Effect of the Length of Branches on the Critical Surface Tension of Poly(n-alkyl Methacrylates) and Copolymers of Stearyl Methacrylate with Methacrylonitrile

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Synopsis

Critical surface tension values γ_c were measured for poly(n-alkyl methacrylates) and copolymers of stearyl methacrylate with methacrylonitrile. Surface tension values γ_L of n-alkyl methacrylate increase with increasing side chain length: $\gamma_L = 23.2$ dynes/cm for methyl methacrylate to 33.2 dynes/cm for stearyl methacrylate, but γ_c values of poly(n-alkyl methacrylate) decrease with increasing side chain length: $\gamma_c = 36.3$ dynes/cm for poly(methyl methacrylate) to 20.8 dynes/cm for poly(stearyl methacrylate). The decrease in γ_c is attributed to a tighter packing of the alkyl chain with a greater concentration of the pendent —CH_3 group at the air/solid interface. Values of γ_c of copolymers hardly depended on the methacrylonitrile content in copolymers and did not satisfy the equation $\gamma_c = N_1\gamma_{c1} + N_2\gamma_{c2}$ proposed by Lee. The difference in γ_c values for casting, annealing, and quenching films of poly(stearyl methacrylate) and the surface structure of copolymers were discussed using electron microscopy and measurement of melting point, heat of melting, and γ_c.

INTRODUCTION

The critical surface tension γ_c, which was used by Zisman[1] as a measure of the wetting properties of polymers, has had frequent application to the studies of adhesive and frictional properties. The interrelation of γ_c and molecular structure of polymers has been studied by many investigators.[1-3]

The influence of chain packing on γ_c was first demonstrated by Zisman and Fox[4] in a comparison of γ_c for a monolayer of octadecylamine and crystal of hexatriacontane. The lower γ_c associated with the crystal (20–22 dynes/cm compared to 22–24 dynes/cm) was attributed to a tighter packing of the alkyl chain with a greater concentration of the pendent —CH_3 group at the air/solid interface.

Recently, Pittman and Ludwig[5] reported the influence of the side chain on γ_c for poly(fluoroalkyl acrylate) containing the alkyl group HCF_2-$(CF_2)_n CH_2$—, where n is 1, 3, 5, 7 or 9. Of this series, the acrylate polymers with $n = 7$ and 9 crystallize partially at room temperature. These polymers presumably have oriented and packed alkyl side chains. Higher γ

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values would be expected owing to poor side chain alignment and exposure of the polymer backbone. Comparison of quenched and annealed films of acrylate polymer ($n = 7$) shows a lower γ_c value and poorer cyrstalline packing of the fluoroalkyl side chain in the quenched than in the annealed film.

In this paper, we discuss the effect of the side chain length of poly(n-alkyl methacrylates) and the composition of stearyl methacrylate–methacrylonitrile copolymers on γ_c values.

EXPERIMENTAL

Monomers

Methyl, ethyl, butyl, hexyl, octyl, lauryl, and stearyl methacrylates and methacrylonitrile were used as monomers. Octyl methacrylate was obtained by the esterification of methacrylic acid (1.4 mole) with octyl alcohol (1 mole) in benzene in the presence of p-toluenesulfonic acid as a catalyst. The refractive index of octyl methacrylate synthesized was in good agreement with the reported value.

Monomers, except stearyl methacrylate, were freed from inhibitor, dried, and purified by distillation under nitrogen at reduced pressure. Stearyl methacrylate was purified by recrystallization from methanol solution.

Preparation of Poly(n-alkyl Methacrylates) and Copolymers

Polymers were obtained by free-radical polymerization of the monomers in the presence of benzoyl peroxide as initiator. Monomers were dissolved in an equal volume of freshly distilled benzene in a three-neck flask fitted with a reflux condenser and a stirrer. Initiator was added (0.5–1 mole-% in benzene), and the flask was then stirred for 8–16 hr at 78°C under nitrogen atmosphere. Polymer was precipitated by adding the reaction mixture to a large amount of methanol. The polymer was then purified by reprecipitation from the system benzene–methanol. Precipitation was repeated three times to completely remove unpolymerized monomer.

