Polymer Vol. 39 Nos. 8–9, pp. 1703–1710, 1998
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0032-3861/97/\$17.00+0.00

PII: S0032-3861(97)00454-0

Structure and molecular motion of polystyrene chains adsorbed on a silica-tethered poly(ethylene oxide) by the spin-label method

Shigetaka Shimada* and Taro Watanabe
Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466, Japan
(Received 27 March 1997; revised 22 April 1997)

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). Spin-labelled polystyrene with a narrow molecular weight distribution, having a weight-average molecular weight ($\bar{M}_w$) of 9.64×10^4, was adsorbed on the surface of the silica-tethered PEO with various grafting ratio lower than 2.1% in carbon tetrachloride solution at 35°C. Electron spin resonance (e.s.r.) spectra were observed at various temperatures after the samples had been dried completely.

The e.s.r. spectra observed at − 196°C were composed of two spectra arising from spin labels attached to 'train' and 'loop' (or 'tail') segments, which were strongly and weakly interacted with the silica surface, respectively. The fractional amount of the 'loop' or 'tail' segments increases dramatically with grafting ratio of the PEO. The transition temperature of molecular motion estimated from the temperature dependence of the e.s.r. spectra decreases also dramatically with the grafting ratio of PEO. The 'loop' or 'tail' segments are attributed to PS chains protruding from the silica surface and/or embedded in the tethered PEO chains, whereas the 'train' segments are trapped near the silica surface. © 1997 Elsevier Science Ltd. All rights reserved.

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

INTRODUCTION

Many investigations have employed the method of electron spin resonance (e.s.r.) spectroscopy to study the adsorption of polymers on silica surfaces[1–4]. In our previous papers[5,6], spin-labelled polystyrenes (PS) with narrow molecular weight distributions were adsorbed on the surface of porous silica gels with different pore diameters in cyclohexane (C_6H_{12}) and carbon tetrachloride (CCl_4) solutions and dried. The conformations and molecular dynamics of the PS chains were studied in detail in order to explore the effect of the surface geometry on their behaviour. The conformational changes of 'train' segments to 'loop' or 'tail' segments with temperature and adsorption time were found. It was also found that the structure and molecular motion are strongly related to the PS–silica interaction which was dependent on the surface geometry, i.e. the size ratio of the average pore diameter to twice the radius gyration of a PS chain.

We also found extremely high mobility of polyethylene (PE) molecules tethered on a fresh surface of poly(tetrafluoroethylene) (PTFE), related to the protruding of PE chains from the PTFE surface[7–9]. These findings motivated us to study the adsorption behaviour of PS chains on silica-tethered polymer chains, and each structure and molecular motion of the PS and the tethered chains. In this paper, we study the adsorption behaviour of PS chains on silica-tethered poly (ethylene oxide) (PEO) by spin labelling of the PS chains.

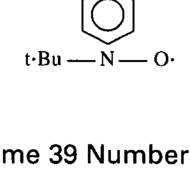
Kawaguchi and co-workers[10,11] studied the adsorption behaviour of PEO and the competitive and displacement adsorption of PS and PEO on a non-porous silica. They concluded that PEO molecules are strongly attached to the silica surface via hydrogen bonding between surface silanol group and the oxygen atoms in the ethoxy segments of PEO. They also found that the PEO molecules were more easily and tightly attached to the silica surface than PS, this difference inducing the preferential adsorption of PEO over PS. It can be expected that the tethered PEO chains are also attached to the silica in the CCl_4 solution like 'train' segments and exclude PS chains from being adsorbed.

Hommel and co-workers[12,13] studied the dynamics of adsorption of PEO chains on silica-tethered PEO and clarified the conformation of the chains, which depended on the concentration of polymer in solution, their molecular weight and the grafting ratio. We are interested in the effects of the tethered PEO on the adsorption behaviour, structure and molecular motion of the PS chains adsorbed on silica-tethered PEO.

EXPERIMENTAL

Materials

A polystyrene having a weight-average molecular weight ($\bar{M}_w$) of 9.64×10^4 (PS-96) was purchased from Tosoh Co. (Tokyo, Japan). The polydispersity of PS-96 was 1.01. The polystyrene was spin-labelled following the method of Bullock and co-workers[14]. The labelled monomer unit has the following structure:



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* To whom correspondence should be addressed

The labelled polymers (SL-PS) were finally purified by precipitating three times from toluene solution by addition of methanol, and were dried under vacuum for more than 1 day at room temperature.

The porous silica particles used for the adsorbent were micro bead (100–200 mesh) silica gels, MB-2000 from Silicia Chemical Co. (Kasugai, Japan). The average pore diameter and surface area of the MB-2000 silica gels are 190.7 nm and 25 $m^2 g^{-1}$, respectively. The silica particles were purified by washing in hot carbon tetrachloride and dried in a vacuum oven at 130–150°C for several days.

