Experimental Report

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Title:	Solvent driven formation of micellar structures at the free interfaceof diblock copolymer films		

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Researh Area: Soft condensed matter

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Samples: Poly(n-butylmethacrylate -block-styrene)

Instrument	Req. Days	All. Days	From	To
FIGARO	4	4	20/05/2013	24/05/2013

Abstract:

We plan to follow the formation of micellar structures in solution cast samples during solvent evaporation of selective solvents using in-situ neutron reflectivity (NR). Two diblock copolymers will be addressed, one consisting of 50 wt% n-butylmethacrylate (PnBMA) and 50 wt% deuterated styrene (dPS) and one copolymer consisting of 65 wt% PnBMA and 35 wt% dPS. By the use of a selective solvent for the PnBMA block we create micelles in the solution which is subjected to drying. We plan to investigate the interplay between film formation and drying. The FIGARO reflectometer offers the necessary horizontal geometry along with a very high flux for the desired high time resolution in this in-situ experiment. Together with the recently performed experiment using non-selective solvents we will get a full understanding on in-situ structure formation in diblock copolymer films out of drying solutions.

Solvent driven formation of micellar structures at the free interface of diblock copolymer films

(Proposal 9-11-1638)

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Solution casting is a widely used technique for the preparation of polymer films both, in science and in industries. Exemplary applications reach from the fields of organic electronics, audio and video tapes to protective coatings and also to adhesive films in daily life or medicine. During the casting process the evaporation rate of the solvent plays an important role in tuning the desired polymer morphology.

Studies exist concerning the drying process of glassy polymer films[1,2] and also computer simulations have been carried out to predict the solvent content of polymer films as a function of time.[3] Diethert el al. had investigated the near surface evaporation during casting of statistical copolymers and found unexpected evaporation regimes in the drying process.[4] But to the best of our knowledge no investigations of this kind have been carried out for diblock-copolymers which show a more complicated behavior compared to homopolymers due to the two components with different glass transitions in the polymer chains, additional segregation effects and most important an already in solution existing structure. In-situ neutron reflectivity (NR) measurements at the instrument FIGARO are the method of choice to investigate the interplay of solvent evaporation and structure formation in the drying film. The instrument provides the necessary setup to measure liquid films with a very high flux leading to a very high time resolution.

In the **performed experiment** we addressed the drying process of a diblock copolymer having a molecular mass of 124k.[5] The diblock polymer consists of 65 wt% n-butylmethacrylate (nBMA) and 35 wt% deuterated styrene (dS). The polymer is dissolved in deuterated solvents for a high contrast in the neutron scattering experiments. The in-situ NR measurements were performed at FIGARO instrument. The substrate was placed in a sample chamber to have a controlled solvent evaporation and carefully aligned to be horizontal. The individual diblock copolymer solutions were deposited and the NR signal was collected during solvent evaporation. Due to the strong changes in sample surface height during evaporation, the sample had to be aligned periodically. Selective solvents such as deuterated dimethylformamide (DMF, $(CD_3)_2NCOD$), N,N-dimethylacetamid (DMAc) and acetone were used.

In case of deuterated DMF (dDMF), Figure 1 a-f shows NR curves at different times, from the freshly dispensed solution to the finally dry state after 48 h. In the beginning the critical edge of the almost pure deuterated solvent is clearly visible with no further visible vertical structure. During the drying process the critical edge moves to smaller q_z values owing to the fact that the mean scattering length density (SLD) evolves towards the average bulk SLD of the diblock polymer. Already after 17 h a shoulder at roughly $q_z \approx 0.02$ A^{-1} is apparent, indicating substructures. The plateau of total reflection drops continuously until no proper reflectivity curve is visible anymore after 38.9 h. Surprisingly, a plateau arises for later times at around 45.5 h before it again drops and loses the shape of a proper NR measurement. The shoulder mentioned above and the drop and rise of the plateau are clear indications of a drying process consisting of several stages. The precise modeling of the whole process is still ongoing.

