Displacement of Polymers by Displacers. 1. Polystyrene at the Silica Surface

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ABSTRACT: Displacement adsorption was examined by first adsorbing polystyrenes with narrow molecular weight distributions onto a nonporous Aerosil 130 silica and then adding five low molecular weight displacers to the system in cyclohexane and in carbon tetrachloride at 35 °C. Extrapolation of the displacement isotherm to the remaining amount of adsorbed polystyrenes, $A_{re} = 0$, gives a critical volume fraction, $\phi_{cr}{}^{d}$, of the displacer. For the same combination of solvent and displacer the $\phi_{cr}{}^{d}$ value was independent of the polystyrene molecular weight. The order of $\phi_{cr}{}^{d}$ in both solvents was well correlated with the adsorption free energy parameters of the polymer from the displacer, which are calculated by the theory of Cohen Stuart, Fleer, and Scheutjens. Below the $\phi_{cr}{}^{d}$ value small polystyrene molecules were desorbed more easily from the silica surface than large ones at the same volume fraction of displacer. We proposed a simple route for evaluation of the free energy parameter of the polymer from solvent using a relationship predicted by Cohen Stuart et al. without individual adsorption data of the displacer.

Introduction

Displacement of adsorbed polymer chains from solid surfaces by displacer molecules including polymer chains has been paid much attention. Particularly, in practical problems, displacement of polymers by a low molecular weight displacer molecule leads to an understanding of the behavior of the steric stabilization of colloid particles[1] upon desorption of a polymer, adsorption chromatography,[2] and the development of adhesive materials.

Desorption of polymers by a displacer,[3] on the other hand, is one clue to estimating a segmental adsorption energy, $\chi_s kT$, where k is Boltzmann's constant, T the absolute temperature, and χ_s the adsorption energy parameter introduced by Silberberg[4] in 1968. Evaluating $\chi_s kT$ is one of the unsolved problems in polymer adsorption and is extremely important for not only predicting the adsorption behavior of a polymer chain but also developing the theoretical works on polymer adsorption onto a solid–liquid interface.

Since 1968, estimates of the χ_s parameter have been performed from adsorption heats by several researchers,[5,6] who used a microcalorimeter. This method is insufficient for adsorption in aqueous solutions where entropically induced hydrophobic bonding may be dominant.

Recently, however, Cohen Stuart et al.[3] derived a theory to evaluate the χ_s parameter from a displacement of adsorbed polymer chains by the addition of low molecular weight displacer molecules and suggested the displacement of polymers by various displacers in a variety of solvents for the experimental determination of the χ_s parameter. Moreover, they examined their theory with the displacement of poly(vinylpyrrolidone) adsorbed onto a silica surface by five different organic compounds in two solvents and compared the determined χ_s parameter with that evaluated by using the microcalorimeter.[5]

Therefore, to estimate the χ_s parameter we have to accumulate data of the displacement of polymers for a number of displacer molecules in different solvents. The aim of this paper is to present the displacement of adsorbed polystyrenes with narrow molecular weight distributions by the addition of several low molecular weight organic compounds under Θ- and good-solvent conditions. The experimental results were compared with the theory of Cohen Stuart et al. and we obtained some important parameters, such as a critical adsorption energy parameter and adsorption energy parameter. Finally, we will suggest one simple route to determine the χ_s parameter without the adsorption data of displacer molecules onto a solid surface.

Experimental Section

Materials. Two polystyrenes with narrow molecular weight distributions purchased from Tosoh Company Co. have the weight-average molecular weights of $M_w = 422 \times 10^3$ and 42.8×10^3 and are designated as PS-400 and PS-40, respectively.

Cyclohexane used as a solvent was distilled, passed through a silica gel column to remove aromatic impurities, and then fractionally distilled just before use. Carbon tetrachloride used as a solvent was distilled twice just before use.

