Study of Switching of Top Layer Composition of Mixed Polymer Brushes with X-ray Photoemission Electron Microscopy

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INTRODUCTION

We have briefly reported our spectro-microscopic study of switching of the top layer composition of poly(styrene-co-2,3,4,5,6-pentafluorostyrene)/poly(methyl methacrylate) (PSF/PMMA) brushes upon exposure to solvents of various selectivity.[1] In that work we used X-ray Photoemission Electron Microscopy (XPEEM) technique[2] which distinguishes between the brush constituent polymers by means of Near Edge X-ray Absorption Fine Structure (NEXAFS)[3] contrast (Figure 1).

The XPEEM technique is a powerful analytical tool for direct sensing of chemical composition of phase-separated surfaces with sub-micron resolution; but only semi-quantitative information can be extracted from it at present days unlike other techniques based on the NEXAFS contrast.[2] In order to estimate the probable mistake in the XPEEM results, we recorded NEXAFS spectra without lateral resolution from the top layer of a PSF/PMMA brush after exposure to three solvents of different selectivity (toluene, chloroform, acetone). The composition of the brush top layer calculated from the recorded spectra was compared with respective results of quantitatively accurate X-ray Photoelectron Spectroscopy (XPS).

EXPERIMENTAL

Synthesis and characterization of the PSF/PMMA brush. The PSF/PMMA brush similar to such brushes reported earlier[1] was synthesized via two-step surface-initiated radical polymerization on polished Si substrates as described in details elsewhere.[4] The synthetic procedure[4] was modified so that a solution of 50 g *methyl methacrylate* (MMA) in 50 g *tetrahydrofuran* (THF) was taken for the second polymerization step. Non-grafted polymers were removed via cold Soxhlet extraction with THF for 1 h after each polymerization step. The weight-averaged molecular weights (Mw) of PSF and PMMA in the mixed brush were estimated $6\cdot10^5$ and $8\cdot10^5$ g/mol, respectively, from size exclusion chromatorgaphy of the bulk polymers assuming that the molecular weights of the respective polymers in the bulk and in the brush are equal.[5] The polydispersity indices (Mw/Mn) of the bulk polymers were ~2 but they can be higher for the polymers in the brush.[6] The ratio of styrene and 2,3,4,5,6-pentafluorostyrene units in PSF was 0.75:0.25 as evaluated from ^{1}H NMR. The grafted amounts of PSF and PMMA were 15 and 29 mg/m^2, respectively, as obtained from ellipsometry after each polymerization step and extraction of the non-grafted polymers. Average distances between grafting points for PSF and PMMA were calculated to be 9 and 8 nm, respectively.

XPS. XPS analysis was performed with AXIS ULTRA XPS spectrometer from Kratos Analytical, England. X-ray source was mono-Al $K\alpha_{1,2}$ (1486.6 eV), its power was 300 W at 20 mA. Photoelectron analyzer pass energy was 160 eV for survey spectra. The sample charging was overcompensated guaranteeing unadulterated peak shapes. Normalized peak areas (Norm.Area) were calculated from peak areas (RawArea) of survey spectra according to the following equation: Norm.Area=RawArea/(RSF·TxFunction), where RSF is a sensitivity factor, experimentally determined for this spectrometer, which accounts variations in proportionality coefficients between the electron yield and the concentrations of emitting atoms. Tx.Function is the spectrometer's transmission function. The molar PMMA fraction in the sample top layers was calculated from ratios of the normalized area of the 1s O XPS peak to the normalized area of the 1s C XPS peak for the spin-coated PMMA film (γ_0) and for the PSF/PMMA brush samples (γ) taking the number of the C and O atoms in the PSF and PMMA monomer units into account: $\varphi(\text{PMMA}) = 8\cdot(\gamma/\gamma_0)\cdot100\%/(5+3(\gamma/\gamma_0))$.

