Photodegradation of Pyrene-Labeled Polystyrene Adsorbed on Silica Surface in Chloroform

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Adsorption of polymers onto particles has been a subject of study because of its importance in the behavior of suspensions.[1,2] To understand the adsorption/desorption process in detail, studies have been carried out with model systems. Some studies have employed polystyrene (PS) adsorbed onto metals, silica, glass, and mica.[3−7] In previous work, we reported on the use of pyrene-labeled PS to study the dynamics of the rearrangement of adsorbed PS after exposing the PS adsorbed on a silica surface to desorption conditions, i.e., after replacing the bulk solution containing unabsorbed PS with pure solvent.[8]

Pyrene has been used widely in the literature as a probe of structure and dynamics in macromolecular systems.[9−11] From the fluorescence emission properties of pyrene labels, such as the I_3/I_1 ratio, the excimer-to-monomer ratio (I_e/I_m), and fluorescence polarization value, one obtains information about the conformation, mobility, and dielectric environment of the pyrene probe within the macromolecule being studied. In this note, we report on the photodegradation of the pyrene labels on PS in chloroform ($CHCl_3$) and adsorbed on silica surface contacting with $CHCl_3$ caused by excitation light under conditions typical for photophysical studies of polymers. We feel this effect should be brought to the attention of the community because of the common use of pyrene as a probe.[12,13]

As published in a previous paper,[8] after the adsorption of labeled PS onto a silica surface has proceeded for a predetermined time in dilute PS/$CHCl_3$ solution, replacing the bulk polymer solution with pure solvent $CHCl_3$ causes a progressive relative increase in excimer emission intensity with time, i.e., an increase in I_e/I_m ratio over time. In this work, we observe that the increase in I_e/I_m ratio was dependent on the total exposure time of the sample to the excitation light in the fluorescence spectrometer.

The synthesis and characterization of the pyrene-labeled PS were reported previously.[8] The polymer used has a molecular weight of 50K and label density of 15 pyrene labels per chain. Porous silica samples were obtained as gifts from Dupont and had average pore sizes of 57 or 122 Å. Solvent $CHCl_3$ was distilled before use.

The preparation of adsorbed, pyrene-labeled PS layers on silica was described before.[8] The bulk polymer concentration for adsorption was 0.1 g/L in $CHCl_3$. After adsorption for a certain time, the bulk polymer solution was replaced with pure $CHCl_3$ by rinsing the solid and transferring it quickly into a fluorescence cell with a 2 mm path length containing pure $CHCl_3$.

The fluorescence emission and excitation spectra were taken on a SPEX Fluorolog 1680 0.22 m double spectrometer with a 450 W xenon lamp using front face excitation. The excitation light beam was directed onto the polymer/silica sediment pack, not the supernatant.

First, the effect of the excitation light on the pyrene labels of the polymer adsorbed on a porous silica was investigated. Typical excitation spectra obtained with successive scans are shown in Figure 1. The excitation spectrum monitored at 480 nm (maximum emission wavelength for pyrene excimer) has several broad unexpected bands in the range 350−450 nm when compared to other reports.[13] It is well-known that the excitation spectra of the preassociated pyrene molecules have similar vibrational structure as the pyrene monomer excitation spectra but are 1−4 nm red-shifted.[13] The observed bands do not correspond to a static excimer of pyrene, which is expected when pyrene molecules are preassociated in the ground state. It was speculated that these bands were caused by other species that emit in the same spectral region as the pyrene excimer. At this point, we decided to investigate whether photodegradation products formed during the spectral collection process while the sample was being irradiated in the sample chamber of the fluorescence spectrometer was the cause of the observation.

On the basis of this hypothesis, it was found that the intensity of the excitation spectra of pyrene labels changed dramatically with cumulative exposure to the instrument excitation light under conditions typical for photophysical studies. The typical observation is that intensities in the monomer excitation spectra decrease with the number of scans taken, while that in the excitation spectra monitored at the excimer emission wavelength increase dramatically, especially in the region of 350−450 nm. These changes could be caused by rearrangement of polymer chains on the surface upon exposure to pure solvent, as suggested earlier, or by photodegradation in the instrument as suggested here. To determine which mechanism was operating, an adsorbed layer of labeled PS on silica was prepared at conditions similar to that described in ref 8 and exposed to solvent for 2 days in complete absence of light, and then its fluorescence excitation spectra were acquired. This sample showed changes in its fluorescence excitation spectra similar to those shown Figure 1 which were taken within minutes after sample preparation. Since, after 2 days under desorption conditions, chain rearrangements should have reached an equilibrium, photodegradation of labels is strongly suspected as the cause of spectrum changes rather than conformational changes for which the labels maintain their chemical integrity. Similar spectral and intensity changes were observed for all the silica samples used in ref 8 and for three other pyrene-labeled PS with different molecular weight and different labeling densities.[14]

