Contact angle of organic liquids on poly(2-ethylhexyl acrylate-*co*-acrylic acid)

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The contact angles of poly(2-ethylhexyl acrylate-*co*-acrylic acid) (P(2EHA-AA)) with organic liquids, such as dispersion, polar and hydrogen bonding liquids, were investigated. The contact angle θ of organic liquids on P(2EHA-AA) decreased exponentially with contact time t, i.e. $\log\theta = -K\log t$. It was suggested that the proportional constant K was influenced by the liquid's surface tension γ_L, viscosity and glass transition temperature of P(2EHA-AA).

(Keywords: poly(2-ethylhexyl acrylate-*co*-acrylic acid); organic liquid; contact angle; time dependence; surface tension; viscosity)

INTRODUCTION

The surface analysis of polymer solids is very important for adhesion, painting, water repellent properties and biocompatibility. In general, the surface structure of solids is investigated by X-ray photoelectron spectroscopy (X.p.s.), secondary ion mass spectrometry (SIMS) and ATR-*FT*i.r. and other physical properties, such as wettability and surface tension evaluated by contact angle measurement.

Recently, in multicomponent polymers, it was reported that surface segregation occurs as the low surface tension component is preferentially enriched on the film surface[1–5]. Patel *et al.* found the surface segregation of siloxane block to occur in polystyrene/sulphone–siloxane–sulphone block copolymer blends using X.p.s. Miki *et al.*[2] also confirmed that surface segregation in poly(trifluoroethyl methacrylate)/acrylate resin blends was exhibited with X.p.s. In the poly(2-ethylhexyl acrylate-*co*-acrylic acid-*co*-vinyl acetate) (P(2EHA-AA-VAc))/poly(vinylidene fluoride-*co*-hexafluoro acetone) (P(VDF-HFA)) blends, the surface segregation of P(VDF-HFA) was observed[34] by ATR-*FT*i.r. with incident angle dependence. In block copolymers of polystyrene with several polymers, Takahara *et al.*[5] reported that the lower surface tension component was segregated on the surface of a sample in contact with air using X.p.s., whereas the hydrophilic component was enriched on the block polymer in water by dynamic contact angle measurement. Saito[6] has pointed out that the rearrangement of polymer chain occurs according to the surface tension of the contacting material and the rate of rearrangement depends on the flexibility of the polymer chain. Therefore, when surface segregation and rearrangement of polymer chain occurs, the time change of the surface structure should be evaluated. The contact angle method is effective for analysing the time change of surface structure[7].

On the other hand, in acrylate adhesives containing a carboxyl group, Kawabe[8] examined the orientation of the carboxyl group and the interfacial interaction to adherend by using ATR-*FT*i.r. Then, he found the time change of orientation of the carboxyl group by the ATR depth profile method. Finally, he pointed out that the time change of peel strength was influenced by the orientation of the carboxyl group in acrylate adhesive.

In a previous paper[9], the contact angle of organic liquids on P(2EHA-AA) was examined by means of the $\log(1+\cos\theta)$ *versus* $\log(\gamma_L)$ plot. The copolymers of 2-ethylhexyl acrylate and acrylic acid are utilized in components of acrylate adhesives. We found that the slope on the $\log(1+\cos\theta)$ *versus* $\log(\gamma_L)$ plot was affected by the liquid species and the contact angle decreased with time. Therefore, it was expected that the surface segregation and orientation of polymer chain on the surface of P(2EHA-AA) occurred. In this paper, we evaluate the time dependence of the contact angle of P(2EHA-AA) with organic liquids, such as dispersion (D), polar (P) and hydrogen bonding (H) liquids. The effects of the liquid's surface tension, γ_L, the viscosity and the glass transition temperature, T_g, of P(2EHA-AA) on the time dependence of contact angle are investigated.

