ESR Studies of the Displacement Adsorption Behavior of Poly(methyl methacrylate) and Polystyrene System at the Solid–Liquid Interface

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The displacement adsorption behavior of a poly(methyl methacrylate) (PMMA) and polystyrene (PS) system onto a nonporous silica surface from a carbon tetrachloride solution was studied by utilizing the ESR method. The fractions of train segments for these polymers were determined from ESR spectra analyses; these values were compared with those of the individual adsorption. When PS was preadsorbed onto silica surface and PMMA solutions of various concentrations were added, the amount of PS desorbed from silica surface was proportional to an increase in the initial concentration of the PMMA solution; at the final concentration, PS was completely replaced by PMMA. This phenomenon was due to the stronger interaction of PMMA with the silica surface arising from its polar character, and the greater hydrogen bonding ability. The amount of adsorption for PMMA, which saturated the silica surface, was lower than that when adsorbed on silica surface individually. The adsorbed PMMA formed a more compressed polymer layer compared with that for the case in which PMMA was adsorbed alone. The amount and conformation of the adsorbed PMMA were affected by the presence of PS in the solution.

The adsorption of polymers at solid–liquid interfaces has been extensively studied.[1)] Among the molecular models proposed for characterizing polymer molecules adsorbed from solution onto a solid surface, past studies have led to the conclusion that a "loop-train-tail" model would be most general and successful.[2)] In order to discuss the conformation of an adsorbed polymer molecule, it is important to estimate the fraction of train segments in the adsorbed polymer, *p*.

A number of techniques have been applied to study the conformation of the polymer adsorbed at the solid–liquid interface, such as: FT-IR,[3—8)] ESR,[2,9—19)] NMR,[20—22)] and ellipsometry.[23,24)] Fontana and Thomas first developed a technique for a quantitative estimation of the segment fraction attached to the surface site through the hydrogen bond using IR spectroscopy.[3)] Robb and Smith first employed the ESR method for studies of the adsorption of poly(*N*-vinyl-2-pyrrolidone) onto a silica surface, mainly from aqueous solution.[12)] Sakai et al. reported on a procedure for estimating the three components of the adsorbed polymer segments (train, short loop, and long loop or tail) from the ESR spectra of spin-labeled polymers.[2)] The present authors reported on the individual adsorption behavior of PMMA,[16)] PS,[17)] and methyl methacrylate-styrene copolymer,[18)] using the ESR method. We also reported on the competitive adsorption behavior of PS and PMMA mixtures, and discussed the difference in the adsorption ability of styrene and methyl methacrylate on a silica surface.[19)]

Several studies have been reported concerning the competitive and displacement adsorption of polymers.[4,19,25—34)] They can be divided into three groups as follows: (1) Competition between chains with different lengths (polydispersity). The use of polydisperse polymers in adsorption studies is the rule, rather than the exception. Kolthoff and Gutmacher[25)] noted that the adsorption, itself, could have a fractionating effect due to the preferential adsorption of a longer chain. (2) Competition between polymers and small molecules. Howard and McConnell[26)] noted that polymer adsorption, although usually impossible by dilution alone, could sometimes be achieved by changing the solvent. They suggested that the desorptive power of an added solvent was due to its stronger interaction with the surface. Kawaguchi et al.[27,28)] studied the displacement of preadsorbed polymers by adding various displacer molecules. (3) Competition between polymers of different chemical species. Kawaguchi et al.[30)] studied the competitive and displacement adsorption of PS and poly(ethylene oxide) (PEO) and reported that PEO adsorbs preferentially over PS, and that the preferential adsorption of large molecules over small molecules occurs, even in the presence of different species. Thies[4)] studied the competitive and displacement adsorption of PS and PMMA mixtures from a trichloroethylene solution using IR spectroscopy. He reported a reversiblity of the adsorption processes in such systems. The present authors reported the competitive adsorption behavior of PS and PMMA mixtures, and discussed the conformation of both adsorbed polymers under this condition.[19)]

As reported in our previous paper,[16)] the value of *p* estimated by the IR method is underestimated compared with that estimated by the ESR method, since the IR method evaluates only the segments adsorbed through a hydrogen bond. Therefore, the ESR method is effective for an accurate evaluation of the state of the adsorbed polymer. We have now studied the displacement adsorption behavior of PMMA and PS systems using the ESR method, based on an estimation of the

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value of p.