For comparison, we tested pyrene-labeled PS in $CHCl_3$ solution under the same conditions in the fluorescence instrument with the results shown in Figure 2. In the fluorescence emission spectra with excitation at 330 nm, multiple scans caused an intensity decrease

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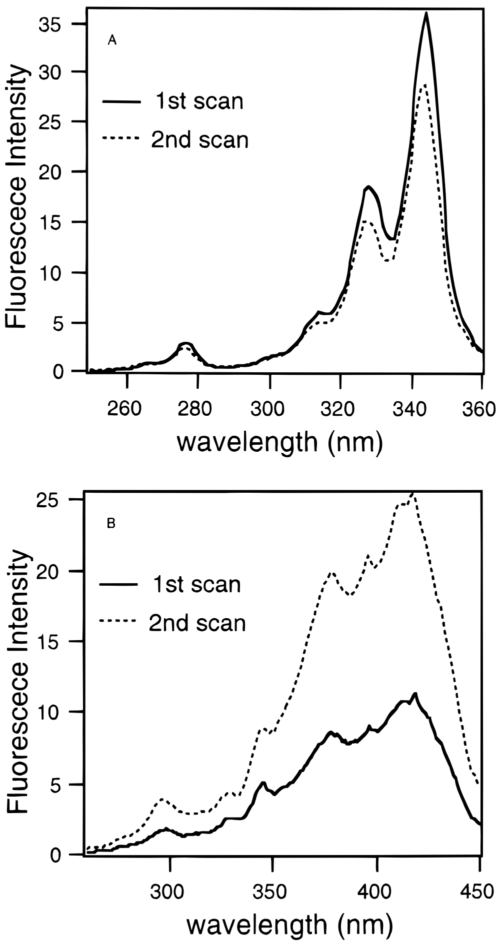

Figure 1. Typical excitation spectra of pyrene-labeled PS adsorbed on porous silica monitored at 375 nm (A) and 480 nm (B). The sample was prepared with 9 h adsorption time and on a silica with an average pore size of 122 Å.

over the whole spectral range, and the degree of decrease was dependent on the number of scans. After the emission measurements, the solution's UV−vis spectrum showed an intensity decrease between 250 and 350 nm and a new tail appearing around 350−450 nm. Also, the intensity of its excitation spectra monitored at the excimer emission maximum (480 nm) decreased in the 250−350 nm range, but there were new, broad bands appearing in the 350−450 nm region. All of these results are consistent with photodegradation of the pyrene labels under the excitation conditions typical for photophysical measurements.

If photodegradation is the cause of the spectral changes observed, minimizing the excitation intensity should reduce or eliminate the effect since the rate of degradation should be directly proportional to the light intensity at a fixed optical density of the sample. Neutral density filters were used to adjust the intensity to lower values. By cutting off 90% of the intensity from the excitation light, the emission intensity of the pyrene-labeled PS solution was stable for 20 min under continuous excitation in the instrument. Under these conditions, the intensity changes of the broad bands in the excitation spectrum of PS on silica monitored at 480 nm were greatly reduced, although their initial intensity was still significant, which suggested that there was already photodegradation present before the fluorescence measurement, possibly during the sample preparation process.

