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Competitive and Displacement Adsorption of Polystyrene and Poly(ethylene oxide)

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ABSTRACT: Competitive and displacement adsorption of polystyrene (PS) and poly(ethylene oxide) (PEO) with narrow molecular weight distributions onto a nonporous silica (Aerosil 130) from carbon tetrachloride solutions at 35 °C was studied by IR and UV spectroscopy. The fraction of silanol groups occupied by styrene or ethylene oxide units was determined from the shift in the IR frequency of the silanol groups. In competitive adsorption, PEO absorbs preferentially over PS, and the preferential adsorption of large molecules over small molecules occurs even in the presence of different species. PS molecules are completely desorbed from the silica surface by addition of PEO (displacer). The degree of displacement of PS by PEO depends on the fraction of styrene units directly attached to the silanol groups as well as on the molecular weights of PS and PEO.

Introduction

Several studies have been reported on competitive and displacement adsorption of different sizes of molecules of a polymer from solution onto a solid.[1-10] Large molecules are in preference to adsorbed small ones, and initially adsorbed small molecules are displaced by larger ones. In an investigation of exchange and competitive adsorption between two chemically different polymers, poly(methyl methacrylate) (PMMA) and polystyrene (PS), it was found that PMMA was preferentially adsorbed, and PS was displaced by PMMA.[11] Similar adsorption studies have been reported[12,13] but they used only one pair of chemically different polymers with polydispersity.

The aim of this paper is to present experimental results on the competitive and displacement adsorption of poly(ethylene oxides) and polystyrenes onto nonporous silica from their carbon tetrachloride solutions at 35 °C. Each sample of both polymers had a narrow molecular weight distribution. Polymer concentrations in solution after adsorption were determined by IR and UV spectroscopy.

Experimental Section

Materials. Samples of PS and PEO were purchased from Toyo Soda Co. Their characteristics from the manufacturer are listed in Table I.

Table I
Characteristics of Polystyrenes (PS) and Poly(ethylene oxides) (PEO)

sample	$M_w \times 10^{-3}$	M_w/M_n
PS-102	102	1.02
PS-775	775	1.04
PS-3840	3840	1.04
PEO-39	39	1.07
PEO-86	86	1.02
PEO-252	252	1.04
PEO-660	660	1.04

The nonporous Aerosil 130 silica (Degussa AG, West Germany) was used as the adsorbent after being cleaned by the procedure described previously.[10,14,15]

Carbon tetrachloride and dioxane were distilled twice just before use.

Adsorption of Polymers. Adsorption isotherms of the PEO samples were determined at 35 °C in 50-mL stoppered glass centrifuge tubes containing 0.16 g of silica and 20 mL of a CCl_4 solution PEO of known concentration C_0. The tube was agitated in a cabinet controlled at 35 ± 0.1 °C for 24 h. The suspension was then centrifuged, and the bulk concentration C_p of unadsorbed PEO remaining in the supernatant solution was determined from its C–H stretching band in the IR at 2900 cm^{-1}.[16]

Competitive adsorption experiments on PS–PEO mixtures (1:1 (w/w)) were performed in the same way. The equilibrium concentration of PEO in the supernatant solution after adsorption was measured by using the IR band of the C–O–C valence vibration at 1107 cm^{-1}.[16] The concentration of PS in the supernatant was determined by evaporating the carbon tetrachloride, drying the residue under vacuum, dissolving it in a definite amount of dioxane, and determining the concentration by UV spectroscopy.

Displacement Adsorption of PS by PEO. PS molecules were adsorbed onto silica (0.16 g) from 20 mL of carbon tetrachloride solution. The PS concentration (0.2 g/100 mL) was chosen to be in the plateau region of PS adsorption isotherms determined previously.[10] After agitation for 24 h at 35 °C and centrifugation, 10 mL of the supernatant solution was withdrawn, and 10 mL of a carbon tetrachloride PEO solution of known concentration was added. The mixture was agitated again for 24 h at 35 °C. After centrifugation, the concentrations of PEO and PS in the supernatant solutions were determined by the spectroscopic procedure described above.

