Experimental report

14/02/2017

Proposal: **9-11-1783** **Council:** 4/2016

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

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: deuterated PMMA and PS, PMMA and PS thin films on silicon substrates

Instrument	Requested days	Allocated days	From	To
D17	6	4	08/12/2016	12/12/2016

Abstract:

In this proposal we are planning to study the early stage of polymer instability at buried interfaces by developing the off-specular neutron reflection. The destabilisation of the interface of a polymer/polymer systems by long range forces will be followed at the early stage by a detail analysis of the off-specular reflection signal analysed in the DWBA approach combined with the specular reflection. The effect of Van der Waal forces on the stabilisation or destabilisation of the interface will be also probed. This project will develop the use of off-specular scattering at ILL, an important tool for the interface analyses still not fully explored in soft matter, and is in the frame of a ILL PhD student that will start in April 2016.

Developing off-specular neutron reflectometry to study the instability at the buried soft interface

Experiment: 9-11-1783

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The physics of the instability of thin polymer layer combines both thermodynamics and fluid flow to produce ordered structures of different length scales [1]. These ordered structures, when created in buried systems, are not easily accessible for in-situ observation since the investigation of the profiles, both perpendicular and lateral, is not possible with imaging techniques. One important dewetting process is via the destabilisation of the thermal fluctuations at the interface: spinodal dewetting. The unstable film, in this case polystyrene (PS) is driven by Van der Waals (VdW) forces: in particular case of PS film of high molecular weight and thickness of around 80 - 300 Å sandwiched between two thick polymethylmethacrylate (PMMA) films and deposited on Si. The PS film will tend to dewet via the spinodal process [2, 3]. The characteristic length will depend on the PS thickness as VdW forces will tend to destabilise the thermal fluctuations at the interface. The interface is expected to grow with a characteristic wavelength related to the growth of the fastest wave and in turn on the thickness of the sample. Finally the layer will break into droplets. This process can be observed indirectly by specular NR or directly using off-specular NR. It is particularly interesting in the early stages where a clear signature of the effect is visible in the off-specular scattering as scattering from a "grating-like" structure. The dewetted structure in this stage of dewetting appears similar to a diffraction grating.

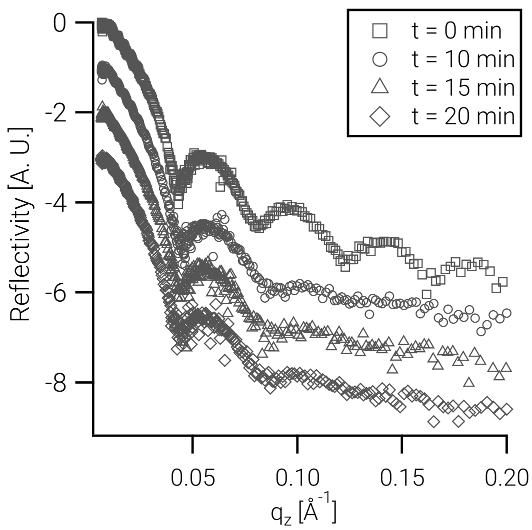
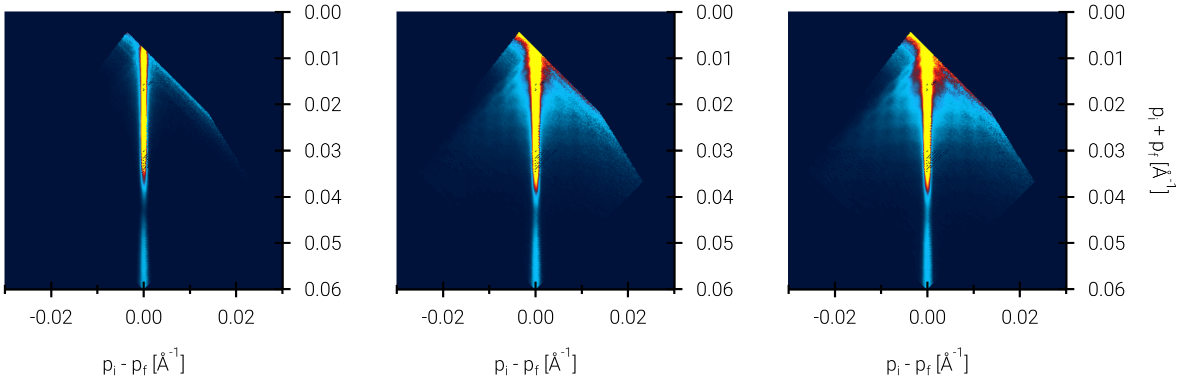


