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Mobility Redistribution of Spin Labels on Adsorbed Polystyrene

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Introduction

Electron spin resonance (ESR)[1] is a spectroscopic technique used to study the resonant transitions between energy levels of the magnetic dipoles due to electronic angular momentum. The usual ESR spectrum is obtained by taking the derivative of the absorption spectrum of a paramagnetic species under microwave excitation in the presence of a ramped magnetic field. The rotational mobility of the paramagnetic species strongly affects the shape of an ESR spectrum since it can affect the relaxation process of the excited state. Techniques for line shape analysis[2] are well established and give information on the mobility distribution of the paramagnetic species in a window of time scales around that for the resonant transitions.

ESR has been employed successfully to study the conformational details of polymer adsorption.[3–5] A three-component model[6–8] has been used to deconvolute spectra from adsorbed, spin-labeled polymers. The experimental spectra are reproduced by summing three components: (a) a sharply peaked component from labels with a rotational correlation time $\leq O(10^{-1}$ ns), denoted "freely mobile" and presumed identical to the spectrum of the labeled polymer in solution; (b) a moderately broadened component from labels with a rotational correlation time $\sim O(10^0$ ns), having "intermediate" mobility and presumed identical to the spectrum of the labeled polymer in the melt state; (c) a "powder pattern" component from labels with a rotational correlation time $\geq O(10^1$ ns), denoted "motion restricted" and presumed identical to the spectrum of the labeled polymer solution at cryogenic temperatures. The basic assumption in all previous ESR work on adsorbed polymers is that the freely mobile, intermediate, and motion-restricted labels correspond to the fractions of segments in long loops and tails, short loops, and trains, respectively.

Based on this composite model, previous studies have determined the apparent conformation of adsorbed macromolecules. For example, Kobayashi *et al*[6,7,9,10] measured the apparent equilibrium fraction of segments in trains, f_{train}, as a function of surface coverage and silanol density for spin-labeled polymers on nonporous silica. With labeled polystyrene (PS), they found that the apparent f_{train} decreases with increasing surface coverage, while the fraction of long loops and tails simultaneously increases. Similar behavior was observed with spin-labeled poly(methyl methacrylate) (PMMA) on nonporous silicas.[9] In another investigation, Sakai *et al.*[8,11,12] studied the effects of solvent quality and polymer molecular weight on the conformation of adsorbed PMMA on nonporous silica.

An aspect of polymer adsorption which has been neglected in all previous ESR studies is the effect of elapsed time after the adsorption is initiated. Some work on dynamic aspects of polymer adsorption using other techniques has been published relatively recently.[13–16] These publications suggest very long time scale surface rearrangements, which progress long after the coverage and layer depth equilibrate. For example, in exchange experiments with protonated and deuterated PS on silicon oxide, Granick *et al.*[13–15] found that the exchange rate depends strongly on the history of the adsorbed layer. Longer incubation of the adsorbed layer in the bulk polymer solution after reaching an "equilibrium" absorbance slows the subsequent exchange process. This was interpreted as a result of the slow rearrangement of the adsorbed chain toward equilibrium conformations with a larger number of contacts per chain. In a study of the development of coverage of PS on gold using a quartz crystal microbalance, Fu *et al.*[16] observed slow, long time scale kinetics with high molecular weight polymer, in which the coverage continues to increase with time long after the layer thickness has equilibrated according to ellipsometry.[17] Although there is indirect evidence, there is no direct spectroscopic observation of these slow surface rearrangement processes.

In this study, we explore the effect of time on the apparent conformation of adsorbed, spin-labeled polystyrene (PST). We monitor the ESR spectra of PST adsorbed on porous silica *in situ*, which shows that the apparent conformational distribution can change slowly with time. In the case of porous silica, the surface chemistry is complex and depends on the silica synthesis and pretreatment conditions.[16–20] Typically, there is a layer of physisorbed water on "as-received" silica. Evacuation procedures can remove the physisorbed water,[18–20] leaving isolated/geminal hydroxyls, hydrogen-bonded "vicinal" hydroxyls, and sterically inaccessible hydroxyls. It has been found[21] that the adsorption of PS on silica occurs mainly through the formation of weak hydrogen bonds between the hydroxyl groups and the aromatic rings. The study by Tripp[22] with nonporous silica suggests that it is the isolated/geminal hydroxyls which attract PS segments via hydrogen bonding. In what follows, we show that trace amounts of water in the system influence the interactions of both the labels and polymer segments with the silica surface and can trigger slow surface rearrangements.

