*Macromolecules* **1990,** *23,* 3957-3962 **3957**

conditions are, from an experimental point of view, less restrictive than ideal Θ conditions and, consequently, they are free of the ambiguity inherent in the definition of $q_\eta$ at the Θ point. Recent renormalization group calculations in the lowest order[15] predict $q_\eta = 0.486$ for Gaussian chains and $q_\eta = 0.561$ in the presence of excluded volume (the former value is much closer to our simulation results than the one provided by the preaveraged theory and is, again, in contradiction with some of the experimental data). Another alternative, discussed in previous work,[12] is to characterize the behavior at the Θ point by means of the Flory parameter Φ, which combines the viscosity and the radius of gyration in the form

$$[\eta] = \Phi \frac{6^{3/2} \langle s^2 \rangle^{3/2}}{M} \qquad (7)$$

where $M$ is the molecular weight of the polymer. The extrapolated results obtained for this parameter are $\Phi = (3.94 \pm 0.02) \times 10^{23}$ for the upper bound limit (very similar to the extrapolated result $\Phi = 4 \times 10^{23}$ reported earlier,[12] obtained with chains of different numbers of units), $\Phi = (3.8 \pm 0.1) \times 10^{23}$ for the lower bound limit, and $\Phi = (3.15 \pm 0.05) \times 10^{23}$ for the trajectories (this latter extrapolation biased again by numerical problems). Experimental data provide $\Phi = (3.4\text{–}4.1) \times 10^{23}$, while the preaveraged theory yields $\Phi = 5.23 \times 10^{23}$. Then, though the scattering shown by experimental data avoids a precise quantitative agreement, it can be concluded that the theoretical approximation clearly overestimates the intrinsic viscosity of ring chains.

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# Ellipsometric Study of Binary Mixed Films of Poly(ethylene oxide) and Poly(methyl methacrylate) at the Air/Water Interface

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ABSTRACT: Binary mixtures of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) spread at the air/water interface have been investigated by using ellipsometry and surface pressure measurements. From the surface pressure measurements both polymers were found to be compatible. This result correlates well with the compatibility of the blends of PEO and PMMA in the bulk state. Ellipsometry gave two quantities for the phase difference (Δ) between the parallel and perpendicular components of the reflected light and the azimuth (ψ) of the amplitude ratio for light polarized parallel and normal to the plane of incidence. The value of Δ was much more sensitive to the presence of polymers at the air/water interface as compared to the ψ value. The changes in Δ and δΔ between pure water and the water surface covered with polymers increased with an increase in the amount spread and approached a plateau value around the PMMA surface concentration of 1.7 mg/m$^2$ in the mixtures, irrespective of the mixed ratio. Their plateau values did not change if the surface concentration was further increased.

## Introduction

The application of ellipsometry to polymer films and fatty acid monolayers spread at the air/water interface has recently been attempted to elucidate their interfacial conformation and surface structures.[1-12] Ellipsometry gives two quantities of the phase difference, Δ, and the azimuth, ψ, of the amplitude ratio for light polarized parallel and normal to the plane of incidence. Kawaguchi et al.[9,10] and Sauer et al.[12] especially have studied almost the same samples, and they reported similar results for the polymer concentration dependence of the changes in Δ between pure water and the water surface covered with polymers. From calculations of the thicknesses of the polymer layer spread as a film at the air/water interface it was found that a series of polymers of varying hydrophilicity preferred to dangle into the water phase rather than stick out of the air side, independent of the hydrophilicity and regardless of the difference in the thickness calculation methods.

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On the other hand, the mixed polymer films spread at the air/water interface have been paid intensive attention in order to clarify the compatibility of the mixed polymers. The compatibility of two polymers in the two-dimensional state is determined from the dependence of the mean areas at a constant surface pressure and/or that of the collapse surface pressures on the molar fraction of one component in the binary mixtures. Gabrielli and co-workers[13-16] have contributed significantly to the investigation of the compatibility of the polymer mixtures, and they concluded that the compatibility of two polymers at the air/water interface strongly depends on their interfacial orientations. Recently, Kawaguchi and Nishida[17] have measured the surface pressures of the binary mixtures for four different polymers, which led them to one important conclusion: the compatibility of the two polymers spread at the air/water interface correlates with that in the bulk state. Similar results were obtained by Wu and Huntsberger.[18] However, there is no study that applies ellipsometry to investigate the interfacial conformation and surface structures of the mixed polymer films spread at the air/water interface.

