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The Configuration of the Adsorbed Polymer at the Solid-Liquid Interface as Depicted by ESR and IR Studies

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Synopsis. Bound segment fractions of adsorbed poly(methyl methacrylate) on silica in CCl_4 were determined by both the spin-labeling technique and infrared spectroscopy. The ESR method yielded considerably larger values than the IR, indicating a highly flattened structure of the adsorbed polymer. However, the greater reliability of the ESR method was pointed out.

Problems of the configurational properties of chain polymer molecules adsorbed at the solid-liquid interface have been receiving much attention in both theoretical and practical fields. In many of the theoretical treatments, it has been predicted that the fraction of the bound segments, p, becomes close to unity in the case of a strong attractive force between the segment and the surface.[1)] The experimental estimation of p was first reported by Fontana and Thomas using IR spectroscopy.[2)] They obtained values of p from 0.3 to 0.4 for the adsorbed poly(alkyl methacrylate) on silica in organic solvents. Later experiments showed a similar tendency.[3),4)] Recently, an ESR technique, the spin-label method, has been employed by Robb *et al.*[5)] for studies of the adsorption of poly(vinylpyrrolidone) onto silica, mainly from aqueous solutions. The ESR values of p from 0.6 to 0.9 were appreciably higher than the results from the IR method. A comparison of the ESR and IR techniques was attempted by Robb and Smith, mainly from the standpoint of utility.[6)] However, it could not be decided whether the large difference in the estimated values of p comes from the differences in the adsorption systems (polymer, solvent, and solid) or from those in the evaluating methods, since they had merely compared their ESR observations with the published data obtained by the IR method. In the present work, we will deal with an experimental comparison of ESR and IR methods using the case of adsorbed poly(methyl methacrylate) on silica from a CCl_4 dilute solution.

Experimental

Spin-labeled PMMA was prepared by the anionic copolymerization of methyl methacrylate and 4-methacryloyloxy-2,2,6,6-tetramethyl-1-piperidyloxyl (molar ratio 450: 1) with a phenylmagnesium bromide catalyst in toluene at 0 °C.[7)] One fraction of the narrow molecular-weight distribution, obtained by repeated fractional precipitation, was used throughout the adsorption experiments. The number-average mol wt of the fraction used was determined to be 1.22×10^5 by membrane osmometry. The spin-label concentration in the polymer was about one label per 400 monomer residues. Cabosil M-5 supplied by Cabot, Far East, Inc., was used as the adsorbent; it had a specified surface area of 220 m^2/g for nitrogen adsorption. The polymer was adsorbed onto the silica from a CCl_4 dilute solution at 25 °C. Measurements of the ESR spectra were performed on a JEOL JES FE-3X spectrometer, while the corresponding IR spectra were recorded on a JASCO, DS 403G spectrometer.

Results and Discussion

In Fig. 1, (a) shows a typical IR absorption of the adsorbed PMMA, while (b) shows the normal spectrum of the free polymer in the CCl_4 solution. The spectrum (c), which was attributed to the H-bonded carbonyl, was obtained by graphical subtraction of (b) from (a), after conversion into a suitable intensity scale. In this case, the H-bonding seems to bring about a frequency shift from 1736 to 1712 cm^{-1} and a line broadening. The fraction of the H-bonded carbonyl groups in the adsorbed polymer was determined by a modification of the method of Kalnin'sh *et al.*[3)] The integrated absorption intensity was used for the calculation instead of the extinction coefficient.

A typical ESR spectrum of the adsorbed PMMA is shown in Fig. 2(e). The line shape indicates that the spectrum is composed of several portions which are easily distinguishable in their molecular motion. These arise from differences in the configurational states of the segments in the adsorbed polymer chain. From the analysis of the line shape, we concluded that the spectrum of the adsorbed polymer could be separated into three component spectra. On the other hand, we obtained three different spectra of PMMA which have different degrees of motional freedom. These are shown in Fig. 2(a), (b), and (c);

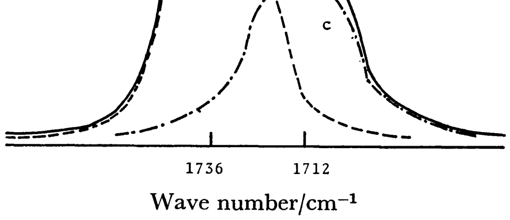

Fig. 1. IR absorption spectra of PMMA at the C=O stretching frequency.
a: Adsorbed on silica in CCl_4, b: in free CCl_4 solution, c: produced by graphycal subtraction of (b) from (a).

