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Molecular-Weight Dependence of the Polymer Adsorption at Solid-Liquid Interfaces as Studied by ESR Spectroscopy

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The conformation of poly(methyl methacrylate) adsorbed from dilute solution on nonporous silica was investigated by ESR method using three-component spectrum analysis. The fraction of the polymer segments in train, short loop, and long loop or tail, as well as the rotational correlation time for the segments were examined with regard to molecular weight (M=10^3—3×10^6), the degree of adsorption, and the particle size of silica. In CCl$_4$, the saturation adsorption, A_s, increased from 6 to 16×10^{-8} g cm^{-2}, the fraction of polymer segments in train, p, decreased from 0.9 to 0.4, and the segment mobility reduced with the increase in molecular weight, respectively. Remarkable changes in A_s and p were found in a range of molecular weight of 5×10^4. In benzene, the values of A_s and p were less dependent on molecular weight than the cases of adsorption in CCl$_4$. Marked effects of intrachain interactions on the conformation were revealed for the adsorption of coiled polymers with high molecular weight from CCl$_4$ solution at low degrees of adsorption, where the loop formation was observed for polymers of $M > 10^4$. The intrachain force was attributed to overlapping among the segments. The difference in the adsorption behavior between the cases in CCl$_4$ and benzene was interpreted by the difference in the degree of deformation of polymer molecules upon adsorption.

The adsorption of linear macromolecules from solution on solid surfaces is a complicated phenomenon with many problems to be clarified. The cause is mainly due to the constitution of macromolecules with a large number of repeating monomeric units. Among molecular models proposed for characterizing adsorbed and deformed polymer molecules at the interface, the "train-loop" model would be most general and successful.

Many investigations have been published on the adsorption of polymers by the IR method; Fontana and Thomas developed the spectroscopic technique for the quantitative estimation of the segment fraction attached to the surface sites through H-bonding.[1-3] Recently, the ESR method using nitroxide spin labels, developed originally for the study of biopolymers, has been applied to the adsorption of synthetic polymers.[4-7] The ESR measurement supplies unique and important information concerning the molecular dynamics as well as the conformation at solid-liquid interface.

The chain mobility of the adsorbed polymer is different between the anchoring train on solid surface and the detached loop extending into the solution. The correlation time τ_c has the most sensitive range ($10^{-7} < \tau_c < 10^{-10}$ s) where the ESR line changes drastically with the time-averaging of anisotropy in hyperfine interaction and g-factor. The ESR spectrum of nitroxide spin labels attached to the polymer chain, therefore, reflects sensitively the difference in the relaxation process between the segments in loop and in train. If any contacts of nitroxide pendant groups with the surface sites can be ignored, the resolution of the ESR spectrum observed for the adsorbed polymer will allow to estimate the average conformation. Thus, the spin-label method seems to be suitable for the polymer adsorption system in which polymer chain has polar functional groups, such as ester, amide, ether, etc.

In our previous studies on the adsorption of spin-labeled PMMA, the ESR spectrum of the adsorbed polymer was resolved into three components: train, short loop, and long loop or tail.[6,7] The three-component analysis of the adsorbed polymer showed a possibility to discuss the conformation and the molecular motion in more detail than the resolution into two components reported by other authors.[4,5] Since the time required for the ESR spectrum analysis has been much saved recently by improving the simulation program using a small computer, it has become possible to treat a lot of spectral data within a short time.

The purpose of this study is to discuss the dependence of adsorption of PMMA on molecular weight over a wide range from 10^3 to 3×10^6, with reference to molecular conformation and molecular motion.

Experimental

Sample Preparation and Measurements. The experimental techniques were basically same as those described in our previous papers.[6,7] The spin-labeled PMMA was prepared by an anionic copolymerization of methyl methacrylate and 4-methacryloyloxy-2,2,6,6-tetramethyl-1-piperidiyloxyl (200—400/1 mol ratios) in toluene at 0 °C using phenylmagnesium bromide catalyst. The polymer was repeatedly fractionated in acetone-water mixture to give narrow molecular weight distributions. The characterization of the polymer samples is listed in Table 1. Each PMMA sample had a highly isotactic microstructure which gave the IR J-value of ca. 26.[8] The spin concentration in the used polymers was in the range of one label per 150 to 450 monomeric residues. The molecular weight was determined by means of viscometry, membrane osmometry, and vapor phase osmometry, and the ratio $\overline{M}_w/\overline{M}_n$ was determined by GPC calibrated with a standard polystyrene.

Two nonporous silica samples, Cabosil M5 (Cabot) and Aerosil OX-50 (Degussa), were used as the adsorbents.