EXPERIMENTAL

Materials

Various copolymer specimens of P(2EHA-AA) having different copolymer compositions and molecular weights

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Table 1 Characteristics of P(2EHA-AA)[a]

	Content of AA (mol%)				
	0	5	10	20	30
$M_n \times 10^{-4}$	2.09	4.29	3.35	2.69	4.32
$M_w \times 10^{-5}$	2.69	3.05	3.85	3.65	4.65
M_w/M_n	12.9	7.1	11.5	13.6	10.9

[a] Equivalent molecular weight to that of polystyrene by g.p.c.

Table 2 Surface tension of liquids at 20°C dyn cm^{-1}[a]

Species	Liquid	γ_L^d	γ_L^p	γ_L^h	γ_L	X_L^d
	n-Nonane	22.9	0	0	22.9	1.00
	n-Decane	23.9	0	0	23.9	1.00
D	n-Undecane	24.7	0	0	24.7	1.00
	n-Dodecane	25.4	0	0	25.4	1.00
	n-Tetradecane	26.7	0	0	26.7	1.00
	n-Hexadecane	27.6	0	0	27.6	1.00
	1,1,2-Trichloroethane[b]	–	–	–	33.6	–
	Hexachlorobutadiene	35.8	0.2	0	36.0	0.994
P	Tetrachloroethane	33.2	3.1	0	36.3	0.915
	1,2-Dibromoethane	–	–	–	38.9	–
	α-Bromonaphthalene	44.4	0.2	0	44.6	0.996
	Tetrabromoethane	44.3	3.2	0	47.5	0.933
	1-Methoxy-2-propanol[b]	–	–	–	27.1	–
	Dipropyleneglycol	29.4	0	4.5	33.9	0.867
	1,3-Butanediol[b,c]	–	–	–	37.8	–
H	Polyethyleneglycol	29.9	0.1	13.5	43.5	0.687
	Diethyleneglycol	31.7	0	12.7	44.4	0.714
	Ethyleneglycol	30.1	0	17.6	47.7	0.631
	Thiodiglycol	39.2	1.4	13.4	54.0	0.726
	Water	–	–	–	72.8	–

[a] Ref. 22
[b] Ref. 23
[c] Surface tension of 1,3-butanediol at 25°C

were prepared by solution polymerization at 70°C for 7 h in a mixed solvent of 95/5 ethyl acetate/toluene using benzoyl peroxide as initiator. The molecular characteristics of P(2EHA-AA) are shown in *Table 1*. The molecular weight was measured by g.p.c. (CP8000 system, Toso Co. Ltd). The copolymers were coated onto poly(ethylene terephthalate) (PET) film of 50 μm thickness at 90°C for 60 s using LINTEC Corporation Universal Coating System. Then, the copolymers were laminated with the release liner. The samples were seasoned at 23±3°C under 65±5% r.h. for 7 days.

Contact angle measurement

The measurement of contact angle was performed at 20°C in the range of 0.5 to 10 min with a contact angle measurement apparatus (type CA-D, Kyowa Kaimen Kagaku Co. Ltd). The surface tensions γ_L of the D, P and H liquids are shown in *Table 2*. Drops of liquid (1.5–2.0 mm diameter) were prepared with a microsyringe and were dropped onto the surface of P(2EHA-AA).

Dynamic mechanical properties

The dynamic viscosity and the dynamic loss tangent, tan δ, of P(2EHA-AA) were measured by the shearing method using a dynamic mechanical analyser (RDS-II, Rheometrics Co. Ltd). The frequency was 1 Hz.

RESULTS AND DISCUSSION

Adhesive properties

The adhesive properties of P(2EHA-AA) are shown in *Table 3*. The 180° peel strength of P(2EHA-AA) with 0, 5 and 10 mol% AA content exhibits cohesive failure in the P(2EHA-AA) layer, and the value of 180° peel strength increases with increasing AA content. On the other hand, interfacial failure between P(2EHA-AA) and stainless steel is observed in P(2EHA-AA) with 20 and 30 mol% AA contents, and the value of 180° peel strength of P(2EHA-AA) with 20 mol% AA content is larger than that of P(2EHA-AA) with 30 mol% AA content. The maximum values of J. Dow ball tack and probe tack are also obtained against AA content. The holding power increases monotonically with increasing AA content. We consider that the adhesive properties of P(2EHA-AA) are influenced by the dynamic mechanical properties and the surface energy.

