Mixed Monolayers of Poly(methyl acrylate) and Its Saponified Polymer

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A film balance study of the mixed monolayers with various ratios of poly(methyl acrylate) and its saponified polymer or of the monolayers themselves was carried out on distilled water, and the mixed monolayers were compared with individual monolayers of the saponified polymers. These mixed monolayers expanded more than individual saponified polymers at the same degree of saponification, giving larger limiting areas. Their limiting areas deviated from the linearity between the limiting area and the degree of saponification, in contrast to the fact that the limiting areas of individual monolayers decreased linearly with an increase in the degree of saponification. This fact can be considered to be due to interactions between the side chains of the ploymers.

Recently, many studies of the mixed monolayers have been reported.[1–3] However, there have been few studies of the mixed monolayers of polymers.[4–6]

In general, when mixtures of two insoluble substances are spread on the water surface, it can be considered that they form either individual monolayers without two components' mixing or an ideal surface mixture by their complete mixing with one another. Mixtures of analogous compounds give the linear relation between the limiting area and the ratio of mixing and the existence of stoichiometric interaction, that is, the additivity of the film areas and the surface potentials. La Mer *et al.* have reported the ideal surface behavior of the mixed monolayers by studying the rate of the evaporation of water through the mixed monolayers.[1] Crisp has shown that the areas and the surface potentials of the mixed monolayers of poly(vinyl acetate) and poly(vinyl alcohol) were linear averages of the individual pure monolayers.[4] However, Labbauf has suggested that the areas obtained for the mixed monolayers of poly(ethyl acrylate) and poly(vinyl acetate) deviated largely, both positively and negatively, from the linear average values.[7]

In this investigation, we have studied the mixed monolayers of poly(methyl acrylate) and its saponified polymers, or the monolayers themselves, and discussed the two-dimensional behavior of polymers in terms of the deviation from the linearity of their limiting areas and the degrees of saponification.

Experimental

Monomer. Methyl acrylate (supplied by Toagosei Co., Ltd.) was used for radical polymerization. It was purified by distillation under reduced nitrogen atomosphere after its inhibitor had been removed by washing it with 5% sodium hydroxide aqueous solution and distilled water and after it had been dehydrated with silicon dioxide.

Polymerization. Poly(methyl acrylate) was prepared by radical polymerization, with α,α'-azobisisobutyronitrile as the initiator, in benzene at 50°C under a flow of nitrogen gas. The polymer thus obtained was purified by reprecipitation from its acetone solution into a large excess of methanol. The average molecular weight of this polymer, as determined by the measurement of the viscosity, was 659000.

Saponification. The saponifications of poly(methyl acrylate) were carried out in a homogeneous system of an acetone-water mixture (5:2 by volume), with sodium hydroxide as the catalyst, at 50°C until all the sodium hydroxide was consumed.[8] After the reaction, the saponified polymers were washed with a hydrochloric acid aqueous solution. They were purified by reprecipitation from an acetone solution into water, methanol, and ethyl ether. The saponification was confirmed by a study of the infrared spectra, while the degrees of saponification (mol%) of these polymers were determined by the elementary analyses to be 13.48, 24.16, and 48.34 mol%.

Surface-pressure Measurement. A modified Wilhelmy-type film balance was used to measure the surface pressure.[9] The film 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 water from a thermostat bath. The distilled water used as the substrate was in the range of pH 5.0—6.0. The trough was coated with highly pure, hard paraffin wax. The sensitivity of the torsion wire was about ±0.1 dyn/cm.

The monolayers were spread on the substrate from a mixed spreading solution of acetone-benzene (1:1 by volume) by means of an "Agla" microsyringe. Various organic liquids were examined as the spreading solvent, but the best was an acetone-benzene mixture (1:1 by volume).

Thirty minutes were allowed for the solvent to evaporate before compression was started. Every reading of the surface pressure was carried out after the films had been left for 5 min. after their compression. The rate of compression was 7.5 cm^2/min.

Results and Discussion

The surface pressure measurements for all the polymers were repeated at least several times; their results were reproducible within the limits of experimental er-

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ror of the ±0.1 Å^2/residue.