NEXAFS spectroscopy. NEXAFS spectra were recorded with a PEEM-2 microscope[7,2] at the beamline 7.3.1.1 of the Advanced Light Source (ALS) synchrotron of the Ernest Orlando Lawrence Berkeley National Laboratory, USA. In the PEEM-2 setup a thin polymer film based on a conductive or semi-conductive substrate is irradiated with a monoenergetic X-ray beam at 30° in ultrahigh vacuum conditions and the emitted photoelectrons are collected with a system of electrostatic lenses and focused at high magnification onto a detector. Images of a sample can be obtained at different photon energies of the incident X-ray radiation with lateral resolution ~60 nm.[1] Herein we report only results extracted from area-averaged NEXAFS spectra, i. e. functions of photoelectron flux on the incident X-ray photon energy.

RESULTS AND DISCUSSION

We recorded NEXAFS 1s C spectra from spin-coated films of PSF and PMMA (Figure 1), and from three samples of the PSF/PMMA mixed brushes which were preliminary exposed to toluene, chloroform, and acetone, respectively.

PMMA being less stable than PSF upon X-ray irradiation may produce an additional peak at 285 eV resulted from the polymer destruction.[2] The PEEM-2 settings were preliminary optimized for the PMMA film to minimize the sample destruction (only a weak PMMA peak is seen at 285 eV in Figure 1), and then they were kept constant for the other samples.

Several (3-7) spectra were recorded for each sample and normalized by the intensity of the incident X-rays. Average spectra were calculated for each sample and normalized by a monocromator function in order to filter off non-linearity in the intensity of the incident X-rays. The monocromator function was recorded for a bear Si-wafer in the same photon energy range and at the same microscope settings as for the polymer spectra. The pre-edge intensity (at 281 eV) of the normalized spectra was set to an arbitrary value of 2. The ratio of the intensity steps over the spectra photon energy range for the bulk PSF and PMMA (Figure 1) was matched with the ratio of the carbon atoms numbers in the respective monomer units (8:5) in accord with the *Thomas-Reiche-Kuhn sum rule*[3].

Table 1. Composition of the PSF/PMMA Brush Top Layer after Exposure to Solvents with Various Selectivity.

Solvent	Normalized PMMA fraction from NEXAFS, %	PMMA fraction from XPS at the take-off angle 0°, %
toluene	58	44
acetone	86	95
chloroform	90	82

The spectra recorded from the samples of the PSF/PMMA brush exposed to different solvents were initially scaled to the same overall intensity step as the bulk PSF spectrum (Figure 2). Then the brush spectra were fitted with linear combinations of the spectra of the bulk PSF and PMMA applying conjugate gradual optimization method. The fitting procedure was done with aXis2000 software written by Adam P. Hitchcock et al. The sum of the calculated PSF and PMMA fraction was 5-20% higher than unity, therefore the polymer fractions were normalized by their sum. The normalized polymer fractions were used for adjustment of the overall intensity steps of the brush spectra to the respective linear combinations of the overall intensity steps of the PSF and PMMA spectra. The adjusted brush spectra were used for the second fitting cycle. The obtained polymer fractions were normalized as described above and used for a new adjustment of the overall intensity steps of the brush spectra. The fitting cycles were repeated until the normalized polymer fractions became unchanged. Three cycles were

done for the brush exposed to toluene and four cycles for the brushes exposed to acetone and chloroform.

The XPS and NEXAFS spectroscopy data on composition of the PSF/PMMA brush top layers differ by 10-15% (Table 1). A probable reason for that is the different sampling depth which is ~15 nm in XPEEM[2] and ~8 nm in XPS at the 0° take-off angle[8]. The NEXAFS spectra of the PSF/PMMA brush with adjusted overall intensity steps are shown in Figure 3. Spectra resulting from the fitting procedure for the brush exposed to acetone are shown in Figure 4 as an example.

