Experimental report

03/10/2017

Proposal: 9-11-1782 **Council:** 4/2016

Title: Probing the effect of polymer adsorption on the thermal fluctuations in polymer/polymer systems by specular and off-specular reflection

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	5	4	24/09/2016	26/09/2016
			07/11/2016	09/11/2016

Abstract:

In this proposal we will study the effect of the adsorption of polymer chains onto solid surfaces on the interfacial width of polymer/polymer system. We expect that the adsorption will tend to suppress the capillary wave contribution of the width (the intrinsic width could also be affected). We will study this by pre-adsorbing the polymer layer, washing the not adsorbed chains and deposing another polymer on top. Moreover by changing he thickness of the films for the adsorbing layer, and in turn the distance of the width from the adsorbing interface, we will try to see the development of the full spectrum of the thermal fluctuations at the interface. The off-specular scattering from the thermal fluctuations will be analysed in term of the DWBA approach. This is in the frame of an ILL PhD student that will be starting in April 2016.

Probing the effect of polymer adsorption on the thermal fluctuations in polymer/polymer systems by specular and off-specular reflectivity

Experiment: 9-11-1782

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The interfacial width between two immiscible polymers is composed of two terms $\Delta^2 = \Delta_0^2 + \langle \Delta\zeta^2 \rangle$, where Δ_0^2 is the intrinsic term and $\langle \Delta\zeta^2 \rangle$ is the capillary wave term: the contribution of the two parts can be studied by combined means specular[1] and off-specular neutron reflectivity: the fluctuations at the interface can be analysed using the Distorted wave Born approximation (DWBA) formalism with the in-plane correlation function equal to the modified Bessel functions of the second kind of 0^{th} order [2, p. 160]. By adsorbing the first layer onto a surface, prior the deposition of the second film, a modification of the capillary wave spectrum could be obtained.

The recent neutron reflection experiment using D17 at ILL had the goal to probe the effect of the chain adsorption on the development of the interfacial width between the two immiscible polymers: we argued that the effect could also depend on the interface-substrate distance and could be experimentally verified as a function of the thickness of the pre-adsorbed layer.

Two different series of samples were prepared in order to study the aforementioned phenomena: one where the bottom layer (with varying d-PS thickness from 90 Å to 1300 Å) was spin coated on to the substrate and then pre-annealed for 48 h at 160 °C in order to reach irreversible adsorption [3]. A thick layer of h-PMMA was then floated on top. Furthermore, the same set of samples was prepared, this time without the pre-annealing step. Both series were then further annealed at 160 °C for 12 h in order to reach equilibrium.

All the measurements were performed on the D17 reflectometer in time-of-flight mode first measuring the specular reflectivity curve for each sample shown in Fig. 1 for 3 representative samples and secondly the off-specular reflectivity. During the reduction process, the off-specular measurements were converted into $(p_i - p_f, p_i + p_f)$ space and are shown in Figs. 2 and 3. There is a clear difference in off-specular scattering between pre-annealed and non-annealed samples of various d-PS layer thickness. Pre-annealed samples show much less off-specular scattering compared to the other series which potentially shows that the thermal fluctuations are being suppressed by the macromolecules adsorbed on the substrate. The data are under a refined analysis.