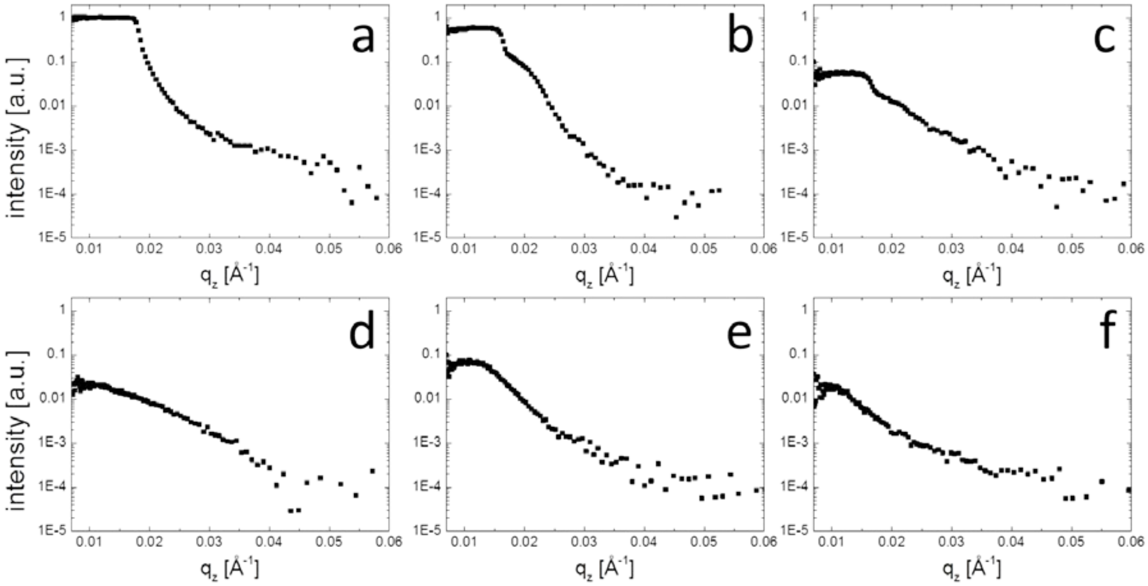

Figure 1. Neutron reflectivity (NR) curves of PnBMA-b-dPS (65wt% and 35wt%, respectively) recorded during drying from dDMF solution. a) NR measurement on the freshly dispensed solution. b) NR measurement taken at time t=17 h. c) NR at t=35.5 h. d) NR at t=38.8 h. e) NR at t=45.5 h. f) NR of the finally dry sample at t=48 h.

In addition to the specular scattering the off-specular scattering was also probed on the area detector of the FIGARO instrument.[5] Figure 2 shows the off-specular scattering along with the specular intensities around the critical edges of dPS and the solvent dDMF versus time. While during the drying process different regimes are clearly visible, the dry state is reached after 48 h. In the first 25 h the off-specular scattering seems to level off and reach a plateau together with the two other curves, but instead strongly increases all of a sudden, shows two peaks and finally levels off with a steep decay to a constant level after 48 h.

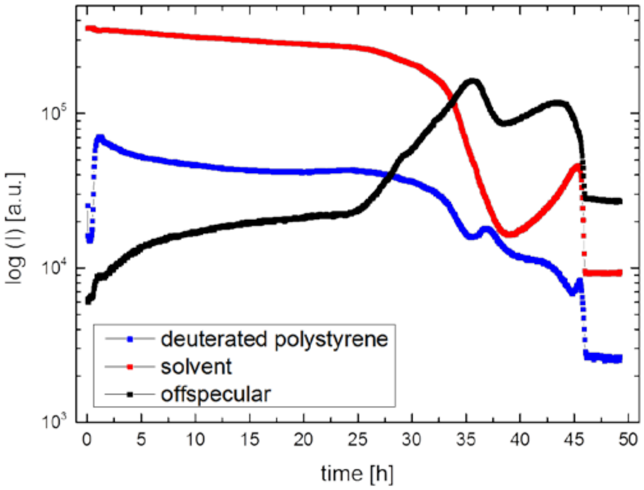

Figure 2. Integrated off-specular intensity evolution (black) along with the integrated intensities around the critical edges of dPS (blue) and dDMF (red).

The features in the three different curves in Figure 2 also correlate, which proves that we observe real reorganization processes. Already without precise fitting of every NR curve a surprisingly complex drying process with several stages is observed. Modeling of the reflectivity data will allow for extraction of precise depth-profiles which will reveal the mechanisms and kinetics of the drying of a micellar solution and its different stages.

References:

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5) Müller Buschbaum, Peter; Gutfreund, Philipp; Metwalli, Ezzeldin; Mosegui Gonzalez, Daniel and Schindler, Markus. (2013). Solvent driven formation of micellar structures at the free interface of diblock copolymer films. Institut Laue-Langevin (ILL) doi:10.5291/ILL-DATA.9-11-1638