Effect of Surface Geometry on Polymer Adsorption. 3. Competitive Adsorption at the Θ Point

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ABSTRACT: Adsorption isotherms of binary mixtures of polystyrenes (PS) with narrow molecular weight distributions and a polydisperse PS on porous and nonporous silica surfaces have been measured in cyclohexane. For the adsorption of the binary mixture on the porous silica, when both PS chains can penetrate into the pores without significant deformation, a complete preferential adsorption of the large PS chain over the small one is observed at the plateau in the adsorption isotherm and the adsorption isotherm has a rounded shape. By contrast, when the large PS component in the mixture adsorbs more than the small PS component at the plateau, i.e., incomplete preferential adsorption, the total amount adsorbed at the plateau is larger than that for the complete preferential adsorption. Furthermore, its magnitude is the same as for the adsorption of the corresponding mixture on the nonporous silica as well as the adsorption of polydisperse PS on the porous and nonporous silicas.

Introduction

Many polydisperse polymers and heterogeneous and porous surfaces are widely used as adsorbates and adsorbents, respectively, in many fields, such as oil recovery, chromatography, suspension, dispersion, coating, and flocculation.[1-3] Nevertheless, it is important to understand the adsorption behavior of mixtures of monodisperse polymers and polydisperse polymers to heterogeneous and porous surfaces; there are few systematic experiments.

Cohen Stuart, Scheutjens, and Fleer[4] theoretically showed a preferential adsorption of a large molecule over a small molecule at smooth surfaces in terms of the polydispersity of samples. Their model was quantitatively compared with several experimental results for adsorption of monodisperse polymer mixtures and polydisperse polymers[4-7] at smooth surfaces, and a good agreement was obtained.

For polymer adsorption on rough surfaces, the introduction of the concept of the fractal geometry has led to the development of methods for dealing with physical problems which involve nontrivial geometries in terms of the fractal dimension.[8] Farin and Avnir[9] have deduced the sample accessibility scaling between the interaction of adsorbates and adsorbents and molecular size, and they obtained the fractal dimension of various adsorbents from the plots of the adsorbed amount against the molecular weight. Moreover, there are several theoretical treatments by using various models, such as Edwards' propagation approach,[10-12] the effective surface model,[13] the renormalization group calculations,[14] the Monte Carlo simulations,[15,16] and the scaling idea,[17] but comparisons of these treatments with the experimental results have not been sufficiently performed.

Furusawa and his co-workers[18-20] have reported the competitive and displacement adsorption of binary and ternary mixtures of monodisperse polystyrene (PS) samples onto well-characterized porous silicas. In their experimental results, it was noticed that there was not observed any complete preferential adsorption of large PS over small PS, where the total amount adsorbed at the plateau, consisting of the large and small PS, is equal to the plateau adsorbed amount of the large PS for the individual adsorption.

Very recently, we have investigated the surface geometry effect on polymer adsorpion of PS with narrow molecular weight distributions in terms of kinetics and the adsorption isotherm.[21,22] Adsorption behavior for the porous silica surfaces was strongly influenced by the surface roughness: when the ratio of the pore size in the silica to twice the radius of gyration of a PS chain in a bulk solution was less than 2, the amounts adsorbed at the plateau were less than those for the nonporous silica.

In this paper, we examine adsorption isotherms for competitive adsorption of binary mixtures of monodisperse PS as well as polydisperse PS onto well-characterized porous and nonporous silica surfaces in cyclohexane. From these experiments, it is possible to make clear the difference in adsorption behavior of polymers with discontinuous and continuous molecular weight distributions. Moreover, we compare these experiments with the results of Furusawa et al. to explain how this work differs from theirs.

