

## Polymer Chain Relaxation: Surface Outpaces Bulk

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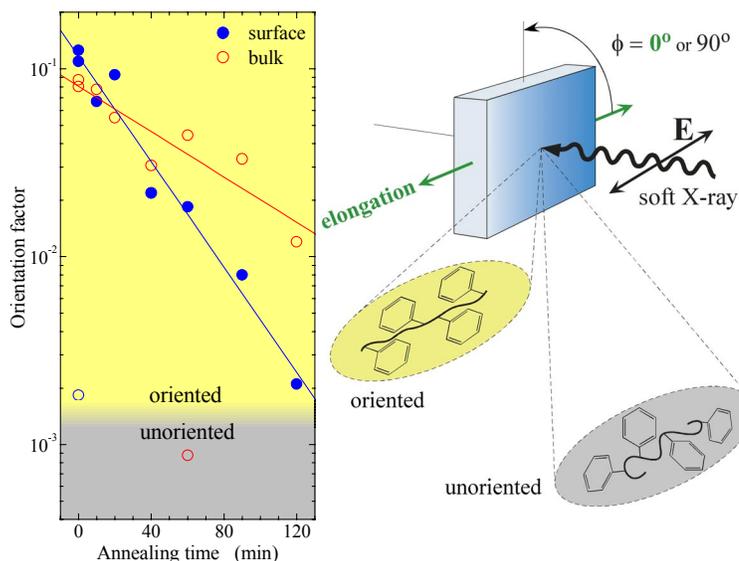
**Introduction:** The time scale that controls polymer chain relaxation profoundly influences the economics of industrial plastics processing. However, not much is known about how fast the surface relaxes relative to the bulk in amorphous polymeric materials. This is in part because no study has reported simultaneous measurement of both surface and bulk chain relaxation dynamics on a single macroscopic sample. In this work we show how carbon near-edge X-ray absorption fine structure (NEXAFS) can be applied to detect both surface and bulk segmental relaxation in uniaxially deformed polystyrene samples. We show that by *simultaneously* monitoring the partial electron yield (PEY, kinetic energy > 150 eV) and the fluorescence yield (FY, carbon  $K_{\alpha}$  277eV) NEXAFS signals, with probing depths of approximately 2 and 200 nm, respectively, one can examine segmental motion throughout a polymer sample. Using this methodology, chain relaxation is found to occur approximately 30% faster at the surface than in the bulk.

**Methods and Materials:** Rectangular samples (12.5 x 12.5 x 6 mm), prepared by vacuum hot-pressing at 150 °C monodisperse polystyrene ( $M = 228,000$  g/mole), were placed into a steel channel die and uniaxially elongated at room temperature along one of the long dimensions to about 130% of their original length. This sample preparation allowed us to examine true bulk samples as encountered in industrial practice and to avoid thin film effects that may alter the free surface behavior. The NEXAFS experiments were conducted on the U7A NIST/Dow Materials Characterization end-station at the National Synchrotron Light Source at Brookhaven National Laboratory. For each sample the PEY and FY carbon K-edge NEXAFS intensities were measured with the incident polarized X-ray beam normal to the sample surface and at two azimuthal sample orientations: with the electric field vector,  $\mathbf{E}$ , parallel ( $\phi = 0^\circ$ ) and perpendicular ( $\phi = 90^\circ$ ) to the elongation direction as shown in Fig. 1.

**Results:** Orientation of the chain backbone was determined by monitoring the C=C phenyl ring  $1s \rightarrow \pi_1^*$  NEXAFS resonance intensity at 285.5 eV, which involves the excitation of carbon  $1s$  electrons to the unfilled  $\pi^*$  antibonding orbitals of the phenyl ring. Enhancement of the  $1s \rightarrow \pi_1^*$  resonance intensity was observed when  $\mathbf{E}$  was parallel to the elongation direction. Since the phenyl  $\pi^*$  orbitals are oriented normal to the phenyl rings, and the phenyl rings, free to rotate around the pendant bond, will have a component normal to the chain axis, the intensity of the  $\pi^*$  signal has been shown to be an unambiguous signature of backbone orientation. This orientation, seen both in the PEY and the FY NEXAFS signals of the elongated samples, provides clear evidence of chain orientation at the outset of the experiment. A direct measure of the chain relaxation rates at the surface and in the bulk can be obtained by defining an orientation factor, OF (see Fig. 1 caption) that is evaluated from the time dependence of the  $1s \rightarrow \pi_1^*$  resonance intensity in the PEY and FY NEXAFS spectra, respectively, during annealing. Figure 1 shows that while the OF for both surface and bulk chains decays as a function of increasing annealing time at 60 °C, the surface orientation is initially greater and decays faster than for the bulk. Fitting the decay rates to exponential functions gives characteristic time constants of approximately 33 and 43 minutes for the surface and the bulk, respectively.

**Conclusions:** These results show conclusively that polystyrene surface chain relaxation dynamics are significantly faster than the bulk. Recalling that chain relaxation rates in amorphous polymers increase with decreasing number of entanglements, our results are in agreement with recent theory that predicts the number of entanglements at the free surface to be significantly reduced compared to the bulk.

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**Figure 1.** Time evolution of the orientation factor, OF, from an elongated (oriented) polystyrene sample reveals that when annealed at 60 °C the surface chains relax to an equilibrium (unoriented) configuration faster than the bulk chains. OF is calculated from  $(I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$ , where  $I_{\parallel}$  and  $I_{\perp}$  are the  $1s \rightarrow \pi_1^*$  resonance NEXAFS intensities collected with the sample elongation direction parallel ( $\phi = 0^\circ$ ) and perpendicular ( $\phi = 90^\circ$ ) to the electric vector of the soft X-ray beam,  $\mathbf{E}$ , respectively.