

Conformational change of polystyrene chains adsorbed on porous silica surfaces by the spin label method

Shigetaka Shimada*, Yoshito Hane and Taro Watanabe

Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan

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The spin-label method was used to study the structure and molecular motion of polystyrene chains adsorbed on three different porous silica surfaces, in order to examine the effect of surface geometry on the conformational structure. Three kinds of spin-labelled polystyrene (PS) samples with narrow molecular weight distributions, having weight-average molecular weight (M_w) = 2.98×10^3 , 96.4×10^3 , and 700×10^3 , were adsorbed on the surface of porous silica gels in cyclohexane (C_6H_{12}) at $35^\circ C$. Electron spin resonance (e.s.r.) spectra were observed at various temperatures after the samples were completely dried. It was found that the observed e.s.r. spectra were composed of two spectra arising from spin labels attached to 'train' and 'loop' (or 'tail') segments on the porous silica surface. The remarkable change of the e.s.r. spectra with temperature was analysed by computer simulation and the transition phenomena from 'train' segments to 'loop' or 'tail' segments were clarified. 'Loop' (or 'tail') segments of adsorbed PS, having $M_w = 700 \times 10^3$ were also converted to 'train' segments with increasing adsorption time when the chains penetrate into the inner part of the porous silica of small pore diameter. The conformational changes are strongly affected by the surface geometry, the size ratio of the average pore diameter to twice the radius gyration of a PS chain, and relaxation of the PS chain. © 1997 Elsevier Science Ltd.

(Keywords: polystyrene; silica surface; adsorption)

INTRODUCTION

Polymer adsorption phenomena have been studied intensively to elucidate the structure and molecular dynamics of polymer chains near solid surfaces¹⁻⁵. In our previous paper⁶, spin labelled polystyrene (PS), having weight-average molecular weight (M_w) = 1.9×10^5 was adsorbed on the surface of porous silica in cyclohexane (C_6H_{12}) and carbon tetrachloride (CCl_4) solutions and dried. The interaction of the adsorbed PS with the silica gel and its molecular mobility in the dried sample were discussed in detail. Only one PS chain in a pore of silica gel had an abnormally high mobility because of the weak interaction of the segment with the silica and the low segmental density. The conversion of 'train' segments to 'loop' or 'tail' segments was also found.

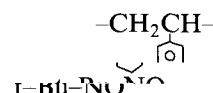
Kawaguchi and coworkers⁷⁻⁹ studied the adsorption behaviour of polystyrene on different porous silica in order to examine the effect of surface geometry on the adsorption. The conformational structure and molecular motion of the PS chain should be affected by the surface geometry. In this paper, we study the molecular weight and pore size dependencies of the electron spin resonance (e.s.r.) spectra of the adsorbed PS chains in detail and explore the effect of the surface geometry on the apparent conformation of the PS chains. We also show that the apparent conformational distribution can change with adsorption time and observation temperature.

In our previous paper⁶, the PS solution was mixed with the silica particles and shaken violently in an ultrasonic cleaner for the adsorption of PS. It was confirmed that an equilibrium adsorption was attained. In the present paper, the sample is shaken gently for a long time in a water incubator for the detection of adsorption time dependence, as mentioned in the Experimental section.

EXPERIMENTAL

Materials

A polystyrene having $M_w = 2.98 \times 10^3$ (PS-3), 96.4×10^3 (PS-96), and 700×10^3 (PS-700) was purchased from Tosoh Co. (Tokyo, Japan). The polydispersity of PS-3, PS-96, and PS-700 were 1.11, 1.01, and 1.05 respectively. The polystyrene was spin-labelled by the method of Bullock *et al.*¹⁰. The labelled monomer unit has the structure,



The labelled polymers (SL-PS) were finally purified by precipitating three times from toluene solution by addition of methanol and dried under vacuum for more than 1 day at room temperature. The porous silica particles used for the adsorbent were micro bead

* To whom correspondence should be addressed

(100–200 mesh) silica gels, MB-300, MB-1000, and MB-2000 of Silica Chemical Co., Kasugai, Japan. The surface area, the pore size and the method of the characterization were mentioned in the references⁷. The average pore diameters (d_p) of the silica gels, MB-300, MB-1000, and MB-2000 are 29.5, 102.3, and 190.7 nm respectively. The silica particles were purified by washing by hot carbon tetrachloride and dried in a vacuum oven at 130–150°C for several days.

Adsorption of polystyrene

Silica gel (0.2 g) was transferred to a 20 ml flask containing 4 ml of cyclohexane. The sample in the glass flask was mechanically shaken to allow to fully penetrate into the pores at 100 rpm in a Yamato BT-23 water incubator attached with a shaker for 24 h.

Next, 0.005 g of SL-PS was dissolved in 2 ml of cyclohexane. The polymer solution was transferred to the 20 ml flask containing the mixture of cyclohexane and silica gel. The polymer solution and mixture in the flask were also shaken to attain equilibrium at 100 rpm in the water incubator. For all experiments, the temperature of the water incubator was controlled to $35.0 \pm 0.1^\circ\text{C}$.

The concentration of the polymer solution, $8.3 \times 10^{-4} \text{ g ml}^{-1}$ does not exceed a critical entanglement concentration, c^* , given by

$$c^* = M / (4\pi R_F^3 N_A / 3) \quad (1)$$

where the coils begin to overlap. In equation (1), M , R_F , and N_A denote molecular weight, the size of one polymer coil in bulk solution, and Avogadro number. When the molecular weight of PS, $M = 700 \times 10^3$ and $R_F = 23.2 \text{ nm}$, the value of c^* is calculated to be $2.3 \times 10^{-2} \text{ g ml}^{-1}$ from equation (1). The concentration of the polymer solution, $8.3 \times 10^{-4} \text{ g ml}^{-1}$ in this study, is about five times more dilute than the value of c^* .

