amount of deposited silane, and (iii) the pH environment imposed by the acid/base properties of the substrate. The degree of chemisorption is the highest on neutral substrates and more dependent on surface chemical functionality for acidic and basic substrates.

The physisorbed layer is capable of diffusing into a matrix resin and consists of unhydrolyzed or partially hydrolyzed monomer and polysiloxane oligomer with a molecular weight up to several thousand. The molecular weight of this physically adsorbed methacryl silane is also a function of the acid/base characteristics of the substrate and decreases in the order neutral > basic ≥ acidic. The acid/base effect can be modeled by adjusting the pH of the treating solution and depositing oligomers in bulk form.

The substrate characteristics which affect the molecular structures of the deposited hydrolyzed trifunctional silanes do so by influencing the rate, extent, and mechanism of condensation. Control of the surface reactions, polymerization, and the resulting molecular structures may be possible with an increased understanding of the surface effects.

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Registry No. Hydrite R, 1318-74-7; calcium carbonate, 471-34-1; [γ-(methacryloxy)propyl]trimethoxysilane, 2530-85-0; iron(III) oxide, 1309-37-1; titanium oxide, 13463-67-7; zirconium oxide, 1314-23-4; aluminum oxide, 1344-28-1; tin(IV) oxide, 18282-10-5; tungsten oxide, 1314-35-8; copper(II) oxide, 1317-38-0; aluminum silicate, 1335-30-4; silica, 7631-86-9; nickel oxide, 11099-02-8; calcium oxide, 1305-78-8; calcium hydroxide, 1305-62-0; magnesium oxide, 1309-48-4; barium hydroxide, 17194-00-2; lead oxide, 1335-25-7; wollastonite, 13983-17-0; calcium metasilicate, 10101-39-0; zinc oxide, 1314-13-2.

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Preferential Adsorption of Monodisperse Polystyrene on Silica Surface

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ABSTRACT: Adsorption of individual and binary mixtures of polystyrenes with a narrow molecular weight distribution onto a nonporous silica (Aerosil 130) from their carbon tetrachloride solutions at 35 °C was studied by IR spectroscopy and GPC. The fraction θ of silanol groups occupied by styrene units and the fraction p of styrene units directly attached to the silanol groups could be determined from the IR frequency shift of the silanol groups. The concentrations of individual polystyrenes both on the surface and in the bulk solution were determined by GPC. Adsorption isotherms of individual polystyrenes are of a high-affinity type; that is, they show a sharp isotherm. For the adsorption of binary mixture the preferential adsorption of large molecules over small molecules can be detected. The adsorption isotherms of the mixtures are compared with the theory of Cohen-Stuart, Scheutjens, and Fleer after confirmation of the validity of their assumptions by taking into account both adsorption isotherms and θ values for individual polystyrenes. The average molecular weights on the surface and in the bulk solution are compared with the expression of Hlady, Lyklema, and Fleer. For both quantitative comparisons a good agreement between calculated and experimental results can be obtained.

Preferential absorption among polymers of the same chemical composition depends on the molecular weight and the concentration of each component.[1] Several experiments have reached the same conclusion that large molecules preferentially adsorb over small ones.[2-9] In some experiments the polymer samples used were polydisperse. However, now polymers with narrow molecular weight distributions ($M_{\rm w}/M_{\rm n} < 1.1$) are available, and the use of such samples is convenient in avoiding the effect of polydispersity on the adsorption.

Recently, Cohen-Stuart, Scheutjens, and Fleer[5] first discussed the preferential adsorption of a binary mixture of monodisperse polymers a and b with the molecular weight of polymer b being larger than that of polymer a based on the following four assumptions.

(1) Adsorption isotherms of polymers a and b are of the high-affinity type. The plateau adsorbance of polymer b is larger than that of polymer a. The surface coverage θ

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in the plateau is independent of molecular weight ($\theta_a^m = \theta_b^m = \theta^m$).

(2) Polymer b is preferentially adsorbed over polymer a.

(3) The sum of the surface coverage of polymers a and b, $\theta_T = \theta_a + \theta_b$, is always equal to θ^m for detectable solution concentrations.

(4) The fractions of adsorbed segments in a polymer chain, p values for individual monodisperse polymers, in the adsorbed layer are equal to the respective values of p^m on the fully covered surface ($\theta_T = \theta^m$).

