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Response of Adsorbed Polystyrene Layers to Desorption Conditions

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Adsorption of macromolecules onto solids plays an important role in many technologies, especially those relying on suspensions, since adsorbed polymer alters the interparticle forces, which largely govern the suspension's properties.[1,2] The technological importance of the adsorption/desorption process has generated interest in understanding the details in model systems.

A number of reports have been published on the adsorption of polystyrene onto model surfaces with weak or moderate segmental sticking energies such as metals, silica, glass, and mica.[3−7] For these systems, a phenomenological understanding of how coverage and thickness develop on a clean solid surface has resulted. These studies indicate that unusually long time scales (days) are needed for adsorbed layers to fully equilibrate. Further, adsorption appears to be nearly irreversible insofar as desorption kinetics into pure solvent are imperceptibly slow. At present, there is no clear molecular-level understanding of these long time scale dynamic features in adsorbed layers.

In this communication, the response of a partially formed adsorbed layer to desorption conditions is followed by a fluorescence label technique. All experiments described herein were performed on a silica−polystyrene system using a hydrated porous silica. Polystyrene labeled with fluorescent active groups is first adsorbed from a good solvent, and we follow the changes in spectral features of the fluorophore as a function of time after exchanging the bulk phase with a pure solvent. Our results show that the adsorbed layer responds dramatically to replacement of bulk polymer solution with pure solvent, though there is no perceptible desorption. Systematic trends in the response are found with changes in the pure solvent and with the layer's preparation history. A complete, systematic study of these effects should lead to a clearer molecular-level view of adsorbed layer dynamics, especially the very long time scale features.

Experimental Procedure. Fluorescence labeling of polystyrene (PS) (molecular weight 45 730, PD = 1.05) was achieved by the aminomethylation method.[8] The functionalization of PS throughout the course of reactions was characterized and confirmed by both IR and NMR. The total conversion to the amine derivative was confirmed by the absence of phthalimide peaks in the aromatic region of the NMR spectra. Pyrenebutyric acid was converted to its acid chloride with thionyl chloride, and the acid chloride was reacted with the amine derivative in the presence of triethylamine to attach the fluorophore. NMR and UV were used to determine the average number of pyrene groups in a chain. The labeling density of PS was 1 pyrene/300 monomer units. (~1.6 labels per chain).

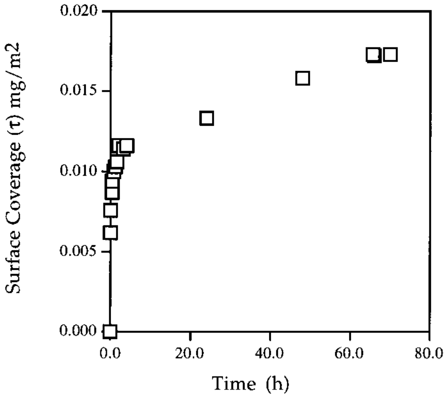

Figure 1. Adsorption kinetics for PS(45.7K) from a 1g/L solution in chloroform. Coverage was determined by depletion of the polymer from the bulk using UV spectroscopy.

In a typical experiment, silica (nominal surface area = 272 m^2/g, pore size = 57 Å, obtained as a gift from Dr. Walter Mahler of Dupont) was first dried at room temperature in a vacuum oven overnight (1 Torr) and then stored in a desiccator until use. No special precautions were taken to exclude moisture from the substrate during subsequent procedures. Consequently, the surface has a layer of physisorbed water. A known amount of silica (~300 mg) was transferred to a flask containing 2 mL of pure chloroform ($CHCl_3$). The solvent was allowed to fully wet the adsorbate by agitating it in a mechanical agitator overnight. A volume of polymer solution at a known concentration was then added, and the adsorption was allowed to proceed on a mechanical agitator for a fixed time at ambient temperature. The solution was then decanted, and the silica washed 3 times with pure $CHCl_3$ on the agitator. "Desorption" of the adsorbed layer was then carried out by transferring the washed solid to a cuvette and adding pure solvent. The steady-state emission spectra of the labeled polymer on the quiescent silica suspension were then recorded as a function of desorption time using a SPEX Fluorolog (DM1680B) in front-face mode. The spectra were obtained by exciting at 332 nm and collecting between 360 and 600 nm. The excimer to monomer intensity ratios are reported by taking the ratio of the peak heights at 480 and 380 nm, respectively. In every case, there was no detectable fluorescence signal in the supernatant solvent, indicating no measurable desorption into the bulk after exchange.