Copolymerizations with different ratios of monomer feeds in a three-neck flask fitted with a reflux condenser and a stirrer were carried out at 78°C under nitrogen atmosphere, benzoyl peroxide being being used as initiator. Polymerization was terminated at low conversion (about 10%) to suppress the appearance of distribution in composition. Copolymer was precipitated by adding the reaction mixture (copolymer and unpolymerized monomer) to a large amount of methanol. The copolymer was then purified by precipitation from the system chloroform–methanol (acetone–methanol for polymethacrylonitrile). Precipitation, in the same manner as poly(n-alkyl methacrylate), was repeated three times to completely remove unpolymerized monomers. The composition of the copolymer (mole fraction of methacrylonitrile), given in Table I, was calculated according to the theory of random copolymerization[6] from the ratio

TABLE I
Temperature, Heat, and Entropy of Melting for Copolymers of Stearyl
Methacrylate with Methacrylonitrile[a]

Sample	Calculated MAN content in co-polymer, mole fraction	Melting point, °C		ΔH_m, kcal/mole		ΔS_m, cal/deg·mole	
		(1)	(2)	(1)	(2)	(1)	(2)
Poly(stearyl methacrylate)	0	35.7	29.5	4.25	2.51	13.77	8.30
Copolymer							
Co-1	0.182	34.5	31.0	2.90	1.73	9.43	5.69
Co-2	0.374	36.6	31.6	2.54	1.01	8.20	3.32
Co-3	0.573	38.8	29.0	2.14	0.29	6.86	0.96
Co-4	0.782	51.0	—	0.66	—	2.04	—
Polymethacrylonitrile	1.0	—	—	—	—	—	—

[a] (1) Sample reprecipitated from benzene–methanol. (2) Sample cooled below its melting temperature at a constant rate of 4°C/min.
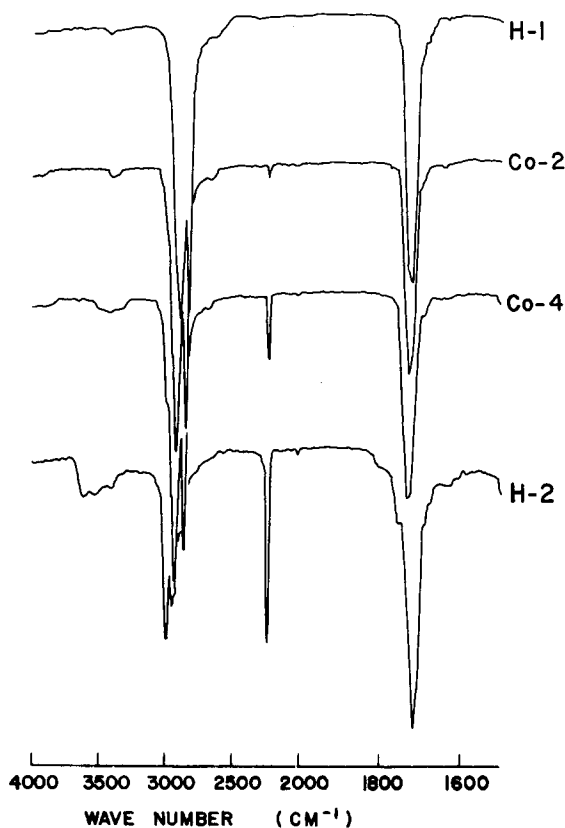

Fig. 1. IR spectra of poly(stearyl methacrylate) (H-1), copolymers of stearyl methacrylate with methacrylonitrile (Co-2, Co-4), and poly(methacrylonitrile (H-2).

of monomer feeds and the monomer reactivity ratios (stearyl methacrylate/methacrylonitrile, $r_1 = 1.13/r_2 = 0.90$).[7]

The heat of melting (ΔH_m) and the melting point of copolymers were measured with a differential scanning calorimeter DSC-1 (made by Perkin-Elmer Corp., U.S.A.) at a constant rate of heating of 8°C/min.