Spectroquality benzene, acetone, and dioxane as well as extra-pure quality ethylbenzene and triethylamine were used as displacers without further purification.

The nonporous Aerosil 130 silica (Degussa AG., West Germany) used as an adsorbent was cleaned by the same procedure as described previously.[7]

Adsorption of Polystyrene. Twenty milliliters of a polystyrene solution of known concentration was mixed with 0.16 g of Aerosil 130 silica in a stoppered centrifugation glass tube, and the mixture was gently stirred by a magnetic chip for 24 h to attain equilibrium at 35 °C. The silica suspensions were centrifuged at 3000 rpm for 10 min to sediment the silica and the supernatant was carefully withdrawn. The polymer concentration in the supernatant, i.e., the equilibrium bulk concentration, C_p, was determined as follows: following the evaporation of the solvent, the residue was dried under vacuum and then dissolved in a definite amount of dioxane, and the equilibrium concentration C_p was determined by using an Ohtsuka Denshi System 77 UV spectrometer.

Displacement of PS by Displacers. We selected the dosage concentration, C_0, for the respective PS molecules in both solvents as follows: $C_0 = 0.2$ g/100 mL for PS-40 and $C_0 = 0.3$ g/100 mL for PS-400 in cyclohexane; $C_0 = 0.15$ g/100 mL for PS-40 and $C_0 = 0.16$ g/100 mL for PS-400 in carbon tetrachloride. They are well in to the plateau regions of the individual adsorption isotherms.

Twenty milliliters of polystyrene solution with a known concentration was mixed with 0.16 g of Aerosil 130 silica in a stoppered glass centrifugation tube and the mixture was conditioned in the incubator controlled at 35 °C during a desired adsorption time, usually 24 h, which is enought time to reach equilibrium. After equilibration the silica was sedimented by a Kubota KR-200B centrifuge and the equilibrium concentration in the supernatant solution was determined by a similar procedure as described for the individual adsorption of PS.

After removing the desired amount of the supernatant solution the same volume of a mixture of displacer and solvent was added to the system. The volume fraction of displacer in the mixture

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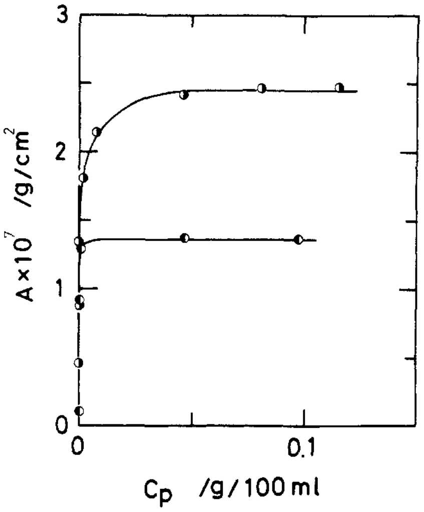

Figure 1. Adsorption isotherms of PS onto Aerosil 130 silica in cyclohexane at 35 °C: (◐) PS-40; (◑) PS-400.

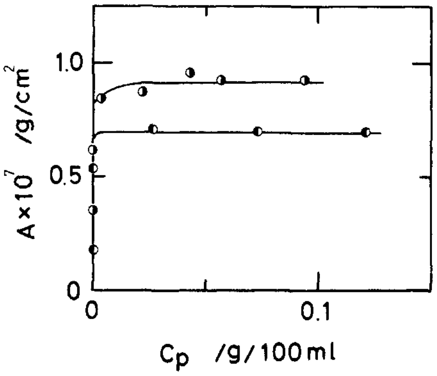

Figure 2. Adsorption isotherms of PS onto Aerosil 130 silica in carbon tetrachloride at 35 °C. The symbols are the same as in Figure 1.

was designated as ϕ^d. The volume fraction of displacer in the solvent mixture after displacement should be less owing to the transfer of displacer to the silica surface. In this paper the term ϕ^d means the dosage volume fraction of displacer. The mixture was agitated again for 24 h at 35 °C in the incubator. After centrifugation the concentration of PS in the supernatant solution was determined by the same spectroscopic procedure as previously described.