In this paper we applied ellipsometry to the binary mixtures of poly(ethylene oxide) (PEO) and poly(methyl methacrylate) (PMMA) spread at the air/water interface together with the surface pressure measurements. We examined whether PEO and PMMA mixtures are compatible or incompatible from the molar composition dependence of both the mean surface areas at a constant surface pressure and collapse surface pressures. The changes in both values of $\Delta$ and $\psi$ between the clean water surface and the film-covered water surface were obtained as a function of the surface concentration of PMMA. Calculation of the layer thicknesses of the binary mixtures allowed us to discuss their conformation in the two-dimensional state. Moreover, we redid the ellipsometry measurements of the individual polymer films for PEO and PMMA in order to confirm the reproducibility of the changes in the value of $\psi$ since their changes were small.

## Experimental Section

**Materials.** Two PEO samples with a narrow molecular weight distribution ($M_w/M_n = 1.1$) were purchased from Tosoh Co. Their molecular weights were determined to be $18 \times 10^3$ and $996 \times 10^3$ by light scattering. PMMA was a commercially available sample from Scientific Polymer Products and was fractionated. One fractionated PMMA sample, having a $M_w = 280 \times 10^3$ as determined from the intrinsic viscosity measurement in benzene, was employed. Its stereoregularity was determined in chloroform-*d* at 55 °C by using a Bruker MSL-400 $^1$H NMR spectrometer. Its content was 9.5% isotactic, 39.0% heterotactic, and 51.5% syndiotactic.

Spectrograde quality benzene was used as the spreading solvent for the two polymers as well as their mixtures. The solvent was used without further purification.

Deionized water, supplied from a Millipore Q-M system, was used in all experiments.

**Surface Pressure Measurements and Ellipsometry.** Surface pressure measurements and ellipsometry of individual films for PEO and PMMA and the binary mixed films of PEO and PMMA spread at the air/water interface were performed with the same instruments as previously used.[9,10] The polymer films were formed by the stepwise addition of the polymer solution or the one-shot spreading using a microsyringe. The water surface was cleaned by aspiration. The temperature of the water phase in a PTHF trough with a diameter of 15 cm placed in a aluminum water jacket was 25 ± 0.1 °C by using circulating, thermostated water. The surface pressures were measured with a sandblasted platinum plate as a Wilhelmy plate hung on a Cahn 2000 electrobalance with a sensitivity of ±0.03 mN/m.

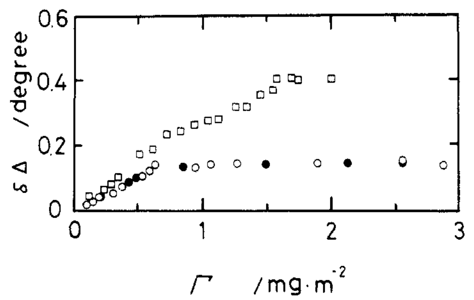

**Figure 1.** Plots of $\delta\Delta$ as a function of polymer concentration: (○) PEO-1 ($M_w = 18 \times 10^3$); (●) PEO-2 ($M_w = 996 \times 10^3$); (□) PMMA.

For the higher concentrations of PMMA in the individual and mixed films, their surface pressures showed a strong time dependence and we regarded the surface pressure, which changes less than 0.05 mN/m for 10 min, as the equilibrium value.

Our ellipsometer is based on conventional null-detection four-zone methods, which have been reviewed in previous publications.[9,10] The precision in the readings of the goniometer mounted with the polarizer, the quarter-wave plate, and the analyzer was 30 s. The experiments were performed at a fixed incident angle of 70° by using monochromatic light with a wavelength $\lambda = 546$ nm, which is obtained from a high-pressure mercury lamp. The changes in $\Delta$ and $\psi$ between the clean water and the water surface covered with polymer films were expressed as $\delta\Delta = (\bar{\Delta} - \Delta)$ and $\delta\psi = (\bar{\psi} - \psi)$, respectively: $\bar{\Delta}$ and $\bar{\psi}$ are for the pure water, and $\Delta$ and $\psi$ are for the water surface covered with the polymers.

