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The Fraction of Bound Segments and the Chain Motion of Adsorbed Poly(methyl methacrylate) at the Solution-Solid Interface as Studied by Electron Spin Resonance

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The configuration of poly(methyl methacrylate) adsorbed on silica from dilute solution (CCl_4, benzene, and $CHCl_3$) was studied from the point of view of the chain motion by a spin-labeling technique. The ESR spectrum of the adsorbed polymer was found to be composed of three portions, which had considerably different degrees of the motional freedom of the local chain segments. The rotational correlation times corresponding to the three portions were estimated by the line shape analysis and the rapid passage technique. These times were 1×10^{-9}, 5×10^{-9}, and longer than 10^{-6} s, and were attributed to the motions in the long loop, short loop, and train, respectively. The large fractions of the bound segments, obtained in all the cases of low surface coverage, showed highly flattened structures of the adsorbed chain molecules. In the adsorption from a poor solvent (CCl_4), a strongly compressed structure with a large number of the short loops was found. The adsorbed layer thickness, indicated by the fraction of the segments in the three states, became much smaller with an increase in the solvent power and a decrease in the surface coverage.

In recent years, the configurational properties of chain polymer molecules adsorbed at the solution-solid interface have attracted the interest of many investigators. From the experimental results as well as the theoretical treatments, it is commonly accepted that an adsorbed molecule consists of sequences of segments restrained in the surface layer (train) and of other sequences that extend into the bulk solution phase (loop or tail).

More recently, experimental techniques such as IR, ESR, NMR, ellipsometry, *etc.*, have been applied to estimate the train and loop contents and the thickness of the adsorbed polymer layer.[1-6] However, each technique was thought to result in uncertainties both in the evaluating methods and in the data interpretation. For example, Robb and Smith pointed out the advantageous and disadvantageous aspects inherent in the ESR technique, by comparing their ESR results with the published data obtained by IR and NMR techniques.[3] In our previous study, we made a direct comparison of the ESR method with the IR method using an identical solution–adsorbent system (PMMA–CCl_4–silica).[4] Based on the experimental results, we pointed out a disagreement: the ESR method gave much larger values of p (fraction of the train segments of the adsorbed polymer) than the IR values.

In the same paper, we reported the new finding that the ESR spectrum of the adsorbed PMMA (nitroxide-labeled) was composed of three portions which were easily distinguishable by the degrees of the motional freedom of the segments. The three spectral components were assigned to the signals from the train, short loop, and long loop segments. These assignments in the previous study, however, had been qualitatively performed by the comparison of the observed line shape with those of three model spectra, obtained from a free polymer solution of low viscosity, a cooled solution to the frozen state, and a highly viscous polymer in the molten state.

In the present study, the rotational correlation times of the three components of the adsorbed PMMA and the model systems were quantitatively estimated. A rapid passage technique was used to examine the very slow motion of the bound segments. The detailed behavior of the train and loop segments is discussed in relation to the solvent effects and the degree of adsorption.

Experimental

The spin-labeled PMMA was prepared by an anionic polymerization, as described in a previous paper.[4] The procedure basically followed the method of Goode, *et al.*[7] A single fraction of the polymer used was obtained by the fractional precipitation from an acetone–water system. M_n/M_w was determined to be about 1.3 by GPC analysis, and M_n was 1.2×10^5 by membrane osmometry. The spin concentration was three labels per polymer molecule. The polymer was essentially isotactic, which gave the IR *J*-value of 26, and was more soluble in CCl_4 than the atactic PMMA.

Cabosil M-5 (Cabot) with a specified surface area of 220 m^2/g for nitrogen adsorption was used as the adsorbent. The silica was essentially nonporous and had an average particle size of 14 nm.

The polymer solution was added to silica, and the mixture was stirred for 4 h with a magnetic stirrer. The adsorption isotherms, shown in Fig. 1, were determined as follows. The silica dispersions were centrifuged, and the polymer concentrations in the supernatant solutions were determined by means of the infrared spectroscopy at the normal carbonyl stretching band near 1740 cm^{-1}. In the case of the benzene solutions, the concentrations were determined by using a calibration curve obtained with the plots of the solution viscosity *vs.* the concn. The amount of adsorption was calculated from the changes in the concn before and after the adsorption.