Experiments

Materials. Anhydrous carbon tetrachloride (99+%) (CCl_4), sodium hydride (NaH), dimethylformamide (DMF), 4-hydroxyTEMPO (HO-TEMPO), polystyrene (PS), and the NMR tubes were purchased from Aldrich Chemical Co. A.C.S.-Certified benzene and toluene were purchased from Fisher Scientific.

Sample Preparation. PS (M_v = 45 730, PD = 1.06) was chloromethylated according to the procedure reported in the literature.[23] The chloromethylated PS was further reacted with 4-hydroxyTEMPO in anhydrous DMF with NaH as catalyst. The spin-labeled polystyrene (PST) was precipitated with 90:10/MeOH:H_2O (by volume) and reprecipitated from $CHCl_3$ in MeOH.

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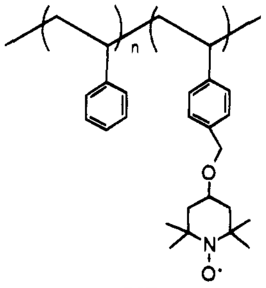
A Ludox porous silica was received from Dr. W. Mahler (DuPont). Microscopy showed that the primary particles are 220 Å in diameter. The primary particles were coagulated into 100 × 100 μm platelets through a freeze–thaw method. The platelets have a surface area of 272 m^2/g and an average pore size of 57 Å, both determined by N_2 adsorption.

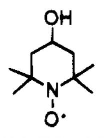
For experiments on "dehydrated" porous silica (pSiDH), 0.2 g of platelets was dehydrated under vacuum ($\sim 10^{-3}$ Torr) at room temperature for 24 h and then prewet with 0.6 mL of anhydrous CCl_4 for another 24 h. For the pSiDH, no special precaution was taken to exclude moisture after evacuation and before addition of the CCl_4, although the intervening time was minimized in all cases. For experiments on as-received silica (pSiAR), the evacuation step was skipped. The prewetting with CCl_4 was assisted by agitating the sample with a mechanical shaker (Janke & Kunkel, Type VX5) at a speed of 200 min^{-1}.

Incubation and Aging. After prewetting the solid, 0.4 mL of 5.0 g/L PST solution in anhydrous CCl_4 was added to produce a nominal polymer concentration in the supernatant of 2.0 g/L. The silica platelets and polymer solution were then mildly agitated throughout an adsorption or "incubation"[26] period. After incubation in the PST solution for a fixed time, the platelets were washed with aliquots (~6 mL) of pure CCl_4, typically 5–8 times, until no nitroxide signal was detectable in the supernatant. Pure solvent was added to the silica, and the slurry was transferred into an NMR tube to "age".[26] ESR spectra were taken on a Bruker EPR300 spectrometer to monitor spectral changes during the aging process. All the operations described above were carried out at room temperature. A few experiments were done with benzene and toluene in place of CCl_4.

Results

Characterization of PST. The spin label is bound to the phenyl ring of PS through an ether linkage, as shown below. The ESR spectrum of the PST in bulk CCl_4 solution (1 g/L, room temperature) exhibits three peaks with unequal intensities (spectrum c in Figure 2), with the highest peak corresponding to the lowest field. The line shape of the ESR spectra of PST solutions in CCl_4 did not change with concentration up to 10 g/L. The labeling degree was estimated by comparing the double-integrated intensities of the ESR spectra of the same volumes (0.1 mL) of a 1.0 g/L PST solution and a standard free 4-hydroxyTEMPO solution. The PST was found to have one label for every ~500 repeating units, which corresponding to ~1 label per chain.


PST


HO-TEMPO

Aging of Adsorbed PST on Dehydrated Porous Silica (pSiDH). Recall that by dehydrated silica, we mean silica which, before incubation in the PST solution, was evacuated and then prewetted with the solvent as described earlier. The initial polymer concentration during incubation was 2.0 g/L (below the bulk overlap concentration $C^* \sim 100$ g/L) but well above the saturation threshold of the adsorption isotherm, C_{sat}, for this system ($C_{sat} < 0.1$ g/L; details are to be published)). Within an hour during incubation, the concentration in the supernatant fell to ~1.2 g/L, which is still well above C_{sat} on the adsorption isotherm, giving rise to a nominal surface coverage of 1.6×10^{-6} g/m^2. This value is significantly lower than what has been reported for PST adsorbed on nonporous silica from CCl_4 under similar conditions ($\sim 10^{-5}-10^{-4}$ g/m^2).[6,28]