The electron microscope was a JME 6A (made by Japan Electron Optics Lab., Co., Ltd., Tokyo, Japan). Thin-film specimens for electron microscopy were obtained by casting from dilute solution on a distilled water surface. The film thickness was about 1000 Å. After slow evaporation of the solvent at room temperature and removal of the residual solvent under vacuum, the film was shadowed with chromium for increased contrast.

Infrared spectra of copolymers were recorded by a grating infrared spectrophotometer EPI-G3 (made by Hitachi Ltd., Tokyo, Japan) at room temperature. IR spectra of copolymers containing varying quantities of methacrylonitrile (MAN) are shown in Figure 1.

Preparation of Samples for Contact Angle Measurement

Smooth stearyl methacrylate (SMA) and octadecane surfaces were obtained by melting SMA (mp 28–29°C) and octadecane (mp 27–28°C) on clean microscope slides kept horizontal.

Polymer-coated glass slides were prepared by immersing the clean glass microscope slides in benzene solutions (acetone for PMAN, chloroform for copolymers Co-1, Co-2, Co-3, Co-4) of the polymers and copolymers (5–6) wt-%). The slides were slowly withdrawn from the solutions and air dried for several hours at 20°C. The slides were held at reduced pressure for a week to remove the solvent completely.

Annealing and quenching samples were prepared for PSMA, Co-1, Co-2, Co-3, and Co-4 in addition to the above-mentioned casting sample. Annealing of polymer-coated glass slides was carried out by heating the slides in the oven to about 5°C past the melting point, then allowing the slides to cool both to a temperature slightly below the temperature where the onset of melting occurred. Quenching of polymer-coated glass slides was carried out by immersing the slides in Dry Ice immediately after removal from the 60°C oven.

Measurement of Contact Angle

The advancing contact angles were measured directly by employing a telescopic device equipped with an ocular protractor (made by Elma Optical Works, Ltd., Tokyo, Japan). Contact angles θ were measured at 20°C and 65% relative humidity for SMA-, octadecane-, and polymer-coated glass slides. Two separate drops of the wetting liquid were placed on the glass slide surface. The contact angle was measured on both sides of the drop, and the θ value used was, in most cases, the mean value of four readings. The drops were equilibrated for a minimum of 10 min prior to reading the contact angle. Reproducibility of the reading was about $\pm 2°$.

TABLE II
Surface Tension of Liquids at 20°C

Liquid	Surface tension, dynes/cm	Literature value
Glycerol	63.3	64.0[8]
Formamide	60.0	52.8[8]
Ethylene glycol	49.0	47.8[8]
Polyethylene glycol P-200	47.0	—
Polyethylene glycol P-300	46.0	—
Dipropylene glycol	34.6	33.1 at 25°C[9]

The liquids used for the estimation of γ_c were glycerol, formamide, ethylene glycol, polyethylene glycol P-200, polyethylene glycol P-300, and dipropylene glycol, the surface tensions of which were measured by a Wilhelmy plate surface tensiometer, Model ST-1 (made by Shimadzu Seisakusho Ltd., Kyoto, Japan) at 20°C and 65% relative humidity (Table II).

RESULTS AND DISCUSSION

Critical Surface Tension of Poly(n-alkyl Methacrylates)

Figure 2 shows Zisman plots (cos θ versus surface tension of test liquid) for poly(n-octyl methacrylate) (POMA), poly(stearyl methacrylate) (PSMA), and poly(n-butyl methacrylate) (PBMA). Zisman plots for the casting, quenching, and annealing samples of poly(stearyl methacrylate) (cast-PSMA, q-PSMA, and a-PSMA, respectively) are shown Figure 3.
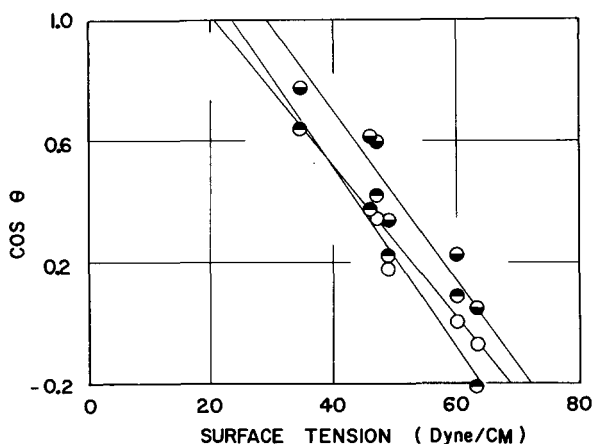

