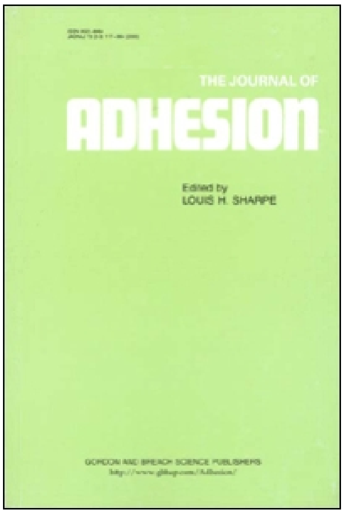
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Peel Morphology of Acrylate Adhesive Polymers

Y. Kano[a]; H. Ushiki[a]; S. Akiyama[a]

[a] Laboratory of Chemistry, Faculty of General Education, Tokyo University of Agriculture and Technology, Tokyo, Japan

To cite this Article Kano, Y. , Ushiki, H. and Akiyama, S.(1993) 'Peel Morphology of Acrylate Adhesive Polymers', The Journal of Adhesion, 43: 3, 223 — 237

To link to this Article: DOI: 10.1080/00218469308026601

URL: http://dx.doi.org/10.1080/00218469308026601

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1993, Vol. 43, pp. 223–237
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

Peel Morphology of Acrylate Adhesive Polymers

Y. KANO, H. USHIKI and S. AKIYAMA

Laboratory of Chemistry, Faculty of General Education, Tokyo University of Agriculture and Technology, 3-5-8, Saiwai-cho, Fuchu-shi, Tokyo 183, Japan

(Received October 26, 1992; in final form August 3, 1993)

The morphology of various acrylate adhesive polymers peeled from Pyrex® glass was investigated. The composition ratios of acrylate polymers [poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate): P(2EHA-AA-VAc)] are 2EHA/AA/VAc = 100/0/0 (PEHA0000), 95/5/0 (PEHA0500), 92/8/0 (PEHA 0800) and 85/5/10 (PEHA0510) (mol%). The peel pattern of PEHA0000 exhibited a greatly elongated saw tooth, while PEHA0500 and PEHA0800 revealed the characteristic branched stringiness at the edge of the saw tooth. The peel morphology of PEHA0510 exhibited the regular saw tooth. The peel morphological pattern differences between the acrylate adhesive polymers were examined using dynamic mechanical thermal analysis, surface tension and the fluorescence probe technique.

KEY WORDS poly(2-ethylhexyl acrylate-co-acrylic acid-co-vinyl acetate); peel morphology; dynamic mechanical properties; surface tension; fluorescence probe technique; relative mean rotational relaxation time; adhesion; pressure sensitive adhesives.

1. INTRODUCTION

Acrylate polymers, such as poly(2-ethylhexylacrylate), poly(butylacrylate) and poly(ethylacrylate), are used as the main components in pressure sensitive adhesives (PSA) because they have low glass transition temperatures ($T_g \leqq -20°C$) and good flexibility. The PSA properties (tack, peel adhesion, holding power) are partially controlled by copolymerization of acrylic acid and vinyl acetate, tackification and crosslinking. In general, the PSA properties are elucidated using dynamic mechanical analysis, surface tension and surface morphology.[1-3] Peel adhesion has been studied by several researchers.[4-11] It is well known that the theoretical equations of peel adhesion use various parameters such as viscoelasticity, thickness, peel angle and work of adhesion, W_A, etc. Saito[12] explained these theoretical equations simply. Recently, Furukawa[13] and Zhu[14] defined new equations for peel adhesion. Urahama *et al.*[15] observed the peel morphology with an optical technique, and found that the backing influenced the peel morphology.

It is reported that the fluorescence probe method is an effective technique for studying chain mobility and dynamic behavior of macromolecules in solution.[16-20] We thought that the study of the dynamic behavior of polymers was very important in the field of adhesive polymers.[21–23] In a previous study,[22] the fluorescence depolarization of chromophores, such as rodamine 6G and fluorescein, was investigated in an acrylate adhesive polymer coated on poly(ethyleneterephthalate) (PET) film. The chromophore's mean rotational relaxation time, ρ, depended on the thickness of the adhesive layer and the PET film. The maximum value of ρ was obtained with a 30 μm thick adhesive layer and a 38 μm thick PET film. We presumed that the orientation of the PET molecule may affect the ρ of a chromophore in the layer of acrylate adhesive polymer. The fluorescence depolarizations results of chromophores in acrylate polymer/toluene mixtures suggests that the extent of interaction between an acrylate polymer and a dissimilar polymer could be evaluated.[21] It was expected that the fluorescence probe technique could well be applied to analyze the chain motion of the acrylate polymer.

In this study, the pressure sensitive adhesive (PSA) properties (peel adhesion, tack, holding power) and peel morphologies of four acrylate adhesive polymers (PEHA0000, PEHA0500, PEHA0800 and PEHA0510) were examined. The dynamic mechanical properties of all of the acrylate adhesives were measured in the bulk state and the fluorescence depolarization was measured in solution (toluene). The surface tensions, γ_s, of the four acrylate polymers were calculated using the solubility parameter, δ. The peel morphology of the acrylate adhesives was correlated with the dynamic mechanical properties, surface tension and the mean rotational relaxation time, ρ, determined from the fluorescence depolarization.

2. EXPERIMENTAL

2.1 Materials

The acrylate polymers {P(2EHA-AA-VAc)} were prepared by radical polymerization at 70°C for 8h using benzoyl peroxide as an initiator in a 95/5 mixture of ethyl acetate and acetone. The composition ratio, molecular weight and molecular weight distribution of P(2EHA-AA-VAc) are shown in Table I. The molecular weights were measured with a Toyo Soda HLC-802UR GPC at 40°C in THF.

2.2 Measurements

Measurements of PSA properties, such as peel adhesion, tack and holding power, were carried out according to JIS (Japanese Industrial Standard)-Z0237. The 180° peel adhesion to stainless steel was measured with a Toyo Baldwin Co., Ltd. TENSIRON/UTM-4-100. The tack was measured using the J. Dow ball tack[24] test with a stainless steel ball at 23°C. Balls of various diameters were rolled onto 100 mm sections of faceup adhesive tape, on a 30-degree incline, with a leading distance of 100 mm. Then, the diameter of the largest ball which stops within 10 cm on the adhesive tape is determined. If the diameter of the ball is (n/32) inch, the tack of the adhesive tape is evaluated as "ball number n." The holding power was measured on stainless steel with a Nitto Rika Kogyo Co., Ltd. NDC-100S creep tester at 40°C. The adhesive test samples were prepared by knife coating a 20 wt% toluene solution onto a 50 μm poly(ethyleneterephthalate) (PET) film. After the samples were dried at 90°C for 2 min, the acrylate polymer films were laminated with the release liner.

