent to equation (2):

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

*Figure 4* shows the plots of $\gamma_l(1+\cos\theta)/2\sqrt{\gamma_l^d}$ against $\sqrt{\gamma_l^p}/\sqrt{\gamma_l^d}$. All the data points, except those for water, fall on fairly straight lines. The values for water should not be adopted since it can dissolve or swell PVAs. In *Figure 5* are plotted the values of $\gamma_s^d$, $\gamma_s^p$ and $\gamma_s$ against the number of carbon atoms, *n*, of an n-alkylthio end group. The dispersion force component, $\gamma_s^d$, first increased with increasing *n*, decreased showing a maximum at $n=8$, and then increased again passing through a minimum at $n=12$, although the changes were small. This complicated change of the $\gamma_s^d$ with *n* may suggest the rearrangements of hydroxy groups near the surface accompanying the introduction of the n-alkyl chains. In contrast, the polar component, $\gamma_s^p$, decreased markedly with an increase in *n*, gave almost zero between $n=8$ and 16 and slightly increased at $n=18$. Then $\gamma_s$ (that is, $\gamma_s^d+\gamma_s^p$) gave a minimum at $n=12$, showing almost the same *n*-dependence as $\gamma_c$.

The above results give some information about the R*n*-PVA/PVA-HCA blend film surfaces. In the case of R*n*-PVA of $n=8$–16, the blend film surfaces are assumed to be predominantly covered with the n-alkyl chains, that is, there exist in the surface layer no hydroxy groups for the liquids to interact with because $\gamma_s^p$ values of the films are substantially zero. There seems to be some difference in the disposition of the n-alkyl chains on the blend surfaces between the R12-PVA/PVA-HCA and R16-PVA/PVA-HCA blends and the R18-PVA/PVA-HCA blend, because both $\gamma_s^d$ and $\gamma_s^p$ of the R18-PVA/PVA-HCA blend are slightly larger than those of the R12-PVA/PVA-HCA and R16-PVA/PVA-HCA blends. This will be discussed later.

*Surface composition*

In order to investigate the surface composition of the R*n*-PVA/PVA-HCA blend films and the disposition of n-alkyl chains on the surface we carried out XPS measurements. *Figure 6* shows the $C_{1s}$ spectra on the air side surface and PET side surfaces for the R12-PVA/PVA-HCA (20/80 by weight) blend. They all indicated two peaks assigned to the carbon atom of C–O (286.7 eV) on PVA and that of C–C (285 eV) on PVA and the n-dodecyl group, respectively. The former peak decreased, especially on the air side surface, by adding R12-PVA to PVA-HCA, indicating that R12-PVA distributed predominantly on the air side surface. This is consistent with the results of the contact angle measurements described above.

The area ratio of $C_{1s}$ peak to $O_{1s}$ peak (C/O ratio) also seems to give some information on the film surface composition. *Figure 7* shows the relationships between the number of carbon atoms *n* of n-alkylthio end groups and the C/O ratio for the R*n*-PVA/PVA-HCA blends with a varying escape angle $\phi_e$, where $\phi_e$ relates the detection depth ($d$) with the electron mean-free path ($\lambda$), as $d=3\lambda\sin\phi_e$. In the case of $\lambda=23$ Å used in this work[16], $d$ is estimated to be 34.5 Å and 69 Å for $\phi_e=30°$ and 90°, respectively. No changes in the C/O ratio were observed for the blends of R*n*-PVAs having *n* below 8, irrespective of escape angle. The ratio measured at 30° increased linearly with increasing *n* for $8<n<18$, whereas the ratio measured at 90° increased linearly with *n* for $8<n<12$, levelling off for larger *n*. These observations indicate that the n-alkyl chains of R*n*-PVA longer than 10 carbon atoms are concentrated on the film in accordance with the observed decreases of $\gamma_c$ and $\gamma_s$. However, the values of $\gamma_c$ and $\gamma_s$ of the R6-PVA/PVA-HCA and R8-PVA/PVA-HCA blends are clearly lower than those of PVA-HCA as mentioned above, which seems to conflict with the C/O ratio result. This is probably because the detection depth, 34.5 Å or 69 Å, was too deep to observe the concentrations of the n-alkyl chains as short as 6 and 8 in *n*. The C/O ratios of the R16-PVA/PVA-HCA and R18-PVA/PVA-HCA blends are larger than that of the R12-PVA/PVA-HCA blend, which seems to contradict the fact that the $\gamma_c$ and $\gamma_s$ of the R12-PVA/PVA-HCA blend are the lowest of all R*n*-PVA/PVA-HCA blends. This is probably caused by

