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Structure and molecular motion of poly(ethylene oxide) chains tethered on silica by the spin label method: effect of polystyrene adsorption

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Electron spin resonance (e.s.r.) spectroscopy of spin-labelled poly(ethylene oxide) (SL-PEO) tethered on silica was studied to characterize the conformation and local dynamics of the chain end. Non-labelled polystyrene (PS) with narrow molecular weight distributions, having weight-average molecular weights ($\overline{M_w}$) of 9.64 × 10^4 (PS-96) and 3.84 × 10^5 (PS-384), were adsorbed on the surface of the silica-tethered PEO with 1.9% grafting ratio in carbon tetrachloride solution at 35°C. E.s.r. spectra of the tethered SL-PEO were observed at various temperatures after the samples were completely dried. The structure and molecular motion of the PEO chains are strongly dependent on the M_w of PS. From the temperature dependence, it was found that the molecular mobility of the tethered PEO chains increased when the large PS-384 molecules were adsorbed on the surface. The chain ends of the PEO chains were mobile even at − 196°C. These facts suggest that the PS chains spread out the PEO chains and are adsorbed on the silica surface as 'train' segments, whereas the PEO chains protrude from the surface as 'tail' segments. On the other hand, when the small PS-96 molecules are adsorbed, the rate of motion of the tethered PEO chains is slowed down by the PS chains. This suggests that the PS chains are distant from the silica surface and entangled with the PEO chains. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: polystyrene; silica-tethered poly(ethylene oxide); adsorption)

INTRODUCTION

In our previous paper[1] the spin label method was used to study the structure and molecular motion of polystyrene (PS) chains adsorbed on a silica-tethered poly(ethylene oxide) (PEO). It was concluded that PS chains having a weight-average molecular weight $\overline{M_w} = 9.64 \times 10^4$ were protruding from the silica surface and/or embedded in the tethered PEO chains in the initial stage of adsorption, and a part of the PS chains took a structure with a strong PS–silica interaction such as 'train' segments with increasing adsorption time. It was also reported that the adsorption behaviour was strongly dependent on the grafting ratio of the PEO. It is very important to elucidate the structure and molecular motion of the tethered PEO chains and compare them with those of the adsorbed PS chains in order to confirm the adsorption behaviour of the PS chains on the silica-tethered PEO, relative to the PS–PEO interaction.

We have developed a spin-label technique to investigate the structure and dynamic behaviour of polymer chains at a particular site in a complicated system[2]. The e.s.r. spectra of the spin-labels of PEO and PS in the same matrices are observed individually to evaluate the rates of motion of the respective polymers in the complicated system. It is well known that the adsorption behaviour of polymers on silica is strongly dependent on the molecular weight of the polymers[3–5]. In this paper, first we report the dependence of the molecular weight of PS on the molecular mobility of the PS chains adsorbed on silica-tethered PEO. Next, the molecular motion of the tethered PEO chains is compared with that of the adsorbed PS chains, which has a strong molecular weight dependence.

EXPERIMENTAL

Materials

Polystyrene having $\overline{M_w} = 9.64 \times 10^4$ (PS-96) and 3.84×10^5 (PS-384) was purchased from Tosoh Co., Tokyo, Japan. The polydispersities of PS-96 and PS-384 were 1.01 and 1.02, respectively. The polystyrene was spin-labelled by the method of Bullock *et al.*[6] mentioned in our previous paper[1].

The porous silica particles used for the adsorbent were also the same as those in our previous paper[1].

A poly(ethylene oxide) (PEO-6) having the number-average molecular weight ($\overline{M_N}$) = 6 × 10^3 was purchased from Katayama Science Co., Tokyo, Japan. The polydispersity of PEO-6 was < 1.20. The PEO-6 was purified by precipitating three times from chloroform solution by addition of diethyl ether and dried under vacuum for more than 1 day at room temperature.

Grafting reaction

The grafting reaction of PEO-6 to the silica gels[7] was performed by the same procedure mentioned in our previous paper[1]. The ends of the tethered PEO chains were spin-labelled by the method of Törmälä and Lindlberg[8]. 3-Carbonyl-2,2,5,5-tetramethylpyroline-1-oxyl (Aldrich Chemical Co., Ltd.) was esterified with the tethered PEO.

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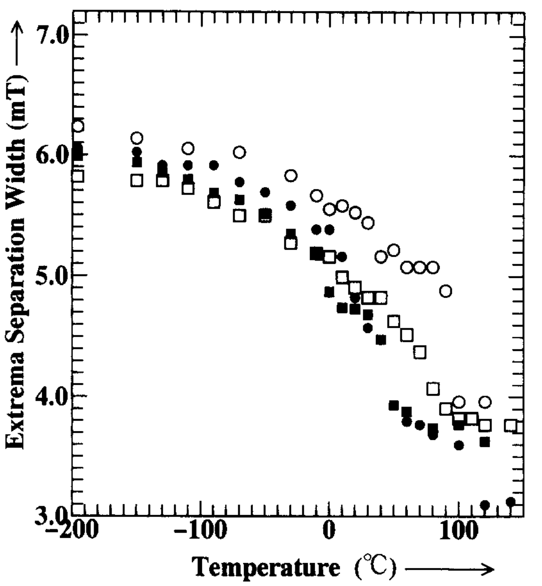