Fig. 2. Zisman plots for poly(butyl methacrylate) (PBMA), poly(octyl methacrylate) (POMA), and poly(stearyl methacrylate) (PSMA): (◓) PBMA; (◓) POMA; (○) PSMA.

The intercept of the straight line at $\cos \theta = 1$ is defined as the critical surface tension of the polymer. Tables III and IV list the monomer surface tension γ_L and the critical surface tensions γ_c of SMA, octadecane, and the polymers.

TABLE III
Surface Tensions of n-Alkyl Methacrylate at 20°C

n-Alkyl methacrylate	Surface tension, dynes/cm
Methyl methacrylate	23.2
Ethyl methacrylate	24.7
Butyl methacrylate	25.0
Hexyl methacrylate	27.7
Octyl methacrylate	25.5
Lauryl methacrylate	30.5
Stearyl methacrylate	33.2

TABLE IV
Critical Surface Tensions of SMA, Octadecane, and the Polymers at 20°C

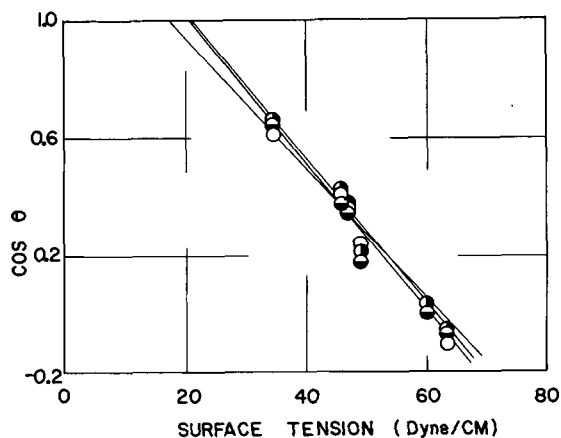|	γ_c, dyne/cm
PMMA	36.3
PEMA	31.5
PBMA	29.0
PHMA	27.5
POMA	23.5
PLMA	21.3
Cast-PSMA	17.3
Q-PSMA	20.8
A-PSMA	20.6
Stearyl methacrylate	28.0
Octadecane	21.6

Fig. 3. Zisman plots for the cast, quenched, and annealed samples of poly(stearyl methacrylate): (○) cast-PSMA; (◑) q-PSMA; (◓) a-PSMA.
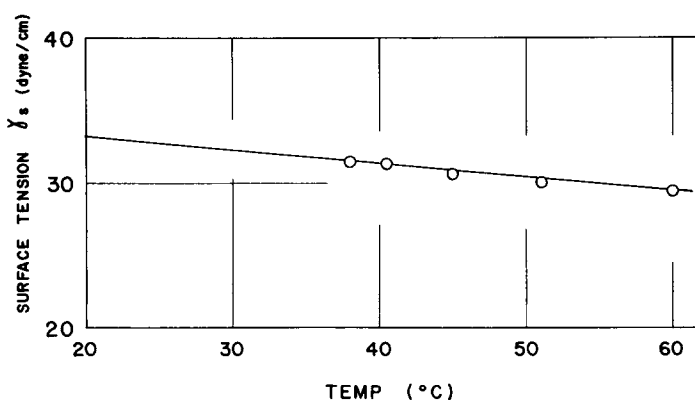
Fig. 4. Dependence of surface tension on temperature for stearyl methacrylate melts.

