Notes

Adsorption of Polystyrenes on a Silica Surface from Binary Mixed Solvents: Comparison of the Displacement by the Same Solvents

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Introduction

Displacement of preadsorbed polymer chains at a solid–liquid interface by addition of low molecular weight displacer molecules is a clue to estimating the segmental adsorption free energy[1–3] and is strongly related to adsorption chromatography.[4] The desorption behavior of preadsorbed polymer chains by displacer molecules is described as follows: the displacer molecules occupy the surface sites with a replacement of the preadsorbed polymer segments. This replacement proceeds until complete desorption of the preadsorbed polymer chains at a given concentration of displacer molecules, which is designated as the critical concentration of the displacer molecules, above which polymer adsorption does not take place. This process is considered as a competitive adsorption between polymer segments and displacer molecules at the solid–liquid interface and is also regarded as the adsorption behavior of polymer chains on the surface from a binary mixture of displacer and solvent molecules. However, there is no comprehensive study comparing the displacement of preadsorbed polymer chains with the individual adsorption in the same concentrations of the displacer molecules.

In general, polymer adsorption should be controlled by the contribution of all polymer–solvent, polymer–surface, and solvent–surface interactions. This general idea could be accepted for polymer adsorption in mixed solvents. In mixed solvents, competition between a polymer segment and a highly adsorptive solvent (displacer molecule) should strongly influence adsorption behavior, and then the adsorption mechanism will be more complex than that from a single solvent. In addition, changes in the components in the mixed solvents induce a change in the solvent power of the polymer chains. Therefore, understanding adsorption of polymer chains in mixed solvents will allow one to tentatively discriminate between solvent competition and solvent power.

In our previous paper[2] we reported the displacement of polystyrenes (PS) by various displacer molecules on silica surfaces in Θ and good solvents. We found that the critical concentration of the displacer molecules is independent of PS molecular weight under the respective solvent conditions. We estimated the segmental adsorption free energy parameter by comparison with the theory of Cohen Stuart, Fleer, and Scheutjens.[1] However, a comparison between the displacement and the individual adsorption of a polymer from binary mixtures of displacer and solvent molecules was not performed.

The aim of this paper is to confirm the reversibility of the displacement of preadsorbed PS by decreasing and increasing the concentrations of the displacer molecules and to compare the remaining amounts in the displacement with the adsorbed amounts from the binary mixture of displacer and solvent molecules at the silica surface for two PS samples.

Experimental Section

Materials. Two PS samples with narrow molecular weight distributions having $M_w = 355 \times 10^3$ (PS-355) and $M_w = 706 \times 10^3$ (PS-706) were purchased from Tosoh Co.

Cyclohexane and carbon tetrachloride were used as solvents. Cyclohexane was spectrograde quality, and carbon tetrachloride was distilled twice before use. Benzene and dioxane displacer molecules were spectrograde quality. Spectrograde quality solvents were used without further purification.

The silica used for the adsorbent was Aerosil 130 (Degussa AG, West Germany) and was purified by the method previously described.[5]

Displacement of PS by Displacer Molecules. The procedure for the displacement of preadsorbed PS on the silica surface was similar to that described in the previous paper.[2] We selected the dosage concentration, C_0, for the respective PS molecules as follows: $C_0 = 0.3$ g/100 mL for PS-355 and 0.4 g/100 mL for PS-706 in cyclohexane; $C_0 = 0.16$ g/100 mL for PS-355 and 0.2 g/100 mL for PS-706 in carbon tetrachloride. These concentrations are well within the plateau regions of the individual adsorption isotherms.[6]

For some systems after the displacement experiment, the addition of the solvent or the displacer molecules into the systems, i.e., a decrease or an increase in the concentration of the displacer molecules, induces adsorption, which we designate as the readsorption experiment in order to examine the reversibility of the displacement. After addition of the solvent or the displacer molecules, the mixture, contained in a stoppered centrifugation glass tube, was stirred with a magnetic chip at 35 °C in an incubator for 24 h. Determination of the PS concentration in the readsorption experiment was similar to the procedure described below for the adsorption of PS from the binary mixed solvents.

