Monolayer Properties of Mixtures of Poly(octadecyl methacrylate) and Poly(butyl methacrylate) and Their Corresponding Copolymers†

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The monolayer properties of mixtures of poly(octadecyl methacrylate) and poly(butyl methacrylate) have been compared with those of their corresponding copolymers of octadecyl methacrylate and butyl methacrylate, using the measurements of their surface pressure-area isotherms at the air/water interface at 20 °C. The results showed that the isotherms of the mixed monolayers had three break points, and the surface pressures of the lower two break points agreed with those of poly(butyl methacrylate). This suggests that at lower surface pressures, the mixtures of the two homopolymers are compatible in a bidimensional state when each phase contains a small amount of the other homopolymer, and otherwise these are incompatible, while at higher surface pressures, up to 70 segment mol% of poly(octadecyl methacrylate) they are incompatible and above 80%, they are compatible. The copolymers showed characteristic isotherms different from those of the mixtures. The properties of the copolymers in the bidimensional state are affected by variations in the vitrified, liquid, or crystalline states with an increase in the mean lengths of the side chains in the three-dimensional state.

Monolayer studies of polymer mixtures or of copolymers of two kinds of monomers have been reported by many authors.[1-10] Kargin *et al.*[1] investigated the monolayer properties of the copolymers of methyl acrylate and hexadecyl acrylate in order to study the influence of the side chain at the air/water interface. Isemura *et al.*[2] showed that surface pressure-area isotherms of the copolymer monolayers of vinyl acetate and vinyl stearate above 50% of vinyl stearate content were almost consistent with the isotherm of poly(vinyl stearate), due to the strong cohesive interaction of octadecyl groups.

However, there have been few studies[3] about the difference of monolayer properties between copolymerized substances from two kinds of monomers, one of which has very long side chains and the other short ones, and mixtures of the corresponding two pure homopolymers.

In this paper, we have studied the monolayer properties of the mixtures of poly(octadecyl methacrylate) and poly(butyl methacrylate) (abbreviated as POMA and PBMA, respectively) and those of the copolymers of octadecyl methacrylate and butyl methacrylate (abbreviated as OMA and BMA, respectively) by surface pressure measurements. Further, the compatibility of the mixtures and the transition of the copolymers at a bidimensional state will also be discussed.

Experimental

Materials. OMA and BMA were supplied by Kyoei Oil Chemical Co., Ltd. These monomers were purified by reduced pressure distillation (nitrogen atmosphere). POMA, PBMA, and the various corresponding copolymers (abbreviated as COP OB-*n* for copolymer; *n*=segment mol % of OMA) 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 benzene 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 determined by viscosity measurements. Their average molecular weights were about 3.85 and 1.22×10^5 (g/mol) for POMA and PBMA, respectively. The composition ratios of the copolymers calculated from the results of the elemental analyses are listed in Table 1 with those of the mixtures (abbreviated as MIX OB-*m* for mixture; *m*=segment mol % of OMA).

Measurements. A modified Wilhelmy-type film balance was used to measure the surface pressure. The apparatus was enclosed in a chamber to allow thermostatic control at 20.0±0.5 °C. The water in the though was kept at 20.0±0.5 °C by circulating the water from the thermostat bath. The trough and the glass barriers were carefully coated with parafin wax. The distilled water used as the substrate had a pH of 5.0—6.0 at 20 °C. The monolayers of two homopolymers and corresponding copolymers were spread on the distilled water from their benzene solutions

TABLE 1. THE COMPOSITION RATIOS OF COPOLYMERS AND MIXTURES

Copolymer	Composition ratio/(segment mol %)	
	OMA	BMA
PBMA	—	100.0
COP OB-20	20.3	79.7
COP OB-45	45.3	54.7
COP OB-63	63.2	36.8
COP OB-82	82.0	18.0
POMA	100.0	—
Mixture	POMA	PBMA
MIX OB-10	10.0	90.0
MIX OB-20	20.0	80.0
MIX OB-30	30.0	70.0
MIX OB-40	40.0	60.0
MIX OB-50	50.0	50.0
MIX OB-60	60.0	40.0
MIX OB-70	70.0	30.0
MIX OB-80	80.0	20.0
MIX OB-90	90.0	10.0

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(0.07 g polymer/100 ml) with an Alfa micro syringe. Thirty minutes were allowed for the solvent to evaporate before the start of film compression. The initial spreading area was 1100 (cm^2)/0.035 (mg). The rate of compression was 20.0 (cm^2/min). The measurement of the surface pressure was done at more than 5 min after the stop of every short compression so that the equilibrium was attained. The results were reproducible within the range of experimental errors.

