

# PEEM studies of thin film bilayers and blends of polystyrene and brominated polystyrene

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## INTRODUCTION

Thin films of polymers have considerable technological importance and are used in numerous applications such as multi-color photographic printing, adhesives, indexed matched optical coatings, and low dielectric electronic packaging. Dewetting and decomposition phenomena of blends and bilayers are crucial for the use of these polymers in, for example, colloidal paint systems where wetting controls the dispersion of color pigments. Compared to bulk properties, relatively little is known about the properties of polymer thin films and surfaces. A detailed understanding of thin film properties, such as composition and morphology, is highly desirable and numerous studies on blends [1-7] and bilayers [8, 9] have recently been undertaken. Most of these studies rely on Atomic Force Microscopy or other methods that do not provide quantitative compositional maps. Hence, blends and bilayers of polystyrene (PS) and brominated polystyrene (PBrS) have recently been studied using the scanning transmission X-ray microscope (STXM) at the National Synchrotron Light Source. STXM provides quantitative composition maps integrated along the direction of the surface normal. These studies [10] reveal the morphology formed as the PS and PBrS phase separates, as well as the morphology that forms as the PBrS dewets the PS substrate layer during annealing at elevated temperature. For example, as the PBrS dewets, round holes form first and subsequently grow in size until they impinge on each other and a network of spines is formed. Upon further annealing, the spines break up and coalesce into drops of PBrS. A thin layer of PS remains present throughout the sample which is much thinner than the original PS layer thickness. STXM data shows that PS wets the spines of PBrS and forms rather thick and tall walls around PBrS spines. STXM data even indicates that the PS is actually encapsulating the PBrS at this point of the dewetting, even though the PBrS started out on top. However, STXM could not conclusively show that encapsulation occurs, as it can not distinguish the surface from the subsurface polymer. We have thus utilized Photoemission Electron Microscopy (PEEM) at the Advanced Light Source to determine the composition of the surface of various PS/PBrS thin films. PEEM combined with tunable X-ray illumination provides the ability to obtain local Near Edge X-ray Absorption Fine Structure (NEXAFS) spectra in the total yield mode with 200 nm spatial resolution. For polymers, this provides information about the composition and bonding on the sample surface with a probing depth of about 10 nm.

## EXPERIMENTAL

Experiments have been performed at beamline 8.0 of the ALS. A Kirkpatrick-Baez pair of mirrors was used to focus the monochromatized X-rays into a 200  $\mu\text{m}$  diameter spot on the sample. The electron optical column of the microscope is used to form an image of the emitted electrons. The microscope is a two-lens system operating at a nominal voltage of 10 kV, and it is described in detail elsewhere [11]. The electron emission caused by the X-rays is proportional to the X-ray absorption. The absorption is a function of the elemental and chemical state of the sample and the

X-ray wavelength. By tuning the X-rays through the absorption edge of the element of interest and taking images at incrementally increased photon energy it is possible to obtain locally resolved NEXAFS spectra with a resolution given by the resolution of the electron optics (200 nm).

Blends and bilayers of PS and PBrS on silicon substrates were used for these studies. The blends contained 50% PS and 50% PBrS and had a total thickness of 43 nm, the bilayers consisted of a 30 nm thick PBrS layer on top of a 30 nm thick PS layer produced by spin casting. For the bilayers, the PS and PBrS were prepared separately, and then the PBrS layer was floated on top of the PS layer. The samples were annealed for different durations at 180°C in a vacuum oven. After annealing the samples were investigated in the PEEM microscope.

## RESULTS AND DISCUSSION

Figure 1 shows the (not spatially resolved) NEXAFS spectra at the carbon K edge of the blend and the bilayer before annealing. The first peak at 285eV can be identified as the PS  $\pi^*$  resonance [10], and it is the dominant feature in both spectra. The peak which is characteristic for the PBrS  $\pi^*$  resonance at 286.3eV is only present in the spectrum of the bilayer which has the PBrS layer on the surface. The blend of 50% Ps and 50% PBrS does not show this resonance. The process of blending and spin casting these two polymers from a toluene solution already initiates the decomposition and the formation of a PS top layer.