Figure 1 Variations of outermost splitting ($2A_{z'}$) with temperature for SL-PS adsorbed on the silica-tethered PEO having *ca.* 1.9% grafting ratio: PS-96 adsorbed for 10 h (●) and 178 h (■); PS-384 adsorbed for 10 h (□) and 178 h (○)

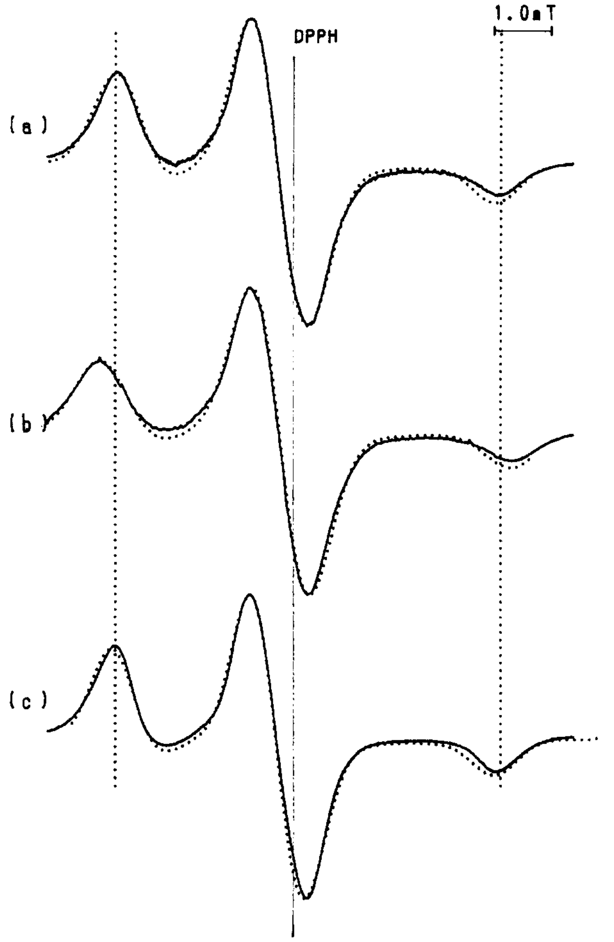

Figure 2 Comparisons of calculated e.s.r. spectra (dotted) and observed spectra (solid) of spin-labelled PEO (SL-PEO): (a) in the homopolymer bulk (SLPEO/Bulk); (b) adsorbed on silica for 1 week (SLPEO/Silica); (c) tethered on silica with a grafting ratio of 1.9% (gSLPEO/Silica). Measurements were carried out at − 196°C. The vertical line indicates the position of the spectrum of DPPH, $g = 2.0036$

In order to compare the molecular mobility of the PEO chains in the PEO homopolymer bulk with that of the tethered chains, the ends of the PEO chains in the homopolymer were also spin-labelled by the same method (SL-PEO).

The adsorption of polystyrene, e.s.r. measurements and computer simulation for the e.s.r. spectra of the spin-labels were also performed by the same procedure mentioned in our previous paper[1]. The signal of diphenylpicrylhydrazil (DPPH) was used as a *g*-value standard.

RESULTS AND DISCUSSION

Molecular motion of PS chains adsorbed on silica-tethered PEO

In the previous paper[1] the molecular motion of the PS chains (PS-96) adsorbed on a silica-tethered PEO was discussed in detail from the temperature dependencies of the e.s.r. spectra of spin-labelled PS. It was found that the PEO chains tethered on the silica increased the rate of motion of the PS segments protruding from the silica surface on increasing the grafting ratio. In this section, the effect of the molecular weight of PS on the molecular mobility of PS chains is clarified. The outermost splitting width ($2A_{z'}$) for SL-PS narrows with increasing motional averaging of the anisotropy of hyperfine splitting (hfs) due to the nitrogen nucleus. In *Figure 1*, the values of $2A_{z'}$ for the various samples are plotted against temperature. The samples have *ca.* 1.9% grafting ratio. The temperature dependence shows a remarkable change with the molecular weight of PS. For example, the narrowing curve of $2A_{z'}$ *versus* temperature for the sample of PS-384 adsorbed for 178 h shifts to temperatures *ca.* 60°C higher than PS-96 adsorbed for 178 h. The results suggest that the molecular motion of the large PS chains is restricted because of their strong interaction with the silica surface.

Kawaguchi and co-workers[3–5] found a preferential adsorption of a large PS chain over a small PS chain in the binary mixture on silica surfaces and attributed its driving force to the conformational entropy loss of the small PS chain: changes in the conformation of the smaller PS chains due to adsorption are much more dramatic than those of the larger ones. It can be concluded that the large PS molecules can spread out the tethered PEO chains, approach the silica surface, and interact more strongly with the silica molecules than the small PS molecules which are embedded in the tethered PEO.

The narrowing curve of $2A_{z'}$ *versus* temperature for the sample of PS-384 also shifts to higher temperatures and the transition temperature regions are much narrowed with increasing adsorption time. The large PS chains are also relaxed to the equilibrium state, take flatter conformations as 'train' segments, and attain a low molecular mobility with increasing adsorption time. The same adsorption behaviour was observed for the small PS chains, as mentioned in our previous paper[1].