Contact angle

The time dependence of contact angle θ of P(2EHA-AA) (AA content, 5 mol%) with H liquids is shown in *Figure 1*. The contact angles of thiodiglycol and dipropyleneglycol on the copolymer decrease exponentially with contact time. *Figure 2* shows the relationship between θ and contact time for polyethylene film (PE, Mitsui Sekiyu Kagaku, Hyzex 5000H) with H liquids, such as thiodiglycol and dipropyleneglycol. The contact angles θ do not change with contact time. In P liquids (tetrabromoethane, tetrachloroethane) and D liquids (hexadecane, undecane), the contact angles of P(2EHA-AA) with 5 mol% AA content also decrease exponentially against contact time as shown in *Figures 3* and *4*. It is presumed that the time dependence of θ for P(2EHA-AA) is affected by the time change of the interfacial tension γ_{SL} between P(2EHA-AA) and the organic liquids.

Table 3 Adhesive properties of P(2EHA-AA)

	AA content (mol%)				
	0	5	10	20	30
180° peel strength (gf per 25 mm)[a]	65[b]	750[b]	3930[b]	1930	1880
J. Dow ball tack	6	9	8	4	>2
Probe tack (g per 5 mm ϕ)	325	696	1097	625	128
Holding power (s)	2[b]	7[b]	25[b]	460[b]	17 860[b]

[a] Adherend, stainless steel; dwell time, 24 h
[b] Cohesive failure of P(2EHA-AA) layer

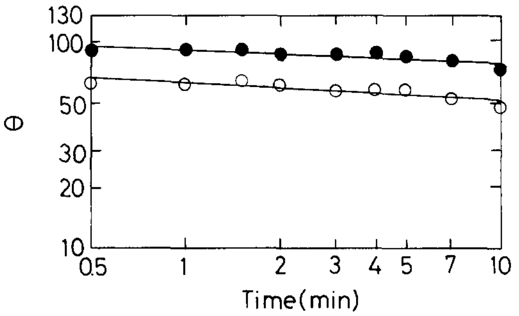

Figure 1 Time dependence of θ for P(2EHA-AA) (AA content 5 mol%) with H liquids: ●, thiodiglycol; ○, dipropyleneglycol

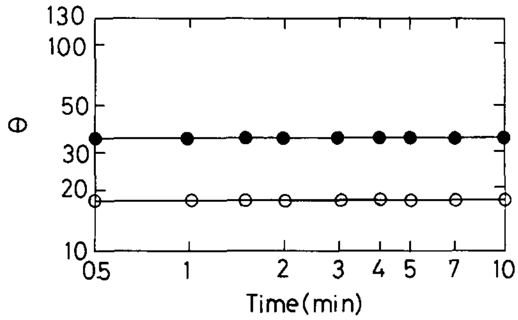

Figure 2 Time dependence of θ for PE with H liquids: ●, thiodiglycol; ○, dipropyleneglycol

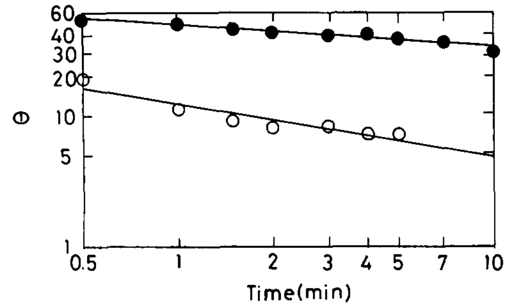

Figure 3 Time dependence of θ for P(2EHA-AA) (AA content 5 mol%) with P liquids: ●, tetrabromoethane; ○, tetrachloroethane

