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Intermolecular Interaction in Mixed Monolayers of *isotactic* and *syndiotactic* Poly(Methyl Methacrylate) at the Air-Water Interface

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Attention has recently been focussed on stereochemical interaction between *isotactic* and *syndiotactic* poly(methyl methacrylate)(PMMA). Various experimental methods have been utilized to clarify the nature of interaction. Beredjick *et al.*,[1,2] were the first not only to show that the film balance technique can differentiate two stereoisomers of PMMA but also that the pressure-area isotherm of 1 : 1 mixture of *synd*- and *iso*- PMMA was closer to that of stereoblock PMMA, thereby indicating strong cohesion between two isomers at the air-water interface. Watanabe *et al.*,[3] found that the mixing of dilute dimethylformamide solutions of two isomers resulted in instantaneous gelation. Liquori *et al.*,[4] reported that stereocomplex is formed between two isomers from their dimethylformamide solution, and the stoichiometry of the complex was 2/1 for the ratio of *synd*/*iso*. They proposed a structure of the complex in which extended *synd*-PMMA molecules are fitted between the grooves of 5_2 helix of *iso*-PMMA. Subsequent studies[5,6] also concluded the 2/1 complex formation. However, Chiang *et al.*,[7] concluded that the stoichio-

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[1] N. Beredjick, R. A. Ahlbeck, T. K. Kwei and H. E. Ries, Jr., *J. Polym. Sci.*, **46**, 268 (1960).

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[4] A. M. Liquori, G. Anzuino, V. M. Corio, M. D'Alagni, P. DeSantis and M. Savino, *Nature*, **206**, 358 (1965).

[5] H. Z. Liu and Kang-Jen Liu, *Macromolecules*, **1**, 157 (1968).

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[7] R. Chiang, J. J. Burke, J. O. Threlkeld and T. A. Orofino, *J. Phys. Chem.*, **70**, 3591 (1966).

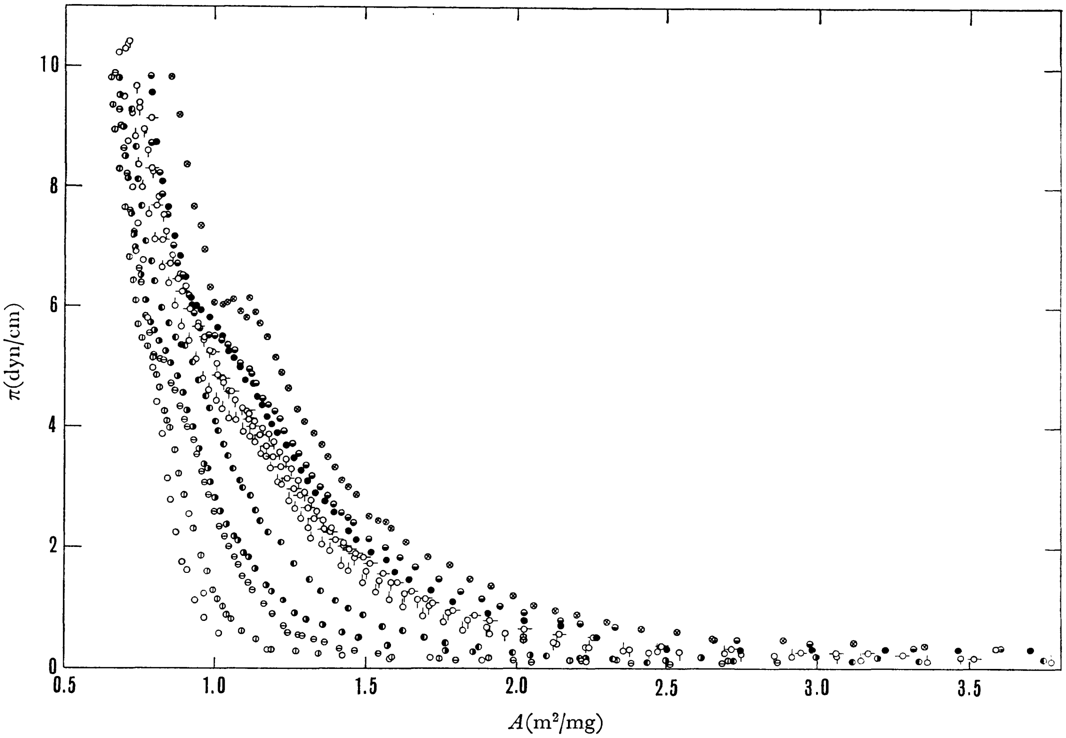

Fig. 1. Pressure-area isotherms for mixtures of *isotactic* and *syndiotactic* poly (methyl methacrylate) at the air-water interface at 25°C.
The ratio of *synd*/*iso*: ⊗ 0/1; ◒ 0.104/0.896; ● 0.178/0.822; -○-0.286/0.714; ♀ 0.418/0.582; ♂ 0.468/0.532; ◐ 0.571/0.429; ◑ 0.717/0.289; ⊖ 0.783/0.217; ⦶ 0.915/0.085; ○ 1/0

metric ratio of *synd*/*iso* in the comlex formation was not as critical as reported by Liquori. Recently, Dayantis *et al.*,[8] determined an equilibrium curve of the concentration of the complex for each composition of *iso*- and *synd*-PMMA mixture in dimethylformamide-benzene solution. The curve has the maximum at the ratio 2/1 of *synd*/*iso*.

