Surface Reorganization of an Amphiphilic Block Copolymer Film Studied by NEXAFS Spectroscopy

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ABSTRACT: The chemical composition of the surface of an amphiphilic diblock copolymer film, comprised of polystyrene and poly(4-(2-(2-(2-acetoxy)ethoxy)ethoxy)styrene), has been characterized upon equilibration in water and in a vacuum, employing surface sensitive near-edge X-ray absorption fine structure spectroscopy. The outermost surface layer exhibits a reversible exchange between the hydrophilic and hydrophobic polymer segments as the equilibrating interface is changed between water and vacuum, respectively. Surprisingly, time-dependent measurements show that a substantial partial molecular reorganization toward a vacuum-equilibrated surface occurs already at 60 °C, which is significantly below the glass transition temperature of the polystyrene block.

Introduction

Surfaces of block copolymers are of significant scientific and technological interest due to the tunability of their properties, which is critically important for the manifold applications of block copolymers such as adhesives, membranes, composite materials, biomaterials, and drug delivery systems, to name a few.[1−3] Consequently, block copolymer surfaces have been intensively studied with a wide spectrum of experimental techniques including contact angle measurements,[4,5] X-ray photoelectron spectroscopy (XPS),[5,6] attenuated total reflectance Fourier transform infrared spectroscopy (ATR−FTIR),[7,8] static secondary-ion mass spectrometry (static-SIMS),[9] high-resolution electron energy loss spectroscopy (HREELS),[10] transmission electron microscopy (TEM),[11,12] and X-ray absorption spectroscopy.[13,14] All these studies confirm the intuitive picture that under dry conditions the more hydrophobic segments with a lower surface energy are enriched in the outermost surface region of the block copolymer films. When the surface is exposed to water, a reorganization of the molecular groups at the surface occurs to reduce the free energy of the new water−polymer interface by placing the more hydrophilic polymer segments in contact with water. In the following we refer to this exchange of molecular groups as "surface reorganization" of copolymer films.

The surface composition of some block copolymers has been investigated upon exposure to air (or vacuum) and water environments as summarized, for example, in ref 15. However, little is known about the detailed reorganization process of block copolymers. This may partly be caused by the limited sensitivity to surface composition of most experimental techniques employed so far. To monitor in detail the reorganization process, the experimental technique should be capable of measuring directly and quickly small changes of the surface composition without interfering with the reorganization process itself. High-resolution carbon K-edge X-ray absorption spectroscopy resolving the near-edge X-ray absorption fine structure (NEXAFS)[16] is a powerful, well-established technique for characterizing the chemical composition of polymer films and their surfaces. For example, this technique has successfully been applied to study relaxation dynamics occurring at surfaces and in the bulk of polymer films.[17−20] We have applied NEXAFS spectroscopy to characterize the surface composition of an amphiphilic block copolymer film after equilibration in water and a vacuum and to follow the surface reorganization in real time. Our results demonstrate that NEXAFS spectroscopy allows an unprecedented insight in the surface reorganization process of amphiphilic block copolymers.

Experimental Section

Materials. Poly(styrene-*block*-4-(2-(2-(2-acetoxy)ethoxy)ethoxy)styrene) (PS-*b*-PAEES) and poly(4-(2-(2-(2-acetoxy)ethoxy)ethoxy)styrene) (PAEES) were synthesized by TEMPO-based controlled radical polymerization, and the reaction details have been published elsewhere.[21] The polymers were characterized by NMR and gel permeation chromatography (GPC) as described previously.[21] Polystyrene was commercially available (Aldrich) and used as received. Milli-Q water (18.2 MΩ cm) was used throughout all water equilibration processes.

Sample Preparation. Spin-coating from a 10 mg/mL THF solution onto silicon wafers (1 cm × 1 cm) resulted in thin films of ∼100 nm thickness after annealing at 150 °C for 14 h in a vacuum. To prepare a film surface equilibrated with water, the polymer films were immersed in 70 °C[22] water for 8 h and subsequently cooled to room temperature while remaining in water. NEXAFS spectra were then recorded within 10 min after transferring the samples from water into the ultrahigh vacuum of the experimental chamber.

