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ESR Studies of the Competitive Adsorption Behavior of Poly(methyl methacrylate) and Polystyrene Mixtures at the Solid-Liquid Interface

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The adsorption from solution of polystyrene and poly(methyl methacrylate) mixtures on a silica surface was studied in order to establish the competitive adsorption behavior of these polymers. The fractions of train segment for these polymers were determined from the ESR spectra analyses, and these values were compared with those of the individual adsorption. When the initial concentrations of the polymer mixtures in solution were fixed and the added amounts of silica adsorbent were varied, the adsorption of polystyrene did not take place until the poly(methyl methacrylate) in solution was completely exhausted. In the simultaneous adsorption, the amount of adsorption of poly(methyl methacrylate) was affected by the presence of polystyrene in the solution. On the other hand, the amount of adsorption of polystyrene was unaffected by the presence of poly(methyl methacrylate) in the system. The conformation of the adsorbed poly(methyl methacrylate) was also affected by the presence of polystyrene when they were simultaneously adsorbed on the silica surface. The conformation of the poly(methyl methacrylate) adsorbed from the mixed solution formed a more compressed polymer layer in comparison with that for the case where the poly(methyl methacrylate) was adsorbed alone.

The adsorption of polymers at solid–liquid interfaces has been studied extensively. 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 most successful.[1)] 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 the study of the conformation of the polymer adsorbed at the solid–liquid interface; FT-IR,[2–7)] ESR,[1,8–16)] NMR,[17–19)] ellipsometry,[20,21)] and so on. Fontana 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.[2)] They obtained values of p from 0.3 to 0.4 for adsorbed poly(alkyl methacrylate) on the silica surface in organic solvents. Robb and Smith first employed the ESR method for studies of the adsorption of poly(*N*-vinylpyrrolidone) onto the silica surface, mainly from aqueous solution.[11)] Sakai et al. reported 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.[1)] The present authors reported the adsorption of poly(methyl methacrylate) (PMMA) on silica surfaces having various silanol densities and estimated the values of the segment fractions anchoring through the hydrogen bond in all train segments of the adsorbed polymer.[15)] We also reported the adsorption of methyl methacrylate-styrene copolymer on the silica surface as functions of the composition in the copolymer. We also discussed the difference in the adsorption ability of styrene and methyl methacrylate on the silica surface.[16)]

Several studies have been reported on the competitive and displacement adsorption of polymers.[3,22–31)] They can be divided into three groups as follows. (1) Competition between chains of different length(polydispersity). The use of polydisperse polymers in adsorption studies is the rule rather than the exception. Kolthoff and Gutmacher[22)] 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[23)] 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.[24,25)] studied the displacement of preadsorbed polymers by adding various displacer molecules. (3)Competition between polymers of a different chemical species. Kawaguchi et al.[27)] studied the competitive and displacement adsorption of polystyrene(PS) and poly(ethylene oxide)(PEO) and reported that PEO adsorbs preferentially over PS, and the preferential adsorption of large molecules over small molecules occurs even in the presence of different species. They[28)] also studied the competitive and displacement adsorption of PS and PMMA or styrene–methyl methacrylate copolymer having a wide range of styrene contents. Thies[3)] studied the competitive and displacement adsorption of PS and PMMA mixtures from trichloroethylene solution using infrared spectroscopy. He reported the reversibility of adsorption processes in such systems.

As reported in our previous paper,[15)] the segments of the PMMA adsorbed on the silica surface can be divided into two groups: one is the segments attached through the hydrogen bond between the carbonyl group of the polymer and the silanol group on the surface site, while the other is the segments attached except for the hydrogen bond. Since the IR method evaluates only the segments adsorbed through a hydrogen bond, the value of p estimated by the IR method is underestimated compared with that estimated by the ESR method. Therefore, we have now studied the competitive adsorption behavior of PMMA and PS mixtures using the ESR method, based on estimation of the values of p.

