Experimental report

18/12/2015

Proposal:	**9-12-387**	**Council:**	10/2014
Title:	Polymer/Fullerene interfaces; Formation of a liquid-liquid equilibrium?		
Research area:	Soft condensed matter		

This proposal is a new proposal

Main proposer:	**Anthony M. HIGGINS**
Experimental team:	Joao T. CABRAL Anthony M. HIGGINS Elizabeth HYNES
Local contacts:	Philipp GUTFREUND

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

Instrument	Requested days	Allocated days	From	To
FIGARO	0	2	20/07/2015	22/07/2015
D17	3	0		

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 efficiency, lifetime and robustness of performance. Polymer/fullerene mixtures can be fabricated into promising devices. However, there is considerable variation in the efficiency of these complex devices as a result of the sensitivity to a host of material and processing parameters. Here, we focus on a model fullerene/amorphous-polymer bilayer. Even in this simplified system (in which only one component can crystallise and the morphology can be well-controlled/characterised) we have uncovered significant complexity in the formation of different forms of fullerene crystal, which is strongly influenced by the thickness of the polymer layer. However, we have discovered that we are also able to use this system to form an interface between amorphous-fullerene and the polymer. This experiment will probe this interface as a function of the polymer MW, and test the hypothesis that the composition profile represents 2 co-existing phases in a liquid-liquid equilibrium.

Polymer/Fullerene interfaces; Formation of a liquid-liquid equilibrium?
Experimental Report 9-12-387

Organic photovoltaics (OPVs) are candidates for the large-scale capture of solar radiation, due to the ability to process these materials in large areas at relatively low cost. However, considerable challenges exist in terms of device efficiency, device lifetime and robustness of performance. This experiment forms part of a wider effort in which our motivation is to complement device optimisation strategies with an in-depth study of structure and kinetics in fullerene-polymer systems aimed at increasing the *fundamental understanding* of the materials science within fullerene/polymer films. This experiment builds on previous work that we have performed to understand the interplay between polymer/fullerene mixing and structure development (including film composition profiles and crystallization behavior) in model bilayers consisting of polystyrene (PS) layers on top of [6,6]-phenyl C61-butyric acid methyl ester (PCBM) layers (on a silicon substrate).[1] Our previous work was focused on the influence of polymer film thickness on behaviour. Experiment 9-12-387 looked at the molecular weight dependence of the composition profile that develops after annealing of the bilayers.

In 2 days of beamtime at Figaro in July 2015, we measured a series of annealed and unannealed PCBM/PS bilayers with various PS molecular weights (MW), ranging from 2000 (2k) to 300,000 (300k), using neutron reflectivity (NR). Around 20 samples were measured altogether. We also performed an initial assessment of the impact of annealing temperature and time (with annealing performed *ex-situ* prior to the NR measurements). We have been able to obtain good fits to most of this data using a simple bilayer model (see fig. 1). The composition profiles for most of the annealed bilayers with MW of 20k and above show a very consistent picture, in comparison to the unannealed bilayers, and in comparison to our previous findings[1]. Unannealed bilayers have a top (pure PS) layer with a scattering length density (SLD) of 1.37 +/-0.07 x 10^{-6} $Å^{-2}$, above pure PCBM (SLD=4.65 +/0.07 x 10^{-6} $Å^{-2}$)-, with a narrow interface (of roughness 4.1+/-2.8 x 10^{-6} Å) between the 2 layers. On annealing, the samples in this MW range all showed an increase in the SLD of the top layer (corresponding to a concentration of around 10% PCBM migrating into this layer), a reduction in the thickness, but not the SLD of the bottom (PCBM) layer, and a significant increase in the PCBM/PS-rich-layer interfacial width. We found very similar composition profiles for different annealing times and different annealing temperatures. For MW below 20k, the samples were more susceptible to dewetting of the top (PS) layer, and to the growth of fullerene crystals. Both of these phenomena can reduce the integrity of the layered structure of the samples and degrade the quality of the extracted fit parameters. This led to some scatter in the information (primarily the fit parameters for the interfacial width and layer SLDs) that we were able to extract for the lower MWs. We plan to submit a continuation proposal, in which we address these issues (by using lower temperatures and/or thicker PS layers) and improve the quality of the data at low MW.

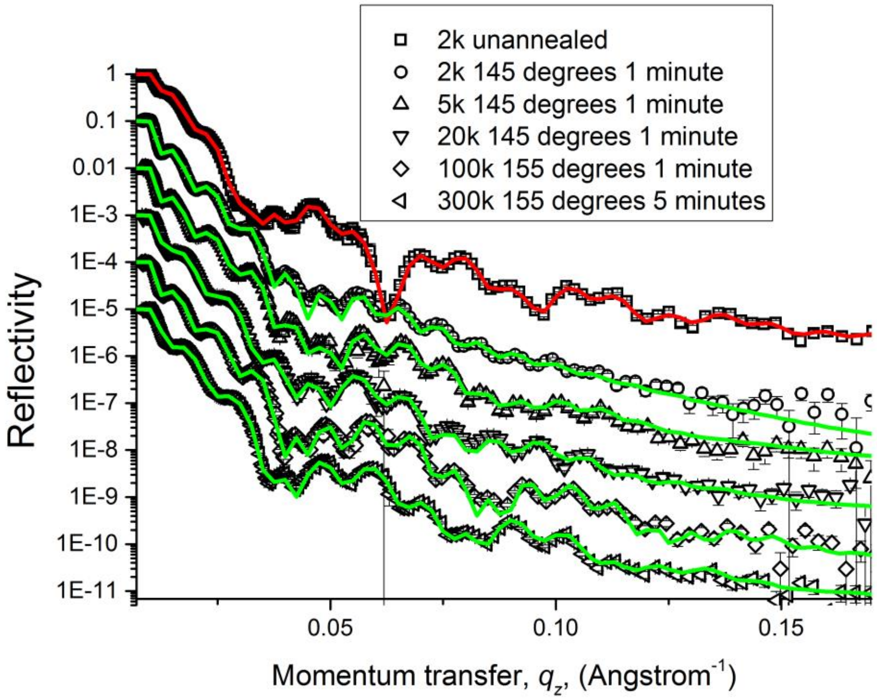

Figure 1 | Specular NR measurements and fits for *ex-situ* annealed PCBM/PS bilayers on silicon. NR versus momentum transfer normal to the substrate (q_z), for annealed and unannealed bilayers. All data shown is fitted with a bilayer model in which the thickness and SLD of each layer is allowed to vary. We also allow the interfacial width between the two layers and the sample surface roughness to vary (the robustness of the fitting procedure with respective to these parameters has been tested, and the surface roughness is also corroborated by AFM measurements). NR curves are offset with-respect-to the y-axis for clarity. Very little off-specular scattering is seen from any of the samples.

[1] Mon et al *Phys. Chem. Chem. Phys.* **17**, 2216 (2015)