## Results and Discussion

We first performed ellipsometry for individual PEO and PMMA films spread at the air/water interface as a function of surface concentration. Figure 1 shows the plot of $\delta\Delta$ as a function of polymer concentration. For the two PEO samples, the $\delta\Delta$ value above $\Gamma = 0.7$ mg/m$^2$ appears to be independent of the molecular weight: the $\delta\Delta$ value increases monotonously with the surface concentration until $\Gamma = 0.7$ mg/m$^2$ or above where it reaches a plateau value of 0.14°. This value does not change if the spread amounts of PEO increase. Also, the surface pressure reaches a constant, i.e., ca. 10 mN/m at $\Gamma = 0.7$ mg/m$^2$. This surface concentration almost corresponds to that where a complete monolayer is formed by adsorption from the bulk aqueous solution of PEO.[19] Therefore, we regard it as the concentration where the water surface is fully covered by PEO. Above this point some segments of PEO molecules that are further added are desorbed from the air/water interface since PEO is soluble in the water phase. Thus, the refractive index of the water phase increases and the lack of contrast between the refractive index of the water phase and the adsorbed PEO layer leads to no additional change in $\delta\Delta$.

For the PMMA film, to confirm the existence of the two kink points in the plots of $\delta\Delta$ versus concentration, we did the ellipsometric measurements for much larger points than those in the previous study. The values of $\delta\Delta$ reproduced the two distinct kinks: the first kink is found at $\Gamma = 0.7$ mg/m$^2$ and the second kink is found at $\Gamma = 1.7$ mg/m$^2$. However, the strange kink at $\Gamma = 1.2$ mg/m$^2$ observed in the previous paper is absent in Figure 1 due to smoothing out by many data points. The kink at $\Gamma = 0.7$ mg/m$^2$ is attributed to the fact that the PMMA monolayer may be patchy. Above $\Gamma = 1.7$ mg/m$^2$ the plateau value of $\delta\Delta = 0.40°$ does not change and the reproducibility was 0.03° or less. This plateau value is larger than that in our earlier paper.[9] This stems from the fact that, in this study, we measured the $\Delta$ and $\psi$ values 1 h after spreading.

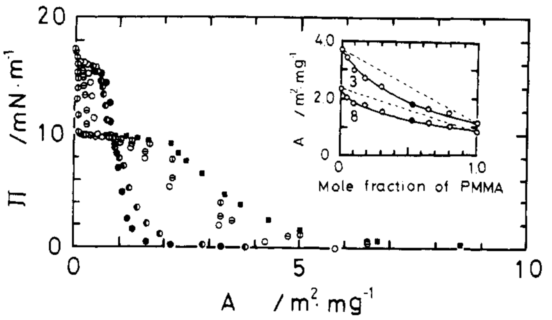

**Figure 2.** Surface pressure–area isotherms for mixtures of PEO and PMMA: (■) PEO; (◑) PEO/PMMA = 0.95/0.05; (⊖) PEO/PMMA = 0.82/0.18; (○) PEO/PMMA = 0.69/0.31; (◐) PEO/PMMA = 0.22/0.78; (●) PMMA. The inset shows the mean areas in the mixtures of PEO and PMMA as a function of the mole fraction of PMMA. The numbers in the inset indicate the surface pressure. The filled circle in the inset is a data point cited from ref 17.

Allowance for 1 h is usually enough to attain the equilibrium surface pressure. In other words, the plateau value reported in the previous paper may not be well in equilibrium. Since PMMA forms a condensed film at the air/water interface, the absence of any change in $\delta\Delta$ may be attributed to the formation of the inhomogeneous layer.

The other values of $\delta\psi$ were 0.01° or less for both polymers, and they were very small and similar to those reported previously. Since the $\delta\psi$ values are not exactly equal to zero, we can in principle extract both the thickness and refractive index of the spread polymer films from the Drude equations by using the experimental values of $\Delta$ and $\psi$. From this fact, in our previous publication,[9,10] we could obtain the values of the thickness and refractive index, regardless of the statement that the $\delta\psi$ value was regarded as zero. In this study, we also could obtain a thickness of 3–4 nm at the full surface coverage for PEO. However, the thicknesses so calculated should contain some uncertainties because of the small values of $\delta\psi$, i.e., the thickness contains a 20% error. Recently, neutron reflection experiments[20] for the PEO spread at the air/water interface gave large thicknesses of 8–9 nm for the molecular weight of ca. $20 \times 10^3$ at full surface coverage. On the other hand, it is possible to calculate the thickness from only the $\delta\Delta$ values. This is discussed further in this study.