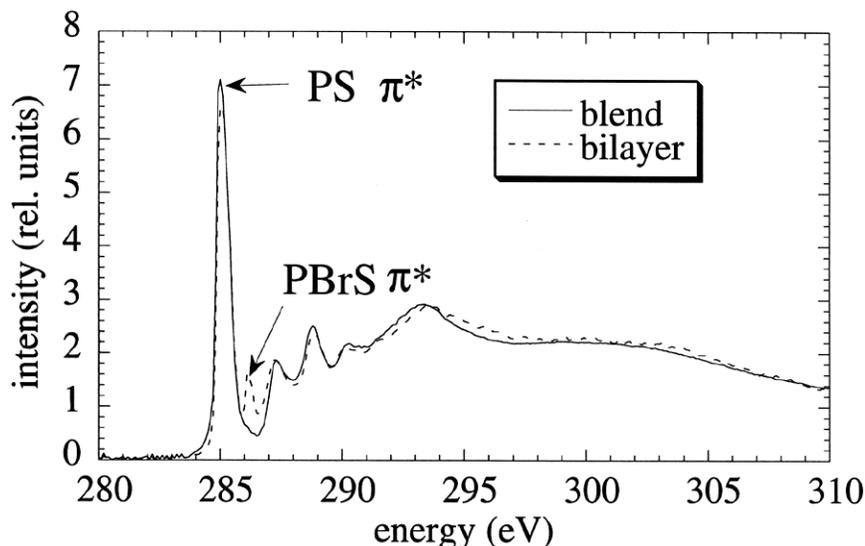


Figure 1: NEXAFS carbon K edge spectra (integrated over a 200  $\mu\text{m}$  spot) of PS/PBrS blend and bilayer before annealing.

Figure 2 shows the NEXAFS carbon K edge spectra of the bilayer after annealing of various duration. The PBrS  $\pi^*$  resonance is still visible after 1 hour of annealing, slightly weaker after 2 days of annealing, and not present anymore after 11 days of annealing.

PEEM microscopy of the 2 days annealed sample confirms that the dewetting process starts locally in small areas. Figure 3a shows a PEEM image of the 2 days annealed sample where we observed a contrast variation in a small spot when the area was imaged at the PS  $\pi^*$  resonance and the PBrS  $\pi^*$  resonance wavelength. The spot appeared in the same brightness as the surrounding at the PS  $\pi^*$  resonance, and dark at the PBrS  $\pi^*$  resonance. The image in Figure 3a is acquired at

286.3eV (PBrS  $\pi^*$  resonance, spot dark). Local NEXAFS spectra were acquired in the spot (Figure 3b, graph 1) and in two adjacent areas outside the spot (Figure 3b, graphs 2 and 3) for reference. The spectra show that in the spot the underlying PS layer is exposed as the PBrS dewetts, whereas outside the spot the PBrS is still at the surface.

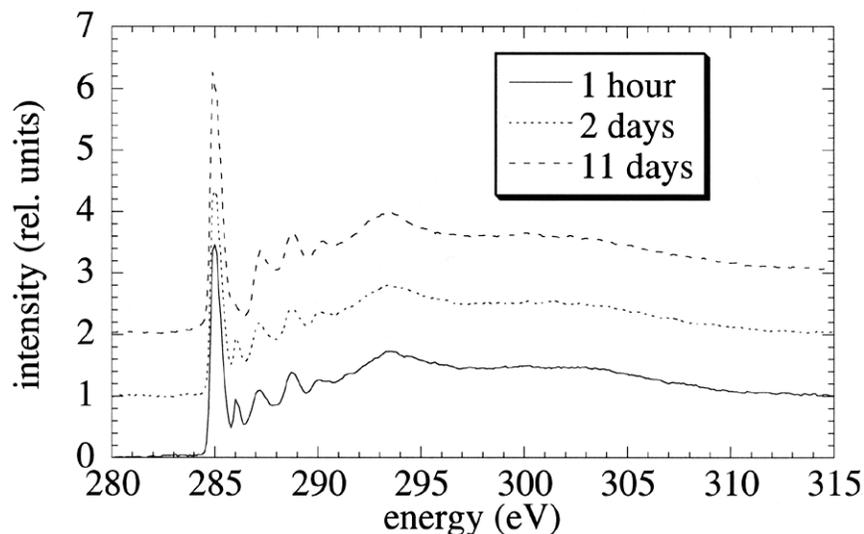


Figure 2: NEXAFS carbon K edge spectra (integrated over a 200  $\mu\text{m}$  spot) of PS/PBrS bilayer after annealing at 180°C of various duration. Spectra are offset for better clarity.