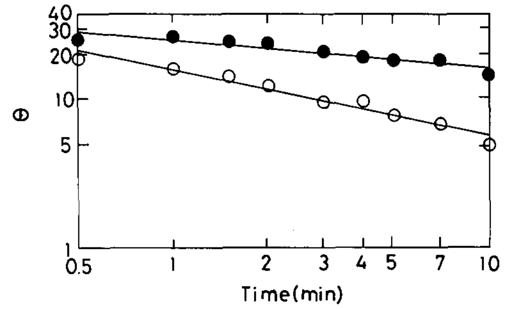

Figure 4 Time dependence of θ for P(2EHA-AA) (AA content 5 mol%) with D liquids: ●, hexadecane; ○, undecane

In general, the contact angle of liquid on solid is expressed by Young's equation[10]:

$$\gamma_L \cos\theta = \gamma_S - \gamma_{SL} - \pi_e \qquad (1)$$

where γ_S and γ_L are the surface tension of solid and liquid, respectively. The spreading pressure π_e can be neglected ($\pi_e \ll \gamma_L$). Good and Girifalco[11–13] represented the work of adhesion W_a as:

$$W_a = 2\Phi_G(\gamma_S\gamma_L)^{0.5} \qquad (2)$$

where Φ_G is the interaction parameter. They[14] have shown this in the equation:

$$\Phi_G = \frac{\frac{3}{4}\alpha_1\alpha_2\frac{2I_1I_2}{I_1+I_2} + \frac{\alpha_1\mu_2^2+\alpha_2\mu_1^2}{2} + \frac{\mu_1^2\mu_2^2}{3\kappa T}}{\left(\frac{3}{4}\alpha_1^2I_1+\alpha_1\mu_1^2+\frac{\mu_1^4}{3\kappa T}\right)^{0.5}\left(\frac{3}{4}\alpha_2^2I_2+\alpha_2\mu_2^2+\frac{\mu_2^4}{3kT}\right)^{0.5}} \qquad (3)$$

where subscripts 1 and 2 refer to phases 1 and 2, respectively, α is the polarizability, I is the ionization potential, μ is the permanent dipole moment, κ is the Boltzmann constant and T is the temperature. The estimation of Φ_G calculated by equation (3) is very difficult because of various parameters. Ward and Neumann[15] expressed the relationship between Φ_G and interfacial tension γ_{SL} as follows:

$$\Phi_G = 1 - 0.075\gamma_{SL} \qquad (4)$$

Interfacial tension γ_{SL} was defined using equation (4) and the equation[16]

$$\Phi_G = (\gamma_S + \gamma_L - \gamma_{SL})/2(\gamma_S\gamma_L)^{0.5}$$

as:

$$\gamma_{SL} = \frac{(\gamma_S^{0.5} - \gamma_L^{0.5})^2}{1 - 0.015(\gamma_S\gamma_L)^{0.5}} \qquad (5)$$

When $\gamma_S = \gamma_L$, the interfacial tension γ_{SL} between solid and liquid exhibits a minimum. Therefore, it is presumed that the time dependence of the contact angle occurs by changing the γ_S value (rearrangement and orientation of polymer chain) to decrease γ_{SL}. It is thought that the time dependence of the contact angle is influenced by the parameters α, I and μ of solid and liquid because Φ_G depends on γ_{SL} from equation (4).