TABLE I
Characteristics of P(2EHA-AA-VAc)[a]

Code	Composition ratio (mol%) 2-Ethyl hexyl acrylate	Acrylic acid	Vinyl acetate	M_n	M_w/M_n
0000	100	0	0	1.7×10^5	9.1
0500	95	5	0	2.5×10^5	4.6
0510	85	5	10	3.0×10^5	5.7
0800	92	8	0	4.1×10^5	5.6

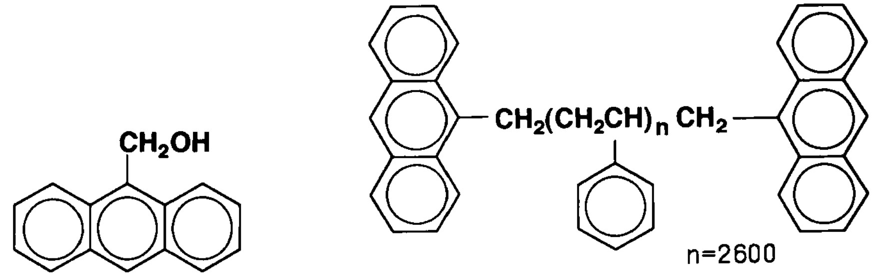
[a] Equivalent molecular weight to that of poly(styrene) by GPC.

These samples were conditioned for 7 days before testing at 23 ± 3°C and 65 ± 5% RH. The dry acrylate adhesive layer was 30 μm thick.

The peel morphology was observed with acrylate polymers coated onto PET film using a peeling behavior observation apparatus made by Miyagi.[25] The peeling angle was 90° and the peeling load was 40~400 (g/25 mm). The adherend was a Pyrex® glass (thickness~2 mm).

The dynamic mechanical properties of the acrylate polymers were investigated by a shearing method, using a Rheometrics Co. RDS-II instrument. The section area and thickness of the acrylate polymer samples were 50 mm^2 and 6 mm, respectively. The frequency was 1 Hz and the dynamic mechanical properties, such as storage modulus G', loss modulus G'', and dynamic loss tangent $\tan\delta$, were measured against temperature.

The fluorescence depolarizations were measured with a fluorescence spectrophotometer (Hitachi 650-40 type) equipped with a data processor (Hitachi 650-0178) and polarizing filters (Hitachi 650-0155). The fluorescence probes are small molecular chromophore (9-hydromethyl anthracene: HMA) and anthryl groups attached to terminal branches of poly(styrene) (APSA). The structures of the fluorescence probes used in this study are shown in Figure 1. The fluorescence probes were put into the P(2EHA-AA-VAc)/toluene mixtures at concentrations between 0.01 and 0.1 (g/dl). The mean rotational relaxation time, ρ, of HMA and APSA was obtained by fluorescence depolarization. The degree of polymerization of poly(styrene) in APSA was 2600.



9-Hydroxymethyl-anthracene (HMA)

APSA

FIGURE 1 Structure of chromophores.

TABLE II
Pressure sensitive adhesive properties of P(2EHA-AA-VAc)

Code	180° Peel adhesion[a] (gf/25 mm)	J. Dow ball tack	Holding power (sec)
0000	CF/65	6	CF/2
0500	CF/750	9	CF/7
0510	CF/1650	9	CF/20
0800	CF/2660	9	CF/20

[a]Dwell time, 24 hours.
CF, Cohesive failure of adhesive.

3. RESULTS AND DISCUSSION

3.1 PSA Properties and Peel Morphology

The PSA properties of the acrylate adhesive polymers are represented in Table II. The 180° peel adhesion testing of all samples exhibits cohesive failure in the acrylate layer, and the peel adhesion increases with increasing acrylic acid content. The 180° peel adhesion of PEHA0510 is between PEHA0500 and PEHA0800. The value of the J. Dow ball tack of PEHA0000 is smaller than that of the other three acrylate adhesive polymers which all have the same value. In all the acrylate polymers, the holding power is unfavorable because they are non-curing. We consider that the PSA properties are influenced by the dynamic mechanical properties and the interfacial interaction between adhesive and adherend. Particularly, since the 180° peel adhesion of these acrylate polymers to stainless steel exhibits cohesive failure in the adhesive layer, it is presumed that the 180° peel adhesion was influenced by the dynamic mechanical properties of the polymers.

The peel morphology of the polymers PEHA0000, 0500, 0510 and 0800 was investigated. The peel patterns of these adhesives on Pyrex® glass are shown in Figure 2. These polymers exhibited interfacial failure between the acrylate layer and the glass. The stringiness of poly(2-ethylhexylacrylate) PEHA0000 results in a markedly elongated saw tooth. In the polymers with acrylic acid content of 5 and 8 (mol%), PEHA0500 and 0800, a characteristic branched stringiness on the edge of the saw tooth appears. When the vinyl acetate unit is added into the PEHA polymer, the stringy peel morphology pattern shows a regular saw tooth form. The peel width and pitch of the acrylate polymers is shown in Table III. As the stringiness pattern changes according to the acrylate polymer composition, and the peels of all acrylate polymers to Pyrex® glass show interfacial failure, it is predicted that the peel morphology is influenced by the mechanical properties of the bulk polymer and the interfacial interaction between the acrylate polymer and the Pyrex® glass. Urahama *et al.*[26] observed the peel morphology of rubber/terpene tackifier resin blend adhesives and found that the stringiness pattern was changed by blending tackifier resin into the rubber. In general, they found that the dynamic mechanical properties, such as storage modulus G′, loss modulus G″ and glass transition temperature T_g, depended on the tackifier resin content. Thus, we thought it important to measure the dynamic mechanical properties of the four acrylate adhesive polymers.