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Table 1. Characterization of PMMA Samples Used

No.	$\bar{M}_n$	$\bar{M}_v$	Methods	$\bar{M}_w/\bar{M}_n$
I-1	1370	—	VPO[a)]	1.1[d)]
I-2	1740	—	VPO	1.1
I-3	2740	—	VPO	1.1
I-4	3770	—	VPO	1.2
I-5	8400	—	VPO	1.4
II-6	16000	—	MO[b)]	1.2
II-7	28000	—	MO	1.3
II-8	56000	—	MO	1.3
II-9	76000	—	MO	1.4
II-10	122000	—	MO	1.3
III-11	—	320000	Viscosity[c)]	1.4
III-12	—	700000	Viscosity	1.4
III-13	—	1.6×10^6	Viscosity	—
III-14	—	3.3×10^6	Viscosity	—

a) VPO: vapor phase osmometry of $CHCl_3$ at 37 °C. b) MO: membrane osmometry in toluene at 38 °C. c) Viscosity: the intrinsic viscosity in benzene was determined at 30 °C, and $\bar{M}_v$ was calculated by $[\eta]=5.2\times10^{-5}\bar{M}_v^{0.76}$.[14] d) The ratio $\bar{M}_w/\bar{M}_n$ was determined by GPC in THF.

Cabosil M5 had a surface area of 220 m^2g^{-1} by N_2 adsorption, and the average particle size of 14 nm. Aerosil OX-50 had the values of 50 m^2g^{-1} and 40 nm, respectively ($g=10^{-3}$ kg). Reagent grade CCl_4 and benzene were used as the solvents after fractional distillation over a desiccant.

The amount of adsorption, A, was determined by the ESR to measure the decrease of polymer concentration after the adsorption, because the peak-to-peak signal amplitude for the polymer solution was proportional to the concentration. The amplitude was calibrated by simultaneous measurement on an equal volume (0.1 cm^3) of the original solution. The typical adsorption isotherms are shown in Fig. 1. Each adsorption curve shows an initial steep rise followed by the plateau at low equilibrium concentration ($C_e=10^{-4}\,g\,cm^{-3}$). Hence, the saturation adsorption, A_s, was determined by taking the plateau values at $C_e=1\times10^{-3}$—$3\times10^{-3}\,g\,cm^{-3}$. The ESR spectrum of the adsorbed polymer was measured in a quartz sample tube which contained ca. 1 cm^3 of silica suspension and sealed under N_2. ESR measurements were made on a JEOL JES FE-3X spectrometer, with a X-band microwave, 100 kHz field modulation, and temperature control of ±1 °C. The g-factor and the sweep width of magnetic field were calibrated by a Mn^{2+} standard.

Analysis of ESR Spectra. The procedures for analyzing ESR spectra are principally same as those described previously with some modifications.[6,7] As shown in Fig. 2, the ESR line shape observed from the adsorption system (spectrum D) was simulated by summation of three model spectra; the triplet line with narrowed width showing high mobility (spectrum A), the intermediately broadened line showing a restricted segment motion (spectrum B), and the powder pattern showing rigid immobilization (spectrum C). The spectrum was normalized by signal intensity obtained from the second integration of first-derivative spectrum. The amplitude of each model spectrum was determined by the least squares method on the multiple regression to fit the summation of the three spectra (spectrum E) with the observed spectrum. The model spectra were selected to make the correlation coefficient close to unity between the observed spectrum and the summation of three model spec-

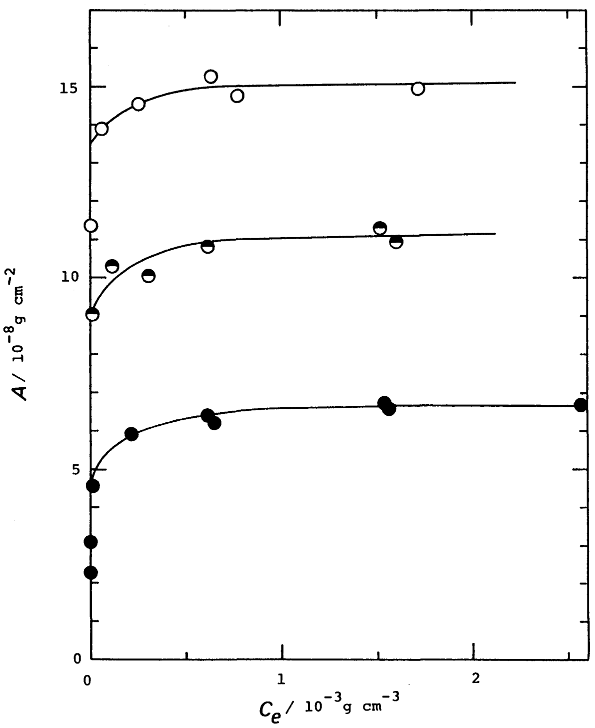

Fig. 1. Adsorption isotherms of PMMA on Cabosil M5 in CCl_4 at 25 °C. ●: M=1370, ◓: 5.6×10^4, ○: 1.22×10^5.