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

Grafting reaction

The grafting reaction[12] of PEO-6 to the silica gels is simply the direct esterification of a surface silanol group, which is naturally abundantly present on the silica, by one of the two hydroxy ends of a macromolecule. The reaction was performed in the polymer melt under vacuum at a desired temperature in the range 140 to 200°C for 30 min. The grafting ratio increases with increasing reaction temperature. For the grafting reaction, the following procedure was carried out. The silica and PEO-6 in a ratio of 5:3 by weight were mixed in a 80 ml sample tube containing a small amount of chloroform and dried in a water bath regulated at *ca.* 70 ± 0.5°C. The mixture was dried completely under vacuum for 1 day at room temperature, evacuated to 6×10^{-4} torr. Next, the sample tube was held at the desired temperature. (The oil bath was controlled within ± 0.5°C.) After the grafting reaction was achieved, the ungrafted polymer was removed by Soxhlet extraction with acetone for 24 h. Finally, the grafted silica was dried under vacuum at 130°C for 1 day. The grafting ratio (weight ratio of PEO to silica) was determined by pyrolysis weight loss between 100°C and 300°C. Thermogravimetry (t.g.) measurements were carried out with a Rigaku-TG 8110D calorimeter. T.g. scans were run from 20°C to 500°C at 5°C min^{-1}.

Adsorption of polystyrene

Silica gel (0.2 g) was transferred to a 20 ml flask containing CCl_4 (4 ml). The sample in the glass flask was mechanically shaken, to allow the CCl_4 to fully penetrate into the pores of the gel, at 100 rev min^{-1} for 24 h in a Yamato BT-23 water incubator attached with a shaker. Next, SL-PS (0.005 g) was dissolved in CCl_4 (2 ml). The polymer solution was transferred to the 20 ml flask containing the mixture of CCl_4 and silica gel. The polymer solution and the mixture in the flask were also shaken to attain equilibrium at 100 rev min^{-1} in the water incubator. For all experiments, the temperature of the water incubator was controlled to 35.0 ± 0.1°C. The concentration of the polymer solution, $8.3 \times 10^{-4} g\ ml^{-1}$, does not exceed a critical entanglement concentration[6].

For kinetic studies of PS adsorption, the following procedure was carried out in each case. The shaking was stopped after a fixed time interval and the silica particles were sedimented. A quantity (0.5 ml) of the supernatant was carefully withdrawn and transferred to an e.s.r. sample tube, and then e.s.r. measurements were carried out in order to estimate the concentration of spin label in the solution. The supernatant in the sample tube was brought back to the 20 ml flask and the shaking was started again. The procedure was repeated many times with increasing adsorption time. The decrease of concentration of the spin label with increasing adsorption time should be caused by the adsorption of PS molecules on the silica surface.

After the adsorption experiment was terminated, the supernatant was carefully removed by an injector. The silica sample in the flask was rinsed with CCl_4 (50 ml) and dried in a vacuum oven at 40°C for several days. After the solvent had been completely evacuated off, e.s.r. measurements were carried out in order to study the structure and molecular motion of PS chains adsorbed on the dried silica. The amount of adsorbed PS on the dried silica was also determined by pyrolysis weight loss as mentioned above.

E.s.r. measurements

E.s.r. measurements were carried out with a JEOL FE3XG and a JEOL ME3XG spectrometer and connected PC9801 computers. 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

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 described in a previous paper[5]. The principal values of **g** and **A** tensors, the fractional amount of B labels, and line widths can be obtained.

RESULTS AND DISCUSSION

Kinetics of polystyrene adsorption on a silica-tethered poly(ethylene oxide)

In order to study the adsorption behaviour of PS on silica-tethered PEO, the intensity of the e.s.r. spectrum of nitroxide spin labels in the CCl_4 solution was detected. *Figure 1* shows plots of the concentration of SL-PS in the supernatant relative to the concentration before the

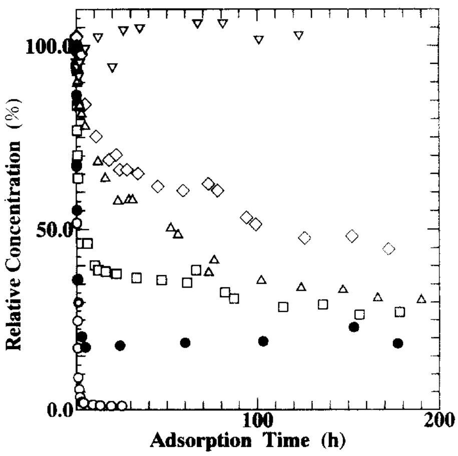

Figure 1 The relative concentration of spin labels in the supernatant as a function of adsorption time for the samples of various grafting ratios: 0% (○); 0.4% (●); 0.9% (□); 1.1% (△); 1.5% (◇); 2.1% (▽)

adsorption as a function of adsorption time. The decreasing concentration with increasing adsorption time should be caused by transfer of PS molecules in the solution to the silica gels. Since twice the radius of gyration of the PS-96, estimated as 23.4 nm, is much smaller than the average pore size of the MB-2000 silica, 191 nm, the PS-96 molecules can easily penetrate into the pores without significant deformation of the PS chain. Then, almost all PS-96 molecules can be expected to be adsorbed very rapidly. In the case of adsorption on non-grafted silica, the relative concentration of spin labels in the solution decreases steeply and attains a plateau value (1%) after only 3 h of adsorption time. It is interesting to study the effect of molecular miscibility of tethered PEO chains with PS chains on adsorption kinetics as a function of the grafting ratio. The effective adsorption area should be reduced by increasing the grafting ratio. The adsorption rates and the adsorption amounts of PS decrease steeply with increasing grafting ratio. The PS chains adsorbed on the silica having only 2.1% grafting ratio could hardly be detected. These experimental facts suggest that PEO chains are more tightly attached to the grafted silica surface than PS chains and exclude PS chains from adsorption because of the low miscibility of PEO and PS chains.