The IR spectra of the sedimented silicas were determined by the method described previously.[10,14,15]

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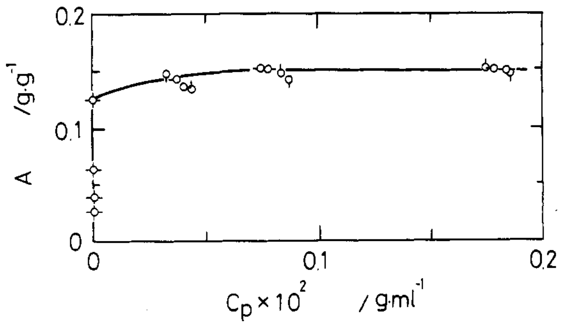

Figure 1. Adsorption isotherms of poly(ethylene oxides) on silica from carbon tetrachloride at 35 °C: (ϙ) PEO-39; (-o) PEO-86; (o-) PEO-252; (ȯ) PEO-660.

Results and Discussion

Adsorption of PEO. Typical equilibrium adsorption isotherms of PEO are shown in Figure 1. The isotherms rise steeply with increasing concentration C_p of the supernatant solution and reach a plateau. The adsorption isotherms are of the high-affinity type, which is characteristic for the adsorption of monodisperse polymers. PEO molecules completely adsorb on the silica surface below the initial added concentration $C_0 = 0.1$ g/100 mL for all samples. The plateau values of adsorbance at the highest C_p are almost independent of PEO molecular weight.

The differential IR spectra between the supernatant solution and the silica on which PEO was adsorbed show two characteristic bands: a band at 3675 cm^{-1} due to the free silanol groups and another band at 3300 cm^{-1} due to the hydrogen bond between silanol and the oxygen of the adsorbed PEO. The peak at 3300 cm^{-1} is usually strong and broad. The positions of the two bands are in good agreement with the previous data of Killmann, Eisenlauer, and Korn.[17] The position of the peak at 3300 cm^{-1} is independent of the molecular weight of PEO.

The extinction coefficient at 3675 cm^{-1} was previously determined to be 69.2 L mol^{-1} cm^{-1}.[10] The extinction coefficient at 3300 cm^{-1} was determined to be 56.5 L mol^{-1} cm^{-1} from an infrared spectrum in which the peak at 3675 cm^{-1} was eliminated by fully covering the silanol groups with adsorbed PEO. The value of the extinction coefficient at 3300 cm^{-1} is almost independent of PEO meolecular weight.

The fraction θ of silanol groups occupied by the ether oxygens of PEO was determined in the same manner as reported previously[10,14,15]

$$\theta = (C_s - C_{OH})/C_s \qquad (1)$$

where C_s and C_{OH} are the numbers of silanol groups before adsorption and free silanol groups after adsorption. Typical plots of θ vs. C_0 for PEO-86 and PEO-660 are shown in Figures 2 and 3, respectively. As seen from the figures the θ value steeply increases and reaches a constant value, $\theta = 1$. For all samples the plateau θ value is unity.

Full coverage of the silanol groups with PEO chains at the relatively low concentration probably reflects the strong adsorption enthalpy and the small steric hindrance to the occupation of the silanol groups. Adsorption enthalpy, which is a measure of the strength of adsorption of monomer units and surface sites, has been related to the infrared absorption shift of surface sites on an adsorbent,[18-20] corresponding to the silanol groups in this experiment. The frequency shift $\Delta\nu_{OH}$ of silanol groups due to adsorption of PEO was 375 cm^{-1}. This value is much larger than the value of $\Delta\nu_{OH} = 94$ cm^{-1} for PS adsorption on a silica surface.[10] This means that PEO chains adsorb more tightly on the silica surface than PS chains. Thus the strong adsorption enthalpy may be responsible for the experimental result that the ellipsometric thickness of PEO adsorbed on solid surface is less than 20 Å.[21]

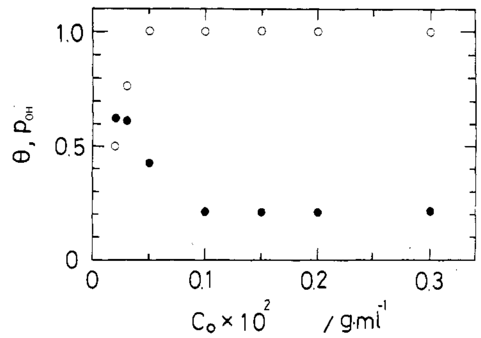

Figure 2. Plots of θ and p_{OH} vs. initial concentration C_0 of PEO-86: (○) θ; (●) p_{OH}.