The purpose of this study is to utilize the ESR method to explore the competitive adsorption behavior of PS and PMMA mixtures onto a nonporous silica surface from carbon tetrachloride solution, and to determine whether polymer incompatibility effects alter the amount of adsorption or adsorbed structure of either polymer when they are simultaneously adsorbed on the silica surface. Therefore, we deal with two kinds of competitive adsorption systems: (1) the competitive adsorption of spin-labeled PMMA and normal PS, (2) the competitive adsorption of normal PMMA and spin-labeled PS. At present, it is impossible to deal with a system having both polymer components labeled, or to analyze the ESR spectrum for the dynamic behavior of PMMA and PS individually.

Experimental

Materials. The normal sample of PMMA (NL-PMMA) was prepared by an anionic polymerization of methyl methacrylate in toluene at 0 °C using phenylmagnesium bromide as a catalyst. The polymer was repeatedly fractionated in an acetone–water mixture to give narrow molecular weight distributions. The normal sample of PS (NL-PS) was purchased from Pressure Chemical Co. The spin-labeled PMMA (SL-PMMA) was prepared by the anionic copolymerization of methyl methacrylate with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl in toluene at 0 °C using phenylmagnesium bromide as a catalyst.[12] 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. The spin-labeled PS (SL-PS) was prepared by the procedure of Regen.[32] The copolymer of styrene and *p*-chloromethylstyrene 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 of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidyloxyl with sodium halide in *N*,*N*-dimethylformamide solution. The SL-PS was repeatedly fractionated in benzene–methanol mixture to give narrow molecular weight distributions. 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.

Table 1. Characterization of the Polymer Samples Used

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

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

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

Carbon tetrachloride used in this work was spectrometric grade and was used without further purification.

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.[15,16] The polymer solution was added to the silica adsorbent, and the mixture was stirred with a magnetic stirrer. The silica dispersions were separated by the use of a centrifuge. The amounts of adsorption, A (g m^{-2}), for PMMA were determined by IR spectroscopy by measuring the difference in the polymer concentrations before and after the adsorption. The characteristic band for PMMA at 1732 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 competitive adsorption studies on PMMA–PS mixtures were carried out in a similar manner to that used for the individual polymers in two modes as follows: (1) Initial concentrations of PMMA and PS in solution were fixed while the added amounts of silica adsorbent (i.e., surface area) were varied. Adsorption isotherms of mixtures were plotted as values of C_e for both polymers as a function of the surface area of the silica adsorbent (m^2); (2) Total initial concentrations of PMMA and PS in solution were varied while the added amounts of silica adsorbent were fixed. In this case, adsorption isotherms of mixtures were plotted as the amounts of adsorption of each polymer as a function of values of C_T. C_T denotes the total concentration of both polymers in solution before adsorption.

The surface coverage, θ_{As} (amount of adsorption / amount of maxiumum adsorption), was determined by using the same procedure as in a previous paper.[15]

Analyses of the ESR spectra of the adsorbed SL-PMMA were performed using the same procedure described in previous papers.[1,15] Analyses of the ESR spectra of the adsorbed SL-PS were basically the same as that of SL-PMMA. As shown in Fig. 1, the ESR line shape observed from the adsorption system (spectrum D) was simulated by the summation of three model spectra; the triplet line with narrowed width showing high mobility (spectrum A), the intermediately broadened line showing restricted segment motion (spectrum B), and the powder pattern showing rigid immobilization (spectrum C). The spectrum was normaliz-