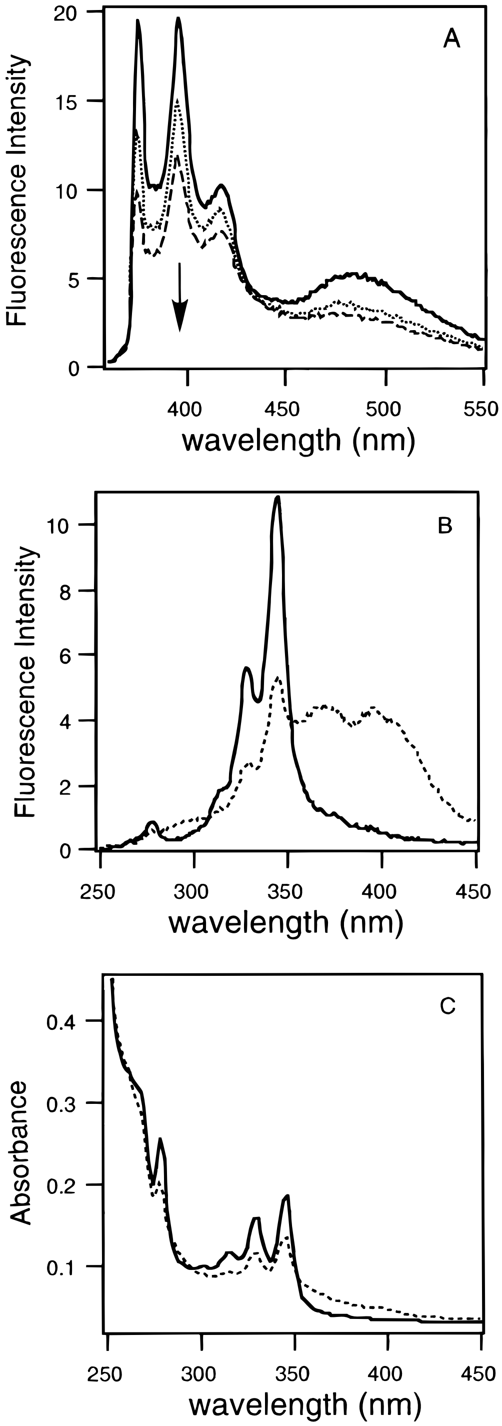

Figure 2. Effect of excitation light on 0.1 g/L pyrene-labeled PS in $CHCl_3$ solution. (A) Fluorescence emission spectra of the 1st (—), 100th (• • •), and 200th scan (- - -). Spectra were taken every 5 min with excitation wavelength of 330 nm. (B) Fluorescence excitation spectra monitored at 480 nm taken before (solid line) and after (broken line) emission measurements. (C) UV absorption spectra taken before (solid line) and after (broken line) emission measurements.

Further, experiments were performed to check whether ambient light had any effect on pyrene labels during sample preparation process (cf. in Figure 3). A sample prepared in dark during the adsorption process gave two superimposable excitation spectra monitored at 375 and 480 nm, which indicated that only dynamic excimers of pyrene were present. For a sample exposed to ambient light during the adsorption process, the 350−450 nm

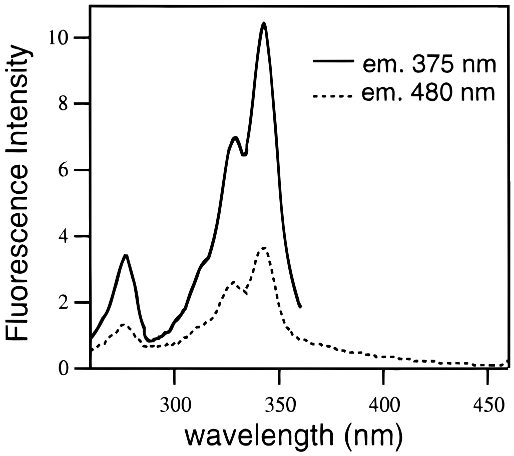

Figure 3. Excitation spectra of pyrene-labeled PS adsorbed on porous silica monitored at 375 nm (solid line) and 480 nm (broken line). The sample was prepared with 2 days adsorption time in the dark and on a silica with an average pore size of 139 Å.

region bands were still observed, indicating that even exposure to ambient light was sufficient to cause measurable decomposition of pyrene labels on PS.

Under conditions of dark preparation and minimal excitation light intensity, the intensity of emission and excitation spectra of adsorbed layers under desorption conditions did not change significantly within 2 days. Thus, the changes in I_e/I_m ratio under desorption conditions that were reported previously[8] are suspected to be an artifact caused by photodegradation.

Last, studies were conducted on the effect of excitation light on pyrene and pyrene-labeled PS in chloroform and benzene solution to examine the source of the degradation in solution. The same evidence of photodegradation was observed for pyrene in $CHCl_3$ as was seen for pyrene-labeled PS in $CHCl_3$. However, in benzene, the photodegradation was evidently insignificant for both pyrene and pyrene-labeled PS. These results indicate that the photodegradation in solution is associated with the combination of pyrene and $CHCl_3$ and probably has little to do with the presence of the polymer. In a previous study of pyrene photodecomposition products in $CHCl_3$, it was suggested that under UV excitation pyrenecarboxaldehydes were formed through reaction of excited singlet state pyrene and $CHCl_3$ with the assistance of oxygen and a trace amount of water.[15]

Larger intensity changes in the excitation spectra monitored at 480 nm occur for polymer adsorbed on silica compared to that in solution (cf. Figure 1b and Figure 2b). We attribute this phenomenon mainly to the different diffusion abilities of pyrene labels in solution relative to those adsorbed on silica surface. In solution, pyrene labels can diffuse with the polymer chain so the degradation products are diluted over the entire solution. On silica, the pyrene labels cannot diffuse away from the light excitation spot because they are partially immobilized on silica through the adsorbed polymer chain. Thus, the fluorescence spectra correspond to the accumulating degradation products in the area of excitation. On the other hand, as demonstrated by Thomas and co-workers, the silica surface could cause photodecomposition of adsorbed pyrene through photoinduced electron transfer reaction between pyrene and silica surface to produce mainly hydroxypyrenes.[16-18] Although this type of silica-mediated pyrene photodecomposition has not been reported for systems under fluorescence instrument excitation and ambient light, we cannot exclude the possibility that additional photodegradation pathways involving the silica surface are present in our system.

In conclusion, the excitation light from a typical fluorescence spectrometer causes photodegradation of pyrene and pyrene-labeled PS in $CHCl_3$ solution and adsorbed on a silica surface contacting with $CHCl_3$. Although it is not clear which intermediates are involved in the photodegradation and what the photodegradation products are, caution should be taken when working with a system involving both pyrene and chloroform.

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