

## Surface Relaxations in Polymers

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**ABSTRACT:** Near-edge X-ray absorption fine structure, NEXAFS, spectroscopy was used to investigate the relaxations of polystyrene, a typical amorphous polymer, near a free surface after the imposition of a small deformation. Using synchrotron radiation, the NEXAFS dichroic ratio was determined for both the Auger and total electron yield processes as a function of temperature to determine the orientation of the polymer in the first 1 and 10 nm from the free surface, respectively. Complete relaxation of the polymer was not seen for temperatures less than the bulk glass transition temperature. No evidence of enhanced mobility at the free surface was found. A planar relaxation of the polymer was found in the first nanometer from the free surface, whereas in the first 10 nm, the dominant relaxation was normal to the surface.

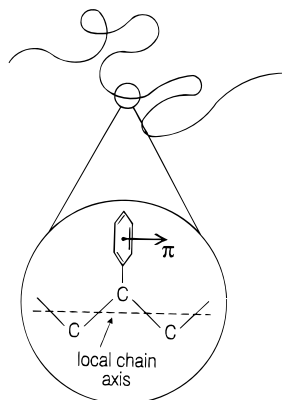
For atomic and molecular solids the breaking of symmetry by a surface strongly influences the fundamental thermodynamic properties of a material, as, for example, the melting point of the solid near a surface.<sup>1–3</sup> Similar issues arise with polymers.<sup>4–8</sup> In the case of amorphous polymers, the mobility of the polymer chains at a surface or interface influences, for example, the initial interdiffusion of two polymers, surface wetting and roughening, and, in general, the interaction of the polymer with other materials. However, the ability to investigate the mobility of polymer chains at surfaces in a direct manner has been lacking. As a consequence, a fundamental question in polymer science has remained unanswered, namely, whether the glass transition temperature,  $T_g$ , or polymer mobility at a free surface is significantly different from that in the bulk. Results from previous studies using different probes have led to different conclusions. Ellipsometric studies on the thermal expansion of polystyrene, PS, films on Si substrates and poly(methyl methacrylate), PMMA, on Au (substrates that do not interact strongly with the polymer) by Keddie et al.<sup>9,10</sup> were interpreted as showing that the  $T_g$  of a polymer surface is much less than that of the bulk. Wu and co-workers,<sup>11,12</sup> on the other hand, used reflectivity methods to measure thermal expansion of PS on silicon oxide and hydrated silicon, found no indication of an increased mobility at the surface, and, in fact, indicated that the mobility at the free surface may be suppressed. Forrest et al.,<sup>13,14</sup> using Brillouin scattering, measured the acoustic properties of PS films as a function of film thickness and reached conclusions similar to those of Keddie et al.<sup>9,10</sup> Positronium annihilation studies of Xie et al.<sup>15</sup> on PS initially

concluded that there was no evidence of increased mobility, but subsequent experiments<sup>16</sup> suggested the presence of a surface layer with enhanced mobility. In an atomic force microscopy study, Kajiyama and co-workers<sup>17,18</sup> concluded that the surface mobility of PS was enhanced only for low molecular weight polymers where the preferential segregation of chain ends to the surface<sup>7</sup> was sufficiently large to enhance the mobility. For higher molecular weight polymers no enhanced mobility at the free surface was found. Meyers et al.,<sup>19</sup> on the other hand, used atomic force microscopy to study the wear of a PS surface and found that the surface behaved more like rubber than like glass. Torkelson and coworkers,<sup>20</sup> using second-harmonic generation, studied poly(isobutyl methacrylate) randomly labeled with a dye and concluded that no change in the mobility was evident. Diffusion studies normal to the surface<sup>21</sup> and parallel to the surface<sup>22</sup> of PS on silicon oxide indicate that the diffusion coefficient is suppressed in thin films and that, if anything, the glass transition temperature in thin films is increased. No indication of an enhancement in the mobility at the free surface was found. Thus, while there are much data in the literature on this subject, the situation is far from clear.