More recently, Cohen-Stuart, Fleer, and Bijsterbosch[9] reported the absorption of fractionated poly(vinylpyrrolidones) from 1,4-dioxane and from water onto silica surface. It was found that the polydispersity effect encountered in adsorption isotherms for a binary mixture of fractionated samples is satisfactorily accounted for by the theory of Cohen-Stuart et al. However, they measured only the total adsorbance but did not measure the adsorbance of each component, θ, and p values.

Hlady, Lyklema, and Fleer[8] extended the theory of Cohen-Stuart et al. for the adsorption of ternary mixtures and applied it to the adsorption for binary and also ternary mixtures of dextrans on silver iodide surface. Hlady et al. concluded that the adsorption isotherms for both binary and ternary mixtures are in good agreement with the calculated ones despite the fact that the molecular weight distribution of the dextran is not sharp. For the comparison with the theory of Cohen-Stuart et al. it is necessary to determine the experimental quantities of adsorbance, θ and p, in order to confirm the four assumptions.

If silica particles whose surface consisting of silanol groups are used as an adsorbent, the fraction p of polymer segments attached to the surface can be determined by IR,[10] ESR,[11] and NMR[12] spectroscopies and microcalorimetry,[13] and moreover the fraction θ of surface sites occupied by polymer can be determined by IR spectroscopy.[10] Since IR spectroscopy is convenient for obtaining both θ and p, we reported adsorption studies[14-17] of several polymers on a nonporous silica surface using IR spectroscopy along with UV spectroscopy and a differential refractometer.

The aim of this paper is to offer experimental results for the adsorption of individual and binary mixtures of monodisperse polystyrenes ($M_w/M_n < 1.1$) onto the Aerosil 130 silica surface from carbon tetrachloride solution at 35 °C. Measurements were carried out by using IR and GPC techniques as functions of concentration and molecular weight. Since GPC measurements are available to determine the concentrations of each component, preferential adsorption of the mixtures can be analyzed. Thus, the quantities appearing in the theory of Cohen-Stuart et al.[5] can be determined. Characteristics of the adsorption of binary mixtures of polystyrenes will be discussed in terms of the theory of Cohen-Stuart et al.

Experimental Section

Materials. Polystyrene samples with a narrow molecular weight distribution were purchased from ArRo Laboratories Co., Pressure Chemical Co., and Toyo Soda Co. The characteristics of the samples are listed in Table I.

Carbon tetrachloride was doubly distilled fractionally just before use.

The nonporous Aerosil 130 silica purchased from Degussa AG (West Germany) was used as the adsorbent after being cleaned by the procedure described in previous papers.[14-17] The surface concentration of silanol groups on the silica surface was determined to be three silanol groups per 100 Å^2 by the reaction with the silanol group and thionyl chloride.[18] According to the manufacturer, the particle diameter is 160 Å with a surface area of 141 m^2/g.

Table I
Characteristics of Polystyrenes

sample	$M_w \times 10^{-3}$	M_w/M_n
PS-0.06[a]	0.6	1.07
PS-0.4[a]	4.0	1.06
PS-0.9[a]	9.0	1.05
PS-4.28[b]	42.8	1.01
PS-10.2[b]	102	1.02
PS-49.8[c]	498	1.07
PS-77.5[b]	775	1.04
PS-200[c]	2000	1.06
PS-384[b]	3840	1.04

[a] Purchased from ArRo Laboratories Inc. [b] Purchased from Toyo Soda Co. [c] Purchased from Pressure Chemical Co.

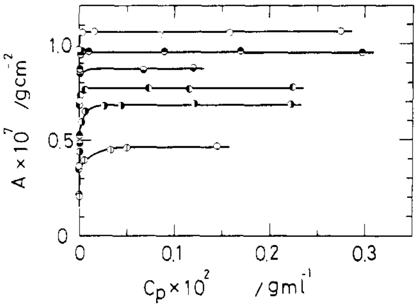

Figure 1. Adsorption isotherms of individual polystyrene onto Aerosil 130 silica surface from carbon tetrachloride at 35 °C: (○) PS-384; (●) PS-77.5; (◒) PS-49.8; (◐) PS-10.2; (◑) PS-4.28; (◓) PS-0.4.