After the shaking was stopped and the silica particles were sedimented, the supernatant was carefully removed by an injector. The residue in the flask was dried in the vacuum oven at 40°C for several days. The same procedures were performed for different silica samples. After the solvents were completely evacuated, e.s.r. measurements were carried out in order to study structure and molecular motion of PS adsorbed on the dried silica. The obtained four specimens were coded as PS-3/MB-2000, PS-96/MB-2000, PS-700/MB-1000, and PS-700/MB-2000, where the samples of PS were adsorbed for a long time (7 days). The PS-700 were adsorbed on the MB-300 silica gel with changing the adsorption time, 1 day, 3 days, and 7 days. The three specimens were coded as PS-700/MB-300/1 day, PS-700/MB-300/3 days and PS-700/MB-300/7 days.

E.s.r. measurements

E.s.r. measurements were carried out with a JEOL FE3XG and a JEOL ME3XG spectrometer and a connected PC9801 computer. The signal of diphenylpicrylhydrazyl (DPPH) was used as a g -value standard. The magnetic field sweep was calibrated with the known splitting constant of Mn^{2+} in MnO .

Simulation

A computer simulation was carried out in order to obtain the principal values of g and A tensors due to the nitrogen nucleus, and to confirm the coexistence of two

kinds of nitroxide spin-labels, A-labels and B-labels, which were attached to strongly and weakly interacted segments with the silica gel, respectively. The simulation method was mentioned in the previous paper. The principle values of A tensors, the fractional amount of B-labels, and line widths can be obtained within small errors.

RESULTS AND DISCUSSION

Conformational transition of PS chains adsorbed on silica surface

Pore size dependence of conformation of PS chains. In the previous paper, e.s.r. spectra of SL-PS adsorbed on silica gel could be interpreted in terms of two components from two different kinds of labels, A-labels and B-labels. A-labels having high values of hyper-fine splitting due to nitrogen nucleus are connected to the segments strongly interacted with the silica as 'train' segments. The high values should be caused by the electric field of the silica surface¹¹. On the other hand, B-labels having low values of hyper-fine splitting are connected to the segments weakly interacted with the silica as 'loop' or 'tail' segments. In this paper, we clarify the factors affecting conformational change of the PS chains adsorbed on the silica surface by using the two components analysis.

Figure 1 shows e.s.r. spectra of SL-PS (PS-700) adsorbed on porous silica gels of the different pore size. The cyclohexane PS solution was mechanically shaken for a long time (1 week) to attain equilibrium, as mentioned in the Experimental section. E.s.r. spectra are observed at -196°C after the solvent is completely evacuated. The values of the widths between the outermost peaks ($2A_{Z'}$) in the samples of PS-700/MB-300/7 days, PS-700/MB-1000, and PS-700/MB-2000 are larger than in the bulk PS. Especially, in the sample of PS-700/MB-300/7 days, the line width is broader than those in the other samples. It can be considered that the higher values of $2A_{Z'}$ are caused by the effect of PS-silica interaction on hyper-fine splitting due to nitrogen nucleus.

Figure 2 shows an example of temperature dependence of the e.s.r. spectra in the sample of PS-700/MB-1000. The outermost peaks in the high and low magnetic field are like plateaux in the e.s.r. spectrum observed at 90°C (Figure 2b). The flat peaks suggest that the two components analysis is reasonable for the e.s.r. spectrum. The dotted line in Figure 2c shows a simulated spectrum for the e.s.r. spectrum observed at -196°C by assuming only one kind of spectrum. The agreement between the simulated spectrum and the observed spectrum (the solid line) is not good. On the other hand, the simulated spectrum by assuming two components shows good agreement with the observed spectra as indicated in Figures 2a and 2b. This result indicates the classification of the spin-labels (A-labels and B-labels) affected by different environments, and is a good approximation as discussed in the previous paper⁶.

The simulated spectra in Figure 1 also show good agreement with the experimental spectra. It is confirmed that all spectra for the adsorbed PS are composed of two components, whereas the e.s.r. spectrum for SL-PS in the homopolymer PS (PS bulk) can be simulated by assuming only one component as shown in Figure 1d. The e.s.r. parameters determined from the spectral simulations are

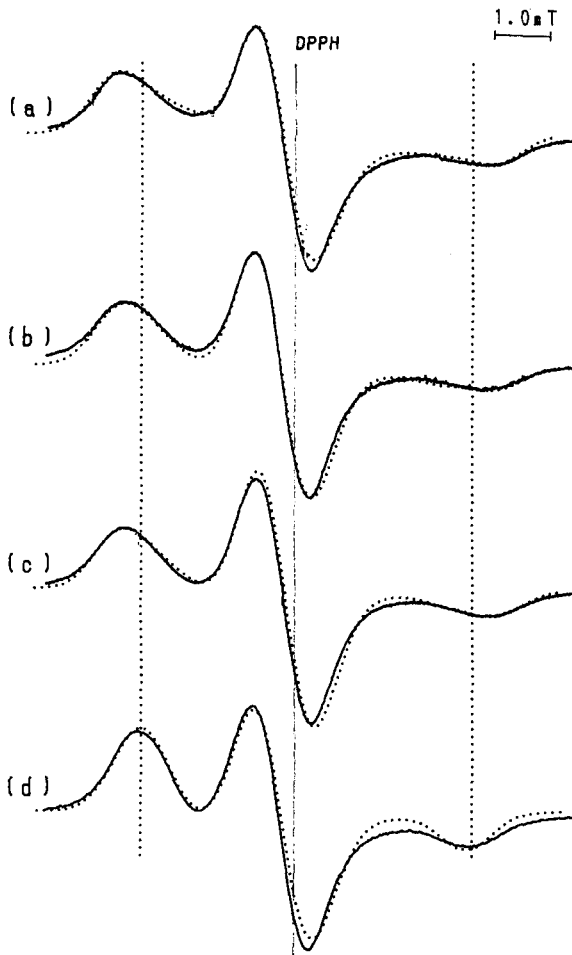


Figure 1 E.s.r. spectra of spin-labelled PS (PS-700) adsorbed on porous silica gels of different pore size: (a) MB-300; (b) MB-1000; (c) MB-2000 and spin-labelled PS (PS-700) in homopolymer matrices. Measurements were carried out at -196°C . Solid and dotted lines are experimental and calculated spectra, respectively

shown in *Table 1*. The following results are found from the simulations.

