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Monolayers of Copolymers of Methyl Acrylate and *n*-Butyl Acrylate and Mixed Monolayers of Thier Homopolymers

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Poly(methyl acrylate), poly(*n*-butyl acrylate), and their copolymers were prepared by radical polymerization. The monolayers of these polymers and the mixed polymers were studied at the air/water interface. The limiting areas obtained experimentally for various copolymers corresponded well to the theoretical values as calculated from the areas per methyl acrylate and butyl acrylate residues. However, those obtained for their corresponding polymer mixtures were larger than the theoretical limting areas.

Many studies of the relation in surface monolayers between several individual polymers and their mixtures have been reported. Crisp[1] established that the areas and the surface potentials of mixed monolayers of poly(vinyl acetate) and poly(vinyl alcohol) were linear averages of the individual pure monolayers. Ries and his co-workers reported their surface pressure-area measurements of mixtures of stearic acid with poly(vinyl acetate)[2] and poly(vinyl benzoate),[3] both of which acted as ideal surface mixtures. Wu and Huntsberger[4] studied the surface mixtures of polymethacrylate and poly(vinyl acetate) and indicated that most polymers are compatible in the monolayers at the air/water interface, although they are incompatible in the bulk. Isemura *et al.* studied various copolymers of vinyl acetate and vinyl stearate.[5]

However, there have been few studies of the relation of copolymers in surface monolayers and their corresponding polymer mixtures.[1] In the present work, we have investigated the relation between the monolayer properties of various copolymers of methyl acrylate and *n*-butyl acrylate and those of polymer mixtures whose monomer components are nearly the same as those of the copolymers. Then, the relation between the limiting area and the composition ratio of the copolymer and that of the corresponding polymer mixture will be dicussed.

Experimental

Sample Polymers. The methyl actylate and *n*-butyl acrylate were supplied by Toagosei Co., Ltd. The methyl acrylate was purified by reduced-pressure distillation (nitrogen atmosphere) after the removal of the inhibitor by washing it with a 5% sodium hydroxide aqueous solution and distilled water and by subsequent dehydration with silicon dioxide. The *n*-butyl acrylate was purified by reduced-pressure distillation (nitrogen atmosphere) after dehydration with silicon dioxide.

Poly(methyl acrylate), poly(*n*-butyl acrylate), and various copolymers of methyl acrylate and *n*-butyl acrylate were prepared by radical polymerization at 60°C under a nitrogen gas flow. α,α'-Azobisisobutyronitrile was used as the initiator, and benzene as the solvent. The products were purified by repeated precipitation from their acetone solutions into a large excess of methanol. The purified polymers were dried by the refrigeration method, and then the trace solvent was removed *in vacuo* at room temperature.

The average molecular weights of these polymers were

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[2] H. E. Ries, Jr. and D. C. Walker, *J. Colloid Sci.*, **16**, 361 (1961).

[3] H. E. Ries, Jr. and N. Beredjick, Proc. 4th Intern. Congr. Surface Activity, **2**, 897 (1967), Gordon and Breach Science Publishers, Inc., New York (1967).

[4] S. Wu and J. R. Huntsberger, *J. Colloid Interfac. Sci.*, **29**, 138 (1969).

[5] T. Isemura, H. Hotta, and T. Miwa, This Bulletin, **26**, 380 (1953).

determined by viscosity measurements. Their average molecular weights were about 6.59, 2.35, 2.89, 3.08, and 2.95 × 10^5 for poly(methyl acrylate), copolymer A, copolymer B, copolymer C, and poly(*n*-butyl acrylate) respectively.

The composition ratios (mol%) of the copolymers were calculated by means of the following equation:

$$\frac{mX/100+b(100-X)/100}{MX/100+B(100-X)/100}\times 100 = C(\%) \qquad (1)$$

where X is the mole percentage of methyl acrylate in the copolymers; where M and B are the apparent molecular weights of a methyl acrylate and a butyl acrylate residue respectively; where m and b are the weights of carbon in a methyl acrylate and a butyl acrylate residue respectively; and where C (%) is the percentage of carbon as obtained by elemental analysis. Table 1 lists the results of elemental analyses and the composition rarios (mol%) of the three copolymers.

