

Monolayers of Poly(methyl acrylate) Saponified Partially in Homogeneous and Heterogeneous Systems

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Poly(methyl acrylate) prepared by radical polymerization of methyl acrylate was saponified partially in acetone-water mixtures (5 : 2 and 100 : 1 by volume), using sodium hydroxide as the catalyst. Saponification in an acetone-water mixture of a 5 : 2 ratio by volume proceeded in a homogeneous state, but the reaction solution of a 100 : 1 ratio by volume was in a white-turbid state, in which saponification proceeded in a heterogeneous state. The properties of the monolayers of polymers saponified in different states were studied at the air/water interface by measuring the surface pressure. The limiting areas obtained on distilled water for each polymer saponified in these two systems decreased linearly with an increase in the degree of saponification. However, the monolayers of polymer saponified in a homogeneous system were more stable on sodium chloride solution than those obtained in a heterogeneous system, and gave the limiting areas on solutions above 5% corresponding with the theoretical values calculated from the areas per methyl acrylate and acrylic acid residue and the degree of saponification. This can be explained by the fact that some of the hydrophilic parts of the saponified polymers submerged into the water phase were squeezed out onto the water surface by the salting out effect. On the other hand, those values obtained in a heterogeneous system neither corresponded to the theoretical values nor gave reproducible areas at high concentrations. These facts may be due to the differences in the states of the saponified polymers.

There have been many studies of the hydrolysis of polymers. In particular, a few studies concerned with the hydrolysis of polyacrylate have been reported. Loecker and Smets reported the hydrolysis of copolymers of methacrylic acid and methyl methacrylate in acid-buffered solution.¹⁾ Sakurada *et al.* studied the saponification of poly(methyl acrylate) in binary mixtures of various compositions of water-acetone and reported the effects of solvent on the rate of saponification.²⁾

However, studies of the hydrolysis of polymers from the two-dimensional point of view have been scarce. Previously, we ourselves investigated the monolayer properties of partially-saponified poly *n*-butyl acrylate at the air/water interface.³⁾ The relationship between the surface properties and the degree of saponification was discussed.

In the present work, we partially saponified poly(methyl acrylate) with sodium hydroxide in mixtures of different compositions of water-acetone (in homogeneous and heterogeneous systems) and studied the properties of the monolayers of those polymers. The saponification reactions of polymer in homogeneous and heterogeneous systems will be discussed on the basis of the two-dimensional behavior of the polymer when the polymer was spread on water and sodium chloride solutions.

Experimental

Sample Polymers. Methyl acrylate was obtained from Toagosei Co., Ltd. The inhibitor was removed by washing it with 5% sodium hydroxide aqueous solution and distilled

water. Methyl acrylate was then purified by distillation under reduced nitrogen atmosphere after having been dehydrated with silicon dioxide. Poly(methyl acrylate) was prepared by radical polymerization in benzene at 50°C under a flow of nitrogen gas, α, α' -azobisisobutyronitrile being used as the inhibitor. After the reaction, this benzene solution was added to a large excess of methanol and the polymer was obtained as precipitate. The polymer thus obtained was purified by repeated precipitation from its acetone solution into a large excess of methanol. The average molecular weight of this polymer was found to be about 659000 by the measurement of the viscosity.

Poly(methyl acrylate) was saponified in a transparent and homogeneous solution of an acetone-water mixture (5 : 2 by volume), with sodium hydroxide as the catalyst, at 50°C until sodium hydroxide was consumed.³⁾ Saponification in a heterogeneous system was carried out under the same conditions except that the mixture had a different composition of acetone-water (100 : 1 by volume) and except that the reaction solution was a white-turbid suspension of polymer. These saponified polymers for each system were obtained by changing the amount of sodium hydroxide. These polymers were purified by repeated precipitation from their acetone solution into water and methanol. Saponification was confirmed by studying the infrared spectra and by elementary analyses. The degrees of saponification (mol%) of these polymers were calculated by putting the analytical values of carbon as determined by the elementary analyses into Eq. (1), they are listed in Table 1.

$$\frac{c \left(\frac{100-X}{100} \right) + d \frac{X}{100}}{a \left(\frac{100-X}{100} \right) + b \frac{X}{100}} \times 100 = C (\%) \quad (1)$$

where X is the degree of saponification; a and b are the apparent molecular weights of a methyl acrylate and of an acrylic acid residue respectively; c and d are the weights of carbon in a methyl acrylate and an acrylic acid residue respectively; C (%) is the analytical value of carbon.