- (a) E.s.r. spectra observed at -196°C are composed of two components, a spectrum with high A_Z and A_i values in comparison with those in the homopolymer PS, reflecting a strong PS-silica interaction (A-labels) and another spectrum with low A_Z and A_i values, reflecting a weak PS-silica interaction (B-labels). The B-labels have the smaller value of A_Z and the larger values of A_X and A_Y than those in the homopolymer PS. The partial averaging of A values suggests that the molecular motion of the segments, weakly interacted with silica, occurs even at -196°C , because of its low segmental density.
- (b) The fractional amount of B-labels decreases with increasing pore diameter of porous silica gel and the values of A_i and A_Z of A-labels adsorbed on the MB-300 silica surface are the largest. These facts indicate that the conformational structure of PS chains adsorbed on the silica surface should be strongly affected by the surface geometry. Twice the radius of gyration of a PS chain¹² in the sample of PS-700/MB-2000 is so much smaller than the average pore diameter, as shown in *Table 2* and then PS chains adsorb unrestrictedly to an energetically stable conformation in comparison with those in the silica

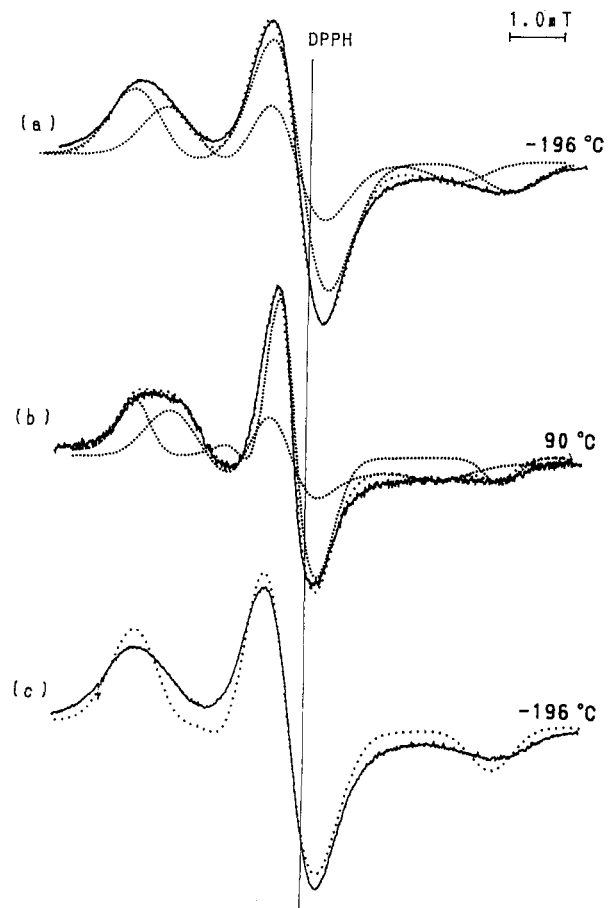


Figure 2 Comparisons of calculated spectra (dotted) and observed (solid) of spin-labelled PS (PS-700) adsorbed on the porous silica gel of MB-1000. Measurements were carried out at -196°C ((a) and (c)) and 90°C (b). Spectra (a) and (b) are calculated by assuming that the spectrum is composed from two different magnitudes of interaction with silica, whereas spectrum (c) is calculated by assuming only one component

gel of the smaller pore size. On the other hand, the distortion of PS chains in the pore increases with decreasing the size ratio. The especially small size ratio (0.64) in the sample of PS-700/MB-300/7 days suggests that PS molecules cannot penetrate easily into a pore of the silica gel discussed in the later section. Only one PS molecule is constrained in a pore of the MB-300 silica as schematically shown in *Figure 3*. Therefore, the amount of the distorted segments weakly interacted with the silica (B-labels) is larger, and the segments connected to A-labels are strongly interacted with the silica.

- (c) The fractional amount (35%) of B-labels observed at -196°C in the sample of PS-700/MB-1000 increases to 59% at 90°C and partial averaging of A- and B-labels also occur at 90°C . The increase of the fractional amount is a reflection of the conversion of 'train' segments to 'loop' or 'tail' segments. The adsorbed segments begin to protrude from the silica surface when the segments have thermal energy equal to the PS-silica interaction energy.

Temperature dependence of conformation of PS chains. In order to evaluate the molecular mobility of adsorbed PS chains related to the PS segment-silica interaction, e.s.r. spectra were observed at various

Table 1 E.s.r. parameters of spectra of spin-labelled PS (PS-700), determined from the spectrum simulation mentioned in the text

	PS-bulk (-196°C)	MB-300 (0.6) (-196°C)		MB-1000 (2.2) (-196°C)		MB-2000 (4.1) (-196°C)		MB-1000 (2.2) (90°C)	
		A	B	A	B	A	B	A	B
g_z	2.0024	2.0024	2.0029	2.0024	2.0029	2.0022	2.0023	2.0026	2.0037
g_y	2.0072	2.0068	2.0061	2.0069	2.0069	2.0066	2.0069	2.0062	2.0063
g_x	2.0072	2.0070	2.0064	2.0071	2.0069	2.0066	2.0070	2.0063	2.0068
$(g_x + g_y + g_z)/3$	2.0056	2.0054	2.0051	2.0054	2.0056	2.0052	2.0054	2.0050	2.0056
A_z (mT)	2.94	3.53	2.65	3.45	2.66	3.46	2.65	3.36	2.48
A_y (mT)	0.52	0.53	0.63	0.48	0.60	0.47	0.59	0.54	0.81
A_x (mT)	0.52	0.53	0.63	0.48	0.60	0.47	0.59	0.54	0.81
$(A_x + A_y + A_z)/3$	1.32	1.54	1.30	1.47	1.29	1.47	1.28	1.48	1.36
Line width (mT)	0.97	0.89	1.37	0.97	0.96	0.93	1.00	0.58	0.98
Fraction (%)	100	52	48	65	35	69	31	41	59