Figure 2 shows plateau values of adsorbed amounts of PS as a function of grafting ratio. The adsorbed amount of PS on the dried silica was estimated by pyrolysis weight loss, whereas the adsorbed amount before rinsing was estimated from the asymptotic concentration in *Figure 1*. It is found that some amounts of PS are desorbed by rinsing with the solvent CCl_4. It seems strange that the amount of PS adsorbed for a short adsorption time (10 h, ■) is larger than that for a long adsorption time (178 h, ●) after rinsing. It can be considered that the PS molecules are adsorbed temporarily in non-equilibrium during the initial stage of adsorption and the PS molecules are rearranged to the equilibrium states, changing the structure of the PS chains. Some PS molecules and others interact more strongly and weakly with the silica, respectively. There are more PS molecules weakly interacted with the silica-tethered PEO and desorbed by rinsing with CCl_4 at the stage corresponding to 178 h of adsorption time than at the stage corresponding to 10 h or short adsorption time. This adsorption behaviour will be also discussed in detail in later sections.

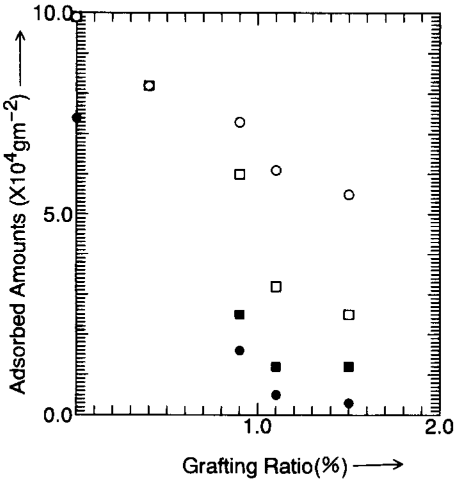

Figure 2 Adsorbed amounts of PS-96 for silica-tethered PEO at $C_0 = 8.3 \times 10^{-4}$g ml^{-1} in carbon tetrachloride as a function of grafting ratio before (○, □) and after (●, ■) rinsing with CCl_4. Adsorption time is 10 h (■, □) and 178 h (●, ○)

Structure of PS chains adsorbed on a silica-tethered PEO

In our previous papers[5,6], the e.s.r. spectra of SL-PS adsorbed on silica gels could be interpreted in terms of two components from two different kinds of label, A labels and B labels. A labels, having high values of hyperfine splitting (*HFS*) due to the nitrogen nucleus, are connected with the segments strongly interacted with the silica as 'train' segments. The high values should be caused by the electric field of the silica surface. The magnitude of *HFS* is an increasing function of PS–silica interaction energy. On the other hand, B labels having low values of *HFS* are connected with the segments that are weakly interacted with the silica as 'loop' or 'tail' segments.

In this paper, we clarify the structure of PS chains adsorbed on a silicatethered PEO by using a two-component analysis of e.s.r. spectra observed at −196°C. *Figure 3* shows an example of the variation of e.s.r. spectra of SL-PS adsorbed on silica with the grafting ratio. The value of the width between the outermost peaks ($2A_{Z'}$) decreases with increasing grafting ratio and the $2A_{Z'}$ values in the sample with 10 h adsorption time are lower than in that with 178 h or long adsorption time, as shown in *Figure 4*.

In order to obtain the exact e.s.r. parameters and clarify the structures of the adsorbed PS segments, spectral simulations for the e.s.r. spectra were performed. *Figure 5* shows examples of the simulated spectra by assuming two components, which agree well with the observed spectra. The e.s.r. parameters determined from the spectral simulations are shown in *Table 1*. The following results are found from the simulations.

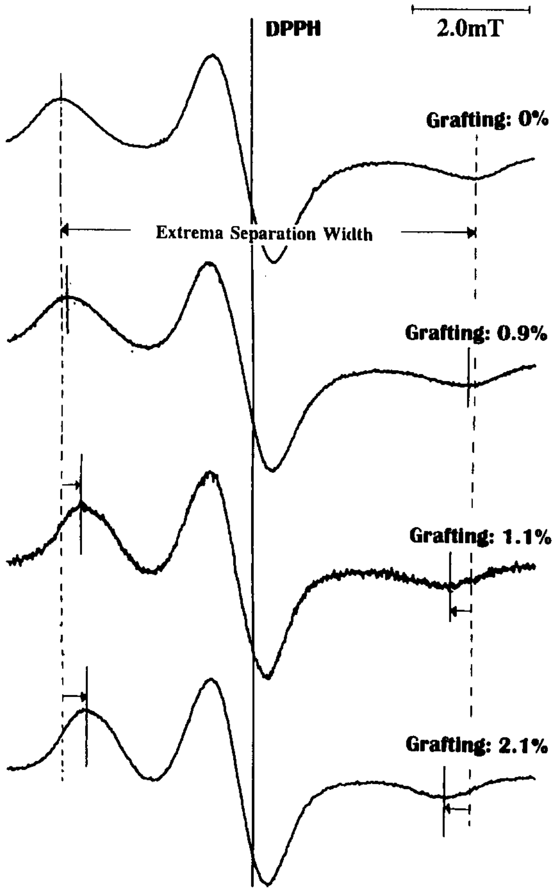

Figure 3 Variation of e.s.r. spectra of SL-PS (PS-96) adsorbed on the silica-tethered PEO with the grafting ratio. Adsorption time is 178 h. Measurements were carried out at −196°C