From the results of *Figures 1*, *3* and *4*, the relationship between θ and contact time for P(2EHA-AA) is expressed by the following equation in the range of 0.5 to 10 min:

$$\log\theta = -K\log t \qquad (6)$$

Figure 5 shows the relationship between the proportional constant K and the surface tensions γ_L of organic liquids, such as D, P and H liquids, for P(2EHA-AA) with 5 mol% AA content. We expect that K is related to the changing rate of γ_{SL}, i.e. the rate of rearrangement and orientation of the polymer chain. K depends on the γ_L value and the species of liquids as shown in *Figure 5*. Using D and P liquids, K decreases with increasing γ_L, whereas K obtained with H liquids shows the minimum at $\gamma_L \approx 50\,\mathrm{dyn\,cm^{-1}}$. The decreasing ratio of K against γ_L with P liquids is smaller than that with D liquids. In D liquids, we believe that the influence of the liquid's surface tension on K is very large. Saito[17] represented the equation between contact angle and γ_L as follows:

$$\log(1+\cos\theta) = -\psi\log(\gamma_L) + \log(2\Phi_0\gamma_S^{0.5-a}) \qquad (7)$$

where the parameter a is defined as the slope $\psi = 0.5 - a$

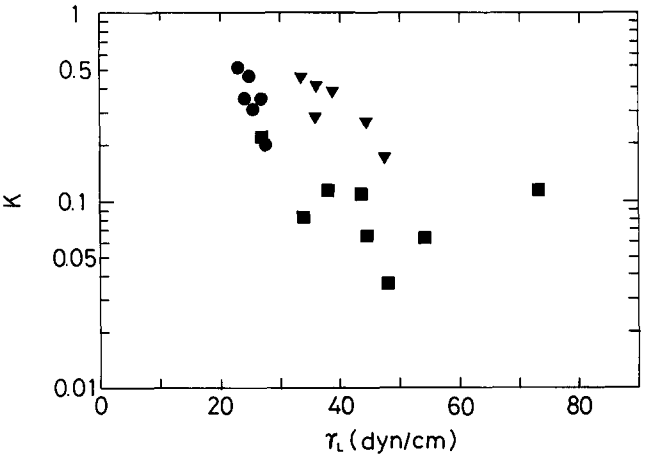

Figure 5 Relationship between K and γ_L for P(2EHA-AA) (AA content 5 mol%) with organic liquids: ●, D; ▼, P; ■, H

in the $\log(1+\cos\theta)$ *versus* $\log(\gamma_L)$ plot and Φ_0 agrees with the Good–Girifalco interaction parameter Φ_G as follows:

$$\Phi_G=\Phi_0+X_{LS}=(X_L^dX_S^d)^{0.5}+(X_L^pX_S^p)^{0.5}+X_{LS} \quad (8)$$

X_j^d and X_j^p denote the dispersion and polarity of the j component, respectively. X_{LS} is an adjustable parameter. We examined the surface tension γ_S and interfacial interaction parameter Φ_G for P(VDF-HFA)[16], vinyl-polybutadiene/terpene resin blends[18] and poly(ethyl acrylate)/P(VDF-HFA) blends[19] by use of equations (7) and (8). We found equations (7) and (8) to be very effective in evaluating interfacial interaction between solid and liquid. It is thought that the time dependence of the contact angle is affected by parameters such as α, I and μ, and polarity X_j^p of solid and liquids, respectively, because γ_{SL} is related to Φ_G. Therefore, we considered that the rate of rearrangement and orientation of P(2EHA-AA) depends on the value and the species of organic liquids. The relationship between K and γ_L for P(2EHA-AA) with 10 mol% AA content in *Figure 6* is similar to *Figure 5*. In the contact angles of H liquids on P(2EHA-AA) with 10 mol% AA content, the increase of K against γ_L is also observed at $\gamma_L > 50\,\mathrm{dyn\,cm^{-1}}$. It is expected that the H liquids with high surface tension, such as thiodiglycol and water, exhibit a specific interaction at the interface between solid and liquid, as suggested by Gutowski[20].