Recently, Hata and Kitazaki[10] reported the influence of the wetting liquids on determining the γ_c of polymers. They suggested a γ_c value determined by saturated hydrocarbon liquids for nonpolar solids. To avoid confusion, only hydrogen-bonding liquids were used as wetting liquids in this paper. Therefore, the γ_c values of PMMA ($\gamma_c = 36.3$ dynes/cm) and PEMA ($\gamma_c = 31.5$ dynes/cm) are lower than the reported values (38 and 33 dynes/cm, respectively).

The γ_L values of the monomers were measured with the Wilhelmy tensiometer. Because the melting point of SMA was observed between 28° and 29°C, the surface tension of SMA was obtained by extrapolating to 20°C the surface tension of molten SMA (shown in Fig. 4). The surface tension of molten SMA was also measured by the ST-1 tensiometer.

The surface tensions of monomers increase with increasing length of side chain, but the critical surface tension of the polymer γ_c decreases. Relations between γ_L, γ_c, and the number of carbon atoms of the alkyl groups in the side chain are shown Figure 5.

Wu[11] obtained the surface tension of PMMA and PBMA at 20°C by extrapolation of the surface tension of polymers measured at 100° to 180°C by the pendent drop method. Values of the surface tension γ_s of the solid polymer thereby obtained were 41.1 dynes/cm for PMMA and 31.2 dynes/cm for PBMA. In Figure 5, these values are indicated in parentheses. Generally, the γ_s values of SMA, PMMA, and PBMA are larger than the γ_c values.

Gardon[2] proposed the following relation between γ_s and the critical surface tension γ_c of a polymer:

$$\gamma_s = \gamma_c/\Phi^2 \qquad (1)$$

where Φ is the ratio between the reversible work of adhesion and the geometric mean of the work of cohesion to components. For low-energy solids, Gardon assumed that Φ is greater than 0.8 but less than 1. The experimental results completely satisfy Gardon's assumption, e.g., estimated Φ values were 0.92 for SMA, 0.94 for PMMA, and 0.96 for PBMA.
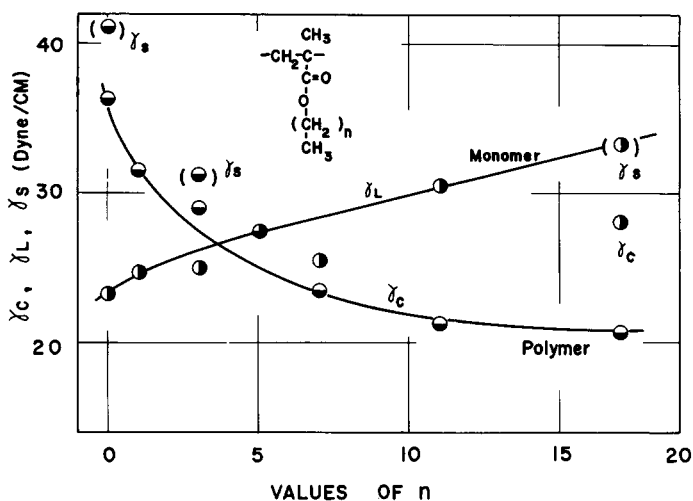
Fig. 5. Effect of branching on surface tension: (◑) surface tension of monomer (γ_L);
(◒) critical surface tension of polymer (γ_c). Parentheses represent surface tension
of PMMA and PBMA, (◒) γ_s, at 20°C by extrapolation of the surface tension of poly-
mers measured at 100° to 180°C by the pendent drop method and the surface tension
of stearyl methacrylate, (◑) γ_s, at 20°C by extrapolation of the surface tension of SMA
measured at 38° to 60°C by Wilhelmy plate method.

The surface tension of normal alkanes increases with increasing number
of carbon atoms. Similarly, the surface tension γ_L of molten n-alkyl
methacrylate increases with increasing number of methylenes in the ester
group. Conversely, the critical surface tension γ_c of poly(n-alkyl meth-
acrylates) decrease with increasing number of methylenes in the ester
group. Comparison of the quenched, annealed, and cast films of PSMA
shows a lower γ_c value in the cast film than in the quenched and annealed
samples.