The surface pressure-area isotherms for poly(methyl acrylate) and its saponified polymers on distilled water are shown in Fig. 1. The limiting area obtained for poly(methyl acrylate) was 21.6 Å^2/residue which corresponded well to 21.5 Å^2/residue by Crisp.(10) This fact suggests that our sample is just the same as Crisp's. The limiting area for each saponified polymer was smaller than that of poly(methyl acrylate), and the theoretical values were calculated as follows. By using the limiting areas of 21.5 Å^2 per methyl acrylate residue and 22.0 Å^2 per acrylic acid residue reported by Crisp,(10) the theoretical value (A_t) of the saponified polymer when all the residues of the polymer were oriented on the water surface was calculated by this equation:

$$A_t = 21.5\left(1-\frac{X}{100}\right) + 22.0\frac{X}{100} \qquad (1)$$

where X is the degree of saponification (mol %).

Figure 2 shows the limiting area of the saponified polymer *vs.* the degree of saponification. The experimental and theoretical limiting areas for each saponified polymer are listed in Table 1. The limiting areas decreased linearly with an increase in the degree of saponification, but deviated from the ideal linearity of Eq. (1). It is considered that some of the hydrophilic residues of the polymer are submerged into the water phase by compressing the films,(11) and that the higher the degree of saponification, the larger the decrease in the limiting area.

Table 1. The limiting areas of poly(methyl acrylate) and its saponified polymer on distilled water

Sample	Limiting Area (Å^2/residue)	
	Experimental	Theoraretical (by Crisp)
Poly(methyl acrylate)	21.6	21.5
13.93 mol% saponified polymer	21.0	21.65
24.16 mol% saponified polymer	19.5	21.69
48.34 mol% saponified polymer	16.8	21.79

The surface pressures of the mixed monolayers of poly(methyl acrylate) and the 48.34 mol% saponified polymer (mixed monolayers of the A series) and the 13.48 mol% and 48.34 mol% saponified polymers (mixed monolayers of the B series), mixed in various ratios, were measured under the same conditions as were used the individual monolayers. The surface pressure-area isotherms obtained for the mixed monolayer of the B series are shown in Fig. 3. The mixed monolayers expanded much more than the individual monolayers and gave larger limiting areas. Furthermore, these limiting areas were larger than those of the individual monolayers at almost the same degree of saponification. The mixed monolayers of the A series showed the same inclinations.