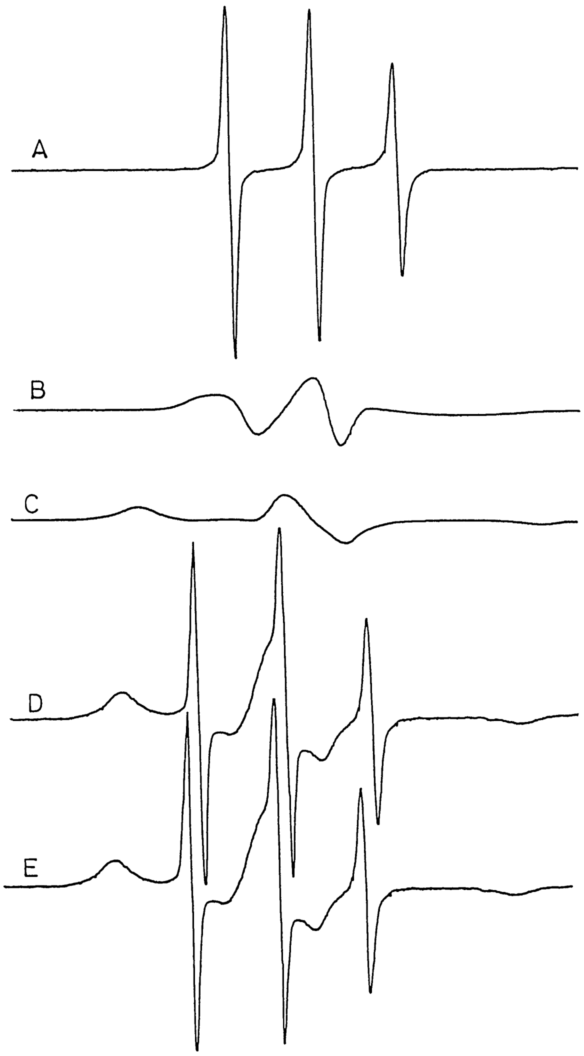

Fig. 1. ESR spectra used for simulation of adsorbed SL–PS on Cabosil M5 from carbon tetrachloride solution. Spectrum A: model for long loop or tail, B: or short loop, C: for train, D: observed from adsorption system, and E: synthesized by summation of A, B, and C.

ed by the signal intensity obtained from the second integration first-derivative spectrum. The amplitude of each model spectrum was determined by the least squares method on multiple regression to fit the summation of the three spectra (spectrum E) with the observed spectrum. The three model spectra were selected to make the correlation coefficient close to unity between the observed spectrum and the summation of three model spectra. In the three-component analysis, close fitting curves were found in every case.

Results and Discussion

Adsorption of Individual Polymers. Typical adsorption isotherms of individual polymers in carbon tetrachloride solution are shown in Fig. 2. Initially, the isotherms rose steeply with the increase in the value of C_e and reached plateau regions. All adsorption isotherms were of the usual high-affinity type, which is characteristic for the adsorption of polymers. As shown in Fig. 2, amounts of saturated adsorption for SL-PMMA and NL-PMMA are almost the same. A similar results 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, as the spin-label concentrations of the two labeled polymer samples are extremely low. The slight difference in the amounts of the adsorption between spin-labeled polymer and non-labeled polymer would be caused by the difference in the molecular weights between the polymers.[14,21]

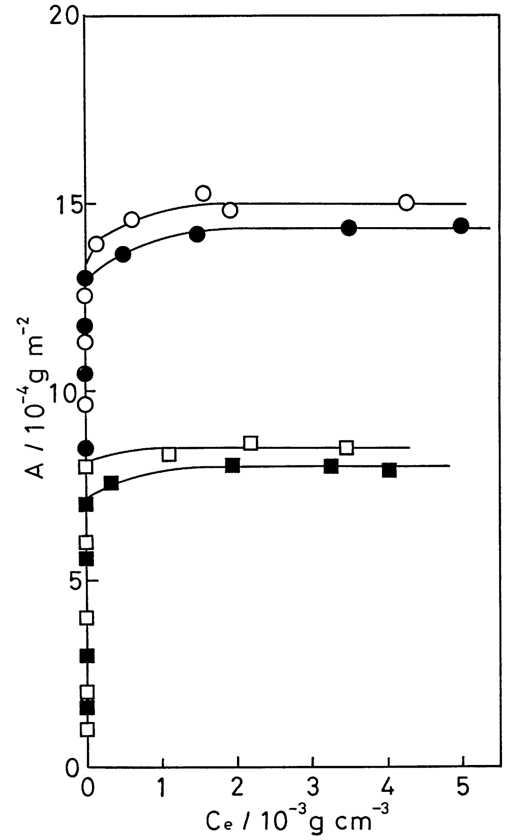

Fig. 2. Adsorption isotherms on Cabosil M5 from carbon tetrachloride solution at 25 °C. ○: SL–PMMA, ●: NL–PMMA, □: SL–PS, ■: NL–PS.