Results

Figures 1 and 2 show adsorption isotherms of PS-40 and PS-400 in cyclohexane and in carbon tetrachloride, respectively. All adsorption isotherms rise steeply with increasing C_p and reach a plateau. The adsorption isotherms are of the high-affinity type, which is characteristic for the adsorption of homodisperse polymers. The plateau adsorbances are dependent on molecular weight in both solvents. The plateau value for adsorbance in cyclohexane (under Θ-solvent conditions) is much larger than that in carbon tetrachloride (under good-solvent conditions). We should remark that the adsorption isotherms are not different from the previous ones.[7,8]

Figure 3 shows typical displacment isotherms, i.e., a plot of remaining amount, A_{re}, for preadsorbed PS-40 versus the logarithm of the volume fraction of displacer molecules, ϕ^d, in cyclohexane. The A_{re} value decreases with log ϕ^d and reaches zero at a given ϕ^d, which we hereafter call the critical displacer concentration and designate ϕ_{cr}^d. Above ϕ_{cr}^d all preadsorbed PS molecules are completely desorbed from the silica surface. We should notice some marked differences among the displacement isotherms. The ϕ_{cr}^d value strongly depends on the displacer and decreases in the order of ethylbenzene (benzene), dioxane, triethylamine, and acetone.

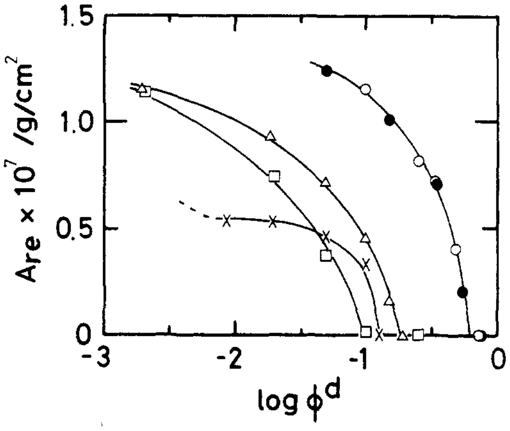

Figure 3. Displacement isotherms of PS-40 for various displacers in cyclohexane: (○) benzene; (●) ethylbenzene; (△) dioxane; (X) triethylamine; (□) acetone.

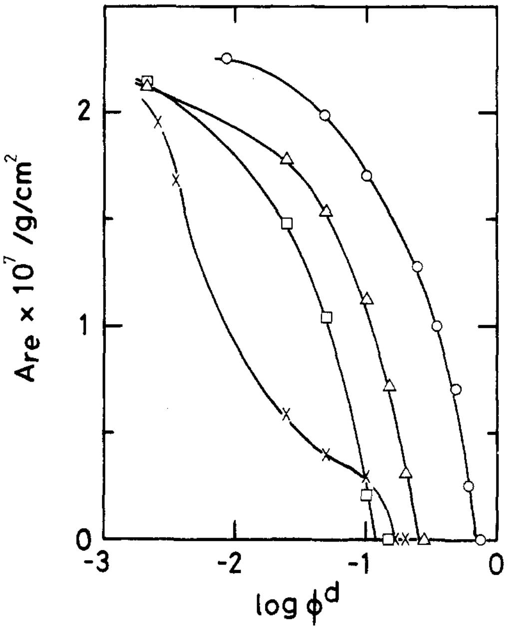

Figure 4. Displacement isotherms of PS-400 for various displacers in cyclohexane. The symbols are the same as in Figure 3.