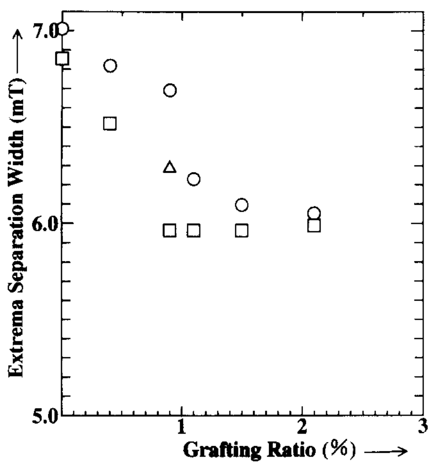

Figure 4 Plots of extreme separation width of e.s.r. spectra of SL-PS (PS-96) at −196°C as a function of grafting ratio. Adsorption time is 10 h (□), 52 h (△) and 178 h (○)

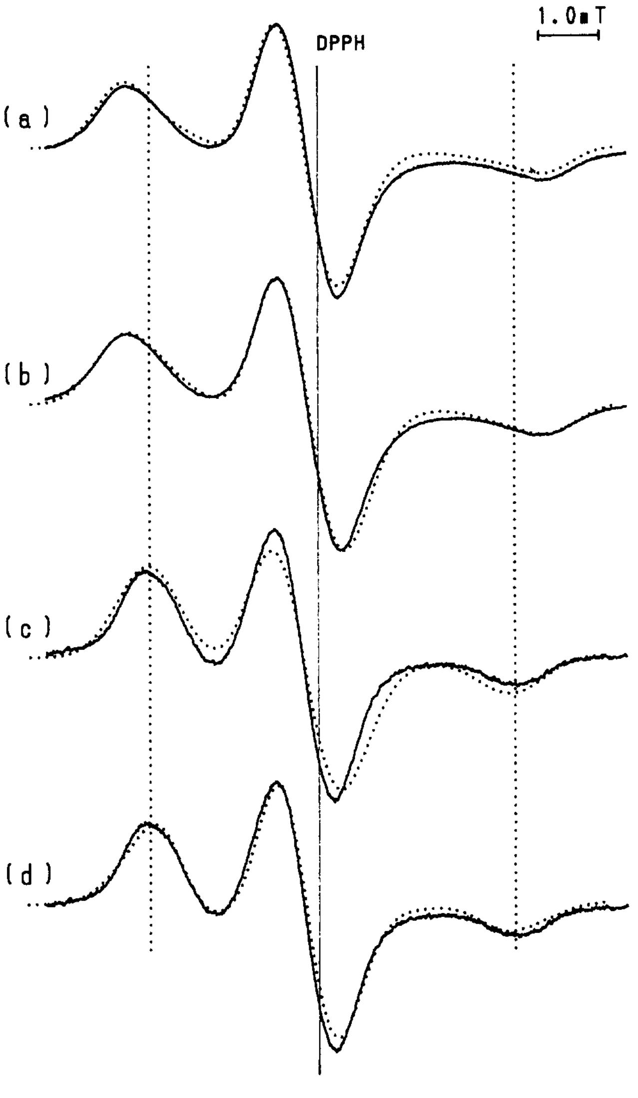

Figure 5 Comparisons of calculated (dotted) and observed (solid) spectra of SL-PS (PS-96) at − 196°C. The PS molecules are adsorbed on the MB-2000 silica gels. (a) Non-grafted silica and 10 h of adsorption time; (b) non-grafted silica and 178 h of adsorption time; (c) silica having 2.1% grafting ratio and 10 h of adsorption time; (d) silica having 2.1% grafting ratio and 178 h of adsorption time

(1) The fractional amount of B labels in the sample with 10 h of adsorption time increases gradually and the amount in the sample with 178 h of adsorption time increases steeply at *ca.* 1.0% with increasing grafting ratio, as shown in *Figure 6*. These results suggest that the PS segments weakly interacted with the silica, like 'loop' or 'tail' segments, increase with increasing grafting ratio because the tethered PEO chains interrupt PS chains from moving to the silica surface and taking a 'train' conformation. The segments are protruded from the silica surface and/or embedded in the tethered PEO chains.

(2) The fractional amounts in the sample with 10 h or short adsorption time are higher than in those in the sample with 178 h or long adsorption time in the whole range, as shown in *Figure 6*. It was also found that the A_Z and A_i values of A labels in the sample with 10 h adsorption time were smaller than those in that with 178 h adsorption time, when the grafting ratio was between 0.3 and 2.0%. These facts suggest that the PS–silica interaction increases with increasing adsorption time.