Near-Edge X-ray Absorption Fine Structure (NEXAFS). The NEXAFS measurements were performed at the high-resolution soft X-ray beamline 10-1 of the Stanford Synchrotron Radiation Laboratory. Carbon K-edge absorption spectra were recorded with an energy resolution of 50 meV in the magic angle geometry (which suppresses sensitivity to molecular orientation) using the surface-

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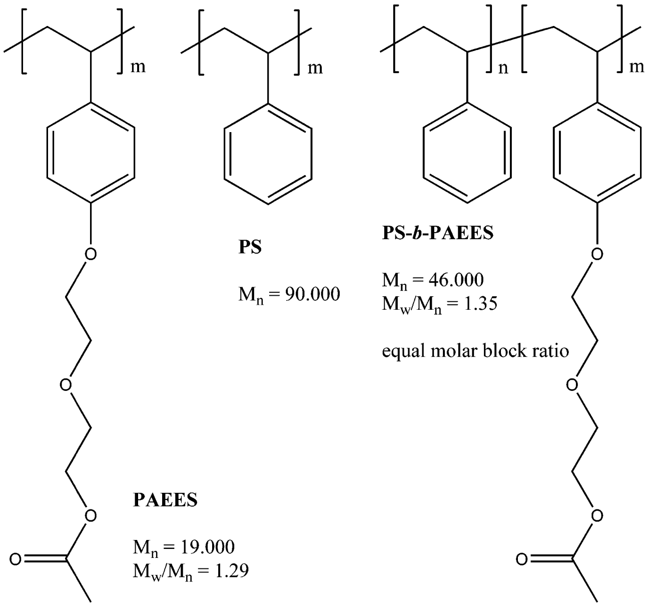
Scheme 1



sensitive Auger electron yield (AEY) detection mode.[16] In this yield method the number of (only elastically scattered) Auger electrons escaping from the sample surface is monitored. Since the 1/e mean free path length of carbon K-shell Auger electrons for typical polymer materials is only on the order of 1 nm,[23] the AEY is in excellent approximation proportional to the absorption coefficient of the outermost surface layer. All NEXAFS spectra are normalized to a common edge jump and thus correspond to absorption intensity per average carbon atom as discussed elsewhere.[16]

Results and Discussion

In this study, we have investigated a novel amphiphilic block copolymer, poly(styrene-*block*-4-(2-(2-(2-acetoxy)ethoxy)ethoxy)-styrene) (PS-*b*-PAEES), and its respective homopolymers, PS and PAEES. This block copolymer (M_n = 46 000, M_w/M_n = 1.35, equal molar block ratio), schematically drawn in Scheme 1, is ideally suited for investigating the surface reorganization due to the strong hydrophilic and hydrophobic character of the PAEES and PS blocks, respectively. Hence, the PAEES blocks are expected to segregate to the interface when the film surface is in contact with water, while an air or vacuum contact should enrich the interface with PS blocks. Moreover, PAEES exhibits a glass transition temperature T_g of −3 °C, while PS's T_g is around 100 °C, thereby practically freezing the overall copolymer structure under ambient condition. For the PS-*b*-PAEES block copolymer two distinct glass transition temperatures are found, thus indicating phase separation. Furthermore, the PS and the PAEES blocks exhibit very distinct NEXAFS spectra as shown below.

Various thin polymer films on silicon substrates have been investigated by NEXAFS. For organic molecules, the fine structure of the C K-edge absorption spectrum results from excitation of the 1s core electrons of the various carbon atoms into the unoccupied π^* and σ^* orbitals of their respective molecular bonds. Intensity differences in these normalized AEY spectra, recorded in the magic angle geometry, therefore indicate differences in the chemical composition of the sampled film surface layer. Hence, NEXAFS spectroscopy can yield quantitative information about the chemical composition of a block copolymer surface, provided that the different segments of a block copolymer can be differentiated by their NEXAFS spectra.