Adsorption of Polystyrene onto Silica. Twenty milliliters of a carbon tetrachloride solution of polystyrene of known concentration was mixed with the silica (0.16 g) in a stoppered centrifuge 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 5000g for 10 min to sediment the silica and the supernatant was carefully removed. The polymer concentration in the supernatant, i.e., the equilibrium bulk concentration, C_p, was determined as follows: Following the evaporation of carbon tetrachloride, the residue was dried under vacuum and then dissolved in a definite amount tetrahydrofuran, and C_p was measured by integrating the peak area of each polystyrene, using a Toyo Soda HLC-802 A gel permeation chromatography instrument with a UV-8 Model II spectrometer. The wavelength used was 254 nm.

Adsorbance, A, expressed in g/cm^2, was determined from the difference between the amount of the polymer initially added, C_0, and that in the supernatant, C_p, and also from the amount of the silica added.

The sedimented silica was subjected to IR measurement according to the method described previously.

Results and Discussion

A. Adsorption of Individual Polymers. Adsorption Isotherms. Typical adsorption isotherms of individual polystyrenes are illustrated in Figure 1. Initially, the isotherms rose steeply with increasing C_p and reached a plateau region. Most adsorption isotherms were of the usual high-affinity type, which is characteristic for the adsorption of monodisperse polymers. The plateau values of adsorbance at the highest C_p are plotted against the molecular weight in a double-logarithmic plot in Figure 2. The plateau adsorbance gradually increases with increasing molecular weight and tends to approach a constant value.

Fraction of Surface Silanol Groups Occupied (θ). The differential IR spectra between the supernatant polymer solution and the silica on which the polystyrene was adsorbed show two characteristic bands in Figure 3:

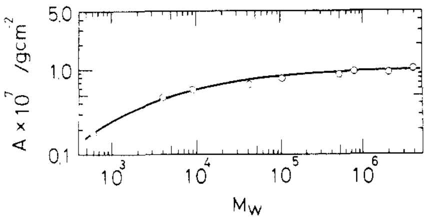

Figure 2. Molecular weight dependence of adsorbance at the highest equilibrium concentration.

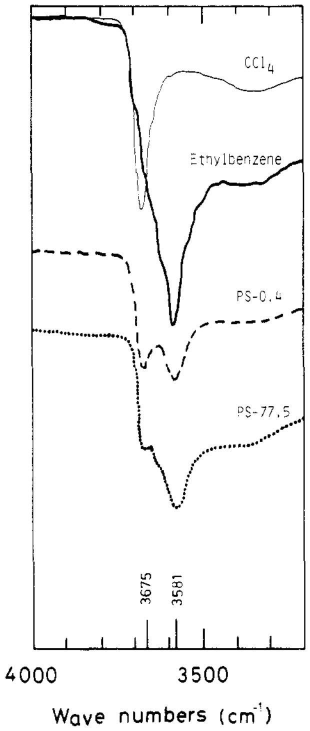

Figure 3. IR spectra of Aerosil 130 silica: (—) immersed in carbon tetrachloride; (—) immersed in ethylbenzene; (- - -) in carbon tetrachloride in the presence of PS-0.4; (···) in carbon tetrachloride in the presence of PS-77.5.

a band located at 3675 cm^{-1} due to the free silanol groups (its peak position agrees well with that for the silica immersed in carbon tetrachloride) and another band located at 3581 cm^{-1} due to the interaction between the silanol groups and the phenyl groups of the adsorbed polystyrene (its peak position is the same as that for the silica immersed in ethylbenzene, which is considered as a model compound for styrene monomer unit). Thus, both the number of free silanol groups (S_{3675}) and the number of occupied silanol groups (S_{3581}) can be determined if the extinction coefficients for the respective absorption bands are known.

From IR spectra of the silica immersed in carbon tetrachloride and in ethylbenzene as shown in Figure 3, the extinction coefficients at 3675 and 3581 cm^{-1} were determined to be 69.2 and 150 L mol^{-1} cm^{-1}, respectively. The fraction θ of silanol groups occupied by the phenyl groups of polystyrene can be calculated from the equation

$$\theta = S_{3581}/(S_{3581} + S_{3675}) \qquad (1)$$

Typical plots of θ vs. C_p for PS-0.4 and PS-77.5 are displayed in Figures 4 and 5, respectively. As seen from the figures the θ value steeply increases at lower C_p and reaches a constant value.