Molecular motion of PS chains adsorbed on a silica-tethered PEO

In order to evaluate the molecular motion of adsorbed PS chains related to the PS–silica or PS–PEO interactions, e.s.r. spectra were observed at various temperatures. *Figure 7* shows the temperature dependence of the e.s.r. spectra of SL-PS adsorbed on the silica-tethered PEO having 0.9% grafting ratio for 10 h adsorption time, which should be compared with that of SL-PS in the homopolymer bulk. The outermost splittings ($2A_{Z'}$) for the SL-PS on the silica are plotted against temperature in *Figure 8*. The value of $2A_{Z'}$ is also a good measure of the mobility of the spin-labelled PS. The width narrowed with increasing temperature because of averaging of the anisotropies of *g* and *HFS* values.

In the solid bulk of polystyrene, the value of $2A_{Z'}$ gradually decreases with increasing temperature. On the other hand, the temperature dependence of $2A_{Z'}$ shows a remarkable change with the grafting ratio. The variations with temperature are very small for the SL-PS on the non-grafted silica and the silica-tethered PEO having 0.4% grafting ratio. This fact suggests that very strong PS–silica interaction causes a hindrance to the mobility associated with relaxation of the PS chains. Next, it is found that the narrowing curves for the silica-tethered PEO having higher grafting ratios, 0.9–2.1%, show remarkable drops in two temperature ranges. Gradual decreases of $2A_{Z'}$ in the lower temperature range below − 40 to 20°C are attributed to a local mode relaxation, whereas steep drops in the higher temperature range above − 40 to 20°C are caused by a micro Brownian type molecular motion[15]. The narrowing of $2A_{Z'}$ for adsorbed SL-PS is much clearer in comparison with that in the homopolymer bulk. The narrowing curves shift to lower temperatures (*Figure 8*) and the transition temperature, T_{50G}, at which $2A_{Z'}$ is 5.0 mT decreases (*Figure 9*) with increasing grafting ratio. These experimental facts indicate that the fractional amount of mobile 'loop' or 'tail' segments in the PS adsorbed on the silica-tethered PEO increases with increasing grafting ratio and the mobile segments are protruded from the silica surface and/or embedded in the tethered PEO chains as concluded in the previous section. Molecular mobility of the PS chains in the PEO matrices is higher than in the PS matrices since the glass transition temperature (T_g) of PEO (−65°C) is lower

Table 1 E.s.r. parameters of the spectra of SL-PS (PS-96) on the silica-tethered PEO, determined from the spectrum simulation mentioned in the text. Dependence of the e.s.r. parameters upon grafting ratio (*GR*). The values in brackets mean adsorption time

	PS bulk	$GR = 0.0\%$ (10 h)		$GR = 0.0\%$ (178 h)		$GR = 2.1\%$ (10 h)		$GR = 2.1\%$ (178 h)	
		A	B	A	B	A	B	A	B
g_z	2.0024	2.0020	2.0020	2.0020	2.0020	2.0022	2.0022	2.0022	2.0024
g_y	2.0072	2.0068	2.0069	2.0067	2.0069	2.0069	2.0069	2.0069	2.0069
g_x	2.0072	2.0070	2.0070	2.0068	2.0069	2.0072	2.0072	2.0072	2.0072
$(g_x + g_y + g_z)/3$	2.0056	2.0053	2.0053	2.0052	2.0053	2.0054	2.0054	2.0054	2.0055
A_z (mT)	2.94	3.45	2.59	3.45	2.59	3.29	2.89	3.31	2.73
A_y (mT)	0.52	0.49	0.60	0.53	0.63	0.51	0.51	0.51	0.51
A_x (mT)	0.52	0.49	0.60	0.53	0.63	0.51	0.51	0.51	0.51
$(A_x + A_y + A_z)/3$	1.32	1.48	1.26	1.50	1.28	1.43	1.30	1.44	1.25
Line width (mT)	0.97	0.88	0.99	0.99	0.94	0.89	1.04	0.91	0.78
Fraction (%)	100	75	25	81	19	8	92	47	53

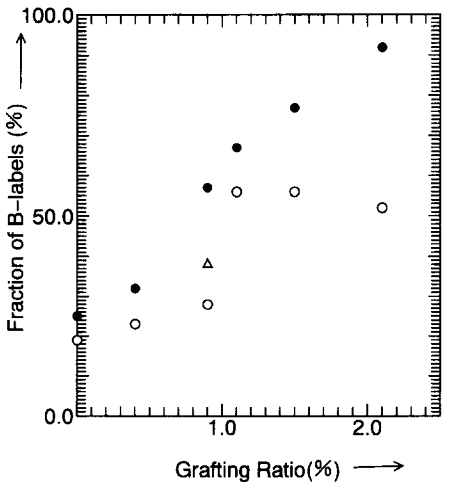

Figure 6 The fractional amount of B labels (%) at −196°C as a function of grafting ratio. Adsorption time is 10 h (△), 52 h (○) and 178 h (●)