The influence of chain packing on γ_c was first demonstrated by Zisman
and Fox[4] in comparison of γ_c for a monolayer of octadecylamine and a
crystal of hexatriacontane. The lower γ_c associated with the crystal (20–22
dynes/cm compared to 22–24 dynes/cm) was attributed to a tighter pack-
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group at the air/solid interface.

Pittman and Ludwig[5] reported the influence of the side chain on γ_c for
poly(fluoroalkyl acrylate) containing the alkyl group $HCF_2(CF_2)_nCH_2$—,
where n is 1, 3, 5, 7, or 9. Of this series, the acrylate polymers with $n = 7$
and 9 crystallize partially at room temperature. These polymers presum-
ably have oriented and packed alkyl side chains. Higher γ_c values would
be expected owing to poor side chain alignment and the exposure of the
polymer backbone. Comparison of the quenched and the annealed films
of acrylate polymer ($n = 7$) shows a lower γ_c value and poorer crystalline
packing of the fluoroalkyl side chain in the quenched than in the annealed
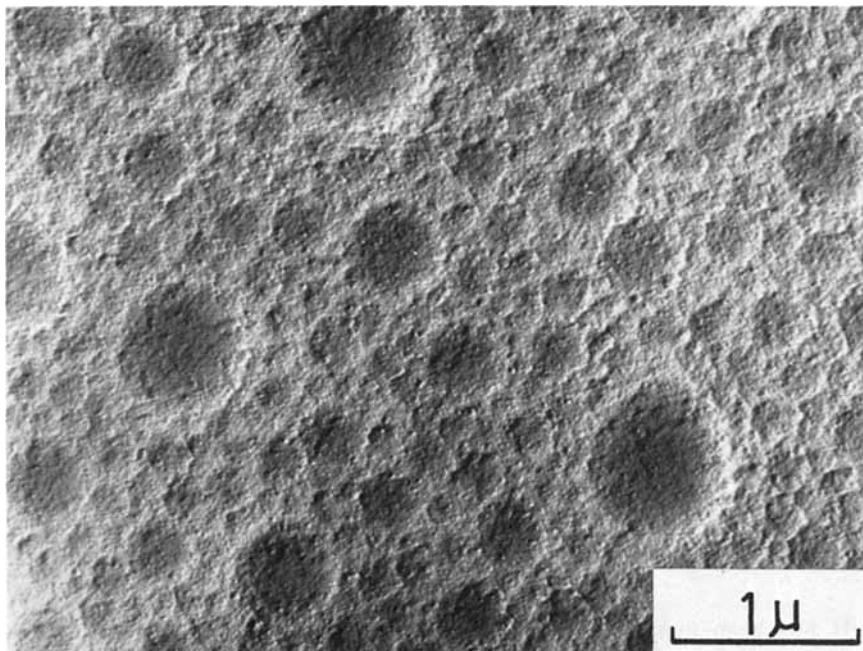film.

Fig. 6. Electron micrograph of poly(stearyl methacrylate).

PSMA is partially crystallized at room temperature, presumably by orientation and packing of alkyl side chain, although the glass transition temperature is $-100°C$.[12] The crystallization of cast film is much larger than that of the quenched or annealed film, as is evident from the DSC result, the cast film causing microroughness of the film surface.

It is believed that the lower γ_c for cast film can be attributed to the microroughness of the film surface. The electron microscope photograph for PSMA is shown in Figure 6. The spots, of diameter 200–300 Å, shown on the surface are crystalline parts of PSMA, but it is doubtful whether a spot represents a partially crystallized alkyl side chain in an electron-beam diffraction image, and a dark-field image is very difficult to obtain. As shown in Figure 5, a collection of spots forms a regular spherical structure (diameter 1000–7000 Å).