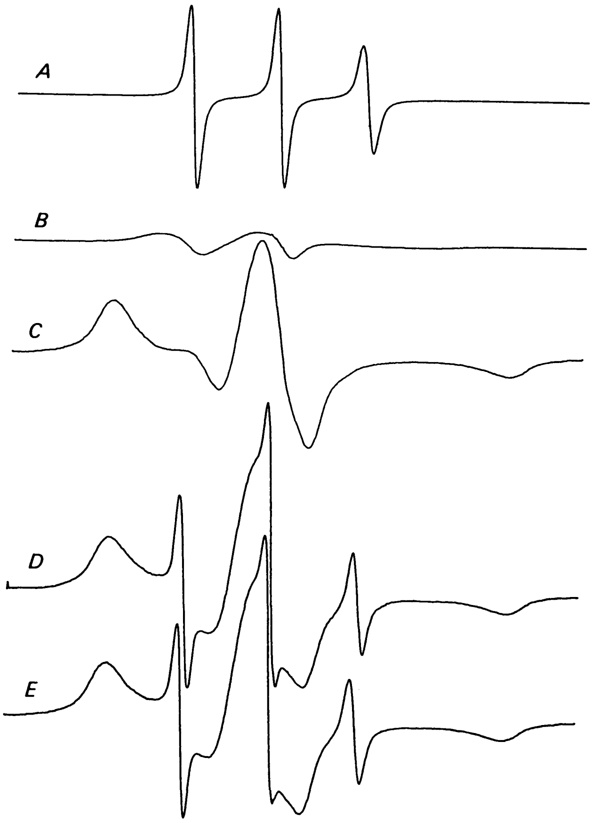

Fig. 2. ESR spectra used for simulation of adsorbed PMMA on Cabosil M5 in CCl_4 at the saturation stage. Spectrum A: model for long loop or tail, B: for short loop, C: for train, D: observed from the adsorption system, and E: synthesized by summation of A, B, and C.

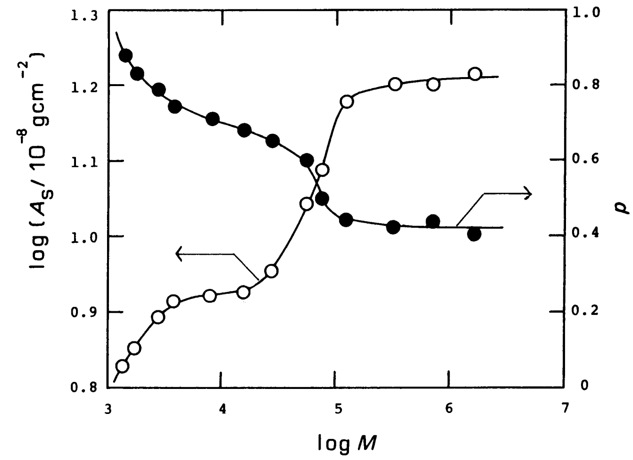

Fig. 3. Plots of logarithm A_s and p-values vs. molecular weight of PMMA adsorbed on Cabosil M5 in CCl$_4$ at 25 °C.

tra. In the three-component analysis, close curve fitting was found in every case. The intermediate components, however, were not negligible; the content was 10—25% in most cases, and good curve fitting could not be obtained without contribution of the intermediates.

The ESR model spectra of motional-narrowing components were observed at various temperatures, and in some cases calculated by Lorentzian and Gaussian approximation with reference to the temperature changes of the peak-to-peak amplitude ratios and the widths of the triplet lines observed for the polymer solution. The model spectra for the intermediate components were obtained from the amorphous polymers in the rubbery state at 120—160 °C. As for the most restricted segments (train), the model spectra were obtained from the adsorbed oligomer PMMA at a low surface concentration at different temperatures. The line shape was almost similar to that of the powder pattern and remained identical even when the temperature was lowered below 25 °C.

The rotational correlation time was calculated by the equations derived by Kivelson[9] and Goldman et al.,[10] who assumed the isotropic rotational diffusion.