Results and Discussion

1. Surface Pressure-area Isotherms of Pure and Mixed Polymer Monolayers. The surface pressure-area isotherms obtained for the monolayers of POMA, PBMA, and nine pairs of their mixtures with various ratios from 10 to 90 segment mol % of OMA on the water at 20 °C are shown in Fig. 1. The isotherm for POMA exhibited a collapse at high surface pressure of 52.6 (dyn/cm). On the other hand, the isotherm for PBMA exhibited two break points, corresponding to a transition and a complete collapse, at 14.3 and 16.7 (dyn/cm), respectively. POMA and PBMA monolayers gave the limiting areas of 24.8 and 32.8 (Å^2/residue), respectively, and formed a solid-condensed film and a liquid-condensed one, respectively. The monolayer properties characteristic of pure POMA and PBMA obtained here were in rather fair agreement with those obtained by Nakahara *et al.*11,12) and Wu and Huntsberger,4) respectively. The isotherms for the mixtures of two homopolymers, shown in Fig. 1, showed shapes similar to those of both POMA and PBMA, and exhibited three break points corresponding to transition or collapse at pressures of about 14, 17, and 44—52 (dyn/cm). For convenience, the three break points are denoted here as (A), (B), and (C) in the order of increasing pressures. Break points (A) and (B) were almost consistent with those for PBMA corresponding to the transition and the collapse at 14.3 and 16.7 (dyn/cm), respectively. On the other hand, break point (C) was located between the collapse pressures of the POMA and the PBMA isotherms. Three break points (A), (B), and (C) of the isotherms for the mixtures can be found clearly at each constant surface pressure up to 70 segment mol % of OMA, as shown in Fig. 2.

On the other hand, the isotherms for the MIX OB-80 and -90 did not show break points (A) and (B) but exhibited only one break point (C) corresponding to the collapse at higher surface pressures, as shown in Fig. 2; the values for their break point (C) increased along the ideal dotted line with an increase in the composition ratios of OMA. Crisp5) has reported as a bidimensional phase rule that if two components are compatible in the monolayer, the surface pressure of the break point is dependent on the composition, and otherwise it is independent of the composition. It may be supported by this rule that, at higher surface pressures, the mixtures of POMA and PBMA are nearly incompatible up to 70 segment mol % of OMA, while they are compatible above 80% in the bidimensional state, as shown in Fig. 2. Such a phenomenon for the incompatible mixtures has also been reported by Gabrielli6) and Wu and Huntsberger.4)