The purpose of this study was to utilize the ESR method in order to explore the displacement adsorption behavior of PMMA and PS systems onto a nonporous silica surface from a carbon tetrachloride solution. Since carbon tetrachloride is as poor a solvent for PS as for PMMA, we can easily discuss the displacement adsorption behavior of both polymers at the solid–liquid interface. Since it is impossible to deal with a system having both polymer components spin-labeled, or to analyze the ESR spectrum for the dynamic behavior of PMMA and PS individually, we deal with two kinds of displacement adsorption systems: (1) the displacement adsorption of spin-labeled PMMA (SL-PMMA) and normal PS (NL-PS), (2) the displacement adsorption of normal PMMA (NL-PMMA) and spin-labeled PS (SL-PS).

Experimental

Materials. NL-PMMA was prepared by an anionic polymerization of methyl methacrylate in toluene at 0 °C using phenylmagnesium bromide as a catalyst.[13] The polymer was repeatedly fractionated in an acetone–water mixture to give narrow molecular weight distributions. NL-PS was purchased from Pressure Chemical Co. SL-PMMA was prepared by an anionic copolymerization of methyl methacrylate with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidyloxyl in toluene at 0 °C using phenylmagnesium bromide as a catalyst.[13] The polymer was repeatedly fractionated by the same procedure as for NL-PMMA. The spin-label concentration of SL-PMMA was approximately one spin per 400 monomer units. SL-PS was prepared by the procedure of Regen.[35] The copolymer of styrene and *p*-(chloromethyl)styrene was prepared by radical copolymerization using α,α'-azobisisobutyronitrile as an initiator at 70 °C. The copolymer was spin-labeled by reaction with a sodium salt of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidyloxyl, which was obtained by the reaction with sodium hydride, in *N*,*N*-dimethylformamide solution. The spin-label concentration of SL-PS was approximately one spin per 1000 monomer units. The polymer samples used in this work are characterized in Table 1.

Cabosil M5, with a specified surface area of 220 $\mathrm{m^2\,g^{-1}}$ for nitrogen adsorption, was used as an adsorbent. The silica had a 2.2 $\mathrm{nm^{-2}}$ silanol density on its surface. The silica was essentially nonporous and had an average particle size of 14 nm.

The carbon tetrachloride used in this work was of spectrometric grade, and was used without further purification.

Table 1. Characterization of the Polymer Samples Used

Sample name	$\overline{M}_w$[a)]	$\overline{M}_w/\overline{M}_n$[a)]
SL-PMMA	224000	1.3
NL-PMMA	219000	1.3
SL-PS	221000	1.5
NL-PS	207000	1.1

a) $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ were determined by means by GPC in THF.

Techniques of Measurements. The experimental techniques for the adsorption of polymers on the silica adsorbents were basically the same as those described in previous papers.[16—19] The polymer solutions were added to the silica adsorbents, and the mixtures were stirred with a magnetic stirrer. The silica dispersions were separated by the used of a centrifuge. The amounts of adsorption, A ($\mathrm{g\,m^{-2}}$), for PMMA were determined by IR spectroscopy by measuring the difference in the polymer concentration before and after adsorption. The characteristic band for PMMA at 1732 $\mathrm{cm^{-1}}$ was utilized for IR analysis. The values of A for PS were determined by means of UV spectroscopy by measuring the decrease in the intensity at 262 nm after the adsorption. C_e denotes the concentration of unadsorbed polymer remaining in the supernatant solution after the adsorption. The surface coverage, θ_{AS}, (amount of adsorption/amount of maximum adsorption), was determined by using the same procedure as in a previous paper.[19]