Results and Discussion

1. Amount of Adsorption and the Fraction of Bound Components. The correlation between the saturation adsorption, A_s, and molecular weight of PMMA adsorbed from CCl$_4$ on Cabosil M5 is illustrated in Fig. 3. The fraction of the bound segments, p-value, is also plotted. The values of A_s increased from 6 to 15×10^{-8} g cm^{-2}, and the p-values decreased from 0.9 to 0.4 with the increase in molecular weight of a lower range from 10^3 to 10^5. Both values approached to constant values, $A_s=16\times10^{-8}$ g cm^{-2} and $p=0.4$, at higher molecular weight range, $M>10^5$. There is a close correlation between the changes in A_s and p; i.e., the loop content increases with the increase in A_s value. The changes in both values with molecular weight, however, were not monotonous but apparent in the molecular weight region of 5×10^4. The feature of the molecular weight dependency was reproducible in the repeated experiments using the polymer samples of different sources.

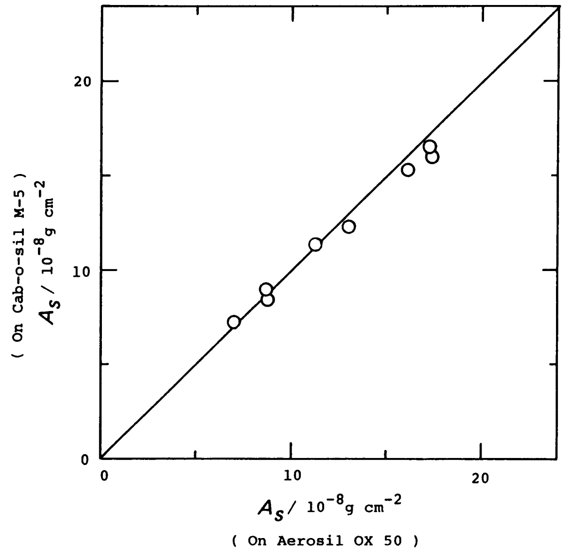

Fig. 4. Correlation diagram between A_s values on two silicas with different particle sizes; Aerosil OX-50 (400 Å) and Cabosil M5 (140 Å).

Similar phenomenon was reported by Kalnin'sh et al.[3] They studied the adsorption of atactic PMMA from several solvents on an Aerosil silica by the IR spectroscopy, and found a rapid drop of p-values with increasing molecular weight near 10^4. They reported a reflection point of p-value at the lower molecular weight region than that in this study. They attributed the rapid drop of p-values to the formation of transitional loops by adsorption of a polymer molecule on several adjacent silica particles, because the size of the polymer coil in solution became commensurate with the adsorbent particle size in the molecular weight region of 10^5.

In order to examine whether or not such a macroscopic interaction effect exists, the adsorption measurements were carried out on Aerosil OX 50 which has larger particle size (average diameter, 400 Å) than that of Cabosil M5 (140 Å) but has similar surface qualities. Figure 4 shows the correlation between the values A_s on Aerosil OX 50 and on Cabosil M5 at various molecular weights in CCl$_4$ solution. The amounts of polymer adsorbed per unit surface area were almost identical at the same molecular weight for both the adsorbents, yielding the same reflection point as that shown in Fig. 3. The changes of p-values with molecular weight were similar. From these results, a relatively strong molecular weight dependence appeared in the molecular weight region of 5×10^4 can not be explained by the sizes of adsorbent and polymer coil in solution. The effect of simultaneous adsorption seems to be negligible.

2. Dynamic Aspects of Adsorbed Molecule. Figure 5 shows the molecular weight dependence of the rotational correlation time, τ_c, estimated for the seg-

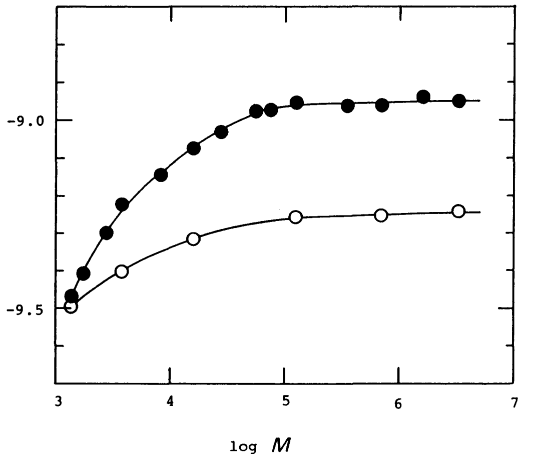

Fig. 5. Double logarithmic plots of rotational correlation time (τ_c) for loop or tail segments vs. molecular weight; ●: in adsorbed polymer, ○: in solution.

ments in long loops or tails, in comparison with that for free segments in CCl_4 solution (C=5×10^{-3} g cm^{-3}) as the reference system. The values of τ_c increase with the molecular weight when $M<10^5$, indicating a decrease of motional freedom in the loop. For $M>10^5$, the values of τ_c approach almost constant values about twice as large as for the free segments in solution. As for extremely short chain molecules, the detached segments appear to have motional freedom which is comparable to that of free segments in solution. This would be due to a contribution of the chain ends in tails.