TABLE 1. THE ELEMENTAL ANALYSES AND THE COMPOSITION RATIOS OF COPOLYMERS

	Elemental analysis (%)		Composition ratio (mol%)	
	Carbon	Hydrogen	Methyl acrylate	*n*-Butyl acrylate
Poly (methyl acrylate)	55.84	6.86	100	—
Copolymer A	59.60	8.00	69.7	30.3
Copolymer B	61.00	8.12	56.3	43.7
Copolymer C	63.76	8.78	24.9	75.1
Poly (*n*-butyl acrylate)	65.63	9.14	—	100

Surface-pressure Measurements. A modified Wilhelmy-type film balance[6] was used to measure the surface pressure. The balance was enclosed in the chamber to allow thermostatic control at 20.0±0.2°C. The water in the trough was kept at 20.0±0.2°C by circulating the water from the thermostat bath. The distilled water used as the substrate had a pH of 5.0—6.0 at 20.0±0.2°C. The polymer solutions (0.03 to 0.04 g polymer/100 m*l* benzene) were spread with an "Agla" microsyringe. Thirty minutes were allowed for the solvent to evaporate before compression was started. The rate of compression was 7.5 cm²/min. The surface pressure value was read after the film has first been allowed to reach equilibrium for 5 min. The surface-pressure measurements for all the polymers were repeated several times; the results were reproducible within the range of experimental error (±0.1 Å²/residue in area).

Results and Discussion

The surface pressure-area isotherms obtained for poly(methyl acrylate), poly(*n*-butyl acrylate), and various copolymers of methyl acrylate and *n*-butyl acrylate are shown in Fig. 1. The limiting areas of poly(methyl acrylate) and poly(*n*-butyl acrylate), as determined from the surface pressure-area isotherms shown in Fig. 1, were 21.6 and 29.5 Å²/residue respectively. These values correspond well to those determined by Crisp (21.5 and 29.3 Å²/residue)[7,8] and to our results.[9,10]

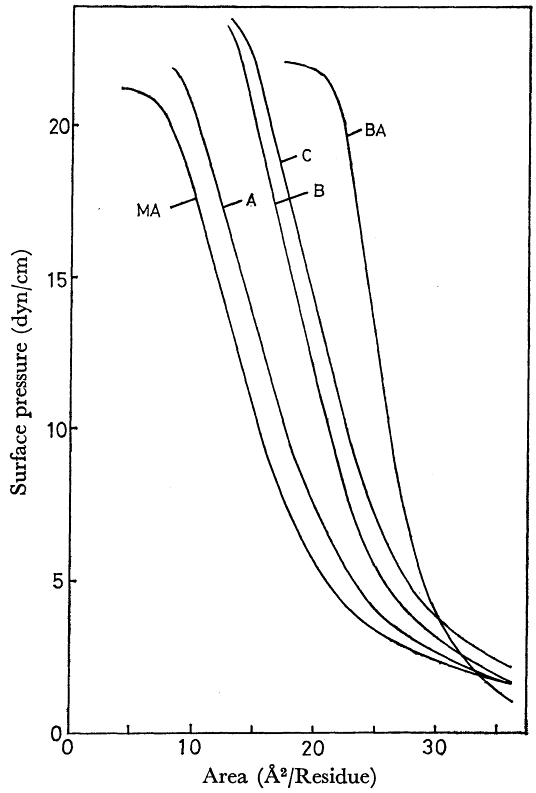

Fig. 1. The surface pressure-area isotherms of copolymers of methyl acrylate and *n*-butyl acrylate on distilled water. MA: poly (methyl acrylate), A: copolymer A, B: copolymer B, C: copolymer C, BA: poly(*n*-butyl acrylate).

With the use of the limiting areas (21.6 Å²/methyl acrylate residue and 29.5 Å²/butyl acrylate residue), the theoretical limiting area (A_t) of the copolymer, assuming the additivity rule between the limiting area and the composition ratio of each polymer component in the copolymer, was calculated by means of the following equation:

$$A_t = 21.6\frac{X}{100} + 29.5\frac{(100-X)}{100} \qquad (2)$$

where X is the mole percentage of methyl acrylate in the copolymer.