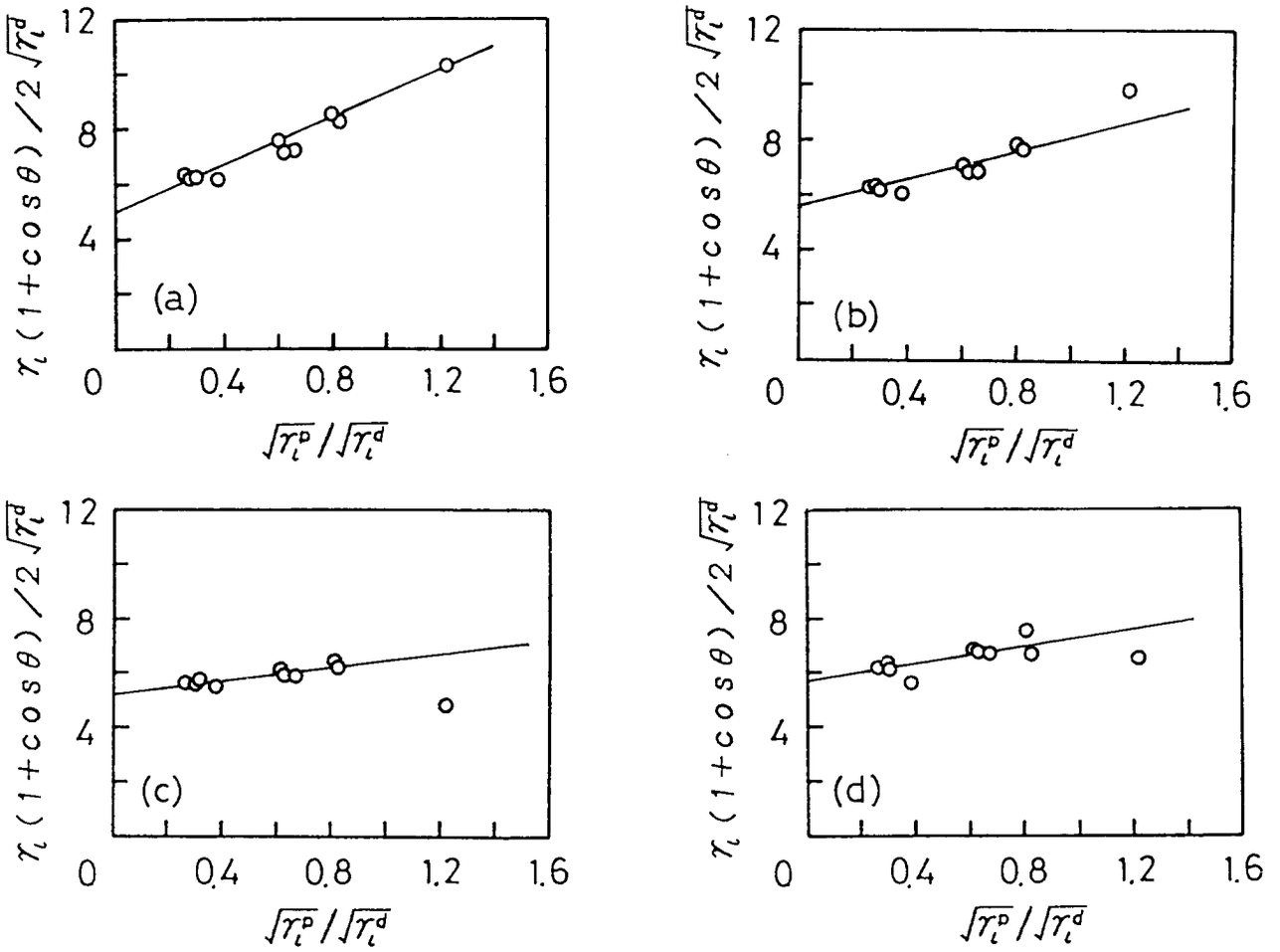


**Figure 4** Plots of $\gamma_l(1+\cos\theta)/2\sqrt{\gamma_l^d}$ against $\sqrt{\gamma_l^p}/\sqrt{\gamma_l^d}$ for the blend films composed of 80 wt% PVA-HCA and 20 wt% R*n*-PVA. (a) PVA-HCA; (b) R6-PVA/PVA-HCA; (c) R12-PVA/PVA-HCA; (d) R18-PVA/PVA-HCA

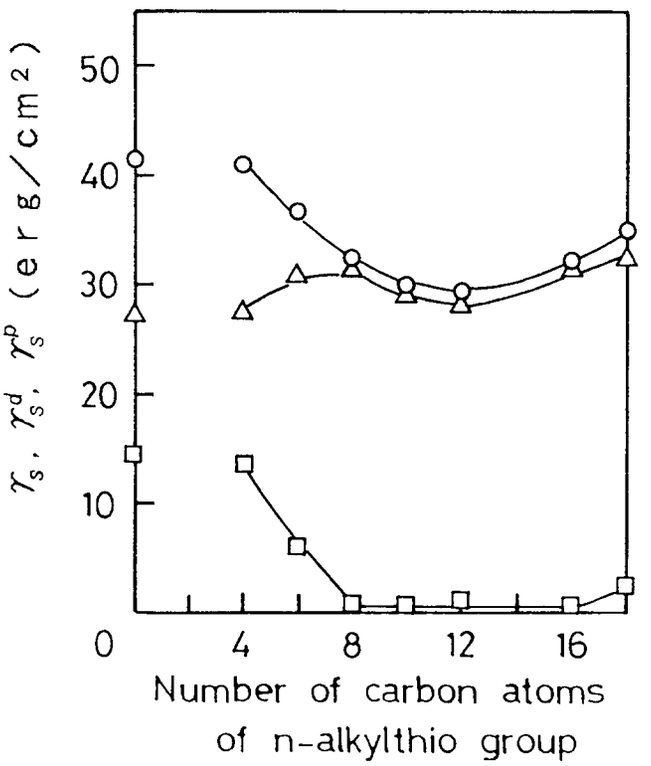


**Figure 5** Relationships between surface-free energy and its components and the number of carbon atoms of the n-alkylthio end group for the blend films composed of 80 wt% PVA-HCA and 20 wt% R*n*-PVA. (○) $\gamma_s$, (△) $\gamma_s^d$, (□) $\gamma_s^p$

the disposition difference between n-dodecyl and n-hexadecyl (or n-octadecyl) chains. In other words, n-dodecyl chains seem to align on the surface layer more densely, regularly and perpendicularly than n-hexadecyl and n-octadecyl chains, from which the lowest $\gamma_s$ for the R12-PVA/PVA-HCA blend may result, in spite of its shorter n-alkyl chain length. The data concerning the composition and disposition of n-alkyl chains seem to give very important information on the film surfaces. It is not possible to distinguish between the C–C of PVAs and that of n-alkyl chains by XPS measurement, which allows no further investigation.

*Figure 8* shows the plot of the C/O ratio measured at 30° against the $\gamma_s$, indicating no clear correlation between these two factors. It is probably because the $\gamma_s$ of polymer surface changes not only with the composition of the surface but also with the disposition or the arrangement of the chains on the surface, as mentioned above.