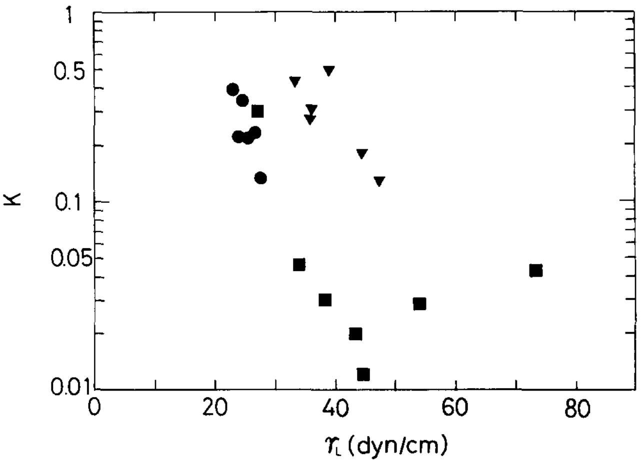

Figure 6 Relationship between K and γ_L for P(2EHA-AA) (AA content 10 mol%) with organic liquids: ●, D; ▼, P; ■, H

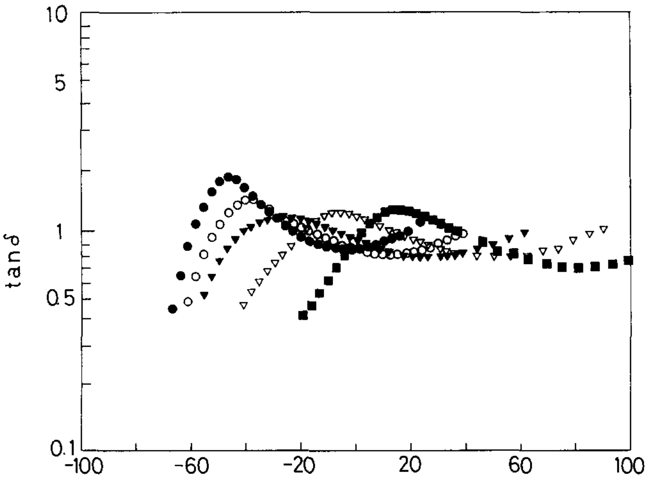

Figure 7 Temperature dependence of tan δ for P(2EHA-AA). AA content (mol%): ●, 0; ○, 5; ▼, 10; ▽, 20; ■, 30

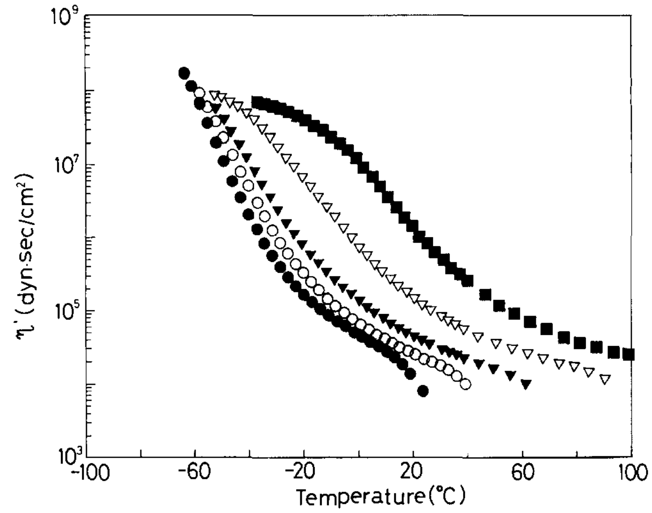

Figure 8 Temperature dependence of η' for P(2EHA-AA). AA content (mol%): ●, 0; ○, 5; ▼, 10; ▽, 20; ■, 30

Table 4 Dynamic viscosity at 20°C and glass transition temperature (T_{Dmax}) of P(2EHA-AA)

	AA content (mol%)				
	0	5	10	20	30
$\eta' \times 10^{-4}$ (dyn s cm^{-2})	1.35	2.47	4.29	14.5	136
T_{Dmax}(°C)[a]	−46.4	−37.3	−26.4	−5.8	16.4

