Experimental report

21/06/2017

Proposal: **9-12-456** **Council:** 4/2016

Title: Continuation Proposal-Polymer/fullerene interfaces; Formation of a liquid-liquid equilibrium?

Research area: Soft condensed matter

This proposal is a continuation of 9-12-387

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Samples: Polystyrene
[6,6]-phenyl C61-butyric acid methyl ester (PCBM)
bis-adduct [6,6]-phenyl C61-butyric acid methyl ester (bis-PCBM)

Instrument	Requested days	Allocated days	From	To
D17	4	3	28/09/2016	01/10/2016

Abstract:

Organic photovoltaics 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 device-lifetime and robustness of performance. Polymer/fullerene mixtures can be fabricated into promising devices, but there is considerable sensitivity to material and processing parameters. This proposal forms part of a wider effort in which we seek to complement device optimisation strategies with an in-depth study of structure and kinetics, aimed at increasing the fundamental understanding of the materials science within fullerene/polymer films. We have discovered that model fullerene/amorphous-polymer bilayers undergo rapid mixing (long before the fullerene crystallises) to form a stable interface, with initial data suggesting broader interfaces for low molecular-weight (MW) polymer. This proposal will probe this interface as a function of the MW, temperature, annealing-time and starting thin-film composition-profile. The aim is to rigorously test the hypothesis that the film composition-profile results from the formation of a liquid-liquid equilibrium interface.

Probing a liquid-liquid equilibrium in polymer-fullerene bilayers;
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Organic photovoltaics (OPVs) offer a low-cost, large-area alternative to silicon-based solar cell technology. However, there are challenges to improving the efficiency and long-term stability and making this technology commercial. One aspect of this is the evolution of morphology and interfacial structure at elevated temperatures. A polymer-fullerene bulk heterojunction, as used in the active layer of many devices, can have complex behaviour with both components being able to crystallise. For this reason we have chosen a model system, PCBM and polystyrene, in a simplified bilayer geometry to enable an exploration of the fundamental science at play in these systems.

In 3 days of beamtime at D17 over September 28th to October 1st 2016 we performed in-situ and ex-situ annealing experiments on our PCBM/PS bilayers to determine the composition profile as a function of temperature, molecular weight and time. We found that after annealing, there is rapid mixing of the fullerene into the PS layer, but a bilayer composition profile is preserved. In comparison with theory (for bulk compositions and interfacial broadening), our evidence suggests that this is indeed an equilibrium situation. Annealing temperature did not play a significant role; annealing above the glass transition for longer than one minute was sufficient to obtain equilibrium.

For the in-situ annealed samples we took 30 second measurements over a limited q range, as well as full q-range measurements before and after annealing. We arrived a day early to calibrate the heater and had some issues with attaching the sample to the heating stage tightly enough to have good thermal & mechanical contact with the sample, but without bending the sample. The initial sample measurements were showing evidence of bending in the detector so we were careful to avoid this. As well as PCBM/PS bilayers we measured PCBM and PS single-layers to measure the thermal expansion that occur during in-situ heating. We obtained good quality data that we were able to fit well with a bilayer model for most samples (see figure below).

We also measured two bis-PCBM/PS bilayers; one in-situ and one ex-situ. This is a popular choice of fullerene derivative in OPVs and is interesting in our study as it does not crystallise, allowing us to explore longer timeframes in our annealing.

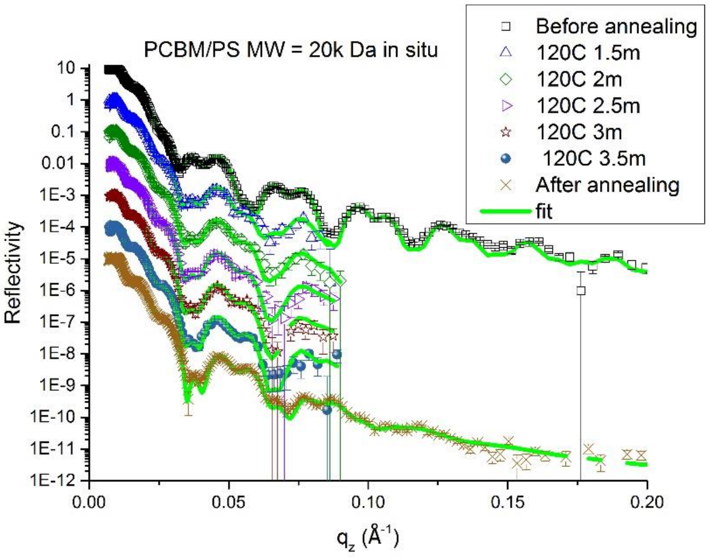

Figure 1:In-situ NR data and fits showing the evolution of the reflectivity curve from the full-q-range before annealing to the full-q-range after annealing, as well as examples of some in-situ 30 second limited-q-range measurements and fits.