Surface-pressure Measurements. The surface pressure-area isotherms were obtained with a modified Wilhelmy-type film balance. The film balance was enclosed in the

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1) W. De Loecker and G. Smets, *J. Polym. Sci.*, **40**, 203 (1959).

2) I. Sakurada, Y. Sakaguchi, and S. Fukui, *Kobunshi Kagaku*, **13**, 355 (1956).

3) S. Hironaka and K. Meguro, *J. Colloid Interfac. Sci.*, **35**, (3), 367 (1971).

TABLE 1. ELEMENTARY ANALYSES OF HYDROGEN AND CARBON AND THE DEGREE OF SAPONIFICATION OF THE SAPONIFIED POLYMERS

Sample	Elementary analysis (%)		Degree of saponification (mol%)
	Hydrogen	Carbon	
Poly(methyl acrylate) theoretical	7.03	55.80	—
Poly(methyl acrylate) experimental	6.86	55.84	—
Homogeneous system			
Saponified polymer	7.20	55.12	13.93
Saponified polymer	6.91	54.59	24.16
Saponified polymer	7.08	53.26	48.34
Heterogeneous system			
Saponified polymer	6.84	55.30	10.38
Saponified polymer	6.88	54.84	18.89
Saponified polymer	6.87	54.24	30.90

chamber adjusted to $20 \pm 0.2^\circ\text{C}$. The distilled water used as the substrate showed a pH of 5.0–6.0. The water in the trough was kept at $20.0 \pm 0.2^\circ\text{C}$ by circulating the water from the thermostat bath. Sample polymers were spread on the distilled water and sodium chloride solutions with an "Agl" microsyringe. A mixture of acetone-benzene (1:1 by volume) was used as the spreading solvent. Thirty minutes were allowed for the solvent to evaporate before compression was started. The rate of compression was $7.5 \text{ cm}^2/\text{min}$.

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

Results and Discussion

The surface pressure-area isotherms on distilled water for poly(methyl acrylate) and polymers saponified in homogeneous and heterogeneous systems are shown in Figs. 1 and 2. The limiting areas obtained for all the saponified polymers of both systems were smaller than that of poly(methyl acrylate) (Figs. 1 and 2); their theoretical values were calculated as follows.

With the use of the limiting areas of 21.5 \AA per methyl acrylate residue and 22.0 \AA per acrylic acid residue reported by Crisp,^{4,5} the theoretical area (A_t) of the saponified polymer, when all the residues of the polymer were oriented on the water surface, without the hydrophilic parts submerged into the water, was calculated by the following equation:

$$A_t = 21.5 \left(1 - \frac{X}{100}\right) + 22.0 \frac{X}{100} \quad (2)$$

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

If the limiting area of the saponified polymer is the sum of the areas of the hydrophilic and hydrophobic parts (acrylic acid and methyl acrylate residues), the measured areas should correspond to the theoretical values calculated by Eq. (2). However, the limiting areas obtained from Figs. 1 and 2 were smaller than the theoretical values and decreased linearly with an increase in the degree of saponification (Fig. 3). The observed decreases in the limiting areas suggest the

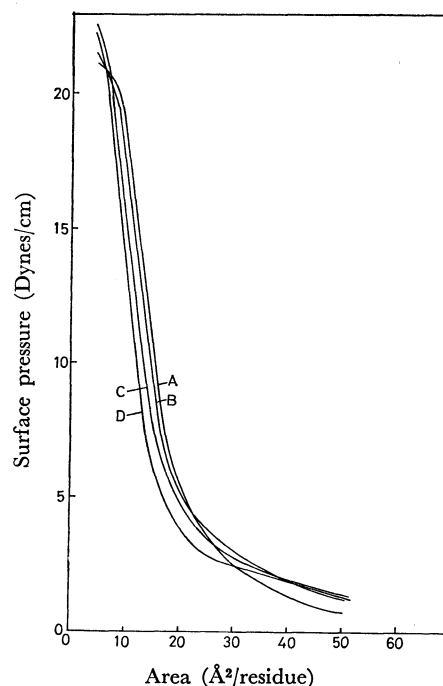


Fig. 1. The surface pressure-area isotherms on distilled water for poly(methyl acrylate) and its saponified polymers in homogeneous system. A-poly(methyl acrylate); B-13.93 mol% saponified polymer; C-24.16 mol% saponified polymer; D-48.34 mol% saponified polymer.

possibility of some of their hydrophilic parts submerging into the water phase in the compressed state of the films.