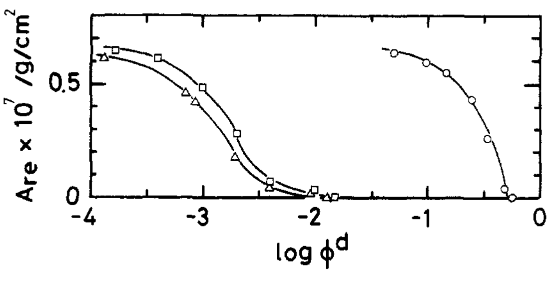

Figure 5. Displacement isotherms of PS-40 for various displacers in carbon tetrachloride. The symbols are the same as in Figure 3.

There are two types of displacement isotherms in Figure 3. The displacement isotherms for ethylbenzene, benzene, dioxane, and acetone are similar in their shapes; i.e., the A_{re} value rather steeply decreases and eventually becomes zero. (We designate it a type I isotherm.) In contrast, the displacement isotherm for triethylamine deviates upward at higher displacer concentrations and shows a rather long tail. (We designate it a type II isotherm.)

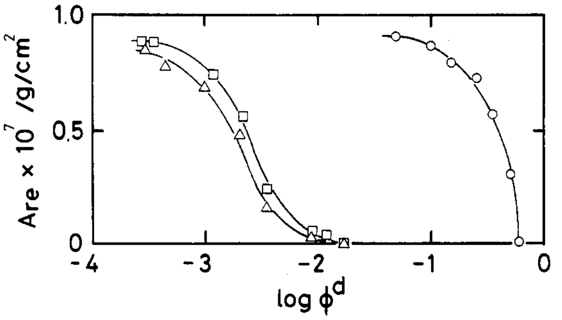

Figure 6. Displacement isotherms of PS-400 for various displacers in carbon tetrachloride. The symbols are the same as in Figure 3.

Table I
Critical Volume Fractions $\phi_{cr}{}^{d}$ of Displacers for Polystyrenes at Aerosil 130 Silica

	$\phi_{cr}{}^{d}$	
displacer	cyclohexane	carbon tetrachloride
benzene	0.69	0.55
acetone	0.11	0.017
dioxane	0.23	0.011
triethylamine	0.13	
pyridine	0.11	

The displacement isotherms of large PS chains in cyclohexane are shown in Figure 4. The shape of the displacement isotherm resembles that for small PS molecules by the respective displacers. Moreover, the magnitude of the $\phi_{cr}{}^{d}$ value is approximately the same as for small PS molecules.

In Figure 5, the displacement isotherms of PS-40 in carbon tetrachloride are illustrated. The shape of the displacement isotherm for benzene is different from those for acetone and dioxane. The former corresponds to the type I isotherm, while the latter is similar to the type II isotherm. The $\phi_{cr}{}^{d}$ value decreases in the order benzene, acetone, and dioxane.

In Figure 6, the displacement isotherms of PS-400 in carbon tetrachloride are displayed. The respective isotherms are fairly similar to those for small PS chains. All $\phi_{cr}{}^{d}$ values in both solvents are summarized in Table I.

Discussion

According to the theory of Cohen-Stuart et al.[3] an equation relating the value of $\phi_{cr}{}^{d}$ to the adsorption energy is given by

$$\chi_s{}^{pd} = \ln \phi_{cr}{}^{d} + \chi_{sc} - \lambda_1\chi^{pd} - (1 - \phi_{cr}{}^{d})(1 - \lambda_1)(\chi^{po} - \chi^{pd} - \chi^{do}) \quad (1)$$

In eq 1, $\chi_s{}^{pd}$ is the adsorption energy parameter of a polymer segment adsorbing from a displacer, χ_{sc} is the critical adsorption energy parameter, and χ^{po}, χ^{pd}, and χ^{do} correspond to the contact free energy parameters between polymer and solvent (po), polymer and displacer (pd), and displacer and solvent (do), respectively. The lattice parameter, $\lambda_1 = 0.25$, corresponding to a hexagonal lattice is employed in their theoretical treatment. Hence, $\chi_s{}^{pd}$ can be estimated if $\phi_{cr}{}^{d}$, χ_{sc}, and three contact free energy parameters, χ^{po}, χ^{pd}, and χ^{do} are known.

