Pressure sensitive adhesives (PSAs) are used for many different applications, such as for example adhesive foils or binding materials. A prominent class of PSA films is based on statistical copolymers. Typically two or three different monomers are combined into the statistical copolymer to balance the different requests of the PSA [1-4]. The adhesive properties of the PSA films are mainly determined by surface-near regions. However, detailed information about surface structures of such adhesive films is still missing.

In the presented work we focus on a PSA model system of the statistical copolymer P(EHA-stat-20MMA) consisting of two different types of monomers, ethylhexylacrylate (EHA) as a soft and sticky component and methylmethacrylate (MMA) which is glassy and thus playing a major role in controlling the mechanical properties of the PSA. The ratio between PEHA and PMMA is 80% to 20% and the molecular weight is 248k. The PSA films were prepared with solution casting on pre-cleaned glass substrates. From a naive point of view, one would have expected homogenous films, which are characterized by the average monomer composition. To investigate the surface structure, we performed grazing incidence small angle x-ray scattering (GISAXS) measurements. X-ray reflectometry (XRR) is used to confirm and extend the data containing structural information normal to the sample surface.

The GISAXS measurements (wavelength of 1.38 Å and beamsize of 40 μm x 20 μm) were performed at the beamline BW4 at HASYLAB. The incident angle on the sample surface was selected to 0.506° and the distance between the sample and the detector was 2.004 m. A 2D-MarCCD detector (2048 x 2048 pixels with a pixel size of 79 μm) was used to record the scattered x-rays from the film surface. Special care was taken to minimize degradation of the PSA film caused by radiation damage. The so called out-of-plane cut through the 2D-scattering pattern is selected in order to look for the evidence of lateral structures. It is oriented parallel to the sample surface.

**Figure 1**: a) Measured and b) simulated 2D GISAXS pattern of a thick P(EHA-stat-20MMA) film, c) selected out-of-plane cut taken at the position of the critical angle of PEHA (symbols) and corresponding fit (black solid line), distributions of d) center-to-center distance, e) radii and f) height of the cylinders used in the model describing the GISAXS data.
surface and perpendicular to the beam direction (along y-axis, see orange line in figure 1a). The out-of-plane cut is made at the critical angle of PEHA.

Figure 1a shows the recorded 2D scattering image of the thick P(EHA-stat-20MMA) film. It is well dominated by a strong scattering in the scattering plane. The out-of-plane cut (figure 1c) clearly shows a shoulder which indicates the presence of a lateral structure inside the PSA film. For analysis the GISAXS data are simulated with the IsGISAXS [5] software (figure 1b). The model used in this simulation, assumes a one-dimensional paracrystal of PMMA cylinders in a depth of 6.6 nm which is embedded in a 200 nm thick PEHA matrix. For the calculation of the form factor the distorted wave Born approximation (DWBA) is used. The substrate in this model has the calculated refractive index of P(EHA-stat-20MMA) being the bulk material as obtained with XRR.

The distribution functions as well as the mean values (red solid line) of the fitted cylinder parameters are depicted in figure 1. In particular we obtain a mean center-to-center distance of 83.9 nm (figure 1d), a mean radius of 34.4 nm (figure 1e) and a mean height of 7.17 nm (figure 1f). Due to the broad distribution of the characteristic lengths no Bragg-like peak is detected.

**Figure 2:**

- **a)** Measured reflectivity of P(EHA-stat-20MMA) in Fresnel-normalized representation (symbols) with corresponding fit (black solid line) and
- **b)** corresponding refractive index profile. The solid lines mark the refractive indices of the statistical copolymer as well as of the corresponding monomers. The dashed line is explained in the text.

Figure 2a shows the reflectivity curve of the described sample in the so-called Fresnel-normalized representation, which is beneficial for thin enrichment layers. The black solid line is the fit to the data performed with Parratt32. The resulting refractive index profile is depicted in figure 2b where z = 0 denotes the sample surface. The black solid lines are positioned at the values of the refractive indices of the corresponding homopolymers and at the calculated refractive index of the copolymer.

The composition as a function of the depth z can be directly derived from the refractive index profile. An oscillating composition profile with two enrichment regions of PMMA is obtained. For values of z > 200 nm the average monomer composition is reached, which is 80:20 for the investigated system.

Combining the XRR and the GISAXS observations, the modeled cylindrical structure in a depth of 6.6 nm (see red dashed line in figure 2b) coincides with the detected PMMA enriched layer situated deeper in the film.

**References**