Experimental report

05/03/2019

Proposal: **9-11-1842** **Council:** 4/2017

Title: Developing off-specular neutron reflection to study the instability at the buried soft interface - continuation proposal

Research area: Soft condensed matter

This proposal is a continuation of 9-11-1783

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Samples: Si
PMMA
PS

Instrument	Requested days	Allocated days	From	To
D17	4	2	19/03/2018	21/03/2018

Abstract:

A bilayer system of two immiscible polymers of certain thickness is destabilised by the van der Waals forces at the interface via spinodal dewetting. We observed that during the first beamtime and obtained new high quality and novel results but the data are not complete due to technical reasons connected to the optimisation of the samples: in order to get a quantitative understanding of the phenomenon and to publish the results, more data are needed. Further measurements of the thickness dependence need to be performed since only one thickness was fully measured at different annealing times. This can easily be accomplished with an additional beamtime. We plan to measure 4 additional samples of the bilayer system Si/dPS/hPMMA of Mw = 60k for dPS and Mw = 298k for hPMMA with varied thickness of dPS: 110, 130, 150, 180 Å at 5 annealing times in order to observe the change in characteristic spinodal dewetting wavelength as a function of the dPS layer thickness. For these systems we can accurately predict the time it takes for the spinodal dewetting to occur.

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This proposal allowed us to finalize the measurements started previously within proposal 9-11-1783 and also extend it to measure additional samples which were based on the experience gained previously.

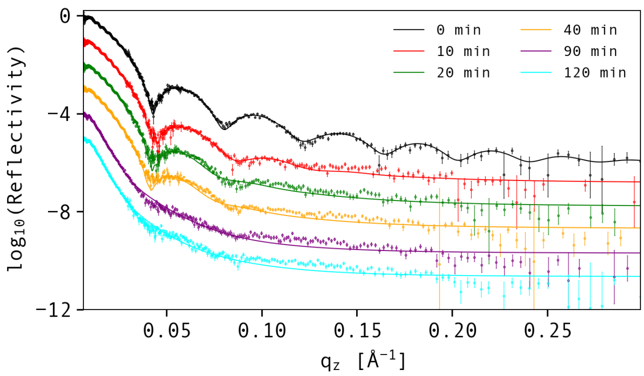
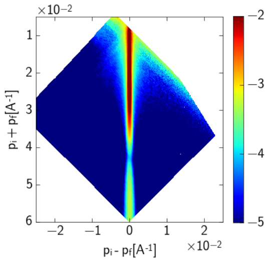


Figure 1: Specular reflectivity for the bilayer sample with increasing annealing times.

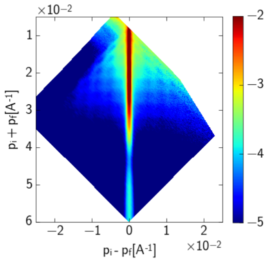
Several bilayer and trilayer samples of polystyrene (PS) and poly methyl methacrylate (PMMA) were prepared and measured. The samples were prepared by first spin coating the bottom layer (protonated PS (hPS) for trilayers and deuterated PS (dPS) for bilayers) onto a silicon substrate and then in the case of bilayers depositing the top hPMMA film with a technique of floating. In the case of trilayers, the middle dPMMA film was spin coated from an acetic acid solution with the top hPS being floated as before.For the systems shown in table , we have been able to record the whole process of film rupture. By using both specular and off-specular measurements, we have allowed the increase of the roughness until the film breaks up completely as no more Kiessig fringes coming from the thin layer are visible (see figure 1).

Sample	Layer 1	Layer 2	Layer 3
Bilayer	dPS (60k) 176 Å	hPMMA (298k) 1485 Å	-
Trilayer	hPS (630k) 1700 Å	dPMMA (53k) 170 Å	hPS (630k) 1700 Å

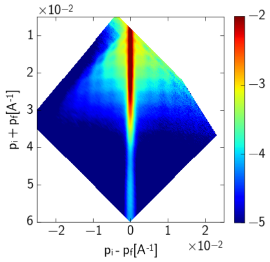
As can be seen in figure 1, the breakup of the bottom layer in the bilayer sample is very well visible in specular reflectivity, where the Kiessig fringes correspond to the dPS layer. With increasing annealing time at $T = 160\,^{\circ}{}^{\circ}\mathrm{C}$ which is well above the glass transition temperature, the fringes start to dissapear. Towards the end of the process also the scattering length density starts to decrease, signifying the breakup of the thin dPS film into domains (droplets). Simultaneously, off-specular measurements were performed and the evolution is well visible also in figure 2. There is an increase in off-specular intensity, signifying the formation of correlated in-plane structure at a buried interface. Complete analysis will be performed in near future based on a novel distorted wave Born approximation (DWBA) algorithm developed for and with the help of these experiments.



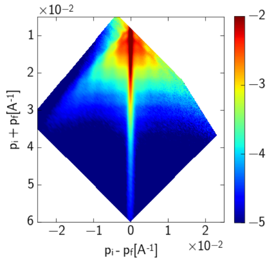
(a) $t_{\mathrm{ann}} = 0\,\mathrm{min}$



(b) $t_{\mathrm{ann}} = 20\,\mathrm{min}$



(c) $t_{\mathrm{ann}} = 40\,\mathrm{min}$



(d) $t_{\mathrm{ann}} = 120\,\mathrm{min}$

Figure 2: Evolution of film rupture in a bilayer observed by off-specular scattering. Different panels show the increasing annealing time at 160 ° °C.