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Adsorption of Poly(methyl methacrylate) on Silica Surfaces Having Various Silanol Densities

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The adsorption of poly(methyl methacrylate) (PMMA) on silica surfaces having various silanol densities was studied by ESR and IR spectroscopies. Three silica samples, Nipsil HD, Aerosil 300, and Aerosil R812, which have 8, 2.2, and 0.54 nm^{-2} silanol densities, respectively, were used as the adsorbents. The amount of adsorption, A, the surface coverage, θ, and the fraction of train segments in the polymer, p, were determined. The values of the segment fractions anchoring through the hydrogen bond in all train segments of the adsorbed polymer, f_{HB}, were also estimated. When PMMA adsorbed on Nipsil HD, the polymer adsorbed predominantly by the formation of hydrogen bonds; on the other hand, when PMMA adsorbed on Aerosil 300, the polymer adsorbed through the hydrogen bond in the part of 30—40%. When PMMA adsorbed onto Nipsil HD, the value of p_{ESR} obtained by the ESR method was almost the same as the p_{IR} obtained by the IR method. When PMMA adsorbed onto Aerosil 300, the value of p_{ESR} was 0.47, twice the value of p_{IR}(0.24).

The adsorption of macromolecules is quite different in many respects from that of small molecules. The difference between them arises from the obvious differences in the size and the resultant flexibility of molecures. Among the molecular models proposed for characterizing polymer molecules adsorbed from solution onto a solid surface, the "loop-train-tail" model would be most general and successful. In order to discuss the conformation of an adsorbed polymer molecule, it is very important to estimate the fraction of train segments in the polymer, p. Usually, IR,[1,2] NMR,[3-5] and ESR[6-8] methods are utilized to estimate the value of p.

Fortana and Thomas first developed a technique for a quantitative estimation of the segment fraction attached to the surface sites through the hydrogen bond using IR spectroscopy.[1] They obtained values of p from 0.3 to 0.4 for the adsorbed poly(alkyl methacrylate) on silica in organic solvents. Robb and Smith first employed the ESR method for studies of the adsorption of poly(*N*-vinylpyrrolidone) onto silica, mainly from aqueous solution.[6] They obtained values of p from 0.6 to 0.9. Sakai et al. studies the conformation of adsorbed poly(methyl methacrylate) (PMMA) by the ESR method using three-component spectrum analysis.[7] They discussed the molecular weight dependence upon the polymer adsorption,[8] and also made a direct comparison of the ESR and IR methods using an identical solution-adsorbent system (PMMA-carbon tetrachloride-silica).[9] Based on their experimental results, they pointed out a disagreement in the obtained p values: the ESR method gave much greater values of p than did the IR method. In the present study one of our purposes was to pursue the cause of this disagreement. It was reported that when PMMA adsorbed on a silica surface, the polymer would mainly adsorb by the formation of a hydrogen bond between a carbonyl group of methyl methacrylate and a silanol group of the surface site.[10] Since the IR method evaluates only the segments adsorbed through a hydrogen bond between the carbonyl group and the silanol group, if the segments in PMMA adsorbed except for the hydrogen bond, the value of p would be understimated. In this paper we report on whether the adsorption of PMMA onto a silica adsorbent is caused exclusively by the formation of hydrogen bonds or not. We studied the amount of adsorption (A), the segment fraction of train (p), and the surface coverage (θ), using three kinds of silica surfaces having various silanol densities.

Experimental

Materials. The experimental procedures were basically the same as those described previously.[7,8] Spin-labeled PMMA was prepared by an anionic copolymerization of methyl methacrylate with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl in toluene at 0 °C using a phenylmagnesium bromide catalyst. The polymer was repeatedly fractionated in an acetone-water mixture to give narrow molecular weight distributions. The number-average molecular weight and the $\overline{M}_{\mathrm{w}}/\overline{M}_{\mathrm{n}}$ ratio of the PMMA sample were determined by GPC, calibrated with a standard polystyrene. They were 1.5×10^5 and 1.6, respectively. The spin-concentration of PMMA was approximately one spin per 400 monomer units. Details of the hyperfine coupling- and g-tensor values of the PMMA sample were published in a previous paper.[7]

Three silica-based adsorbents were used (Table 1). Nipsil HD (Nippon Silica Industrial) is a silica of surface area 263 $\mathrm{m^2\,g^{-1}}$, as determined by N_2 adsorption; it contains a relatively high level of silanol groups, 8 per nm^2. Aerosil 300 (Degussa) is a silica of surface area 303 $\mathrm{m^2\,g^{-1}}$ with a lower content of silanol groups, 2.2 per nm^2. A sample of surface-

