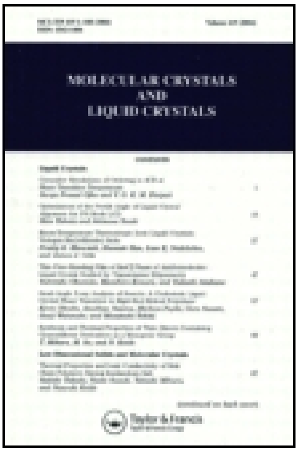

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Miscibility of Poly(methyl methacrylate)-/Poly(vinyl acetate) Blend in 2-Dimensional State at the Air/Water Interface

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Miscibility of Poly(methyl methacrylate)–/ Poly(vinyl acetate) Blend in 2-Dimensional State at the Air/Water Interface

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The miscibility in binary polymer systems in 2-dimensional state at the air/water interface was investigated by the relationship between the mean molecular area at a constant surface pressure and the mole fraction of one component in the binary mixtures of poly(methyl methacrylate)(PMMA) and poly(vinyl acetate)(PVAc). Compatibilization of the immiscible PMMA/PVAc blend at the air/water interface was achieved by introducing carboxyl acid to either of the two component polymers.

Keywords: miscibility; polymer blends; air/water interface; poly(methyl methacrylate)(PMMA); poly(vinyl acetate)(PVAc)

INTRODUCTION

Investigation of polymer monomolecular films spread at the air/water interface leads to the interest of miscibility as well as static and dynamic properties in the two-dimensional system. It is not easy, however, to choose a good pair to compare the miscibility in the bulk state with that in the film spread at the air/water interface, since most polymers do not form stable monolayers at the air/water interface[1].

In the present work, from measurements of the surface pressure-area isotherms for the binary mixed monolayers of polymers spread at the air/water interface according to the Kawaguchi and Nishida[2], we report on the miscibility of the polymers having very similar molecular structures at the air/water interface to get the information concerning the general reasons for miscibility in the two-dimensional state. The polymers used in this study are PMMA and PVAc. We also synthesized hydrolyzed PMMA, methyl methacrylate (MMA)/oleic acid(OA) and vinyl acetate(VAc)/acrylic acid(AA) copolymers to clarify the effects of the introduction of carboxylic groups to the homopolymers on the miscibility at the air/water interface.

EXPERIMENTAL

Poly(methyl methacrylate)(PMMA, Mw.=120,000) and poly(vinyl acetate)(PVAc, Mw=78,800) were purchased from Aldrich Co. and Junsei chemical Co., respectively. Hydrolyzed PMMA(H9-PMMA) with 9 mol % of carbonyl group, poly(methyl methacrylate-co-oleic acid)(poly(MMA-co-OA)), and poly(vinyl acetate-co-acrylic acid) (poly(VAc-co-AA)) were synthesized in this work. The ^{1}H-NMR spectroscopy confirmed that the content of oleic acid and acrylic acid is 6 and 8 mol %, resprectively, in the copolymers. Surface pressure-area(π -A) isotherms were recorded by using a LAUDA film balance. The temperature of the aqueous subphase was controlled at 25 ± 0.1℃ by circulating water with a constant temperature. The compression rate was 0.6 cm^2/sec.

RESULTS AND DISCUSSION

Figure 1 shows the π -A isotherms of PMMA and PVAc monolayers at the air/water interface spread from two different spreading solvents, benzene and a mixture of 35/75(v./v/) dimethyl formamide(DMF) and chloroloform. The shapes of the surface pressure-area isotherms for the two different spreading solvents are comparable but the shift of the isotherm for the monolayer spread from DMF/chloroform mixed solvent should be noted, indicating the film loss due to the dissolving surface-active materials with DMF and chloroform into the aqueous subphase[4]. For this reason, benzene was used as a spreading solvent for the homopolymer monolayers unless otherwise specified. Fairly reproducible π -A isotherms were obtained for the homopolymers when benzene was used as a spreading solvent. Similarly, N,N-dimethylacetoamide (DMAA)/benzene(5/5 by v/v) was used as a spreading solvent for the blends of polymers containing the carboxylic group. Thus, the choice of a spreading solvent is very important. The isotherms were reproduced three times in order to rule out impurities and potential insufficient weighing accuracy.

It may be suggested that the criterion of the negative deviation behavior on the plot of mean area against mole fraction of one component in polymer mixtures is valid only in the condensed state or, at least, in the transition state near the condensed state, in which stable films can be obtained until the surface pressure reach at the collapse pressure at the air/water interface.

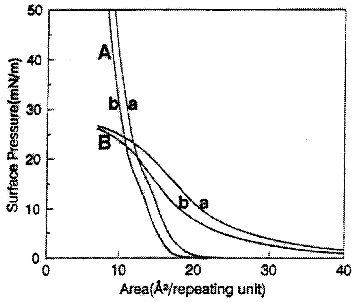
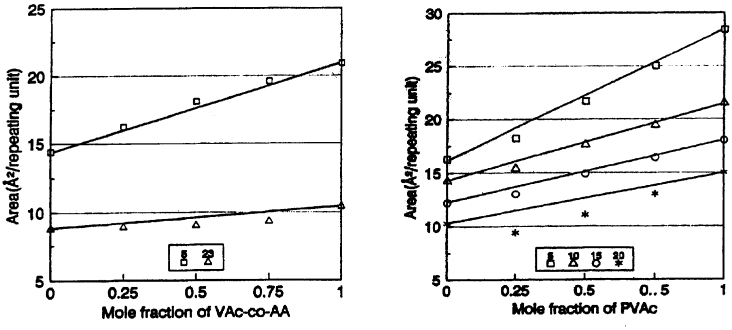


Figure 1. π -A isotherms of PMMA(A) and PVAc (B). (Spreading solvent: benzene (a), DMF/chloroform, 35/75 by vol. (b))

Even though PMMA and PVAc shows phase separation in the bulk state [3], the poly(VAc-co-AA) shows miscibility in the bulk state with PMMA through the specific interaction of the carboxylic acid, AA and carbonyl group in PMMA. The use of specific interaction also leads to the miscibility of the two components at the air/water interface. The copolymer as well as PVAc showed the surface pressure at a larger surface area than H9-PMMA films and exhibited the expanded film behavior. At 23 mN/m of surface pressure, the plot of mean area vs. mole fraction gives a negative deviation behavior, as shown in Figure 2. The result again means that the H9-PMMA is miscible with poly(VAc-co-AA) due to the molecular interactions between the two components by the introduction of the functional group such as carboxylic group. Here, the plot of surface area versus mole fraction at lower surface pressure, i.e. 5 mN/m, shows just immiscible mixture behavior. Figure 2 also shows the plot of mean areas at four different surface pressures versus mole fraction of poly(MMA-co-OA) in the mixture with PVAc. The negative deviation behavior at the larger surface pressure is larger than that for the smaller one. The negative deviation means that the intermolecular interaction between OA in poly(MMA-co-OA) and PVAc is attractive and that the mixture of the copolymer and PVAc at the air/water interface is miscible. In this figure, one can see also that the negative deviation behavior is not clearly seen at low surface pressure, in other words,when the mixture monolayers are in an expanded state.



(a) (b)

Figure 2. (a) Mean surface areas vs. mole fraction of poly(VAc-co-AA) in the H9-PMMA/poly(VAc-co-AA) mixtures and (b) Mean surface areas vs. mole fraction of PVAc in the mixture of poly(MMA-co-OA)/PVAc mixtures. The numbers in the figures indicate the surface pressure (mN/m).

Acknowledgment

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