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Following the Kinetics of a Chemical Reaction in Ultrathin Supported Polymer Films by Reliable Mass Density Determination with X-ray Reflectivity

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Ultrathin supported films of polymers are frequently used for applications such as transistors,[1] sensors,[2] intelligent materials,[3] and model systems,[4] to name but a few. Many of these functionalities involve chemical reactions, but analysis of such films is challenging because of the minute amount of film material in contrast to the copious amount of substrate. Often the surface morphology is probed by atomic force microscopy and the film thickness with ellipsometry or profilometry, while the chemical composition is determined by X-ray photoelectron spectroscopy (XPS) or various surface-sensitive applications of IR or Raman spectroscopy. Mass densities of ultrathin polymer films, however, have rarely been reported. In this communication, we report that reliable determination of the mass density of an ultrathin polymer film by X-ray reflectivity (XRR) is feasible within limited thickness regimes. Furthermore, we demonstrate how the density analysis can be applied to follow the kinetics of a chemical reaction occurring within the film. Previous efforts to measure the density of organic films have imposed limitations on the instruments or materials, requiring a special (multichannel) detector[5] or deuterated samples.[6] This also includes the recently introduced resonant soft X-ray reflectivity technique designed to enhance the contrast within polymer bilayers, which utilizes a synchrotron beamline for data collection.[7] A more effortless method to follow organic reaction kinetics on solid supports by magnetic levitation was published recently by Mirica et al.,[8] but this method is not applicable to thin films with lateral dimensions of macroscopic scale.

It is well-recognized that XRR is able to probe the electron density of thin films from hard (inorganic) materials.[9] The seminal problem with polymers and XRR, on the other hand, lies in the relatively small electron density of organic materials. If the density of the substrate exceeds that of the film, the XRR determination of density becomes increasingly unreliable. The usual way to determine the mass density is to deduce it from the position of the critical angle, but this method is not sensitive enough for soft materials.[5]

The qualities that are quantified in an XRR analysis include the thickness, roughness, and density of the supported film. In fact, these values do not directly emerge from an XRR measurement; they are parameters obtained from a numerical fit to the Parratt formalism,[9,10] which attempts to simulate the reflectivity curve. While the thickness value from this fit is entirely accurate for any film material, one can estimate arbitrary density values close to the actual density for sparser (organic) materials and still obtain a reasonable fit. This unreliability stems largely from the influence of film roughness on the reflectivity curve, as will be demonstrated in the following. What has remained unnoticed, however, is that within certain thickness intervals, the density determination is reliable. The key requirement here is that the reflectivity curve must exhibit a local minimum directly after the critical angle α_c (i.e., the angle below which total reflection of X-rays occurs). Figure 1a shows calculated XRR curves for 10 nm thick films of polystyrene-like materials (C_8H_7) with densities of 1.00−1.10 g cm^{-3} on silicon (Si/SiO$_x$) substrates. (The density of polystyrene is close to 1.05 g cm^{-3}.) Below α_c, total reflection takes place, after which interference fringes occur. The period (width) of the fringes indicates the thickness of the film. The density, on the other hand, affects the amplitude. It is important to note that changing the density in the simulation has a measurable effect only at the local minima between the interference fringes, whereas the change as measured in the logarithmic scale is roughly equal between the minima (i.e., α_c remains unchanged for the diverse densities).

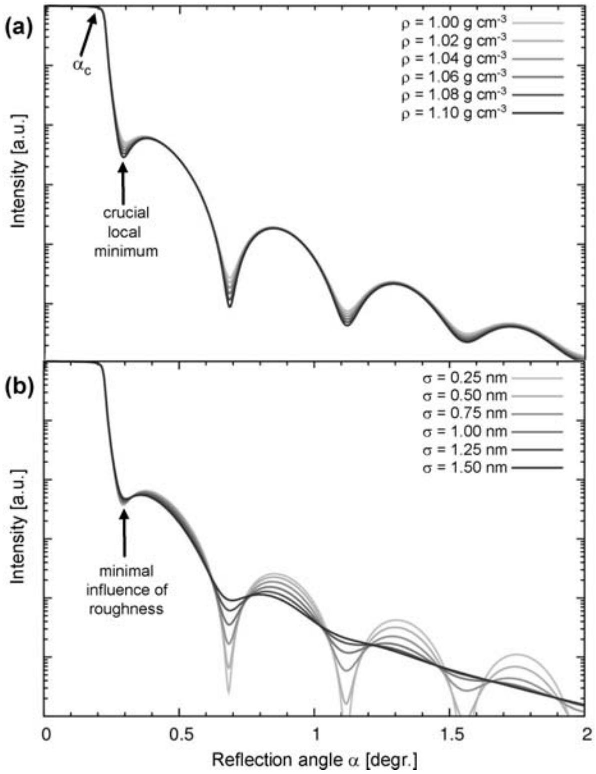

Figure 1. Calculated XRR curves for a structure containing 10 nm of a polystyrene-like material (C_8H_7) on a Si/SiO$_x$ substrate. (a) Influence of mass density variation (constant roughness of 0.75 nm). (b) Influence of roughness variation (constant density of 1.05 g cm^{-3}).