Figure 1: Specular reflectivity of a PS/PMMA bilayer. Fall in intensity of Kiessig fringes attributed to the thinner layer can be observed with increasing annealing time. Curves are offset by factor 10 for clarity reasons.

A number of measurements in specular and off-specular NR were performed on the D17 reflectometer in time-of-flight mode on bilayer dPS/hPMMA and trilayer hPMMA/dPS/hPMMA samples of various layer thicknesses where the bottom layer was spin coated onto the surface of a Si substrate. Further layers were floated on top. During the experiment, the samples are annealed above $T_g = 160\,^{\circ}\mathrm{C}$. Due to technical reasons connected to finding the onset of spinodal dewetting, only one trilayer and one bilayer sample yielded successful results. However, this gives very encouraging results, as for a given molecular weight and composition we are now able to predict the time scale and given more beamtime further measurements should be straightforward.

The rupture of the layer into droplets has two distinct phenomenological stages. First, the thermal fluctuations at the interface start to increase in amplitude. Off-specular signal can be observed, but for now without any pronounced structure. In specular reflectivity curves this can be seen as a decrease in amplitude and eventually disappearance of Kiessig fringes at higher



(a) t = 0 min (b) t = 15 min (c) t = 20 min

Figure 2: Dewetting process as seen by off-specular reflectivity at 3 different annealing times.

q_z values. When the spinodal dewetting starts to proceed with a single pronounced wave, an ordered diffraction pattern appears in the off-specular signal. It resembles a diffraction grating, with regular spacing between the peaks. At the same time a steeper slope of the specular reflectivity curves can be seen. This is usually connected to a smaller SLD value, but can in our case be attributed to the projected roughness being so high that the layers already start mixing. At that time it is hard to speak about stratified layers anymore and fitting with simple SLD models becomes impossible. The evolution of the process in specular reflectivity can be seen in Fig. 1 and in off-specular reflectivity in Fig. 2.

As can be seen a dPS/hPMMA bilayer with dPS thickness of 150 Å clearly shows a very regular and structured off-specular signal after $\sim$ 30 min. The decrease in specular reflectivity is only presented for the bilayer, but a trilayer (which is one of our previous measurements and was this time confirmed as being well reproducible) shows the exact same behaviour described before. It is also visible that the samples still contain a fairly pronounced layer composition, as the amplitude of the first Kiessig fringe is very high. This means that they could be annealed for a few further steps, should time permit. The grating-like pattern visible in off-specular would then also increase. For true quantitative data analysis in the scope of DWBA, we need to record more data in order to obtain better statistics. That means measuring further samples of various thicknesses, e.g. 100 Å, 120 Å, 140 Å, 170 Å and 190 Å. Now that some samples were successfully measured and the time which is required for spinodal dewetting to start has been determined, measuring additional samples should be straightforward. The plan is to apply for additional beamtime in order to complete the data series and prepare for publication.

Bibliography

[1] Richard A. L. Jones and R. W. Richards. *Polymers at surfaces and interfaces*. Cambridge University Press, Cambridge ; New York, 1999. ISBN 978-0-521-47440-5.

[2] Michele Sferrazza, M. Heppenstall-Butler, Robert Cubitt, D. Bucknall, J. Webster, and Richard Anthony Lewis Jones. Interfacial instability driven by dispersive forces: The early stages of spinodal dewetting of a thin polymer film on a polymer substrate. *Physical review letters*, 81(23):5173, 1998.

[3] J. P. de Silva, M. Geoghegan, A. M. Higgins, G. Krausch, M.-O. David, and G. Reiter. Switching Layer Stability in a Polymer Bilayer by Thickness Variation. *Physical Review Letters*, 98(26), June 2007. ISSN 0031-9007, 1079-7114.