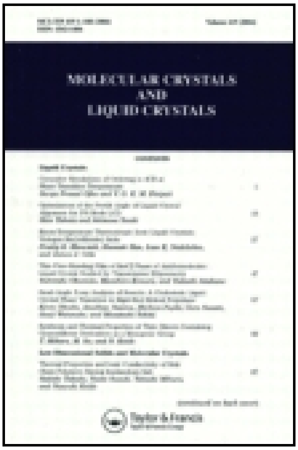

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Intermolecular Interaction between Polymer Monolayers and Poly(ethylene glycol) Monostearates at Air/Water Interface

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Intermolecular Interaction between Polymer Monolayers and Poly(ethylene glycol) Monostearates at Air/Water Interface

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Intermolecular interaction between PEG monostearate with two ethylene glycol units (N=2) and several polymer monolayers at air/water interface was investigated. For polymer monolayers, poly(methyl methacrylate) (PMMA) and poly(isopropenyl acetate) (PIPA) were spread on the distilled water. It was observed that the positive or negative deviation behavior between the mean surface area and the composition of the mixed monolayers in the condensed state is in good agreement with the miscibility behavior of the blends of the component polymers in the bulk state.

Keywords poly(ethylene glycol) (PEG) monostearate; polymer monolayer; air/water interface

INTRODUCTION

Monolayers of polymer mixtures at the air/water interface have been attracting much interest to study molecular interactions between polymers [1-5]. Particularly, the surface pressure-area (π -A) isotherms of the monolayers strongly depend on the hydrophilic-hydrophobic balance, the chemical structures, orientation and packing of the molecules [6].

In this study, we investigated intermolecular interaction between poly(ethylene glycol) (PEG) monostearate and several polymer monolayers such as poly(methyl methacrylate) (PMMA) and poly(isopropenyl acetate) (PIPA) at air/water interface. The miscibility of polymer mixture at the air/water interface was investigated in terms of the deviation from the additivity rule in the plot of the mean surface area vs. the composition of the mixture.

EXPERIMENTAL

Materials

Poly(methyl methacrylate) (PMMA) (Mw=120,000; isotac. 2.2, Syndio. 57.2%) was purchased from Aldrich Co. PEG monostearate with two ethylene glycol units (N=2) were obtained from Tokyo Kasei Kogyo Co. Ltd. Poly(isopropenyl acetate) (PIPA) was prepared by polymerizing in toluene using 2-azobisisobutyronitrile at 65℃ for 72 hr and precipitating in hexane. The synthesized polymer was identified by FT-IR and ^{1}H-NMR spectroscopy.

Measurements of Surface Pressure-Area Isotherms

Monolayers were spread from the benzene solutions onto distilled water as a subphase. A LAUDA film balance was used for measuring surface pressure (π) as a function of molecular area (A) at 25±0.1℃ through a compression rate of 0.6 cm^2/sec.

RESULTS AND DISCUSSION

Figure 1 shows typical π -A isotherms for the mixed monolayers of PMMA or PIPA with PEG monostearate (N=2) at different compositions, spread on the distilled water. PMMA was formed to be relatively condensed and compressible monolayers. The obtained π -A isotherm of PMMA is similar to that reported by other works [7-9], and the molecular area at 15 mN/m is about 14 Å^2/repeating unit. The collapse pressure and the corresponding area are 50 mN/m and 11 Å^2/repeating unit, respectively. The PIPA monolayer shows plateau regions around a surface pressure of 23 mN/m. The width of the plateau regions in terms of molecular areas ranges from 18 to 8 Å^2/repeating unit. The mixtures show condensed state at higher surface pressure such as 30 mN/m even though an expanded state at 10 mN/m.

A relation between the mean areas (A) at a given surface pressure and the molar ratios of component 1 (x_1) and component 2 (x_2) in the mixture ($x_1 + x_2 = 1$) is expressed by equation (1) if the two components are ideally miscible or completely immiscible [10].

$$A = x_1A_1 + x_2A_2 \tag{1}$$

where A_1 and A_2 correspond to the molecular areas of the components 1 and 2, respectively. This relation can be applied to the mixed polymer films by using the values of A, A_1, and A_2 as an area per unit mass of the repeating unit instead of a molecular area.

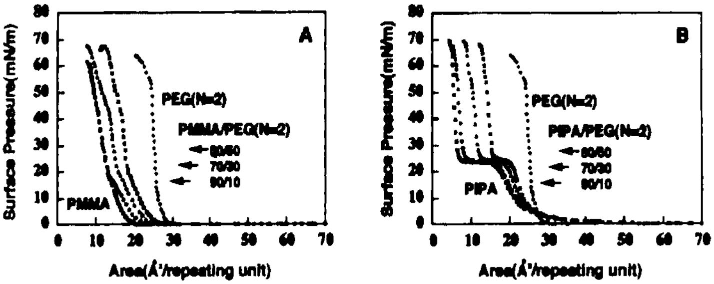

FIGURE 1 π -A isotherms for mixtures of PMMA/PEG monostearate (N=2) (A) and PIPA/PEG monostearate (N=2) (B) on the distilled water. The numbers in the figures indicate the mole fraction of mixture.

Figure 2 shows the mean surface areas in the mixed monolayers of PMMA or PIPA with PEG monostearate(N=2) at two different surface pressures, i.e. 10 and 30 mN/m, against the composition for the mixture. The plots of the mean area versus the mole fraction of PMMA show negative deviation behaviors at 30 mN/m, whereas those give an ideal additivity behavior at 10 mN/m. From the negative deviation behaviors, it can be seen that the intermolecular interaction of PEG and PMMA is larger than that between PEG and PIPA, which coincides with the miscibility behaviors in the bulk state.

It was assumed that there exists interfacial interaction between hydrophilic parts of the polymers and PEG molecules in the expanded state on the aqueous subphase. It was concluded that the criterion on the miscibility is valid only in the condensed state of the mixed monolayers, since the conformation of polymers is changeable at the expanded state in the mixed monolayers on the aqueous subphase.

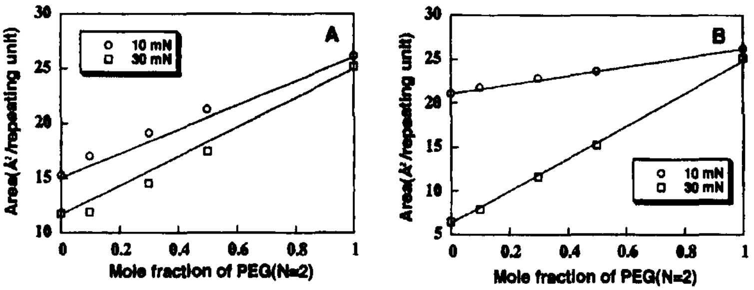

FIGURE 2 Mean surface areas in the mixtures of PMMA/PEG monostearate(N=2)(A) and PIPA/PEG monostearate(N=2)(B) at the air/water interface. Comparisions were made at two different surface pressures: 10 and 30 mN/m.

Acknowledgement

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