Experimental report

23/08/2023

Proposal: 9-11-2090 **Council:** 10/2022

Title: Hysteresis in polymer/small-molecule mixtures for OPV applications

Research area: Soft condensed matter

This proposal is a new proposal

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Samples: Polystyrene
bis-adduct phenyl-C60-butyric acid methyl ester

Instrument	Requested days	Allocated days	From	To
D17	4	4	22/06/2023	26/06/2023

Abstract:

Organic photovoltaics (OPVs) are candidates for the large-scale capture of solar radiation, due to the potential to process these materials in large areas at low cost. However, considerable challenges exist in terms of lifetime and robustness of performance. This proposal forms part of a wider effort in which our motivation is to complement device optimisation strategies with in-depth studies of model systems, aimed at increasing the fundamental understanding of the materials science within polymer nanocomposite thin-films.

This proposal builds on the understanding that we have recently developed by systematically studying equilibrated polymer/small-molecule bilayer systems, using in-situ thermal annealing/neutron reflectometry. Equilibration occurs on annealing at sufficiently high temperature. However, in a number of cases we have observed examples of `non-equilibrium mixing¿ during isothermal annealing at lower temperatures; here extensive mass transfer occurs, but the system does not achieve thermodynamic equilibrium. The current proposal seeks to systematically investigate this behaviour, which is of key importance for working OPVs.

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The aim of this experiment was to measure the mixing between fullerene (BisPCBM) and polystyrene (PS) molecules in a bilayer geometry and investigate the 'non-equilibrium mixing' that can sometimes occur during isothermal annealing. During this experiment we performed neutron reflectivity (NR) measurements while *in-situ* annealing the samples in the beam. This was performed on a range of PS/BisPCBM bilayers. A relaxed resolution was used, enabling a full NR curve to be collected in 10 minutes (2 mins measurement with an incident angle of 0.8° and 8 minutes at 3°). After initial measurement at 80 °C (a temperature at which there is no mixing between the layers) samples were annealed isothermally for extended periods (between 1 and 3.5 hours), under vacuum, at a range of set-point temperatures (150, 160 or 170 °C – the actual sample surface temperatures were a few degrees below this). Some samples were then subjected to temperature cycling to measure the thermal reversibility of the sample composition profiles (which change as a function of temperature) and assess whether the samples have equilibrated. During thermal cycling the annealing temperature was raised to either 180 or 190 °C, then cooled in 10 °C steps to around 130 °C, then heated a second time in 10 °C steps to 180 or 190 °C, before final cooling to 80 °C. After a short wait time for temperature stabilisation (around 6-8 minutes following a 10 °C temperature step), NR measurements were performed at each temperature. Other samples underwent more limited investigations; these were just heated isothermally (at 150 or 160 °C) and measured repeatedly for an hour or so, then briefly heated/measured at either 180 or 190 °C and finally remeasured at the isothermal annealing temperature for another hour or so.

We measured samples containing both high molecular weight (MW) PS (300k) and low MW PS (5k). In all samples the bottom layer was initially pure BisPCBM, while the top layers were sometimes pure PS and sometimes a PS/BisPCBM mixture. While there was some evidence of Yoneda scattering on some of the 5k-PS/BisPCBM samples at incident angles of 0.8°, the 300k-PS/BisPCBM samples showed very little evidence of off-specular scattering. Examples of data and fits from a 300k-PS/BisPCBM bilayer (sample AH47, which initially had a pure PS top layer) that was isothermally annealed at 150 °C and then underwent temperature cycling, are shown in figures 1-3. The fits use bilayer models with 6 adjustable parameters; the thickness and scattering length density (SLD) of each layer, plus the buried interfacial roughness (interfacial width) and the sample surface roughness. The resolution in each fit was taken as that of the instrument (given in the data file). The fits for this sample (with the reduced NR data containing around 270 points) have a goodness-of-fit, χ^2, parameters of around 400 for all measurements. Figure 4 shows how the SLD of the (initially pure PS) changes as this sample is isothermally annealed, temperature cycled and finally cooled to 80 °C.