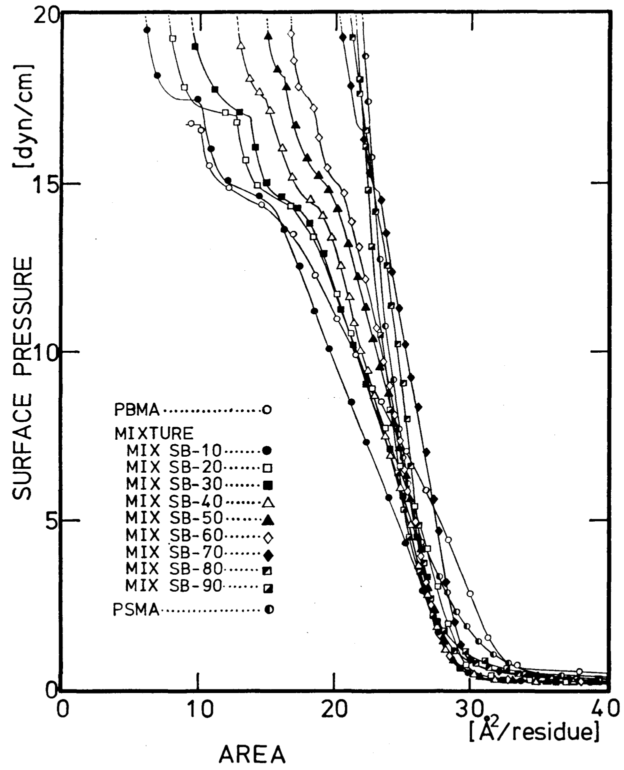

Fig. 1. Surface pressure-area isotherms of PSMA, PBMA, and their mixtures on distilled water at 20 °C.

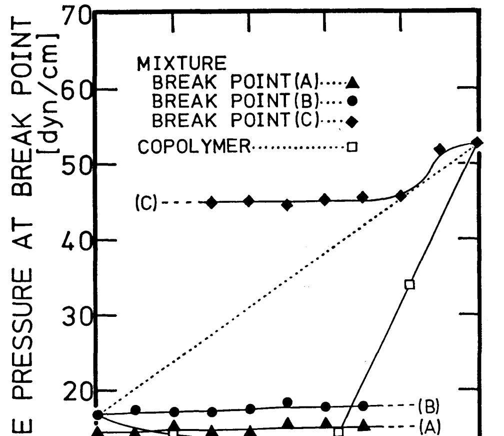

Fig. 2. Surface pressures at break points of copolymers (□) and mixtures (▲, ●, ◆) as a function of composition ratio.

In order to find the precise properties of the mixed monolayers in lower surface pressures, their limiting areas are plotted against the segment molar ratios of POMA in Fig. 3. The limiting areas for the mixtures containing a very small amount of POMA in PBMA exhibited intermediate values between those of POMA and PBMA, and then decreased

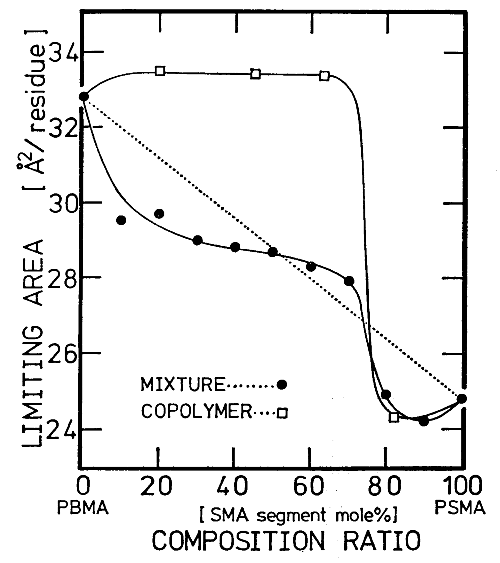

Fig. 3. Limiting areas of copolymers (□) and mixtures (●) as a function of composition ratio.