## CONCLUSION

It was confirmed by contact angle measurements and XPS analysis that in the blend films composed of R*n*-PVA ($n=4$–18) and PVA-HCA, R*n*-PVA distributed preferentially on the air side surface rather than on the opposite surface depending on the chain length *n*. The critical surface tension, $\gamma_c$, and surface-free energy, $\gamma_s$, of

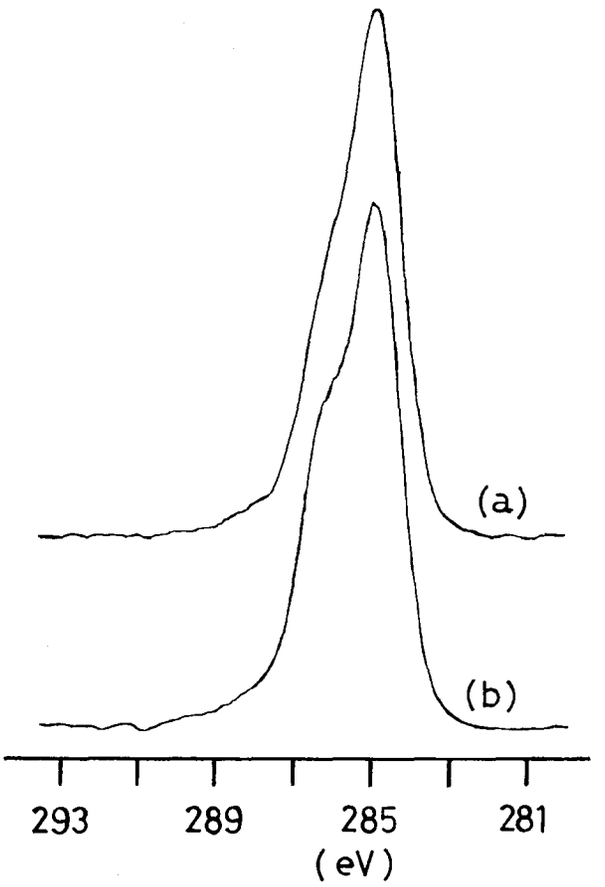


**Figure 6** $C_{1s}$ spectra on the air side surface and PET side surface for PVA-HCA film and the blend film composed of 80 wt% PVA-HCA and 20 wt% R12-PVA. (a) Air side surface; (b) PET side surface

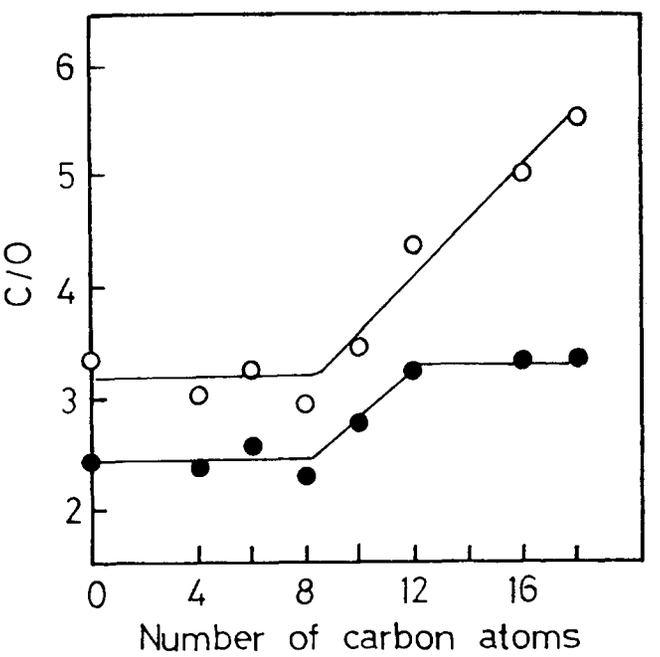


**Figure 7** Relationships between the C/O ratio and the number of carbon atoms of the n-alkylthio end group for the blend films composed of 80 wt% PVA-HCA and 20 wt% R*n*-PVA. (○) measured at 30° of escape angle; (●) measured at 90° of escape angle

