ESR Studies of the Adsorption Behavior of Polystyrene at the Solid-Liquid Interface

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Synopsis. The adsorption of spin-labeled polystyrene on the silica surface from a carbon tetrachloride solution was studied by ESR spectroscopy. The fraction of train segments in the adsorbed polymer was determined from ESR spectrum analysis. The adsorption behavior of polystyrene is discussed as a function of surface coverage.

Many investigations have been published concerning the adsorption of polymers by the IR method.[1,2] Fontana and Thomas developed a spectroscopic technique for a quantitative estimation of the fraction of train segments in the adsorbed polymer, p.[1] Recently, the ESR method using nitroxide spin labels has been applied to the adsorption of synthetic polymers.[3-7] Sakai et al. studied the conformation of the adsorbed poly(methyl methacrylate)(PMMA) by the ESR method and reported that the ESR spectrum of the adsorbed polymer was resolved into three components: train, short loop, and long loop or tail.[4] We studied the adsorption of 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.[6] In this paper, we discuss the adsorption behavior of polystyrene(PS) using the ESR method, in order to confirm the greater effectiveness of this method.

Experimental

Spin-labeled polystyrene(SL-PS) was prepared by a procedure of Regen.[8] 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 a benzene-methanol mixture to give a narrow molecular weight distribution. The weight-average molecular weight of SL-PS used in this experiment was determined to be 22.1×10^4 by GPC calibrated with standard PS. The spin-label concentration in the polymer was about one label per 1000 monomer residues. The normal sample of polystyrene(NL-PS) was purchased from Pressure Chemical Co. The weight-average molecular weight of NL-PS was 20.7×10^4. Two nonporous silica samples, Cabosil M5 (Cabot) and Aerosil R812 (Degussa), were used as the adsorbents. According to the manufacturer, Cabosil M5 has a 2.2 nm^{-2} silanol density on the surface, while Aerosil R812, which is a surface-modified silica, has no silanol groups. The carbon tetrachloride used in this work was of spectrometric grade. The experimental techniques for the adsorption of polymers on the silica adsorbents were basically the same as those described in previous papers.[4,6]

Results and Discussion

The adsorption isotherms for SL-PS and NL-PS on Cabosil M5 from a carbon tetrachloride solution are illustrated in Fig. 1. Initially, both isotherms rose steeply with an increase in the equilibrium concentration, C_e, in the supernatant solution after the adsorption and reached a plateau region. The adsorption isotherms are of usual high-affinity type, which is characteristic for the adsorption of polymers. The amounts of saturated adsorption for these polymers are almost the same; therefore, a spin-label reagent has no influence on the adsorption of PS. No adsorption of SL-PS and NL-PS onto Aerosil R812, which has no silanol groups, took place. We therefore conclude that the adsorption of PS onto the silica surface occurs only by the formation of a hydrogen bond between a phenyl group of styrene and a silanol group of the surface site.

Figure 2 shows the ESR spectra of SL-PS adsorbed on Cabosil M5 from a carbon tetrachloride solution. The line shapes indicate that each spectrum comprises several portions which are easily distinguishable through their molecular motion. The ESR signals from the nitroxide labels attached to the polymer chain sensitively reflect any changes in the motion of the adsorbed chain segments arising from differences in the configurational states, whether in the loop or the train form. The spectral intensity ratio of the wings (marked with * in Fig. 2) to the inner parts (**) increased with a decrease in the surface coverage, θ_{As}

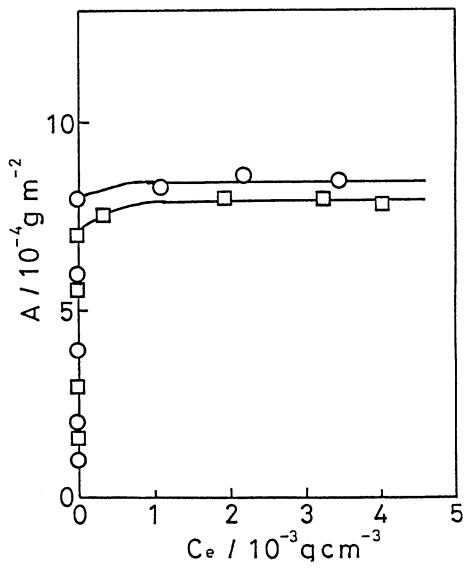

Fig. 1. Adsorption isotherms of SL-PS and NL-PS on Cabosil M5 at 25 °C. ○: SL-PS, □: NL-PS.

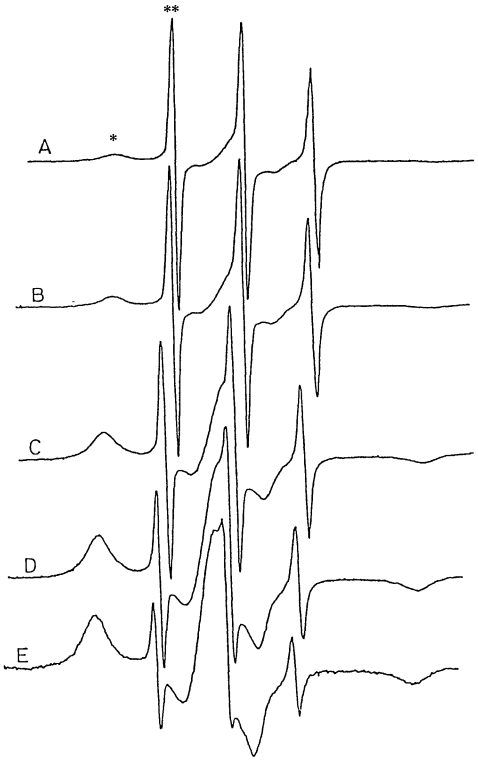

Fig. 2. ESR spectra of the SL-PS adsorbed on Carbosil M5 from carbon tetrachloride solution. A: θ_{As}=1, B: 0.94, C: 0.47, D: 0.24, E: 0.12.