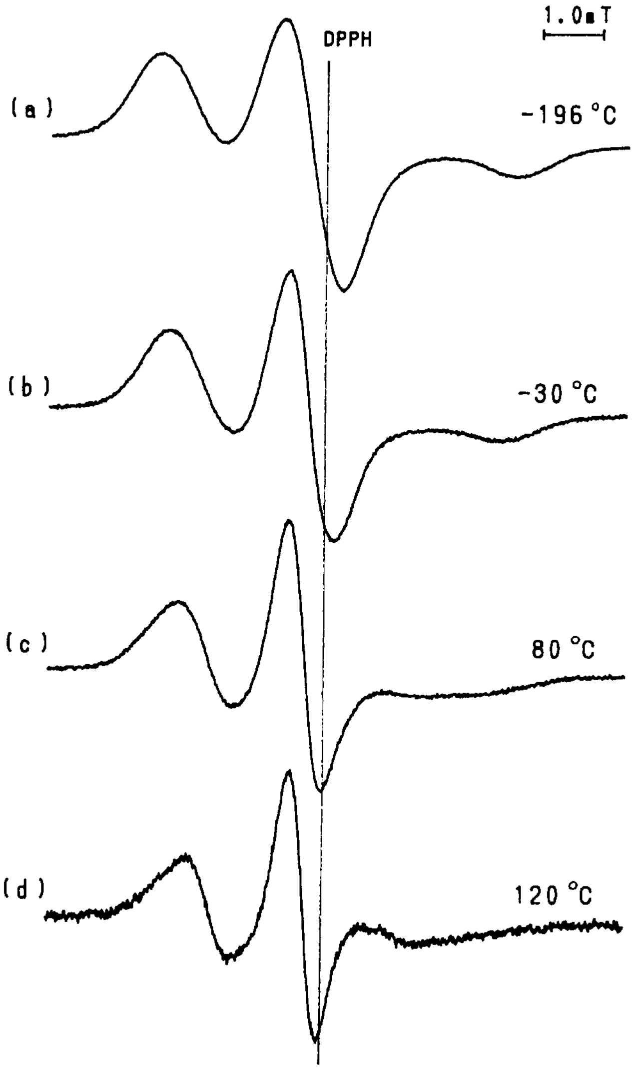

Figure 7 Temperature-dependent e.s.r. spectra of SL-PS (PS-96) adsorbed on the silica-tethered PEO having 0.9% grafting ratio for 10 h adsorption time

than that of PS (87°C)[16]. The tethered PEO chains accelerate the molecular motion of the PS segments protruded from the silica surface. Consequently, the transition temperature shifts to a low temperature and becomes lower than that for the homopolymer PS bulk with increasing grafting ratio.

Figure 10 shows also plots of $2A_{Z'}$ for the SL-PS on the silica-tethered PEO for long adsorption time (178 h) as a function of temperature. The temperature dependences should be compared with those in *Figure 8*. The narrowing curves shift to higher temperatures and the transitions are much narrowed with increasing adsorption time. The variations with temperature below −80°C are very small and the transition temperature, T_{50G}, is higher than that for short adsorption time as shown in *Figure 9*. These experimental facts suggest the following adsorption behaviour. The PS molecules are adsorbed in non-equilibrium during the initial stage of adsorption and have a structure with a wide distribution of correlation time for the molecular motion. Next, the PS molecules are rearranged to the equilibrium state and take a structure with a strong PS–silica interaction. Then, the arrangement gives the PS chains a low molecular mobility with a narrow distribution of correlation time.

In order to confirm the adsorption time dependence of the narrowing curve of $2A_{Z'}$ *versus* temperature, the experimental results for SL-PS on the silica-tethered PEO having 0.9% grafting ratio are shown in *Figure 11*. The outermost splittings in the lower temperature range increase with increasing adsorption time. Surprisingly, the broad e.s.r. spectra for 10 h adsorption time, observed at higher temperatures above 50°C, split into two-component spectra with larger and smaller values of $2A_{Z'}$, corresponding to the labels with slow and fast rates of motion. The two kinds of

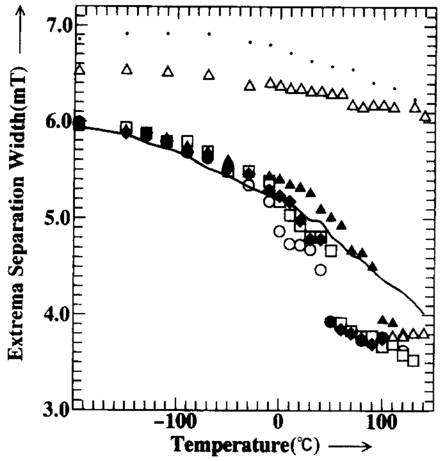

Figure 8 Variations of outermost splitting $(2A_{Z'})$ with temperature for solid bulk (PS-96) (————) and PS-96 adsorbed on the silica-tethered PEO having various grafting ratios: 0% (•); 0.4% (△); 0.9% (▲); 1.1% (□); 1.5% (◆); 2.1% (○). Adsorption time is 10 h (●)

