Electronic Supplementary Material (ESI) for Soft Matter.

Energy Dependent XPS Measurements on Thin Films of a Poly(vinyl methyl ether)/Polystyrene Blend in Dependence on Film Thickness – Concentration Profile on a Nanometer Resolution to Understand the Behavior of Nanofilms

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Three-layer model:

The three-layer model considers firstly of an adsorbed layer at the substrate, where the segments have a reduced mobility, causing an increase of T_g^{therm}. It is worth to note that the adsorbed layer has a two-part substructure. A "strongly bounded" adsorbed subpart, with higher density and reduced mobility is formed at short adsorption times by pinning the segments directly on the substrate leading mainly to trains. The kinetics of the adsorption process changes its time-dependence at a crossover time. There, the adsorbed layer further grows by diffusion and/or changes in the conformation of the segments, through the already existing layer, on the expense of their entropy. This yields a "loosely bounded subpart" of the adsorbed layer at larger distance from the substrate where the segments have a different mobility, compared to that of the strongly bounded one. It consists mainly of loops and tails. Recently, ref. showed that the thickness of the loosely bounded layer is not only dependent on the molecular weight but also on the original film thickness.

Secondly, a bulk-like layer in the middle of the film, where the segments have more or less bulk-like mobility and properties. It is worth to note that with decreasing film thickness, the thickness of the bulk-like layer decreases. Thirdly, a surface layer present at the polymer/air interface, where due to missing segment/segment interactions, the segments have a higher molecular mobility leading to a decrease of T_g^{therm}. [1-5]The thickness of the surface layer was found to be between 5 and 15 nm for polymer blend films with a thickness of 200 nm.[1] The measured thermal glass transition temperature of the whole film is a complicated average of all of these effects of the different layers.

Preparation of the films:

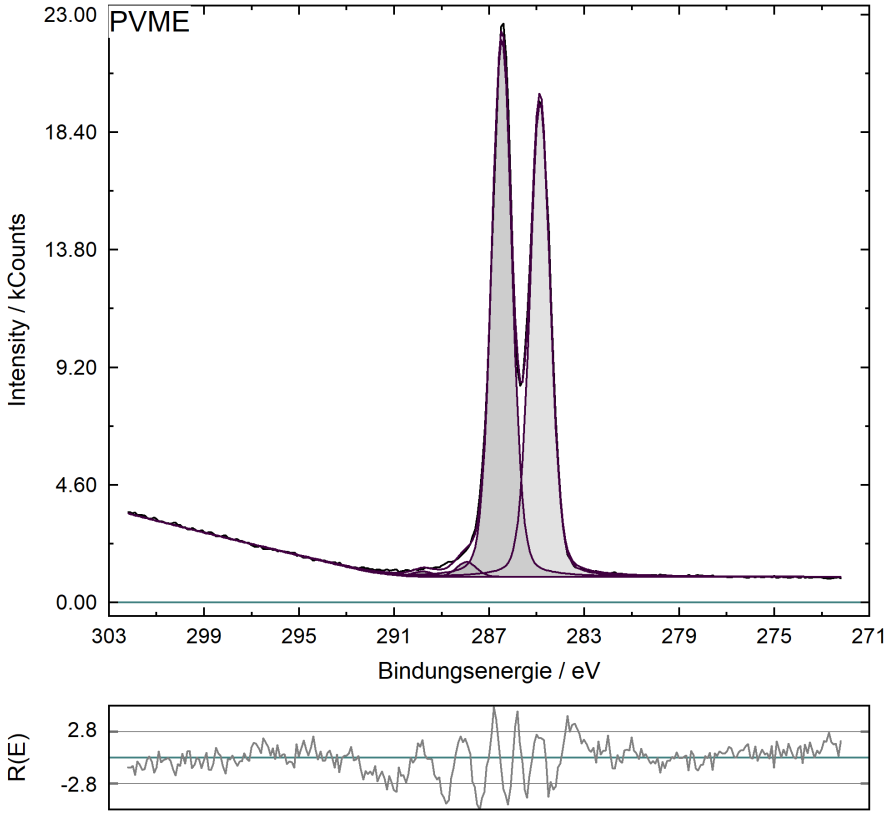
A concentrated polymer solution of PVME and PS with the weight ratio of *25 wt%* to *75 wt%* was prepared using toluene (Master solution). Diluted solutions prepared from the master solution were filtered (Minipore, 0.2 µm) and then spin coated with *3000 rpm* and an acceleration of *2000 rpm/s* for *60 s* on cleaned silicon substrates in a flow box. The thickness of the films was controlled by the concentration of the solution.

Photon energies and corresponding information depth:

Photon energy / eV	Information Depth / nm
392	1.5
525	2.7
676	3.8
775	4.6
849	5.1
1486.6	9.6

Table S1: Photon energy vs. information depth.