The reduced degree of the motional freedom for higher molecular weight polymers will be interpreted from the increased segment density in the loop layer, because the A_s values increase and the p-values decrease with molecular weight as illustrated in Fig. 3. The segment motion is restricted by the intra- and interchain interactions in a dense surface layer. Above results will also predict the "compressed conformation" for higher molecular weight polymers at the interface as will be described later.

The values of τ_c of the intermediate components in ESR spectra (short loop) were in the range from 4 to 6×10^{-9} s, and were larger than the values for long loop or tail segment. Those values were less dependent on the molecular weight.

Figure 6 shows the ESR spectra of oligomer molecule (M=1370) adsorbed at a low surface coverage (θ=0.3) on Cabosil M5 in CCl_4 at various temperatures. The line shape of the spectrum at 25 °C is close to the powder pattern which reflects a complete train conformation of the adsorbed molecules. When the temperature was raised, the extreme separation width (W) of the spectrum reduced, indicating a recovery of the segment motion. However, even after keeping the adsorption system at 72 °C for 2 h, the ESR line shape indicated that the adsorbed oligomer molecules remain the deposited conformation. This would be an evidence of persistent adsorption which is characteristic of polymeric chains and different from the case of monomeric molecules.

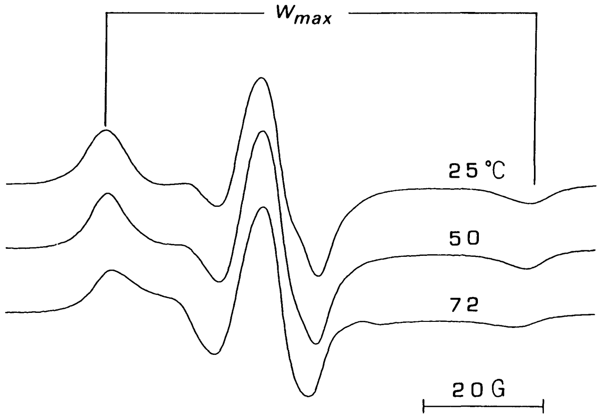

Fig. 6. ESR spectra of adsorbed oligomer molecule, M=1370, at unsaturated stage (θ=0.3) on Cabosil M5 in CCl_4 at various temperatures indicated in right side.

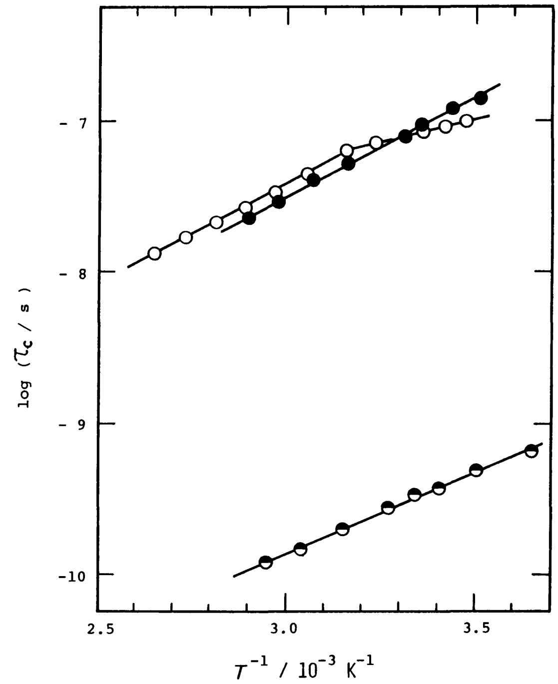

Fig. 7. Arrhenius plots of τ_c for oligomer PMMA (M=1370). ●: For train segments adsorbed on Cabosil M5 in CCl_4, ○: for amorphous solid state polymer, ◓: for free segments in CCl_4 solution (C=5×10^{-3} g cm^{-3}).