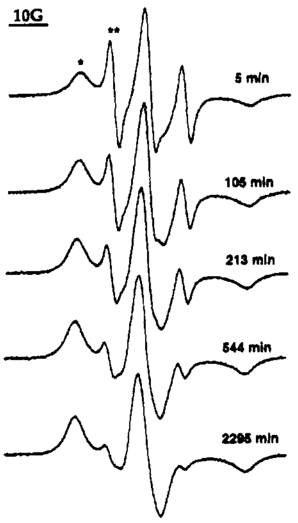


Figure 1. ESR spectra of PST adsorbed on dehydrated silica (pSiDH) during aging in pure CCl_4. The sample had been incubated in 2.0 g/L PST–CCl_4 solution for 1 h. The spectra from top to bottom are after aging in pure CCl_4 for 5, 105, 213, 544, and 2295 min. The peaks denoted with * and ** are the signals given by labels with restricted mobility and free mobility, respectively.

After incubating the silica in PST–CCl_4 solution, the bulk was exchanged with pure CCl_4 to begin an "aging"[26] process. The main purpose of replacing the bulk solution with pure solvent is to eliminate the signal contributed by polymer in the bulk so that only the signal from the adsorbed polymer is seen. For all the aging experiments done, no detectable ESR signal was found in the supernatant, indicating there was no perceptible desorption of polymer into the pure solvent, bulk phase.

The ESR spectra of PST on pSiDH during aging in pure CCl_4 after 1 h of incubation in polymer solution (Figure 1) were similar to the spectra of PST on nonporous silica reported by Kobayashi *et al.*[6] The spectra contain a characteristic broad peak at low field (marked with * in Figure 1) from motion-restricted labels, usually associated with trains. They also show a sharp peak at a slightly higher field (marked with ** in Figure 1) from freely mobile labels, presumably due to tails and long loops. From the beginning of the aging process for up to 2 days, the intensity of the broad peak increased with time at the expense of the intensity of the sharp peak. After 1 week of aging in CCl_4, the sharp peak had disappeared completely, resulting in a spectrum similar to the motion-restricted spectrum of bulk PST solution at cryogenic temperature. The only difference between the long-time spectrum on dehydrated silica and that of a frozen solution is that the motion-restricted spectrum obtained from the former is somewhat broader than that from the latter (Figure 2a); *i.e.*, the hyperfine coupling constant is larger for PST completely immobilized on silica. A similar broadening was reported by Lozos,[27] who studied adsorption of nitroxide radicals on silica. This feature was ascribed to the difference in polarity of the label environment on silica and in a frozen solution.[2]

Deconvolution of ESR Spectra. In our analysis of the experimental spectra (Figure 2), we made two

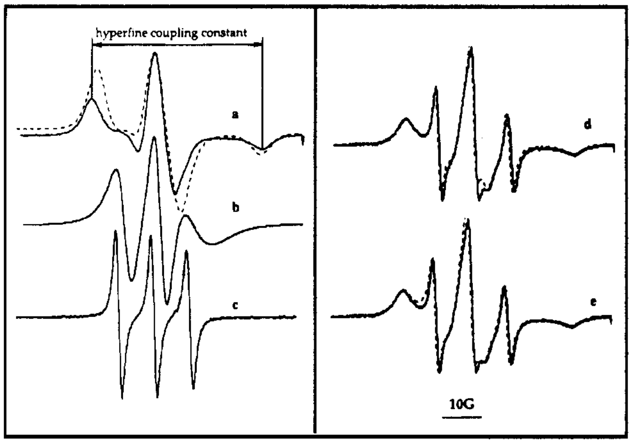


Figure 2. Deconvolution of ESR spectra of PST adsorbed on dehydrated porous silica (pSiDH): (a) solid line, ESR spectrum of PST adsorbed on pSiDH after 2 weeks of aging in CCl_4, for modeling the motion-restricted component; dashed line, ESR spectrum of frozen PST solution (~−140 °C); (b) ESR spectrum of PST in the melt state (~150 °C), for modeling the intermediate-mobility component; (c) ESR spectrum of 1.0 g/L PST−CCl_4 bulk solution at room temperature, for modeling the mobile component; (d) typical ESR spectrum after incubation (solid line) and computed spectrum (dashed line) with components (a) (84%) and (c) (16%) only; (e) typical ESR spectrum after incubation (solid line) and computed spectrum (dashed line) with components (a) (82.5%), (c) (14.5%), and (b) (3%).