C1s XPS spectrum for the PVME film:



Peak name _|43|1	Peak height/ Counts	Lorentzian	Position/ eV	FWHM/ eV	abs. Area/ Counts·eV	rel. Area/ %
C-C, C-H	18585.6	0.2	284.8642	1.00597	21668	46.14
C-O-C	21081.1	0.2	286.471	0.99619	24343	51.84
C=O	596.629	0.2	287.9602	1	691.55	1.47
O-C=O	221.537	0.2	289.7859	1	256.74	0.55

Figure S1: C1s XPS spectrum of a pure PVME film. The spectra shows also a small amount (< 2 wt%) of oxidation products

Fit parameters obtained for the spectra in Figure 3:

Peak name C1s_1	Peak height/ cps	Lorentzian contribution	Position/ eV	FWHM/	Abs. Area/ cps eV	Rel. Area/ %
C-C, C-H	71816.2	0.2	285.0	1.98	162774	94.5
C-O	4179,6	0.2	287.6	1.97	9437	5.5

Lorentzian and FWHM were fixed for all spectra, for the binding energies a variation of ± 0.2 eV was allowed. The relative uncertainties of the peak areas were below 4 % with a confidence value of 95 %.

Test of the exponential decay:

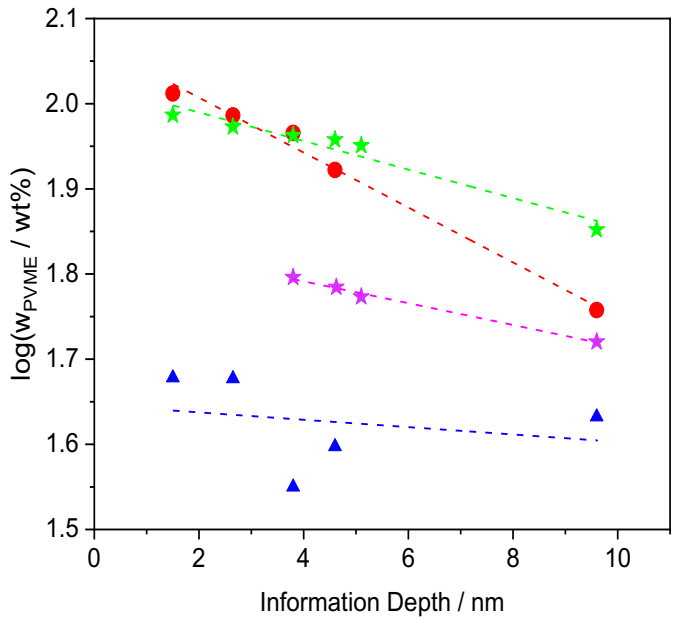


Figure. S2: PVME concentration vs. information depth of the photons for different film thicknesses: red circles -32 nm, green asterisk – 45 nm, violet asterisk – 62 nm, and blue triangle – 187 nm.The dashed lines are linear regression to the corresponding data.

Concentration profiling:

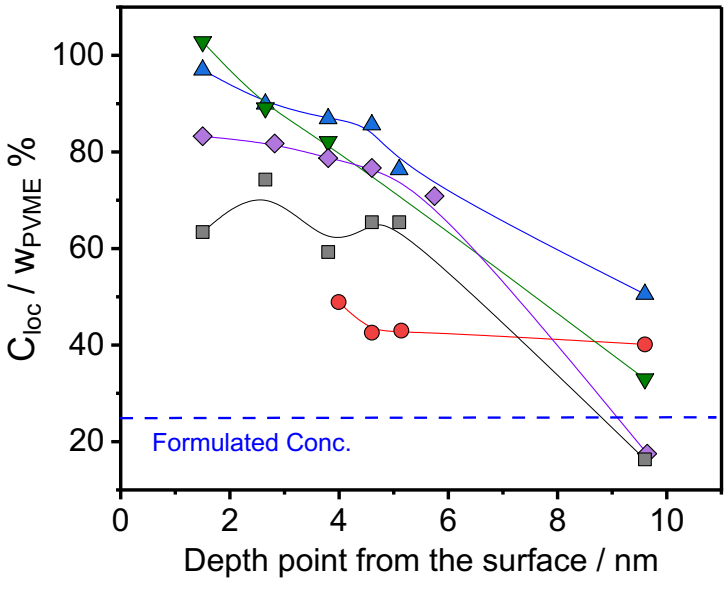


Figure. S3 Local PVME concentrations at different depth points (Yi) for 187 nm – black pentagons, 82 nm – red circles, 45 nm – blue triangles, 32 nm – green downside triangles, 24 nm – grey squares, and 15 nm – purple rhombuses. The sloid lines are just for eye guidance. The dashed blue line marks the formulated concentration.

References:

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