In Fig. 3, the segment fractions of train, short loop, and long loop for the adsorption of SL-PMMA are plotted against the surface coverage, θ_{As}. Increasing the value of θ_{As}, the number of train segments decrease, whereas the number of long loop segments increase. At relatively low θ_{As}, most of the segments were highly localized near the surface. As a result, the adsorbed polymer was considered to be flattened and formed a thin layer. At the saturated adsorption ($\theta_{\mathrm{As}}=1$), the fraction of train segments(the value of p) reduces to ca. 0.4, which indicates that the adsorbed PMMA has a flat conformation.

In Fig. 4, the segment fractions of train, short loop, and long loop for the adsorption of SL-PS are plotted against the value of θ_{As}. Increasing the value of θ_{As}, the number of train segments decrease, whereas the number of long loop segments increases. In contrast to the adsorption of PMMA, over the whole range of θ_{As}, it can be seen that the fraction of short loop segments is smaller. At the saturated adsorption-($\theta_{As}=1$), the fraction of train segments (the value of p) reduces to ca. 0.28. In contrast to the adsorption of PMMA, the trend toward lower values 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.

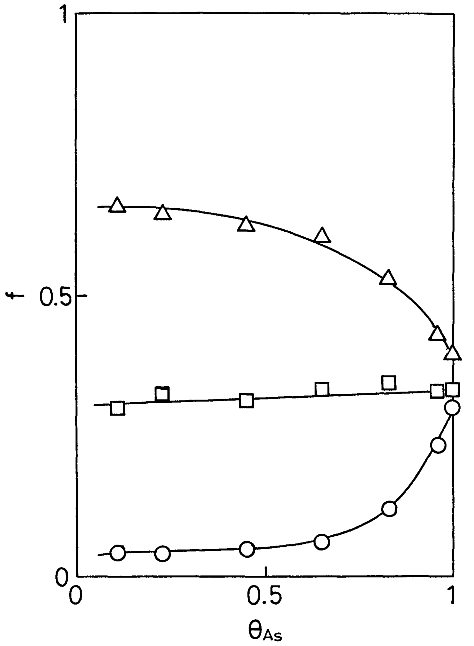

Fig. 3. Plots of the segment fractions, f, of train, short loop, and long loop against the value of θ_{As} for adsorbed SL-PMMA from carbon tetrachloride solution. △: train, □: short loop, ○: long loop.

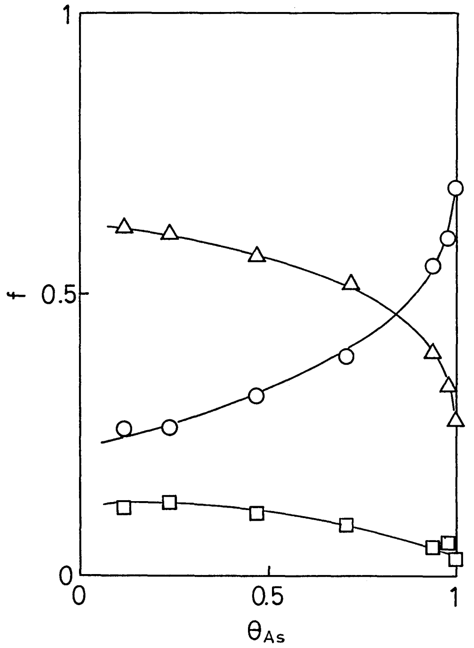

Fig. 4. Plots of the segment fractions, f, of train, short loop, and long loop against the value of θ_{As} for adsorbed SL-PS from carbon tetrachloride solution. △: train, □: short loop, ○: long loop.