Previously, we investigated the monolayer properties of partially saponified poly *n*-butyl acrylate⁹ and discussed them. Saponified polymer monolayers on sodium chloride solution expanded more than those on water. Their limiting areas increased as the salt concentration was increased. The limiting areas obtained on salt solutions above a certain concentration corresponded well to the theoretical values as calculated from the areas per butyl acrylate and per acrylic acid residue. One explanation of this is that the submerged hydrophilic residues of the saponified polymers were forced out of the water phase onto its

4) D. J. Crisp, *J. Colloid Sci.*, **1**, 49 (1946).

5) D. J. Crisp, *ibid.*, **1**, 161 (1946).

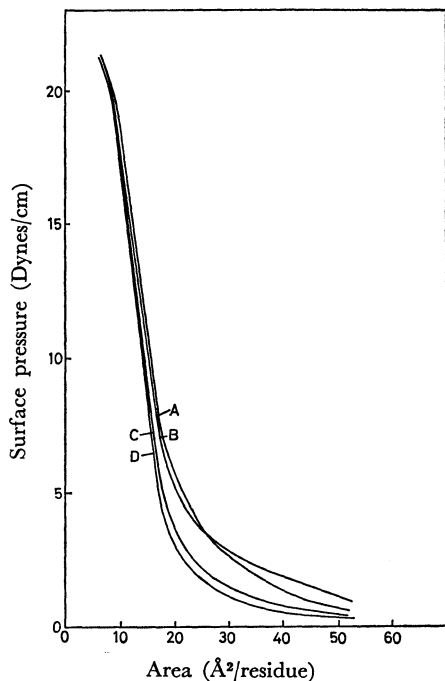


Fig. 2. The surface pressure-area isotherms on distilled water for poly(methyl acrylate) and its saponified polymers in heterogeneous system. A-poly(methyl acrylate); B-10.38 mol% saponified polymer; C-18.89 mol% saponified polymer; D-30.90 mol% saponified polymer.

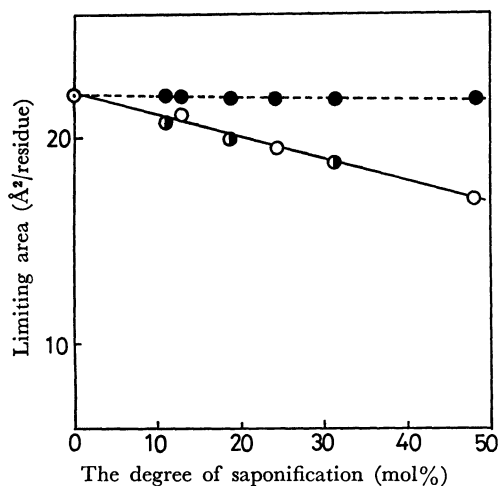


Fig. 3. Plots of the limiting areas of the saponified polymers against the degree of saponification. ○-saponified polymers in homogeneous system; ●-saponified polymers in heterogeneous system; ◐-poly(methyl acrylate); ●-theoretical values.

surface *via* the salting out effect.

Figure 4 shows the effect of the salt concentration on the surface pressure-area isotherms for the 48.34 mole% saponified polymer obtained in a homogeneous system. Figure 5 shows the plots of the limiting areas obtained for each saponified polymer *vs.* the concentration of sodium chloride. These curves approached nearly horizontal straight lines on salt solutions above 5%. The extrapolated values of these portions to a zero concentration of sodium chloride were in good agreement with the theoretical values within the limits of experimental error, as Table 2 shows. The agree-