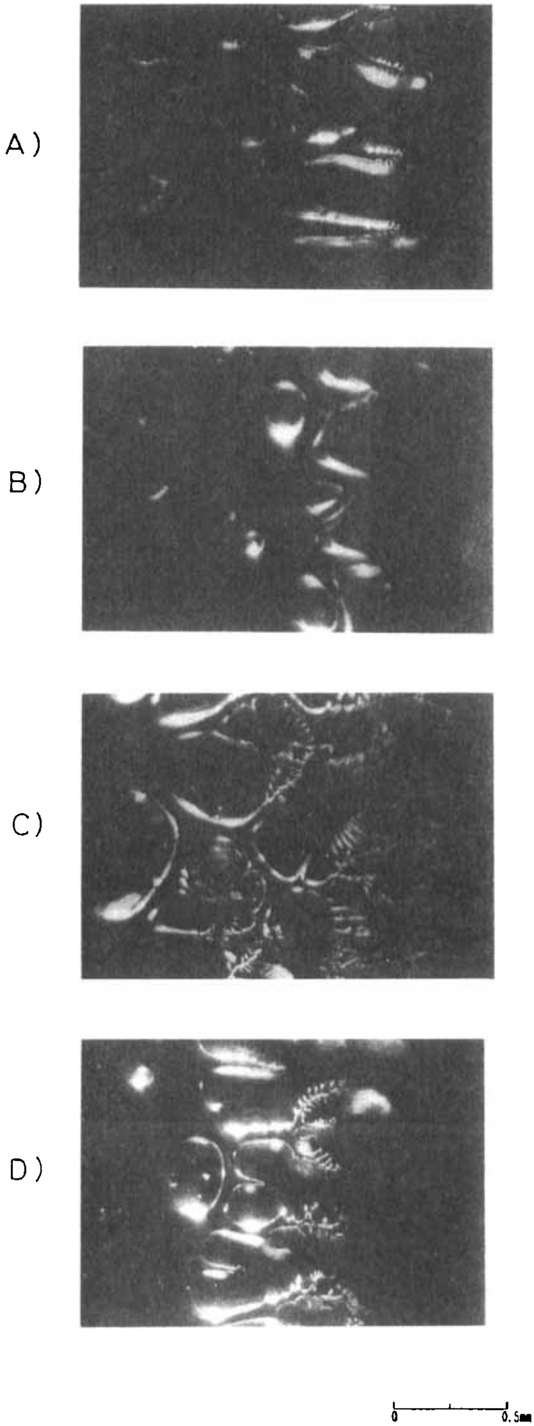


FIGURE 2 Peeling morphology of acrylate polymers. Code: A) 0000, B) 0510, C) 0800, D) 0500.

TABLE III
Peel width and pitch of P(2EHA-AA-VAc)

Code	Width (mm)	Pitch (mm)
0000	0.7	0.25
0500	0.7	—
0510	0.25	0.35
0800	1.25	—

3.2 Dynamic Mechanical Properties

The temperature dependence of G′ for the acrylate polymers is shown in Figure 3. The values of G′ for PEHA0000 are smaller than for the other acrylate polymers. Urahama[27] studied the peel morphology of a non-cured type acrylic pressure sensitive adhesive (PSA) to a glass plate and reported that the peel morphology exhibited a greatly-elongated peel pattern. The peel pattern of PEHA0000 is similar to that of the non-cured type PSA. Thus, we think that the greatly-elongated peel pattern is related to the lower G′ value (the G′ of PEHA0000 is 3.8×10^5 (dyn/cm^2) at room temperature). On the other hand, in the acrylate polymers containing acrylic acid and vinyl acetate, the magnitude of G′ increases

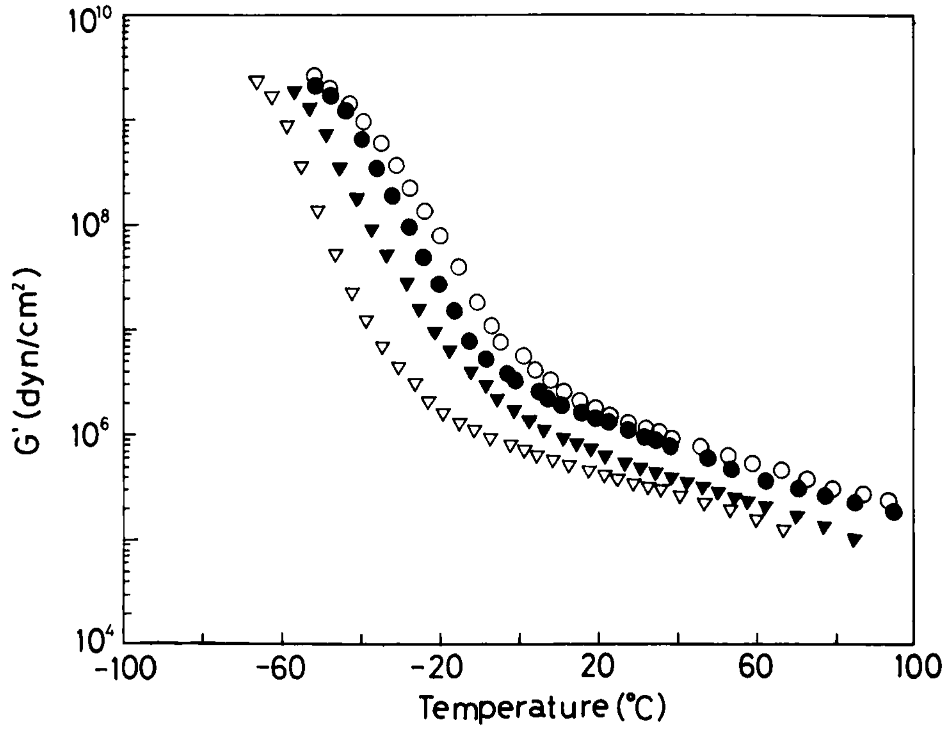


FIGURE 3 Temperatre dependence of G′ for acrylate polymers. Acrylate polymer code: ● 0510, ○ 0800, ▼ 0500, ▽ 0000.