Competitive Adsorption of Mixtures. When initial concentrations of PMMA and PS mixtures in solution were fixed at 1:1 by weight and the added amounts of silica adsorbent (i.e., surface area) were varied, the equilibrium adsorption isotherms are presented in Figs. 5 and 6. The numbers in the graph are the values of p at that point. In the figures, the dashed lines represent the calculated relationship between the values of C_e for PMMA and PS and the surface area. These relations are estimated from the date for the amount of adsorption in Fig. 2, and are based on the following assumptions: (1) PMMA is completely adsorbed before any PS adsorbs and PS in solution has no influence on the amount of adsorption of PMMA; (2) PS adsorbs once PMMA adsorption is complete and the presence of PMMA on the silica surface has no effect on the amount of adsorption of PS.

As shown in Figs. 5 and 6, the adsorption of PS does not take place until the PMMA in solution was

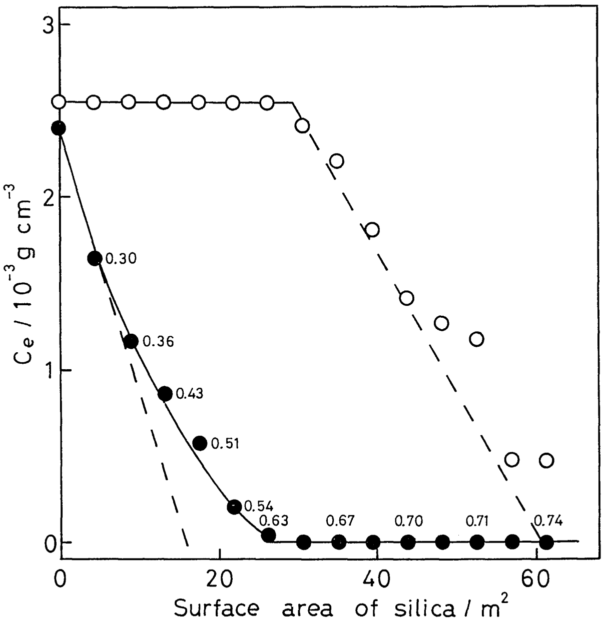

Fig. 5. Equilibrium adsorption isotherms for 1:1 (by weight) PMMA-PS mixtures. The dashed lines shown represent the calculated relationship between the values of C_e for PMMA and PS and the weight of silica adsorbent (i.e., surface area), assuming complete adsorption of PMMA occurs before PS is adsorbed. The numbers on the graph are the values of p at that point. ●: SL-PMMA, ○: NL-PS.

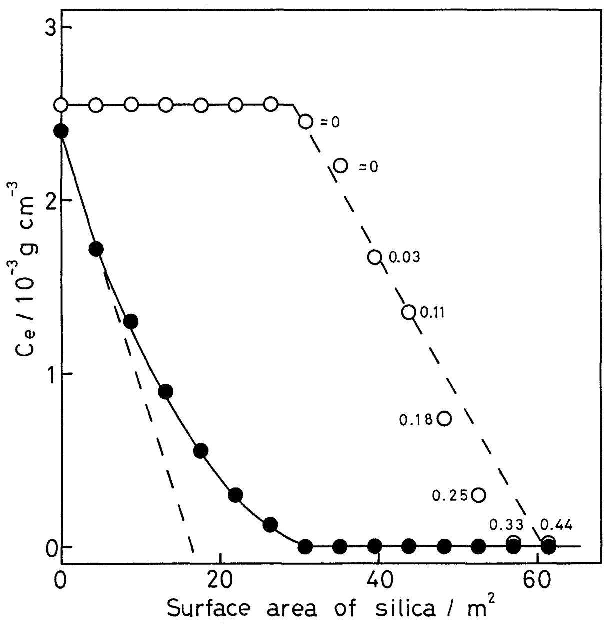

Fig. 6. Equilibrium adsorption isotherms for 1:1 (by weight) PMMA–PS mixtures. The dashed lines shown represent the calculated relationship between the values of C_e for PMMA and PS and the weight of silica adsorbent (i.e., surface area), assuming complete adsorption of PMMA occurs before PS is adsorbed. The numbers on the graph are the values of p at that point. ●: NL–PMMA, ○: SL–PS.