[a] Temperature exhibiting maximum value of tan δ

Takahara *et al.*[5] have reported that the rate of rearrangement and orientation of polymer chain depends on the glass transition temperature T_g. We investigated the relationship between T_g and K for P(2EHA-AA). The temperature dependence of the dynamic loss tangent tan δ for P(2EHA-AA) is shown in *Figure 7*. The temperature exhibiting the maximum value of tan δ (T_{Dmax}) related to T_g increases with increasing AA content. We measured the dynamic viscosity η' of P(2EHA-AA) because the chain motion of polymer segment affects the rearrangement and orientation. *Figure 8* shows the relationship between η' and temperature for P(2EHA-AA). The η' decreases with rising temperature and increases with increasing AA content. The glass transition temperature $T_g(T_{Dmax})$ and η' at 20°C for P(2EHA-AA) are represented in *Table 4*. It is expected that the rearrangement and orientation of polymer chain occur because the T_g of P(2EHA-AA) is lower than room temperature ($T_r = 20$°C) and P2EHA possessing low T_g (−46.4°C) and low η' (1.35×10^4 dyn s cm^{-2}) most easily induces the rearrangement and orientation of polymer chain in bulk. On the other hand, we consider P(2EHA-AA) with 30 mol% AA content induces the least chain motion of polymer segment. The time dependence of the contact angle for P(2EHA-AA) with undecane is shown in *Figure 9*. The contact angle of undecane on P(2EHA-AA) decreases exponentially with contact time and the proportional constant K decreases with increasing AA content. *Figure 10* shows the relationship between K and AA content with D

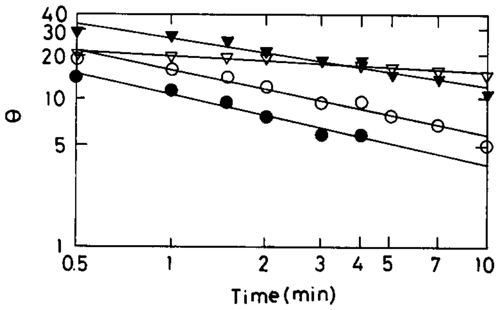

Figure 9 Time dependence of θ for P(2EHA-AA) with undecane. AA content (mol%): ●, 0; ○, 5; ▼, 10; ▽, 20

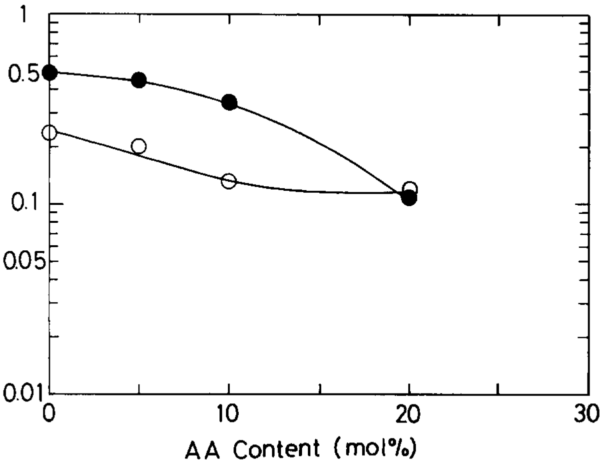

Figure 10 Relationship between K and AA content for P(2EHA-AA) with D liquids: ●, undecane; ○, hexadecane

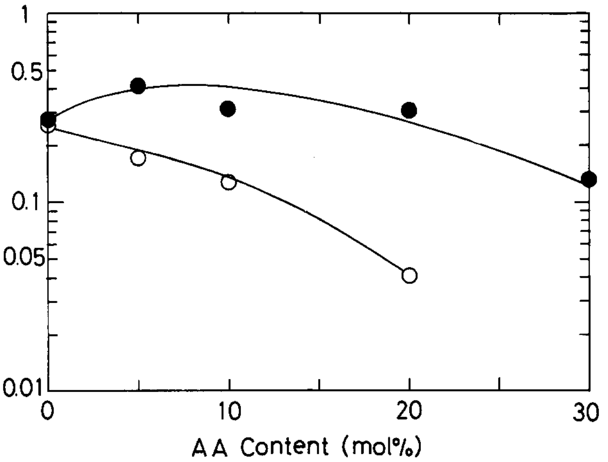

Figure 11 Relationship between K and AA content for P(2EHA-AA) with P liquids: ●, tetrabromoethane; ○, tetrachloroethane