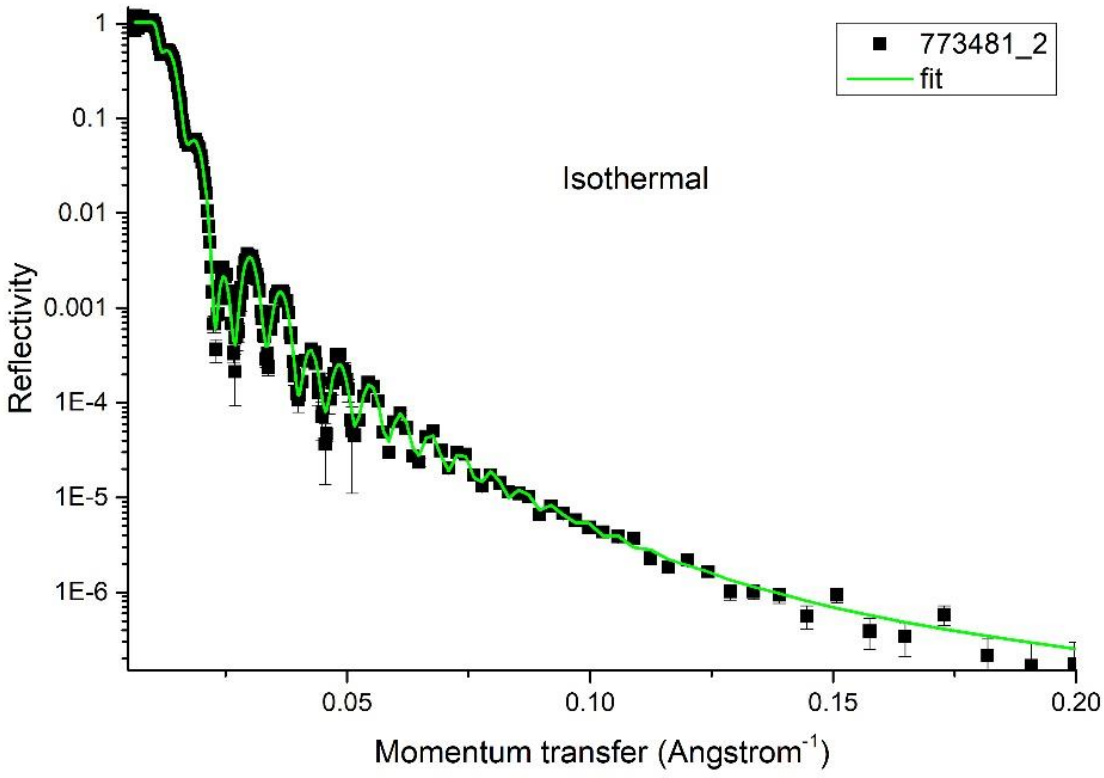

Figure 1; NR curve and fit for sample AH47 measured at 150 °C after isothermal annealing for 200 minutes.

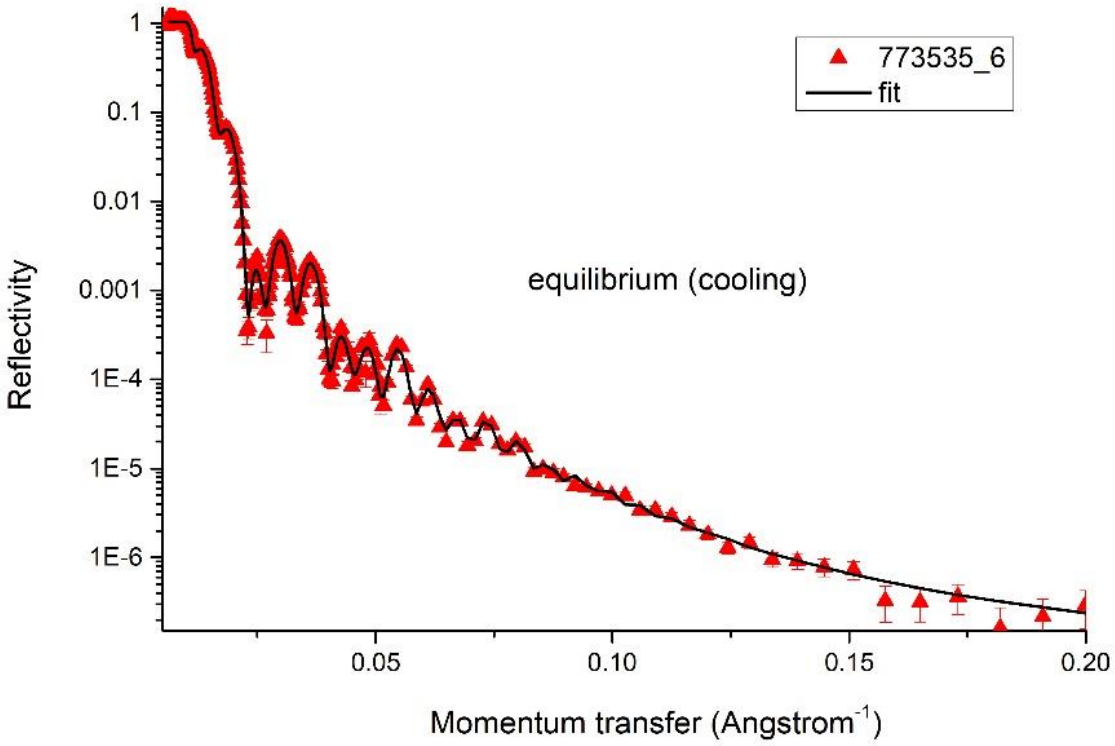

Figure 2; NR curve and fit for sample AH47 measured at 150 °C during thermal cycling (during first cooling).