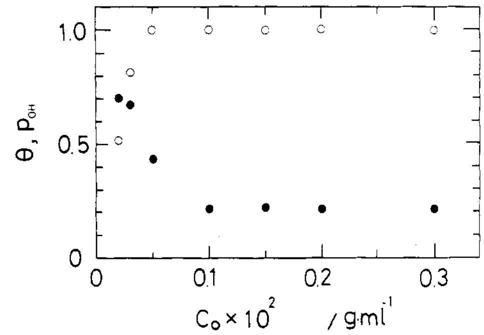

Figure 3. Plots of θ and p_{OH} vs. C_0 of PEO-660. Symbols are the same as in Figure 2.

The fraction p_{OH}, defined by eq 2, represents the relation

$$p_{OH} = (C_s - C_{OH})/C_A \qquad (2)$$

of the number of silanol groups occupied by adsorbed polymer to the total number of polymer segments in the adsorbed layer. C_A is the quantity of adsorbed polymer expressed as $(C_0 - C_p)$. The value p_{OH} is identical with the fraction of attached polymer segments only when one ether group occupies one silanol group. Plots of p_{OH} against C_0 for PEO-86 and PEO-660 are shown in Figures 2 and 3, respectively. The p_{OH} value at low C_0 is large, then decreases, and becomes constant. The plateau value p_{OH} is around 0.2 independent of molecular weight and is the same as observed by Killmann et al.[17]

Adsorption of Mixtures of PS and PEO. Typical adsorbed amounts of PS and PEO are given in Figures 4a, 5a, and 6a as a function of the initial concentration C_0 of each polymer for nine different PS-PEO mixtures. All concentrations examined were below the plateau region for individual adsorption of both polymers. At these concentrations PEO molecules completely adsorb on the silica surface. In contrast, PS molecules adsorb on the silica surface only at low C_0, and no additional adsorption occurs at $C_0 > 0.03$ g/100 mL. It appears that PEO molecules preferentially adsorb over PS molecules on the silica surface. Preferential adsorption of PEO is mainly attributed to the strong interaction with the silica surface arising from its more polar character and greater hydrogen-bonding ability than PS. Related to this result is the observation[16,22] that PEO can adsorb on the silica surface from its benzene solution.

As seen from the figures the adsorbance of PS increases with increasing PS molecular weight at constant PEO molecular weight (Table II). On the other hand, at constant PS molecular weight the amount of PS adsorbed

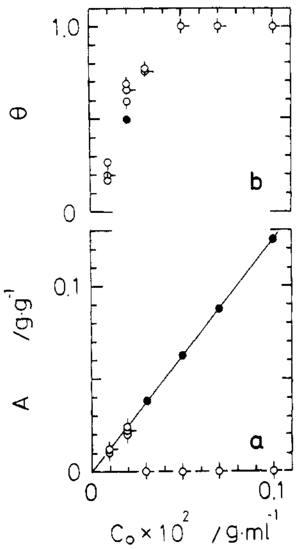

Figure 4. (a) Adsorbed amounts for 1:1 (by weight) PS–PEO mixtures of PS-102 and PEO-86, PS-775 and PEO-86, and PS-3840 and PEO-86 as a function of initial concentration C_0 of each polymer: (ϙ) PS-102; (o-) PS-775; (ȯ) PS-3840; (●) PEO-86. (b) Plots of θ vs. C_0 for the same mixtures as in (a). Filled circle indicates the θ value for individual adsorption of PEO-86.

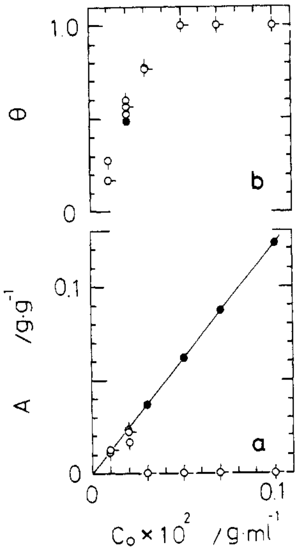

Figure 5. (a) Adsorbed amounts for 1:1 (by weight) PS–PEO mixtures of PS-102 and PEO-252, PS-775 and PEO-252, and PS-384 and PEO-252 as a function of initial concentration C_0 of each polymer: (ϙ) PS-102; (o-) PS-775; (ȯ) PS-3840; (●) PEO-252. (b) Plots of θ vs. C_0 for the same mixtures as in (a). Filled circle indicates the θ value for individual adsorption of PEO-252.

