Ellipsometric Study of Competitive and Displacement Adsorption of Polymers at the Θ Condition

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ABSTRACT: Competitive adsorption and displacement adsorption of polystyrene (PS) molecules onto a platinum plate from *trans*-decalin solutions at 20.4 °C (Θ condition) were studied by ellipsometry for two different combinations of PS molecules. Adsorbance and thickness of the adsorbed layer were measured as a function of adsorption time at a constant bulk concentration of each PS molecule. The thickness of the adsorbed layer attained an equilibrium earlier than adsorbance for each adsorption experiment. In competitive adsorption the magnitude of the thickness of the adsorbed layer was the same as that of large-size PS molecules while the adsorbance was slightly lower than that of large ones. On the other hand, in displacement adsorption adsorbance and the thickness of the adsorbed layer depend strongly on the molecular weight of previous adsorbed PS molecules.

Introduction

The adsorption of polymer mixtures, particularly mixtures of the same chemical structure, at the solid–solution interface has been studied extensively.[1-8] Some theoretical works on this subject have been reported:[9,10] It is generally agreed that large molecules preferentially adsorb over small ones, and small molecules adsorbed early can be displaced by large molecules.

Most experiments of mixture adsorption have measured the adsorbed amount, the surface coverage of the surface sites by adsorbed polymer units, and the fraction of polymer segments directly attached to the surface. These data are very useful to compare with existing theories, and good agreement between experiments and theories has been reported.[6-8] However, the thickness of the adsorbed layer on the solid surface for the competitive adsorption and displacement adsorption of polymers has not yet been reported. Accumulation of such data is very important for further developing theoretical work. We can measure the thickness by several experimental techniques, for example the hydrodynamic method, photon correlation spectroscopy, and ellipsometry.[11]

In this study we used ellipsometry, which is a suitable technique for simultaneously measuring the thickness of the adsorbed layer and the adsorbance. The aim of this paper is to obtain experimental results on the thickness of the adsorbed layer as well as the adsorbance for competitive adsorption and displacement adsorption of polystyrene molecules, each polystyrene sample having a narrow molecular weight distribution on a platinum plate from *trans*-decalin solution at 20.4 °C (Θ condition)[12] by ellipsometry. The thickness of the adsorbed layer and absorbance will be discussed as functions of adsorption time and the molecular weight of polystyrenes in comparison with the adsorption of single, monodisperse polystyrenes.

Experimental Section

Materials. Three polystyrenes (PS) with narrow molecular weight distributions were purchased from Toyo Soda Co. Their characteristics are listed in Table I.

Table I
Characteristics of Polystyrenes

sample	$M_w \times 10^{-3}$	M_w/M_n
PS 102	102	1.02
PS 422	422	1.04
PS 775	775	1.01

trans-Decalin, a Θ solvent for PS at 20.4 °C, was purchased from Tokyo Kasei Kogyo Co. The solvent was distilled twice under vacuum (29 mmHg at 82.5 °C) before use.

Platinum plates (15.2 × 30.3 × 1.2 mm) were used as the substrates. Prior to the experiments the platinum plates were cleaned by the previously described method.[13]

Ellipsometry. We used a Shimadzu horizontal ellipsometer. The ellipsometric measurements and the analysis of ellipsometric data are described in detail in ref 14. All adsorption experiments were carried out in *trans*-decalin–PS solution at 20.4 °C. A total of 20 mL of solution was put in a trapezoidal glass cell, which had a platinum plate on its bottom. The incident angle was 70°.

The adsorption of the component polystyrenes was performed at several bulk concentrations C_p. For competitive adsorption we used two different mixtures of small and large PS molecules (1:1 (w/w)) at component bulk concentrations of $C_p = 0.1$ g/100 mL. Displacement adsorption was performed by first adsorbing to complete equilibrium smaller PS molecules (PS 102 or PS 422) at a bulk concentration of $C_p = 0.1$ g/100 mL, then carefully removing 10 mL of the supernatant, and finally adding 10 mL of PS 775 solution with a bulk concentration of $C_p = 0.2$ g/100 mL.