Table 1. Characterization of Silica Sample

Sample name	Specified surface area/$\mathrm{m^2\,g^{-1}}$	SiOH/nm^2
Nipsil HD	263	8
Aerosil 300	303	2.2
Aerosil R812	245	0.54

modified silica, Aerosil R812 (Degussa), was prepared by treating Aerosil 300 with trimethylchlorosilane; this treatment converts most of the silanols to trimethylsilyl groups. It was reported that the differences of the particle sizes and the specific surface coverage in the used samples do not influence the amount of adsorption, A, and the train segment in polymer, p.[8]

Carbon tetrachloride and benzene used in this work were spectrometric grade.

Techniques of Measurements. The adsorption isotherms of PMMA on the various silica surfaces at 25 °C were measured by ESR spectroscopy, as described previously.[7] Solutions (10 ml) of various polymer concentrations were shaken vigorously with a solid adsorbent (0.1 g) in order to disperse the solid, then tumbled slowly over 24 h to ensure that equilibrium had been reached. The suspensions were then centrifuged and the ESR spectra of the supernatant solution and the adsorbed polymer were recorded. All ESR spectra were recorded with a JEOL JES FE-3X spectrometer.

The surface coverage (fraction of surface silanol groups occupied), θ_{IR}, was determined by the method of Kawaguchi et al., using infrared spectroscopy.[2] The differential IR spectra between the supernatant polymer solution and the silica on which PMMA was adsorbed show two characteristic bands: a band located at 3730 cm^{-1} due to the free silanol groups and another band located at 3420 cm^{-1} due to an interaction between the silanol groups and the carbonyl groups of the adsorbed PMMA. If we know the molar extinction coefficients (L mol^{-1} cm^{-1}) at 3730 and 3420 cm^{-1}, both the number of free silanol groups (S_{3730}) and the number of occupied silanol groups (S_{3420}) can be determined, and the surface coverage, θ_{IR}, can be calculated from the equation

$$\theta_{IR} = S_{3420}/(S_{3420} + S_{3730}). \tag{1}$$

All IR spectra were recorded with JASCO FT-IR 7000 spectrometer. In the case of Aerosil R812, we could not decide on the surface coverage, θ_{IR}, since the absortion of the silanol group was broad and did not shift before and after adsorption. Therefore, instead of θ_{IR}, we determined the surface coverage, θ_{As} (amount of adsorption/amount of maximum adsorption), of Aerosil R812 by using the same procedure as in a previous paper, from data regarding the amount of adsorption.[8]

Analyses of the ESR spectra of the adsorbed polymers were performed using the same procedure described in a previous paper.[7] The ESR line shape observed from the adsorption system was simulated by the summation of three model spectra: a triplet line with a narrowed width showing high mobility, an intermediately broadened line showing a restricted segment motion, and a powder pattern showing rigid immobilization. The spectrum was normalized by the singal intensity obtained from a second integration of the first-derivative spectrum. The amplitude of each model spectrum was determined by a least-squares method on the multiple regression to fit the summation of the three spectra with the observed spectrum. The model spectra were selected to make the correlation coefficient close to unity between the observed spectrum and the summation of the three model spectra. In the three-component analysis, close curve fitting was found in every case.

Results and Discussion

The adsorption isotherms for labeled PMMA from carbon tetrachloride and benzene onto the three kinds of adsorbents are shown in Fig. 1, indicating that the solvent has a strong influence on the affinity of the polymer for the surface. Here, Nipsil HD showed no indication of saturation over the concentration observed. In a benzene solution, relatively small amounts of polymer were required to saturate the surface. In a carbon tetrachloride solution, the adsorption of PMMA was more favored. The difference in the adsorption of PMMA adsorbed from carbon tetrachloride and benzene would be caused by the fact that carbon tetrachloride is a poorer solvent than benzene for PMMA and that benzene has a stronger affinity for a silica surface than does carbon tetrachloride. In both solvents, the adsorption of PMMA decreased with a decrease in the silanol density of the surface (Fig. 1). In the cases of Aerosil 300 and Nipsil HD, the adsorption of PMMA were of a high-affinity type and increased steeply under low equilibrium concentration.