Results and Discussion. An adsorbed layer is first formed by contacting the clean solid with PS in $CHCl_3$ solution. Subsequently, the bulk is exchanged with pure solvent; we refer to this step as desorption hereafter, although no measurable desorption occurs. The initial structure of the adsorbed layer was varied by varying the adsorbing conditions. Figure 1 shows the kinetics of adsorption of the labeled PS onto the substrate from a 1 g/L solution in $CHCl_3$.[9] Clearly, a layer obtained by adsorbing in a 1 g/L PS/$CHCl_3$ solution for 15 min differs from one obtained by adsorbing for 1 or 20 h.

Figure 2 shows the emission spectra obtained at different time intervals during "desorption" in $CHCl_3$ of an adsorbed layer formed from a 1 g/L solution for 0.5 h. An obvious feature of these spectra is the relative increase in excimer emission intensity with time. It has to be noted here that a 1 g/L solution of this polymer in $CHCl_3$ shows very little excimer. Clearly, the concentration of the fluorophore is higher in the adsorbed layer than in the bulk polymer solution, favoring excimer

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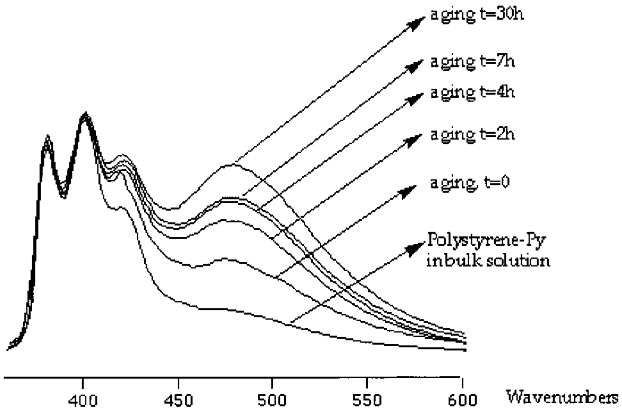

Figure 2. Typical fluorescence spectra of an adsorbed PS layer desorbing in chloroform which shows an increase in the excimer emission with desorption time. The spectra are normalized by the monomer emission peak height.

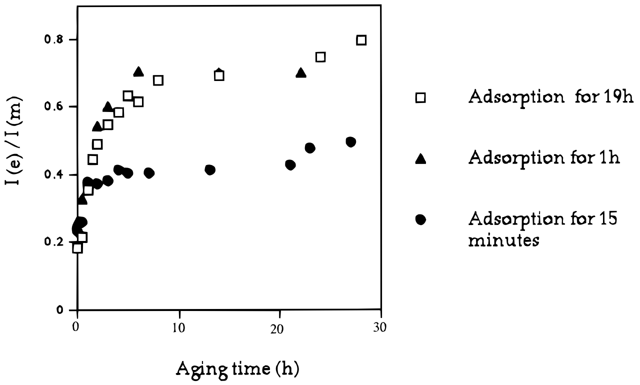

Figure 3. Plot of the changes in the excimer to monomer ratios for a series of adsorbed layers incubated for different time intervals and desorbed in chloroform. The adsorption was done from a 1g/L solution of pyrene-labeled PS in chloroform.

formation. Furthermore, the supernatant in contact with silica after addition of pure solvent did not show any fluorescence. This indicates that desorption has not occurred, and the changes in the spectral features reflect the changes in the adsorbed layer during contact with pure $CHCl_3$. We note that a similar observation was made in another study.[12]

The excimer to monomer ratio for layers prepared with different adsorption times in a 1 g/L PS/$CHCl_3$ solution is plotted as a function of desorption time in $CHCl_3$ in Figure 3. The adsorption time for preparation of the layer was varied from 15 min to 19 h. The general trend in all three plots is the same. There is an initial rapid increase in the excimer to monomer ratio (I_e/I_m) which eventually reaches a plateau after some characteristic time. There are two basic features of the plot which deserve comment.