Table II
Calculated $\chi_s{}^{pd}$ and Three Contact Free Energy Parameters χ^{po}, χ^{pd},[a] and χ^{do}[b]

solvent	displacer	χ^{po}	χ^{pd}	χ^{do}	$\chi_s{}^{pd}$
cyclohexane	dioxane	0.5	0.46	0.58	−0.87
	acetone	0.5	~0.8	0.58	−1.36
carbon tetrachloride	dioxane	0.46	0.46	0.31	−3.90
	acetone	0.46	~0.8	0.31	−3.30

[a] Reference 13. [b] Reference 14.

The value of $\phi_{cr}{}^{d}$ is obtained from the displacement isotherm by an extrapolation of the remaining amount of polymer to zero. The χ_{sc} value also can be estimated from the displacement isotherm of a given polymer by a polymer repeating unit analogue. Among the three contact free energy parameters, both χ^{po} and χ^{pd} corresponding to the Flory–Huggins interaction parameters are obtained from osmometry and thermodynamic analysis by using the Stockmayer–Fixman plot for the intrinsic viscosity data. The χ^{do} value is obtained from the Hildebrand[9]–Scatchard[10] theory by using the solubility parameter as follows:

$$\chi^{do} = (V_o/RT)(\delta_o - \delta_d)^2 \quad (2)$$

where V_o is the molar volume of a solvent, R is the gas constant, T is the absolute temperature, and δ_o and δ_d are the solubility parameters of a solvent and a displacer molecule, respectively.

Since the chemical structure of ethylbenzene resembles the repeating unit of PS, we can assume $\chi_s{}^{pd} = 0$ for the displacement of PS by ethylbenzene. In other words, PS molecules do not adsorb from ethylbenzene solution. No adsorption of PS in ethylbenzene onto the silica surface is confirmed experimentally.[11] Putting $\chi_s{}^{pd} = 0$ into eq 1 gives the following equation:

$$\ln \phi_{cr}{}^{d} = -\chi_{sc} + \lambda_1\chi^{pd} + (1 - \phi_{cr}{}^{d})(1 - \lambda_1)(\chi^{po} - \chi^{pd} - \chi^{do}) \quad (3)$$

As seen in Figure 3 we should notice that the displacement isotherm for ethylbenzene falls approximately on that for benzene and the experimental $\phi_{cr}{}^{d}$ value is obtained as 0.69 both for ethylbenzene and benzene. Therefore, we would say that benzene behaves like ethylbenzene for desorption behavior of PS. It is well-known that PS molecules do not adsorb onto the silica surface from benzene solution.[12] For a calculation of the χ_{sc} value from eq 3, $\chi^{po} = 0.5$, $\chi^{pd} = 0.44$[13], $\chi^{do} = 0.161$[14], and $\phi_{cr}{}^{d} = 0.69$ in cyclohexane, while $\chi^{po} = 0.46$[15], $\chi^{pd} = 0.44$, $\chi^{do} = 0.048$[14], and $\phi_{cr}{}^{d} = 0.55$ in carbon tetrachloride are employed. The χ_{sc} values so calculated are 0.46 and 0.50 in cyclohexane and carbon tetrachloride, respectively. Both calculated χ_{sc} values are positive and the χ_{sc} value under θ-solvent conditions is somewhat smaller than that under good-solvent conditions.

On the other hand, the numerical values of χ_{sc} obtained in theoretical works[4,16,17] depend on the lattice used and are positive (0.2–0.75). Cohen Stuart et al.[3] employed an χ_{sc} of 0.288 for a hexagonal lattice model and compared it with their experimental displacement isotherms. As a result, our experimental χ_{sc} value is comparable to the theoretical χ_{sc} value and the displacement of a polymer by a polymer monomeric analogue would provide a reasonable value for the critical adsorption energy parameter.