in the order: PEHA0500<0510<0800. It is presumed that the regular saw tooth pattern (PEHA0510) and the characteristic branched stringiness on the edge of the saw tooth peel morphology is observed around $G' = 6.0 \times 10^5 \sim 1.4 \times 10^6$ (dyn/cm^2) at room temperature. Figure 4 shows the temperature dependence of loss modulus G″ for the acrylate polymers. The curves of G″ *vs.* temperature are similar to those of G′ *vs.* temperature and the magnitude of G″ also increases in the order: PEHA0000<0500<0510<0800. The maximum value of G″ may appear in the lower temperature region (< −60°C). The temperature dependence of the dynamic loss tangent, tan δ, for the acrylate polymers is shown in Figure 5. The maximum of tan δ (T_{Dmax}) for the polymers (PEHA) shifts towards higher temperatures in the order: PEHA0000<0500<0510<0800. In the PEHA polymers, the ordering of the T_{Dmax} values is the same as that of the G′ and G″ values. The T_{Dmax} relates to the glass transition temperature, T_g. The dynamic mechanical properties (G′, G″) at 23°C and T_{Dmax} for the acrylate polymers are shown in Table IV. The order of 180° peel adhesion values also corresponds to that of the dynamic mechanical properties for the four acrylate adhesive polymers. It is, therefore, presumed that the 180° peel adhesion of PEHA polymers is influenced by the bulk properties (dynamic mechanical properties) of the polymers. The values of G′, G″ and T_{Dmax} for PEHA0000 is smaller than those of the other acrylate polymers. In the peel morphology of PEHA0000, it is considered that the markedly-elongated saw tooth depends on the lower G′, G″ and T_{Dmax} of this polymer. On the other hand, it is suggested that the characteristic branched stringiness on the edge of the saw tooth

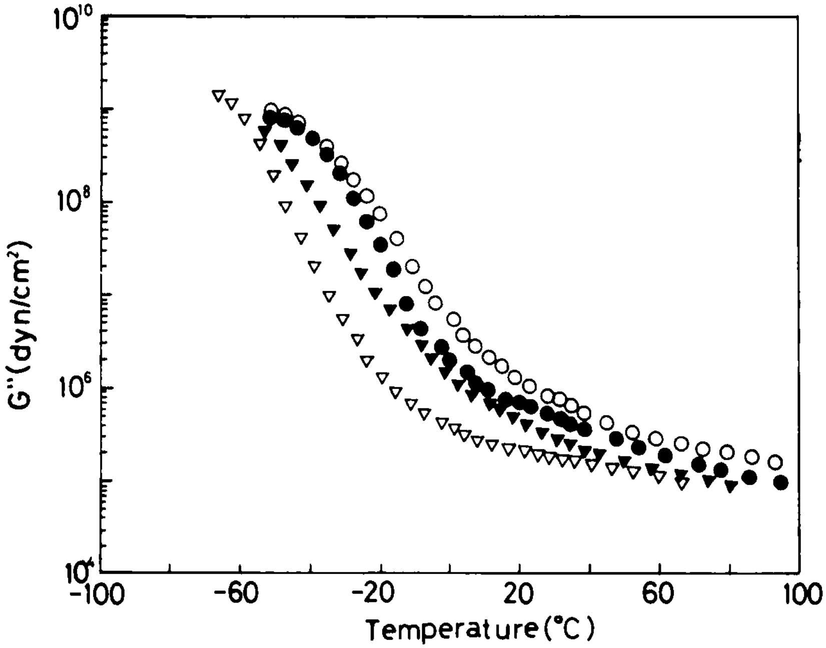


FIGURE 4 Temperature dependence of G″ for acrylate polymers. Acrylate polymer code: ● 0510, ○ 0800, ▼ 0500, ▽ 0000.

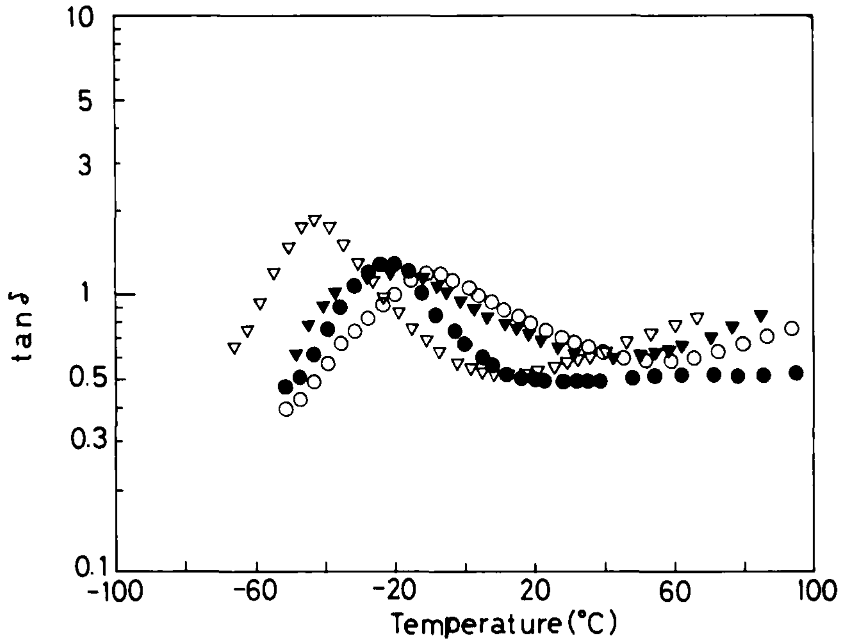


FIGURE 5 Temperature dependence of tan δ for acrylate polymers. Acrylate polymer code: ● 0510, ○ 0800, ▼ 0500, ▽ 0000.

TABLE IV
Dynamic mechanical properties at 23°C and T_{Dmax} of acrylate polymers

Code	G′ (dyn/cm^2)	G″ (dyn/cm^2)	T_{Dmax} (°C)
0000	3.82×10^5	3.19×10^5	−42.6
0500	6.02×10^5	4.04×10^5	−21.3
0510	1.27×10^6	9.70×10^5	−20.0
0800	1.38×10^6	1.61×10^6	−11.1

and the regular saw tooth forms of peel morphology for the other acrylate polymers is related to the higher G′, G″ and T_{Dmax}. Figure 6 shows the heightened scale of peeling morphology (the characteristic branched stringiness on the edge of the saw tooth form) of the acrylate polymers with acrylic acid content of 5 and 8 (mol%) (PEHA0500, 0800). In the acrylate polymer containing 5 (mol%) acrylic acid (PEHA0500), the branched stringiness observed on the edge of the saw tooth exhibits the twigged peel morphology. The peel pattern of PEHA0800 also shows the twigged peel morphology; however, the peel features of PEHA0800 are very complicated. When the acrylic acid is copolymerized with 2-ethylhexyl acrylate, G′, G″ and T_g increase with increasing acrylic acid content because of hydrogen bonding and the higher T_g of acrylic acid. In the copolymer of 2-ethylhexyl acrylate and acrylic acid, it is thought that the feature of twigged peel morphology is influenced by the mechanical properties, such as modulus and T_g, of the bulk acrylate polymer.