The ESR spectra were recorded on a JEOL JES FE 3-X spectrometer utilizing 100 kHz field modulation and X-band microwaves. Temperature was controlled by a cooled and rewarmed nitrogen-gas-flow system. To detect the spectrum of the adsorbed polymer itself, the silica was washed before the measurements with pure solvent to eliminate the free polymer. In the regions of unsaturated adsorption, the measurements were made without the washing, since the contribution from the unadsorbed polymer into the spectrum was negligible.

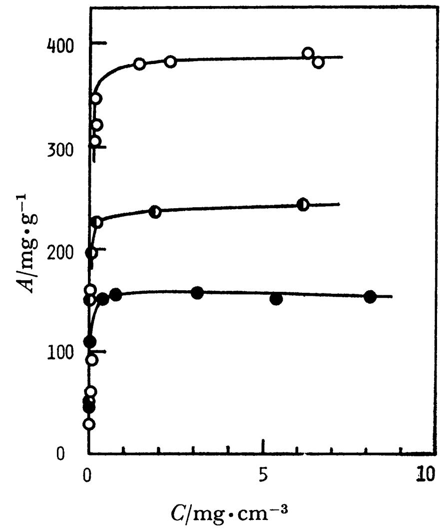

Fig. 1. Adsorption isotherms of PMMA at 25 °C. From ○: CCl_4 solution, ◐: benzene, ●: $CHCl_3$.

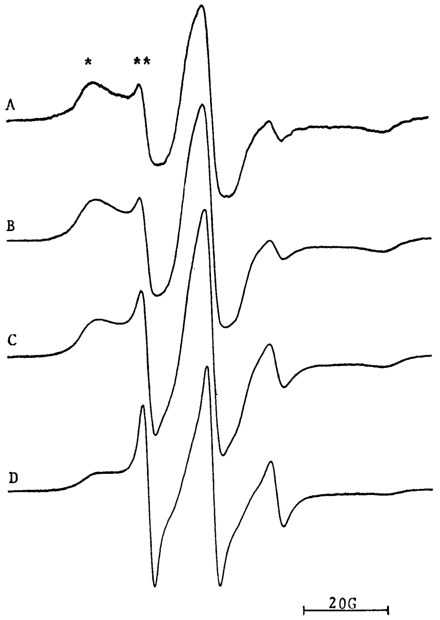

Fig. 2. ESR spectra of the adsorbed PMMA on silica from CCl_4 at 25°C.
A: θ=0.07, B: 0.15, C: 0.28, D: 0.89.

An adiabatic rapid passage technique, developed by Hyde, *et al.*,[8] was also applied to the examination of the very slow tumbling motion of the adsorbed chain segments. The first harmonic of the dispersion signal was detected at 90° out-of-phase with respect to the Zeeman modulation. The saturation-transfer spectra were observed under the conditions of moderately saturating microwave field.

Calculation of Rotational Correlation Times. For the region of motionally narrowed line shape, 10^{-9} to 10^{-11} s, the correlation times (τ_c) were calculated by the equation:[9,10]

$$\tau_c = c\,\Delta H_{\mathrm{msl}}[(h_0/h_{-1})^{1/2} - (h_0/h_{+1})^{1/2}]. \tag{1}$$

Here, ΔH_{msl} is the maximum slope width of the center field line, and h_{-1}, h_0, and h_{+1} are the signal heights of high, center and low field lines, respectively. The constant c is a parameter depending on the anisotropies of the hyperfine interaction and the g-factor.

In the region of relatively slow motion from 10^{-7} to 10^{-9} s, τ_c was estimated by the expression of Goldman, *et al.*:[11]

$$\tau_c = a(1 - S)^b, \tag{2}$$

where $S=A'_z/A_z$, A'_z is one-half the separation width of the hyperfine extrema (W), and A_z corresponds to the rigid limit value ($W_{\max}$). The parameters, a and b, are dependent on the rotational diffusion model and the intrinsic line width in the spectrum. In this work, the values for the moderate jump diffusion model, $a=1.1\times10^{-9}$ and $b=-1.01$, was used for the calculation.

