Polymer Chain Relaxation: Surface Outpaces Bulk

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Received December 6, 2000

Revised Manuscript Received April 9, 2001

The time scale that controls polymer chain relaxation has taken on a new importance as the paradigm for polymer innovation evolves from three dimensions to two.[1] Nanotechnology initiatives, involving the design and fabrication of highly confined polymer layers, drive the need for a comprehensive description of chain dynamics as bulk polymers become thinner and more surface-like. In this study we apply near-edge X-ray absorption fine structure (NEXAFS)[2,3] to measure directly both surface and bulk segmental relaxation throughout a uniformly deformed polystyrene slab. Using this methodology, in a single experiment, chain relaxation is found to occur almost 50% faster at the surface than in the bulk.

Much work has been performed on investigating chain relaxation dynamics in a wide variety of bulk polymer systems[4,5] including polystyrene.[6−9] The study of surface chain relaxation dynamics is much newer. Experiments in this area have often been based on measuring colligative properties, typically mechanical (for example, atomic force microscopy[10−13]). There are only a few studies that follow the specific molecular-scale bond reorientation of polymer chains at surfaces as a function of time and temperature. An important study of this type is that of Liu et al.[14] where near-edge X-ray absorption fine structure (NEXAFS) was used to examine the relaxation of buffed polystyrene thin film surfaces as a function of temperature for a fixed annealing time. Here the authors find that chains within the first 1 nm of the free surface, as well as those within the first 10 nm, relax at the same rate from a state of uniaxial alignment to a random configuration. Upon the assumption that the first 10 nm of the sample represents the sample bulk, the authors conclude that "segmental mobility of high molecular weight, amorphous polymer chains at a free surface is not significantly different from that in the bulk."

More recently, Schwab et al.[15,16] have rubbed with velour cloth thick (10 μm) polystyrene films to increasing degrees (that is, distance rubbed) and discovered through optical birefringence measurements a depth-dependent reduction in the glass transition temperature in the near surface region. The maximum reduction, about 15 K, was found for light rubbing where chain alignment was estimated to extend only 7 nm into the sample. The minimum reduction, about 6 K, was found for heavily rubbed films with chain alignment extending an estimated 32 nm into the sample. Comparison was made to separate measurements of the bulk glass transition temperature.

In this Communication we report on probing *true segmental dynamics* in preoriented *bulk* polystyrene samples. By simultaneously monitoring the time dependence of the partial electron and X-ray fluorescence yield NEXAFS signals, whose probing depths are ≈2 and ≈200 nm, respectively, a realistic simultaneous direct comparison of surface and bulk chain relaxation dynamics is obtained without resorting to two separate measurements. Using this setup, relaxation of the surface chains to an equiaxed conformation was seen to occur faster than the relaxation of the bulk chains. This indicates that segmental mobility of high molecular mass, amorphous polymer chains at a free surface is significantly different from the bulk.

Rectangular samples (12.5 × 12.5 × 6 mm), prepared by vacuum hot-pressing at 150 °C monodisperse polystyrene ($M_W = 228\,000$ g/mol, bulk radius of gyration[17] approximately 13.4 nm), 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.[15] Partial electron yield (PEY, kinetic energy > 150 eV) and fluorescence yield (FY, carbon Kα 277 eV) carbon K-edge NEXAFS intensities, with probing depths of approximately 2 and 200 nm, respectively, were recorded simultaneously at the NIST/Dow Soft X-ray Materials Characterization Facility at the National Synchrotron Light Source at Brookhaven National Laboratory.[3,18] For each sample, PEY and FY 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, **E**, parallel ($\phi = 0°$) and perpendicular ($\phi = 90°$) to the elongation direction as shown in Figure 1.

Orientation of the chain backbone was determined by monitoring the C═C phenyl ring 1s → π^* NEXAFS resonance intensity at 285.5 eV,[19] which involves the excitation of carbon 1s electrons to the unfilled π^* antibonding orbitals of the phenyl ring. Enhancement of the 1s → π^* resonance intensity was observed when **E** was parallel to the elongation direction. Since the phenyl π^* 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 π^* signal has been shown to be an unambiguous signature of backbone orientation.[14] This orientation, seen in both 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 Figure 1 caption), that is evaluated from the time dependence of the 1s $\rightarrow \pi_1^*$ resonance intensity in the PEY (relative uncertainty ±0.01%) and FY (relative uncertainty