In the present studies the relaxation of PS segments at the free surface as a function of temperature was investigated using near-edge X-ray absorption fine structure, NEXAFS, spectroscopy.<sup>23</sup> By combining the surface sensitivity of NEXAFS and the polarized nature of a synchrotron X-ray beam, it is shown that the relaxation of the polymer within the first nanometer from the free surface is parallel to the surface or planar, i.e., two dimensional, whereas in the first 10 nm the dominant relaxation occurs normal to the free surface. Full relaxation of the surface was found for temperatures above the bulk glass transition temperature. Thus, using this direct probe, no indication of an

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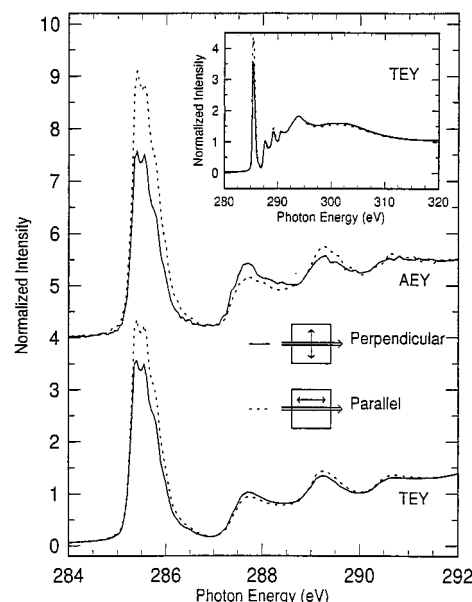


**Figure 1.** Schematic diagram of a polystyrene chain that has undergone deformation. The enlargement shows a detailed diagram of a phenyl group and its orientation with respect to the local chain axis.

enhanced mobility of the polymer chains at the free surface was found.

PS, having a weight-average molecular weight of  $9.6 \times 10^4$  with a polydispersity of 1.04, was purchased from Polymer Laboratories and used without further purification. The polymer denoted 96K PS was dissolved in toluene and spin coated onto cleaned Si(100) wafers having a native oxide layer. The concentrations of the solutions were varied to produce films with thicknesses ranging from 25 to 170 nm. The samples were heated to 80 °C to remove solvent then heated to 150 °C for 1 h to relax the film. The surfaces of the films were unidirectionally rubbed at room temperature<sup>24</sup> with a velvet cloth under a load of 2 g/cm<sup>2</sup> over a distance of 300 cm at a speed of 1 cm/s.

NEXAFS studies were performed at the Stanford Synchrotron Radiation Laboratory on beamline 10-1, which is equipped with a spherical grating monochromator. The horizontally polarized X-ray beam impinged upon the sample at normal incidence, with the polarization direction either parallel or perpendicular to the orientation or rubbing direction. The X-ray energy was then changed through the carbon K absorption edge and the Auger and total electron yield spectra, AEY and TEY, respectively, were recorded with a spectral resolution of 100 meV.<sup>25</sup> The escape depth of the Auger electrons is 1 nm, and, consequently, AEY probes only the first nanometer from the free surface. TEY, on the other hand, provides information on the first 10 nm from the free surface. Of interest in these studies is the intensity of the dominant  $\pi^*$  resonance associated with the phenyl ring in PS. The phenyl antibonding  $\pi^*$  orbitals are oriented normal to the phenyl rings and so, as shown schematically in Figure 1, are predominantly parallel to the local chain axis of the polymer. Thus, comparing the NEXAFS spectra with the electric field vector of the X-rays parallel and perpendicular to the buffing direction yields a dichroic ratio which is related to the segmental orientation of the polymer.<sup>25</sup> Experiments were performed as a function of temperature where the sample was heated to a specific temperature for a half hour. Prior to measurements, the heater was shut off to eliminate extraneous signals from the heater circuit. Thus, the dichroic ratio reflects the state of orientation after relaxation at the annealing temperature. Subsequent to the measurements reported here, studies were performed as a function of the annealing time. In these studies NEXAFS spectra were recorded at 10 min intervals after the sample reached a preset