Figure 7 shows the change in the electron-beam diffraction image for PSMA. The electron beam diffraction image changes from a distinct diffraction image to a halo during the observation period. From Figure 7, it is seen that crystallized alkyl side chains of PSMA fuse quickly.

The higher γ_c values associated with quenched and annealed films were attributed to a tighter packing of the pendent —CH_3 group at the air/solid interface. The γ_c values obtained for quenched PSMA (q-PSMA), annealed PSMA (a-PSMA), octadecane, and SMA are 20.8, 20.6, 21.6, and 28 dynes/cm, respectively, and the values for q-PSMA, a-PSMA and octadecane were in good agreement with the value (20–22 dynes/cm) sug-
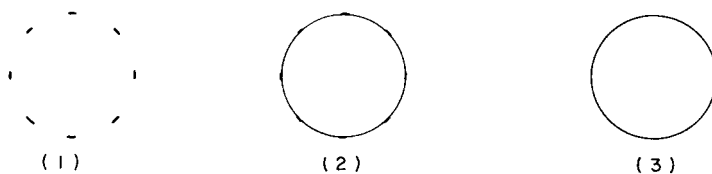
Fig. 7. Schematic representation of electron diffraction pattern of poly(stearyl methacrylate): (1) immediately, electron beam irradiation; (2) after about 2 sec; (3) after about 10 sec.

gested by Zisman and Fox in a tighter packing of the alkyl chains with a concomitant greater concentration of —CH₃ groups at the air/solid interface. The γ_c of SMA is 28 dynes/cm, and this higher value than that of PSMA may be attributed to the effect of ester groups. The γ_c of PLMA is 21.3 dynes/cm. When the number of methylene groups exceeds 11, the γ_c values of poly(n-alkyl methacrylate) is almost constant (20–22 dynes/cm).

Critical Surface Tension of Copolymers of Stearyl Methacrylate with Methacrylonitrile

It has been mentioned that the γ_c values for the poly(n-alkyl methacrylates) decrease with increasing side chain length (36.3 dynes/cm for PMMA to 20.6–20.8 dynes/cm for PSMA). For the γ_c values of copolymer and polymer blend, Lee[8] proposed the following relation between γ_c and composition of copolymer and polymer blend:

$$\gamma_c = N_1\gamma_{c_1} + N_2\gamma_{c_2} \tag{2}$$

where N_1 and N_2 are mole fraction of monomer in copolymer and blend ratio in polymer blend, respectively, and γ_{c_1} and γ_{c_2} are γ_c values of homopolymer.

The γ_c values of random copolymers of stearyl methacrylate with methacrylonitrile (MAN) containing cyano groups (CN—) with high polarity are shown in Figure 8. All samples were annealed. As shown in Figure 8, values of γ_c of copolymers hardly depend on the MAN content in copolymers and did not satisfy eq. (2) proposed by Lee. The γ_c of PMAN is 43 dynes/cm and is nearly equal to the γ_c of polyacrylonitrile ($\gamma_c = 44$ dynes/cm).[8]

As shown in Table I, the mp and ΔH_m of the Co-4 annealed sample could not be observed. Increasing the MAN content in the copolymer causes the distance between the methylene side chains to increase, and methylene side chain does not crystallize. But the air/solid interface of copolymer is occupied by —CH₃ groups and the influence of the cyano group hardly depends on the γ_c value of the copolymer.