completely exhausted. The amount of adsorption of PMMA is affected by the presence of PS in solution, while the amount of adsorption of PS is unaffected by the presence of PMMA in the system. Once the adsorption of PMMA is complete, the adsorption of PS begins immediately. Although the measured values of C_e for PS are somewhat scattered, the amount of adsorption of PS is nearly independent of the surface coverage by PMMA. These results demonstrate that under equilibrium condition PMMA is preferentially adsorbed on the silica surface from carbon tetrachloride containing PMMA–PS mixtures. This reflects the stronger interaction of PMMA with the silica surface arising from its more polar character and greater hydrogen bonding ability.

When SL-PMMA and NL-PS mixtures adsorbed simultaneously on the silica surface, the segment fractions of train, short loop, and long loop segment for SL-PMMA can be plotted against the amounts of silica adsorbent (i.e., surface area) in Fig. 7. Until the PMMA molecules in solution are completely exhausted, the fraction of train segment(p) increases dramatically, while the fraction of long loop segment decreases. That is, the adsorbed PMMA varies dramatically from a loopy conformation to a flat conformation with an increase in the available surface site. After the complete removal of PMMA molecule from solution (i.e., surface area of silica in excess of *ca.* 30 m^2) where PMMA and PS may coexist on the silica surface, the conformation of adsorbed PMMA varies toward a more compressed polymer layer accompanied by a decrease in the fraction of short loop segment with the increase in the adsorbed amount of PS.

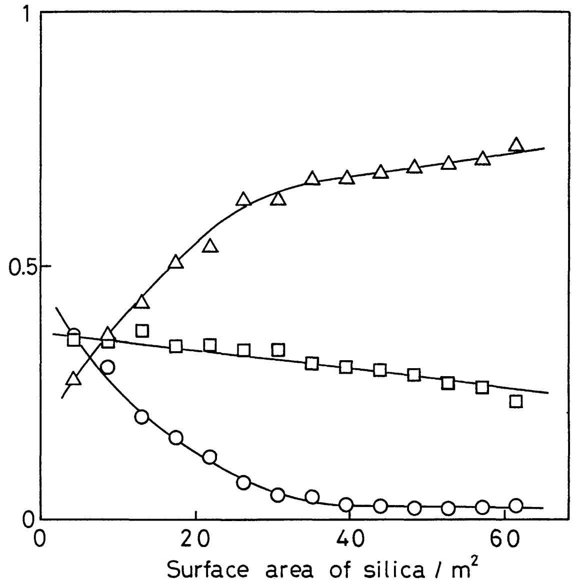

Fig. 7. Plots of the segment fractions, f, of train, short loop, and long loop against the surface area of silica for SL-PMMA adsorbed from carbon tetrachloride solution. △: train, □: short loop, ○: long loop.

When NL-PMMA and SL-PS mixtures are adsorbed simultaneously on the silica surface, the segment fractions of train, short loop, and long loop segment for SL-PS can be plotted against the amounts of silica adsorbent (i.e., surface area) as in Fig. 8. After the complete removal of the PMMA molecules from solution, the adsorption of PS begins immediately. The fraction of long loop segment for SL-PS decreases steeply with the increase in the surface area of silica, accompanied by an increase in the segment fractions of short loop and train. That is, the adsorbed PS varies dramatically from a loopy conformation to a flat conformation with an increase in the available surface site.