According to the theory of Cohen Stuart et al.[3] the shift of the displacement isotherm curve versus log ϕ^{d} is induced by changing $\chi_s{}^{pd}$. As the negative $\chi_s{}^{pd}$ value increases, the $\phi_{cr}{}^{d}$ is reduced without further changes in the shape of the displacement isotherm. We can calculate a $\chi_s{}^{pd}$ from eq 1 using the experimental values of χ_{sc} and $\phi_{cr}{}^{d}$ and also the three contact free energy parameters. Some $\chi_s{}^{pd}$ values calculated from eq 1 are listed in Table II together with three contact free energy parameters used in the calculation. The $\chi_s{}^{pd}$ values so calculated should be independent of solvent, but $\chi_s{}^{pd}$ in carbon tetrachloride is much smaller that in cyclohexane for both displacers. However, the order of the magnitude of the $\chi_s{}^{pd}$ values so calculated is in good agreement with the order of the magnitude of the critical volume fraction, $\phi_{cr}{}^{d}$. At this stage we do not have

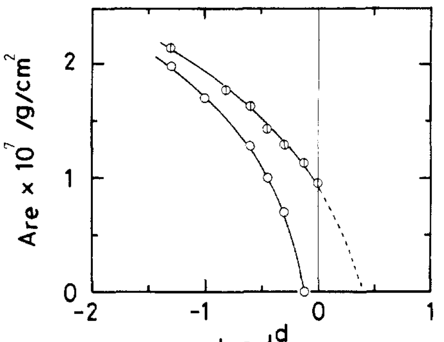

Figure 7. Displacement isotherms of PS-400 for benzene (○) and carbon tetrachloride (⊖) in cyclohexane.

a satisfactory explanation for different χ_s^{pd} values. In spite of different χ_s^{pd} values, we would propose a route for evaluation of χ_s parameter by eq 1.

Though Cohen Stuart et al.[3] have suggested that the displacement of preadsorbed polymer chains by displacer molecules and individual adsorption of displacer molecules provide a χ_s parameter, we would expect that the χ_s parameter can be calculated from eq 1 provided that a value of ϕ_{cr}^d could be obtained from the displacement isotherm by a solvent (for a displacer) in another solvent. In Figure 7 the displacement adsorption of PS molecules for carbon tetrachloride in cyclohexane is displayed. A value of ϕ_{cr}^d is determined to be 2.40 by extrapolating the displacement isotherm into the vertical region, $\phi^d > 1$, as seen in Figure 7. Putting $\phi_{cr}^d = 2.40$, $\chi^{po} = 0.5$, $\chi^{pd} = 0.46$[15], $\chi^{do} = 0.0286$,[14] and $\chi_{sc} = 0.46$ into eq 1 we obtain $\chi_s^{pd} = 1.23$, corresponding to the adsorption energy parameter χ_s for the adsorption of PS from carbon tetrachloride. Thus, we can obtain a χ_s value by selecting a good combination of two solvents, that is, a poor solvent is used for a solvent and a good solvent for a disperser, without the individual adsorption of the displacer, although an extrapolation in Figure 7 could contain some artifacts.

The reason why acetone and dioxane behave as a stronger displacer for desorption of PS than benzene (ethylbenzene) is attributed to the presence of an ester and ether bond in their compounds. Therefore, their desorbabilities seem to depend on the strength of hydrogen bonding between the functional group in the displacer molecules and the silanol group. The strength of the hydrogen bonding has been correlated with the infrared absorption shift of the surface sites on an adsorbent,[18,19] corresponding to the silanol group in this study.