Structure of PEO chains tethered on silica

Figure 2 shows e.s.r. spectra of SL-PEO observed at −196°C. The value of the outermost splitting width ($2A_{z'}$) for SL-PEO adsorbed on the silica surface (SLPEO/Silica) is larger than those for SL-PEO in the bulk of PEO (SLPEO/Bulk) and for tethered SL-PEO on the silica surface (gSLPEO/Silica). The high value should be caused by the electric field of the silica surface[1,9,10]. The magnitude of

Table 1 E.s.r. parameters of spectra of spin-labelled PEO, determined from the spectrum simulation mentioned in the text[a]

				gSLPEO/Silica + PS (−196°C)		
	SLPEO/Bulk	SLPEO/Silica	gSLPEO/Silica	A	B	gSLPEO/Silica + PS (−269°C)
g_z	2.0021	2.0023	2.0023	2.0026	2.0049	2.0024
g_y	2.0065	2.0061	2.0064	2.0074	2.0056	2.0074
g_x	2.0080	2.0079	2.0085	2.0075	2.0061	2.0077
$(g_x + g_y + g_z)/3$	2.0055	2.0054	2.0057	2.0058	2.0055	2.0058
A_z (mT)	3.30	3.58	3.32	3.13	2.25	3.08
A_y (mT)	0.43	0.40	0.43	0.51	0.77	0.47
A_x (mT)	0.43	0.40	0.43	0.51	0.77	0.47
$(A_x + A_y + A_z)/3$	1.39	1.46	1.39	1.38	1.26	1.34
Line width (mT)	0.83	0.87	0.76	1.08	0.89	1.20
Fraction (%)	100	100	100	83	17	100

[a]Sample codes are described in the text and the caption to *Figure 2*. (+ PS) means adsorption of PS molecules and the values in parentheses indicate the observation temperature

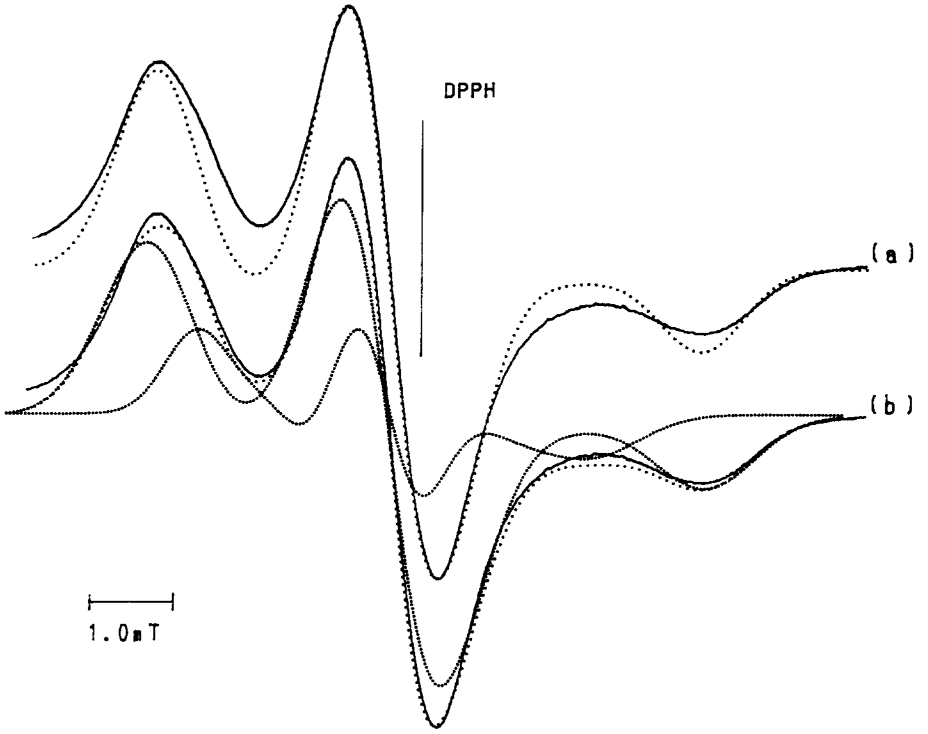

Figure 3 Effect of PS (PS-384) adsorption at a concentration of 5.0 × 10^{-3} g ml^{-1} on the e.s.r. spectra of tethered SL-PEO on silica having 1.9% grafting ratio. Measurements were carried out at − 196°C. Solid lines are experimental spectra and dotted lines (•••) are simulated spectra by assuming only one component (a) and two components (b) (fine-dotted lines (· · ·)). Solid lines in (a) and (b) are identical. The vertical line indicates the position of the spectrum of DPPH, $g = 2.0036$

the hfs due to the nitrogen nucleus is an increasing function of PEO–silica interaction energy.