In Fig. 7, the values of τ_c for the train segments estimated from the changes in W are plotted against the reciprocal of temperature, together with τ_c for solid polymer and free polymer in solution. The τ_c value for the train was estimated to be ca. 1×10^{-7} s at 25 °C. The relaxation time was longer than that estimated for an amorphous polymer in glassy state at 25 °C. The activation energy of rotational diffusion was estimated to

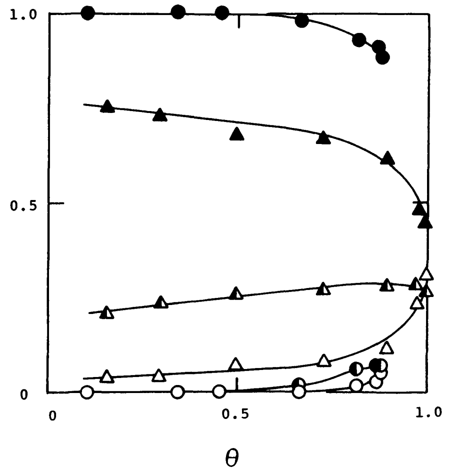

Fig. 8. Plots of the values of p (●,▲), f_{sl} (◐,◭) and f_{ll} (○,△) vs. θ for two polymers adsorbed on Cabosil M5 in CCl_4 at 25 °C. The data are shown with circles for M=1370 and with triangles for M=1.22×10^5.

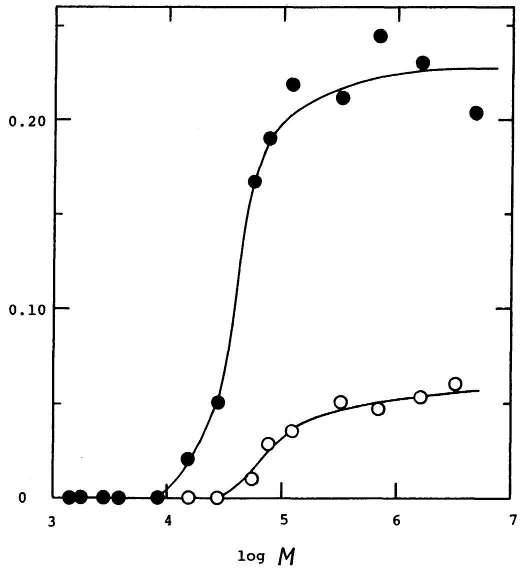

Fig. 9. Plots of values of f_{sl} (●) and f_{ll} (○) vs. logarithms of molecular weight at θ=0.1 on Cabosil M5 in CCl_4 at 25 °C.

be ca. 26 kJ mol^{-1}. This value is eqivalent to that for the rubbery state polymer, but higher than that for free polymer in solution.

In the cases of the molecules with higher molecular weight than 10^5, the values of W were equal to the rigid limit value, and no longer changed over the temperature range of −120 to 70 °C. The values of τ_c for the train segments in polymers with higher molecular weight will exceed 10^{-7} s, because W did not reduce even at ca. 70 °C. In the previous study using an adiabatic rapid passage technique, we revealed that τ_c for the train segment is over 10^{-6} s in a similar adsorption system.[6] These results demonstrate that the train segments in a coiled molecule were immobilized more rigidly than segments of short chain molecule. The stronger restriction of segment motion in higher molecular weight polymers would be caused by a "compression" onto the first layer (train) from the loop layer.

3. Influence of Surface Concentration on the Conformation. The fraction of the segments in train (p), in short loop (f_{sl}), and in long loop or tail (f_{ll}) was examined at various polymer concentrations in the surface layer, in order to elucidate the contribution of intra- and interchain interactions to the conformation. The segment distribution in adsorbed two polymers with different molecular weight is shown in Fig. 8 as a function of θ. The value of θ was determined from the following experimental results: The amount of polymer segments attached directly to the surface ($p \times A_s$) increased slightly (ca. 10%) with increasing molecular weight, and became almost constant at high molecular weight range ($M > 10^5$). The results gave a saturation value $(pA_s)_{max}$ of 6.7×10^{-8} g cm^{-2}. From this value, the surface area occupied per monomer unit in the train was calculated to be 25 Å^2, which is agree with the literature value determined for the case of PVAc adsorbed at a liquid-air interface.[11] The value of θ was obtained by the ratio, $\theta = pA/(pA_s)_{max}$, on an assumption that the surface sites saturate with the polymer segments at the saturation adsorption of high molecular weight polymers.

For the polymer with molecular weight of 1370, the p-values were close to unity (f_{sl}=0 and f_{ll}=0) at unsaturated adsorption stages ($\theta < 0.6$). This means a completely deposited conformation of short chain molecules. When the adsorption approaches the saturation, the p-value reduced to ca. 0.9 with slight increases in f_{sl} and f_{ll}. On the other hand, the higher molecular weight polymers ($M > 10^5$) contain higher amount of looped conformation even at low θ; the content of loop segments is ca. 20—30%. The p-values decreased gradually with increasing θ, and then dropped to ca. 0.4 at the saturation adsorption with relatively rapid increase in f_{ll}.