Experimental Section

Materials. Three polystyrenes (PS) with narrow molecular weight distributions, having MW = 37.9×10^3 (PS-38), 96.4×10^3 (PS-96), and 355×10^3 (PS-355), were purchased from Tosoh Co. One polydisperse PS (PS-126) was prepared by radical polymerization in benzene with an initiator of AIBN. Its molecular weight of 126×10^3 was determined from the intrinsic viscosity measurements in benzene at 25 °C.[23] The polydispersities of the PS-38, PS-96, PS-355, and PS-126 were determined to be 1.01, 1.01, 1.02, and 4.26, respectively, using a Toyo Soda HLC-802 A gel permeation chromatography (GPC) instrument with a UV-8 Model II detector. The wavelength was 254 nm. The eluent used was tetrahydrofuran (THF).

Cyclohexane used as a solvent for polymer adsorption experiments and dioxane used as a solvent for determination of the PS concentration in the supernatant by UV spectroscopy were of spectrograde quality and were used without further purification. THF used as a solvent for PS and an eluent for GPC measurements was of guaranteed reagent grade and used without further purification.

The adsorbents used were a porous microbead (100-200 mesh) silica gel (MB-800; Fuji-David Chemical Co., Kasugai, Japan) and a nonporous Aerosil 130 silica (Japan Aerosil Co., Yokkaichi, Japan). The surface area (S) of 45 m^2/g and the average pore diameter (d) of 81.3 nm for the MB-800 were determined from N_2 adsorption and a mercury porosimeter, respectively. The latter method also characterizes the pore size distribution. From the pore distribution, we characterized the breadth and the skewness of the distributions by $D(90)$ and $D(10)$: 90% of the pore diameters are larger than the value of $D(90)$ = 75 nm and 10% are larger than that of $D(10)$ = 112 nm. Thus, the size

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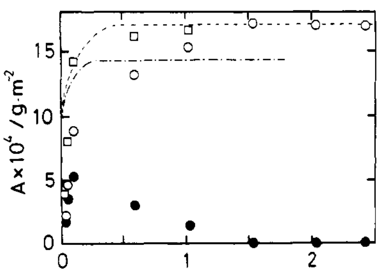

Figure 1. Adsorption of a mixture of PS-38 and PS-96 for the MB-800 silica: total adsorbed amount (□); adsorbed amount of PS-38 (●); adsorbed amount of PS-96 (○). Dashed–dotted and dashed lines indicate the adsorption isotherms of the individual adsorptions of PS-38 and PS-96 for the MB-800, respectively.

distribution is relatively narrow. The purification and drying methods were the same as described in our previous papers.[21,22]

From the manufacturer of the Aerosil 130, the average particle diameter is 16 nm, the surface area is 141 m^2/g, and there are three silanol groups per 1 nm^2. The purification of the Aerosil 130 silica was the same as described previously.[24]

Adsorption of PS. Individual PS and 1:1 (w/w) mixtures of PS-38/PS-96, PS-96/PS-355, and PS-38/PS-355 were dissolved in cyclohexane to desired concentrations. The mixture in the glass flask was mechanically shaken at a constant speed, usually 100 rpm in a Yamato BT-23 water incubator attached with a shaker for 24 h to determine adsorption isotherms. The temperature of the water in the incubator was controlled to 35 ± 0.1 °C.

An 0.087-g sample of the Aerosil 130 silica was mixed 20 mL of polymer solution in a stoppered glass centrifugation tube. After equilibration by stirring with a magnetic stirrer chip at 35 °C in an air incubator, the supernatant was separated to sediment the silicas by using a Kubota KB-200 B centrifuge.

The amount of PS adsorbed at the silica surfaces was determined from the difference in the concentrations between the dosage (C_o) and the supernatant (C_p) and from the added silica amount. The value of C_p was determined as follows: after the evaporation of the solvent, the residue was dried in a vacuum oven at room temperature for 24 h and then dissolved in a fixed amount of dioxane, and finally C_p was measured using an Ohstuka Denshi System 77 UV spectrometer. The intensities of the dioxane solutions were measured at $\lambda = 266$ nm, where the extinction coefficient was 76.5 L mol^{-1} cm^{-1}. There was one reason why we took such a complex procedure to determine the C_p: there is the possibility that a cyclohexane/PS solution would be turbid at ambient temperature since its Θ point is 35 °C.