In Figure 6 the plateau value of θ at the highest C_p is plotted against molecular weight. The value of θ gradually increases with increasing molecular weight and becomes constant above $M_w = 42.8 \times 10^3$.

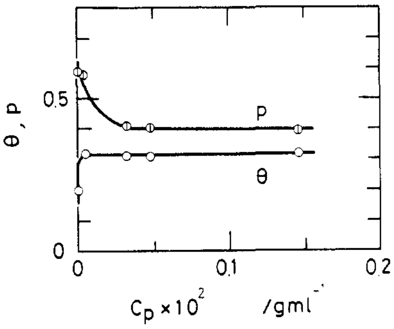

Figure 4. Plots of θ and p vs. equilibrium concentration for PS-0.4: (O) θ; (Φ) p.

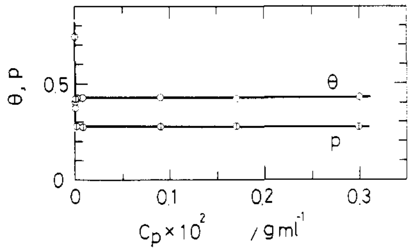

Figure 5. Plots of θ and p vs. equilibrium concentration for PS-77.5. Symbols are the same as in Figure 4.

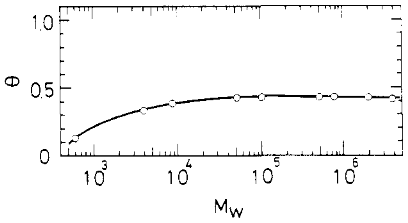

Figure 6. Molecular weight dependence of θ at the highest equilibrium concentration.

Fraction of Styrene Units Adsorbed (p). The fraction of styrene units directly attached to the silanol groups can be calculated from the equation derived by Fontana and Thomas:[10]

$$p = \frac{\text{(weight of attached styrene units per unit area)}}{\text{(weight of total adsorbed polystyrene per unit area)}} \qquad (2)$$

The numerator is obtained from the product of the number of silanol groups occupied (S_{3581}) and the molecular weight of styrene unit. The denominator corresponds to the adsorbance.

Plots of p against C_p for PS-0.4 and PS-77.5 are shown in Figures 4 and 5, respectively. The p value at lower C_p is large near 1 and then decreases and becomes constant.

B. Adsorption of Mixture. Adsorption Isotherm. Four samples, PS-0.4, PS-4.28, PS-10.2, and PS-77.5, were selected for adsorption of mixture: 1:1 (w/w) mixtures of PS-77.5 and PS-10.2, PS-77.5 and PS-4.28, PS-77.5 and PS-0.4, and PS-4.28 and PS-0.4 were examined. Figure 7a shows an adsorption isotherm of a mixture of PS-77.5 and PS-10.2. In the same figure the adsorbances of individual components in the mixture are also displayed. The shape of the adsorption isotherm for the mixture of PS-77.5 and PS-10.2 is different from the high-affinity-type adsorption isotherm characteristic for the individual adsorption of PS-77.5 and PS-10.2. The adsorption isotherm consists of the following four regions: (i) an initial steeply rising part where ($C_0 < 0.10$ g/100 mL) the two compo-

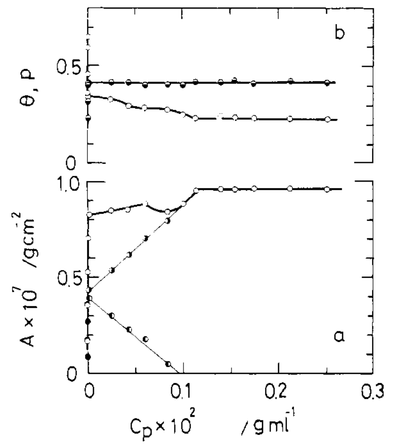

Figure 7. (a) Adsorption isotherm for a mixture of PS-77.5 and PS-10.2: (○) mixture; (◑) PS-77.5 in mixture; (◐) PS-10.2 in mixture. The solid circles denote the same adsorbed amount of each component. (b) Plots of θ (◒) and p (○) vs. equilibrium concentration for a mixture of PS-77.5 and PS-10.2.