The G′, G″ and T_{Dmax} of PEHA0510 lie between those of PEHA0500 and 0800,

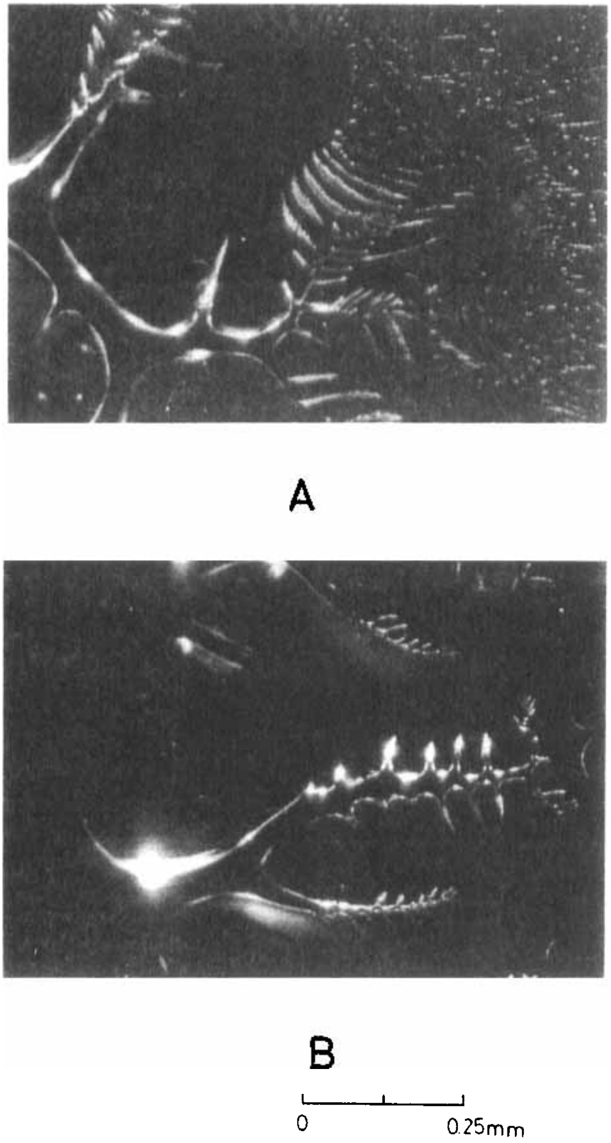


FIGURE 6 Peeling morphology of acrylate polymers. Code: A) 0800, B) 0500.

while the pattern of peel morphology of 0510 differed from the peel morphologies of 0500 and 0800. We took note of the values of dynamic mechanical properties and peel morphology (regular saw tooth) for PEHA0510. It is supposed that the pattern of peel morphology is affected by the dynamic mechanical properties of the acrylate adhesive polymers and other factors, *i.e.*, the interfacial interaction between the adhesives and the adherend and the surface tension of the adhesives.

3.3 Surface Tension

In general, pressure sensitive adhesive properties, such as tack and 180° peel adhesion, depend on the surface tension. For example, Toyama *et al.*[28] found that tack and peel adhesion were influenced by the difference between the surface tensions of the adhesive polymer and adherend. The pattern of peel morphology may, therefore, also be related to the difference between the surface tensions of the acrylate polymers.

In this study, the surface tensions, γ_s, of the acrylate polymers were estimated using the solubility parameter, δ, and the following equations:

$$\gamma_s = 0.07147\cdot\delta^2\cdot V^{1/3} \qquad (1)$$ [29]

$$\delta = 4.1(\gamma_s/V^{1/3})^{0.43} \qquad (2)$$ [30]

$$\gamma_s = 0.062\cdot\delta^2\cdot V^{1/3} \qquad (3)$$ [31]

where V is the molar volume. The δ is calculated from the molar attraction constants, F_i, using Hoy's table.[32]

$$\delta = \Sigma\ (F_i/V) \qquad (4)$$

As the acrylate polymers are composed of 2-ethylhexyl acrylate (2EHA), acrylic acid (AA) and vinyl acetate (VAc), the codes a, b and c are expressed as the monomer ratios of 2EHA, AA and VAc, respectively. Thus, δ is obtained with the monomer ratios a, b and c as follows:

$$\begin{aligned}\delta &= \delta_{2EHA}\cdot\delta_{AA}\cdot\delta_{VAc}\\ &= [\Sigma\ (F_{i\,(2EHA)}/V_{2EHA})]^a\ [\Sigma\ (F_{i\,(AA)}/V_{AA})]^b\ [\Sigma\ (F_{i\,(VAc)}/V_{VAc})]^c \qquad (5)\end{aligned}$$

The γ_s calculated by equations 1, 2, 3 and literature values of γ_s, for acrylate polymers are shown in Table V. The γ_s obtained by the four methods are different from each other (27~34 (dyn/cm)); however, the γ_s are unchanged in these acrylate polymers. This result suggests, therefore, that the γ_s do not, in fact, affect the pattern of peel morphology.

TABLE V
Surface tensions of acrylate polymers (dyn/cm)

Code	γ_s (Eq. 1)	γ_s (Eq. 2)	γ_s (Eq. 3)	γ_s (Ref.)
0000	31.2	33.3	27.1	27.4[a]
0500	31.5	33.9	27.3	28.0[a]
0510	31.5	33.8	27.3	28.3[b]
0800	31.7	34.1	27.5	28.6[a]

[a] T. Kasemura, M. Inagaki and T. Hata, *Kobunshi Ronbunshu* **44**, 131 (1987).
[b] Y. Kano, K. Ishikura, S. Kawahara and S. Akiyama, *Polym. J.* **24**, 135 (1992).