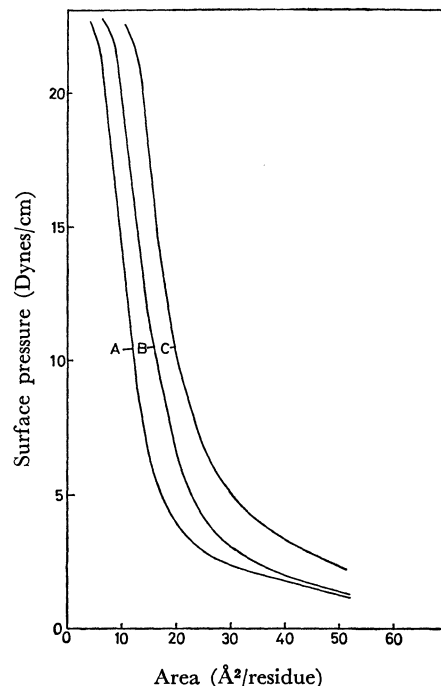


Fig. 4. The surface pressure-area isotherms of 48.34 mol% saponified polymer in homogeneous system on distilled water-(A); 2%-(B); and 5-10% sodium chloride solution-(C).

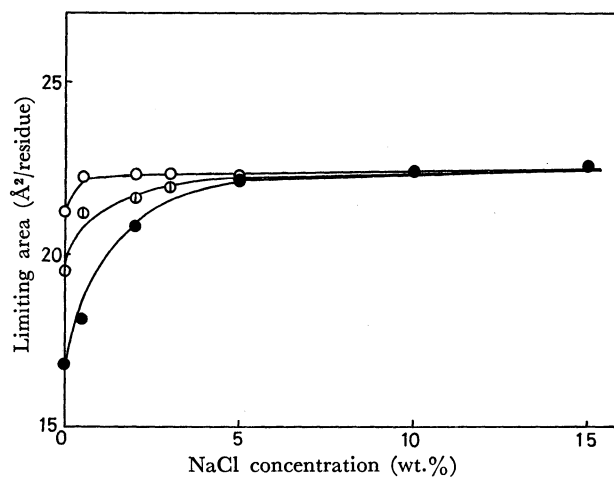


Fig. 5. Plots of the limiting areas of the saponified polymers in homogeneous system against concentration of sodium chloride in the bulk. ○-13.93 mol% saponified polymer; ◐-24.16 mol% saponified polymer; ●-48.34 mol% saponified polymer.

ment suggests that the monolayers of the saponified polymers spread completely on salt solutions above about 5%.

Also, the ratios of the portion submerging into the water phase and the portion remaining on it were estimated from the theoretical and observed values of the limiting areas in Fig. 3.³⁾ These ratios showed a good linearity against the degree of saponification. In the present work, this linearity was confirmed to hold (in Fig. 6). It can be suggested that the saponification of poly(methyl acrylate) in a homogeneous system proceeds evenly.

On the other hand, the monolayers of polymers

TABLE 2. THE LIMITING AREAS OF POLY(METHYL ACRYLATE) AND ITS SAPONIFIED POLYMERS

Experimental: the values extrapolated to zero concentration of sodium chloride (from Figs. 1 and 2).

Theoretical: the values calculated by Eq. (2).

Sample	Limiting area ($\text{\AA}^2/\text{residue}$)	
	Experimental	Theoretical
Poly(methyl acrylate)	21.6	21.5 (by Crisp)
Homogeneous system		
13.93 mol% saponified polymer	21.8	21.6
24.16 mol% saponified polymer	21.8	21.6
48.34 mol% saponified polymer	21.9	21.7
Heterogeneous system		
10.38 mol% saponified polymer	22.8	21.6
18.89 mol% saponified polymer	21.9	21.7
30.90 mol% saponified polymer	20.3	21.7

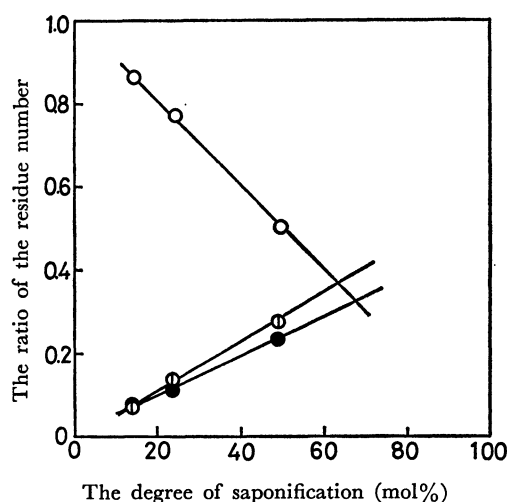


Fig. 6. Plots of the ratio of each residue number against the degree of saponification. The methyl acrylate residue—○, the acrylic acid residue in water—●, the acrylic acid residue on water—⊙.