In order to obtain the exact e.s.r. parameters, spectral simulations for the e.s.r. spectra are performed. The simulated spectra show good agreement with the observed spectra as indicated in *Figure 2*. The e.s.r. parameters determined from the spectral simulations are shown in *Table 1*. The high values of A_z (3.58 mT) and $A_i = (A_x + A_y + A_z)/3$ (1.46 mT) for the SL-PEO adsorbed on the silica surface are caused by the strong electric field of the silica surface. For instance, the PEO segments connected with the SL-PEO are strongly interacted with the silica as 'train' segments[11,12]. On the other hand, the values of A_z (3.32 mT) and A_i (1.39 mT) for the tethered PEO on the silica having 1.9% grafting ratio are the same as those of SL-PEO in the homopolymer PEO. This is a reflection of the weak interaction of the tethered SL-PEO with the silica. The segments connected with the tethered SL-PEO behave like 'tail' segments on the silica surface[13].

STRUCTURE AND MOLECULAR MOTION OF PEO CHAINS TETHERED ON SILICA: EFFECT OF PS ADSORPTION

Effect of adsorption of PS having $\overline{M_w} = 3.84 \times 10^5$

E.s.r. spectra of tethered SL-PEO on the silica surface are observed after the PS-384 is adsorbed on the silica-tethered PEO. The PS adsorption was carried out at a

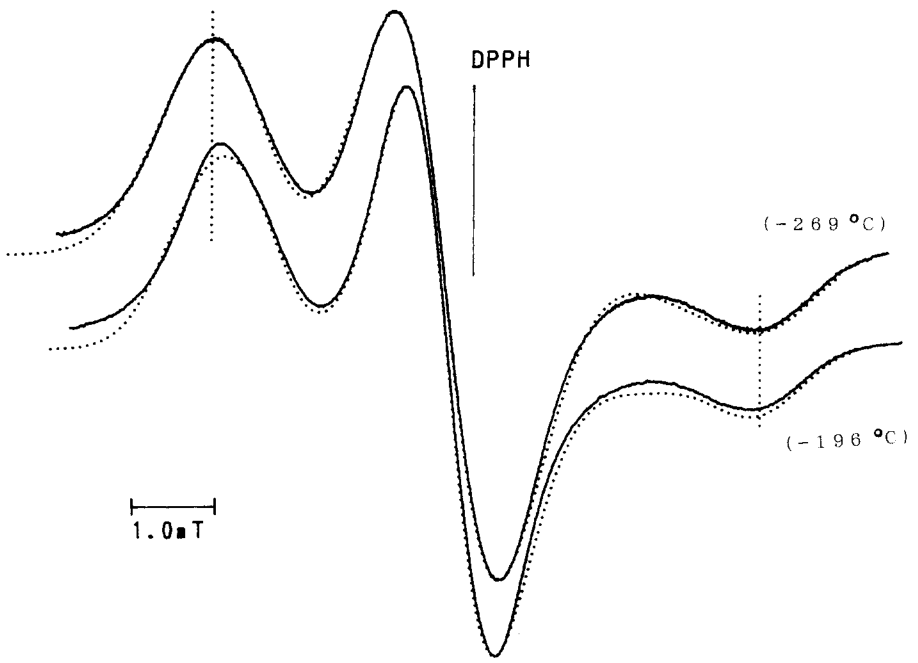

Figure 4 Effect of PS (PS-384) adsorption at a concentration of 5.0×10^{-3} g ml^{-1} on the e.s.r. spectra of tethered SL-PEO on silica having 1.9% grafting ratio. Measurements were carried out at − 269 and − 196°C. Solid and dotted lines are experimental and calculated spectra, respectively. The vertical line indicates the position of the spectrum of DPPH, $g = 2.0036$