We think that the difference between the peel patterns of the acrylate polymers (PEHA0500, 0800 and 0510) is related to the vinyl acetate unit. In the previous paper,[21] we investigated the fluorescence depolarization of chromophores in acrylate polymer/toluene mixtures based on the fluorescence probe technique. We found that this technique is an effective method for evaluating the interaction between an acrylate adhesive polymer and a dissimilar polymer. To examine the effect of the vinyl acetate unit on the difference between the peel patterns for the acrylate polymers, the fluorescence probe technique in solutions (acrylate polymer/toluene mixtures) was employed. The mean rotational relaxation time, ρ, of chromophores in acrylate polymer/toluene mixtures was measured by means of a fluorescence depolarization method.

3.4 Fluorescence Depolarization

The emission anisotropy, γ, relates to the mean rotational relaxation time, ρ. By assuming the rigid sphere approximation, the relationship between γ and ρ is expressed as follows:

$$\gamma_0/\gamma = 1 + (3\tau_0/\rho) = 1 + (\kappa\ \tau_0/V)\ (T/\eta) \tag{6}$$

where τ_0 is the excited single lifetime of the chromophore, γ_0 the emission anisotropy in rigid solution, η the viscosity, V the apparent rotational volume of the chromophore, κ the Boltzmann constant and T the absolute temperature. Thus, the ratio ρ/τ_0 can be calculated by following equation:

$$\rho/\tau_0 = 3\gamma_0^{-1} \cdot I_F/(\gamma^{-1} - \gamma_0^{-1}) \cdot I_F^0 = (3V/\kappa\ \tau_0)\ (\eta/T) \tag{7}$$

where I_F and I_F^0 are the fluorescence intensities at various polymer concentrations, F, and 0% polymer concentration, respectively. Therefore, ρ is calculated from the emission anisotropy which is measured by the fluorescence depolarization.

To investigate the interaction between the acrylate polymer and a dissimilar polymer [poly(styrene)], the relative mean rotational relaxation time, ρ, of HMA and APSA was evaluated by fluorescence depolarization. Figure 7 shows the dependence of ρ, for the chromophores APSA and HMA, *versus* η/T for various acrylate polymer/toluene mixtures. The viscosity, η, at 25°C of different PEHA/toluene mixtures as a function of acrylate polymer concentration in the various polymers was reported in the previous paper.[21] In the acrylate polymer codes, 0000, 0500 and 0800, the change of the apparent mean rotational relaxation time of APSA against η/T is little. On the other hand, the apparent mean rotational relaxation time of APSA in PEHA0510/toluene mixtures increases with increasing η/T, monotonically. It is expected that the interaction between PEHA0510 and APSA is stronger than those between the other acrylate polymers and APSA. Using HMA as the chromophore, polymers 0510, 0800 and 0500 show an increase in the apparent mean rotational relaxation time with increasing η/T, whereas the mean rotational relaxation time does not change with η/T for PEHA0000.

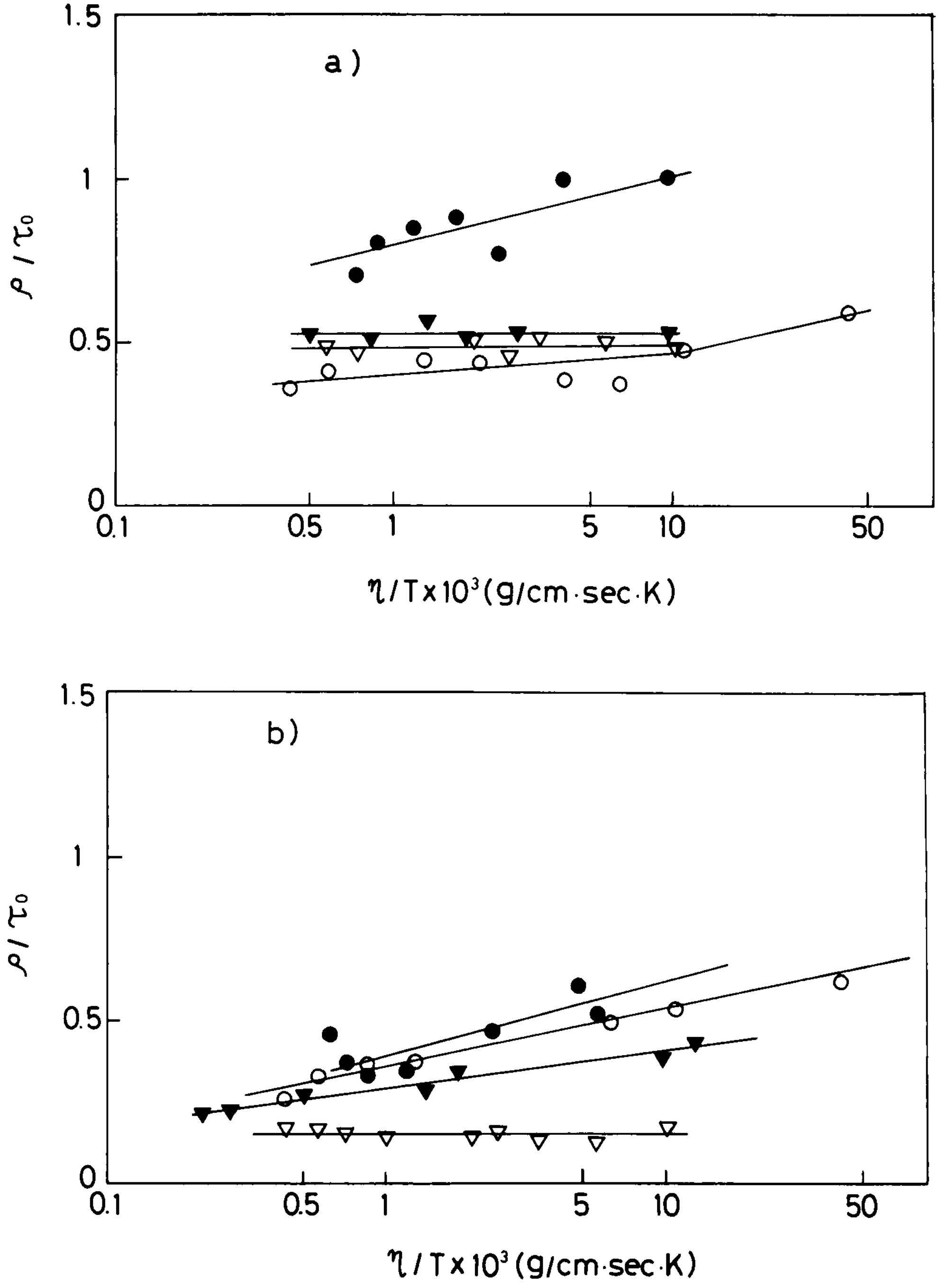


FIGURE 7 Relationship between relative mean rotational relaxation time of chromophores and η/T for various acrylate polymer/toluene mixtures. Chromophore: a) APSA, b) HMA. Acrylate polymer code: ● 0510, ○ 0800, ▼ 0500, ▽ 0000.