On the other hand, determination of the composition of the supernatant was carried out using gel chromatography as follows: after evaporation of the solvent and drying the residue as described above, it was dissolved in THF, and finally the THF solution was analyzed. These experimental techniques are almost the same as described in a previous paper.[22]

Results and Discussion

Adsorption of Mixtures. Figure 1 displays the total adsorbed amount of the PS-38/PS-96 mixture and the adsorbed amounts of each component in the mixture as a function of the equilibrium concentration, C_p, of the mixture. In the figure the adsorption isotherms of the individual adsorptions of PS-38 and PS-96 are also shown by dashed–dotted and dashed lines, respectively.[21,22] A comparison of the chain diameter of an isolated PS chain in cyclohexane, which is calculated from the relation between the radius of gyration and the molecular weight determined by Berry,[25] with the average pore size (*d*) shows that both PS-38 and PS-96 molecules can easily penetrate into the pores in the MB-800. Since there is no steric effect for both PS molecules due to the pore size, the plateau adsorbed amount below MW = 100 × 10^3 for the MB-800 silica is almost similar to that for the Aerosil 130 silica.[22] Furthermore, a complete preferential adsorption of PS-96 over PS-38 is observed at the plateau region, and its driving force is attributed to the conformational entropy loss of the small PS chain: changes in the conformation of the smaller PS chains due to adsorption are much more dramatic than the larger ones and hence prevent adsorption of the smaller species.[26]

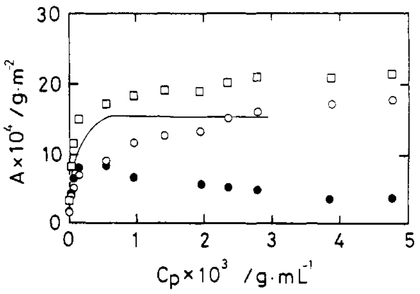

Figure 2. Adsorption isotherms of a mixture of PS-38 and PS-355 for the MB-800 silica: total adsorbed amount (□); adsorbed amount of PS-38 (●); adsorbed amount of PS-355 (○). The solid line indicates the adsorption isotherm of the individual adsorption of PS-355 for the MB-800. The adsorption isotherm of the individual adsorption of PS-38 is almost the same as that of PS-355.

The adsorption isotherms of the mixture are of rounded shape, consisting of the following three regions: (1) an initial steeply rising part where all PS-96 chains adsorb, whereas PS-38 chains only remain in the supernatant; (2) a region in which $0.05 < C_p < 0.15$ g/100 mL where both PS components remain in the supernatant; (3) a region above $C_p = 0.15$ g/100 mL where only PS-96 chains adsorb and its adsorbed amount attains the plateau value, and it is in agreement with that for the individual adsorption of PS-96. Our isotherm is similar in shape to the results of Furusawa et al.,[18] where there is not observed a complete preferential adsorption, and it also agrees with our experimental results for the complete preferential adsorption for the porous silica surface in carbon tetrachloride.[22]

Figure 2 shows an adsorption isotherm of the mixture of PS-38 and PS-355, together with the adsorbed amount of each component in the mixture and the individual adsorption isotherms[21,22] of PS-38 and PS-355. As seen from Figures 1 and 2, the adsorption isotherm of the total amounts for the PS-38/PS-355 mixture is different in shape from that for the PS-38/PS-96 mixture, and the discontinuous pattern is observed for a region in which $0.2 < C_p < 0.3$ g/100 mL. Similar results were first predicted by the model of Cohen Stuart, Scheutjens, and Fleer[3] and experimentally observed.[3-5]

The adsorption isotherms of the respective components in the mixture are different from those of the mixture of PS-38 and PS-96: especially in the low concentration region up to $C_p = 0.01$ g/100 mL, the small size component adsorbs more than the large one due to diffusion-limited adsorption and preferential adsorption of the large component over the small one occurs with an increase in C_p. Such a preferential adsorption behavior is governed by the entropy loss of the small PS chain.[26] These results are different from those of Furusawa et al.,[18] who reported that the isotherm is one of rounded shape and the adsorbed layer consists more of the adsorbed amount of the large PS than the small one in the entire concentration range when both PS chains have smaller diameters in bulk solution than the pore size in the silica.