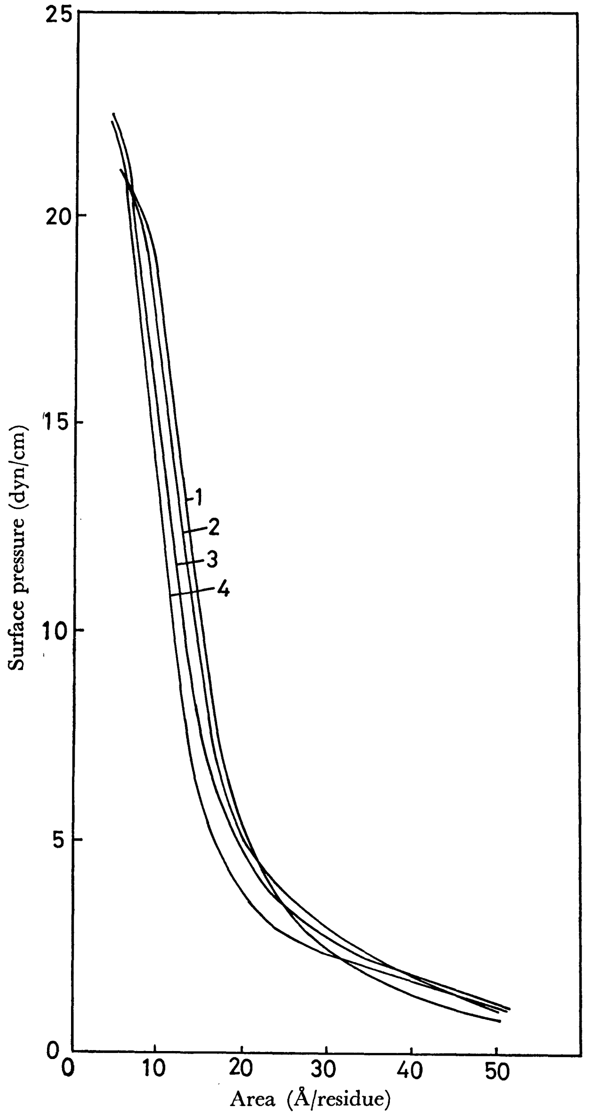

Fig. 1. The surface pressure-area isotherms of poly (methyl acrylate) and its saponified polymer on distilled water.
1- poly(methyl acrylate); 2- 13.93 mol% saponified polymer; 3- 24.16 mol% saponified polymer; 4- 48.34 mol% saponified polymer.

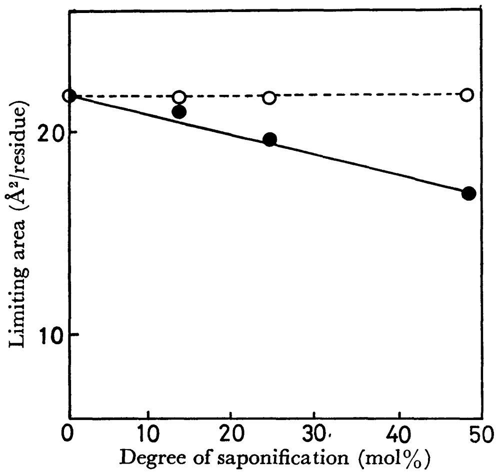

Fig. 2. The limiting areas of the saponified polymer *vs.* the the degree of saponification. ○: theoretical; ●: experimental; ◑: poly(methyl acrylate).

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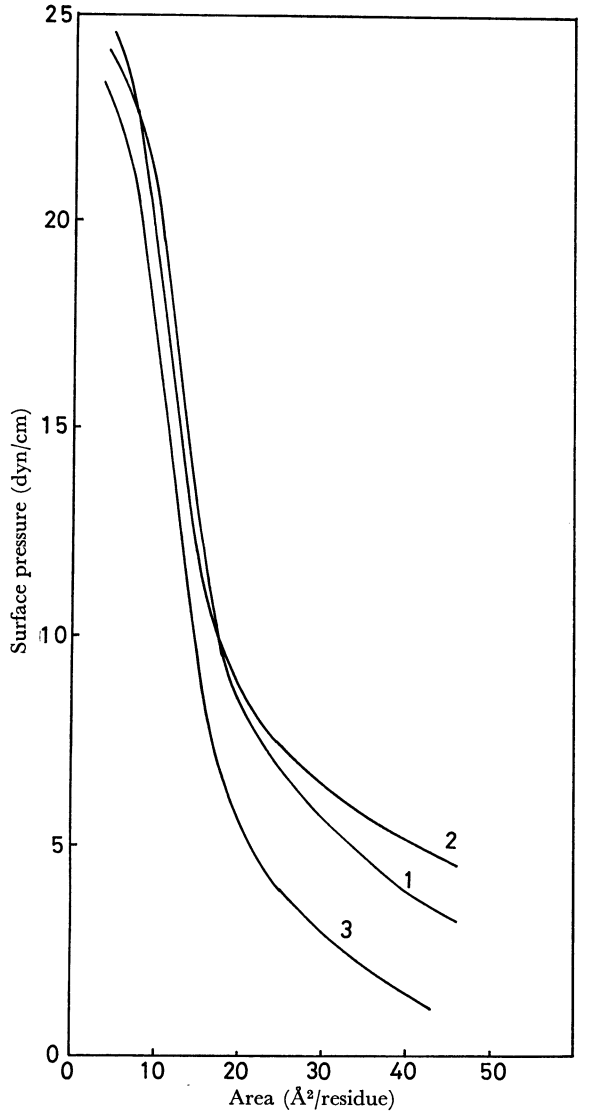

Fig. 3. The surface pressure-area isotherms of mixtures of 13.93 mol% saponified polymer and 48.34 mol% saponified polymer. 1- 19.95 mol% mixed polymer; 2- 29.97 mol% mixed polymer; 3- 39.95 mol% mixed polymer.

