

# Orientation of fibrils in polymer crazes studied by STXM

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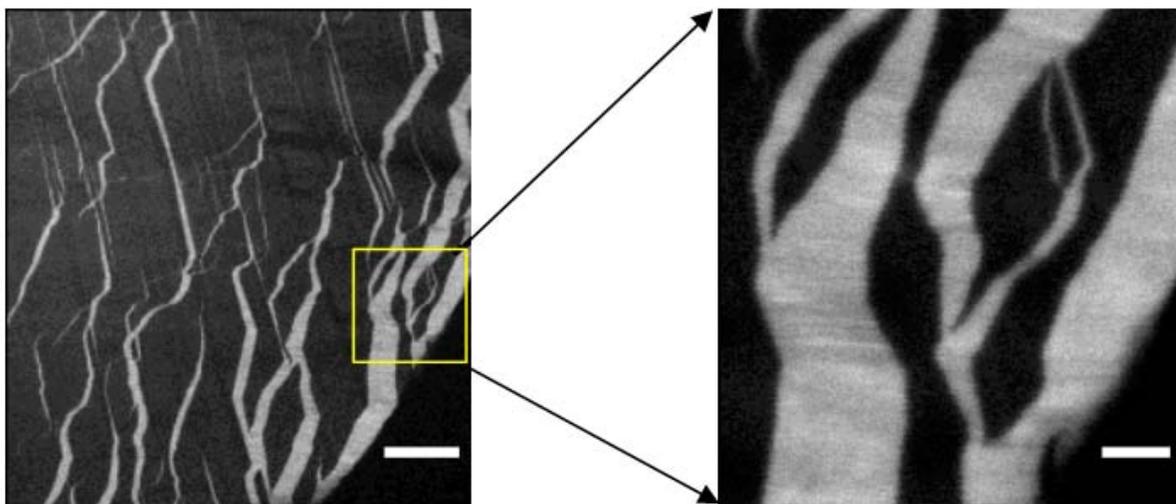
## INTRODUCTION

Many important thermoplastic polymers are very brittle in their neat form and thus one of the most important areas of endeavour for the polymer scientist is to improve and control the toughness of common polymeric systems. An understanding of the fundamental fracture mechanics of polymers should facilitate the design of tougher materials. Failure of brittle polymers generally occurs by crack formation. The crack begins as a craze, in which the separating polymer surfaces are bridged by small filaments or fibrils of polymer. The fibrils are formed as polymer molecules are pulled out from the bulk material. One would presume that the polymer chains would be strongly aligned along the fibril direction. Knowledge of the degree of orientation prior to break and the variation of this property for different size crazes, and different materials will provide data important to any mathematical model of polymer deformation. If reliable, such a model could be used to design better materials. However, until now the quantitative data at high spatial resolution needed to test any proposed model has not been accessible by any known method. The enhanced spatial resolution and improved stability of the new scanning transmission x-ray microscope (STXM) at BL 5.3.2 [1,2] offer the opportunity to obtain this data. We report here our first, and successful attempt at this kind of measurement.

## RESULTS AND DISCUSSION

The absorption intensity in near edge x-ray absorption (NEXAFS) is determined by the projection of the transition dipole moment operator onto the electric field vector of the light. Thus, polymer orientation can be determined from the change in transition intensity as a function of sample angle [3]. In polystyrene, the C 1s  $\rightarrow \pi^*_{\text{ring}}$  transition at 285.2 eV is oriented perpendicular to the ring. Since the ring planes are approximately perpendicular to the polymer axis [4] the polarization dependence of the strong 285.2 eV resonance is a convenient monitor of molecular orientation. In principle, one can quantify degree of polymer alignment by comparing the NEXAFS spectrum measured with the fibril axis aligned along the photon E vector, with that measured with the sample positioned at 90° to that orientation. In practice, this is very challenging since sample rotation in the STXM is difficult, the E-vector cannot be rotated (yet) [5], and since the fibrils are known from transmission electron microscopy (TEM) to be about 10-40 nm in diameter, somewhat smaller than the ~50 nm resolution of the STXM [2].

Another issue that needs to be considered is the possibility of beam damage caused by the measurement [6]. Early attempts to record the NEXAFS spectra of the matrix and the fibrils by using image spectral sequences [7] did in fact suffer from detectable damage, which in the case of PS has been shown to occur by degradation of the  $\pi^*_{\text{ring}}$  resonance [6]. To avoid that, we report here an approach resulting in the lowest possible damage.

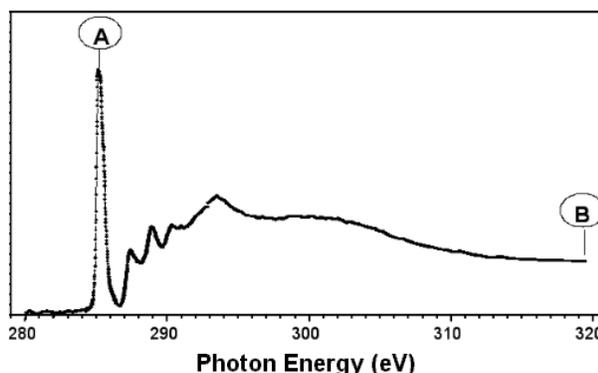


**Fig. 1** STXM images at 285.2 eV of crazed PS. The image on the right was the crazed region used for dichroism measurements. Scale bars: left: 5 microns, right: 1 micron.