Adsorbance A was calculated from the ellipsometric data on the refractive index n_f and the thickness t of the uniform adsorbed layer as follows:

$$A = t(n_f - n_0)/(\partial n/\partial c) = tC_f \qquad (1)$$

n_0 is the refractive index of the solvent, $\partial n/\partial c$ is the refractive index increment of the polymer in the solvent, and C_f is the average concentration in the adsorbed layer. In this study $n_0 = 1.4711$ for *trans*-decalin at 20.4 °C and $\partial n/\partial c = 0.130$ mL/g for PS in *trans*-decalin at 20.4 °C.

Results and Discussion

Adsorption of Component Polystyrenes. Typical plots of adsorbance of PS 775 against adsorption time are shown in Figure 1. At each bulk concentration C_p the adsorbance increases with increasing adsorption time and attains equilibrium after about 20 h. The equilibrium values are then unchanged, even over 3 days.

Figure 2 shows the thickness of the adsorbed layer as a function of adsorption time. The thickness of the adsorbed layer attains its equilibrium value faster than adsorbance. This is interpreted in terms of a conformational rearrangement, in which the PS chains adsorbed early take a flattened conformation on the sparsely populated surface and the PS chains adsorbed later must occupy a small number of vacant sites and therefore must adopt a more extended conformation. From comparison of Figures 1 and 2 the thickness of the adsorbed layer attains a plateau value at lower concentration than the adsorbance. This result indicates that the adsorbed chain takes an equilibrium extended conformation on the surface even at low concentrations, but some unoccupied sites where other

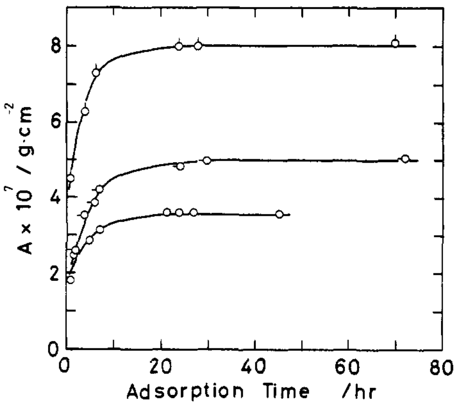

Figure 1. Typical adsorbances of PS 775 as a function of adsorption time: (○-) bulk concentration C_p = 0.013 g/100 mL; (-○) C_p = 0.051 g/100 mL; (○̍) C_p = 0.1 g/100 mL.

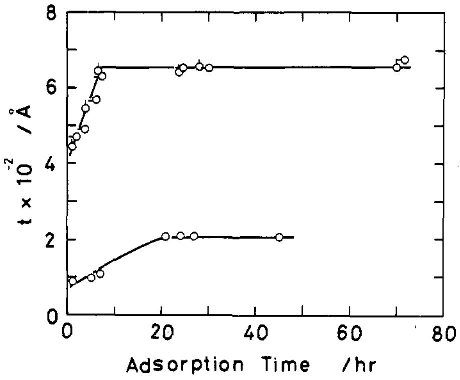

Figure 2. Typical thickness of the adsorbed layer for PS 775 as a function of adsorption time. The symbols are the same as in Figure 1.

Table II
Plateau Adsorption Data and Diameter of PS Chains at the Θ Condition

	t/Å	$A \times 10^7/(\mathrm{g{\cdot}cm^{-2}})$	$2\langle S^2\rangle_0^{1/2}$/Å
PS 102	95	0.95	179
PS 422	380	2.7	364
PS 775	640	7.8	494

polymer chains can adsorb still remain.

The thickness of the adsorbed layer for each sample reaches a plateau value at a bulk concentration of C_p = 0.1 g/100 mL. Table II compares the plateau thickness of the adsorbed layer with the diameter (twice the radius of gyration) of the PS chain in the solution calculated from the relation[12] between the radius of gyration and the molecular weight of PS in *trans*-decalin at 20.4 °C. The absolute magnitude of the thickness of the adsorbed layer is larger than the diameter except for the PS 102 sample. This indicates that PS molecules would be adsorbed by taking a conformation with some distortion from the chain configuration in the solution. PS 102 molecules probably take a more flattened conformation than large PS molecules.