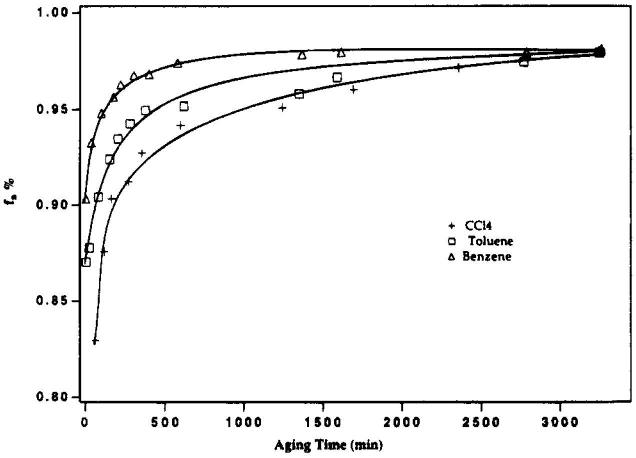


Figure 3. Fraction of motion-restricted labels, f_a, during aging in three solvents for PST adsorbed on pSiDH from the corresponding solution. The samples were incubated in an initially 2.0 g/L PST solution for 1 h.

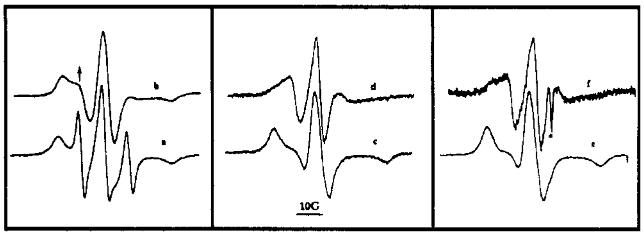


Figure 4. ESR spectra at the beginning of aging in CCl_4: (a) PST on pSiDH; (b) PST on pSiAR (the arrow marks the signal from labels with intermediate mobility); (c) HO-TEMPO on pSiDH; (d) HO-TEMPO on pSiAR; (e) PST adsorbed on pSiDH at the end of aging; (f) same as in (e) after adding 0.004 mL of water and agitating. Samples a, b, and e were prepared by incubating the silica with an initially 2.0 g/L PST−CCl_4 solution for 1 h; samples c and d were prepared by incubating the silica with 10^{-4} M HO-TEMPO−2.0 g/L PS−CCl_4 solution for 1 h.

modifications of the standard procedure:[6−8] (i) The motion-restricted contribution is taken as the spectrum from PST adsorbed on dehydrated silica in the long-time limit (2 weeks) of aging in the pure solvent instead of spectrum of a frozen PST solution. This is because the latter spectrum is narrower than the former and permits a much better representation of the experimental spectra. (ii) In some cases, we found that the spectra are actually better reproduced with just two components, from labels with restricted and free motions (Figure 2a,c), instead of three; *i.e.*, the inclusion of a component from labels with intermediate mobility, presumably on short loops (Figure 2b), did not provide a good deconvolution, as shown in Figure 2d,e.

The fraction of motion-restricted labels, f_a, obtained by the above deconvolution process is plotted against the aging time in the pure solvent in Figure 3 for aging in several solvents after 1 h of incubation in an initially 2.0 g/L solution of PST in the corresponding solutions. For CCl_4, even at the beginning of the aging, f_a is found to be very high (~82%), suggesting that most of the labels are directly adsorbed or are contained in trains[6−8] of adsorbed segments. The restricted fraction increased with aging in CCl_4 until after 2 days it approached 95%. Similar trends were observed in the other solvents, toluene and benzene, although f_a begins at a higher value relative to CCl_4 (Figure 3).

Aging of PST on As-Received Porous Silica (pSiAR). The ESR spectrum of PST adsorbed on as-received porous silica, pSiAR, differed significantly from that of PST on pSiDH (Figure 4a,b). There are three important differences between the results for pSiDH and pSiAR. First, pSiAR adsorbed significantly more PST than pSiDH. In the case of pSiAR, the concentration of the PST solution at the end of 1 h of incubation is about one-fifth of that for pSiDH (~1.2 g/L). This is just above C_{sat} on the adsorption isotherm (to be reported) and corresponds to a nominal coverage of twice that on pSiDH. Second, the spectra from pSiAR show significant contributions from labels with intermediate mobility instead of contributions from labels with restricted and free mobility as in the case of pSiDH. Finally, the change of the spectroscopic features during aging on pSiAR are much less obvious than what was observed on pSiDH. These data clearly indicate that physisorbed water present on pSiAR plays an important role in the binding of the spin labels and/or polymer segments, as reflected by the dramatically different mobility distributions of PST on as-received and dehydrated substrates.