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10.1021/ma002075t CCC: $20.00

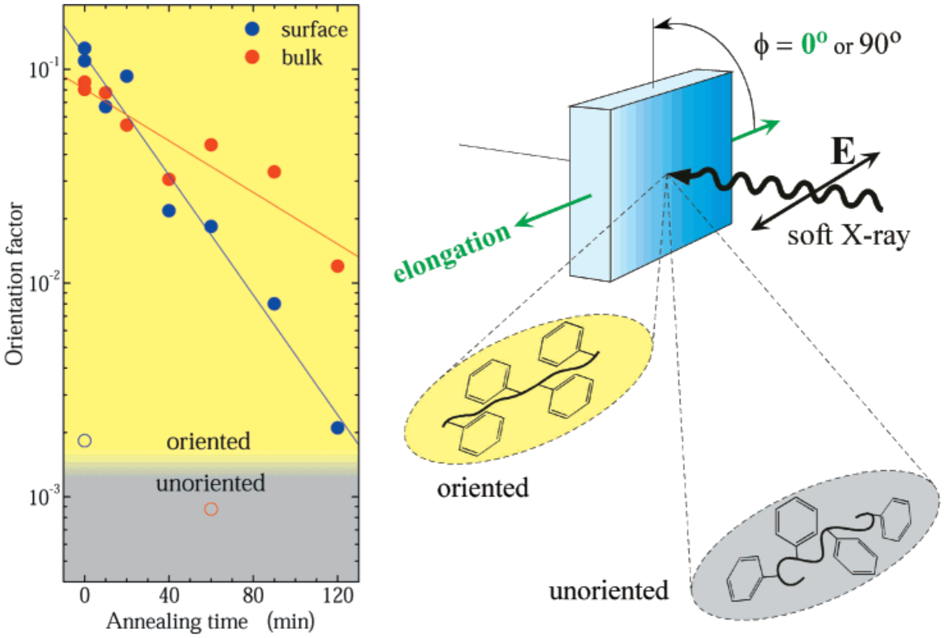

Figure 1. Time evolution of the orientation factor, OF, from an elongated (oriented) polystyrene sample reveals that when annealed at 60 °C the surface chains relax to an equilibrium (unoriented) configuration faster than the bulk chains. OF is calculated from $(I_{\parallel} - I_{\perp})/(I_{\parallel} + I_{\perp})$, where $I_{\parallel}$ and $I_{\perp}$ are the $1s \rightarrow \pi^*$ resonance NEXAFS intensities collected with the sample elongation direction parallel ($\phi = 0°$) and perpendicular ($\phi = 90°$) to the electric vector of the soft X-ray beam, **E**, respectively. The blue circles denote OF from the partial electron yield NEXAFS signal (surface region), and the red circles represent the fluorescence yield NEXAFS signal (bulk region), measured simultaneously. The closed and open circles depict OF evaluated from data collected on elongated specimens and those not subjected to elongation, respectively. The solid lines represent exponential decay fits to the experimental data on the elongated samples; the rate decay constants are reported in the text. The schematic on the right details the sample geometry for the incident polarized soft X-ray beam normal to the polystyrene sample surface with the elongation direction parallel to **E** ($\phi = 0°$). The insets in the lower right represent chain configurations in oriented (before annealing) and unoriented (after annealing) elongated samples.

±0.05%) 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,[7] 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 50 min (with corresponding R^2 values of 0.90 and 0.91) for the surface and the bulk, respectively.

These results show conclusively that polystyrene surface chain relaxation dynamics are significantly faster than the bulk. Our results are in accord with recent theory predicting that collective motion on chain loops extended to the sample surface is responsible for a rapid increase of chain mobility near the surface region of the film (top $\approx$ 5 nm).[20] The finding that the polystyrene surface segmental mobility greatly outpaces the bulk is expected to be a universal property of polymeric chains profoundly influencing the design, processing, and application of polymeric materials.

Acknowledgment. This research was supported by the NCSU COE start-up funds and the NSF CAREER award, Grant DMR98-75256. NEXAFS experiments were carried out at the National Synchrotron Light Source, Brookhaven National Laboratory, which is supported by the U.S. Department of Energy, Division of Materials Sciences and Division of Chemical Sciences. The authors gratefully acknowledge fruitful discussions with Professor P. G. de Gennes (Collège de France).

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MA002075T