Next, we performed the surface pressure measurements and ellipsometry of the binary mixtures of PEO and PMMA using the small molecular weight PEO for six mixtures of 0.95/0.05 (8/1), 0.90/0.10 (4/1), 0.82/0.18 (2/1), 0.69/0.31 (1/1), 0.36/0.64 (1/4), and 0.22/0.78 (1/8), of which these ratios of PEO and PMMA are expressed in monomer molar fraction and weight fraction in parentheses, respectively. Typical surface pressure–area isotherms and the mean surface areas at constant surface pressures of 3 and 8 mN/m as a function of the molar PMMA in the mixtures are displayed in Figure 2. The isotherms at the higher PEO contents have plateau regions around 10 mN/m, which correspond to the collapse surface pressure of the PEO film. Below the plateau regions the surface pressure at the same area decreases with an increase in the PMMA composition. Above the plateau surface pressure, on the other hand, the composition dependence of the surface pressure is quite the reverse.

The width of the plateau regions increases with the molar fraction of PEO. This fact is demonstrated more clearly in a plot of the surface pressure versus the surface concentration of PMMA, $\Gamma_{PMMA}$, as displayed in Figure 3. For comparison, the surface pressure of the PEO homopolymer is displayed by a dashed line in Figure 3. For the lower PEO contents in the mixed films, there is a kink below $\Gamma_{PMMA} = 1.0$ mg/m$^2$ and the surface pressure at the kink is below 10 mN/m. Both the plateau surface pressure and the surface pressure at the kink could be regarded as a kind of collapse surface pressure, and its magnitude is not constant and depends on the composition of the PEO/PMMA mixtures.

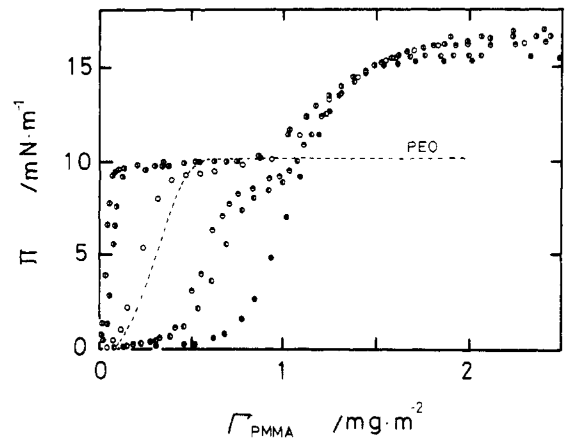

**Figure 3.** Surface pressures as a function of PMMA concentration in the mixtures of PEO and PMMA: (◑) PEO/PMMA = 0.90/0.10; (◒) PEO/PMMA = 0.36/0.64. The other symbols are the same as in Figure 2. The dashed line indicates the concentration dependence of the surface pressure of PEO homopolymer.

Goodrich[21] and Gaines[22] derived the molar excess free energy of mixing, $\Delta G^{\pi}_{ex}$, of two pure monolayers to form as mixed monolayer at constant temperature and surface pressure. The value of $\Delta G^{\pi}_{ex}$ is defined as the difference between the molar free energy of mixing at surface pressure, $\pi$, and that at zero surface pressure and is given by

$$\Delta G^{\pi}_{ex} = \int_0^{\pi} (A - X_1A_1 - X_2A_2)\, d\pi \qquad (1)$$

where $A$ is the mean area in the mixed monolayer at a given surface pressure, $X_1$ and $X_2$ are the molar ratios of components 1 and 2, and $A_1$ and $A_2$ are the molecular areas of components 1 and 2 at the same surface pressure, respectively. If the mixed monolayers behave ideally, $\Delta G^{\pi}_{ex}$ vanishes so that a relation is obtained from eq 1:

$$A = X_1A_1 + X_2A_2 \qquad (2)$$

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 instead of a molecular area and by adopting the values $X_1$ and $X_2$ as a monomer molar fraction.

From the inset in Figure 2, the mean areas deviate negatively from the dashed line, which represents the additivity line of eq 1. The negative deviation means that the intermolecular interaction between PEO and PMMA is attractive and that the mixture of PEO and PMMA at the air/water interface is nonideally miscible and stable. Moreover, both polymers more easily interpenetrate each other.