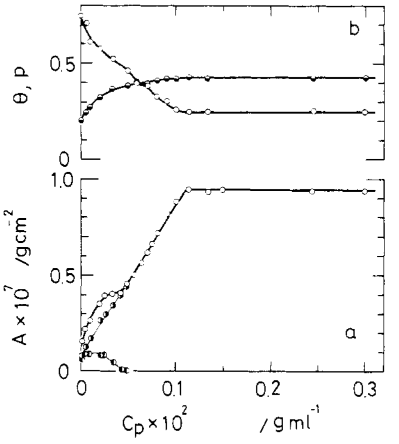

Figure 8. (a) Adsorption isotherm for a mixture of PS-77.5 and PS-0.4: (○) mixture; (◑) PS-77.5 in mixture; (◐) PS-0.4 in mixture. (b) Plots of θ (◒) and p (○) vs. equilibrium concentration for a mixture of PS-77.5 and PS-0.4.

nents adsorb completely with equal adsorbed amounts, (ii) a region below $C_p = 0.084$ g/100 mL ($0.10 < C_0 < 0.18$ g/100 mL) where PS-77.5 molecules preferentially adsorb over PS-10.2 molecules and only PS-10.2 molecules remain in the bulk solution, (iii) a region where $0.084 < C_p < 0.11$ g/100 mL ($0.18 < C_0 < 0.22$ g/100 mL) where only PS-77.5 molecules are adsorbed on the surface and the adsorbance linearly increases with C_p, and (iv) a region above $C_p = 0.11$ g/100 mL where the adsorbance reaches a plateau and its value is almost equal to the plateau adsorbance for the individual adsorption of PS-77.5. The shape of the adsorption isotherm of a mixture of PS-77.5 and PS-4.28 is similar to that for the mixture of PS-77.5 and PS-10.2.

An adsorption isotherm of a mixture of PS-77.5 and PS-0.4 is illustrated in Figure 8a. The adsorbances of each component are also displayed in the figure. The shape of the adsorption isotherm is somewhat different from those of the mixture of PS-77.5 and PS-10.2 and the mixture of PS-77.5 and PS-4.28. There is no region i where both components adsorb completely: Region ii corresponds to the initial part with $C_p < 0.055$ g/100 mL ($0.02 < C_0 < 0.11$ g/100 mL), region iii corresponds to $0.055 < C_p < 0.115$ g/100 mL ($0.11 < C_0 < 0.22$ g/100 mL), and the plateau region iv corresponds to $C_p > 0.115$ g/100 mL. The plateau adsorbance does not change with increasing C_p and almost equals the plateau value of PS-77.5 for the individual adsorption. For a mixture of PS-4.28 and PS-0.4 a similar adsorption isotherm was obtained.

Fraction of Silanol Groups Occupied (θ). The peak positions in the IR spectra of the silica on which polystyrene mixtures were adsorbed are the same as in the case of individual polystyrenes. The total θ values for mixtures were also calculated from eq 1. Figure 7b shows the plot of θ against C_p for a mixture of PS-77.5 and PS-10.2. The value of θ steeply increases at lower C_p and reaches a constant value at the equilibrium concentration, where PS-10.2 molecules begin to be excluded from the surface. The constant value of θ equals the plateau value of θ for the individual adsorption of PS-77.5. A similar concentration dependence of θ was obtained for the mixture of PS-77.5 and PS-4.28.

As seen from Figure 8b the value of θ more gradually increases with increasing C_p than in the case of adsorption of the mixture of PS-77.5 and PS-10.2 and reaches a constant value above $C_p = 0.055$ g/100 mL. The constant value of θ is almost equal to the plateau value for the individual adsorption of PS-77.5. A similar result was obtained for the adsorption of the mixture of PS-4.28 and PS-0.4. The plateau value of θ for the mixture equals the plateau value for the individual adsorption of PS-4.28.

Fraction of Styrene Units Attached to the Silanol Groups (p). The total p values for mixtures were estimated by using eq 2. Figure 7b shows a plot of p vs. C_p for the mixture of PS-77.5 and PS-10.2. Initially p steeply decreases, around $C_p = 0.084$ g/100 mL a distinct decrease in p is observed, and then p reaches a constant value above $C_p = 0.11$ g/100 mL. The constant value is nearly equal to that for the individual adsorption of PS-77.5. A similar concentration dependence of p was observed for the mixture of PS-77.5 and PS-4.28. The distinct change in p is also observed at the equilibrium concentration where the small molecules are excluded from the surface.