The measurement of the free energy of complex formation has not yet been reported, since its determination in bulk is cumbersome. In order to investigate the nature of interaction, we have carried out the measurements of pressure-area isotherms of mixtures of two stereoisomers of PMMA as a function of the ratio of *synd*/*iso*, and determined the molar excess free energy of mixing of monolayers of two stereoisomers at the air-water interface.

Experimental

Materials. The *isotactic* form was prepared by anionic polymerization, and purified by precipitation from a benzene solution into *n*-hexane and by freeze-drying from benzene. The *syndiotactic* form was synthesized by γ-irradiated polymerization at -70°C. Purification and drying were carried out in the same way as in the case of *isotactic* form. Viscosity average molecular weights were 1×10^6 for the *iso*-PMMA and 1×10^5 for the *synd*-PMMA, respectively. Tacticities were determined according to the NMR method of Bovey and Tiers.[9] The tacticity of *iso*-PMMA was *iso*=83.3%, *hetero*=8.2% and *synd*=10.5%; that of *synd*-PMMA was *iso*=0%, *hetero*=13.8% and *synd*=86.2%.

Film Balance. Teflon trough (20 cm × 120 cm) was used and surface pressures were measured at 25°C by a film balance similar in design to that of Inokuchi.[10] The spreading solvent was three times distilled benzene, and the substrate was three times distilled water. Benzene solutions of specified mixtures of two isomers were spread from an Agla microsyringe.

Results and Discussion

Pressure-area isotherms for specified mixtures are shown in Fig. 1. In the low pressure region, reproducibility was excellent. The isotherms obtained for both *iso*-PMMA and *synd*-PMMA are quite similar to that reported by Beredjick *et al.*,[1,2] the *iso*-PMMA is more expanded, while the *synd*-PMMA is clearly condensed. The isotherm of *iso*-PMMA has distinct segments, and has a transition point at 6 dyn/cm; the extra-

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[10] K. Inokuchi, This Bulletin, **26**, 471 (1953).

polated area is 18 and 15.5 Å^2/monomer unit, respectively. The transition point at 6 dyn/cm could be attributed to conformational transformation involving 5_2 helices from extended form.[1] The monolayer of *synd*-PMMA is more tightly packed than that of *iso*-PMMA. The extrapolated area is 14 Å^2/monomer unit.

Below surface pressure, $\pi=6$ dyn/cm, the isotherms for all mixtures fall in the region limited by that of two isomers, however, above $\pi=6$ dyn/cm, the isotherms shift to lower area with the increase of the composition of *synd*-PMMA. In particular, when the ratio of *synd*/*iso* exceeds 2/1, the isotherms lie on the left hand side as compared to that of *synd*-PMMA alone.

The molar excess free energy of mixing, $\Delta G^{\pi}_{xs,m}$, of two pure monolayers to forms as mixed monolayer at constant temperature and surface pressure was derived by Goodrich[11] and Gaines[12] and is given by

$$\Delta G^{\pi}_{xs,m} = \Delta G^{\pi}_{m} - \Delta G^{0}_{m} = \int_{0}^{\pi}(A_m - N_iA_i - N_sA_s)\mathrm{d}\pi \quad (1)$$

where ΔG^{π}_{m} is the molar free enrgy of mixing at surface pressure π, and ΔG^{0}_{m} is that at zero sufrace pressure. A_m is the molecular area measured in the mixed monolayer, N_i and N_s are the segment mol fractions of the *iso*- and *synd*-PMMA and A_i and A_s are the segment molar areas in the *iso*- and *synd*-PMMA monolayers at the same sufrace pressure. In evaluating the integral, we neglected the surface pressure of the polymer monoleyer in equilibrium with its surface vapor. If the mixed monolaryer behaves ideally, $\Delta G^{\pi}_{xs,m}$ vanishes so that the area of the mixed monolayer is the average of two isomer monolayers, thus

$$A_m = A_iN_i + A_sN_s \quad (2)$$

If A_m shows negative deviation from the average value, $\Delta G^{\pi}_{xs,m}$ will become negative. This indicates attractive interaction and compatibility. However, it is important to note that the linear additivity of areas holds also in the case of incompatibility.

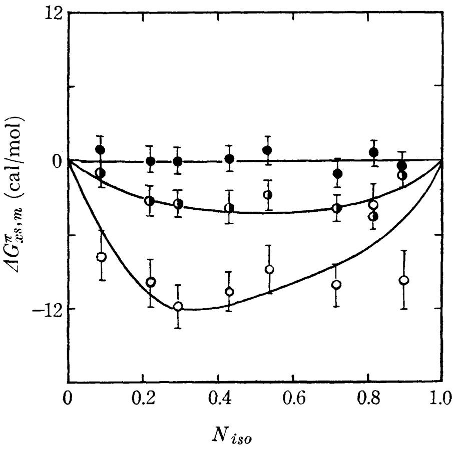

Fig. 2. Excess free energy of mixing of mixed monolayers of *iso*- and *synd*-PMMA at the surface pressures, ● 3; ◐ 6; ○ 10 dyn/cm (25°C).