The dependence of p-value on θ for the high molecular weight polymers was stronger than the published results of other polymers such as poly(alkyl methacrylate), atactic PMMA, etc.[1] The statistical mechanical treatment of polymer adsorption, however, gave evident difference between p-values of saturation adsorption (θ=1) and of an isolated molecule ($\theta \rightarrow 0$).[12] The relatively strong dependence of p-value on θ found in this study is in accord qualitatively with the theoretical prediction.

Under the adsorption conditions at low θ, intrachain interaction and interaction between polymer segments and surface sites affect the conformation, whereas interchain forces are weak. The molecular weight dependence of the conformation was examined at low θ of ca. 0.1, in order to elucidate intrachain forces.

Figure 9 illustrates the fractions of the polymer segments in short loops (f_{sl}) and in long loops or tails (f_{ll}) as a function of molecular weight. The powder pattern of the ESR spectrum was observed for the adsorbed PMMA of lower molecular weight than 10^4. (Consequently, $f_{sl}=0$, $f_{ll}=0$, and $p=1$ for $M<10^4$.) The short chain molecules were completely flattened on the surface at low θ. In the range of higher molecular weight than 10^4, the adsorbed molecules take the looped conformation. The value of f_{sl} and f_{ll} increased with the increase of molecular weight from 10^4 to 10^5, and became constant at $M>10^5$.

These phenomena suggest that there is a difference in the interaction with the surface between the lower ($M<10^4$) and the higher molecular weight polymers. The difference determines whether the molecules behave as coiled chains to the surface or not. The reason why the higher molecular weight polymers are not adsorbed with a flat conformation as the lower molecular weight polymers even at low θ is probably due to intrachain overlapping among the segments. The overlapping in chain polymer reduces the p-value and affects on excluding a volume at the surface. Effects of intrachain interaction on the conformation have been studied by statistical mechanics on the adsorption of macromolecular chain. Several authors reported recently from the computer enumeration a marked reduction in p-value owing to the excluded volume effect.[13]

4. Deformation of Polymer Coil upon Adsorption. Koral et al., studied the adsorption of PVAc, and treated experimental results of the amount of adsorption, A_s, by an adsorption model that adsorbent surface is completely covered by spherical polymer coils.[11] They discussed the deformation of the polymer coil lateral to surface plane, by comparing the experimental values of A_s with the theoretical value expected from the radius of gyration, R, of the polymer in solution. A_s can be related to the surface area (S_s) occupied per polymer coil by

$$A_s = M/S_s N_0 \text{ (g per unit area)},$$

where N_0 is Avogadro's number. If the cross section ($S_b=\pi R^2$) of the polymer coil in solution is estimated, a factor which describes the degree of deformation of polymer coil, β, lateral to the surface when the polymer collapses on the surface can be defined as

$$\beta^2 = S_s/S_b.$$

In the series of adsorption of polymers with different molecular weights, the molecular weight dependence would be more explicitly described by the lateral deformation factor. If one considers important the relative changes of β with molecular weight, the factor β would be a meaningful parameter to describe the behavior of adsorbed polymers at the interfaces.

The dimension of PMMA in a poor solvent, CCl_4, was taken from the published data on the unperturbed chains of isotactic PMMA in a theta solvent.[14] Taking the relationship between the root-mean-square end-to-end distance and molecular weight, $\langle \bar{r}_0^2 \rangle = 7\times10^{-9} M^{0.50}$ (cm), the radius of gyration (R) was obtained from the relation, $R_0^2 = \langle \bar{r}_0^2 \rangle/6$. In this case, the difference between R and R_0 was ignored in considering relative changes of β with molecular weight. For the cases in benzene, R was estimated from the intrinsic viscosity-molecular weight relationship, assuming $\alpha^{2.43}=[\eta]/[\eta]_\theta$, where α is the expansion factor defined as $\alpha=R/R_0$, and $[\eta]$ and $[\eta]_\theta$ is the intrinsic viscosity in benzene and in a theta solvent, respectively.[14]