The experimental limiting areas of the copolymers and the theoretical limiting areas calculated by means of Eq. (2) *vs.* the composition ratios of methyl acrylate and *n*-butyl acrylate in the copolymers are shown in Fig. 2. It is found that the limiting areas obtained experimentally for various copolymers coincided well with the theoretical ones calculated by means of Eq. (2). The fact that the copolymers did not show such transition points in the surface pressure-area isotherms as were observed in the mixed monolayers suggests that copolymers are very slightly contaminated with traces of the homopolymer. Generally, the monolayers of copolymers do not behave as mixtures of the corresponding homopolymers would, and the introduction of a little comonomer often produces effects far out of proportion to its amount. Isemura

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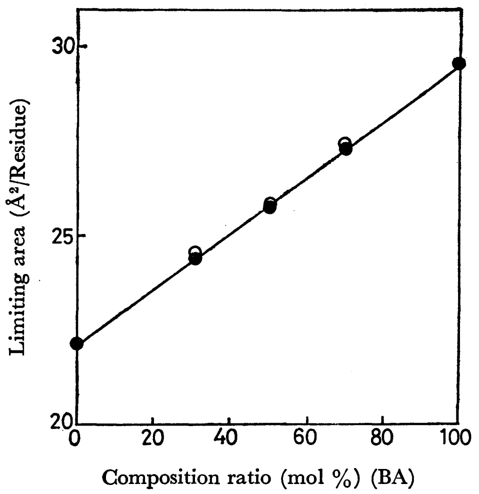

Fig. 2. The limiting areas of copolymers *vs.* their composition ratios. ○: experimental, ●: theoretical, BA: poly(*n*-butyl acrylate).

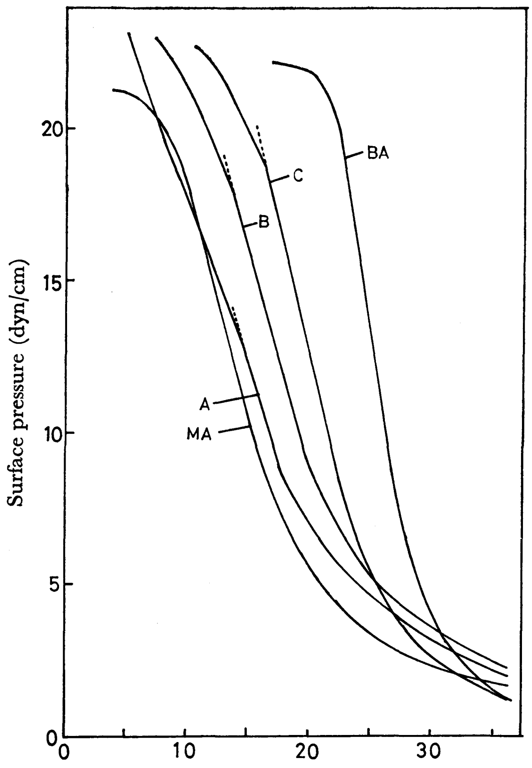

Fig. 3. The surface pressure-area isotherms of mixtures of poly(methyl acrylate) and poly(*n*-butyl acrylate) on distilled water. MA: poly(methyl acrylate), A: mixture A, B: mixture B, C: mixture C, BA: poly(*n*-butyl acrylate).

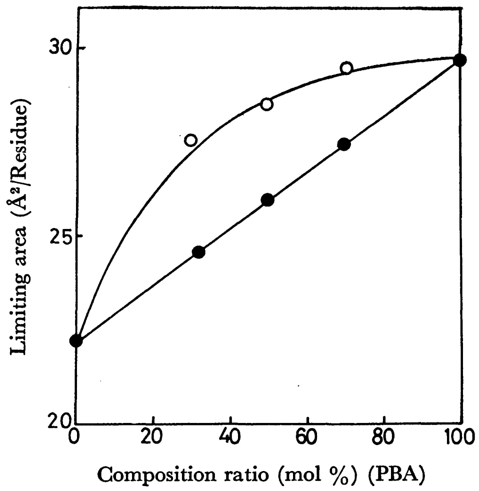

Fig. 4. The limiting areas of mixtures of poly(methyl acrylate) and poly(*n*-butyl acrylate) *vs.* the composition ratio by mixing. ○: experimental, ●: theoretical, PBA: poly(*n*-butyl acrylate).