Table II
Ratio of Adsorbed PS Amount to PS Amount Assuming That Complete Adsorption of PS Occurs in Competitive Adsorption at the Initial Added Concentration C_0 = 0.02 g/100 mL of Each Polymer

	PS-102	PS-775	PS-3840
PEO-86	0.82	0.92	0.96
PEO-252	0.59	0.89	0.92
PEO-660	0.52	0.80	0.86

decreases with increasing size of the PEO molecule. These results indicate that the preferential adsorption of large molecules over small molecules occurs even if other polymer species are present. The differences in PS adsorbance were relatively small, but the reproducibility of the experiments was fairly good.

The θ value increases with increasing C_0 (Figure 4b, 5b, and 6b). The θ value at $C_0 < 0.02$ g/100 mL is attributed to both polymers and is larger than that observed for adsorption of PEO molecules alone. Since the infrared absorption peak at 3581 cm^{-1} due to the interaction between the silanol groups and the phenyl groups of adsorbed PS was weak, we could not calculate individual θ values for PS and PEO molecules. With $C_0 > 0.03$ g/100 mL, where no PS molecules can adsorb on the silica surface, the θ value is almost the same as for PEO adsorption. In general, the difference in θ between the adsorption of mixed and individual PEO at $C_0 = 0.02$ g/100 mL increases with decreasing PEO molecular weight and with increasing amounts of PS adsorbed.

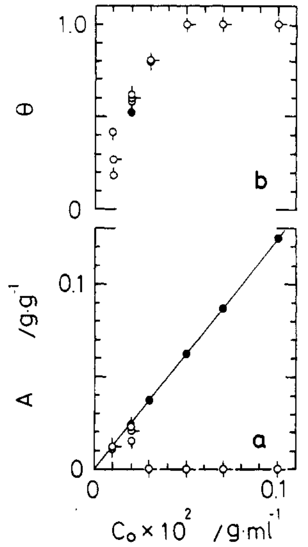

Figure 6. (a) Adsorbed amounts for 1:1 (by weight) PS–PEO mixtures of PS-102 and PEO-660, PS-775 and PEO-660, and PS-3840 and PEO-660 as a function of initial concentration C_0 of each polymer: (ϙ) PS-102; (o-) PS-775; (ȯ) PS-3840; (●) PEO-660. (b) Plots of θ vs. C_0 for the same mixtures as in (a). Filled circle indicates the θ value for individual adsorption of PEO-660.

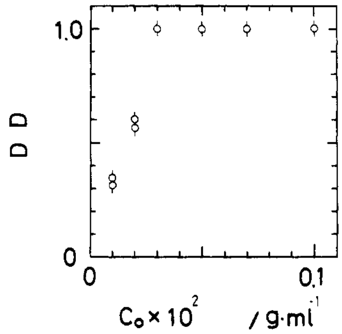

Figure 7. Degree of displacement of PS-102 by two types of PEO as a function of initial PEO concentration C_0: (ϙ) PEO-86; (ȯ) PEO-660.

At $C_0 = 0.03$ g/100 mL about 20% free silanol groups still remain, but PS molecules cannot adsorb on the silica surface. Thus, adsorbed PEO chains appear to block sterically the remaining free silanol groups.

Displacement of PS by PEO. The displacement of PS by PEO was examined by first fully adsorbing PS on the silica surface and then adding PEO to the system. The initial concentrations C_0 of PEO, ranging from 0.01 to 0.1 g/100 mL, are lower than the concentrations at which plateau adsorbance of PEO is attained.

The degree of displacement (DD) of PS by PEO, defined by eq 3, is shown as a function of C_0 in Figures 7–9 for eight

$$\mathrm{DD} = \frac{\text{amt of PS desorbed from silica surface}}{\text{amt of PS adsorbed initially}} \qquad (3)$$

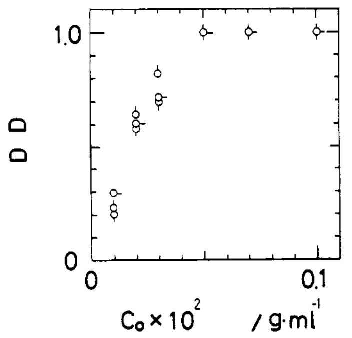

Figure 8. Degree of displacement of PS-775 by three types of PEO as a function of initial PEO concentration C_0: (○) PEO-252. Symbols are the same as in Figure 7.