Results and Discussion

ESR Spectra. Figure 2 shows the ESR spectra of PMMA adsorbed on silica from CCl_4 solution. The line shapes indicate the diverse motion of the adsorbed chain. The ESR signals from the nitroxide labels attached to the polymer chain reflect sensitively the changes in the motion of the adsorbed chain segments arising from the differences in the configurational states, whether in the loop or the train. The spectral intensity ratio of the wings (marked with * in Fig. 2) to the inner parts (**) decreased with an increase in the surface coverage: the amount of adsorption relative to the saturated adsorption. This shows an increase in the content of the mobile segments. These ESR spectra are composed of three portions which have different mobilities of the local chain, as described in a previous publication.[4] In conclusion, the three portions were attributed to the signals from train, short loop, and long loop parts of the adsorbed chain. As shown in Fig. 3 for an example, an ESR spectrum of the adsorbed PMMA 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. The spectrum A was observed in the unadsorbed polymer in CCl_4 solution at 10 °C, and consisted of three motional-narrowing lines due to the rapid rotational motion of the segments in the low viscosity medium. The spectrum B was obtained from the cooled polymer solution in the frozen state at −120 °C, and showed a typical powder pattern due to a rigid immobilization. The solid polymer in the molten state at 146 °C gave an incompletely averaged pattern due to an intermediate restriction of the chain motion (spectrum C). These three model spectra were superimposed upon one another on a computer to match the observed spectrum of the adsorbed polymer. As a result of the repeated runs, spectrum D gave a good fit to the line shape of the observed spectrum E. Thus, it was decided that the adsorbed polymer chain was constructed with three portions.

The Motion of the Adsorbed Chain Segments. The rotational motion of the loop segments is somewhat restricted by the fixing of the two loop ends by the surface, and will strongly depend on the length and the distance from the surface. The value of τ_c of the most mobile component was 1×10^{-9} s, while that of the intermediate portion was approximately 5×10^{-9} s. Therefore, resonable assignments for the relatively mobile components are as follows: the most freely

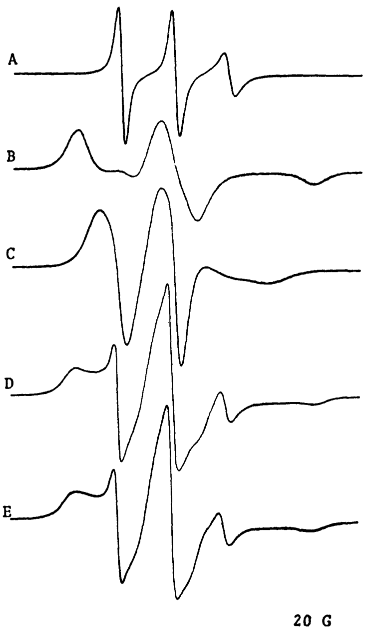

Fig. 3. ESR spectra of the spin-labeled PMMA.
A: Unadsorbed in CCl_4 at 10°C, B: unadsorbed in CCl_4 at -120 °C, C: in the molten state at 146 °C, D: reproduced by superposition of above three model spectra, E: adsorbed on silica in CCl_4 at 25 °C.

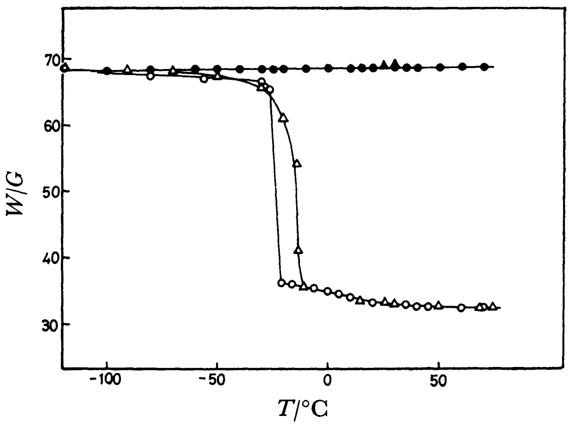

Fig. 4. Extreme separation width (W) of the ESR spectra *vs.* temperature.
●: Adsorbed in CCl_4, ▲: adsorbed in benzene,
○: unadsorbed in CCl_4, △: unadsorbed in benzene.

rotating segments are in long loops, while the intermediately restricted segments are in short loops. The value of τ_c of the long loop segments was about twice as long as the unadsorbed polymer in solution at the same temperature, 25 °C. The sequences of the detached segments were considered to be long enough to allow the rapid tumbling motion, although each segment behaves in a less mobile way than does the free polymer in solution. The intermediate restriction of the short loop segments, 5×10^{-9} s, should be caused by a close neighboring with the train segments. Robb and Smith demonstrated the presence of short loops of about 2 or 3 segments, from a comparison of their ESR results with the IR.[3] They thought that the ESR counted the short loops as the train. However, we suggest that the intermediately restricted portion of the adsorbed chain corresponds to the short loops of a few segments.