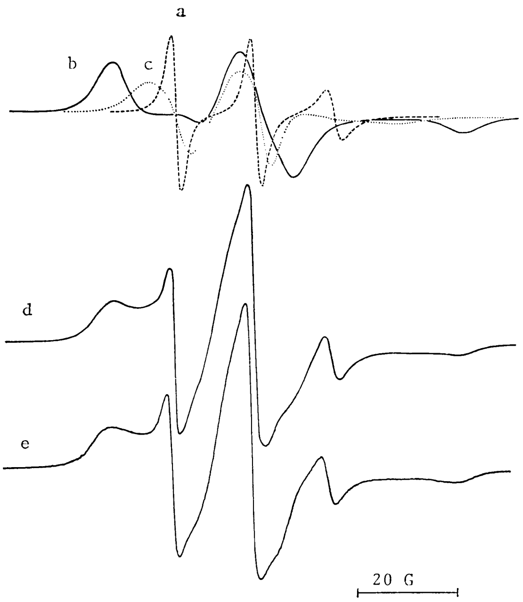

Fig. 2. ESR spectra of spin-labeled PMMA.
Top: a; in CCl_4 solution at 10 °C, b; in the frozen solution at −120 °C, c; of the molten state at 146 °C. Center: d; reproduced by superposition of above three model spectra. Bottom: e; adsorbed on silica in CCl_4 at 25 °C.

(a): a free polymer solution of a low viscosity at 10 °C (2 mg/ml), (b): a solution cooled to the frozen state at −120 °C, (c): a highly viscous polymer in the molten state at 146 °C. Apparently, the chain mobility decreased in the order of (a), (c), and (b). From the observation of the apparent line shape, the three spectra were found to correspond roughly to the three components of the adsorbed polymer. These three reference spectra were superimposed upon one another with suitable intensity ratios to reproduce the observed spectrum (e). The reproduced spectrum (d) closely fits in the observed line shape. In the polymer chain lying on the solid surface, the sequences of the segments directly bound to the surface should have restricted motion, while the detached segments should be much more mobile. Therefore, the component in a very strongly immobilized state was assigned to the train segments directly bound to the surface. The other two components, in relatively mobile states, were assigned to the free segments which are forming a short loop or a long loop. Our experimental evidence that the spin labels do not have a stronger affinity for the silica surface than the original MMA monomer demonstrates that specific adsorption through the nitroxide labels does not proceed during the polymer-adsorption process.

The values of p obtained by the ESR analysis are plotted against θ in Fig. 3. Here, θ is the amount of adsorption relative to the saturated adsorption, By our preliminary experiments, the saturated amount of adsorption was almost independent of the molecular weight of the polymer, while p decreased moderately with an increase in the mol wt. The fractions of the H-bonded carbonyl groups obtained by the IR analysis are also plotted in Fig. 3. The results from ESR exhibit a much higher level than the IR results. Both ESR and IR values of p were moderately decreased with an increase in θ. At the initial stage of a small amount of adsorption, $\theta = 0.27$, the ESR value of p was 0.67, which showed an appreciably flattened structure of the adsorbed polymer.

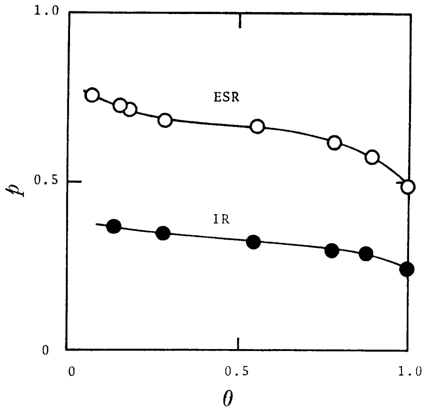

Fig. 3. Fraction of bound segments (p) *vs.* relative amount of adsorption (θ).

Cabosil silica has, as is well known, a partially hydrolized surface and a relatively small density of silanol groups on its surface. Most of those silanol groups are "isolated hydroxide" groups which are distant from one another beyond 4 Å. The density of the surface silanol available for the H-bonding with the polymer carbonyl was estimated to be about 3 OH per 100 $Å^2$ or less from the results obtained for the saturation adsorption (1.77 mg/m^2), where 24% of the carbonyls of the adsorbed PMMA were H-bonded. If a sequence of the segments is anchored only by the H-bonding with such dilute silanols, the absorbed sequence should be highly elongated along the surface.

One possible explanation for the large differences in our results from ESR and IR methods is as follows; some of the segments in a train interact with the silanol groups, while the remaining train segments interact with "non-hydroxylic sites"[8] on the silica surface. The IR method evaluates only the segments adsorbed through the H-bonding between the carbonyl and the silanol, whereas the ESR method evaluates the segments adsorbed in any mechanism. Therefore, the conventional IR method tends to estimate p values smaller than the actual values. On the other hand, we consider that the ESR method is more advantageous, as it visualizes the actual structure of the adsorbed polymer.

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