First, the plateau of (I_e/I_m) for each depends on the conditions under which the layer was formed. In this case, more polymer is adsorbed for longer adsorption times, suggesting that the higher ultimate excimer to monomer ratios for samples adsorbed longer reflect the higher average fluorophore content in those layers. This is reinforced by the fact that there is a larger difference in the plateau ratios of I_e/I_m between layers incubated for 15 min and 1 h than between the 1 and 19 h samples, while the adsorption kinetics (Figure 1) show large changes in the coverage within the first hour, with subsequent changes in the coverage being much less. One is tempted to guess that the plateau value of I_e/I_m depends only on the coverage achieved during incubation. Secondly, a layer built out of short adsorption times (15 min) reaches the plateau faster than one obtained after extended adsorption. A similar behavior has been observed by Granick *et al.* in exchange experiments involving polystyrene and deuteriopolystyrene on silicon oxide surfaces.[6] These authors measured a time constant to exchange, which increases exponentially with aging time. This clearly indicates greater difficulty after longer aging times in restructuring a preformed layer during a subsequent perturbation.

Similar trends were observed by changing the chemical potential driving force during the adsorption step. Desorption kinetics were monitored after adsorbing from 0.1 and 1 g/L solutions of $CHCl_3$ for 1 h. Both samples exhibited an initial increase in the excimer to monomer ratio, after which the ratio reached a plateau. However, the final plateau value was far less for adsorption in a 0.1 g/L solution than in a 1 g/L solution. Although we cannot precisely define the structural differences in the preformed adsorbed layers for this case at present, it is probable that the higher driving force results in a greater coverage after a fixed adsorption time, which should give a higher ultimate excimer to monomer ratio during "desorption".

The simplest molecular-level interpretation is that increasing I_e/I_m corresponds to increasing the (average) segmental mobility in the preformed layer, which is facilitated by the detachment of bound segments. Figure 4 schematizes this mechanism. To explore whether this is true, we "desorbed" layers built from PS in $CHCl_3$ in several other solvents. Two parameters will control the response in this situation: the segmental sticking energy $\chi(s)$ and the bulk solvent/segment interaction parameter χ. Values of $\chi(s)$ or χ for the desorbing solvent lower than for chloroform should favor detachment of bound segments and enhance I_e/I_m relative to the response in pure $CHCl_3$. In Figure 5, the excimer to monomer ratios are plotted as a function of desorbing time for desorption in $CHCl_3$, methanol, and toluene.[13] Note that for methanol, a nonsolvent for PS, there is hardly any change in I_e/I_m relative to the result for $CHCl_3$. Surprisingly, toluene, a good solvent for polystyrene, reduces the amount of excimer during desorption to well below that in methanol, a nonsolvent. When the layer is desorbed in 10% methanol−toluene mixture, a higher excimer to monomer ratio is obtained than when desorbed in pure toluene. The implication is that the adsorbed layer's segmental mobility is enhanced during "desorption", the most in chloroform, followed by methanol and then toluene.

These solvent effects can be explained by considering the relative interaction parameters of the polystyrene−silica−solvent systems. Table 1 collects these for the PS/silica/solvent systems of interest. Methanol has a very high value of $\chi = 1.5$, making it a nonsolvent for PS. This χ value exceeds chloroform's (0.08), which favors collapse of initially adsorbed chains, resulting in decreased mobility of the pyrene segments and low excimer formation. On the other hand, $\chi(s)$ for the PS/silica/MeOH system ($=-9.3$) is quite unfavorable compared to PS/silica/chloroform ($=-0.03$), which should have the opposite effect; i.e., methanol should displace bound segments, enhancing mobility and therefore excimer formation. The net effect is, evidently, a cancellation and almost no change in I_e/I_m upon exposure to methanol.

In the case of toluene, a similar argument holds. The χ parameter for toluene slightly exceeds that for chlo-