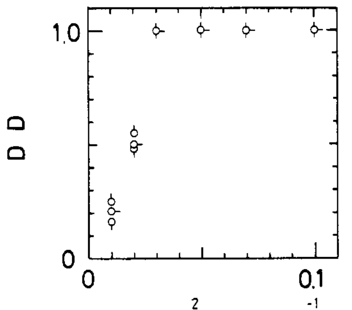

Figure 9. Degree of displacement of PS-3840 by three types of PEO as a function of initial PEO concentration C_0: Symbols are the same as in Figure 8.

different combinations of PS–PEO pairs. In all cases the displacement of PS molecules increases with increasing C_0 and finally all PS molecules are completely desorbed from the silica surface. Therefore, PEO effects complete PS displacement, with no PEO left in the supernatant solution after adsorption. As seen from the figures the DD values significantly depend on C_0 and the molecular weights of both polymers. Particularly, the complete displacement of PS by PEO molecules was observed with $C_0 > 0.03$ g/100 mL for PS-102 and PS-3840 and with $C_0 > 0.05$ g/100 mL for PS-775, independent of PEO molecular weight. Thus of the three PS molecules, PS-775 molecules are most tightly adsorbed on the silica surface

The desorbability of adsorbed polymer chain by a displacer should depend on factors such as the interaction parameter between polymer and surface, the fraction of polymer segments directly attached to the surface, the concentration of displacer, and the molecular sizes of adsorbed polymer and displacer. Here we attempt to interpret our experimental results on the basis of two aspects: (1) the fraction of adsorbed segment and (2) the molecular dimensions of adsorbed and displacer polymers.

In the three PS samples PS-775 molecules were displaced completely at the highest PEO concentration. The reason for this is that the difference in the fraction of PS segments directly attached to the silica surface would be more strongly affected than the sizes of adsorbed and displacer polymers because the plateau fraction p_{OH} values were 0.28 ± 0.02 for PS-102 and PS-775 and 0.20 ± 0.02 for PS-3840.[10] The p_{OH} values show that PS-3840 molecules adopt a more extended conformation than smaller PS chains on the silica surface. We can expect that adsorbed chains with a more extended conformation should be desorbed more easily than flattened conformation chains with large p_{OH} values. This expectation coincides with the difference in desorption between PS-775 and PS-3840 molecules. The difference in desorption between PS-102 and PS-3840 is attributed more to the molecular size of adsorbed chains than to the p_{OH} value: small molecules desorb more easily than large molecules. As seen from Figures 7–9 the large displacer (PEO) has a greater exchangeability than the small one.

At $C_0 < 0.03$ g/100 mL, some PS molecules still remain adsorbed, giving the peak at 3581 cm^{-1}. With increasing C_0 this peak decreases, and disappears if complete displacement of PS occurs. However, we cannot calculate the respective coverages of silanol groups by PS and PEO molecules because the infrared absorption peak at 3300 cm^{-1} is strong and broad and sometimes overlaps with the peak at 3581 cm^{-1}. Thus, the total coverage of silanol group with polymer chains was determined by eq 1. At concentrations where both polymers are adsorbed, the θ value is larger than that for the individual PEO adsorption. Above the concentrations where PS molecules are completely desorbed from the silica surface, the absolute value of θ is almost equal to that for the individual PEO adsorption.

Conclusions

(1) In adsorption from PS–PEO mixtures polar PEO molecules preferentially adsorb on the silica surface. Large molecules adsorb more readily than small molecules even in the presence of other species.

(2) For the desorption of PS by PEO molecules, the exchangeability is mainly controlled by the fraction of adsorbed segments of PS molecules and also by the molecular sizes of adsorbed and displacer polymer chains. The complete displacement of PS by PEO demonstrates the reversibility of the PS adsorption process and agrees with previous observations.[11]

Registry No. PS, 9003-53-6; PEO, 25322-68-3; silica, 7631-86-9.

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