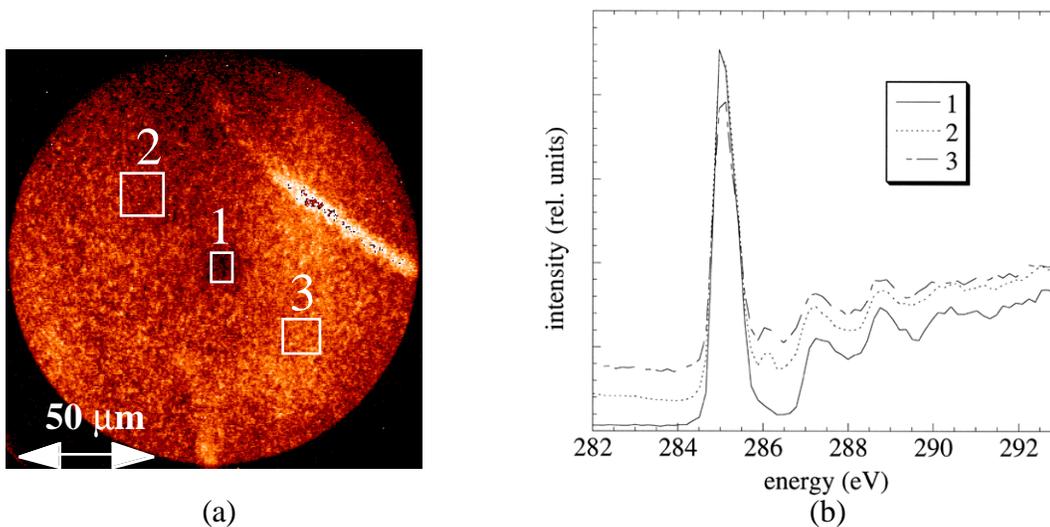


Figure 3: (a) PEEM image of a 2 days annealed PS/PBrS bilayer taken at 286.3eV. The image indicates the 3 areas where the local NEXAFS spectra were taken. (b) Local carbon K edge NEXAFS spectra of the areas in (a). Spectra offset for clarity.

Images acquired of bilayers annealed for longer duration (Figure 4a) show the same network of spines as observed with STXM. Contrast is based solely on topography, and no chemical contrast was observed. In all areas at the surface only PS was found (Figure 4b).

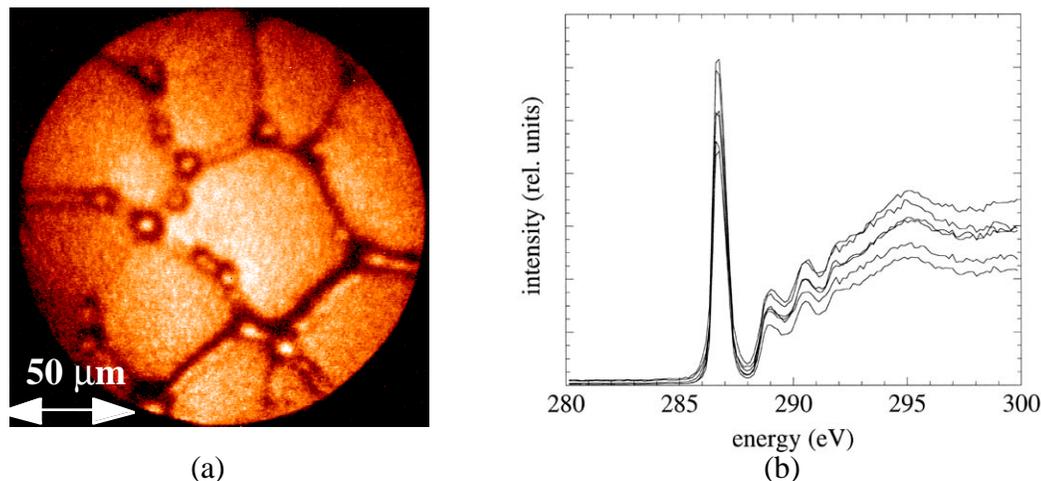


Figure 4: (a) PEEM image of a 4 days annealed PS/PBrS bilayer taken at 286.3eV. (b) Local carbon K edge NEXAFS spectra taken at 6 different areas of (a). None of the spectra shows the PBrS  $\pi^*$  resonance at 286.3eV.

## CONCLUSIONS

The PEEM results showed that the dewetting of the PBrS polymer from the PS sublayer initially exposes a pure PS surface in small areas, while in most areas PBrS is still present at the surface. The formation of spines as the dewetting progresses was observed with both methods. STXM could identify that the spines are composed of PBrS, but only PEEM observation could show that these PBrS spines are covered by a thin PS layer. The combination of these two methods allows the study of complex polymer systems, and both methods yield complementary information which, if combined, give a complete understanding of the processes taking place during dewetting of the polymer systems.

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