When the interaction between the acrylate polymers and a dissimilar polymer is evaluated, the ratio of mean rotational relaxation time in each chromophore, ρ_P/ρ_S, is expressed as follows:

$$\rho_P/\rho_S = \frac{[I_{FP}\, I^0_{FS}\, \tau_{0P}\, \gamma_{0P}^{-1}\, (\gamma_S^{-1} - \gamma_{0S}^{-1})]}{[I^0_{FP}\, I_{FS}\, \tau_{0S}\, \gamma_{0S}^{-1}\, (\gamma_P^{-1} - \gamma_{0P}^{-1})]} \tag{8}$$

where subscripts P and S denote the chromophore attached to the terminal branches of poly(styrene) (APSA) and the small molecule chromophore (HMA), respectively. As $\gamma_{0P} \approx \gamma_{0S}$ and $\tau_{0P} \approx \tau_{0S}$, ρ_P/ρ_S can be calculated with the following equation

$$\rho_P/\rho_S = \frac{(I_{FP}\cdot I^0_{FS}/I^0_{FP}\cdot I_{FS})\,[\gamma_S\,(\gamma_{0S} - \gamma_P)]}{[\gamma_P\,(\gamma_{0S} - \gamma_S)]} \tag{9}$$

where the γ_0^{-1} value of HMA is 7.8.[18]

In order to clarify the interaction between the acrylate adhesive polymer and the dissimilar polymer, the relationship between ρ_P/ρ_S and η/T is plotted as shown in Figure 8. From Eq. 7, the ratio of apparent rotational volume (V_P/V_S) can be expressed by:

$$\rho_P/\rho_S = V_P/V_S \tag{10}$$

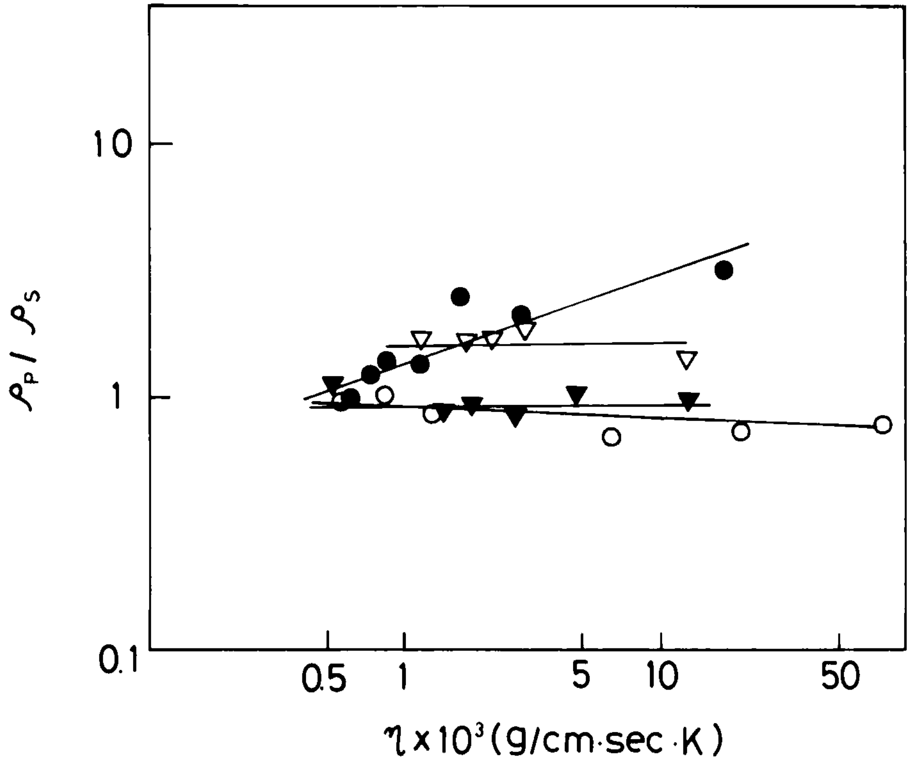


FIGURE 8 Plots of ρ_P/ρ_S against η/T for various acrylate polymer/toluene mixtures. Acrylate polymer code: ● 0510, ○ 0800, ▼ 0500, ▽ 0000.

As shown in Figure 8, the increasing ratio of ρ_P/ρ_S to η/T in the PEHA0510/toluene mixtures is larger than those in the mixtures of the other acrylate polymers with toluene. Thus, the increasing ratio of V_P/V_S in PEHA0510/toluene mixtures is larger than that in PEHA0000, 0500 and 0800/toluene mixtures. It is presumed that interaction between PEHA0510 and the dissimilar polymer [poly(styrene)] is stronger than those between the other acrylate polymers and the dissimilar polymer in toluene. The PEHA0510 contains the vinyl acetate unit, whereas the other acrylate polymers, PEHA0000, 0500 and 0800 do not contain vinyl acetate. We expect that adding vinyl acetate units to the acrylate polymer enhances the interaction with a dissimilar polymer, because the vinyl acetate can reduce the hydrogen bonding force of the acrylic acid group and easily entangle with another polymer [poly(styrene)].

From the results of the fluorescence depolarization technique, the change in the mean rotational relaxation time ratio, ρ_P/ρ_S, *versus* η/T in PEHA0510/toluene mixtures was very large. If the interaction between PEHA0510 and poly(styrene) in solution is equivalent to that between PEHA0510 and Pyrex® glass in the solid state, we may expect that the regular saw tooth form of peel morphology for PEHA0510 is related to the effects of vinyl acetate (reducing hydrogen bonding force, advancing entanglement to another polymer). On the other hand, the ρ_P/ρ_S ratio of the chromophore in the PEHA0000, 0500 and 0800/toluene mixtures does not change against η/T. It is considered that the patterns of peel morphology for PEHA0000, 0500 and 0800 (the markedly-elongated saw tooth, characteristic branched stringiness on the edge of the saw tooth) are affected by the dynamic mechanical properties of the acrylate polymers.