However, the contrast between the different densities is lost when the roughness of the film varies, as shown in the simulations for corresponding films in Figure 1b. Indeed, a small change in film roughness, which could easily occur during a chemical reaction or

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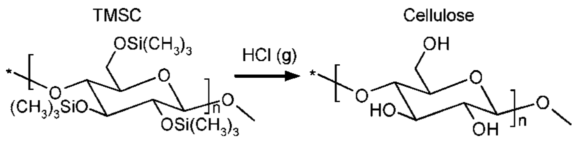
Scheme 1



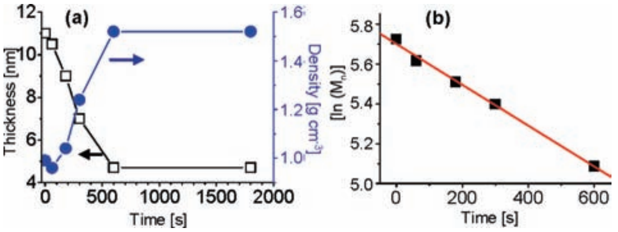


Figure 2. (a) Thickness and mass density of TMSC during the course of its hydrolysis to cellulose, as monitored by XRR. (b) Natural logarithm of the average molar mass of TMSC during the course of its hydrolysis to cellulose, as calculated from the thickness and density values.

swelling of the film, for example, results in drastic alterations in the XRR curves, and these alterations are severe enough to hide the subtle contrast caused by the mass density (Figure 1b vs 1a). In other words, the mass density determination is bound to be unreliable if the roughness of the film is unknown. However, the alterations due to varying roughness do not appear in the first local minimum of the fringe that is closest to α_c (Figure 1b). It is therefore necessary that both local minima in the fringe closest to α_c are properly visible. Because the film thickness determines the period of the fringes, the existence of the first fringe with both local minima depends strongly on the thickness. The simulations indicate that the ultrathin thickness regime where the fringe nearest to α_c is present with both of its local minima is 5−17 nm. The next corresponding ultrathin thickness range is 40−50 nm. In other words, supported polymer films with thickness values in the range 5−17 or 40−50 nm are eligible for reliable determination of mass density using XRR. The thickness constraints also depend on the mass density of the film and must be tested separately for each material. A mathematical treatise on the problem is featured in the Supporting Information.

The method was tested on a small set of samples consisting of common synthetic polymers and biopolymers deposited as ultrathin films on silicon supports with thicknesses of 6−17 nm. The densities correlated well with the literature values (Table S1 in the Supporting Information). We emphasize that the density determination is feasible with ordinary, untreated polymers and supports and can be performed with most conventional X-ray diffractometers.

If the thickness and density of an ultrathin film can be monitored and the stoichiometry is known, it is possible to follow the course of a chemical reaction in the film. As a sample reaction, we chose the hydrolysis of trimethylsilyl cellulose (TMSC) to cellulose by vapor-phase HCl (Scheme 1). This is a well-characterized reaction whose occurrence in ultrathin films has been established in several instances.[11] At room temperature, the reaction spans ~10 min when the HCl concentration is 0.5 M,[12] which is a pragmatically attractive rate for this study.

Figure 2a reveals the phases of the reaction in an ultrathin TMSC film as it gradually hydrolyses to cellulose. The removal of the bulky TMS group and the formation of a tight hydrogen-bonding network of cellulose results in a decrease in thickness. Similarly, the density of the film increases because of the contrast between the denser cellulose and sparser TMSC. In 600 s, the transformation to cellulose is complete. The time scale correlates well with previous characterization by XPS and IR spectroscopy of the same reaction with similar films.[12]

An ultrathin film is essentially a two-dimensional structure, meaning that only its thickness is bound to change during the reaction, not its lateral dimensions. Obviously, the awareness of mass density, thickness, and stoichiometry of the reaction (Figure 2) enables the calculation of the average molar mass of the film (M_n) at a certain point of the reaction (see the Supporting Information).

When the natural logarithm of the molar mass is plotted as a function of time, the order and rate constant of the reaction of TMSC to cellulose with 0.5 M HCl can be resolved (Figure 2b). Since the plot in Figure 2b has a linear fit, the reaction is first-order, and the rate constant obtained from the slope of the fit is $k = 1.02 \times 10^{-3}\ \mathrm{s}^{-1}$.

In principle, it is also feasible to follow the reaction kinetics in ultrathin polymer films with, for example, reflection absorption IR spectroscopy or XPS. However, IR spectroscopy requires calibration for reliable quantitative analysis, which can be a laborious task especially in the case of ultrathin films. Quantification of XPS data, on the other hand, depends on the escape depth of photoelectrons, which exhibits exponential decay over the sample cross section. In addition, the decay is different for different materials.[13] Because the principle of XRR is based on the interference between the substrate−sample and sample−air interfaces, it provides uniform information over the whole cross section without the need for calibration.

In summary, reliable determination of the mass density for ultrathin supported polymer films by XRR within certain thickness constraints has been demonstrated. Simultaneous mass density and thickness determination can be used to follow a chemical reaction in an ultrathin polymer film.

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Supporting Information Available: Experimental details, mathematical treatise on the density determination, experimental results from density determinations for various polymer films, and calculation of molar mass from density data. This material is available free of charge via the Internet at http://pubs.acs.org.

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