Adsorption of PS from the Binary Mixed Solvents. PS was dissolved in a binary mixture of displacer and solvent molecules. Twenty milliliters of a PS solution with the same C_0 as in the displacement adsorption was mixed with 0.16 g of Aerosil 130 silica in a stoppered centrifugation glass tube. The mixture was gently stirred by a magnetic chip for 24 h to attain equilibrium at 35 °C in the incubator. The silica suspensions were centrifuged at 3000 rpm for 10 min with a Kubota KB-200B centrifuge to sediment the silica. The supernatant was then carefully withdrawn. The PS concentration in the supernatant, i.e., the equilibrium bulk concentration of PS, C_p, was determined as follows: after evaporation of the solvent mixture, the residue was dried under vacuum and then dissolved in a definite amount of carbon tetrachloride or dioxane; the C_p in carbon tetrachloride was determined with a Nihon Bunko FT-IR-3 spectrometer at a characteristic wavenumber of 3027 cm^{-1}, and the C_p in dioxane was determined with an Ohstuka Denshi System 77 UV spectrometer at a characteristic wavelength of 264 nm. To confirm the reproducibility of the experiments, we performed at least two measurements for the same concentrations. The errors in both the remaining amounts and the adsorbed amounts of PS, A_{re}, are less than 5%.

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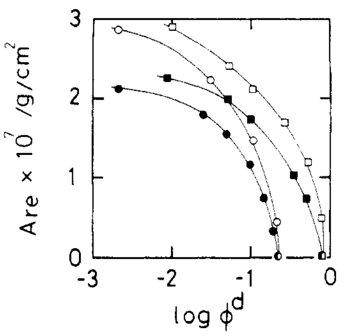

Figure 1. Displacement isotherms of PS-706 and PS-355 for benzene and dioxane in cyclohexane: (□) PS-706 for benzene; (■) PS-355 for benzene; (○) PS-706 for dioxane; (●) PS-355 for dioxane.

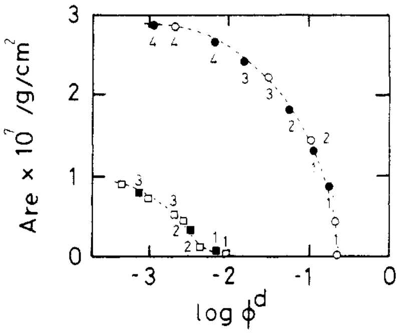

Figure 2. Comparison between the displacement and readsorption experiments for PS-706 in cyclohexane and carbon tetrachloride: (○, ●) displacement and readsorption experiments for dioxane in cyclohexane; (□, ■) displacement and readsorption experiments for dioxane in carbon tetrachloride. The numbers indicate the corresponding displacement and readsorption experiments. The primes on 1 and 4 indicate that the definite content of dioxane is further added after the content of dioxane in the mixture is reduced by the addition of the cyclohexane solvent.

Results and Discussion

Figure 1 shows the displacement isotherms of PS-355 and PS-706, i.e., a plot of remaining amount for the preadsorbed PS versus the logarithm of the volume fraction, ϕ^d, of the displacer molecules. The volume fraction of displacer in the solvent mixture after displacement should be less due to the transfer of the displacer to the silica surface. In this paper, the term ϕ^d indicates the dosage volume fraction of the displacer.

The displacement isotherms for both displacer molecules, in which the remaining amount of PS rather steeply decreases and eventually becomes zero, are similar in their shapes. The shape of these displacement isotherms corresponds to a type I isotherm, which had been designated in a previous study.[2] We noticed that the critical concentrations of the displacer molecules are independent of molecular weight and their magnitude is almost equal to that in the previous paper[2] for both displacer molecules.