The adsorption isotherms for the individual adsorptions of PS-38 and PS-355 are almost the same, and the amount adsorbed at the plateau for PS-355 is less than that for the

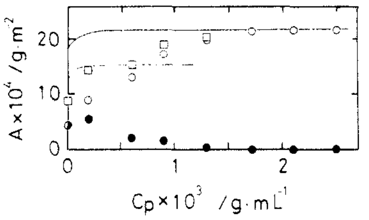

Figure 3. Adsorption isotherm of a mixture of PS-38 and PS-355 for the Aerosil 130 silica. The symbols are the same as in Figure 2. Dashed-dotted and solid lines indicate the adsorption isotherms of the individual adsorptions of PS-38 and PS-355 for the Aerosil 130 silica, respectively.

Aerosil 130.[22] This indicates that PS-355 chains cannot easily penetrate into the pores in the MB-800 silicas; nevertheless, the average pore size is twice as large as the chain diameter. However, a preferential adsorption of PS-355 over PS-38 chains should stem from the difference in the molecular size. Moreover, adsorption of PS-355 chains in the mixture is enhanced; namely, the amount adsorbed at the plateau for PS-355 in the mixture is larger than that for the individual adsorption of PS-355. As a result, the total amount adsorbed at the plateau region is larger than that for the mixture of PS-38 and PS-96. This complex adsorption phenomenon is difficult to explain at the moment. However, such an enhanced adsorption may be related to an easy entanglement of PS chains in the adsorbed layer under Θ solvent conditions because of no excluded volume effect. Moreover, the adsorption behavior of the same mixture for the Aerosil 130 and that of the polydisperse PS for both the MB-800 and the Aerosil 130 silicas, which will be described in the following section, may lead to a clue to quantitatively understanding such a complex adsorption phenomenon.

Figure 3 displays an adsorption isotherm of the mixture of PS-38 and PS-355 for the Aerosil silica, together with adsorbed amounts of each component in the mixture as well as the adsorption isotherm[27] of the individual adsorptions for each component in the mixture. Since the mean particle size (16 nm) of a particle of the Aerosil 130 silica is comparable with the diameter of an isolated PS chain, PS chains can adsorb simultaneously some particles, and it leads to a sort of bridging flocculation of silica particles. At the Θ point the higher adsorbed amount is obtained since the polymer–particle interaction is relatively strong.[21] Thus, it is expected that there is a trend toward more compact flocs with closer particle–particle separations, which results in fractal-type aggregates. The fact that the silica slurry in cyclohexane becomes turbid by adding the PS/cyclohexane solution is positive evidence regarding the flocculation of silica particles. Moreover, a small-angle neutron scattering experiment[28] and computer simulation[29] indicated the short-range structure of flocs formed by polymer bridging of monodisperse particles. As a result, it is not too much to say that PS chains adsorb on physically rough surfaces, which are induced by the flocculation of silica particles.

As seen from Figure 3 the shape of the isotherm of the mixture and the total amount adsorbed at the plateau in the mixture are similar to those for the MB-800 silica. However, the discontinuous pattern of the isotherm is more clearly observed at a region in which $0.05 < C_p < 0.15$ g/100 mL, and a complete preferential adsorption of PS-355 over PS-38 is observed. This shows that there is less steric hindrance for the preferential adsorption on the aggregated Aerosil silica particles than that for the MB-800. Similar results were observed for the competitive adsorption of the binary mixtures of monodisperse PS on the Aerosil 130 silica in carbon tetrachloride.[6] Moreover, the total amount adsorbed at the plateau in the mixture agrees with that for the individual adsorption of PS-355.