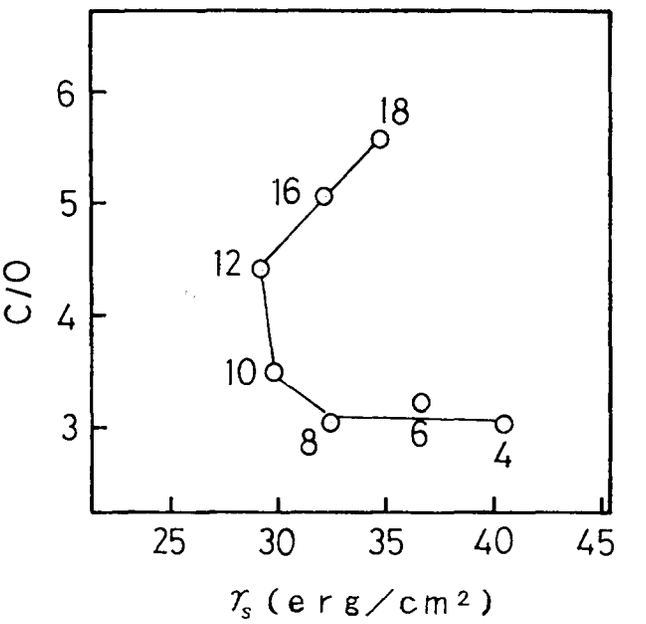


**Figure 8** Plots of the C/O ratio measured at 30° of escape angle against the $\gamma_s$ values for the blend films composed of 80 wt% PVA-HCA and 20 wt% R12-PVAs. Numbers in the figure represent the number of carbon atoms of the n-alkylthio end group

the R12-PVA/PVA-HCA blend were the lowest of all R*n*-PVA/PVA-HCA blends. The polar component of the surface-free energy, $\gamma_s^p$, of R*n*-PVA blends with *n* between 8 and 16 was substantially zero, which suggests that the film surfaces are predominantly covered with the n-alkyl chains.

The C/O ratio, the ratio of the carbon atoms to the oxygen atoms in the surface layer estimated by an XPS analysis, had some correlation with $\gamma_c$ and $\gamma_s$.

## REFERENCES


1 Ray, B. R., Anderson, J. R. and Scholz, J. J. *J. Phys. Chem.* 1958, **62**, 1220
2 Matsunaga, T. and Ikada, Y. *J. Colloid Interface Sci.* 1981, **84**, 8
3 Shiomi, T., Nishioka, S., Tezuka, Y. and Imai, K. *Polymer* 1985, **26**, 429
4 Nakamae, K., Miyata, T., Yamashita, S. and Matsumoto, T. *Kobunshi Ronbunshu* 1983, **40**, 65
5 Okaya, T. and Imai, K. to be submitted
6 Sato, T. and Okaya, T. *Makromol. Chem.* 1993, **194**, 163
7 Sato, T. and Okaya, T. *Polym J.* 1992, **24**, 849
8 Scofield, J. H. *J. Electron Spectrosc.* 1976, **8**, 129
9 Sato, T. and Okaya, T. *J. Appl. Polym. Sci.* 1992, **46**, 641
10 Kitazaki, Y. and Hata, T. *Nippon Setchakku Kyoukaishi* 1972, **8**, 178
11 Fox, H. W. and Zisman, W. A. *J. Colloid Sci.* 1952, **7**, 428
12 Shafrin, E. G. and Zisman, W. A. *J. Colloid Sci.* 1952, **7**, 166
13 Fowkes, F. M. *Ind. Eng. Chem.* 1964, **56**, 40
14 Owens, D. K. and Wendt, R. C. *J. Appl. Polym. Sci.* 1969, **13**, 1741
15 Ikada, Y. and Matsunaga, T. *Kobunshi Kako* 1978, **14**, 427
16 Dickle, R. A., Hammond, J. S., deVries, J. E. and Holubka, J. W. *Anal. Chem.* 1982, **54**, 2045