The displacement adsorption studies on the PMMA-PS system were carried out as follows. In the first place, PS was preadsorbed on silica adsorbents to saturation; the supernatant solutions were removed. Then PMMA solutions of various concentrations were added to silica adsorbents. The mixtures were stirred and separated by centrifuging. The values of A for PMMA, A_{PMMA}, and the values of A for PS, A_{PS}, were measured. The ESR spectra of the adsorbed polymers were also measured. C_0 denotes the added concentration of PMMA. Incidentally, we do not deal with a system in which after PMMA is preadsorbed on a silica surface the PS solution is added, since PMMA cannot be displaced by PS, as reported in previous papers.[4,19]

Analyses of the ESR spectra of the adsorbed spin-labeled polymers were performed using the same procedure described in previous papers.[2,19]

Results and Discussion

Adsorption of Individual Polymers. Typical adsorption isotherms of individual polymers in a carbon tetrachloride solution are shown in Fig. 1. Initially, the isotherms rose steeply with an increase in the value of C_e, and reached plateau regions. All of the adsorption isotherms were of the usual high-affinity type, which is characteristic of the adsorption of polymers. As shown in Fig. 1, the amounts of saturated adsorption for SL-PMMA and NL-PMMA are almost the same. A similar result was obtained for the adsorption of SL-PS and NL-PS. The influence of the spin-label agent on the amounts of the adsorption is negligible, since the spin-label concentration of the two labeled polymer samples are extremely low. The slight difference in the amounts of the adsorption between spin-labeled polymers and non-labeled polymers would be caused by the difference in the molecular weights between the polymers.[15,24]

In Fig. 2, the segment fractions of train, short loop, and long loop for the adsorption of SL-PMMA are plotted against the value of θ_{AS}. Upon increasing the value of θ_{AS}, the values of p decrease, whereas the fractions of the long loop segments increase. At relatively low θ_{AS}, most of the segments were highly localized near to the

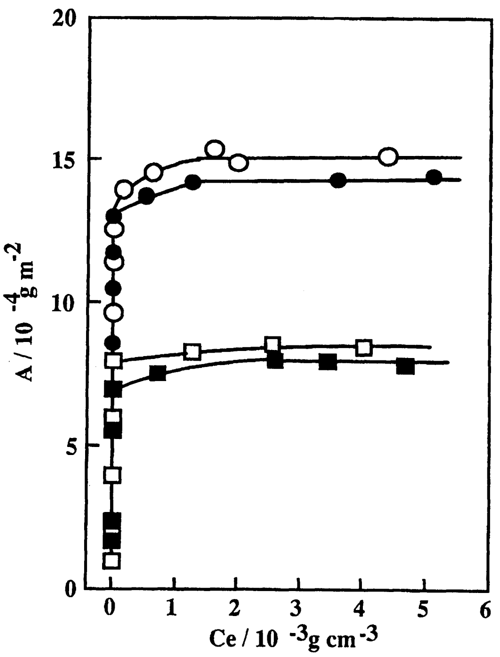

Fig. 1. Adsorption isotherms of polymers on Cabosil M5 from carbon tetrachloride solution at 25 °C. ○: SL-PMMA, ●: NL-PMMA, □: SL-PS, ■: NL-PS.