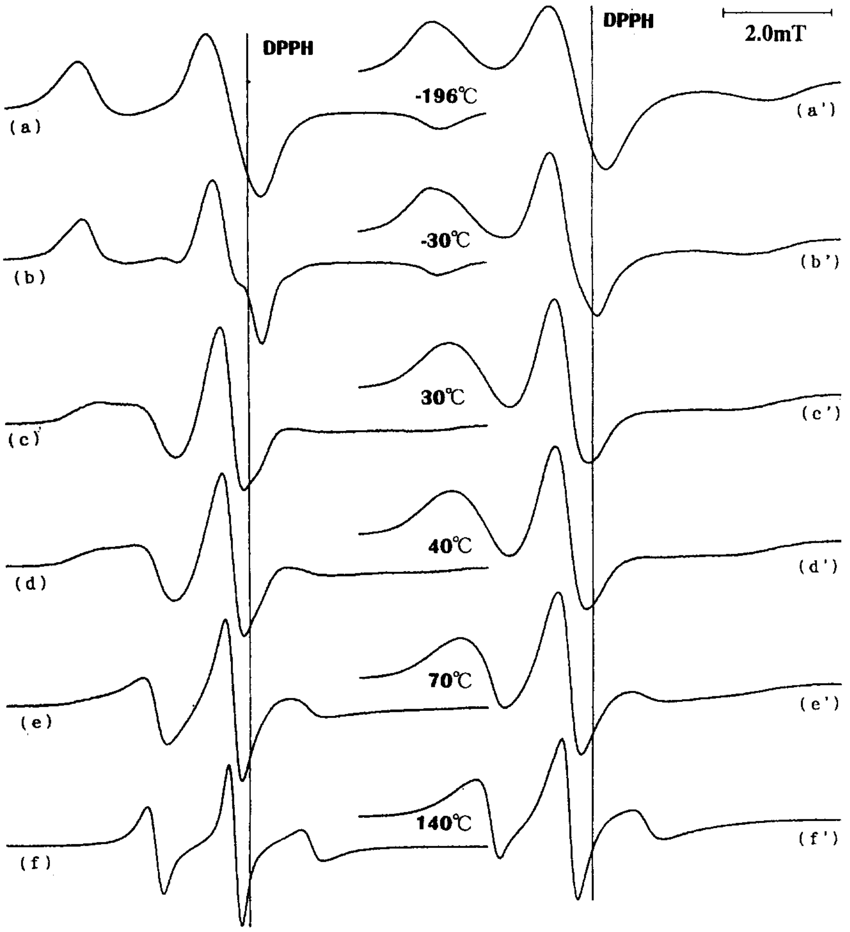

Figure 5 Temperature-dependent e.s.r. spectra of tethered SL-PEO on silica having 1.9% grafting ratio before (a–f) and after (a′–f′) PS (PS-384) adsorption at a concentration of 5.0×10^{-3} g ml^{-1}. Measurements were carried out after the solvents were completely evacuated. The vertical lines indicate the positions of the spectra of DPPH, $g = 2.0036$

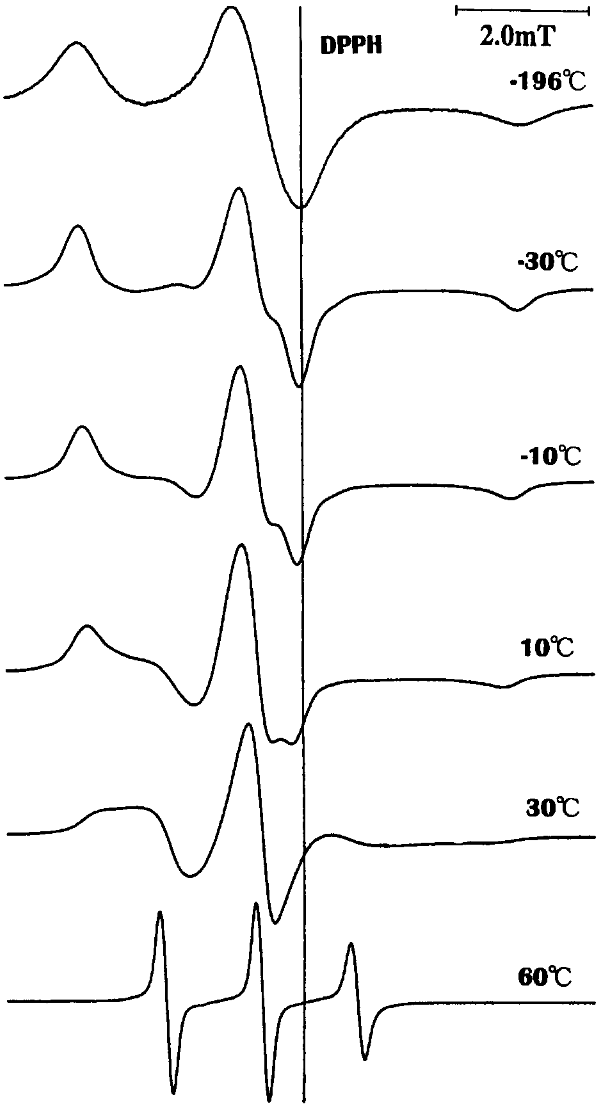

Figure 6 Temperature-dependent e.s.r. spectra of SL-PEO in the homopolymer bulk. The spectrum of DPPH, $g = 2.0036$, is the vertical line

concentration of 5.0×10^{-3} g ml^{-1} PS in carbon tetrachloride. The concentration is five times as dilute as a critical entanglement concentration, where the coils begin to overlap.

Figure 3 shows the e.s.r. spectrum of SL-PEO tethered on the silica surface at − 196°C after the adsorption of PS-384. It is found that the e.s.r. spectrum becomes broad and the extreme separation width decreases in comparison with that before the adsorption (*Figure 2c*). The agreement between the observed spectrum (the solid line in *Figure 3a*) and the simulated spectrum (the dotted line in *Figure 3a*) by assuming only one kind of spectrum is not good. On the other hand, the simulated spectrum by assuming two components shows good agreement with the observed spectrum as indicated in *Figure 3b*. This result indicates that the classification of the spin-labels into two kinds of labels (A- and B-labels) affected by different environments is a good approximation. A-labels having a high value of hfs are connected to the segment strongly interacted with the silica. On the other hand, B-labels having a low value of hfs are connected to the segment weakly interacted with the silica.