The adsorbance also attains a plateau value at C_p = 0.1 g/100 mL for the three samples used, and the plateau adsorbances are listed in Table II. Both the magnitude of the thickness of the adsorbed layer and the adsorbance are very similar to previously obtained data of the ellipsometric adsorption of PS on a chrome plate from cyclohexane solutions at 35 °C (Θ condition).[14]

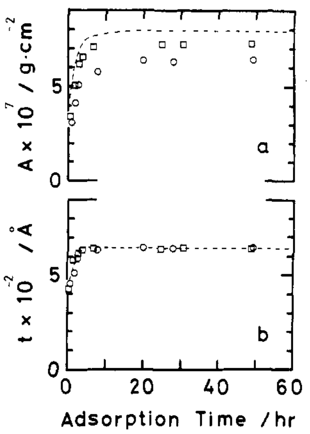

Figure 3. (a) Adsorbances for competitive adsorption of PS 102–PS 775 (○) and PS 422–PS 775 (□) as a function of adsorption time at C_p = 0.1 g/100 mL for each polymer. The dashed line indicates the adsorbance for individual adsorption of PS 775 at C_p = 0.1 g/100 mL. (b) Thickness of the adsorbed layer for competitive adsorption of PS 102–PS 775 (○) and PS 422–PS 775 (□) as a function of adsorption time. The dashed line indicates the thickness of the adsorbed layer for individual adsorption of PS 775 at C_p = 0.1 g/100 mL.

Table III
Equilibrium Adsorption Data of Competitive Adsorption and Displacement Adsorption of Polystyrene at the Θ Condition

	competitive adsorption		displacement adsorption	
combination	t/Å	$A \times 10^7/(\mathrm{g{\cdot}cm^{-2}})$	t/Å	$A \times 10^7/(\mathrm{g{\cdot}cm^{-2}})$
PS 102–PS 775	640	6.4	580	5.7
PS 422–PS 775	640	7.2	640	6.5

Adsorption of Mixtures. Figure 3a shows adsorbances for PS 102–PS 775 and PS 422–PS 775 mixtures as a function of adsorption time. The adsorbance of PS 775 at a bulk concentration of C_p = 0.1 g/100 mL is also displayed in the same figure. As seen from the figure the adsorption of the mixtures reaches an equilibrium value within 24 h within experimental error. The equilibrium adsorbance was unchanged after a week. The time required for attaining the equilibrium is almost the same as that for the individual adsorption.

Plots of the thickness of the adsorbed layer against adsorption time for PS 102–PS 775 and PS 422–PS 775 mixtures are shown in Figure 3b. In the figure, for comparison, the thickness of the adsorbed layer for PS 775 at a bulk concentration of C_p = 0.1 g/100 mL is also shown as a function of adsorption time. The thickness of the adsorbed layer of the mixtures steeply increases with increasing adsorption time and reaches an equilibrium value after 5 h. The time for reaching the equilibrium is independent of the mixture of PS pairs and is almost the same as for individual adsorption. The absolute values of the thickness of the adsorbed layer for the two mixtures at the equilibrium state are equal and are the same as the value for individual adsorption of PS 775 molecules within experimental error. The equilibrium thickness was unchanged after a week. From the agreement between the equilibrium thickness of the adsorbed layer for competitive adsorption with that for individual adsorption of large-size PS, we can state that apparent preferential adsorption of large molecular size over small molecular size completely occurs in this experiment. However, in contrast to the thickness of the adsorbed layer, the adsorbances of the mixtures (Table III) are lower than that of the individual adsorption of PS 775 but are larger than that of small PS molecules. Therefore, in the adsorbed layer two different species of large and small PS molecules are adsorbed, and preferential adsorption of large molecules over small molecules is not complete.