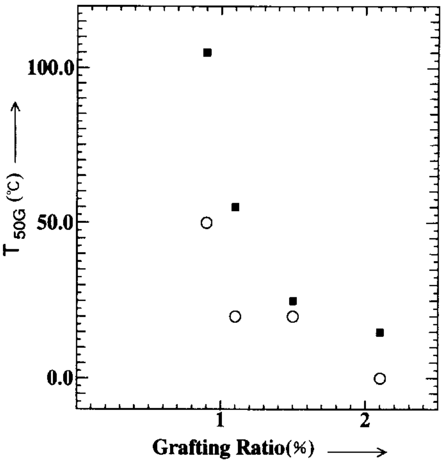

Figure 9 Plots of T_{50G} as a function of grafting ratio. Adsorption time is 10 h (○) and 178 h (■)

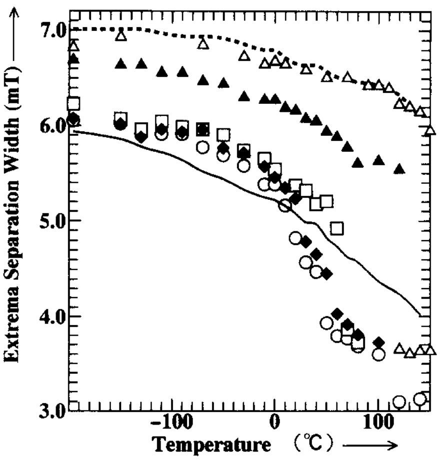

Figure 10 Variations of outermost splitting $(2A_{Z'})$ with temperature for solid bulk (PS-96) (————) and PS-96 adsorbed on the silica-tethered PEO having various grafting ratios: 0% (– ■ –); 0.4% (△); 0.9% (▲); 1.1% (□); 1.5% (◆); 2.1% (○). Adsorption time is 178 h (○)

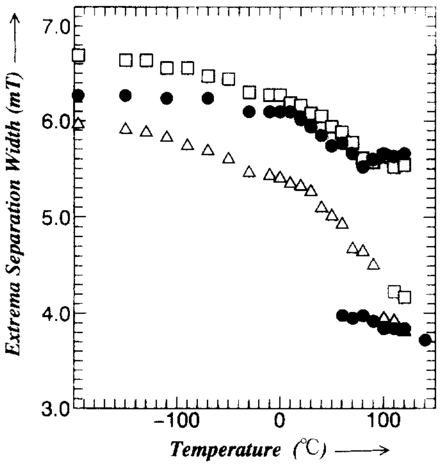

Figure 11 Variations of outermost splitting $(2A_{Z'})$ with temperature for PS-96 adsorbed on the silica-tethered PEO having 0.9% grafting ratio. Adsorption time is 10 h (△), 52 h (●) and 178 h (□)

label are attached to 'train' and 'loop' (or 'tail') segments, respectively. Next, the labels with the fast rate of motion disappear for 152 h or long adsorption time. From these experimental results, it can be concluded that some PS segments of quasi-stable state during the initial stage of adsorption become more strongly interacted with the silica, others become more weakly interacted with the silica and PEO molecules, and the PS molecules with the latter segments are desorbed, finally.

Effect of structure of tethered PEO chains on adsorption behaviour of PS chains

The adsorption behaviour of PS chains on a silica-tethered PEO is depicted schematically in *Figure 12*. The PS chains are adsorbed on the silica surface directly, as shown in *Figure 12a*, when the grafting ratio (*GR*) is lower than the characteristic ratio (*GR**) at which the overlap of the PEO chains starts.

Tajouri *et al.*[17] recently studied the organization of a layer of PEO chains grafted on silica and concluded that the chains adopt a flat conformation on the surface at a low grafting ratio, whereas the chains adopt more extended conformation, perpendicular to the surface, at a high grafting ratio. We agree with their models for the adsorption structure of the tethered PEO chains. PS adsorption behaviour on the silica-tethered PEO has a strong dependence on the grafting ratio. The adsorption rate is a decreasing function of the grafting ratio and approaches zero around a grafting ratio of 1.5–2.1%, as shown in *Figure 1*. This result suggests that tethered PEO chains on the silica having *ca.* 1.5% grafting ratio cover the whole surface of the silica. For instance, an amount of PEO segments forms one monolayer on the surface and the tethered PEO chains interrupt all PS segments from being adsorbed on the silica surface, directly. A tethered PEO chain occupies roughly a hemisphere with a radius comparable to the Flory radius, R_F, for a coil. $R_F = N^{0.5}a$, where N is the number of repetitions and a is the length of a segment. It can be obtained that a tethered PEO chain having $M_n = 6000$ occupies part of the surface area of the silica given by πR_F^2, i.e. 2.8 nm^2, and 0.009 g of PEO chains can form a monolayer on 1 g of the silica, which has a surface area of 25 $m^2 g^{-1}$. Above the grafting ratio 0.9% (*GR**), the PEO coils begin to overlap; a modification to the structure arises. The calculated value of *GR** is nearly equal to