Typical plots of the values of θ_{IR} and θ_{As} against the equilibrium concentration for the PMMA adsorbed on various silica surfaces from carbon tetrachloride solution are displayed in Fig. 2. The values of θ_{IR} increased steeply at a low concentration and reached a

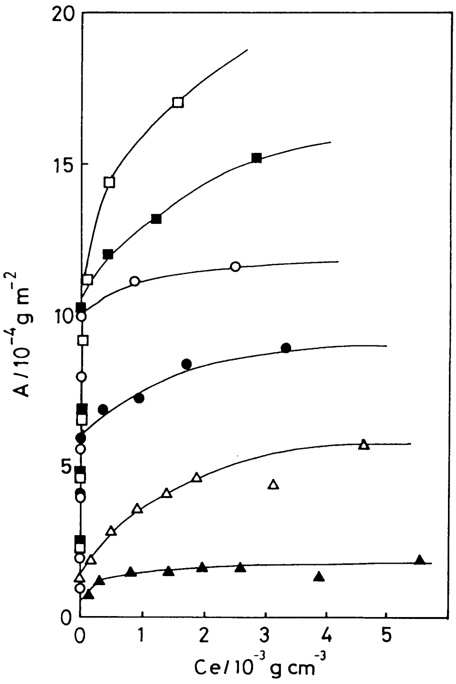

Fig. 1. Adsorption isotherms of PMMA on the three silica samples at 25 °C. □: Nipsil HD in CCl$_4$, ■: Nipsil HD in C$_6$H$_6$, ○: Aerosil 300 in CCl$_4$, ●: Aerosil 300 in C$_6$H$_6$, △: Aerosil R812 in CCl$_4$, ▲: Aerosil R812 in C$_6$H$_6$.

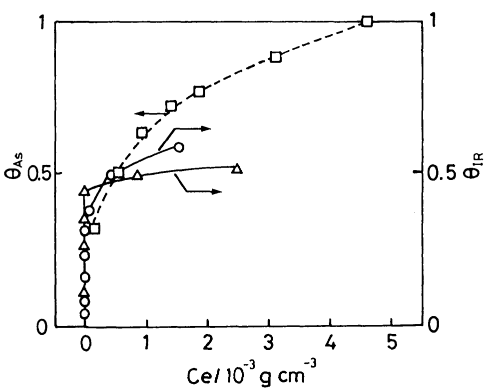

Fig. 2. Plots of the values of θ_{IR} and θ_{As} against the equilibrium concentration for adsorbed PMMA from CCl_4. O: Nipsil HD, Δ: Aerosil 300, □: Aerosil R812.

constant value. The values of θ_{As} gradually increased and reached naturally to unity.

When the affinity of the polymer for the surface is relatively weak, the adsorbed polymer molecules are likely to be held rather loosely and have an abundance of loops and tails. When the affinity of the polymer for the surface is strong, the adsorbed chains are held more strongly on the surface. The resulting motionally restricted conformations tend to be relatively flat and to have an abundance of trains. Such conformational differences are apparent in the ESR spectra of the adsorbed labeled PMMA. The spectra of the PMMA adsorbed on the three kinds of silica surfaces from a carbon tetrachloride solution are illustrated in Fig. 3. The ESR spectra of PMMA adsorbed on Nipsil HD and Aerosil 300 are virtually identical and are composites of broad and motionally-nallowed lines, indicating that some of the segments at the surface are located in loops or tails which are relatively free and more mobile. The ESR spectra of PMMA adsorbed on the Aerosil R812 have motionally-nallowed lines, suggesting a loopy conformation.

When PMMA molecules are adsorbed onto an Aerosil 300 silica surface, the segment fractions of train, short loop, and long loop segments against the surface coverage, θ_{IR}, can plotted as in Fig. 4, which shows a decrease in the number of train segments and an increase in the number of long loop segments with an increase in θ_{IR}. At relatively low θ_{IR}, most of the segments were highly localized near the surface. As a result, the adsorbed polymer was flattened and formed a thin adsorbed layer. All of the theoretical treatments predict that a flexible chain polymer molecule would be strongly attracted by a solid surface and would have an appreciably flat structure with a large fraction of train segments, in the case of a high level of the adsorption energy between the segments and the surface. The revealed structures roughly agree with the theoretical predictions.