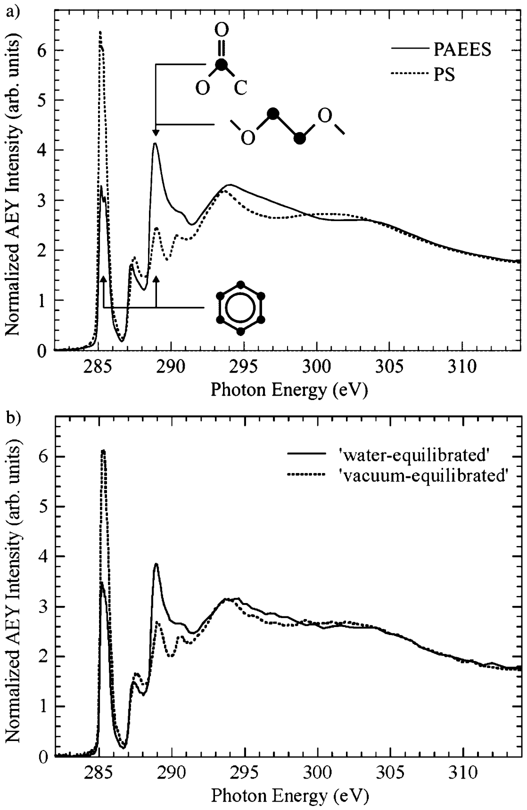


Figure 1. (a) Normalized Auger electron yield carbon K-edge NEXAFS spectra of poly(4-(2-(2-(2-acetoxy)ethoxy)ethoxy)styrene) ("PAEES", solid line) and polystyrene ("PS", dotted line), recorded at room temperature with the X-ray incidence angle matching the magic angle geometry.[16] The resonance at 285.2 eV originates from excitation of 1s electrons of the phenyl ring carbon atoms (filled circles) into the first unoccupied phenyl π^* orbital. A second phenyl π^* orbital gives rise to the weaker resonance at 289.0 eV. Superimposed to this, one finds for PAEES a strong resonance corresponding to the excitation of carbon 1s electrons into σ^* orbitals of the C−O and π^* orbitals of the C═O double bonds of the hydrophilic side chains from the carbon atoms. (b) Normalized Auger electron yield NEXAFS spectra of the PS-*b*-PAEES block copolymer after equilibration in water by immersing in 70 °C water for 8 h ("water-equilibrated", solid line) and after subsequent reequilibration by annealing in a vacuum at 120 °C for 2 h ("vacuum-equilibrated", dotted line), both recorded at room temperature with the magic angle X-ray incidence.

All thin polymer films have been equilibrated before NEXAFS measurements. For simplicity, we refer to the polymer film equilibrated in water at 70 °C for 8 h as "water-equilibrated", while the film equilibrated in a vacuum by annealing at 120 °C for 2 h is referred to as "vacuum-equilibrated".

The near-edge region of the normalized AEY carbon K-edge absorption spectra of the two homopolymers, polystyrene (PS) and poly(4-(2-(2-(2-acetoxy)ethoxy)ethoxy)styrene) (PAEES), are shown in Figure 1a. The assignment of the pronounced peaks to excitation of carbon 1s core electrons into particular molecular orbitals, denoted in this figure, is taken from the literature.[16,20] Since the backbone of PAEES is identical to that of PS, the two spectra share certain common features, while the differences arise from the additional contributions of the hydrophilic side groups of PAEES, especially the C−O and C═O bonds.[24] For example, the absorption at 285.2 eV corresponding to excitation of carbon 1s core electrons into unfilled π^* orbitals of the phenyl rings is much less pronounced in PAEES than in PS, since in comparison to PS the homopolymer PAEES has a significantly smaller fraction of carbon atoms in the phenyl rings. On the other hand, the absorption peak at 289.0 eV is stronger for PAEES, since the excitations to σ^* orbitals of C−O and π^* orbitals of C═O bonds of the hydrophilic side groups make