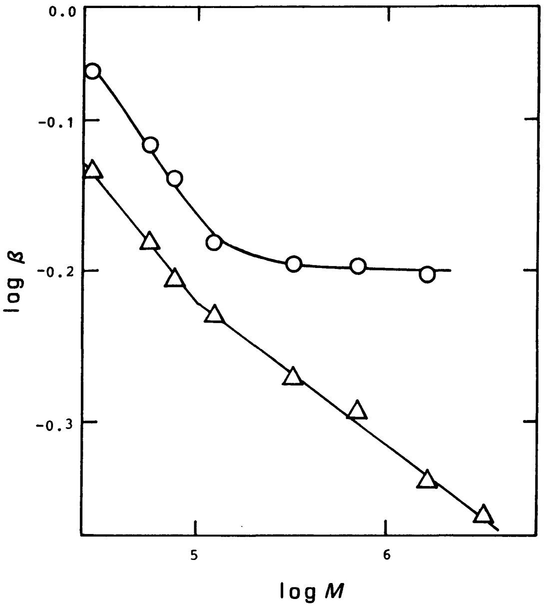

Fig. 10. Double logarithmic plots of β vs. molecular weight for PMMA with high molecular weight adsorbed on Aerosil OX 50 in CCl_4 (○) and in benzene (△) at 25 °C.

Figure 10 illustrates the relation between β for coiled molecules and molecular weight. The logarithm β is a negative function of molecular weight. Namely, the larger the polymer coil in solution is, the smaller the lateral deformation factor upon the adsorption is. The polymer coils seem to be laterally compressed to the surface, occupying narrower space than the cross section of the polymer coil in solution. In CCl_4, the factor β tends to be constant for $M>10^5$. On the other hand, the adsorption data obtained in benzene are expressed by $\beta \propto M^{-0.1}$.

The degree of lateral deformation of the polymer coil is considered to be more significantly influenced by molecular weight in a better solvent than in a poor solvent. It is probably related to higher expansion of the polymer coil in the better solvent. In a poor solvent, the polymer molecule will be in a more compact conformation than in a good solvent, and consequently resistant to the lateral compression when the polymer collapses on the solid surface.

The total number of segments adsorbed per surface site (θ/p) was estimated from the ratio $A_s/(pA_s)_{max}$. This value is a measure of the thickness of adsorbed

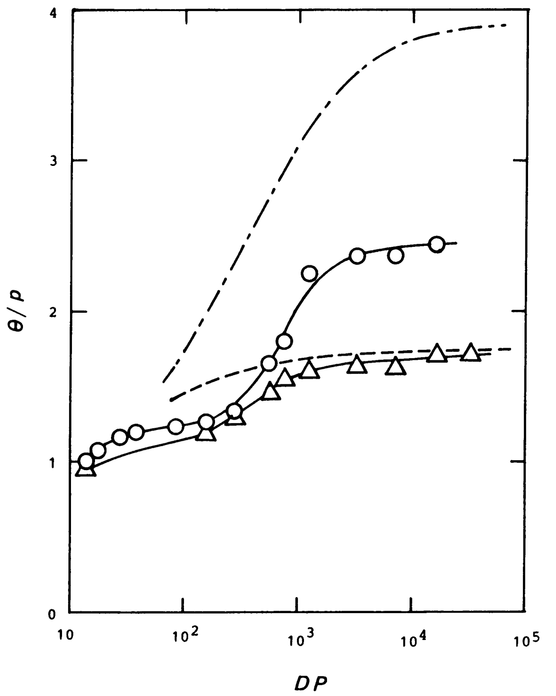

Fig. 11. Plots of θ/p vs. degree of polymerization, *DP*, ○:In CCl_4, △:in benzene. Dependence predicted by Silberberg's theory is shown with —·— for the case of adsorption from a theta solvent and with ---- for that from an athermal solvent.

polymer layer, and would reflect the feature of the deformation in the axis normal to the surface, as well as the fractions of polymer segments (p, f_{s1}, and f_{l1}) in the surface layer. In Fig. 11, the values of θ/p are plotted against the degree of polymerization (*DP*). The values predicted by Silberberg's theory are also plotted for the case of adsorption from a theta solvent and an athermal solvent. Here, the values are derived from the given original parameters; $\Phi^*=10^{-4}$, $\gamma_b\gamma_s=0.1$, and $\chi_s=\infty$(namely $\theta=1$).[12]

In the case of short chain molecules ($M<2\times10^4$), the values of θ/p were nearly unity both in CCl_4 and benzene. This means monomolecular layer adsorption. The molecular weight dependence of θ/p in the better solvent (benzene) was weaker than that in the poor solvent (CCl_4), and the larger molecules still remained the flat conformation, within $\theta/p<2$. These data are consistent with the theoretical values predicted for the case of athermal solvent. In CCl_4, the values of θ/p were ca. 2.4 for $M>10^5$, and considerably lower than the predicted values for the adsorption from a theta solvent.

In the case of adsorption from the better solvent, benzene, the degree of deformation of the polymer coils seems to be much higher than the case of adsorption from CCl_4, because the polymer coil is not only flattened but laterally compressed on the surface.

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