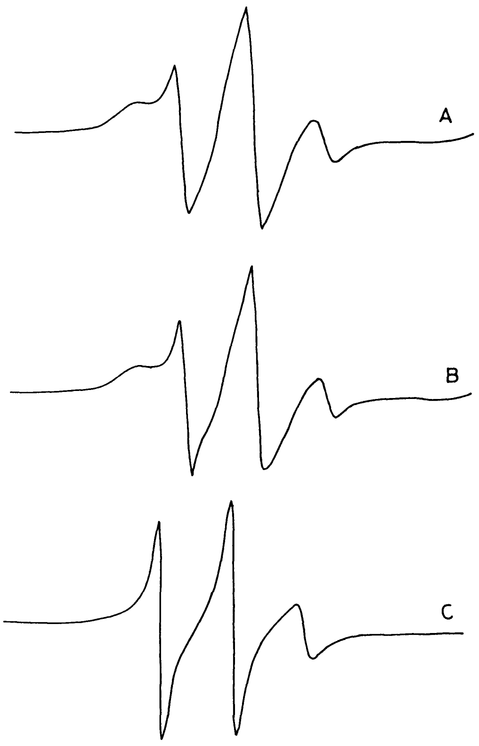

Fig. 3. ESR spectra of the adsorbed PMMA adsorbed on the three silica surfaces. A: Nipsil HD, B: Aerosil 300, C: Aerosil R812.

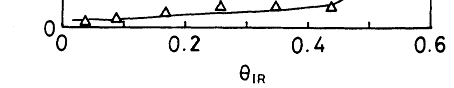

Fig. 4. Plots of the segment fractions, f, of train, short loop, and long loop against the surface coverage, θ_{IR}, for OMMA adsorbed onto the Aerosil 300 silica surface. □: train, O: short loop, ▲: long loop.

The segment fractions of train, short loop, and long loop at the maximum surface coverage are listed in Table 2. In both solvents the fraction of train segments decreased and that of long loop segments increased with a decrease in the silanol densities of the surface. On the three kinds of silica surfaces in benzene, the fraction of train segments is smaller and the fraction of long loop segments is larger than those in carbon tetrachloride. The obtained results in both solvents (Table 2) indicate that when PMMA adsorbs onto Nipsil HD and Aerosil 300, the polymer would

Table 2. Segment Fractions of Adsorbed Polymer

Solvent	Adsorbent	Train	Short loop	Long loop
CCl_4	Nipsil HD	0.50	0.30	0.20
	Aerosil 300	0.47	0.28	0.25
	Aerosil R812	0.12	0.16	0.72
C_6H_6	Nipsil HD	0.48	0.28	0.24
	Aerosil 300	0.41	0.20	0.39
	Aerosil R812	0.11	0.09	0.80

Table 3. Fraction of Hydrogen Bond

Solvent	Adsorbent	A_{train}	A'_{train}	f_{HB}
		$\times 10^{-4}$ g m^{-2}	$\times 10^{-4}$ g m^{-2}	
CCl_4	Nipsil HD	8.5	7.7	0.91
	Aerosil 300	5.5	1.9	0.34
	Aerosil R812	6.8	—	—
C_6H_6	Nipsil HD	7.3	6.8	0.93
	Aerosil 300	3.6	1.5	0.40
	Aerosil R812	2.0	—	—

have flat conformations; however adsorption onto Aerosil R812 would have a loopy conformation.

The values of the segment fractions anchoring through the hydrogen bond in all train segments of the adsorbed polymer, f_{HB}, are listed in Table 3.

In the table A_{train}(g m^{-2}) indicates the weight of a train segment in terms of the amount of adsorption, and is given by

$$A_{\mathrm{train}} = A_{\mathrm{s}} \times p, \tag{2}$$

where A_{s} is the amount of saturated adsorption. A'_{train}(g m^{-2}) also indicates the weight of segment anchoring through the hydrogen bond in a train segment of a polymer, and is given by

$$A'_{\mathrm{train}} = N_{\mathrm{SiOH}} \times \theta_{\mathrm{IR}} \times M, \tag{3}$$

where N_{SiOH} is the mumber of silanol per unit area and M is the molecular weight of the methyl methacrylate monomer. Consequently, f_{HB} is denoted $A'_{\mathrm{train}}/A_{\mathrm{train}}$ and is used for the notation of the segment fraction anchoring through the hydrogen bond in all train segments of the adsorbed polymer. As can be seen from the table, when PMMA is adsorbed on Nipsil HD, the polymer adsorbs predominantly by the formation of hydrogen bonds; however, when PMMA is adsorbed on Aerosil 300, the polymer adsorbs through hydrogen bonds in a ratio of 30—40%. The value of f_{HB} of the PMMA adsorbed on Aerosil 300 is similar to the result of Sakai and Imamura,[9] who made a direct comparison of the ESR method with the IR method using an identical solution-solvent system (PMMA-carbon tetrachloride-silica).