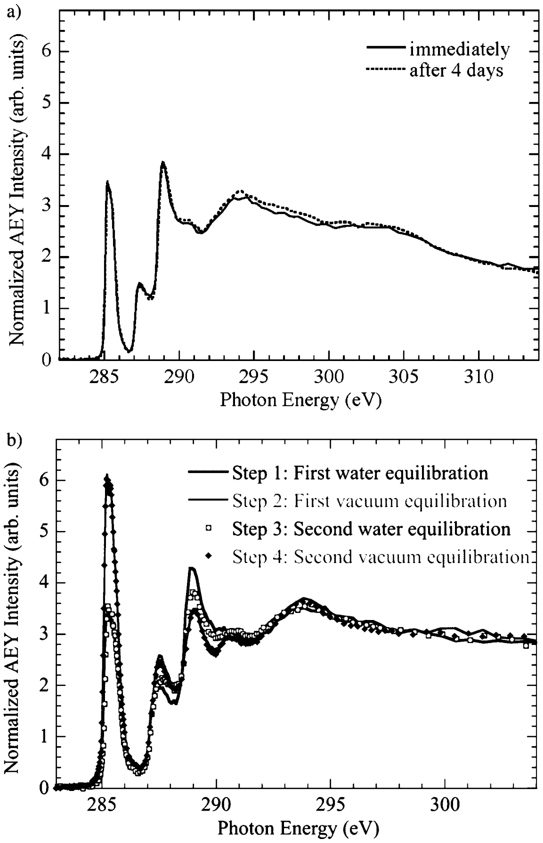


Figure 2. (a) Carbon K-edge NEXAFS spectra recorded on the "water-equilibrated" copolymer film immediately after transfer into the vacuum chamber (solid line) and after storing the sample in a vacuum at room temperature for 4 days (dashed line). (b) The carbon K-edge NEXAFS spectrum recorded after consecutive water equilibration and vacuum equilibration cycles of the copolymer film. The NEXAFS spectra recorded after the second equilibration steps show that the surface is again enriched with the respective segments of the diblock copolymer.

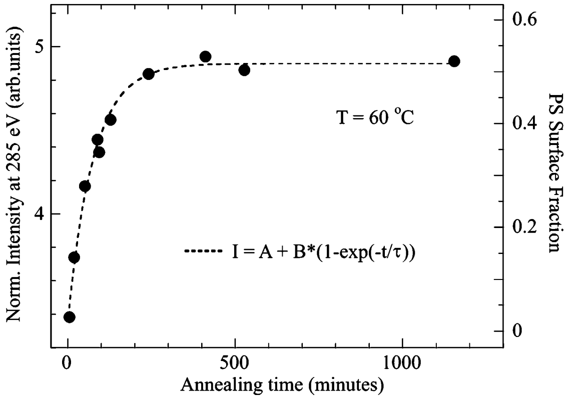


Figure 3. In-situ characterization of the surface reorganization while annealing the copolymer film at 60 °C. Plotted versus the annealing time is the intensity of the phenyl ring π^* resonance at 285.2 eV, which is proportional to the relative concentration of PS segments within the outermost surface layer.

much stronger contribution to this peak than the second π^* resonance of the phenyl carbon atoms.

The large differences between the two spectra demonstrate that the two segments of the PS-*b*-PAEES block copolymer can be well differentiated by NEXAFS spectroscopy, allowing the analysis of the chemical composition of the block copolymer film surface and its variation. This is indeed demonstrated by the two carbon K-edge absorption spectra shown in Figure 1b, where the solid line labeled "water-equilibrated" represents the NEXAFS spectrum recorded after the block copolymer film has been immersed in 70 °C water for 8 h, as described above. The close match of the NEXAFS spectrum of this water-equilibrated surface to that of the PAEES homopolymer is compelling, showing that the outermost surface layer of the water-equilibrated copolymer film is dominated by hydrophilic PAEES segments. This clearly confirms the intuitively expected enrichment of the copolymer surface with the hydrophilic PAEES blocks in water, preferentially placing the C−O and C═O moieties at the film surface.