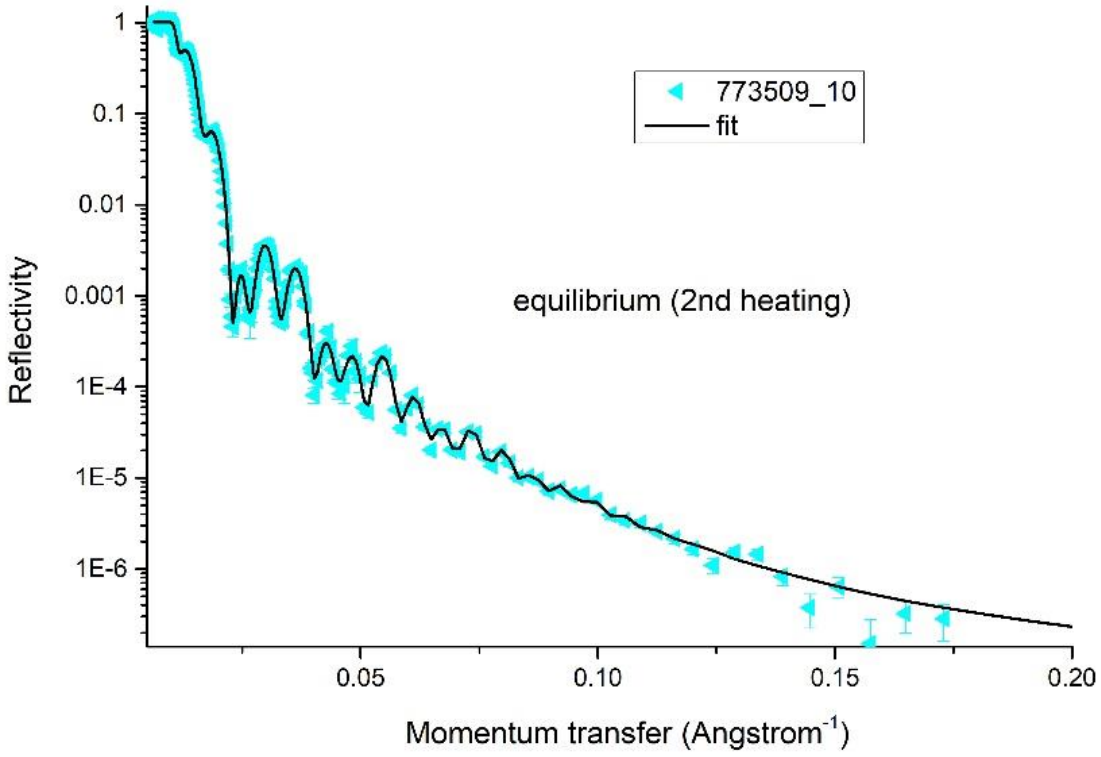

Figure 3; NR curve and fit for sample AH47 measured at 150 °C during thermal cycling (during second heating).

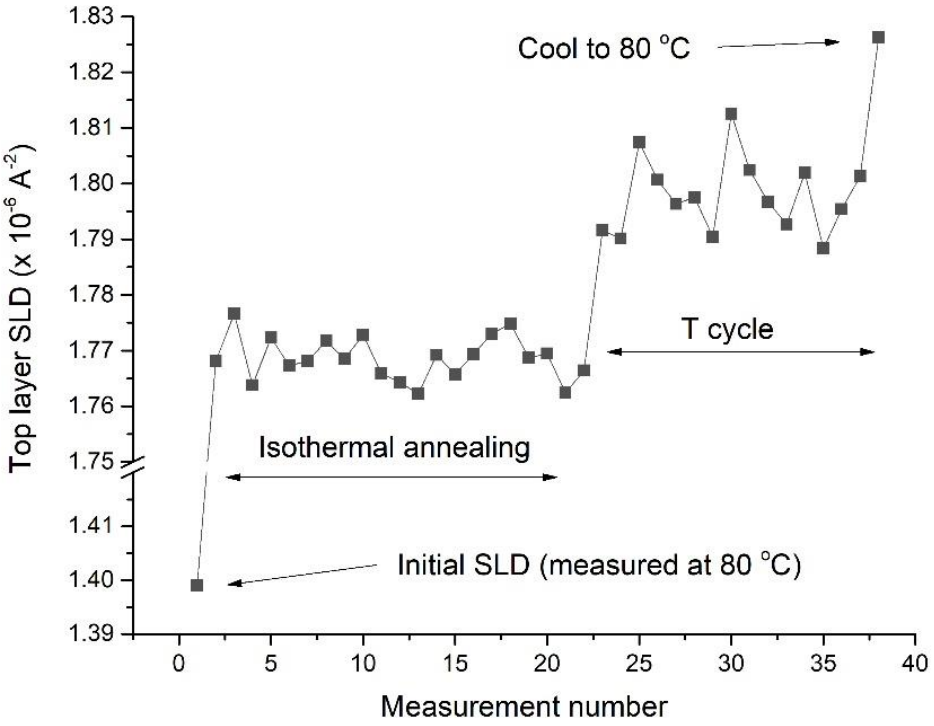

Figure 4; Top layer SLD fit parameter for sample AH47 during isothermal annealing at 150 °C and during temperature cycling (which involves equilibration at 180 °C followed by cooling to 130 °C, a second heating to 180 °C, and a final cooling to 80 °C).