

Near-surface solvent content profiles during solution casting

Polymer coatings such as paints, corrosion protections, adhesives or organic electronic devices play a key role in science, industry and everyday life. One widely-used processing method is to dissolve the polymer, spread the solution onto the desired support and let the solvent evaporate. This “solution casting” technique permits thicknesses ranging from a few nanometers to millimetres. There is also almost no limitation to the shape of the polymer film.

Solvent evaporation can be one of the driving forces influencing the surface roughness or morphology of polymer coatings; good knowledge of the underlying kinetics is therefore of utmost importance [1]. Solvent loss rates reported in the literature depend on time t as t^k , where k can vary between $\frac{1}{2}$ and 1. These studies consider the total amount of solvent as a function of time. We, in contrast, focus on the near-surface part of drying polymer films, using *in situ* neutron reflectometry (NR) on ILL’s FIGARO. With this method even small concentration variations as a function of distance from the sample surface can be detected.

To be more precise, the near-surface solvent content profile of solution-cast polymer films is monitored as a function of time and of molecular weight. We start from freshly coated, toluene-based poly(*n*-butylacrylate-*stat*-methylacrylate) (P(*n*BA-*stat*-MA)) solutions, which present a model system for pressure-sensitive adhesives, and we perform continuous NR experiments until the extractable solvent has evaporated. By choosing protonated polymers and deuterated toluene we ensure that the neutrons provide very high contrast between the solvent and the polymers; the components of the copolymer are deliberately not distinguishable.