The frequency shift of the silanol groups interacting with organic compounds containing ester and ether bonds was found by several researchers[20,21] to be 3–4 times as large as that interacting with benzene. Particularly, Curthoys et al.[21] have extensively evaluated the energies, q, of the formation of hydrogen bonding between the silanol group and various adsorbed organic compounds using IR spectroscopy and microcalorimetry. They obtained $q = 0$ for cyclohexane and carbon tetrachloride, $q = 6.1$ kcal/mol for dioxane, $q = 6.9$ kcal/mol for acetone, and $q = 10.3$ kcal/mol for triethylamine. The order of q correlates well with the order of our experimental ϕ_{cr}^d value for the type I isotherm in cyclohexane. Regardless of the largest q for triethylamine, its ϕ_{cr}^d value is larger than that for acetone. We have no adequate interpretation for this reverse. However, it may be correlated with the type II isotherm for the displacement isotherm by triethylamine in cyclohexane. This correlation also would hold for the reverse order of the ϕ_{cr}^d value between acetone and dioxane in carbon tetrachloride.

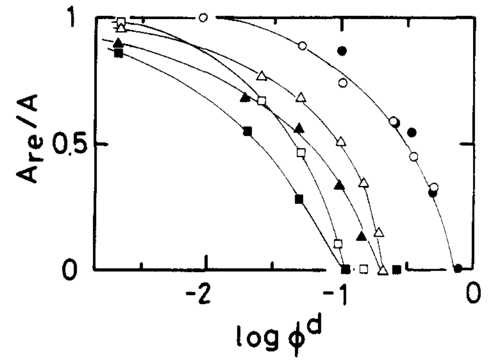

Figure 8. Degree of desorption A_{re}/A as a function of log ϕ^d in cyclohexane: (●) PS-40 for benzene; (○) PS-400 for benzene; (▲) PS-40 for dioxane; (△) PS-400 for dioxane; (■) PS-40 for acetone; (□) PS-400 for acetone.

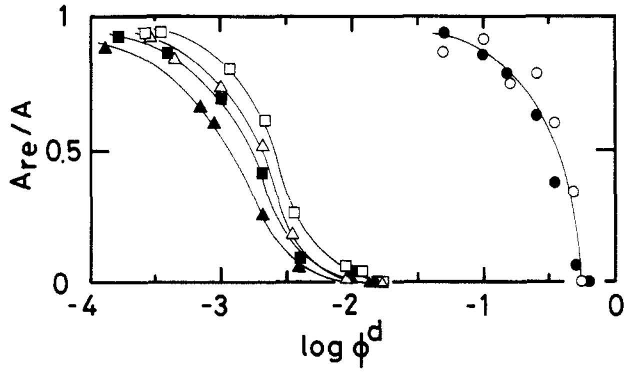

Figure 9. Degree of desorption A_{re}/A as a function of log ϕ^d in carbon tetrachloride. The symbols are the same as in Figure 8.

Figures 8 and 9 show the difference in the desorbability between large and small PS molecules by various displacers such as benzene, acetone, and dioxane in cyclohexane and carbon tetrachloride, respectively. Below the ϕ_{cr}^d value, for acetone or dioxane the ratio, A_{re}/A, of remaining and fully preadsorbed amounts for large PS molecules is clearly larger than that for small ones at the same ϕ^d value under both solvent conditions. Thus, large PS molecules are not desorbed more easily than small ones at the same displcer concentration. This molecular weight dependence on desorbability is in good agreement with the displacement of polymers by different chemical polymer chains.[22,23] However, when using benzene as a displacer a single curve can be drawn in the plot of A_{re}/A verses log ϕ^d under the respective solvent conditions. Close inspection shows that in cyclohexane the difference in the desorbability between large and small PS molecules is small, while in carbon tetrachloride, except for lower concentrations of benzene, small PS chains are more easily desorbed from the silica surface than large ones at the same displacer concentration.