On the other hand, the most immobilized portion could be attributed to the train segments. Their motion was examined by the dependence of the extreme separation width (W) upon the temperature and the rapid-passage experiments. In Fig. 4, the values of W in various systems are plotted *vs.* the temperature. In the case of the adsorbed polymer, W values remained constant over the wide temperature range of -120 to 70 °C. The value of 68.5 G is in good agreement with the rigid limit (W_{max}) of the unadsorbed polymer in CCl_4 or benzene in the frozen states at -120 °C. These results mean that τ_c of the most immobilized component is at least longer than 10^{-7} s, since this time is the useful rigid limit for the motion of the nitroxide-spin labels to be detected by normal ESR measurements. In addition, W_{max} values of the adsorbed systems were significantly smaller than those in hydrogen-bonding media.[12] For example, the polymer solutions containing methanol or phenol gave the values of 73 and 76 G, respectively. Therefore, in the case of the adsorbed polymer phase, the direct H-bonding between the nitroxide labels and the surface silanol groups was negligible, and any specific adsorption through the nitroxide labels was not predominant over that between the original polymer segments and the surface. From the adsorption experiments using the unlabeled PMMA and the monomeric species (MMA and the labeled MMA), the same conclusion was obtained.

When the first harmonics of the dispersion mode were detected at 90° out-of-phase with respect to the field modulation under the conditions of a moderately saturating-microwave field, the rapid passage spectra could be observed. The spectrum A shown in Fig. 5 was obtained from the unadsorbed polymer in benzene solution in the frozen state at -50 °C. The spectrum B was obtained from the adsorbed polymer in benzene solution at 25 °C, and showed a slight effect of the saturation transfer. These spectra were quite similar

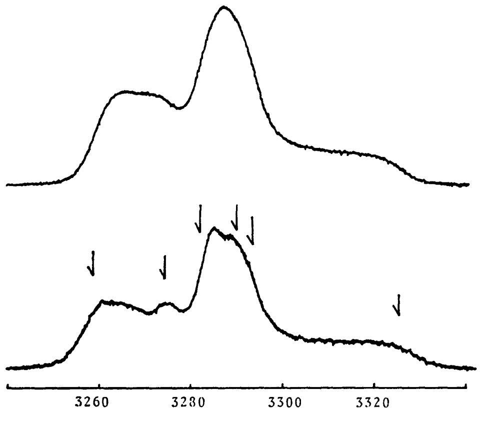

Fig. 5. Rapid passage dispersion spectra detected at 90° out-of-phase with respect to the field modulation of 5 G. Top: Unadsorbed in benzene at -50 °C, bottom: adsorbed on silica in benzene at 25 °C. The arrows show the turning points. Full scale is an interval of 100 G.

to the undifferentiated absorption spectra in the shape of the actual spectral distribution of spins. When τ_c is close to the reciprocal of the modulation frequency, approximately 10^{-6} s in this case, the spectral response is most sensitive to changes in τ_c.[8] The signal intensity would remarkably reduce with decreasing τ_c, in the regions between the turning points shown with arrows in Fig. 5. These turning points are the resonance fields where the magnetic principal axis of the nitroxide is oriented parallel or perpendicular to the applied field direction. The observed line shapes showed a very strong immobilization of the adsorbed polymer chain. If one neglects any contribution from a small amount of the mobile components on the spectrum, τ_c of the most immobile portion can be taken as longer than 10^{-6} s. Such a strong restriction demonstrates a rigid binding of the train segments by the surface sites. The motion was considerably slower than in the case of adsorbed monomeric species (labeled MMA) on silica. In general the rearrangements of the conformation of adsorbed polymeric molecules requires a relatively long period.[13] Such a strong restriction, due to the strict binding by the surface as described above, would disturb the rearrangement and consequently prevent the desorption process.