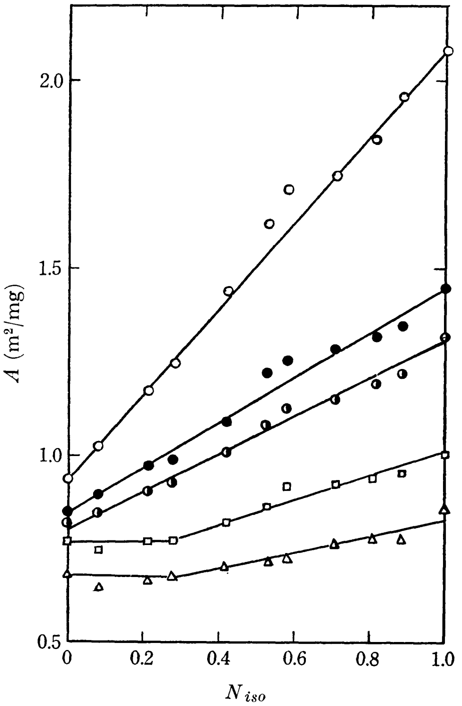

Fig. 3. Monolayer area *vs*. composition at the specified surface pressures for mixtures of *iso*- and *synd*-PMMA. π is, ○ 1; ● 3; ◐ 4; □ 6; △ 10 dyn/cm.

The $\Delta G^{\pi}_{xs,m}$ values were calculated by Eq. (1) from the results shown in Fig. 1 using graphical integration. The results are shown in Fig. 2. In Fig. 3, areas of mixtures A_m at the specified surface pressures are plotted against isomer composition. Below 5 dyn/cm, $\Delta G^{\pi}_{xs,m}$ is almost zero and the additivity of areas holds as expected. Above 6 dyn/cm, $\Delta G^{\pi}_{sx,m}$ becomes negative, and at 10 dyn/cm it becomes minimum for the ratio 2/1 of *synd*/*iso*. At the same time, A_m shows negative deviation from the ideal behavior and has an inflexion point for the same ratio of *synd*/*iso*. These results indicate that, at the composition, *i. e.*, *synd*/*iso* is 2/1, the attractive interaction between two isomers is the strongest, and their efficient packing resulted under the surface pressure exceeding 6 dyn/cm.

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[11] F. C. Goodrich, Proc. Intern. Congr. Surface Activity, 2nd, London, **1**, 85 (1957).

[12] G. L. Gaines, Jr., "Insoluble Monolayers at Liquid Gas Interface," Interscience, New York, N.Y. (1966).

According to Crisp,[13] and Defay and Prigogine,[14] the surface phase rule is expressed as

$$F=C^{B}+C^{S}-P^{B}-q+3 \tag{3}$$

where T, P and π are variables, F is the number of freedom, C^B is the number of components in the bulk phases, C^S is the number of componetns confined to the surface phase, P^B is the number of bulk phases, and q is the number of surface phases in equilibrium with one another. As is clear from Fig. 1, the transition point of surface pressures of mixtures, π_t, varies with the composition of monolayers; *viz.*, starting at $\pi_t=6$ dyn/cm for *synd/iso*=0/1, gradulally decreases with the increase of the ratio, reaches a minimum at 4 dyn/cm where the ratio is 0.468/0.532, and then increases with the increase of *synd.* content. Thus, we have one degree of freedom at T and P constant. We may consider four possible cases at the transition point with one degree of freedom.[15] (1) Compatible monolayer with phase transition ($C^B=2$, $C^S=2$, $P^B=2$ and $q=2$); (2) compatible monolayer with squeezing out of one component ($C^B=3$, $C^S=1$, $P^B=3$ and $q=1$); (3) compatible monolayer which becomes incompatible at π_t ($C^B=2$, $C^S=2$, $P^B=2$ and $q=2$); (4) incompatible monolayer which becomes compatible at π_t ($C^B=2^2$ $C^S=2$, $P^B=2$ and $q=2$). Of these four possibilities, case (3) may be discarded since the attractive interaction is shown to be above above π_t. Beredjick, *et al.*,[1] concluded that *iso*-PMMA is transformed to helical form from extended conformation at $\pi_t=6$ dyn/cm. Moreover, the isotherms of mixed monolayer with the ratio of *synd/iso* higher than 2/1 are almost superposed on those of the pure *synd*-PMMA monolayer above 5 dyn/cm. Thus, it is likely that an overlayer is formed. If we adopt a tentative layer model of the stereocomplex where *synd*-PMMA are snugly fitted between grooves of *iso*-PMMA helix as proposed by Liquori *et al.*,[4] case (1) is most likely, though no structural evidence such as an electron diffraction of built-up film of the mixed monolayer is present. It appears that the stereocomplementary molecular packing between two isomers at the air-water interface is promoted under pressure.

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