We noticed the existence of another collapse surface pressure at above $\Gamma_{PMMA} = 1.7$ mg/m$^2$ in Figure 3. This high collapse surface pressure, i.e., 15–17 mN/m, increases with an increase in PEO. Thus, the compatibility of PEO and PMMA at the air/water interface is guaranteed by the composition dependence of both the mean surface area at constant surface pressure and at constant collapse surface pressures. This result correlates with the compatibility of the blends of the corresponding polymers in the bulk state.[20]

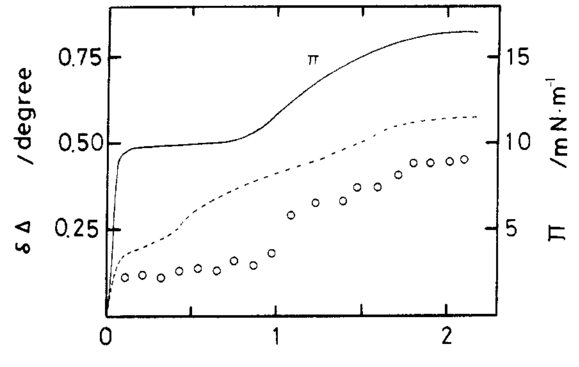

**Figure 4.** Comparison between $\delta\Delta$ and surface pressure as a function of PMMA concentration in the PEO/PMMA molar ratio of 0.95/0.05. The dashed line indicates the additive curve for $\delta\Delta$.

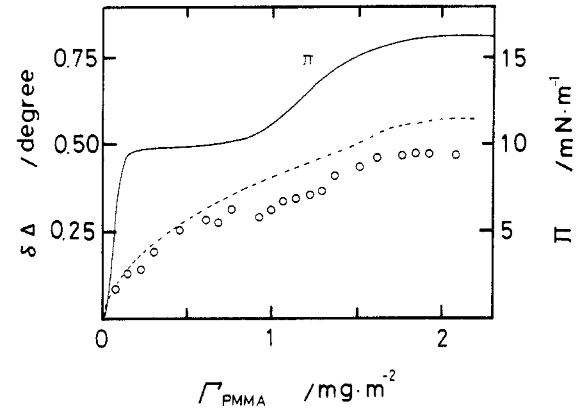

**Figure 5.** Comparison between $\delta\Delta$ and surface pressure as a function of PMMA concentration in the PEO/PMMA molar ratio of 0.90/0.10. The dashed line indicates the additive curve for $\delta\Delta$.

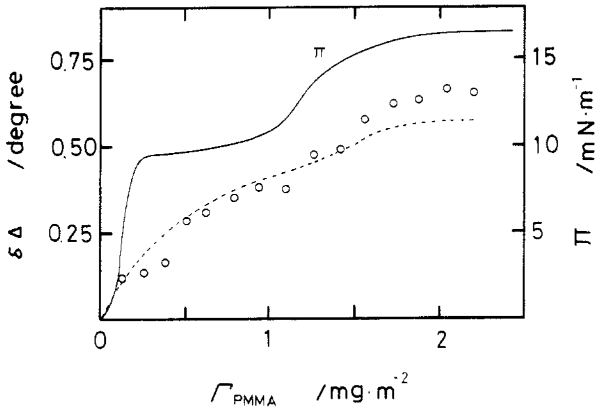

**Figure 6.** Comparison between $\delta\Delta$ and surface pressure as a function of PMMA concentration in the PEO/PMMA molar ratio of 0.82/0.18. The dashed line indicates the additive curve for $\delta\Delta$.

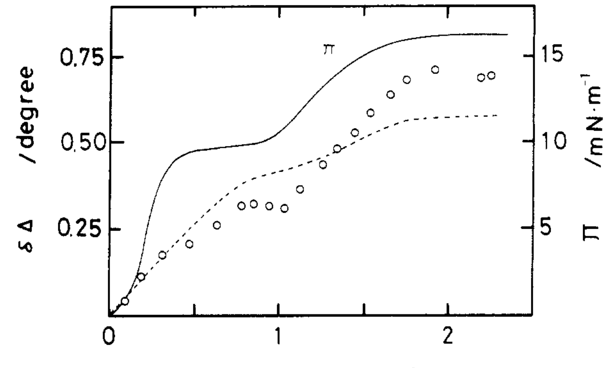

**Figure 7.** Comparison between $\delta\Delta$ and surface pressure as a function of PMMA concentration in the PEO/PMMA molar ratio of 0.69/0.31. The dashed line indicates the additive curve for $\delta\Delta$.