On the other hand, for the mixture of PS-77.5 and PS-0.4 such a distinct change in the plot of p vs. C_p is not observed as shown in Figure 8b. The p values at both $C_p = 0.05$ and 0.07 g/100 mL are almost the same. This constant p value may correspond to the distinct change in p described above, since around $C_p = 0.07$ g/100 mL the PS-0.4 molecules are excluded completely from the surface. Similar results were obtained for the mixture of PS-4.28 and PS-0.40.

Comparison with the Theories of Cohen-Stuart et al. and Hlady et al. The preferential adsorption of large molecules over small ones is completely achieved in the present experiments. The first theoretical interpretation for such a preferential adsorption was attempted by Cohen-Stuart, Scheutjens, and Fleer.[5] Subsequently, Hlady, Lyklema, and Fleer[8] extended the theory of Cohen-Stuart et al. for the ternary mixture.

When the experimental data are compared with the theory of Cohen-Stuart et al., it is desirable to confirm the validity of the four assumptions described earlier. Application of IR spectroscopy to polymer adsorption permits the simultaneously determination both of θ and p and provides the possibility of verifying assumptions introduced by Cohen-Stuart et al. However, it seems to be impossible to estimate p for the individual polymers in the adsorption of a mixture from IR spectroscopic measurements. The validity of the assumptions was discussed by Cohen-Stuart et al., who concluded that it is more difficult to verify assumption 4.[5] Therefore, we will verify assumptions 1, 2, and 3 but not assumption 4.

Since the preferential adsorption of large molecules over small molecules is observed for all binary mixtures, assumption 2 is satisfied. As seen from Figures 1, 2, and 6, the adsorption isotherm is of a high-affinity type and the plateau adsorbance increases with increasing molecular weight; moreover, the plateau value of θ becomes constant independent of molecular weight above $M_w = 42.8 \times 10^3$. This indicates that the binary mixtures of PS-77.5 and PS-10.2 and PS-77.5 and PS-4.28 satisfy assumption 1. For these two binary mixtures at the equilibrium concentration, where small molecules are exluded from the surface, the θ value ($\theta_a + \theta_b$) reaches a plateau value, θ^m, and therefore assumption 3 is satisfied. As a result, the binary mixtures of PS-77.5 and PS-10.2 and PS-77.5 and PS-4.28 are suitable to compare with the theory of Cohen-Stuart et al.

According to the theory of Cohen-Stuart et al.,[5] an adsorption isotherm of a binary mixture of monodisperse polymers a and b with mass fractions w_a and w_b ($w_a + w_b = 1$) and molecular weights M_a and M_b (with $M_b > M_a$) consists of three regions, described below. Adsorbance Γ is expressed in g/g and a nonadsorbed amount Γ^* is defined as $C_p/(S/V)$ in the same units as Γ to eliminate the effect of the surface area/solution volume ratio, where S is the area of adsorbent and V is the volume of the solution. Γ and Γ^* contain contributions from each component as follows:

$$\Gamma = \Gamma_a + \Gamma_b \tag{3}$$

$$\Gamma^* = \Gamma_a^* + \Gamma_b^* \tag{4}$$

The total amount of polymer is defined as the sum of Γ and Γ^*.

(I) In the rising part where both polymers a and b are completely adsorbed on the surface, the value of Γ ($=\Gamma_0$) is given by

$$1/\Gamma_0 = w_a/\Gamma_a^m + w_b/\Gamma_b^m \tag{5}$$

where Γ_a^m and Γ_b^m are the plateau adsorbances of polymers a and b, respectively.

(II) Polymer b preferentially adsorbs over polymer a and adsorbs completely ($\Gamma_0 < \Gamma \leq \Gamma_b^m$, $0 < \Gamma^* < \Gamma_1^*$), where Γ_1^* is denoted as a nonadsorbed amount until small molecules are completely displaced by large ones. Γ is written by

$$\Gamma = \Gamma_0 + (\Gamma_0/\Gamma_a^m - 1)\Gamma^* \tag{6}$$

(III) Above $\Gamma^* > \Gamma_1^*$, Γ equals Γ_b^m and no futher increase in Γ is observed even if the concentration of the bulk solution increases. This region is equivalent to the plateau region.