et al. indicated this for the surface pressure-area isotherms of various copolymers of vinyl acetate and vinyl stearate.⁵⁾

Figure 3 shows the surface pressure-area isotherms for mixtures of poly(methyl acrylate) and poly(*n*-butyl acrylate). The experimental limiting areas obtained for the mixed polymers were larger than those obtained for the copolymers with the same ratios of components and the theoretical ones calculated by Eq. (2). Figure 4 shows the experimental and the theoretical limiting areas *vs.* the composition ratios of the mixed polymers. The experimental values deviated largely and positively from the theoretical limiting areas. When the deviation ratio was calculated by means of the following equation:

$$\text{Deviation ratio} = \frac{A_e - A_t}{A_t} \times 100 \qquad (3)$$

the values calculated for mixtures A, B, and C were 12.7, 10.4, and 6.9% respectively. A_e is the experimental limiting area and A_t is the theoretical limiting area, as calculated by Eq. (2). The mixture rich in poly(methyl acrylate) showed the largest positive deviation from the theoretical limiting area. These deviations can be explained by the assumption that the monolayer of poly(methyl acrylate) can expand more than that of poly(*n*-butyl acrylate).

The transition points were observed for the isotherms of each mixed polymer (in Fig. 3). The transition points obtained for mixtures A, B, and C were about 14, 18, and 19 dyn/cm respectively. These values were smaller than the collapse pressures of the individual pure monolayers (20.5 dyn/cm for poly(methyl acrylate) and 22.1 dyn/cm for poly(*n*-butyl acrylate)). The surface pressure at the transition increased with an increase in the amount of poly(*n*-butyl acrylate). Further, the reductions of area occurred after the transition point. The reduction of area after the transition point increased with the amount of poly(*n*-butyl acrylate) present in the mixed polymer. While the mixture rich in poly(*n*-butyl acrylate) had a high transition point and acted like that of poly(*n*-butyl acrylate) below the transition point, the mixture rich in poly(methyl acrylate) behaved at low surface pressures as poly(methyl acrylate) did. The behaviors of these mixed polymers may be affected by the composition. The mixture rich in poly(*n*-butyl acrylate) is mainly subject to poly(*n*-butyl acrylate) and gives the higher transition point, but it also produces the larger reduction of area because of the condensation of poly(*n*-butyl acrylate) at rela-

TABLE 2. THE COMPOSITIONS AND THE LIMITING AREAS OF THE COPOLYMERS AND THEIR CORRESPONDING MIXED POLYMERS

	Components of copolymer (mol%)		Limiting area (Å²/residue)		Deviation ratio (%)
	Methyl acrylate	*n*-Butyl acrylate	Experimental	Theoretical	
Poly(methyl acrylate)	100	—	21.6	21.5 (by Crisp)	
Copolymer A	69.7	30.3	25.0	24.4	2.5
Copolymer B	56.3	43.7	25.8	25.9	−0.4
Copolymer C	24.9	75.1	27.7	27.4	1.1
Poly(*n*-butyl acrylate)	—	100	29.5	29.3 (by Crisp)	
	Components of corresponding polymer mixture (mol%)				
	Poly(methyl acrylate)	Poly(*n*-butyl acrylate)			
Mixture A	69.9	30.1	27.5	(24.4)	12.7
Mixture B	49.4	50.6	28.6	(25.9)	10.4
Mixture C	29.4	70.6	29.3	(27.4)	6.9

tively high pressures.

Finally, the limiting areas of the copolymers were compared with those of mixed polymers in which the compositions were nearly the same as those of the corresponding copolymers. Table 2 shows the compositions and the limiting areas of the copolymers and their corresponding mixed polymers. The limiting areas of the mixed polymers deviated largely and positively from the theoretical limiting areas as calculated by Eq. (2), while those of the copolymers corresponded well to the theoretical ones. This difference suggests that poly(methyl acrylate) in the mixed polymer can expand more than the methyl acrylate component in the copolymer. The additivity holds good in copolymers, but the mixed polymers expand to give larger limiting areas than the theoretical ones.