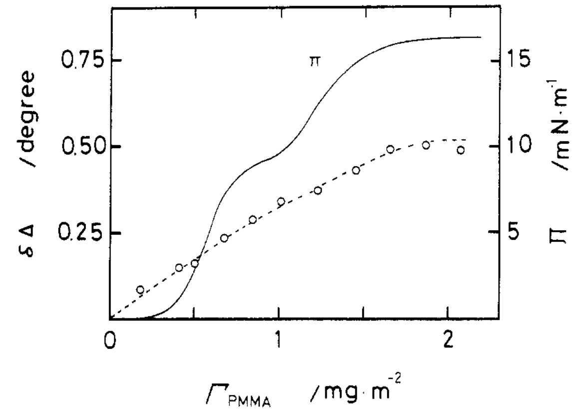

**Figure 8.** Comparison between $\delta\Delta$ and surface pressure as a function of PMMA concentration in the PEO/PMMA molar ratio of 0.36/0.64. The dashed line indicates the additive curve for $\delta\Delta$.

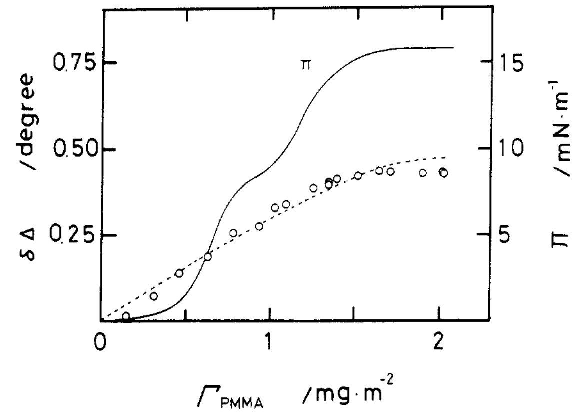

**Figure 9.** Comparison between $\delta\Delta$ and surface pressure as a function of PMMA concentration in the PEO/PMMA molar ratio of 0.22/0.78. The dashed line indicates the additive curve for $\delta\Delta$.

Ellipsometry of the mixed films shows that the $\Delta$ values are much more sensitive to the spread amounts of both polymers than the $\psi$ values: the values of $\delta\Delta$ increase with an increase in the spread amounts of polymer, whereas the $\delta\psi$ values are less than 0.01° over most surface concentrations for all compositions. Plots of $\delta\Delta$ versus $\Gamma_{\mathrm{PMMA}}$ are given in Figures 4–9 for the mixtures of 0.95/0.05, 0.90/0.10, 0.82/0.18, 0.69/0.31, 0.36/0.64, and 0.22/0.78, respectively. In these figures the surface pressures are also displayed. The plots of $\delta\Delta$ depend on the compositions in the mixtures, and we noticed two features in the plots. First, for the mixtures of 0.95/0.05, 0.90/0.10, 0.82/0.18, and 0.69/0.31, there is a kink around at $\Gamma_{\mathrm{PMMA}}$ = 0.6–1.0 mg/m$^2$, where the low-collapse surface pressure is observed. Second, for all the mixtures the values have a plateau value above $\Gamma_{\mathrm{PMMA}}$ = 1.7 mg/m$^2$ at which the surface pressures are near the high-collapse surface pressure. The kink may be concerned with the patchiness of the PEO/PMMA mixtures.

For both the 0.36/0.64 and 0.22/0.78 mixtures, since the individual concentration of PEO even at $\Gamma_{\mathrm{PMMA}}$ = 2 mg/m$^2$ is lower than $\Gamma_{\mathrm{PEO}}$ = 0.7 mg/m$^2$, which corresponds to the onset of the full surface coverage of PEO, PEO molecules also contribute to the changes in $\delta\Delta$ without its desorption from the water's surface. The $\delta\Delta$ values for the 0.36/0.64 mixture are larger than those for the 0.28/0.72 mixture in the entire concentration range.