To analyze the room temperature stability of the film surface enrichment with hydrophilic PAEES blocks, a water-equilibrated film was kept in a vacuum for 4 days. The NEXAFS spectrum recorded after 4 days (Figure 2a, dashed line) is essentially identical to the one recorded right after the sample was inserted into the vacuum chamber (Figure 2a, solid line).The essentially identical pattern of the spectra reveals that no significant changes in the chemical composition have occurred. This indicates that the hydrophilic surface is trapped kinetically by the immobilized PS blocks at room temperature.

However, after annealing the water-equilibrated film in a vacuum for 2 h at 120 °C, i.e., well above the glass transition temperature of PS, the NEXAFS spectrum looks substantially different, as shown by the dotted line in Figure 1b. Overall, the spectrum of this vacuum-equilibrated copolymer film is very close to that of the PS homopolymer. This indicates a nearly complete replacement of the hydrophilic PAEES segments within the outermost film surface by the hydrophobic PS segments. This surface reorganization is completely reversible; a second water equilibration (at 70 °C for 2 h) leads to an enrichment of the film surface with hydrophilic PAEES segments, which are again replaced by hydrophobic PS segments upon annealing in a vacuum at 120 °C This is shown by the spectra in Figure 2b. The slightly lower degree of chemical segregation achieved in this second water equilibration is most likely due to the shorter time the film was immersed in water due to time constraints. Subsequently annealing in a vacuum restores again the PS-enriched copolymer film surface.

To study the dynamics of the surface reorganization process, we have rapidly[25] heated a sample polymer film, which was water-equilibrated (70 °C, 8 h), from room temperature to 60 °C and then recorded a series of consecutive NEXAFS spectra at constant temperature in a vacuum. To avoid artifacts from radiation damage, each spectrum has been recorded on a new sample spot. The time evolution of the chemical composition at the film surface is summarized in Figure 3 where the intensity of the phenyl ring peak at 285.2 eV is plotted as a function of annealing time. From the reference spectra of the homopolymers shown in Figure 1a we know that the normalized intensity of this peak varies linearly with the relative concentration of the PS segments between the values of about 3.3 (pure PAEES) and 6.4 (pure PS). On the basis of these values, we can derive quantitatively from the normalized intensities the surface composition, which are given by the ordinate on the right-hand side of Figure 3. Hence, the initially rapid increase with annealing time indicates a strong segregation of PS segments to the film surface, which levels out after about 400 min. At this state 52% of the surface composition has reorganized from hydrophilic PAEES block segments to hydrophobic PS block segments. The time dependence is well fitted by a simple, empirical exponential function (solid line), which yields a time constant of about $t = 75$ min. It is interesting to note that the surface equilibrium reached at 60 °C has a significantly lower relative PS concentration than the one reached after annealing at 120 °C, i.e., above the glass temperature of the PS block. This observation seems to show that the glass temperature T_g of the PS blocks close to the film surface is substantially lower than the T_g of the bulk PS sample, in accordance with the literature results,[26] and the incomplete reorganization is caused by the increased T_g of the PS blocks further away from the film surface.

Conclusion

In conclusion, we have shown that NEXAFS spectroscopy is ideally suited to measure directly the surface reorganization of an amphiphilic block copolymer film by investigating a novel block copolymer, PS-*b*-PAEES, which is comprised of two polymer segments with a large difference in hydrophilic character. The distinct NEXAFS signatures of the two respective blocks allowed us to reveal the nearly complete and reversible surface reorganization upon equilibration in water and vacuum. By recording consecutive NEXAFS spectra at a constant, elevated temperature, we have been able to follow the time evolution of the surface reorganization process. A surprising finding is that a substantial partial reorganization toward the "vacuum equilibration" takes place at 60 °C, significantly below the glass transition temperature of the PS block ($T_g = 100$ °C). A more detailed investigation of the temperature−time dependence, combining NEXAFS and AFM measurements, is currently under way to better understand the kinetic and morphological aspects of the surface reorganization process of amphiphilic block copolymers.

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