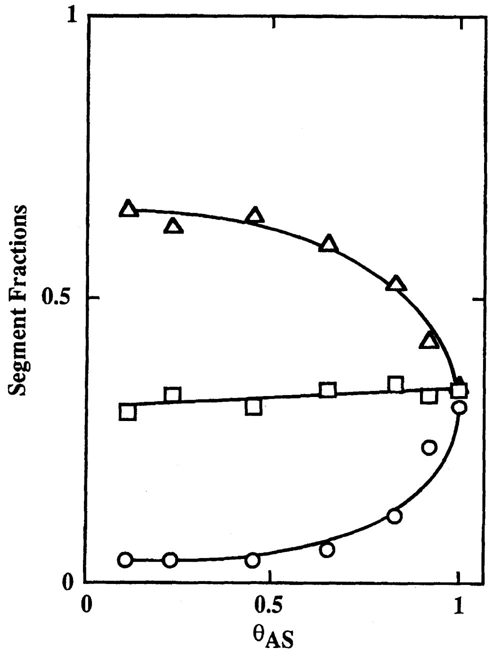

Fig. 2. Plots of the segment fractions of train, short loop, and long loop against the value of θ_{AS} for SL-PMMA adsorbed from carbon tetrachloride solution. △: train, □: short loop, ○: long loop.

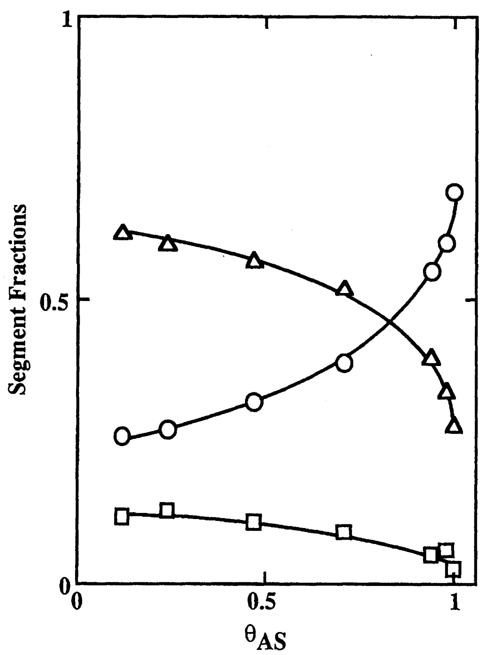

Fig. 3. Plots of the segment fractions of train, short loop, and long loop against the value of θ_{AS} for SL-PS adsorbed from carbon tetrachloride solution. △: train, □: short loop, ○: long loop.

surface. As a result, the adsorbed polymer was considered to be flattened, forming a thin layer. At saturated adsorption ($\theta_{AS}=1$), the value of p was reduced to 0.35, indicating that the adsorbed PMMA has a relatively flat conformation.

In Fig. 3, the segment fractions of train, short loop, and long loop for the adsorption of SL-PS are plotted against the value of θ_{AS}. Upon increasing the value of θ_{AS}, the values of p decrease, whereas the fractions of long loop segments increase. In contrast to the adsorption of PMMA, over the entire range of θ_{AS}, it can be seen that the fractions of short-loop segments are smaller. At the saturated adsorption ($\theta_{AS}=1$), the value of p is reduced to ca. 0.28. In contrast to the adsorption of PMMA, the trend toward lower value of p indicates that a more extended adsorbed structure (i.e., loopy conformation) is formed as the silica surface is filled with the adsorbed PS.

Displacement Adsorption of PMMA and PS System. When PS is preadsorbed on a silica surface from a carbon tetrachloride solution to saturation, and then PMMA solutions of various concentrations are added, the amounts of adsorption of PMMA and PS are plotted against the initial concentration of the added PMMA solution (Figs. 4 and 5). The numbers in the graph are the values of p at that point. The adsorption isotherm of PS represents the desorbed amounts of PS by the adsorbed PMMA. As shown in Figs. 4 and 5, PS is desorbed from the silica surface, accompanied by an increase in the initial concentration of the added PMMA; finally, PS is completely replaced by PMMA. Therefore, this indicates a stronger interaction of PMMA with the silica surface, arising from its polar character and greater hydrogen bonding ability. The amount of adsorption for PMMA, which saturates the silica surface, is obviously lower than that when adsorbed on silica surface individually, as shown in Fig. 1;