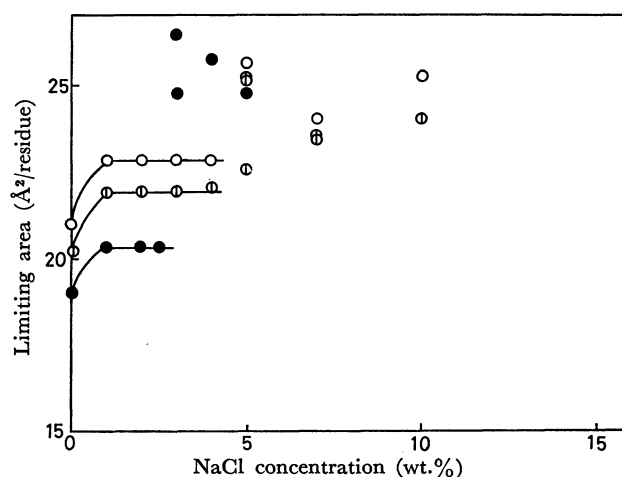


Fig. 7. Plots of the limiting area of the saponified polymers in heterogeneous system against concentration of sodium chloride in the bulk. ○—10.38 mol% saponified polymer; ⊙—18.89 mol% saponified polymer; ●—30.90 mol% saponified polymer.

saponified in a heterogeneous system were confirmed to be unstable on salt solution as compared with those in a homogeneous system. Furthermore, the films of these substances had a tendency to show similar linear plots only in the range of low concentrations, as is shown in Fig. 7, and the extrapolated values did not agree with the theoretical ones. In the range of higher concentrations above 2.5–4%, the films were less stable than those at low concentrations and were not reproducible, giving much larger limiting areas than the theoretical ones.

The monolayers of polymers saponified under different conditions showed the different two-dimensional behaviors. This may be due to the difference in the saponified states of the polymers. Probably, saponification in a homogeneous solution of the polymer proceeded evenly.

On the other hand, the results obtained for polymers saponified in a heterogeneous system suggest that the states of saponification of the polymers are not steady. Perhaps polymers may be either those saponified in block or mixtures of saponified and unsaponified polymers. If they are mixtures, their monolayers should

give the behaviors of the mixed monolayers. Their monolayers, however, did not give the same surface pressure-area isotherms as the mixed monolayers. Therefore, saponification presumably proceeds in block and the saponified polymers consist of both those saponified in block and those not saponified at all.

The unstability and the further expansion of the monolayers of the saponified polymers on salt solutions above 2.5–4% suggest that the parts saponified in block were salted out strongly, exposing many neighboring carboxylates at the water surface. This resulted in an expansion of the monolayer, which was favored by the repulsion between $-\text{COO}^-$ ions formed by their dissociation.

The effect of the pH on the monolayers was further examined by adding hydrochloric acid and sodium hydroxide into the water phase, but the films of polymers obtained in both the homogeneous and heterogeneous systems were hardly affected below pH 6, while they expanded a little in the pH range of 8–9.

In conclusion, on distilled water the monolayers of polymers saponified under different conditions showed the same tendency for the limiting areas to decrease

linearly with the increase in the degree of saponification (Fig. 3); the results obtained on salt solutions suggested the difference in the saponified states of polymers detectable by the differences in the stabilities and the reproducibilities of the limiting areas. Further, the submergence theory held good only for polymers saponified in a homogeneous system. A linear relation was obtained by assuming the submergence theory, by assuming, that is, that some of the hydrophilic groups of the saponified polymers submerge into the water phase and are squeezed out of

it by the salting out effect. This fact suggests that, while some of the hydrophilic groups are easily submerged into the water phase by compressing the films, one or two hydrophilic groups of both sides of the saponified portions are next to hydrophobic anchors, such as methyl acrylate residues, and remain on the water surface.

On the basis of the above discussion, it may be suggested that studies of the monolayers are of use in connection with the saponification reaction of polymers.