Hlady et al.[8] calculated the average molecular weights $\bar{M}_m^*$ in the supernatant solution and $\bar{M}_m^\sigma$ in the adsorbed layer for the adsorption of a ternary mixture using the theory of Cohen-Stuart et al. We can easily calculate the values of $\bar{M}_m^*$ and $\bar{M}_m^\sigma$ for the bnary mixture by modification of the relationship of Hlady et al. as follows. In region II the values of $\bar{M}_m^*$ and $\bar{M}_m^\sigma$ are defined as

$$\bar{M}_m^* = M_a \tag{7}$$

$$\bar{M}_m^\sigma = \bar{M}_m + (\bar{M}_m - M_a)/(\Gamma_0/\Gamma^* + \Gamma_0/\Gamma_a^m - 1) \tag{8}$$

where the average molecular weight $\bar{M}_m$ in the mixture is defined as $w_aM_a + w_bM_b$. In region III the respective molecular weights are given by

$$\bar{M}_m^* = M_b - w_a(M_b - M_a)(1 + \Gamma_b^m/\Gamma^*) \tag{9}$$

$$\bar{M}_m^\sigma = M_b \tag{10}$$

For representative comparisons with the theories of Cohen-Stuart et al. and Hlady et al., we choose the adsorption of the mixture of PS-77.5 and PS-10.2 and employ the following values for comparisons: $M_a = 102 \times 10^3$, $M_b = 775 \times 10^3$, $\Gamma_a^m = 0.106$ g/g, $\Gamma_b^m = 0.134$ g/g, and $w_a = w_b = 1/2$. As seen from Figure 9, an excellent agreement between the measured and calculated adsorption isotherms for the mixture of PS-77.5 and PS-10.2 is observed concerning $\Gamma = \Gamma_0$ at $\Gamma^* = 0$, $\Gamma = \Gamma_b^m$ at $\Gamma^* = \Gamma_1^*$, and $\Gamma = \Gamma_b^m$ above $\Gamma^* = \Gamma_1^*$. However, in the neighborhood of $\Gamma^* = \Gamma_1^*$ the measured value of Γ deviates below the theoretical straight line. In this region only PS-77.5 molecules are adsorbed on the surface. The discrepancy is often considered to be due to no attainment of real adsorption equilibrium. However, such a conjecture does not come true. Because the filled circles displayed in Figure 9 correspond to data points measured after both 1 day and 1 week, this confirms that 1 day is sufficient to reach the real equilibrium adsorption of the mixture.

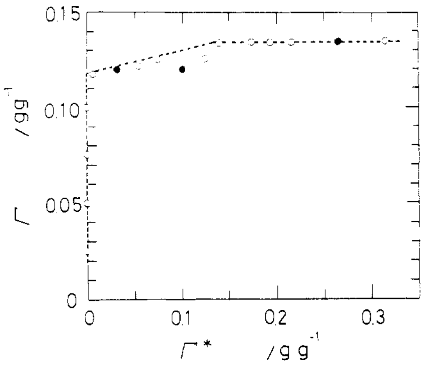

Figure 9. Plots of Γ vs. nonadsorbed amount Γ^* for a mixture of PS-77.5 and PS-10.2. Dashed line is calculated from the theory of Cohen-Stuart et al.

For another mixture of PS-77.5 and PS-4.28, it was found that the measured and calculated positions of the second kind of $\Gamma = \Gamma_b^m$ at $\Gamma^* = \Gamma_1^*$ and the plateau value of $\Gamma = \Gamma_b^m$ are in good agreement, but below $\Gamma^* = \Gamma_1^*$, the measured Γ is lower than the calculated one. This lower measured value of Γ may be caused by overwhelming preferential adsorption of large molecules over small ones, and, moreover, probably such an overwhelming preference is enhanced by the larger in the difference of the molecular weights of two polymers used.