For the mixtures of 0.95/0.05, 0.90/0.10, 0.82/0.18, and 0.69/0.31, on the other hand, the values of $\delta\Delta$ at the higher $\Gamma_{\mathrm{PMMA}}$, where the PEO contents in the corresponding mixtures are above the threshold of full surface coverage of PEO by the PEO homopolymer, decrease with the PEO contents, regardless of the high total amounts of PEO and PMMA. This result may be interpreted by the similar reason why the $\delta\Delta$ values for the PEO homopolymers do not change above the onset of the fully saturated PEO surface. In other words, PEO molecules do not significantly contribute to the changes in $\delta\Delta$ at the higher percent PEO mixtures due to the desorption of PEO from the air/water interface. Moreover, for the 0.95/0.05 mixtures, the values of $\delta\Delta$ at the lower $\Gamma_{\mathrm{PMMA}}$ are nearly consistent with the plateau value of the pure PEO.

Since the $\delta\Delta$ value clearly depends on the total spread amounts, it is interesting to compare the observed $\delta\Delta$ with that calculated from the simple addition of $\delta\Delta$ for the individual polymers at a given surface concentration. However, there is no theoretical reason to use the simple addition of $\delta\Delta$, and it will be hard to deduce any understanding. Here, we only made an attempt. The additive curves are displaced in Figures 4–9 with a dashed line. The observed $\delta\Delta$ is in agreement with the additive curve for the two mixtures of 0.36/0.64 and 0.22/0.78. Except for the two mixtures, the observed $\delta\Delta$ values deviate from the additive curves. For the mixtures of 0.90/0.10 and 0.95/0.05, the negative deviation from the additive curves is observed over the entire concentration ranges. The value of $\delta\Delta$ above $\Gamma_{\mathrm{PMMA}} = 1.7$ mg/m$^2$ shows a convex curve as a function of the molar fraction of PMMA in the mixtures, and they are all larger than that of the individual PMMA film.

Ellipsometry provides both the thickness and the refractive index of the adsorbed layer using the Drude equation and the two values of $\Delta$ and $\psi$. As previously mentioned, since the $\delta\psi$ values are much smaller than $\delta\Delta$, the reproducibility of the calculation for both the thickness and refractive index of the adsorbed layer is not good when the iteration method is used where the thickness and refractive index values are sought, which reproduce the measured ellipsometric parameters of $\Delta$ and $\psi$: we did not obtain any solutions for some $\Delta$ and $\psi$ data. Even if a solution was found, it contained a 30% error. Thus, we stopped calculation of the thickness and the refractive index from both values of $\Delta$ and $\psi$.

When the value of $\delta\psi$ is small, one could calculate the layer thickness from only the value of $\delta\Delta$. This calculation method was sometimes employed for the analysis of the ellipsometry for gas adsorption on a solid surface.[24,25] The thickness, $t$, with an upper limit of the order of 1 nm is related with the value of $\delta\Delta$ as

$$\delta\Delta = \alpha t \tag{3}$$

where $\alpha$ is a constant determined by the angle of incidence of the beam, $\phi$, the wavelength of the light, $\lambda$, and the refractive indexes, $n_s$ and $n_f$, of the surface and film, respectively. The value of $\alpha$ monotonously increases with $n_f$ below $n_f = 2.00$ at fixed values of $\phi$, $\lambda$, and $n_s$.

More recently, Sauer et al.[12] applied eq 3 to the polymer films spread at the air/water interface and extracted the layer thicknesses of polymers. According to the model of Sauer et al., the refractive index, $n_f$, of the polymer layer is assumed to be dependent on the surface coverage, $\theta$, of the water surface with the polymers and to be equal to that in the bulk state at the full surface coverage, and the film layer has a constant thickness consisting of polymer and water below the full surface coverage. Below the full surface coverage the value $n_f$ was assumed to be expressed by the Lorentz–Lorenz equation using three refractive indexes of $n_f$, $n_p$, and $n_s$.

$$(n_f^2 - 1)/(n_f^2 + 2) = \theta(n_p^2 - 1)/(n_p^2 + 2) + (1 - \theta)(n_s^2 - 1)/(n_s^2 + 2) \tag{4}$$

There is no distinct rule for choosing the full surface coverage, but there are some choices: the surface concentration at which the limiting area is obtained by extrapolation of surface pressure to zero, the surface concentration at the onset of the plateau surface pressure, and the surface concentration at the threshold of the plateau, $\delta\Delta$.