The data of the readsorption experiment by decreasing or increasing dioxane content in cyclohexane and carbon tetrachloride for PS-706 are denoted by filled circles and filled rectangles in Figure 2, respectively. They are well fitted on the curve of the corresponding displacement isotherms (open circles and open rectangles). Decreasing dioxane content should induce a reduction of the solvent power and the number of silanol groups occupied by dioxane molecules. In contrast, if the content of dioxane increases, the solvent power increases and the adsorbed amount of PS decreases. These results show that the displacement of the preadsorbed PS by the displacer molecules is reversible.

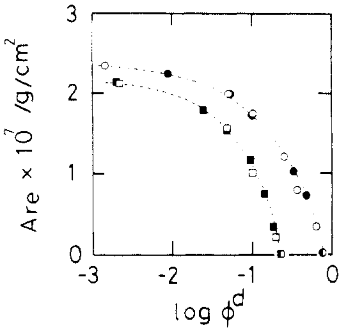

Figure 3. Comparison between the displacement isotherms and the adsorbed amounts of PS-355 from the binary mixture of displacer and cyclohexane: (●) displacement by benzene; (○) adsorbed amounts from benzene mixture; (■) displacement by dioxane; (□) adsorbed amounts from dioxane mixture.

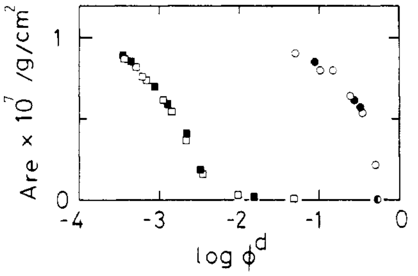

Figure 4. Comparison between the displacement isotherms and the adsorbed amounts of PS-355 from the binary mixture of displacer and carbon tetrachloride: (●) displacement by benzene; (○) adsorbed amounts from benzene mixture; (■) displacement by dioxane; (□) adsorbed amounts from dioxane mixture.

Thus, the reversibility of the displacement process has been certainly confirmed by the readsorption experiments. This confirmation provides justification for the comparison of the displacement of preadsorbed PS by the displacer molecules with the theory of Cohen Stuart et al.[1] in our previous work[2] since their theory is established on the basis of the reversibility of the displacement of polymer chains by the addition of the displacer molecules. Ellerstein and Ullman[7] also reported that the readsorption and desorption of poly(methyl methacrylate) (PMMA) on an iron surface was apparently reversible upon changing the components of benzene and acetonitrile (displacer molecule) during adsorption.

In addition, the displacement isotherm for carbon tetrachloride in Figure 2 deviates upward at the higher dioxane content and has a tail. We have designated such a isotherm as a type II isotherm in the previous paper,[2] which occurs during displacement by a strong displacer.[1,8] This isotherm is not different from those previously reported.[2]

Figure 3 shows a plot of adsorbed amounts of PS-355 in binary mixed solvents of cyclohexane and benzene or dioxane versus the logarithm of the volume fraction of displacer molecules, together with the corresponding displacement isotherm curves. The shapes of the adsorption isotherms in the binary mixed solvent are similar to that of the displacement isotherm over the entire range of the displacer contents. We noticed that the concentrations of zero adsorption in the mixed solvents, that is, the points extrapolated to zero adsorbed amount of PS, coincide with the critical concentrations of the displacer molecules for the respective displacement isotherms.

On the other hand, the adsorption data of PS-355 in mixed solvents of carbon tetrachloride and benzene or dioxane are shown in Figure 4. The data points are fitted on the respective displacement isotherms displayed by the filled circles and rectangles. The benzene concentration of zero adsorption in the mixed solvent agrees with the critical concentration. Thus, it is found that the remaining amounts in the displacement are coincident with the adsorbed amounts from the binary mixtures at the same contents of the displacer molecules in the equilibrium state: the experimental time of 24 h is long enough to reach an equilibrium since a kinetic study[9] shows that the displacement and adsorption processes were in their equilibrium states within 1 h and 10 h, respectively.

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Registry No. PS, 9003-53-6; benzene, 71-43-2; dioxane, 123-91-1; Aerosil 130, 7631-86-9.