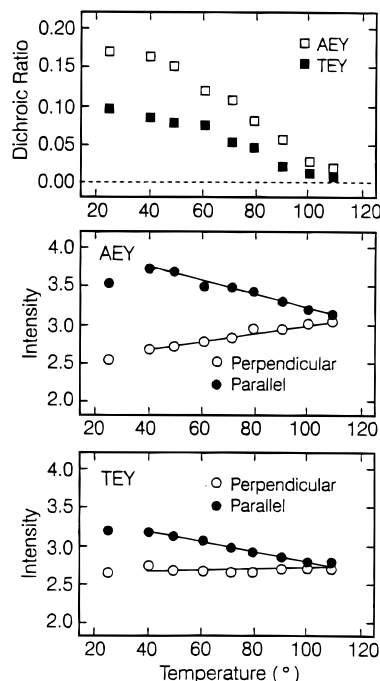
**Figure 2.** Near-edge X-ray absorption fine structure spectra for an oriented 31 nm thick 96K PS sample at room temperature. The Auger electron yield (AEY) and the total electron yield (TEY) spectra are shown when the polarization direction of the incident X-ray beam is parallel and perpendicular to the orientation direction. Normalized TEY spectra over a larger energy range are shown in the inset demonstrating equal intensities for  $I^{\parallel}$  and  $I^{\perp}$  well above and well below the carbon absorption edge.

temperature. No change in the spectra was observed with annealing.

Shown in Figure 2 are the AEY and TEY NEXAFS spectra for a 96K PS as a function of the incident X-ray energy with the polarization direction (**E** vector) parallel and perpendicular to the rubbing direction. The spectra were normalized as discussed previously.<sup>25</sup> The inset shows complete TEY spectra demonstrating that, well above and below the absorption edges, the spectra superpose. The intensities of the dominant  $\pi^*$  phenyl resonance at 285.5 eV change markedly with the polarization direction. Owing to the high spectral resolution of the spectra, the phenyl  $\pi^*$  resonance is seen to be composed of several peaks. These arise from the structural inequivalence of the various phenyl c atoms and the resulting chemical shifts.<sup>23</sup> Changes are also observed for the smaller resonances at 287.8 (phenyl C-H) and 289.3 eV (phenyl  $\pi^*$ ) but will not be discussed here in detail. The intensity of the prominent  $\pi^*$  resonance in the parallel geometry,  $I^{\parallel}$ , is much greater than that in the perpendicular geometry,  $I^{\perp}$ . The  $\pi^*$  resonance at 289.3 eV exhibits the same behavior, while the C-H resonance at 287.8 eV exhibits the opposite polarization dependence, as expected.<sup>23</sup> A convenient means of monitoring the orientation in a sample is by the dichroic ratio,  $R$ , defined as

$$R = (I^{\parallel} - I^{\perp}) / (I^{\parallel} + I^{\perp}) \quad (1)$$

Shown in Figure 3 is the dichroic ratio for the AEY and TEY phenyl  $\pi^*$  resonance intensities as a function of temperature. At 25 °C the AEY dichroic ratio is greater than that for TEY. This shows that, as expected, the first 1 nm of the film is oriented more than the first 10 nm. Increasing the temperature results in a gradual decrease in the dichroic ratio. For unrubbed samples the dichroic ratio was zero at room temperature and, therefore, no studies were done at higher temper-



**Figure 3.** Dichroic ratio and corresponding AEY and TEY integrated phenyl  $\pi^*$  resonance intensities in the parallel and perpendicular geometries as a function of the sample annealing temperature.

atures. Similar results have been seen in birefringence studies on unrestrained, stretched PS films in the bulk by Kovacs and Hobbs.<sup>26</sup> The gradual relaxation has been attributed to local segmental relaxations and changes in the torsional angle populations introduced during the deformation.<sup>27</sup> It is important to note that the temperature dependence of the birefringence of a uniaxially oriented PS held under a constant strain produces markedly different results.<sup>28</sup> In this case a rapid decrease in the birefringence is found at the bulk  $T_g$  (105 °C). This suggests that the free surface of a PS film is behaving in an unconstrained manner.