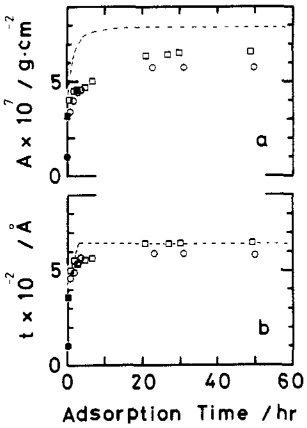

Figure 4. (a) Adsorbances for displacement adsorption of both PS 102 by PS 775 (○) and PS 422 by PS 775 (□) as a function of adsorption time at C_p = 0.1 g/100 mL. The filled circle and square indicate the equilibrium adsorbances for individual adsorption of PS 102 and PS 422 at C_p = 0.1 g/100 mL, respectively. The dashed line indicates the adsorbance for individual adsorption of PS 775 at C_p = 0.1 g/100 mL. (b) Thickness of the adsorbed layer for displacement adsorption of both PS 102 by PS 775 (○) and PS 422 by PS 775 (□) as a function of adsorption time at C_p = 0.1 g/100 mL. The filled circle and square indicate the equilibrium thickness for individual adsorption of PS 102 and PS 422 at C_p = 0.1 g/100 mL, respectively. The dashed line indicates the thickness of the adsorbed layer for individual adsorption of PS 775 at C_p = 0.1 g/100 mL.

We attempted to measure the composition of PS molecules in supernatants for the competitive adsorption by GPC, but we could not observe a difference in the composition of PS molecules between the initial added solution and supernatants. This is probably due to the small area of adsorbent.

Displacement of PS Molecules. Figure 4a shows the adsorbance for displacement adsorption of small PS molecules previously adsorbed by large PS molecules as a function of adsorption time for the PS 102–PS 775 and PS 422–PS 775 combinations. The zero adsorption time in the figure corresponds to the time of addition of 10 mL of PS 775 solution to 10 mL of small PS molecules from the supernatant that had attained full equilibrium adsorption. For comparison, the adsorbance of displacer molecules, i.e., PS 775, is also shown in the figure. Adsorbance initially increases with increasing adsorption time and then attains equilibrium. A more careful inspection of the figure shows that the adsorbance of a combination of PS 102 and PS 775 increases more steeply than that of the other combination at early adsorption time. Both combinations reach the equilibrium values after 20 h, and their equilibrium values are shown in Table III. The equilibrium values for the PS 422–PS 775 combination is lower than that for the PS 102–PS 775 combination. The equilibrium values of both combinations are lower than that for the individual adsorption of the displacer molecules. Moreover, they are lower than those for adsorption of the corresponding mixtures.

The adsorption time dependence of the thickness of the adsorbed layer is shown in Figure 4b for the displacements of PS 102 and PS 422 by PS 775. The thickness of the adsorbed layer for displacer molecules is indicated by a dashed line in the figure. The thickness of the adsorbed layer for both combinations increases with adsorption time and attains the equilibrium value. The PS 102–PS 775 combination can attain the equilibrium thickness of the adsorbed layer earlier than the PS 422–PS 775 combination. The equilibrium thickness of the adsorbed layer for the PS 422–PS 775 combination is much larger than that for the PS 102–PS 775 combination and is also almost equal to the equilibrium value for the individual adsorption of the displcer polymer.

After the attainment of equilibrium, both the equilibrium adsorbance and the thickness of the adsorbed layer were unchanged after a week. The equilibrium adsorbance and thickness for the PS 102–PS 775 combination is lower than those for the PS 422–PS 775 combination. This is so even beyond the expectation that the small molecules adsorbed (PS 102) should be desorbed from the surface more easily than the large molecules adsorbed (PS 422). The reason for this is that the equilibrium thickness of the adsorbed layer of PS 102 is much smaller than the diameter of the polymer chain in the solution in comparison with PS 422 molecules (Table II). In other words, desorption of PS 102 molecules from the surface is more difficult than desorption of PS 422 molecules due to a relatively flattened conformation. Therefore, displacement of small molecules by large molecules at the Θ condition is not complete. Such experimental results coincide with the previous observation[5] of displacement adsorption of PS molecules on a silica surface at the Θ condition.

Conclusion

Ellipsometry has been applied to competitive absorption and displacement adsorption of PS molecules at the Θ condition. Apparently, if we judge from only data on the thickness of the adsorbed layer, complete preferential adsorption of large molecules over small molecules takes place. Adsorbance, however, is clearly lower than that of large PS molecules alone. Thus, it appears that the segment density distribution far from the surface of the large polymer chain, which contributes to the thickness measurement, can be detected. In the case of displacement adsorption, small PS molecules are not completely displaced by large ones. The degree of displacement depends strongly on the molecular weight of the previously adsorbed PS molecules. It is therefore concluded that in *both competitive adsorption and displacement adsorption* a complete preference for larger molecular weight adsorption does not occur at the Θ condition.

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