When PMMA is adsorbed onto Nipsil HD, f_{HB} is nearly equal to 1. It is then expected that the values of p_{ESR} and p_{IR}, obtained by ESR and IR methods, respectively, at the maximum surface coverage, θ_{IR}, are identical. The values of p_{ESR} and p_{IR} in the adsorption onto Nipsil HD, are plotted against the surface coverage, θ_{IR}, in Fig. 5. The values of p_{ESR} and p_{IR} decreased moderately with an increase in θ_{IR}. At a maximum surface coverage, $\theta_{\mathrm{IR}}=0.58$, the value of p_{ESR} is almost the same as p_{IR}. This fact is consistent with the result given in Table 3. At a relatively low θ_{IR}, some of the train segments in the polymer adsorb through the hydrogen bond; and the remaining train segments adsorb except for the hydrogen bond. At the maximum surface coverage, most of the train segments in the polymer adsorb through the hydrogen bonds.

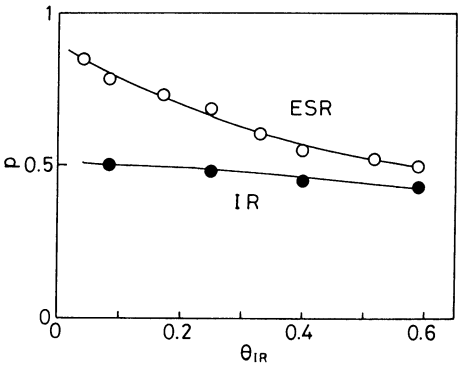

Fig. 5. Plots of the values of p_{ESR} and p_{IR} against the surface coverage, θ_{IR}, for PMMA adsorbed onto Nipsil HD. ○: p_{ESR}, ●: p_{IR}.

When PMMA is adsorbed onto Aerosil 300, f_{HB} is 0.3—0.4; it is expected that the values of p_{ESR} are a much higher level than those of p_{IR}. The values of p_{ESR} and p_{IR} for the PMMA adsorbed onto Aerosil 300 are plotted against the surface coverage, θ_{IR}, in Fig. 6. The values of p_{ESR} and p_{IR} were moderately decreased

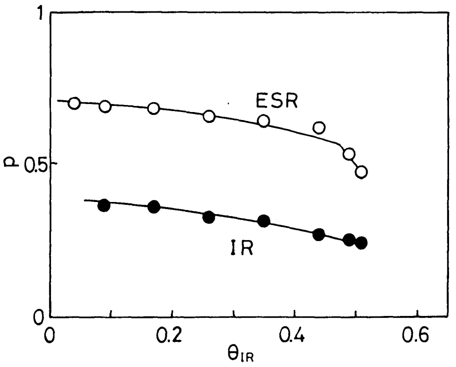

Fig. 6. Plots of the values of p_{ESR} and p_{IR} against the surface coverage, θ_{IR}, for PMMA adsorbed onto Aerosil 300. ○: p_{ESR}, ●: p_{IR}.

with an increase of θ_{IR}. At the maximum surface coverage, $\theta_{IR}=0.51$, the value of p_{ESR} was 0.47. It was twice as the value of p_{IR}, 0.24. This fact is consistent with the result given in Table 3. From the results of Figs. 5 and 6, when Nipsil HD, which has a relatively high level of silanol groups (8 per nm^2) was used as the adsorbent, the value of p_{ESR} was identical with the value of p_{IR}. When Aerosil 300, which has a lower content of the silanol group, 2.2 per nm^2, was used as the adsorbent, the results from the ESR method exhibit a much higher level than those of the IR method.

One possible explanation for the large differences in Figs. 5 and 6, is as follows: some of the train segments in the polymer interact with the silanol groups, while the remaining train segments interact with "non-hydroxylic sites"[11] on the silica surface. The IR method is used to evaluate only the train segments adsorbed through hydrogen bonds between carbonyl groups and silanol groups, whereas the ESR method is used to evaluate the train segments adsorbed through any mechanism. On Nipsil HD, train segments in the adsorbed polymer mainly adsorbed by the formation of hydrogen bonds between carbonyl groups of methyl methacrylate and silanol groups of the surface site; thus, the results obtained from the ESR and IR methods are identical. Since on Aerosil 300, train segments in the adsorbed polymer are anchored with or without hydrogen bonds, the results obtained from the ESR method exhibited a much higher level than those of the IR method.

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