(the amount of adsorption relative to that of the saturated adsorption). This shows a decrease in the content of the mobile segments(i.e., loop segments).

The procedures for analyzing the ESR spectra are principally the same as those described previously concerning the adsorption of spin-labeled PMMA.[5,6] As shown in Fig. 3, for example, the ESR spectrum of the adsorbed SL-PS (spectrum A) could be synthesized by superposing three reference spectra (obtained from the following model systems in which each polymer chain had different degrees of the motional freedom). Spectrum B was observed in the unadsorbed polymer in a carbon tetrachloride solution at 25 °C, and consisted of three motional-narrowing lines due to the rapid rotational motion of the segments in the low-viscosity medium. Spectrum C was obtained from a solid polymer in the molten state at 150 °C, and comprises an intermediately broadened line showing a restricted segment motion. Spectrum D was obtained from a cooled polymer solution in the frozen state at −120 °C, and showed a typical powder pattern due to rigid immobilization. These three model spectra were superimposed upon one another on a computer to match the observed spectrum of the adsorbed polymer (spectrum A). The amplitude of each model spectrum was determined by a least-squares method involving multiple regression to fit a summation of the three spectra (spectrum E) with the observed spectrum (A). In a three-component analysis, close curve fitting was found in every case. Therefore, the ESR spectra of SL-PS adsorbed on the silica surface are composed of three portions which have different local-chain mobilities, like those previously described for

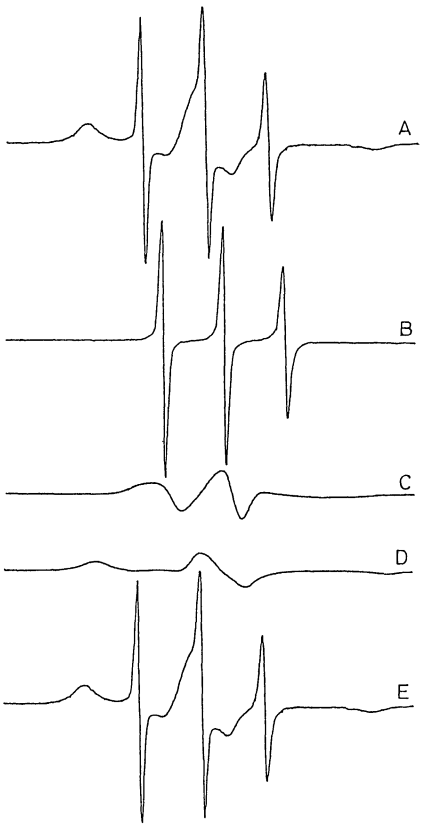

Fig. 3. ESR spectra used for simulation of SL-PS adsorbed on Cabosil MS from carbon tetrachloride solution. Spectrum A: observed from the adsorption system, B: model for long loop or tail, C: for short loop, D: for train, and E: synthesized by summation of A, B, and C.

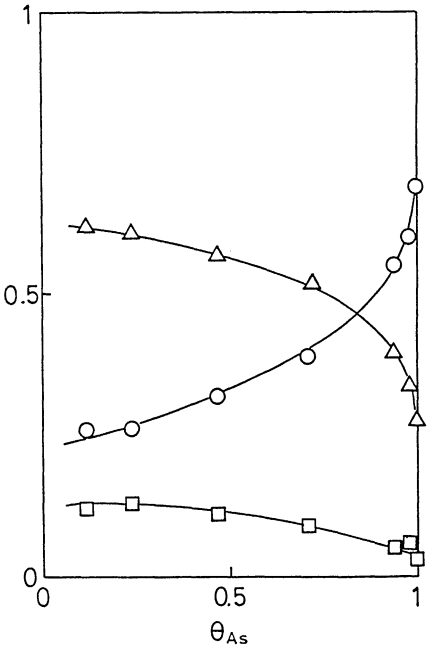

Fig. 4. Plots of the segment fractions of the SL-PS adsorbed from carbon tetrachloride solution as a function of the surface coverage (θ_{As}). △: train, □: short loop, ○: long loop.

the adsorption of PMMA.[4,6] In conclusion, the three portions are attributed to signals from the train, short-loop, and long-loop parts of the adsorbed chain.

The segment fractions of train(p), short loop, and long loop segments for the SL-PS adsorbed on Cabosil M5 from carbon tetrachloride solution are plotted against the value of θ_{As} in Fig.4. The fraction of the train segment(p) is larger and the fraction of long-loop segments is smaller at relatively low values of θ_{As}. When the adsorption approaches saturation, the fraction of train segments(p) reduces to ca. 0.28 with a relatively rapid increase in the fraction of long loop segments. The fraction of short-loop segments remained constant against the value of θ_{As}. This behavior (Fig. 4) is almost the same as that described previously for the adsorption of PMMA,[4,6] and is characteristic for the adsorption of polymers.

As discussed above, if the adsorption of PS occurs only by the formation of a hydrogen bond between a phenyl group of styrene and a silanol group of the surface site, the IR method utilizing the frequency shift due to the hydrogen bond should give the same value of p estimated by the ESR method. In practice, the value of p at the saturated adsorption($\theta_{As}=1$) in Fig. 4 is almost the same as that described previously by Kawaguchi et al., who studied the adsorption of PS using an identical solution-adsorbent system(PS-carbon tetrachloride-silica) by IR method.[2]

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