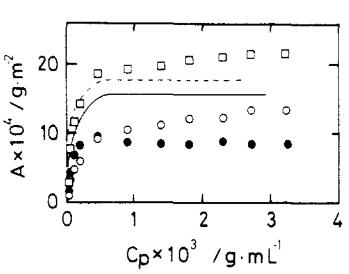

Figure 4. Adsorption isotherm of a mixture of PS-96 and PS-355 for the MB-800 silica: total adsorbed amount (□); adsorbed amount of PS-96 (●); adsorbed amount of PS-355 (○). Dashed and solid lines are the same as in Figures 1 and 2, respectively.

In Figure 4, an adsorption isotherm of the mixture of PS-96 and PS-355 for the MB-800 is displayed, together with the adsorbed amounts of each component in the mixture and the adsorption isotherm[21,22] of the individual adsorptions for each component in the mixture. The adsorption behavior of the mixture is similar to that of the PS-38/PS-355 mixture: in the low concentration region up to $C_p = 0.05$ g/100 mL the adsorbed amount of PS-96 is larger than that of PS-355, the concentration region where the preferential adsorption of the small PS over the large one occurs is relatively wider than that for the PS-38/PS-355 mixture, and finally with an increase in C_p PS-355 adsorbs more than PS-96 and at the plateau the amounts of both PS are less than those for the respective individual adsorptions. However, the total amount adsorbed at the plateau is larger than that for the individual adsorption, and its absolute value is almost the same as the mixture of PS-38 and PS-355. Thus, this preferential adsorption is dominated by the molecular size and is not related with the plateau adsorbed amounts of each component in the mixture for the individual adsorptions.

Such a preferential adsorption behavior is in disagreement with that in carbon tetrachloride,[22] where PS-96 chains adsorb more than PS-355 chains in the entire concentration range and the total amount adsorbed at the plateau is almost equal to the individual adsorption of PS-96. This reverse preferential adsorption in a good solvent seems difficult to explain in terms of the conformational entropy loss adopted for an explanation of preferential adsorption in the Θ solvent, and it should be mainly governed by the spatial effect: the larger PS chains are forced to more significantly deform than the smaller ones in order to penetrate into the pores. Furthermore, since carbon tetrachloride is a good solvent for PS chains, repulsion of polymer chains owing to the excluded volume effect plays a role in adsorption. However, the respective amounts adsorbed at the plateau are less than the individual adsorptions, and this behavior is similar to that in carbon tetrachloride.[22]

As mentioned above, several models for polymer adsorption on physically heterogeneous surfaces have been proposed, and they have led to a conclusion that the geometrical roughness increases the tendency for a polymer to adsorb. At the moment, however, it seems difficult to discuss our preferential adsorption experiments in terms of these theoretical treatments.

Adsorption of Polydisperse PS. Figure 5 displays adsorption isotherms of PS-126 for the MB-800 and the Aerosil 130 silicas. The adsorption isotherm for the MB-800 is different in shape from those of the PS-38/PS-96, PS-38/PS355, and PS-96/PS-355 mixtures for the MB-800; the latter isotherm has a round-shaped isotherm, such as is often observed for adsorption of polydisperse polymers

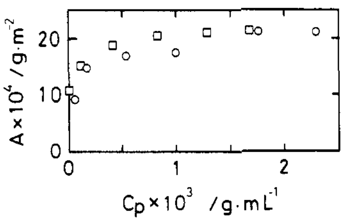

Figure 5. Adsorption isotherms of PS-126 for the MB-800 (○) and the Aerosil 130 (□) silicas.