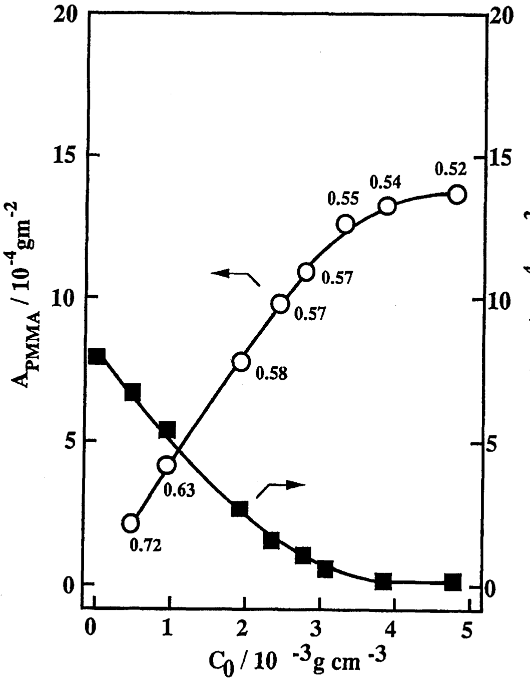

Fig. 4. Adsorption isotherm of SL-PMMA and desorption isotherm of NL-PS against the added concentration of SL-PMMA. The numbers in the graph are the values of p at that point. ○: SL-PMMA, ■: NL-PS.

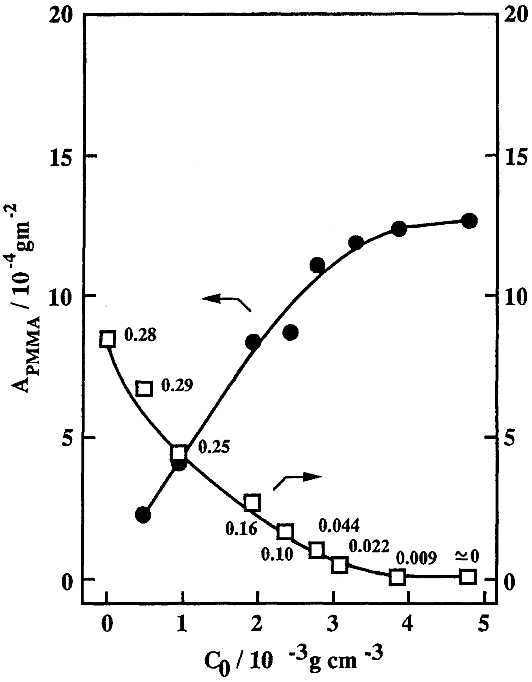

Fig. 5. Adsorption isotherm of NL-PMMA and desorption isotherm of SL-PS against the added concentration of NL-PMMA. The numbers in the graph are the values of p at that point. ●: NL-PMMA, □: SL-PS.

that is, the adsorbed PMMA has a flatter conformation (p=0.52) than that in individual adsorption (p=0.35). In conclusion, it has been clarified that the PS molecule in solution affects both the amount and the conformation of the adsorbed PMMA. The results represented here are consistent with our previous observations regarding the competitive adsorption of PMMA and PS mixtures.[19)]

In Fig. 6, the segment fractions of train, short loop and long loop for SL-PMMA can be plotted as a function of C_0, accompanied by the displacement of NL-PS. As shown in Fig. 6, the values of p gradually decrease, while the segment fractions of short loop and long loop increase. That is, the adsorbed PMMA varies from a flat conformation to a loopy conformation with an increase in C_0. When a PMMA solution of low concentration is added to the silica surface preadsorbed by PS, the value of p is relatively high (p=0.72; i.e., flat conformation). This reason is due to the low surface coverage, θ_{IR} (θ_{IR}=0.16) of silica surface saturated by PS, as previously reported.[18)] Therefore, PMMA may adsorb to the open space of the surface with a high p-value.