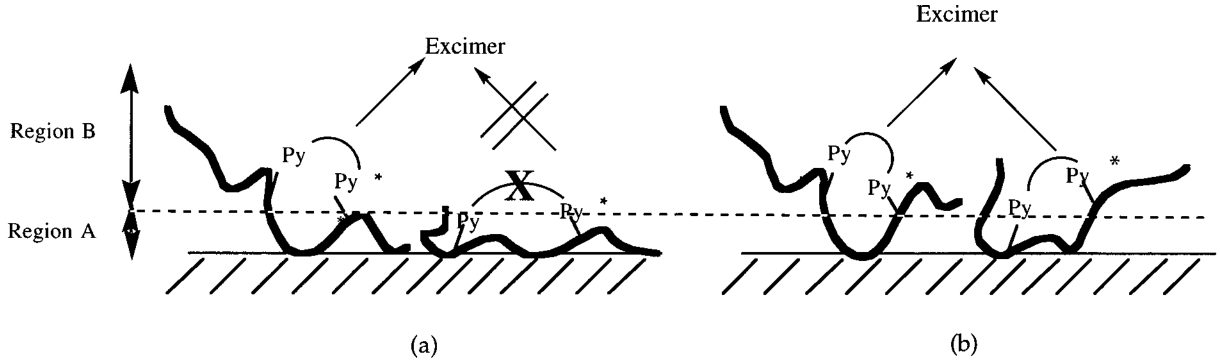

Figure 4. Schematic of molecular events associated with increased I_e/I_m. Region A consists mainly of trains and short loops and has a high fraction of immobile segments, inhibiting excimer formation. Region B consists mainly of long loops and tails and contains a high fraction of mobile segments. (a) Is favored with higher χ and χ(s) values, while (b) is favored with lower χ and χ(s) values. Increased I_e/I_m corresponds to conversion of segments from region A to region B via detachment of bound segments (a to b).

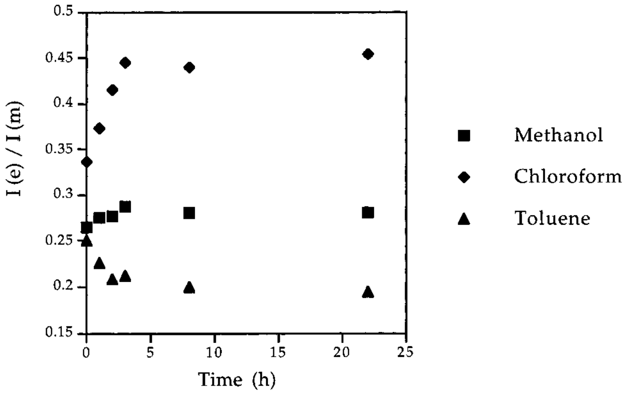

Figure 5. Plot of change in the excimer to monomer ratio as a function of aging time for aging in three different solvents. Adsorption was done from a 0.1 g/L solution of chloroform for 1 h.

Table 1. Interaction Parameters for PS/Silica/Solvent Systems

solvent	interaction parameter (χ)[a]	surface interaction parameter [χ(s)][b]
methanol	1.5	−9.321
chloroform	0.085	−0.0352
toluene	0.268	−0.3133

[a] Reference 12. [b] Reference 15.

roform, suggesting that a weak compaction of the layer might occur. However, the difference in χ(s) between toluene and chloroform is relatively small, and hence there is only a weak energetic driving force for displacement of bound segments. It is therefore not surprising to find I_e/I_m less than for methanol in this case.

Chloroform appears to be an energetically special case, being a very good solvent for PS ($\chi = 0.085$) and causing a very weak segmental−surface interaction for PS/silica. According to data in ref 11, the segmental sticking energy is marginally unfavorable in this case (see Table 1), but our adsorption data suggest χ(s) is, in fact, marginally favorable for the silica employed in this study. The special energetics enable us to monitor the molecular-scale processes during desorption on convenient time scales.

Conclusion. These preliminary studies show the possibility of systematically studying the dynamic response of adsorbed layers to osmotic perturbations. A critical piece of information for the success of such studies is to determine the molecular-level significance of increases in I_e/I_m during desorption. This work suggests that increases in I_e/I_m corresponds to enhanced chromophore mobility in the adsorbed layer facilitated by the displacement of pinned segments by solvent, which permits excimer formation by diffusive encounters. Establishing the validity of this picture, and exploiting it in a systematic study of adsorbed layer dynamics, is the subject of current work.

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(9) The adsorption kinetics were measured by the depletion method using UV spectroscopy. The coverages reported are lower by 1−2 orders than the typical values of τ (mg/m^2) reported for PS on SiO_2[4,6,7] or metals[5] from either good or poor solvents. The two main reasons for this are as follows: (a) We used porous silica with a characteristic pore size on the order of the coil dimensions, in which confinement is known to suppress coverage relative to nonporous material.[10] (b) Adsorption was done from chloroform, which has been classified as a displacer in other studies.[11] We, however, do find significant adsorption of PS from chloroform onto silica, indicating marginally favorable energetics, which may contribute to the low coverages observed.
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(13) Toluene and methanol are displacers according to ref 11. Although we did not measure significant desorption into the quiescent supernatant for either of these solvents on the time scales of observation, PS does desorb from silica on longer time scales under agitation, consistent with ref 11.
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