Since the concentrations of individual components are available both in bulk solution and in the adsorbed layer, the molecular weights $\bar{M}_m^*$ and $\bar{M}_m^\sigma$ can be calculated from the following equations:

$$\bar{M}_m^* = \frac{M_a\Gamma_a^* + M_b\Gamma_b^*}{\Gamma_a^* + \Gamma_b^*} \tag{11}$$

$$\bar{M}_m^\sigma = \frac{M_a\Gamma_a + M_b\Gamma_b}{\Gamma_a + \Gamma_b} \tag{12}$$

Such molecular weights of $\bar{M}_m^*$ and $\bar{M}_m^\sigma$ will be compared with the theoretically calculated ones according to eq 7–10, respectively. An plot of $\bar{M}_m^*$ and $\bar{M}_m^\sigma$ as a function of Γ^* is displayed in Figure 10 for the adsorption of the mixture of PS-77.5 and PS-10.2. Plots of both $\bar{M}_m^*$ and $\bar{M}_m^\sigma$ vs. Γ^* are in good agreement between the measured and theoretical values.

Conclusions

Application of both IR and GPC techniques to the adsorption of polystyrene mixtures on silica surface permits determination of θ, p, and the concentrations of each component in the adsorbed layer and in the bulk solution. On the basis of these quantities, the validity of the assumptions of Cohen-Stuart et al. is discussed. The adsorption isotherms of binary mixtures of polystyrenes cannot be completely interpreted by the theory of Cohen-Stuart et al. However, both the plateau adsorbance

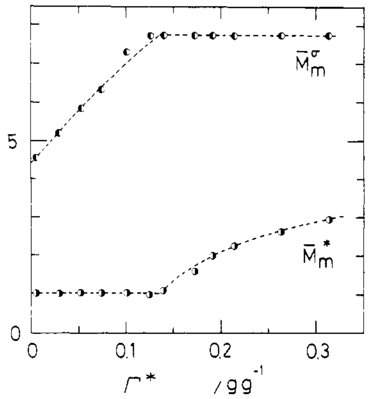

Figure 10. Plots of the average molecular weights $\bar{M}_m^{\sigma}$ (◐) on the surface and $\bar{M}_m^{*}$ (◑) in the bulk solution vs. nonadsorbed amount of Γ* for a mixture of PS-77.5 and PS-10.2. Dashed lines are calculated from eq 7-10.

and the equilibrium concentration where the adsorption is attained to be the plateau excellently agree with the values calculated from the theory. This discrepancy may be due to the overwhelming preferential adsorption of large molecules over small molecules.

Another interesting aspect of the present work is the determination of the average molecular weights on the surface and in the bulk solution using polystyrene samples with a narrow molecular weight distribution and also the GPC technique. Therefore, we note that important conclusions are obtained since the validity of assumptions based on the theoretical prediction is confirmed experimentally.

Registry No. Polystyrene (homopolymer), 9003-53-6; silica, 7631-86-9.

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On the Role of Intermolecular Hydrogen Bonding in Miscible Polymer Blends

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ABSTRACT: The results of a Fourier transform infrared study of poly(vinylphenol) blends with poly(vinyl acetate) and ethylene-vinyl acetate copolymers are presented. Infrared bands attributed to intermolecular hydrogen-bonding interactions involving the phenolic hydroxyl group with the acetate carbonyl group are identified. A quantitative measure of the fraction of hydrogen-bonded carbonyl groups in the blends has been obtained as a function of temperature. The results are considered in terms of an effective equilibrium constant, and an estimation of the strength of the intermolecular interaction has been gained. Ramifications concerning polymer-polymer miscibility and the effect of temperature, solvent, and glass transition temperature on the structure of polymer blends are discussed.

Introduction

In a series of previous publications,[1-8] we have presented the results of Fourier transform infrared (FT-IR) studies of a number of binary compatible polymer blend systems. Perhaps the most significant conclusion of this work is that infrared spectroscopy can be employed to detect and identify the presence of intermolecular interactions occurring between different polymeric components in many compatible blends. An excellent example is the study of the compatible polymer blend system containing the poly(hydroxy ether of bisphenol A) (Phenoxy) and poly(ϵ-caprolactone) (PCL).[5] A hydrogen-bonding type of intermolecular interaction was unambiguously identified involving the PCL carbonyl group with the hydroxyl group of the Phenoxy polymer. Furthermore, it was demonstrated that the relative strength of this intermolecular interaction was weaker than that occurring in pure Phenoxy (self-association).

These intermolecular interactions are considered to play a key role in polymer compatibility. As discussed in the elegant paper of Patterson and Robard,[9] polymer-polymer compatibility may be viewed as a balance between a free volume term (which is always unfavorable to mixing) and an interactional term (potentially favorable). If the latter

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