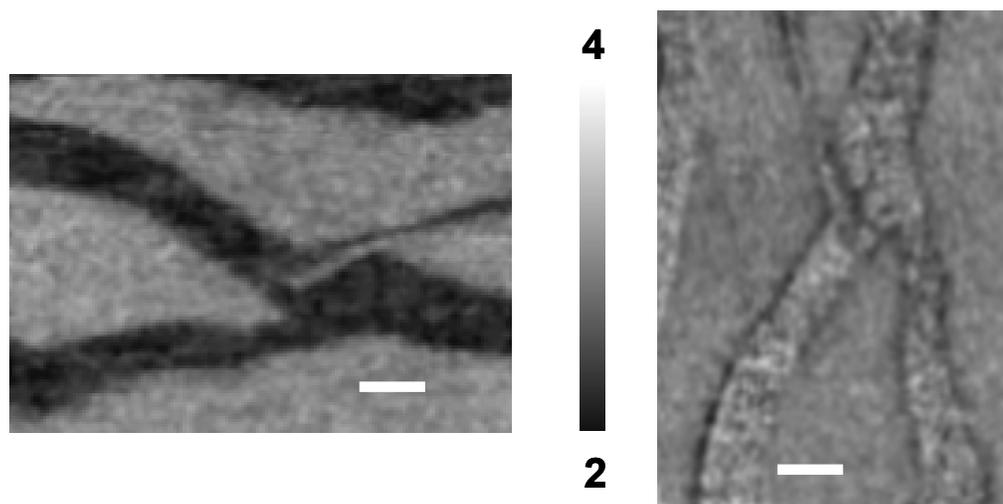
A microtomed thin section of general purpose PS (molecular weight approximately 100,000 Daltons) was placed on a copper TEM grid which had been pre-treated with an adhesive. A miniature deformation stage was used to stretch the grid and thereby stretch the PS section until crazes had formed. This process was monitored using a visible light microscope. This sample was then analyzed in the STXM.

Images measured at 285.2 eV are reproduced at two different magnifications in Figure 1. The lighter areas are the crazes and the darker material is the intact bulk PS. Although the fibrils are not completely resolved, their presence is discerned by the irregular haziness of the space between the dark regions of bulk PS. Two images were acquired per orientation set. The first image was at 285.2 eV, the top of the  $\pi^*_{\text{ring}}$  resonance, labelled A in Figure 2. The second image was acquired at 320 eV, labelled B in Figure 2, an energy well away from any absorption resonance, where variations in the carbon thickness are the only contrast mechanism. This was used to correct for the thickness differences between matrix and crazes as described below.

Both images were converted to optical density  $OD = -\ln(I/I_0)$ , where  $I$  is the signal being detected through the sample in transmission and  $I_0$  is the incident beam intensity. To compensate for density differences and thereby allow using the bulk PS as a reference, we have normalized the 285.2 eV images by dividing them by the 320 eV images. The image ratios for the fibrils oriented approximately parallel (horizontal) and perpendicular (vertical) to the electric vector of the photon field are compared in Figure 3. One sees that the fibrils in the crazes are brighter than the matrix when the E vector (in the horizontal plane of the image) is parallel to the fibrils. When the sample is rotated by  $90^\circ$  to put the E vector perpendicular to the fibril direction, the craze region is much

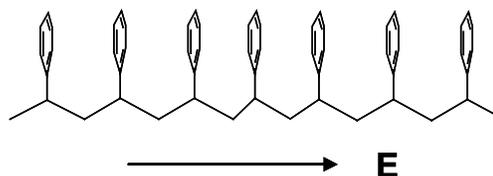


**Fig. 2** C 1s spectrum of polystyrene. A and B indicate the energies where images were recorded to determine orientation.



**Fig. 3** Ratio of images at 285.2 and 320 eV. (left) sample with the crazes approximately parallel to E-vector (fibrils perpendicular to E-vector). (right) orthogonal sample orientation, craze perpendicular, fibrils parallel to E-vector. Bar is 1 micron.

darker compared to the matrix. These observations are consistent with the hypothesis that the fibrils are oriented PS chains across the crazes, with the phenyl rings approximately perpendicular to the fibril axis, and thus parallel to the craze. In this orientation, the E-vector should be perpendicular to the craze direction for maximum intensity of the  $C\ 1s \rightarrow \pi^*_{\text{ring}}$  (Fig. 4), consistent with the observation (Fig. 3). In order to quantify the degree of orientation one needs to correct for the open area around the fibrils which ‘dilutes’ the dichroic signal.



**Fig. 4** Sketch to illustrate the suggested orientation of phenyl rings relative to the chain axis. The rings are all shown on the same side and the zigzag planar structure is used only for simplicity.

## SUMMARY

NEXAFS dichroism has been used for the first time to directly confirm the orientation of molecular chains within fibrils in crazed polymers. Further experiments are planned to make more quantitative measurements and to study more complex polymeric systems. The information gleaned from these studies will contribute to our understanding of fracture properties of materials at a very fundamental and microscopic level.

## REFERENCES

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