Figure 4 shows the variation of the e.s.r. spectrum with temperatures of −269 and −196°C. The e.s.r. spectrum

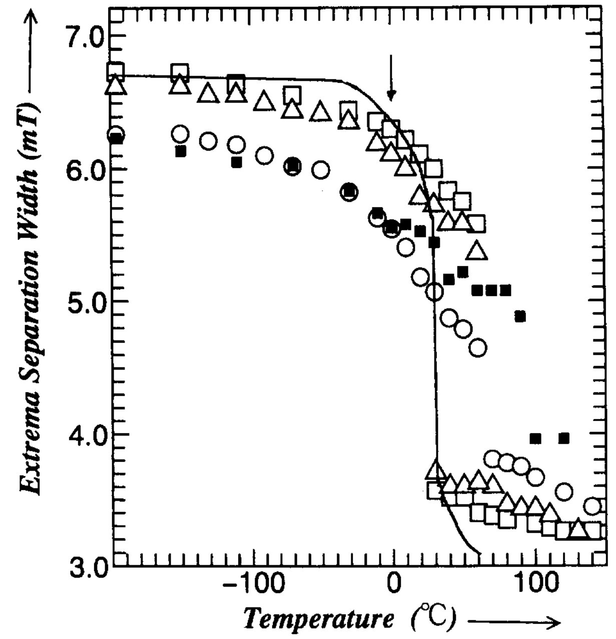

Figure 7 Variations of outermost splitting $(2A_{z'})$ with temperature for spin-labelled polymers: SL-PEO in the homopolymer bulk (—); SL-PEO tethered on silica-tethered PEO having 1.9% grafting ratio (□). Effect of PS (PS-384) adsorption at a concentration of 8.3×10^{-4} (△) and 5.0×10^{-3} g ml^{-1} (○) on the variation for the tethered SL-PEO; SL-PS adsorbed on the silica-tethered PEO at a concentration of 8.3×10^{-4} g ml^{-1} (■)

observed at −269°C can be simulated by assuming only one component (a). E.s.r. parameters determined from the spectrum simulation are also indicated in *Table 1*. Surprisingly, the values of A_z for the tethered SL-PEO on the silica containing the adsorbed PS (gSLPEO/(Silica + PS)(− 196°C) at − 196°C are much lower than those for the SL-PEO in the homopolymer PEO (SLPEO/Bulk) and the tethered PEO on the silica (gSLPEO/Silica). The low values of A_z (3.13 mT for A-label and 2.25 mT for B-label) and the high values of A_x and A_y (0.51 mT for A-label and 0.77 mT for B-label) are caused by motional averaging of the anisotropic hfs interaction. This suggests that the end sites of the PEO chains move even at −196°C and some extremely mobile segments bonded to B-labels protrude from the layer of the tethered PEO chains. The extremely high mobility of the end site of the PEO chains is due to a large free space around the end part. The low value of A_z (3.08 mT) and the high value of A_x and A_y (0.47 mT) at −269°C for the sample of gSLPEO/(Silica + PS) indicate that the end sites of the PEO chains are still mobile at −269°C. On the other hand, the molecular motion of the PS chains (PS-384) is restricted because of the strong interaction with the silica as mentioned in the previous section.

In order to evaluate the molecular motion of PEO chains tethered on the silica above −196°C and compare it with that of PS chains, e.s.r. spectra were observed at various temperatures. *Figure 5* shows the temperature dependencies of e.s.r. spectra of SL-PEO tethered on the silica having 1.9% grafting ratio before and after the adsorption of PS-384. The dependencies should be compared with that of SL-PEO in the homopolymer bulk as shown in *Figure 6*. The e.s.r. spectra of SL-PEO in the bulk narrow steeply around 30°C, because of the phase transition of PEO from the crystalline to the liquid state[8], whereas those of SL-PEO on the silica are still broad at 140°C. The rate of motion

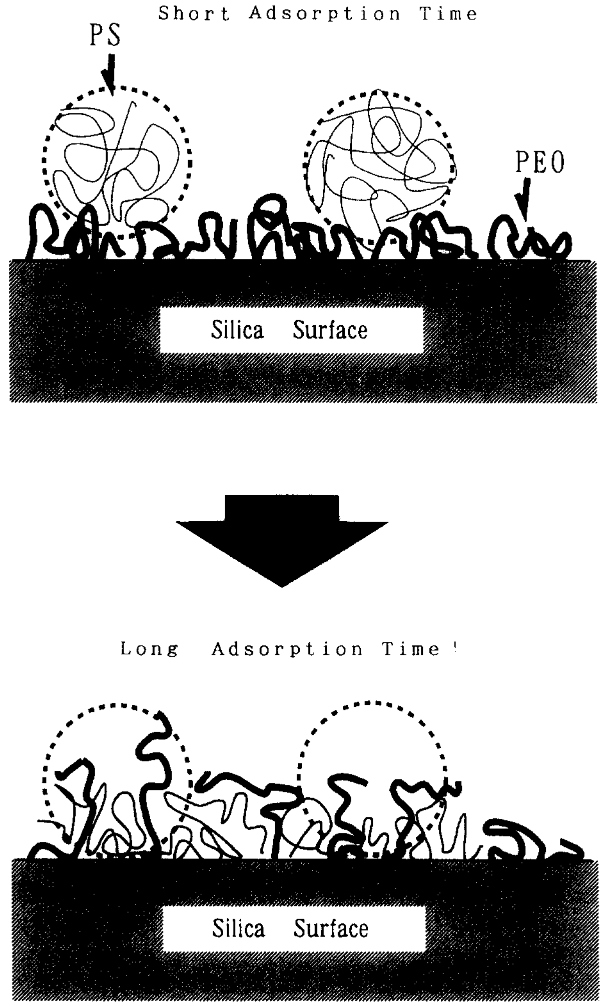

Figure 8 Schematic representations of conformational changes of PS and PEO segments on the silica-tethered PEO. Effect of PS (PS-384) adsorption