Adsorption of Free Spin Probes on Porous Silica. A change in mobility of labels on the adsorbed polymer, such as that discussed above, can arise from changes in label−site interaction or segment−site interaction, which indirectly affects the attached labels. In order to assess the relative importance of these two effects, the interaction of the label alone with silica was investigated by studying the adsorption of HO-TEMPO on pSiAR and pSiDH from unlabeled PS solutions. For these experiments, the PS concentration was 2 g/L while the HO-TEMPO concentration was 10^{-4} M, which corresponds closely to the nominal bulk label concentration in the aging experiments with PST. The same protocol was used as in the aging experiment with PST, *i.e.*, prewetting of the solid with CCl_4 followed by 1 h of incubation in the HO-TEMPO−CCl_4 solution and finally aging in CCl_4. On pSiDH, the HO-TEMPO adsorbs and is completely immobilized (Figure 4c). The ESR spectrum of the adsorbed HO-TEMPO on pSiDH (Figure 4c) resembles that of the adsorbed PST in the long-time

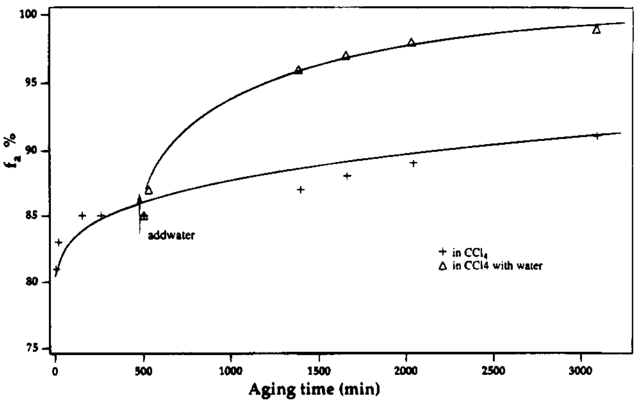


Figure 5. Plot of f_a as a function of aging time with and without addition of trace water at the beginning of aging. The sample was prepared by incubating pSiDH in an initially 0.2 g/L PST−CCl$_4$ solution for 1 h.

limit of aging (Figure 4e). On pSiAR, the adsorbed HO-TEMPO exhibits only intermediate mobility (Figure 4d). In both cases, almost all HO-TEMPO in solution went to the silica surface, giving a nominal surface coverage of $\sim 1.3 \times 10^{-7}$ g/m^2. The residual HO-TEMPO supernatant concentration in the case of pSiAR ($\sim 10^{-7}$ M) was one-third of that with pSiDH, suggesting that the physisorbed water enhances the adsorption of HO-TEMPO, but the effect is uncertain. The difference in coverages corresponding to the different supernatant concentrations is only 10^{-10} g/m^2, comparable to the experimental uncertainty. Further experiments showed that the presence of PS during the adsorption of HO-TEMPO has no effect on the mobility of the adsorbed spin probes.[29]

Effect of Trace Water on Aging. Deliberate addition of a trace amount of water (less than 0.005 mL of H_2O for 0.2 g of silica in 2 mL of CCl_4) to the pSiDH samples with adsorbed PST after extended aging initiated an increase in the mobility of the labels, until the final spectrum resembled that of HO-TEMPO adsorbed on pSiAR (Figure 4d). When a trace of water was added at the start of aging on pSiDH, where the ESR spectrum exhibits a significant contribution from the fast-motion component, the fast-motion component did not convert directly into the intermediate one. Instead, adding water at the early stage in aging accelerated the increase of the motion-restricted fraction at the expense of the freely mobile fraction. The increase of f_a during aging for PST on pSiDH with and without trace water added at the beginning of the process is shown in Figure 5.

Discussion

The results from aging experiments on dehydrated porous silica (pSiDH) indicate that a relatively slow redistribution of mobility of spin labels attached to the polymer occurs after its initial deposition, leading to a greater fraction of labels with restricted motion. Two interesting questions arise in connection with this observation: (i) What is the molecular-level interpretation of the mobility distribution? (ii) What physical processes control the kinetics of mobility change on pSiDH?