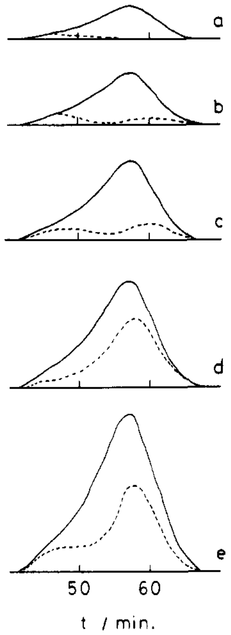

Figure 6. GPC chromatograms of PS-126 solution before (—) and after (- - -) adsorption on the MB-800 silica for various initial added concentrations (C_0): a, C_0 = 0.06 g/100 mL; b, C_0 = 0.10 g/100 mL; c, C_0 = 0.15 g/100 mL; d, C_0 = 0.20 g/100 mL; e, C_0 = 0.30 g/100 mL.

at smooth surfaces. This is attributed to less steric hindrance for the aggregated Aerosil silica than the MB-800. The amount adsorbed at the plateau is the same, irrespective of the silica, and its absolute value is in agreement with those of the PS-38/PS-355 mixture for the MB-800 and Aerosil 130 silicas and that of the PS-96/PS-355 mixture for th MB-800 silica. Thus, such a plateau adsorbed amount, irrespective of both the surface roughness and the polydispersity of PS, seems to attain the limiting plateau, where the available adsorption surface areas of the porous silicas are most effectively used.

It is interesting to understand what parts preferentially adsorb in the polydisperse PS chains from GPC chromatograms. In Figure 6, GPC chromatograms of PS-126 in the supernatant solutions before and after adsorption on the MB-800 are displayed by solid and dashed lines, respectively. At lower concentration, small components preferentially adsorb, with an increase in concentration the small components are excluded from the silica surface, whereas adsorption of the middle components proceeds with little adsorption of larger components, and finally relatively large components preferentially adsorb over the small components. Such a preferential adsorption behavior is in qualitative agreement with that for the adsorption of mixtures of monodisperse polymers described above, and it is clear evidence for a sieve effect of polymer adsorption.

On the other hand, GPC chromatograms of PS-126 in the supernatant solutions before and after adsorption on the Aerosil 130 silica are shown by solid and dashed lines in Figure 7, respectively. For the Aerosil 130 silica large

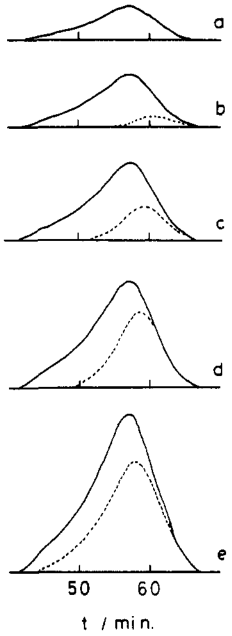

Figure 7. GPC chromatograms of PS-126 solution before and after adsorption on the Aerosil 130 silica for various initial concentrations. Symbols are the same as in Figure 6.

components preferentially adsorb over small ones at every concentration. Similar results were obtained by several researchers.[30]

Conclusions

For the adsorption of the binary mixtures of monodisperse PS polymers at the porous silica surface, preferential adsorption of the large PS chain over the small one is governed by the conformational entropy loss of the small chain, whereas the reverse preferential adsorption is dominated by the pore size effect; i.e., the small chain can easily penetrate into the pores in the silica, and the large one must significantly deform for penetration into the pores. When the large PS chains adsorb more than the small ones, i.e., incomplete preferential adsorption, the amount adsorbed at the plateau region in the adsorption isotherm is somewhat larger than that for the individual adsorptions of the respective polymer chains and also that for the complete preferential adsorption, where the large chain only adsorbs. Furthermore, its magnitude is equal to the amount adsorbed at the plateau for the adsorption of the binary mixture on the smooth surface and that for the adsorption of the polydisperse sample on the rough and smooth surfaces.

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