In Fig. 7, the segment fractions of train, short loop and long loop for SL-PS can be plotted as a function of C_0 accompanied by the displacement of SL-PS by NL-PMMA in solution. As shown in Fig. 7, the values of p decrease monotonously with an increase in C_0, while the fractions of long loop segments increase. That is, the adsorbed PS gradually varies from a flat conformation to a loopy conformation with an increase in C_0.

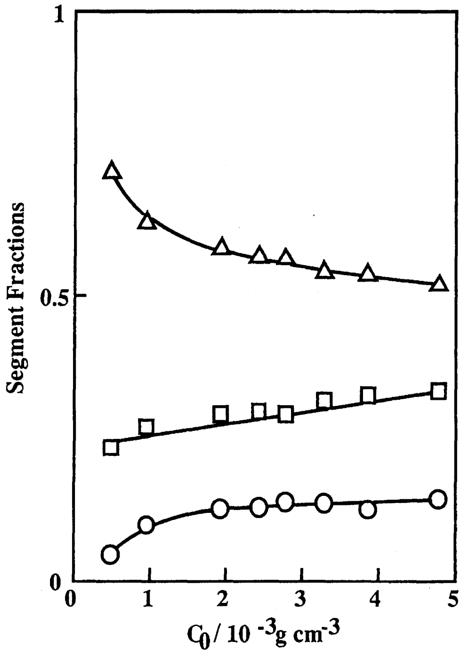

Fig. 6. Plots of the segment fractions of train, short loop, and long loop for SL-PMMA against the added concentration of SL-PMMA, with the displacement of NL-PS. △: train, □: short loop, ○: long loop.

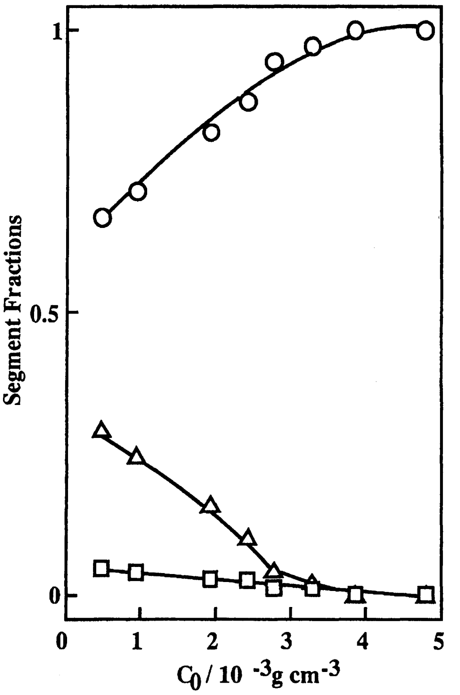

Fig. 7. Plots of the segment fractions of train, short loop, and long loop for SL-PS against the added concentration of NL-PMMA, with the displacement of SL-PS. △: train, □: short loop, ○: long loop.

Significantly, PMMA displaces PS from the silica surface, although a greater number of PS-surface attachments must be ruptured in order to effect a displacement. As soon as the silica surface is saturated with both PMMA and PS, PMMA molecules in solution displace PS molecules. This behavior has been pointed out in the simultaneous adsorption of PS and PEO by Kawaguchi et al.[30] The complete displacement of PS by PMMA observed throughout this study demonstrates the reversibility of the PS adsorption process, which is consistent with the results of the competitive adsorption of PMMA and PS mixtures.[19] It is also consistent with a previous observation that preferential adsorption of more surface-active molecules could effect polymer displacement.[36,37] Silberberg[38] and others[39,40] stressed that polymer adsorption is reversible under suitable conditions, showing that no irreversible polymer-surface bonds are formed.

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