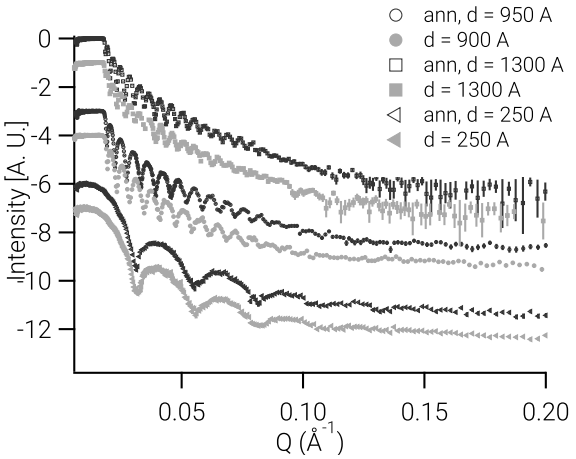
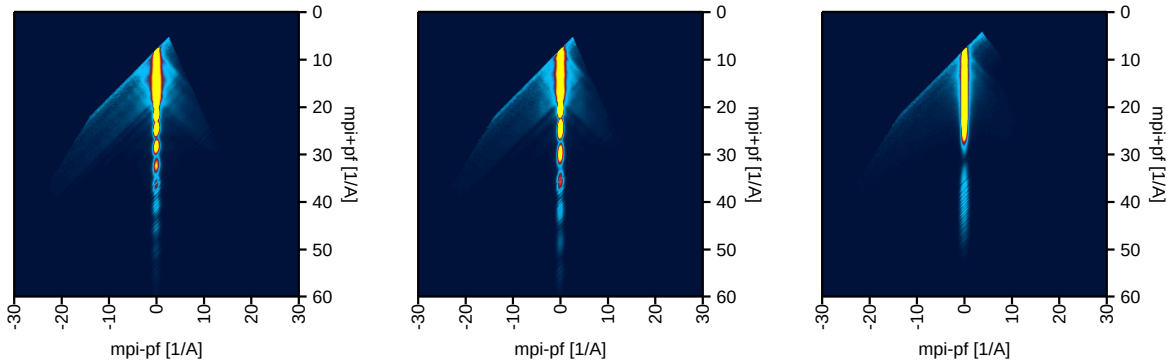
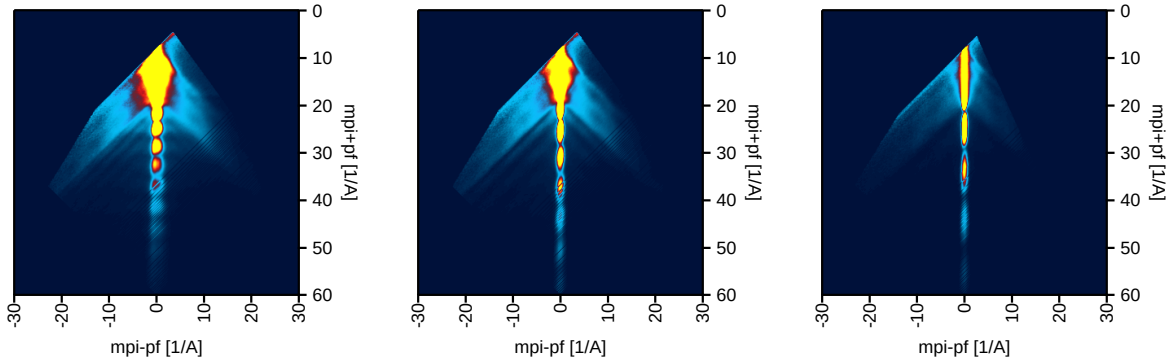


Figure 1: Specular reflectivity of selected pre-annealed (ann) and non pre-annealed samples of PS/PMMA polymer bilayer. Curves are offset and grouped together for clarity reasons.



(a) Adsorbed, $d_{\text{d-PS}} = 1300\,\text{Å}$ (b) Adsorbed, $d_{\text{d-PS}} = 950\,\text{Å}$ (c) Adsorbed, $d_{\text{d-PS}} = 250\,\text{Å}$

Figure 2: Off-specular reflectivity of pre-annealed samples of different thickness of d-PS layer.



(a) Non-adsorbed, $d_{\text{d-PS}} = 1300\,\text{Å}$ (b) Non-adsorbed, $d_{\text{d-PS}} = 900\,\text{Å}$ (c) Non-adsorbed, $d_{\text{d-PS}} = 250\,\text{Å}$

Figure 3: Off-specular reflectivity of non pre-annealed samples of corresponding thicknesses to Fig. 2.

Bibliography

[1] Michele Sferrazza, C. Xiao, Richard Anthony Lewis Jones, David G. Bucknall, J. Webster, and J. Penfold. Evidence for capillary waves at immiscible polymer/polymer interfaces. *Physical review letters*, 78(19):3693, 1997.

[2] Jean Daillant and Alain Gibaud, editors. *X-ray and Neutron Reflectivity*, volume 770 of *Lecture Notes in Physics*. Springer Berlin Heidelberg, Berlin, Heidelberg, 2009.

[3] Caroline Housmans, Michele Sferrazza, and Simone Napolitano. Kinetics of Irreversible Chain Adsorption. *Macromolecules*, 47(10):3390–3393, May 2014.