The values in brackets mean the size ratio of pore diameter (d_p) to twice the radius of gyration ($2\langle R^2 \rangle^{1/2}$). E.s.r. spectra were observed at temperatures shown under sample code names

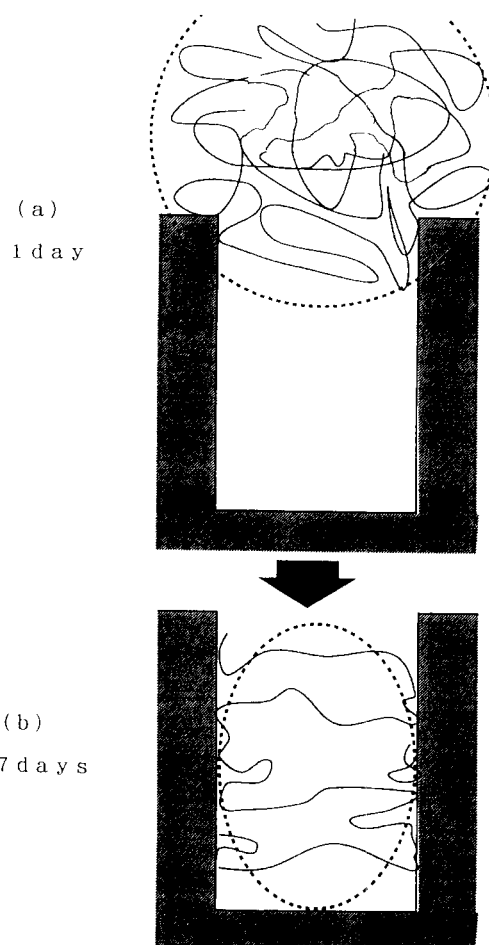
Table 2 Molecular characteristics of PS chains and the size ratio of the average diameter (d_p) to twice the radius of gyration of a PS chain ($2\langle R^2 \rangle^{1/2}$)

Sample	$M_w \times 10^{-3}$	$2\langle R^2 \rangle^{1/2}$ in cyclohexane (nm)	$d_p/2\langle R^2 \rangle^{1/2}$		
			MB-2000	MB-1000	MB-300
PS-3	2.98	2.1	90	49	14
PS-96	96.4	17	11	6.0	1.7
PS-700	700	46	4.1	2.2	0.64

temperatures after the solvents were completely evacuated. Figure 4 shows the temperature dependence of the e.s.r. spectra of the spin-labelled PS (PS-700) on the MB-2000 silica, which should be compared with that of the SL-PS in the homopolymer bulk (Figure 5). The outermost splitting ($2A_z$) for the PS adsorbed on the silica is plotted against observation temperature in Figure 6. The value of $2A_z$ is a good measure of the mobility of the spin-labelled PS, as mentioned above.

The width narrowed with increasing temperature, because of increasing averaging of the anisotropy of the hyperfine coupling. In the solid bulk of polystyrene (Figure 6), the outermost peaks gradually changed around 60°C and narrowed sharply at 100°C. Decreases of the outermost separation width in the lower and higher temperature ranges are attributed to a local mode relaxation, and a micro-Brownian type molecular motion, respectively^{13,14}. In the PS chains adsorbed on the porous silica, the variation in the lower temperature range is so small and the absolute values of $2A_z$ are high in comparison with those in the solid bulk of PS. These experimental facts indicate that the strong PS segment-silica interaction cause a hindrance of the molecular mobility in the lower temperature range.

Figure 7 shows the fractional amount of B-labels with temperature from the spectral simulation. The fractional amount increases with increasing temperature. The temperature dependence seems to be a transition phenomenon. For example, we can find a broad temperature range of transition, -150 to -70°C in the sample of PS-700/MB-1000. This transition is a reflection of the conversion of 'train' segments to 'loop' or 'tail' segments. The broadness of the transition is caused by a broad distribution of conformation of the train segment. The adsorbed segments begin to protrude from the silica

**Figure 3** Schematic illustrations of conformational change of PS chains (PS-700) adsorbed on the silica gels of MB-300 with adsorption time