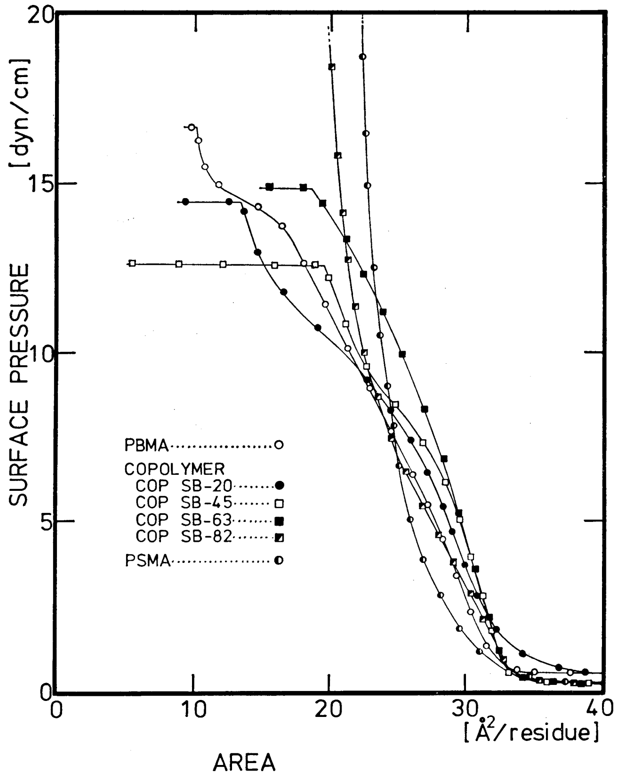

Fig. 4. Surface pressure-area isotherms of PSMA, PBMA, and copolymers of SMA and BMA on distilled water at 20 °C.

slightly with an increase in composition ratios of POMA up to 70 segment mol %. On the other hand, above 80%, their values were almost the same as that of POMA. These results imply that the mixtures containing small amounts of POMA are compatible in a bidimensional state at lower surface pressures, and become gradually incompatible with an increase in composition ratios of POMA up to 70 segment mol %, even at lower surface pressures, as shown in Fig. 3. These findings suggest that the mixed monolayers are gradually separated into one POMA rich film and another PBMA rich one with an increase in surface pressure, and near the collapse pressure of PBMA (break point (B)) the PBMA rich films are squeezed out from the incompatible monolayers, and then the other POMA rich films collapse completely at break point (C).

On the other hand, above 80%, the mixtures are considered to form more stable and compatible films due to the intermolecular cohesive forces of the large amount of octadecyl groups in POMA, at both lower and higher surface pressures, as shown in Figs. 2 and 3.

2. Surface Pressure-area Isotherms of Copolymer Monolayers. The surface pressure-area isotherms for four copolymers with various composition ratios of OMA and BMA on the water at 20 °C are shown in Fig. 4, together with those of POMA and PBMA for comparison. Their isotherms of the copolymers had only one break point, corresponding to the break point (B) or (C) for the mixtures, as shown in Fig. 2, and showed very different shapes from those of binary mixtures of homopolymers. With increasing OMA content of the copolymers the surface pressures corresponding to the break point decreased and then the long plateaus appeared at the break point. Subsequently, above 50 segment mol % of OMA the surface pressures corresponding to the break point increased again rapidly and the plateau disappeared gradually.

Each isotherm of COP OB-20, -45, and -63 formed liquid condensed films, while that of COP OB-82 formed a solid one similar to that of POMA. On the other hand, at the three-dimensional state, PBMA exhibited a vitrified state, and COP OB-20, -45, and -63 exhibited liquid states, while COP OB-82 and POMA exhibited solid cristalline ones at 20 °C. These results suggest that the properties in the bidimensional state are affected by those in the three-dimensional state.

The changes of the monolayer properties of copolymers from liquid condensed to solid states can be seen clearly from the curve in Fig. 2. These results imply that the transition from liquid condensed films to solid ones occurs at about 70 segment mol % of OMA. This transition is also recognized in Fig. 3. Up to 70% of OMA, their limiting areas gave approximately the same values as that of PBMA (32.8 Å²/residue), but above 80% of OMA, COP OB-82 gave the same limiting area as that of POMA (24.8 Å²/residue). From these results, the monolayer of COP OB-82 is considered to form a strongly condensed film, due to the intermolecular and intramolecular cohesive forces among a number of octadecyl groups in the same molecules, and also to have properties similar to the mixture monolayer having the same composition ratio.

Nakahara *et al.*[12] have reported that the poly(*n*-alkyl methacrylate) series form many kinds of films at 20 °C, depending on their side chain lengths, such as liquid ones for poly(nonyl, dodecyl, and tetradecyl methacrylate), a solid one for POMA, and an intermediate one between liquid and solid state for poly(hexadecyl methacrylate). As COP OB-20, -45, -63, and -82 have the mean lengths of the side chains corresponding to 6.8, 10.3, 12.8, and 15.5 carbon numbers, respectively, their isotherms suggest the changes of the monolayer properties from liquid condensed to solid state due to the difference of the mean lengths of their side chains.

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