

## Soft X-ray Microscopy and Spectroscopy of Polystyrene/Poly(methyl methacrylate) Blends

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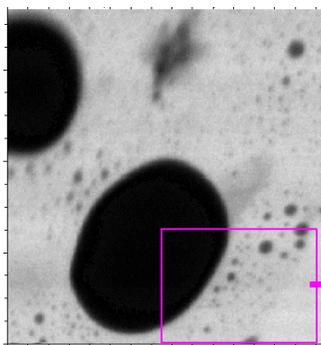
Beamline(s): U4B, U7A, X1A

In recent PEEM investigations with 100 nm spatial resolution of annealed thin film samples of polystyrene (PS) and poly(methyl methacrylate) (PMMA) a PS signal was detected in the PMMA domains[1]. As thermodynamics predicts almost complete phase separation at our preparation conditions (molecular weights 21,000g/mol, annealed at 165°C, 99% pure phases), this signal cannot be explained by a mixed phase, but we had to consider a thin PS-skin on top of the PMMA-domains. To test this hypothesis we investigated the samples by scanning transmission x-ray microscopy (STXM, at X1A), total electron yield (TEY, at U4B) and partial electron yield NEXAFS spectroscopy (PEY, at U7A).

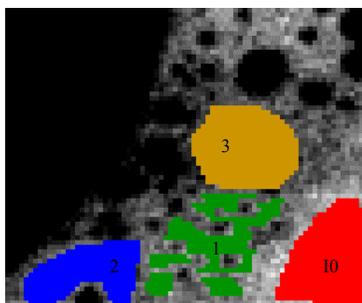
High resolution (step size 40nm) and long dwell time (50ms) STXM images reveal a wide range of PS domains size (from the resolution limit to several micrometers, **Figure 1**). We determined the PS-thickness by averaging over a carefully chosen region of the PMMA matrix. (#1 in **Figure 2**. Regions #2 and #3 contain some small PS domains.) The absorption difference observed from images at 281.8eV and 285.1eV in region #1 is 0.011 units of optical density, would correspond to a PS-skin thickness of 5Å. This would be in the range of the noise level of the STXM. This small PS signal can, however, be explained by the modulation transfer properties of the STXM.

The PEY spectrum of an identically prepared sample shows a higher PS and a lower PMMA signal than the respective TEY spectrum (**Figure 3**). From the integrated  $\pi^*$  intensity of the PEY signals we calculate a PS volume fraction of 41% and of 27% from the TEY signals, respectively. On the other hand, the surface fraction of PS domains determined from the STXM images is around 40% and the PEY method is very surface sensitive (sampling depth  $\approx 10$  Å). Therefore, the PEY PS signal can be explained by PS domains on top of the PMMA and we can exclude a PS skin as possibility. The TEY PS signal is smaller than the PEY signal because its sampling depth is higher and a larger amount of PMMA under small PS domains is detected.

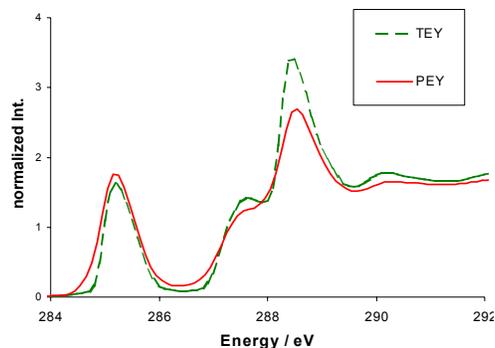
Both STXM and surface NEXAFS yield consistent results that exclude a PS skin on the samples.



**Figure 1.** STXM image at 285eV of a PS/PMMA blend (image size 8 $\mu$ m x 8 $\mu$ m)



**Figure 2.** Enlarged part of Fig. 1, used for evaluation. The absorption difference between 285.1eV and 281.8eV is 0.012 for area 1, 0.016 for area 2 and 0.034 for area 3.



**Figure 3:** PEY (solid line) and TEY (dashed line) NEXAFS spectra of a PS/PMMA blend. (The spectra are normalized to unity at 310eV)

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**References:** [1] K. Kaznatcheyev, A.P. Hitchcock, C. Morin, H. Ikeura-Sekiguchi, S. Urquhart, D.G. Castner, A. Scholl, F. Nolting, personal communication