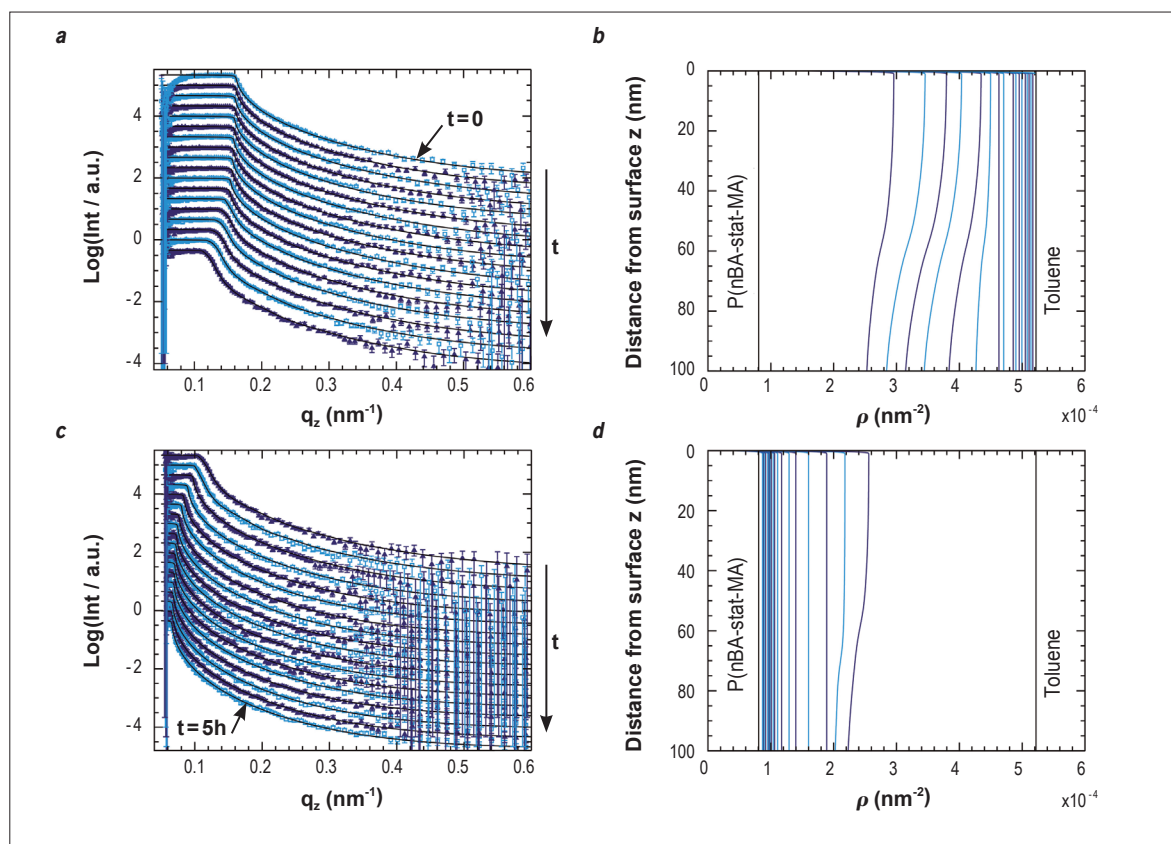


Figure 1: (Left) *In situ* NR data for the drying process of P(*n*BA-*stat*-MA) with a molecular weight $M_w = 600 \cdot 10^3$ g/mol. For clarity, the curves have been shifted along the y-axis and presented in separate graphs. The sample age increases from top to bottom. (Right) The corresponding SLD profiles, in which the sample age increases from left to right. The SLDs of the materials involved are marked by the vertical lines (see labels).

Figures 1a and 1c show (from top to bottom) the evolution with time of the reflectivity curves in the first 5 hours after casting the solution onto the substrate, for a molecular weight of $M_w = 600 \cdot 10^3$ g/mol (symbols). The data of several measurements was summed up on the basis of the counting rates and evaporation speed. The black solid line shows the fit to the data. The first curve is still equal to the NR data of liquid toluene. After this, the shift of the critical edge accelerates before it converges to zero for large t .

Figures 1b and 1d show the corresponding scattering length density (SLD) profiles. The data is fitted assuming homogeneously distributed toluene except for a time interval of 20 min (see curves 13 to 20 counting from the top). There is a 60 nm region in this time interval at the top of the sample in which the solvent concentration is higher here than in the bulk. The length of the corresponding time interval and the amplitude of the difference in concentration between bulk and surface increase with increasing molecular weight.

To our knowledge, there are no theoretical predictions of this phenomenon, although recent molecular dynamics simulations have shown comparable effects [2]. The free-volume theory [3, 4] may provide an explanation: close to the sample surface the chain end density deviates from the bulk value and this allows further trapping of the solvent.

Figure 2 shows the solvent loss $1-n(t)$ as a function of time, normalised to the point at which deviation from pure toluene NR data is detected; $n(t)$ is the solvent concentration. For the stages of inhomogeneous solvent distribution, $n(t)$ is determined by averaging the SLD profiles over the interval $z \in [0; 100$ nm].

For the samples with the two highest molecular weights, the solvent loss is proportional to time in the early stages; this is also called case II diffusion and is classically predicted for glassy polymers. Beyond the early stages, near-surface solvent evaporation accelerates showing power law behaviour exactly proportional to t^3 . To our knowledge this exceeds all reported evaporation velocities. It has to be considered, however, that our experiment focuses on

the near-surface region. It is possible that the solvent trapped in the enhanced near-surface free volume is released in this phase and contributes in addition to the ongoing case II evaporation.

For the sample with the lowest molecular weight, the early stages of solvent loss cannot be split into two regions. This might be attributable to a lower degree of near-surface solvent trapping. If we neglect the first two data points, a best fit to the data leads to a power law in which the solvent loss is proportional to t^2 . There is still, nevertheless, strong deviation from a case II diffusion.

In summary, the complete near-surface solvent evaporation process for a polymer melt has been monitored *in situ* for the first time. We have revealed a new aspect of the process by focusing on the region close to the sample surface. Further experimentation with other classes of polymer and other solvents would almost certainly provide even more insight.

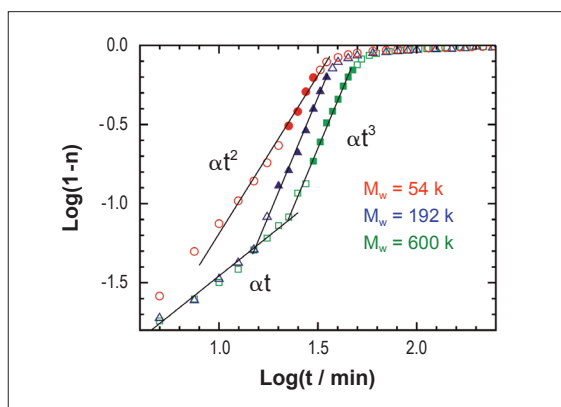


Figure 2: Near-surface solvent loss $1-n$ as a function of time t for $P(nBA\text{-}stat\text{-}MA)$ with $M_w = 54 \cdot 10^3$ g/mol (circles), $M_w = 192 \cdot 10^3$ g/mol (triangles) and $M_w = 600 \cdot 10^3$ g/mol (squares). The data points for stages with solvent enrichment at the surface are shown as filled symbols, whereas open symbols represent a homogenous distribution of the solvent.

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