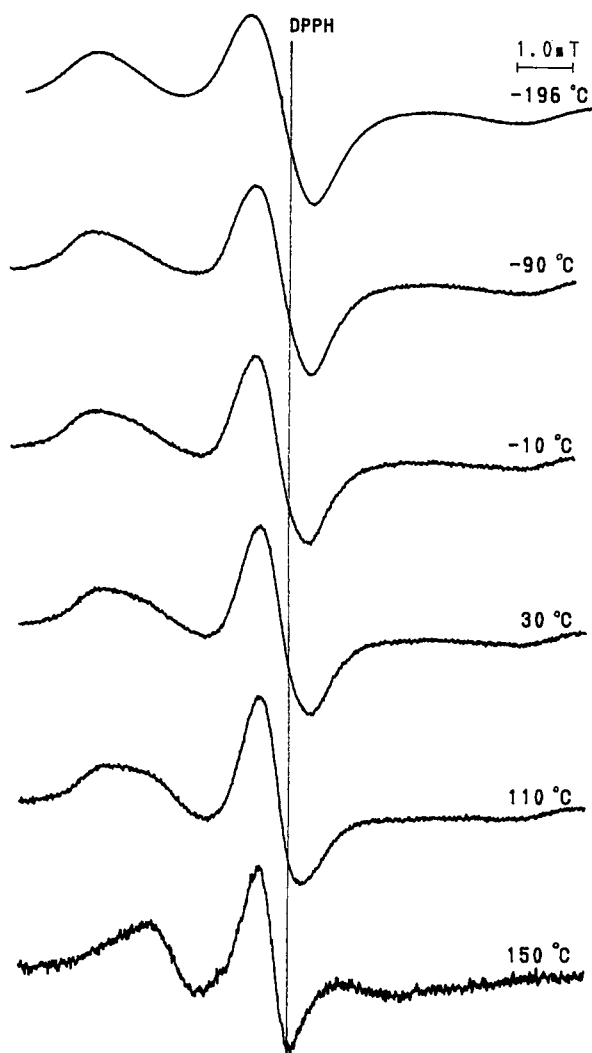


Figure 4 E.s.r. spectra of spin-labelled PS (PS-700) adsorbed on the silica gel of MB-2000 at various temperatures

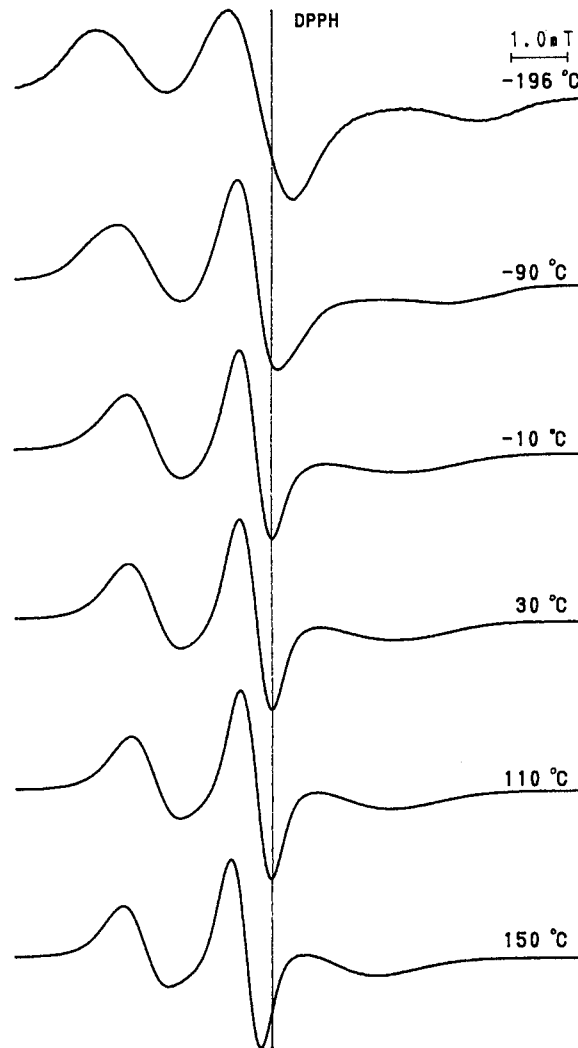


Figure 5 E.s.r. spectra of spin-labelled PS (PS-700) in homopolymer matrices at various temperatures

surface and convert to 'loop' or 'tail' segments when the segments have thermal energy equal to the PS-silica interaction energy, which has a broad distribution. After the release of the interaction, the molecular motion is still restricted, because one side or both sides are tethered on the silica surface.

Molecular weight dependence of conformation of adsorbed chains. Figure 8 shows e.s.r. spectra of SL-PS (PS-3, PS-96, and PS-700) adsorbed on the porous silica gel of MB-2000, observed at -196°C . The simulated spectra obtained by two-component analysis show good agreement with the experimental spectra. The value of $2A_z'$ increases with decreasing molecular weight of PS in the samples. This fact can be interpreted in terms of the relative intensity of the components. Decreasing the amount of B-labels (increasing the amount of A-labels) spreads the outermost splitting. The fractional amount of A-labels, 86% in the sample of PS-3/MB-2000, is larger than 69% in PS-700/MB-2000. Figure 9 shows the fractional amounts of B-labels with temperature from the spectral simulation mentioned above. The fractional amount increases with temperature. The conversion of 'train' segments to 'loop' or 'tail' segments occurs in the higher temperature range as discussed in

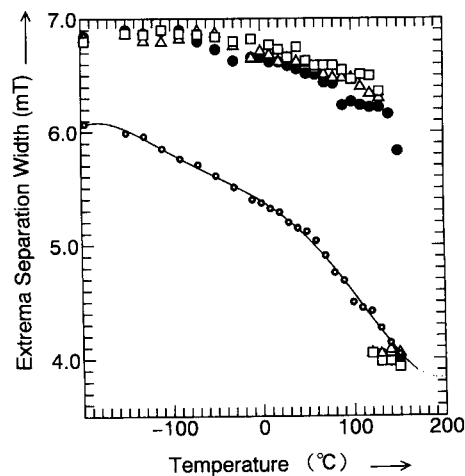


Figure 6 Variation of outermost splitting ($2A_z'$) with temperature: solid bulk of PS (\circ); spin-labelled PS (PS-700) adsorbed on the solid silicas, MB-300 (\bullet), MB-1000 (\triangle), and MB-2000 (\square)

the section of the pore size dependence. The higher the molecular weight of PS is, the higher the fractions are in the whole temperature range. The PS chains of low molecular weight (PS-3) can adsorb unrestrictedly on