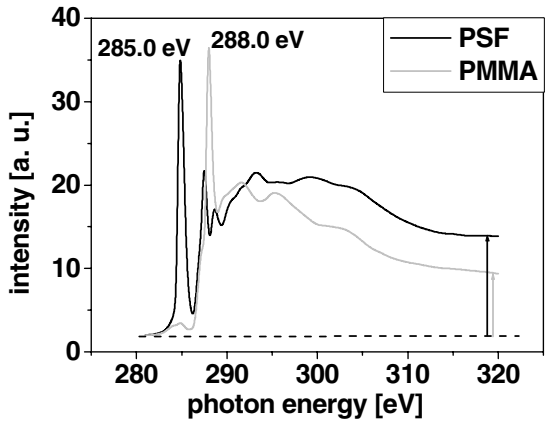

Figure 1. NEXAFS 1s C spectra of the spin-coated bulk PSF and PMMA normalized by the monocromator function. The main peaks of PSF and PMMA at 285.0 and 288.0 eV correspond to $\pi^*_{C=C}$ and $\pi^*_{C=O}$ electron transitions[2], respectively. The intensity steps over the entire photon energy range (marked with arrows) were set in accord with the ratio of C atoms in the monomer units of the polymers (8:5).

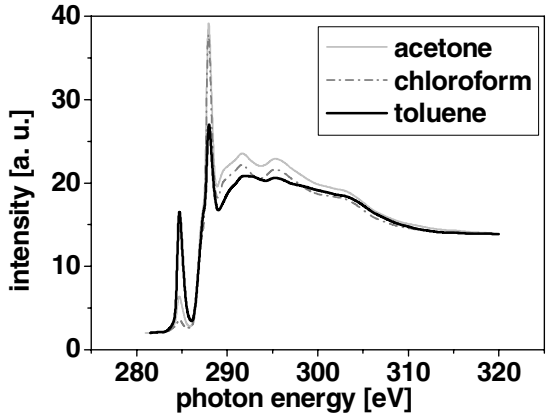

Figure 2. NEXAFS 1s C spectra of the PSF/PMMA brush samples after exposure to 3 different solvents. The spectra are scaled to the same overall intensity step as the PSF spectrum in Figure 1.

In summary, our recent experiments demonstrate good quantitative agreement for the surface composition of the mixed polymer brushes measured by two different techniques XPS and XPEEM. For the one brush both methods were applied after exposure of the sample to three different solvents. In all cases both methods have demonstrated very similar quantitative data. The results give evidence for the correct interpretation of the XPEEM experiments and prove the XPEEM methods to be a powerful tool for study chemical patterning and switching of surface composition in thin polymer films.

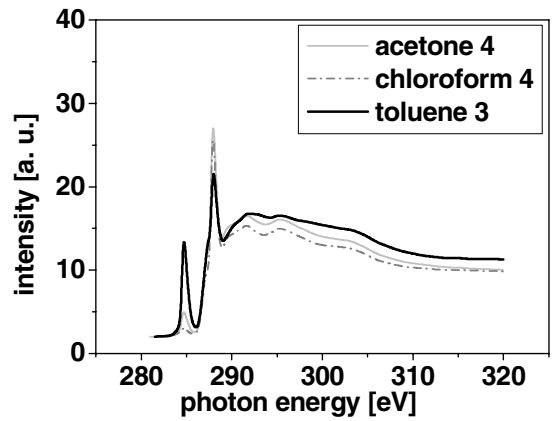

Figure 3. NEXAFS 1s C spectra of the PSF/PMMA brush after exposure to 3 different solvents. The overall intesity steps are adjusted to linear combinations of such steps of the PSF and PMMA spectra in accord with the normalized fractions of the constituents in the brush top layers. The numbers of the fitting cycles are indicated.

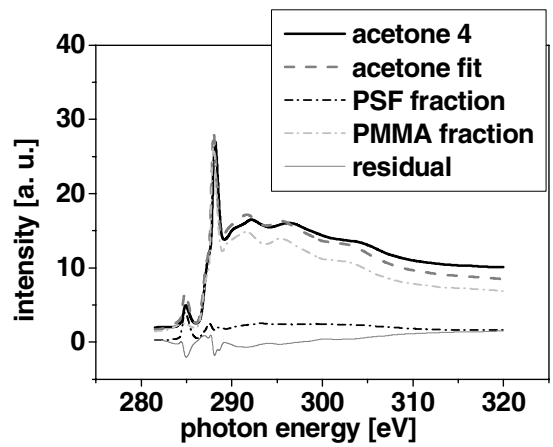

Figure 4. Decomposition of the NEXAFS 1s C spectrum of the PSF/PMMA brush exposed to acetone into a linear combination of the spectra of the brush constituent polymers after 4 fitting cycles.

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