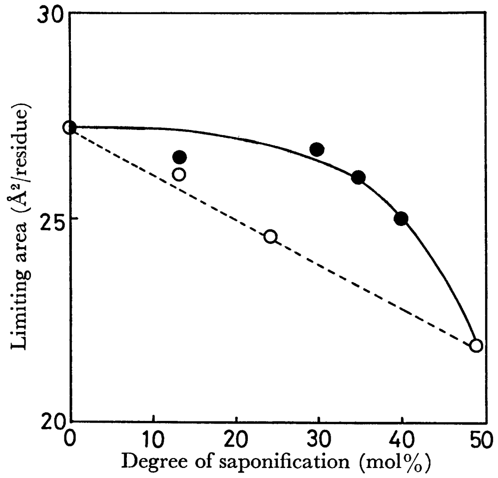

Fig. 4. The limiting areas of mixtures of poly(methyl acrylate) and 48.34 mol% saponified polymer *vs.* the degree of saponification by mixing. ○: pure saponified polymer; ●: mixed polymer; ◑: poly(methyl acrylate).

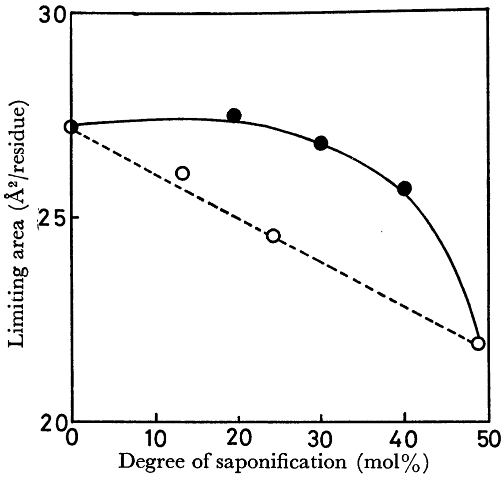

Fig. 5. The limiting areas of mixtures of 13.93 mol% saponified polymer and 48.34 mol% saponified polymer *vs.* the degree of saponification by mixing. ○: pure saponified polymer; ●: mixed polymer; ◑: poly(methyl acrylate).

The behavior of the ideal surface mixtures is generally exhibited by mixtures of close members of a homologous series.[1,4,12)] The plots of the limiting areas of the mixed monolayers *vs.* the degrees of saponification by mixing are given in Figs. 4 and 5. If these mixed monolayers form the ideal surface solution, the plots should have the ideal mixing linearity, that is, the linearity between the limiting areas and the degrees of saponification obtained for the individual monolayers. However, the results of A and B series deviated largely and positively from the ideal mixing linearity and behaved like the nonideal surface solutions. This fact suggests that the behavior and orientations of the mixed monolayers are different from those of the individual monolayers. The individual monolayers have such orientations as some of their hydrophilic groups are submerged into the bulk, while one or two of them are hung with such hydrophobic anchors as methyl acrylate residues and so remain on the water surface. Therefore, they have limiting areas smaller than the theoretical values. On the other hand, with regard to the mixed monolayers, it is considered that the two component polymers have interactions between each other's sidechains, though they consist of binary mixtures of homologous polymers, and that the interactions exceed the decrease in the areas because of the submergence of some of the hydrophilic groups. Furthermore, it is conceivable that the dissociation of the hydrophilic groups facilitates this interaction between sidechains. As evidence for these suggestions, the mixed monolayers were more expanded and unstable than the individual monolayers at all surface pressures. Specially, at low surface pressures, the mixed monolayers were much more expanded than the individual monolayers. This suggests that the molecules of polymers have larger spaces for their free movements because of the interactions.

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Conclusion

Although the individual monolayers gave smaller limiting areas than the theoretical values because some of hydrophilic groups are submerged into the bulk, they exhibited a linearity between the limiting area and the degree of saponification. The mixed monolayers did not show the behavior of the ideal surface mixtures in spite of their consisting of close members of a homologous series, and their limiting areas deviated largely and positively from the ideal linearity upon mixing. These unexpected results suggest an interaction between sidechains of two component polymers which exceeds the decrease in the areas as a result of the submergence of some of the hydrophilic groups.