In this study, the peel patterns of the four kinds of acrylate adhesives were compared with the results of the fluorescence depolarization experiments in the solution state to examine the interfacial interaction between the adhesive polymers and the adherend (Pyrex® glass). However, it is supposed that the ρ_P/ρ_S ratio of the chromophores in acrylate adhesive polymer/toluene solutions may be influenced by the degree of polymerization of the poly(styrene) in the APSA and the polarity of the liquid (because of the solution state). The effect of the vinyl acetate unit may be different in the solution state (fluorescence depolarization technique) from what it is in the solid state (peel morphology). In the future, we would like to investigate the effect of these parameters on the peel pattern and on the ρ_P/ρ_S of chromophores in the adhesive polymer (solid state) on PET film.

4. CONCLUSIONS

In the four acrylate adhesive polymers [PEHA0000, 0500, 0800 and 0510], the peel morphology was examined with the peel behavior observation apparatus. The peel pattern of PEHA0000 exhibited a greatly-elongated saw tooth, whereas those of PEHA0500 and PEHA0800 exhibited a characteristic branched stringiness on the edge of the saw tooth. The pattern of peel morphology of PEHA0510 revealed a regular saw tooth. The difference of peel morphology for the four acrylate adhesive polymers was investigated by comparing their dynamic mechanical properties, their surface tension, γ_S (bulk state), and their mean rotational relaxation time, ρ, based on the fluorescence depolarization technique (solution state). The γ_S did not change in these acrylate polymers. It is, therefore, presumed that the difference of peel patterns for PEHA0000, 0500 and 0800 was influenced by the dynamic mechanical properties, such as G', G'' and T_{Dmax}. On the other hand, the peel pattern (regular saw tooth) for PEHA0510 was related to the vinyl acetate unit (the decreasing hydrogen bonding force and the increasing entanglement effect), because the increase in the ratio ρ_P/ρ_S with increasing η/T for PEHA0510 was much larger than for the other polymers.

Acknowledgments

The authors express their thanks to Dr. Y. Urahama of Nitto Denko Co. Ltd. for peeling observation and to Dr. Y. Kitazaki of Nichiban Co. Ltd. for supplying acrylate polymers.

References

1. M. A. Krenceski, J. F. Johnson and S. C. Temin, *Macromol. Chem. Phys.* **C26,** 143 (1986).
2. D. Satas, *Handbook of Pressure Sensitive Adhesive Technology,* 2nd ed. (Van Nostrand Reinhold, New York, 1989).
3. M. Toyama, *Kanatsu Setchakuzai* (Kobunshi Kankokai, Kyoto, 1991).
4. J. J. Bikerman, *J. Appl. Phys.* **28,** 1484 (1957).
5. J. L. Gardon, *J. Appl. Polym. Sci.* **7,** 643 (1963).
6. D. H. Kaelble, *J. Colloid Sci.* **19,** 413 (1964).
7. D. H. Kaelble, *J. Adhesion* **1,** 102 (1969).
8. M. Toyama, T. Ito and H. Moriguchi, *J. Appl. Polym. Sci.* **14,** 2039 (1970).
9. A. N. Gent and G. R. Hamed, *Polym. Eng. Sci.* **17,** 462 (1977).
10. D. W. Aubrey and M. Sherriff, *J. Polym. Sci. Polym. Chem. Ed.* **16,** 2631 (1978).
11. D. W. Aubrey and M. Sherriff, *J. Polym. Sci. Polym. Chem. Ed.* **18,** 2597 (1978).
12. T. Saito, *Nippon Setchaku Kyokaishi* **21,** 228 (1985).
13. J. Furukawa, *Nippon Setchaku Kyokaishi* **24,** 403 (1988).
14. C. X. Zhu, *Nippon Setchaku Gakkaishi* **28,** 436 (1992).
15. Y. Urahama, Y. Tokunaga and Y. Tanaka, *Nippon Setchaku Gakkaishi,* a) **26,** 333 (1990); b) **26,** 386 (1990).
16. H. Ushiki and I. Mita, *Polym. J.* **17,** 1297 (1985).
17. H. Ushiki, K. Hirayanagi, Y. Shindo, K. Horie and I. Mita, *Polym. J.* **17,** 671 (1985).
18. H. Ushiki and F. Tanaka, *Eur. Polym. J.* **21,** 701 (1985).
19. H. Ushiki, I. Wada, S. Onuki, K. Horie and I. Mita, *Chem. Phys. Lett.* **125,** 174 (1986).
20. H. Ushiki and M. Ozu, *Eur. Polym. J.* **22,** 835 (1985).
21. H. Ushiki, Y. Kano, S. Akiyama and Y. Kitazaki, *Eur. Polym. J.* **22,** 381 (1986).
22. S. Akiyama, H. Ushiki, Y. Kano and Y. Kitazaki, *Eur. Polym. J.* **23,** 327 (1987).
23. S. Akiyama, H. Ushiki and H. Sugiyama, *Rep. Prog. Polym. Phys. Jpn.* **31,** 455 (1988).
24. J. Dow, *Proc. Inst. Rubber Ind.* **1,** 105 (1954).
25. Z. Miyagi, *Nippon Setchaku Kyokaishi* **20,** 288 (1984).
26. Y. Urahama, Y. Shibata, K. Yamamoto and Z. Miyagi, Dai 25kai Setchaku Kenkyu Happyoukai Yoshi (Japan), 1986, p. 121.
27. Y. Urahama, Doctor Thesis, Meiji University, Japan, 1989.
28. M. Toyama, T. Ito, H. Nukatsuda and M. Ikeda, *J. Appl. Polym. Sci.* **17,** 3495 (1973).
29. P. Becher, *J. Colloid Interface Sci.* **38,** 291 (1972).
30. H. Burrell and N. J. Clitor, *Polymer Handbook,* 2nd ed., J. Brandrup and E. H. Immergut, Eds. (Wiley, New York, 1975), p. vi-337-359.
31. M. Imoto, *Nippon Setchaku Kyokaishi* **24,** 395 (1988).
32. K. L. Hoy, *J. Paint Technol.* **42,** 76 (1970).