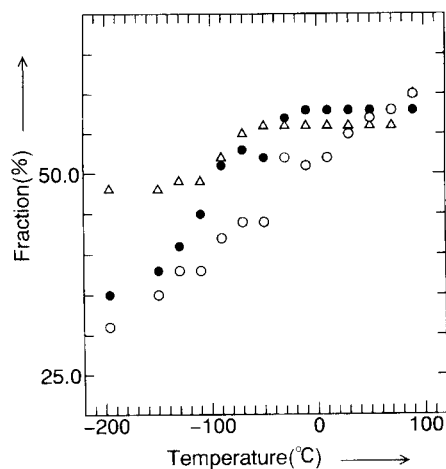


Figure 7 Variation of fractional amount of B-labels (%) with temperature: PS-700/MB-300/7 days (Δ), PS-700/MB-1000 (\bullet), and PS-700/MB-2000 (\circ)

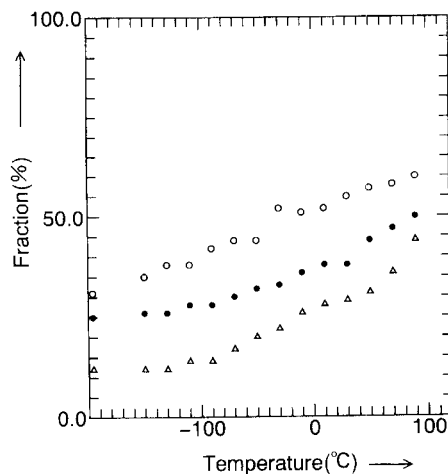


Figure 9 Variation of fractional amount of B-labels (%) with temperature: PS-3/MB-2000 (Δ), PS-96/MB-2000 (\bullet) and PS-700/MB-2000 (\circ)

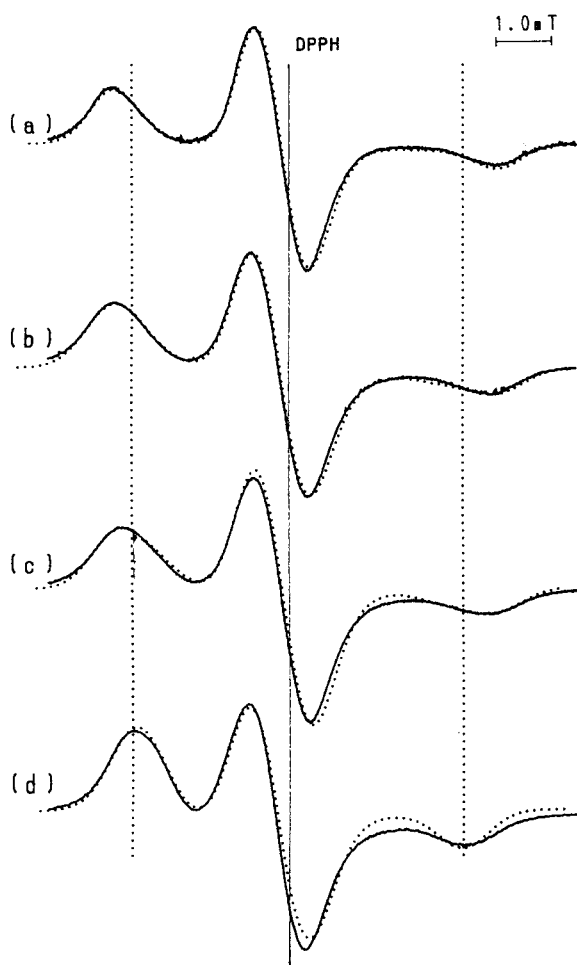


Figure 8 E.s.r. spectra of spin-labelled PS (PS-3 (a), PS-96 (b), and PS-700 (c)), adsorbed on the porous silica gels of MB-2000 and spin-labelled PS (PS-700) in homopolymer matrices (d). Measurements were carried out at -196°C . Solid and dotted lines are experimental and calculated spectra, respectively

the porous silica of large pore diameter to an energetically stable conformation, i.e. a 'train' segment. The distortion of PS chains increases with increasing molecular weight in the case of even the silica gel of MB-2000 of large pore size. The molecular weight dependence

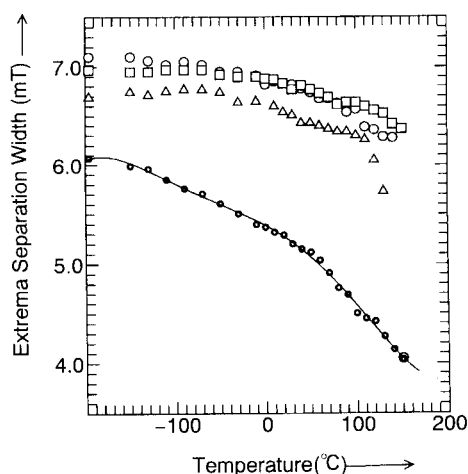


Figure 10 Variation of outermost splitting ($2A_z$) with temperature: solid bulk of PS (\circ); PS-3 (\circ), PS-96 (\square), and PS-700 (Δ) adsorbed on the solid silicas, MB-2000

of the fraction on *Figure 9* is caused by the magnitude of the constraint of PS chains in the pore. The outermost splitting for the samples of the different molecular weight adsorbed on the silica gel of MB-2000 is shown in *Figure 10*. The adsorbed PS chains of PS-700 has a high mobility, in spite of high molecular weight in comparison with the other adsorbed chains (PS-3 and PS-96). The molecular weight dependence is also caused by the magnitude of the constraint of the chains.