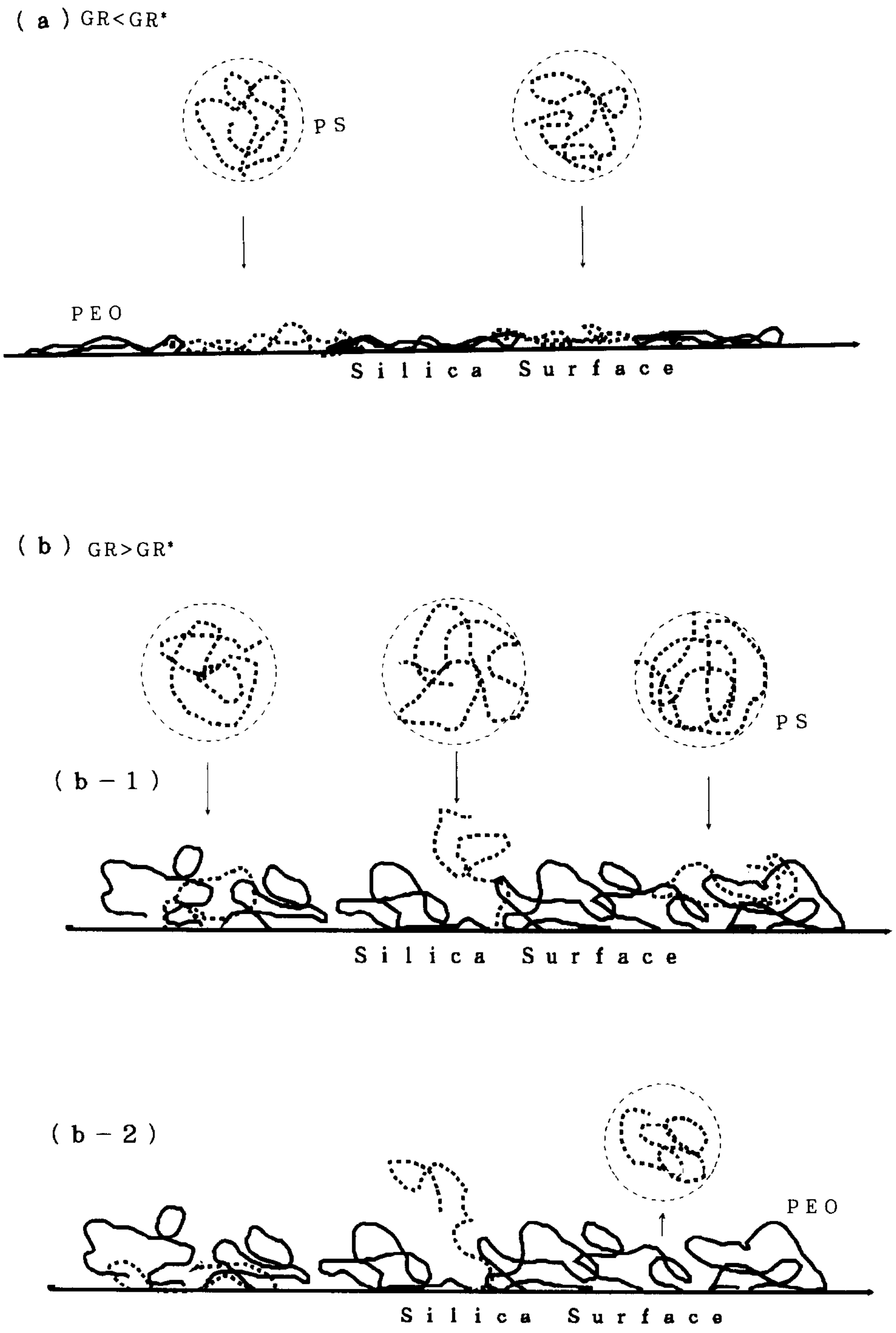

Figure 12 Schematic representations of conformational changes of PS and PEO segments on the silica-tethered PEO. The meaning of *GR** is mentioned in the text

1.5% grafting ratio, at which the adsorption behaviour changes. The fractional amount of B labels for long adsorption time increases steeply at the crossover grafting ratio, *GR**, as shown in *Figure 6*. PS chains are adsorbed selectively on the silica surface which is not occupied by tethered PEO chains because the silica surface is more attractive for the PEO chains and the chains adopt a flat conformation at low $GR < GR^*$. On the other hand, at $GR > GR^*$, PS chains are adsorbed indirectly on the silica, entangling with the PEO chains because the PEO chains start to overlap and protrude from the silica surface as shown in *Figure 12b*(1). Then, the fractional amount of B labels attached to 'loop' or 'tail' segments increases to a limiting value.

The PS molecules with the strong PS–silica interaction and the desorbed molecule after long adsorption time mentioned previously are also depicted in *Figure 12b*(2). The fractional amount of B labels at $GR < GR^*$ is a function of the PS–silica interaction, which has a molecular weight dependence as discussed in the previous paper[6]. The grafting ratio dependences the of molecular motion of PS chains have also crossover points, as shown in *Figures 9 and 10*. At $GR < GR^*$, molecular mobility increases with increasing grafting ratio. The density of tethered PEO segments is not uniform on the silica surface. The PS chains adsorbed on the silica surface increase the interaction with the PEO segments which accelerate their molecular motion, with increasing grafting ratio. At $GR > GR^*$, all chains are embedded in the tethered PEO chains, the density of which becomes uniform. Then, molecular mobility of the PS chains become less dependent on the grafting ratio.

The structure and molecular motion of the tethered PEO chains on the silica will be discussed in detail in a forthcoming paper.

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