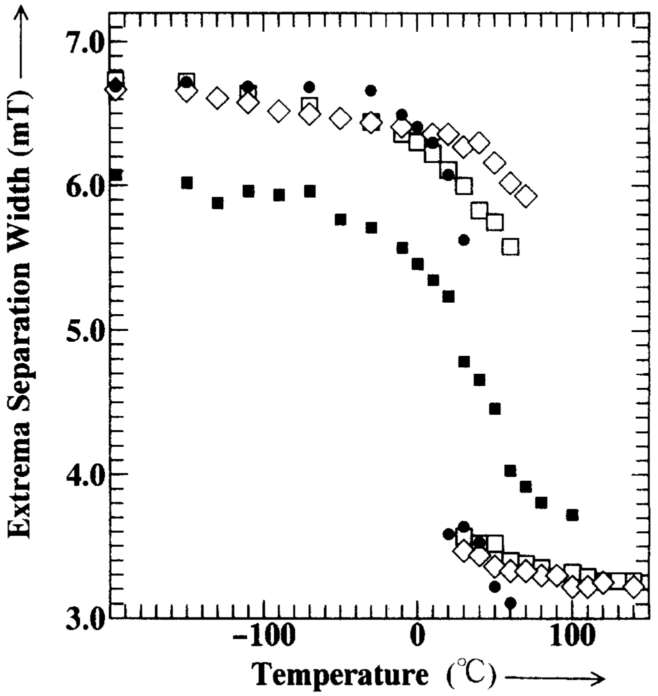

Figure 9 Variations of outermost splitting ($2A_{z'}$) with temperature for spin-labelled polymers: SL-PEO in the homopolymer bulk (●); SL-PEO tethered on the silica-tethered PEO having 1.9% grafting ratio (□). Effect of PS (PS-96) adsorption at the concentration of 8.3×10^{-4} g ml^{-1} (◇) on the variation for the tethered PEO. SL-PS adsorbed on the silica-tethered PEO at the concentration of 8.3×10^{-4} g ml^{-1} (■)

of the tethered SL-PEO even at 140°C is lower than that of SL-PEO in the bulk at 60°C because one of the chain ends is bonded to the silanol group on the silica surface and the mobility of another chain end should be constrained. It is found that the line widths of the e.s.r. spectra of the tethered SL-PEO increase and their outermost splitting widths decrease when PS molecules are adsorbed on the silica-tethered PEO as indicated in *Figure 5*. The broad line width should be caused by a broad distribution of the PEO–silica and PEO–PS interactions in the chain end sites. On the other hand, the small outermost splitting can be interpreted in terms of the weak PEO–silica and PEO–PS interactions which give rise to high molecular mobility and low electric field for SL–PEO.

The outermost splittings for the SL–PEO are plotted against temperature in *Figure 7*. The value of $2A_{z'}$ as a function of temperature is also a good measure of the mobility of SL-PEO. The width narrowed with increasing temperature. In the solid bulk of PEO, the outermost separation width begins to decrease around − 30°C and drops steeply at 30°C. On the other hand, in the tethered SL-PEO on silica the narrowing curve of $2A_{z'}$ *versus* temperature (*Figure* 7(□)) shows a remarkable fall in four temperature ranges, near −150–0, 0–60, 60 and 60–120°C. The e.s.r. spectra observed at temperatures between 30 and 60°C split into two components of spectra with larger and smaller values of $2A_{z'}$, corresponding to slow and fast rates of motion. The two kinds of labels are attached to the end segments strongly and weakly interacted with the other segments, respectively. The fall in the four temperature ranges in *Figure 7* should arise from many different modes of molecular motion[14]. The small decrease of $2A_{z'}$ due to a local mode relaxation of a small amplitude in the lowest temperature region, −150– − 30°C cannot be detected in the bulk sample. This result indicates that the chain end of the tethered PEO has high mobility because of the weak interaction of the end segment with other segments, reflecting the low segmental density around the end site and excess free volume in comparison with that in the bulk of PEO. The second local mode relaxation of larger amplitude begins around 0°C as indicated by an arrow in *Figure 7* and the steep relaxation corresponding to a micro-Brownian-type molecular motion[14] occurs at 60°C. It is found that the narrowing curves of $2A_{z'}$ *versus* temperature for A-labels after the adsorption of PS-384 shift to lower temperatures (*Figure* 7(△,○)) than that before the adsorption. The effect of the PS adsorption on the molecular motion of the tethered PEO increases with an increase in the concentration of PS.