The polymer segments in the first 1 nm reorient more than those in the first 10 nm (approximately a factor of 2 would superpose the data), and the dichroic ratio remains finite up to  $\sim 110$  °C. Consequently, complete relaxation of the surface and near-surface regions does not occur over the time scale of the measurements (30 min annealing) until the measurement temperature exceeds the glass transition temperature of the bulk. These results show that the mobility of the polymer at the free surface is not enhanced significantly over that in the bulk. If this were the case, then the AEY dichroic ratio would have decreased to zero well below the bulk  $T_g$ , whereas some orientation would still have been evident in the TEY data.

In Figure 3 it is seen that the dichroic ratio does not decrease to zero precisely at the bulk  $T_g$ . This residual dichroism or orientation in unconstrained amorphous polymers results from a deformation of the entire polymer chain near the surface that has not had sufficient time to relax. For temperatures only slightly in excess of  $T_g$ , a complete relaxation of the polymer chain along its own contour requires long times to occur. Similar results have, also, been seen in measurements of the birefringence of unconstrained bulk PS,<sup>26,29,30</sup> which underscores the similarity of the bulk and surface behavior.

The extent of the relaxations observed here, as well as in bulk samples, will depend upon the time scale over

which the measurements are made. Consequently, any relaxations that occur are rapid relative to the 30 min time scale of the present experiments. In comparison to other techniques like differential scanning calorimetry, dilatometry, dielectric spectroscopy, and dynamic mechanical spectroscopy, techniques routinely used to measure the  $T_g$  of bulk films, the time scale of the studies here is much longer.

It is important to examine more closely the AEY and TEY  $\pi^*$  resonance intensities from which the dichroic ratios were derived. Shown in parts b and c of Figure 3 respectively are the integrated AEY and TEY phenyl  $\pi^*$  resonance intensities as a function of temperature in the parallel and perpendicular geometries. The plotted intensities correspond to energy integrated intensities from 284.5 to 286.9 eV (see Figure 2). The data at 25 °C show clearly that the chain segments within 1 nm from the free surface are oriented. Heating the samples to 40 °C shows a distinct increase in the AEY intensities in the parallel and perpendicular geometries, which suggests that the chain segments are becoming more oriented at the surface. This is in contrast to expectations and arises from a relaxation of stresses built within the film during rubbing and the relaxation of bond angle distortions imposed during deformation. With further increase in temperature, the AEY and TEY  $\pi^*$  resonance intensities exhibit markedly different behavior. In the case of AEY, the intensity in the parallel geometry decreases gradually with temperature, whereas that in the perpendicular geometry increases with temperature in exactly the opposite way; i.e., the sum of the intensities remains constant. Since the polarization-dependent NEXAFS intensity is constant when averaged over all polarization directions, the results shown here imply a purely in-plane reorientation of the phenyl  $\pi$  system. This is exactly the behavior exhibited by a two-dimensional or planar process, where the loss of segmental relaxation in the deformation direction results in a compensating increase perpendicular to this direction. This is not the case for the TEY data. Here, in the parallel geometry, a continuous decrease in the  $\pi^*$  resonance intensity is seen with increasing temperature. However, in the perpendicular geometry, the  $\pi^*$  resonance intensity is constant. Because of the polarization sum rule mentioned above, these results show that the dominant relaxation mechanism for chain segments within the first 10 nm from the surface is one where some of the chain segments reorient normal to the surface plane. Consequently, the type of segmental relaxation exhibited by the polymer depends upon the distance the segments are from the interface. For both AEY and TEY the retention of orientation up to  $\sim 110$  °C is evident.

The studies presented here have quantitatively shown that the segmental mobility of high molecular weight, amorphous polymer chains at a free surface is not significantly different from that in the bulk. Chain ends can enhance the surface mobility; however, in order to have high enough chain-end concentrations, the molecular weight of the polymer must be sufficiently low to have an effect. It has been shown that, for amorphous polymers oriented by rubbing, within the first 1 nm from the free surface the segmental relaxations of the polymer chains are effectively two-dimensional. In contrast, within the first 10 nm, the dominant relaxation occurs normal to the surface plane. NEXAFS spectroscopy has provided a unique means of examining the surface

reorientation in polymers in a noninvasive and direct manner.

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