When the total initial concentrations of SL-PMMA and NL-PS mixtures in solution were varied and the added amounts of silica adsorbent were fixed, typical adsorption isotherms of mixtures are shown in Fig. 9 as a function of values of C_T. The numbers in the graph are the values of p for SL-PMMA at that point. The appearance of the adsorption isotherm for the mixture of SL-PMMA and NL-PS is different from that of usual high-affinity type, which is characteristic for the individual adsorption. The adsorption isotherm consists of the following three regions: (1) a region below $C_T=2\times10^{-3}$ g cm^{-3} where both SL-PMMA and NL-PS adsorb completely with the equal

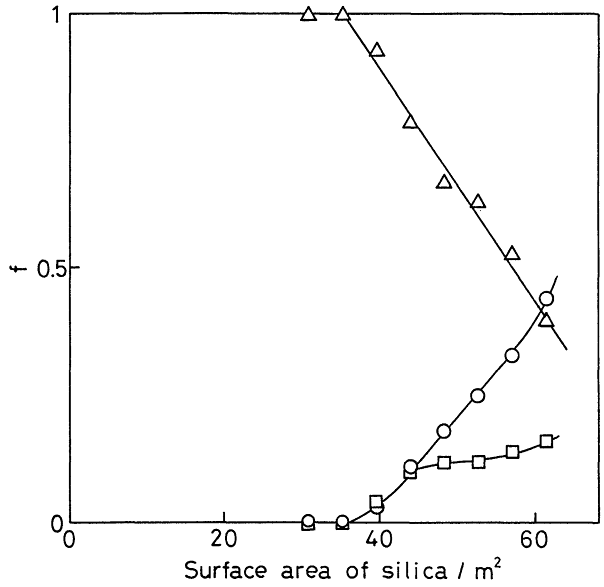

Fig. 8. Plots of the segment fractions, f, of train, short loop, and long loop against the surface area of silica for SL-PS adsorbed from carbon tetrachloride solution. ○: train, □: short loop, △: long loop.

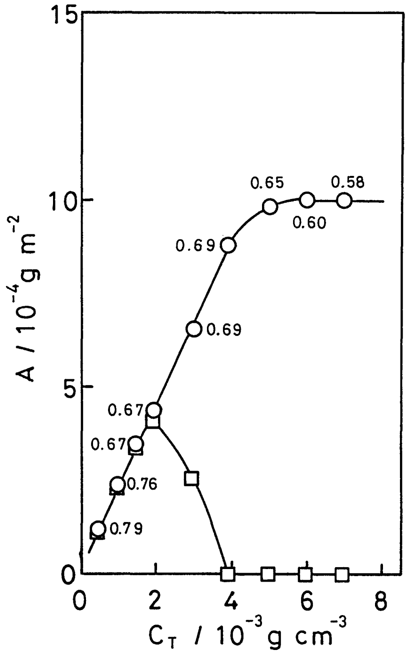

Fig. 9. Typical adsorption isotherms for SL-PMMA and NL-PS mixtures as a function of the values of C_T. The numbers on the graph are the values of p at that point. ○: SL-PMMA, □: NL-PS.

amounts of adsorption, (2) a C_T region of 2 to 4×10^{-3} g cm^{-3} where the amounts of adsorption for SL-PMMA further increase, accompanied by a decrease in the amount of adsorption of NL-PS, (3) a region above $C_T=4\times10^{-3}$ g cm^{-3} where the silica surface is filled with only SL-PMMA and no NL-PS is adsorbed.