Conclusions

Displacement of polystyrenes by the addition of various low molecular weight displacer molecules under Θ- and good-solvent conditions allows us to estimate χ_{sc}, χ_s^{pd}, and χ_s in comparison with the theory of Cohen Stuart et al. by taking into account three contact free energy parameters between polymer and solvent, polymer and displacer, and displacer and solvent. The χ_{sc} value is a positive quantity, which is generally accepted in polymer adsorption theories. The χ_s^{pd} values lead to reasonable interpretation of each displacement isotherm regardless of the presence of two different shaped isotherm. We could show a good example for evaluation of χ_s from only displacement isotherms if we select a good combination of two solvents; that is, one behaves as a solvent and another as a displacer.

Registry No. Polystyrene, 9003-53-6; silica, 7631-86-9; benzene, 71-43-2; acetone, 67-64-1; dioxane, 123-91-1; triethylamine, 121-44-8; pyridine, 110-86-1.

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Random Copolymer Adsorption. 1. Infrared Study at a Silica Surface

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ABSTRACT: Adsorption of styrene–methyl methacrylate (SM) copolymers covering the entire range of chemical composition on a silica surface from trichloroethylene was investigated by using IR and UV spectrometers together with the adsorption of the homopolymers of styrene and methyl methacrylate. Fractionated and well-characterized SM copolymers had mostly similar molecular weights. Adsorbance, the fractions of silanol groups occupied by styrene (θ_s) and by methyl methacrylate units (θ_m), and the fractions of styrene (p_s) and methyl methacrylate units (p_{COH}) that are directly attached to the silanol groups were separately determined. The plateau adsorbance and p_{COH} were dependent on the chemical composition in the SM copolymers. These results were fairly different from the data of Herd et al. (*J. Polym. Sci., Part C* 1971, *34*, 211), and the difference could be interpreted by taking into account the polydispersity effect; that is, large molecules preferentially adsorb over small molecules. The features of SM copolymer adsorption were identified in comparison with the adsorption of ethylene–vinyl acetate as well as that of styrene–butadiene copolymers.

Introduction

There are many copolymer adsorption studies.[1-11] The adsorption behavior of a copolymer at the liquid–solid interface, in general, should be governed by two effects: (1) the solubility of the respective components in a copolymer, i.e., a solvent is a poor solvent for one component and is a good solvent for another component; (2) the interaction strength between components in a copolymer and the surface, i.e., the stronger interaction between a component in the copolymer and the surface than that of another component. For adsorption studies on copolymers of ethylene oxide–propylene oxide[1] in water as well as in benzene and of styrene–butadiene in cyclohexane,[9] the plateau amount adsorbed on the silica surface was dependent on the components in the copolymers, where the results are mainly governed by effect 1. On the other hand, for adsorption studies on copolymers of ethylene–vinyl acetate[2-4,10,11] in various solvents and of styrene–methyl methacrylate[5] in several solvents, the plateau adsorbed amount was independent of chemical composition since vinyl acetate and methyl methacrylate units showed the overwhelming strength of the carbonyl–silanol interaction for the respective adsorption, where effect 2 was dominant.

However, our recent data[11] for the adsorption of fractionated ethylene–vinyl acetate copolymers having different compositions on the silica surface showed a slight but clear composition dependence of the plateau adsorbed amount regardless of the vinyl acetate units only interacting (adsorbing) with the silica surface. This result was clearly different from the previous data[4] and could be induced by using the fractionated ethylene–vinyl acetate copolymers with relatively narrow molecular weight distributions. Thus, the results have shown that one could expect to obtain a much clearer dependence of the plateau adsorbed amount on the component for the adsorption of the styrene–methyl methacrylate (SM) copolymer than for that of the ethylene–vinyl acetate copolymer since both styrene and methyl methacrylate units should interact with the surface. Moreover, the SM copolymer can be easily prepared by radical polymerization in the entire range of components and fractionated to obtain relatively narrow molecular weight distribution samples.

The aim of this paper is to offer experimental data for the adsorption of fractionated SM copolymers onto a