The electron microscope photographs for the copolymers are shown in Figure 9. In comparing it with the electron microscope photograph of PSMA (Fig. 6), the spot of diameter 200–300 Å is shown in the surface, but the spherical structure of diameter 1000–7000 Å is not shown. Further, the electron-beam diffraction image for copolymers does not show an
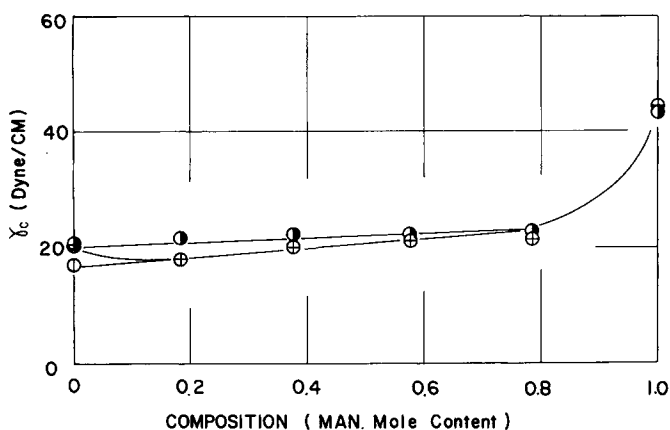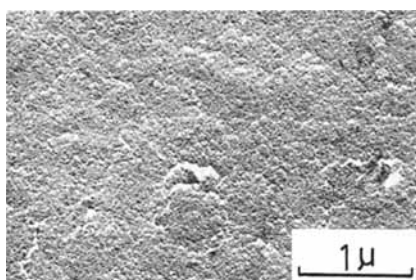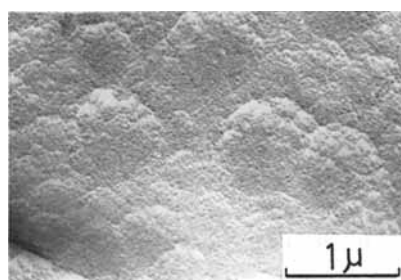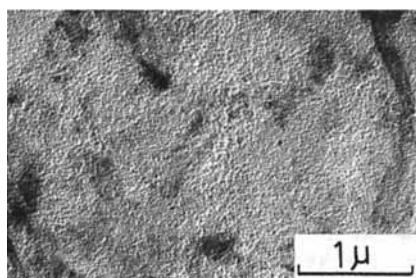
Fig. 8. Relationship between γ_c of copolymer and composition.
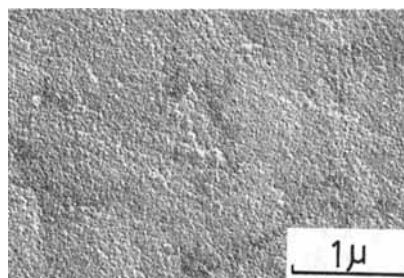

Co-1

Co-3

Co-2

Co-4

Fig. 9. Electron micrographs of copolymer.

image as in Figure 7a, but was changed from (b) to (c) by the applied electron-beam irradiation. It is believed that these phenomena are caused by restraining of crystallization of side chains owing to copolymerization with MAN.

CONCLUSIONS

The γ_c values for poly(n-alkyl methacrylates) decrease with increasing side chain length and approach the constant value for the poly(n-alkyl

methacrylate) containing a long side chain than poly(lauryl methacrylate). The constant value was 20–22 dynes/cm and was in good agreement with the value suggested by Zisman and Fox in a tighter packing of the alkyl chain with a concomitant greater concentration of $-CH_3$ groups at the air/solid interface. In the author's results, the γ_c value for octadecane was 21.6 dynes/cm at 20°C. But the γ_c value for SMA was 28 dynes/cm and was larger than 20–22 dynes/cm under the influence of ester groups. The γ_c value for PSMA cast film was 17.3 dynes/cm and was unusually small compared with annealed and quenched films. With the electron microscope it was observed that on the surface of cast PSMA spots having a diameter of 200–300 Å build up a spherical structure having a diameter of 1000–7000 Å.

The spherical structure was not observed on the surfaces of annealed and quenched PSMA. It is believed that the unusually small γ_c value for PSMA cast film has an influence on microconvex surfaces. The γ_c values of copolymers of stearyl methacrylate with methacrylonitrile did not satisfy the equation proposed by Lee. The γ_c value of the copolymer having a methacrylonitrile content of 78.2% was 22.3 dynes/cm, and its value is much smaller than the value of PMAN (γ_c = 43 dynes/cm), which is approximately equal to the values of annealed or quenched PSMA. On the basis of the experimental results, we considered that the γ_c value of the copolymer of stearyl methacrylate with methacrylonitrile was affected significantly by the long side chain of SMA.

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