Concerning the first question, in past ESR studies with nonporous silica,[6-8] the relative contribution from motion-restricted labels was equated to the fraction of segments in trains. According to this model, the changes observed in our study during aging would be interpreted as an increase in the fraction of segments in trains, *i.e.*, an increase in the bound fraction of segments. By this interpretation, the bound fraction approaches 100% during aging in this system (Figure 3), which seems excessive.

The control experiments using free HO-TEMPO clarify the situation somewhat. The spectra of HO-TEMPO adsorbed on pSiDH were similar to those from PST adsorbed on pSiDH after extended aging. Adding trace water caused the latter to become very similar to that of free HO-TEMPO on hydrated silica, pSiAR. It is apparent that the spin labels in this system interact directly with the surface sites and that the physisorbed water introduces a population of relatively weak binding sites for the label.

On the other hand, comparing the spectra of adsorbed HO-TEMPO and PST on pSiAR, one sees a significant number of TEMPO labels on PST with restricted mobility, while under the same conditions, the adsorbed HO-TEMPOs have only intermediate mobility. This suggests an interaction between polymer segments and the hydrated silica (pSiAR) surface gives rise to a motion-restricted component. So, in interpreting the results from ESR spectral analysis, the realistic view is that the mobility-restricted component corresponds to labels which interact with the surface directly *and* labels pinned in train segments. Thus, the increase of the motion-restricted fraction should be viewed as an increase in direct interactions of the spin labels with active sites and/or the indirect effect of polymer segments binding in trains with the active sites on the silica surface, and not simply equated with the train fraction. At this stage, we cannot separate the two contributions definitively.

With this in mind, consider the second question. Since more PST adsorbs on pSiAR (hydrated silica) than on pSiDH (dehydrated silica), it is clear that physisorbed water modifies the surface sites on silica to increase the surface's affinity for polymer segments. This suggests that the aging kinetics of PST on pSiDH are triggered by the modification of surface sites by ambient water. The modified surface, being more attractive to segments, and possibly to labels, results in the conversion of freely mobile to restricted components and more tightly bound adsorbed layer. This picture is consistent with the progressive increase in the motion-restricted component during PST aging on pSiDH (Figure 3), with the acceleration of this process by addition of trace water at the beginning of aging (Figure 5), and with the invariance of the spectra of PST on pSiAR. Since the time scale for the dispersion of water through the system is extremely short[30] compared with the aging kinetics, it is clear that they are controlled by macromolecular rearrangements on the silica surface.

Conclusions

We report here a preliminary observation of mobility redistribution of spin labels attached to monodisperse polystyrene adsorbed on dehydrated porous silica. By deconvoluting the ESR spectra of adsorbed polymer during aging in contact with the pure solvent, it is found that the fraction of motion-restrictd labels increases with time while the fraction of labels with free mobility decreases. Progressive increases in both segment−site and label−site interactions, triggered by an increase in the level of physisorbed water on the silica, are clearly responsible for the mobility redistribution. Evidently, the operation of replacing the bulk polymer solution with pure solvent does not have an overriding influence in this system. The effects of water content, molecular weight of the polymer, porosity of the silica, and incubation time on this conformational redistribution are under investigation.

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(26) Here, incubation refers to the initial adsorption process where a new silica sample contacts the polymer solution. The term aging refers to the process of contacting a silica sample with previously adsorbed polymer with a pure solvent.

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(28) This could be due to the relative sizes of the polymer molecule and the pores in the silica. In a study of the effect of porosity on PS adsorption onto silica, Kawaguchi *et al.*[24,25] observed that PS adsorbed much less onto porous silica than onto the nonporous varieties when the ratio of the pore diameter (PD) to the twice of the radius of gyration ($2R_G$) of polymer was smaller than 2; $PD/2R_G$ for the system under investigation is $\sim 1/2$. According to Kawaguchi *et al.*, when the size of the pores falls significantly below the polymer molecule, it is very difficult for polymer segments to penetrate into the pores, thus leaving a certain fraction of the surface sites inaccessible to the polymer.

(29) Only trace amounts of HO-TEMPO were detected in the supernatant of samples with no PS in solution. Evidently, PS competes with free HO-TEMPO for adsorption sites, but the effect is weak since the difference in HO-TEMPO adsorbance caused by the presence of PS is $\sim 10^{-10}$ g/m^2 or $\sim 0.1\%$ of the total surface coverage.

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