Upon calculation of the thickness from eqs 3 and 4, there is no reason why the refractive index of the adsorbed polymer layer at full coverage should be equal to that in bulk polymer, since the optical constants of the adsorbed layers of water-soluble and hydrophilic polymers, in this study such as PEO, might differ from those in their bulk state. Neutron reflection experiments supported that the refractive index of the adsorbed layer of PEO was less than that in the bulk state.[20] However, PMMA may satisfy with this assumption since PMMA is formed as a condensed film at the air/water interface. Upon calculation of the PMMA thickness, the concentration of 1.7 mg/m$^2$, in which the surface pressure becomes constant, is chosen as the full surface coverage. This PMMA concentration is somewhat lower than that determined by Sauer et al.,[12] who chose the concentration at the onset of the plateau surface pressure. The difference between them may be attributed to the difference in the microstructures of PMMA used. Moreover, we employed $n_s = 1.3340$ for the pure water, which was determined from ellipsometry.[9] We obtained the film thickness of 1.2 ± 0.05 nm by employing the refractive index of the film at the fully occupied water surface with the polymer using the refractive index of 1.490.[26] This film thickness is in good agreement with the data of Sauer et al.

We tried to calculate the thickness of the mixed polymers for only the mixtures of 0.36/0.64 and 0.22/0.78, since the small amount of PEO in both mixtures would not desorb from the interface. Since both polymers were compatible, we could estimate the refractive indexes, $n_f$, of the polymer mixtures by using the Lorentz–Lorenz relation with the refractive indexes of the corresponding polymers (1.455 for PEO).[26] We chose $\Gamma_{\mathrm{PMMA}} = 1.7$ mg/m$^2$ as the full surface coverage for the mixtures, since above this concentration both the value of $\delta\Delta$ and the surface pressure attain the respective plateau value. The thicknesses so calculated are 1.5 ± 0.05 and 1.3 ± 0.05 nm for the mixtures of 0.36/0.64 and 0.22/0.78, respectively. Both thicknesses are somewhat larger than that for PMMA.

## Conclusions

Ellipsometry was first applied to the binary mixtures of PEO and PMMA spread at the air/water interface. Both polymers were found to be compatible from the surface pressure measurements. The changes in $\Delta$ values were more sensitive than those in $\psi$ values over the entire concentration ranges. This behavior was similar to that of the individual polymers. Since the changes in $\psi$ values were small, the thickness and refractive index of the mixed polymer layer could not be accurately extracted from the values of $\Delta$ and $\psi$. The changes in $\Delta$ as a function of

PMMA concentration in the mixtures were discussed by comparing their surface pressures.

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# Characterization of Film Formation from Polystyrene Latex Particles via SANS. 1. Moderate Molecular Weight

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ABSTRACT: Deuterated and protonated polystyrene latexes of 275-Å radius and 250 000 g/mol were mixed together to give 6 mol % of deuterated polystyrene. After removal of the aqueous phase and surfactants, the dry latex particles were sintered to full density at 110 °C under a pressure of 9.0 MPa by using a vacuum hot press for 40 min. These sintered films were annealed at 144 °C from 5 min to 48 h. Small-angle neutron scattering, SANS, measurements were made to evaluate the interdiffusion through an apparent increase in size of the deuterated polystyrene-rich particles, while tensile strength measurements were carried out on the corresponding protonated samples. For the present system, the minimum depth of molecular diffusional penetration for full tensile strength ($3.04 \times 10^7$ N/m$^2$) was found to be about 110–120 Å, comparable to the weight-average radius of gyration, $R_g^w$, of the whole polystyrene chain. An elbow in the tensile strength–penetration depth relationship was found at 45–50 Å, corresponding to the critical molecular weight for entanglement. After an apparent induction period, the tensile strength increased with time to the one-fourth power, as predicted by Wool et al. After 48 h of annealing at 144 °C, complete molecular mixing was achieved via interdiffusion of deuterated and protonated species.

## Introduction

The process of film formation from a latex can be divided into three stages: (a) evaporation of water, (b) coalescence and deformation of latex particles, and (c) interdiffusion of polymer chains between adjacent particles. Extensive research has been devoted to the first and second stages of film formation, while the interdiffusion problem has received little attention because of instrumental limitations. The present experiments utilize small-angle neutron scattering (SANS) to determine the latex particle and polymer radii of gyration in the films as a function of annealing time, from which molecular interdiffusion can be evaluated and compared with tensile strength buildup.

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