These experimental facts suggest that the PS chains spread out the tethered PEO chains and are adsorbed near the silica surface like 'train' segments, whereas the PEO chains protrude from the silica surface as 'tail' segments. The filled square symbols in *Figure 7* show the temperature variation of $2A_{z'}$ values for SL-PS in the same matrices as those where the molecular motion of the tethered SL-PEO is elucidated in *Figure* 7(△). The rigid-to-isotropic pattern change of SL-PS caused by a micro-Brownian-type molecular motion occurred at *ca.* 100°C, whereas the change of SL-PEO was observed at the lower temperature, *ca.* 60°C. The segmental mobility of the PEO chains is

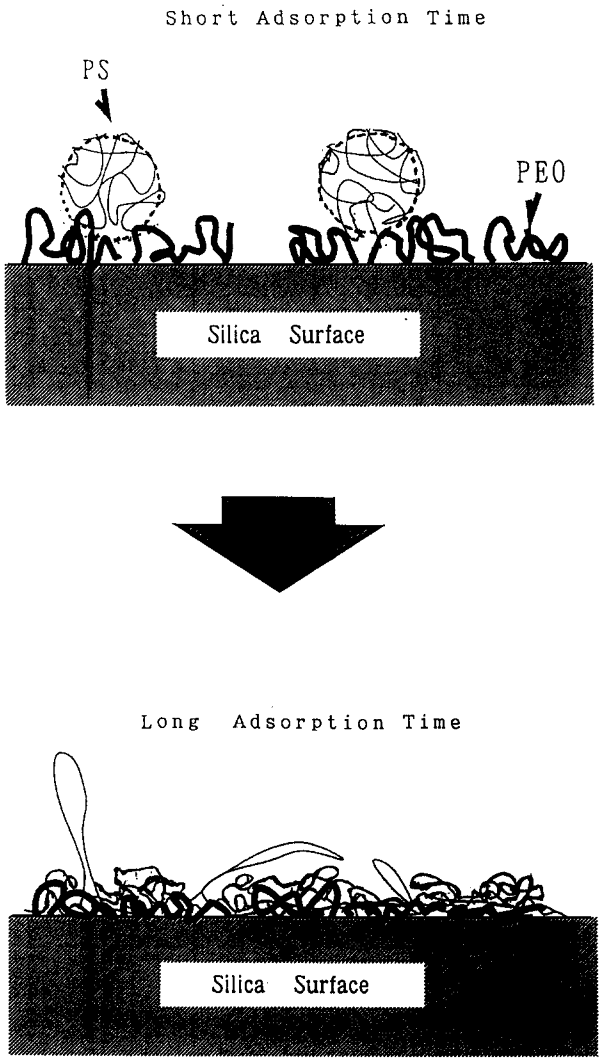

Figure 10 Schematic representations of conformational changes of PS and PEO segments on the silica-tethered PEO. Effect of PS (PS-96) adsorption

higher than that of the PS chains. These molecular dynamics are consistent with the structural changes, as discussed previously. The structural change of the tethered PEO chains affected by the adsorption of PS-384 molecules is shown schematically in *Figure 8*.

Effect of adsorption of PS having $\overline{\mathrm{M}_w} = 9.64 \times 10\{-4\}$. The molecular motion of PS chains adsorbed on silica-tethered PEO has a strong molecular weight dependence of PS, as mentioned previously. The smaller PS chains (PS-96) on silica have a much higher mobility than the larger PS (PS-384) on silica and in the homopolymer bulk. This result predicts the different behaviour of PS-96 on the silica-tethered PEO from those of PS-384. *Figure 9* shows that the outermost splittings with temperature for the tethered SL-PEO are affected by the adsorption of PS-96. The narrowing curve of $2A_{z'}$ *versus* temperature is similar to those for the adsorption of PS-384. However, the curve of *Figure 9* (◇) shifts to higher temperatures with the adsorption of PS-96, whereas the curves of *Figure 7* ((△), (O)) shift to lower temperatures with the adsorption of PS-384. This result suggests that the tethered PEO chains are compressed and the rate of motion is slowed down by the smaller PS molecules.

The filled square of in *Figure 9* show the temperature variation of $2A_{z'}$ for SL-PS in the same matrices as those where the molecular motion of the tethered SL-PEO are elucidated in *Figure 9* (◇). The mobility of the PEO chains is lower than that of the PS chains. In particular, the rigid-to-isotropic pattern change of SL-PS caused by a micro-Brownian-type molecular motion occurred at *ca.* 20°C, whereas the change of the tethered SL-PEO was observed at the higher temperature, *ca.* 60°C. These experimental results are contrary to those for the adsorption of PS-384. A large number of segments of the small PS molecules are distant from the silica surface and entangled with the tethered PEO chains. In other words, the mobile PS segments more weakly interacted with the silica should be protruded from the silica surface and/or embedded in the tethered PEO chains.

We can evaluate individually the rates of motion of the adsorbed PS and tethered PEO chains in the complicated system composed of PS, PEO and silica.

In our previous paper, we clarified the adsorption time dependence of the adsorption behaviour of PS-96 on the silica-tethered PEO by using spin-labelled PS. The high molecular mobility of the PS chains on the silica having a high grafting ratio also decreases with an increase in adsorption time. The result could be interpreted in terms of migration of PS segments from the surface of the tethered PEO to the inner region near the silica surface as indicated in *Figure 10*. In order to confirm the adsorption behaviour, the molecular motion of the PEO segments was observed by using the spin-labelled PEO in the present paper. The motion of the PS chains on the silica is accelerated by the tethered PEO molecules and the rate of motion of the PEO chains is slowed down by the PS molecules. It can be considered that the PS molecules (PS-96) should take a structure such as 'loop' or 'tail' conformation and/or mix with the tethered PEO molecule on a molecular level as shown schematically in *Figure 10*.

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