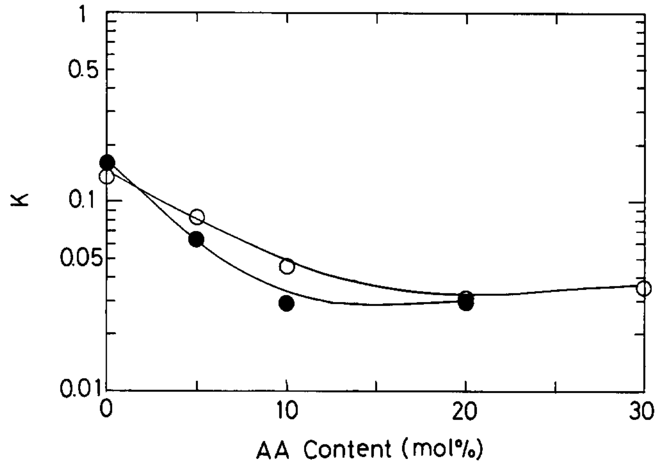

Figure 12 Relationship between K and AA content for P(2EHA-AA) with H liquids: ●, thiodiglycol; ○, dipropyleneglycol

liquids (undecane, hexadecane). In D liquids, it is suggested that the rate of rearrangement and orientation of polymer chain are elevated by decreases in T_g and η' of P(2EHA-AA) because K decreases with AA content. The relationship between K and AA content with P liquids (tetrachloroethane and tetrabromoethane) is shown in *Figure 11*. The proportional constant K decreases with increasing AA content in tetrachloroethane, whereas K obtained with tetrabromoethane exhibits a convex curve. It is suggested that the rate of rearrangement and orientation of P(2EHA-AA) is defined by the liquid's parameters, such as α, I and μ, the polarity X_L^p in tetrabromoethane and dynamic mechanical properties (T_g, η'). The relationship between K and AA content with H liquids (thiodiglycol, dipropyleneglycol) for P(2EHA-AA) as shown in *Figure 12* is represented by a concave curve. We may consider, in the increasing region of K against AA content, that the parameters such as α, I, μ and polarity of solid and liquid greatly affect the rearrangement and orientation of polymer chain. Miki *et al.*[21] found that the concentration at the surface of poly(trifluoroethyl methacrylate) cast film and the interface between the film and the substrate depended on the surface tension γ_S of the substrate.

In this study, it was suggested that the time dependence of contact angle of P(2EHA-AA) with liquid was influenced by the rearrangement and orientation of polymer chain through decreasing γ_{SL}. Then, we expected that the rate of rearrangement and orientation (proportional constant K) between P(2EHA-AA) and organic liquids was affected by the surface tension and species of liquid, the parameters (α, I, μ and polarity X_j^p) and dynamic mechanical properties (T_g and η'). In the future, it will be necessary to investigate the time dependence of the polymer concentration at the interface between P(2EHA-AA) and organic liquids by X.p.s.

CONCLUSIONS

The contact angles θ for organic liquids, such as dispersion, polar and hydrogen bonding liquids, on the surface of P(2EHA-AA) decreased with contact time. It was expected that the rearrangement and orientation of P(2EHA-AA) affected the time dependence of θ through decreasing interfacial tension γ_{SL}. The relationship between θ and contact time t (0.5–10 min) was expressed by:

$$\log\theta = -K\log t$$

The proportional constant K depended on the surface tension γ_L and species of liquid, dynamic mechanical properties (T_g, η') and the parameters (α, I, μ and X_j) of P(2EHA-AA) and liquids.

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