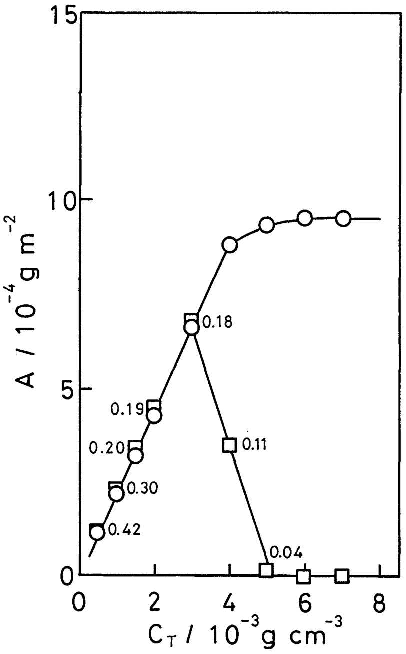

Fig. 10. Typical adsorption isotherms for NL-PMMA and SL-PS mixtures as a function of the values of C_T. The numbers on the graph are the values of p at that point. ○: NL-PMMA, □: SL-PS.

In region (1) the values of p decrease gradually with the increase in the value of C_T; that is, the fractions of loop segment increase. In region (2) the amount of adsorption for SL-PMMA is further increased with the desorption of NL-PS. This behavior implies that at $C_T=2\times10^{-3}$ g cm^{-3} the silica surface is initially saturated with SL-PMMA and NL-PS. Later the NL-PS on the silica surface is displaced from the interface by SL-PMMA in solution. This desorption of NL-PS by SL-PMMA molecule, as shown in Fig. 5, is mainly attributed to the stronger interaction of PMMA with the silica surface arising from its molar polar character and greater hydrogen bond ability. In region (3) the silica surface is filled with only SL-PMMA and no NL-PS is adsorbed. The amount of adsorption for SL-PMMA in this region is much smaller than that of adsorption on the silica surface individually as shown in Fig. 2. The values of p for SL-PMMA is much larger than that when adsorbed on the silica surface individually as shown in Fig. 3; that is, the PMMA adsorbed from the mixed solution has a flatter conformation than that in the individual adsorption. In conclusion, the influence of PS on the adsorption of PMMA is clarified and the results represented here are consistent with those shown in Figs. 5 and 6.

When the total initial concentrations of NL-PMMA and SL-PS mixtures in solution were varied and the added amounts of silica adsorbent were fixed, typical adsorption isotherms of mixtures are shown in Fig. 10 as a function of values of C_T. The numbers in the graph are the values of p for SL-PS at that point. The change of the amounts of adsorption for NL-PMMA and SL-PS against the value of C_T is almost same as that shown in Fig. 9. Regions (1), (2), and (3) are defined in a similar manner as Fig. 9. In a region (1) below $C_T=3\times10^{-3}$ g cm^{-3} where both NL-PMMA and SL-PS adsorb completely with the equal amounts of adsorption, the values of p for SL-PS reduces remarkably from 0.42 to 0.18. This implies that the conformation of adsorbed PS varies from a flat conformation to a loopy conformation. In region (2) of C_T ranging from 3 to 5×10^{-3} g cm^{-3} where the amounts of adsorption of NL-PMMA further increase with the desorption of SL-PS, the values of p for SL-PS reduces from 0.18 to 0.04. This implies that the conformation of the adsorbed PS varies toward a more loopy conformation.

Significantly, PMMA displaces PS from the silica surface even though PS and PMMA are incompatible polymers. The PS molecule in the mixed solution affects the amount and the conformation of the adsorbed PMMA. As shown in Figs. 9 and 10, some PS is adsorbed initially when PS–PMMA mixtures are added to the silica adsorbent and then is completely displaced from the interface by excess PMMA in the solution, although a greater number of PS-surface attachments must be ruptured in order to effect displacement. The fact that PMMA completely displaces PS from the silica surface establishes that PMMA readily penetrates the adsorbed PS layer. 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.[27] The complete displacement of PS by PMMA observed throughout this study demonstrates the reversibility of the PS adsorption process. It is consistent with previous observations that preferential adsorption of more surface-active molecules could effect polymer displacement.[33,34] Silberberg[35] and others[36,37] stressed that polymer adsorption is reversible under suitable conditions, showing that no irreversible polymer-surface bonds are formed.

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