Conformational change of PS chains with adsorption time

Change of PS-silica interaction. It was concluded in the previous section that only one PS molecule, having $M_w = 700 \times 10^3$, is the most constrained in a pore of silica gel of MB-300, because of the smallest size ratio of the pore diameter to twice the radius of gyration of PS. The effect of the surface geometry of the PS adsorption motivated us to study the adsorption time dependence of structure and molecular motion of PS chains on the silica gel. *Figure 11* shows the variation of e.s.r. spectra of SL-PS (PS-700) adsorbed on the porous silica gel of MB-300 with adsorption time. The value of the

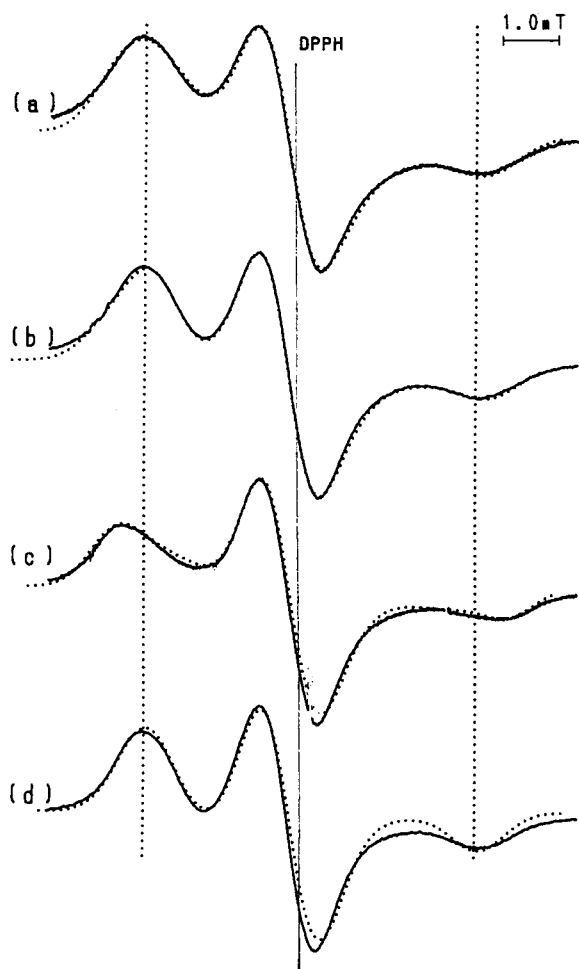


Figure 11 Variation of e.s.r. spectra of spin-labelled PS (PS-700) adsorbed on the porous silica gels of MB-300 with adsorption time: (a) 1 day; (b) 3 days; (c) 7 days; (d) spin labelled PS (PS-700) in homopolymer matrices. Measurements were carried out at -196°C . Solid and dotted lines are experimental and calculated spectra, respectively

width between the outermost peaks ($2A_z'$) in the samples of PS-700/MB-300/1 day and PS-700/MB-300/3 days are smaller than that in the sample of PS-700/MB-300/7 days. The line width in the sample of PS-700/MB-300/1 day seems to be very broad. In order to obtain the exact

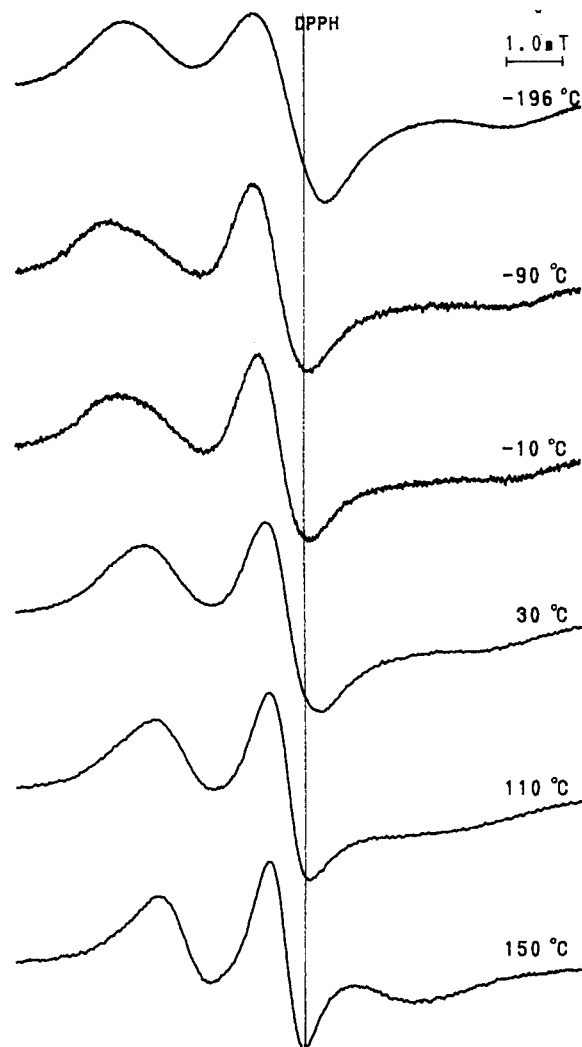


Figure 12 E.s.r. spectra of spin-labelled PS (PS-700) adsorbed on the silica gel of MB-300 at various temperatures. The PS was adsorbed for 1 day

e.s.r. parameters, spectral simulations for the e.s.r. spectra are performed by the method mentioned above. The following results are found from the e.s.r. parameters, as shown in Table 3.

Table 3 E.s.r. parameters of spectra of spin-labelled PS, determined from the spectrum simulation mentioned in the text

	PS-bulk	MB-300 (0.6) (1 day)		MB-300 (0.6) (3 days)		MB-300 (0.6) (7 days)	
		A	B	A	B	A	B
g_z	2.0024	2.0037	2.0029	2.0037	2.0029	2.0024	2.0029
g_y	2.0072	2.0057	2.0064	2.0056	2.0065	2.0068	2.0061
g_x	2.0072	2.0075	2.0064	2.0074	2.0066	2.0070	2.0064
$(g_x + g_y + g_z)/3$	2.0056	2.0056	2.0052	2.0056	2.0053	2.0054	2.0051
A_z (mT)	2.94	3.34	2.70	3.40	2.70	3.53	2.65
A_y (mT)	0.52	0.51	0.63	0.51	0.63	0.53	0.63
A_x (mT)	0.52	0.51	0.63	0.51	0.63	0.53	0.63
$(A_x + A_y + A_z)/3$	1.32	1.46	1.32	1.47	1.32	1.54	1.30
Line width (mT)	0.97	0.95	1.60	0.94	1.45	0.89	1.37
Fraction (%)	100	36	64	39	61	52	48