Miyamoto and Cantow studied the adsorption of isotactic PMMA onto silica from $CHCl_3$ solution using high-resolution NMR spectroscopy.[5] Since all of the signals from the adsorbed PMMA on the solid surface could not be detected, they concluded that the chain motion was strongly restricted at most of the segments, and the adsorbed molecule had an uniform and relatively compressed structure. In the present case of the ESR method, however, the spectrum seems to be composite, because the monitor attached to the polymer chain reflects sensitively the changes in the local segment motion over the wide range of τ_c from 10^{-7} to 10^{-11} s. The slow motional region in the long time scale is important in the case of the adsorbed chain. The considerable change in the motion arising from the differences in the configurational states of the adsorbed polymer segments, whether they are in train or loop, can be detected individually. The presence of three portions in the ESR spectrum was revealed by the line shape analysis in our study.

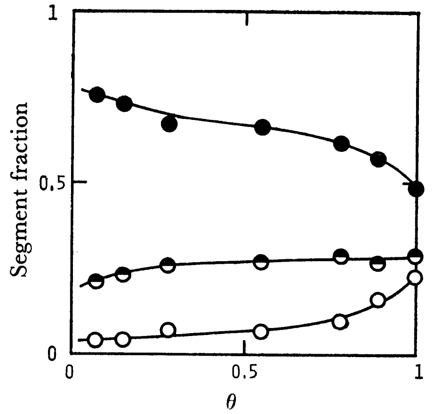

Fig. 6. The segment fractions of adsorbed PMMA in CCl_4 at 25 °C as a function of the surface coverage (θ). ●: In train, ◓: short loop, ○: long loop.

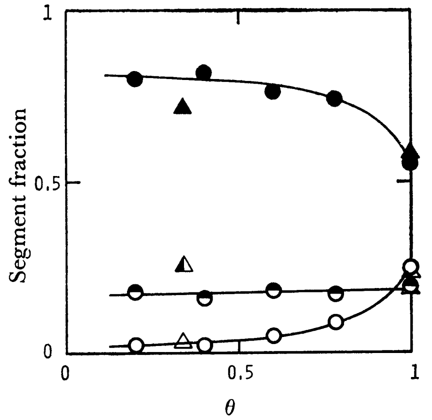

Fig. 7. The segment fractions of adsorbed PMMA on silica at 25 °C.
From benzene, ●: train, ◓: short loop, ○: long loop; from $CHCl_3$, ▲: train, ◭: short loop, △: long loop.

Effects of Solvent and Surface Coverage. The segment fractions in the three states were estimated from the integrated intensities of the signal components divided into three parts. Figures 6 and 7 show the fractions of the train, short loops and long loops as a function of the surface coverage (θ). At relatively low θ, most of the segments were highly localized near the surface. Consequently, the adsorbed polymer was flattened and formed a thin adsorbed layer. All of the theoretical treatments predict that a flexible chain polymer molecule will be strongly attracted by a solid surface and 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. In the present case, the adsorption is regarded to be caused by a strong attractive force much above 1 kT; the solvents used would not seriously perturb the adsorption energy, since H-bonding is the predominant interaction between the polymer and the surface. The revealed structures roughly agree with the theoretical prediction.

The thickness of the adsorbed layer increased moderately with an increase in θ. The intermolecular interactions such as the adsorption competition among the molecules were encountered at the high concentration of the adsorbed polymer, and would cause the thickening. However, even at the saturation adsorption, a flat configuration still remained. In a previous publication, we reported that one adsorbed PMMA molecule had 24% of the H-bonded carbonyls. The surface area occupied by one molecule was estimated to be approximately 1.2×10^2 nm^2 at the saturation. This value is much smaller than the cross section of the random coil in solution estimated from the unperturbed dimension of PMMA.[14] Therefore, the adsorbed molecule seems to have a "compressed structure" at the CCl_4-silica interface.

The thickness was smaller in the good solvents (benzene and $CHCl_3$) than in the poor solvent (CCl_4). On the other hand, the maximum amount of adsorption (A_s) was appreciably decreased with increasing solvent power, in the order of CCl_4, benzene, and $CHCl_3$. The decrease in A_s can be explained by the fact that a randomly coiled polymer is so extended in a good solvent that it occupies a larger surface area than in a poor solvent. The extension results in the decrease in the thickness under a strongly attractive force field. Particularly, there was a higher tendency of the short loop formation in the case of adsorption from CCl_4. In a poor solvent, such as CCl_4, the polymer molecule coiled and tended to form a large number of short loops. This tendency is consistent with the results from the computational statistical study by Clark *et al.*[15)]

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