The values in brackets mean the size ratio of pore diameter (d_p) to twice the radius of gyration ($2\langle R^2 \rangle^{1/2}$). The samples of PS-700 were adsorbed for durations shown under sample code names

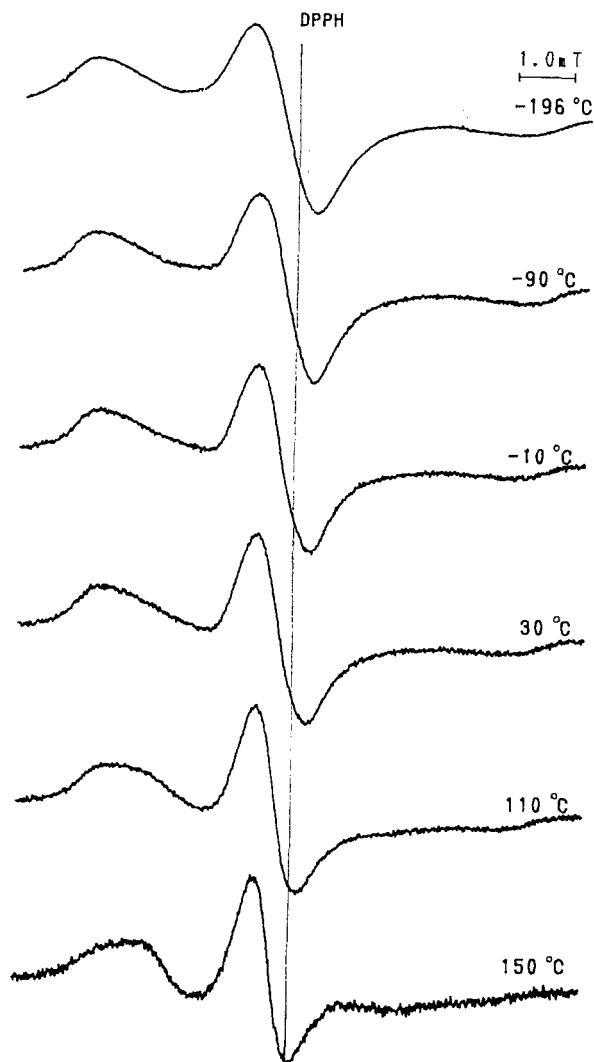


Figure 13 E.s.r. spectra of spin-labelled PS (PS-700) adsorbed on the silica gel of MB-300 at various temperatures. The PS was adsorbed for 7 days

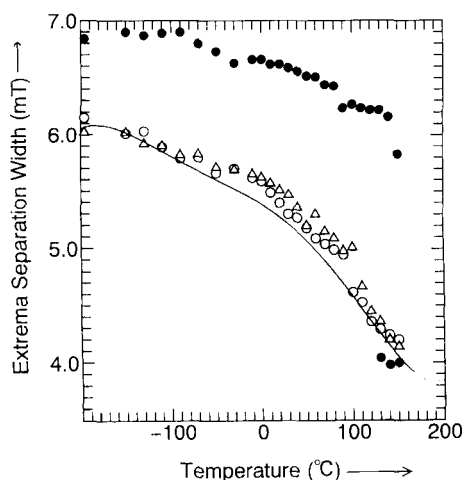


Figure 14 Variation of the outermost splitting ($2A_z$) with temperature: solid bulk of PS (—); PS-700 adsorbed on the solid silica gel of MB-300 for 1 day (○), 3 days (△), and 7 days (●)

- (a) A_z and A_i values for A-labels, reflecting a strong PS–silica interaction increase with increasing adsorption time.
- (b) The fractional amount of B-labels decrease with increasing adsorption time.

These results, (a) and (b), indicate that a PS molecule cannot penetrate easily into a pore of the silica gel, because of the small size ratio. In the first stage, a small amount of segments adsorb, strongly interacting with silica. A part of PS molecules can penetrate into the inner part of the pore and the amount of ‘train’ segments increase with increasing adsorption time, increasing the interaction energy with the silica, as schematically shown in Figure 3.

- (c) The line widths decreased with increasing adsorption time. This fact indicates that the structure of the PS adsorbed chains in the first stage has a broad distribution and next, approach to an equilibrium state, decreasing the breadth of the distribution with increasing adsorption time.

Change of molecular motion of PS chains. Figures 12 and 13 show the temperature dependence of the e.s.r. spectra of SL-PS in the samples of PS-700/MB-300/1 day and PS-700/MB-300/7 days, respectively. The e.s.r. spectra in PS-700/MB-300/1 day are broad, in spite of the small values of the outermost splitting ($2A_z'$) in the whole temperature range. In Figure 14, the values of $2A_z'$ are plotted against observation temperature. The narrowing curves for the samples of PS-700/MB-300/1 day and PS-700/MB-300/3 days are similar with that for the solid bulk of PS. The variations in the lower temperature range (–196 to –40°C) is small, and the outermost peak narrows sharply at 100°C. On the other hand, the variation of $2A_z'$ in the temperature range of –196 to 40°C is only 0.65 mT in the sample of PS-700/MB-300/7 days. The transition temperature of molecular motion in the sample shift *ca* 40°C to a higher temperature. These experimental results indicate that the PS segments–silica interactions increase with increasing adsorption time, and the strong interaction causes a hindrance of the molecular mobility of the adsorbed PS chains. It is very interesting that conformational change of PS chains with time can be related to the PS–silica interaction and molecular motion.

On the other hand, the remarkable change of PS conformation with adsorption time was not detected for the sample having the large pore size ratio. For instance, the PS molecules can easily penetrate into the large pore without significant deformation, and an equilibrium state was attained rapidly.

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