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Neutron polarisation analysis of Polymer:Fullerene blends for organic photovoltaics

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ABSTRACT

The photogeneration process in polymer-fullerene organic solar cells relies strongly on the nanostructure and on the nano/picosecond dynamics occurring in these complex blends. Elastic and inelastic neutron scattering techniques are valuable tools with which to investigate those features in the appropriate time and space domains. In particular, quasi-elastic neutron scattering (QENS) connects useful structural and dynamical information by the measurement of dynamical incoherent (single particle) fluctuations in soft materials as a function of lengthscale. Extraction of these fluctuation rates can, however, be hampered by the presence of coherent contributions, originating from elastic scattering, and/or inelastic scattering modes which overlap in the space/time domain with the incoherent single-particle motions. As we have already seen in a previous study [1], this happens in poly(3-hexylthiophene) (P3HT) and [6,6]-Phenyl C_{61} butyric acid methyl ester (PCBM) solid blends, in which the coherent contribution arising from the PCBM crystalline phase seems to affect the interpretation of the polymer dynamics. Here, we utilise neutron polarisation analysis as an effective tool to separate coherent and incoherent contributions and make QENS data analysis of these blends more reliable.

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1. Introduction

Blends of conjugated polymers and fullerene derivatives are the current paradigm for state-of-the-art polymer photovoltaic diodes. These belong to the class of excitonic solar cells, in which the photocurrent originates from the splitting of the photogenerated bound electron-hole pairs, so-called *excitons*, which for organic low dielectric constant materials ($\varepsilon = 2–3$) exhibit a relatively high binding energy [2] and a diffusion length confined to a few monomers (5–10 nm) [3]. The bulk-heterojunction (BHJ) architecture, in which the formation of an interpenetrated network between the electron-donor and acceptor materials upon blending has the potential to partially overcome these limitations [4,5], enables power conversion efficiencies approaching 10% [6]. The nanoscale structural/dynamical features of these solid blends, such as the crystallisation of the fullerene molecules [7–9] as well as the reorganisation of the polymer amorphous and crystalline domains [10], control the optoelectronic response of the active material and, hence, the efficiency of the photovoltaic process. Therefore, in order to boost the performance of this class of devices, it is important to gain deeper insight into the thermodynamic and kinetic phenomena that occur upon blending and post-process treatments.

Neutron scattering has been employed as a sensitive and non-destructive tool to investigate the structure/dynamic/efficiency relationship in polymer/fullerene blends for organic photovoltaics [10–12]. One advantage of using neutron scattering to study these polymer-nanocomposite systems stems from the strong contrast in scattering between polymer chains and fullerene particles, as the neutron scattering length of fullerene derivatives differs considerably from that of highly hydrogenated conjugated polymers. For instance, if we consider the benchmark blend for BHJ organic solar cells, which is based on regioregular poly(3-hexylthiophene) (P3HT) as the electron donor and [6,6]-Phenyl C_{61} butyric acid methyl ester (PCBM) as the electron acceptor [13], the scattering length densities (SLD) are 7×10^{-7} Å^{-2} and 3.6×10^{-6} Å^{-2} for P3HT

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and PCBM, respectively. Therefore, elastic and inelastic neutron scattering techniques are extremely powerful in mapping a variety of phenomena at the nanoscale, such as polymer-fullerene phase separation and mutual diffusion at their interfaces. Quasi-elastic neutron scattering (QENS), in particular, is well adapted to the measurement of molecular motions in soft matter over a large dynamical range; such as fast vibrations and rotations as well as slower segmental relaxations and diffusion, with the advantage of mapping their nanoscale spatial dependence as a function of the momentum transfer, Q [14]. As QENS is highly sensitive to hydrogen dynamics due to its high incoherent scattering cross section, the fact that P3HT holds thirteen H atoms on the side chain and only one on the backbone can be used to highlight the dynamical fluctuations of the side-chain in this functional polymer.

In recent years, QENS has started to be employed in the study of side-chain dynamics of pure poly(alkylthiophenes) [15,16] and in blends with carbon nanotubes [17] or fullerene derivatives [18]. In this context, we have carried out a QENS study of P3HT-PCBM blends [1] as a function of blending and solvent choice, using the high-resolution backscattering spectrometer IRIS at the ISIS Neutron and Muon Facility (UK) [19], in the picosecond time range. We found that the addition of PCBM frustrates polymer motion, possibly related to polymer confinement within PCBM domains. However, it seems that there is some excess elastic signal fraction at Q-values that correspond to the characteristic distance of PCBM crystals (discussed further in the Results section). Calculation of the different contributions to the scattering cross-sections for a 1:1 P3HT:PCBM concentration yields incoherent and coherent contributions of ca. 75.5% and 5.5% for P3HT respectively, and 14% and 5% for PCBM respectively. Thus, three possible scenarios arise: i) the frustration of P3HT polymer dynamics is real (slowing down or increased elastic fraction), and it is due to P3HT-PCBM interaction and/or polymer confinement within PCBM domains; ii) the increase of the elastic fraction is largely due to the increase of coherent signal caused by PCBM addition and crystallisation; iii) a combination of the two effects. It is therefore important to assess whether the excess of coherent contribution in this Q-range affects the data interpretation. To this end, neutron polarisation analysis can be a powerful method to disentangle collective events from single-particle motions in complex systems. Although this technique has been already employed to discriminate between localised and non-localised motions in ionic liquids [20], it has never been used to investigate blends of semi-crystalline conjugated polymers with fullerene derivatives.

In the work presented here, we use neutron polarisation analysis to separate the coherent/incoherent scattering contributions in pure P3HT and in blends with PCBM (Fig. 1), by making use of the diffuse scattering spectrometer D7 at ILL [21]. We observe that, although the polymer motion seems to fall outside the instrumental time-window, this technique can be used effectively to discriminate the coherent/incoherent contributions in a multi-component polymer:fullerene blend and, in general, in those systems in which the coherent contribution can make data analysis/interpretation non-trivial, i.e. in polymer:nanocomposite systems [22].

2. Materials and methods

2.1. Materials and sample preparation

Regioregular P3HT (Mw = 10,000–40,000 g/mol) and PCBM were purchased from American Dye Source and used without further purification steps. Films of pure P3HT and blends of 50 wt% P3HT-PCBM were prepared by dissolving the two materials in chloroform separately with a concentration of 20 mg/mL, and mixing them in a 1:1 ratio. The resulting solutions were stirred overnight and drop-cast onto aluminium foil, yielding sample films of around 150 μm (as needed for the QENS neutron scattering experiments to achieve transmissions of ~85% and minimize multiple scattering effects). The samples were vacuum-dried overnight at room temperature (RT = 20–25 °C) to remove any residual solvent.

2.2. D7 experiment

The diffuse scattering spectrometer D7 measures neutron scattering with polarisation analysis and, hence, unambiguously separates collective (nuclear coherent) and single-particle (nuclear incoherent) and magnetic scattering processes by means of *xyz*-polarisation analysis. This is a valid claim in cases where the incoherent scattering is dominantly *spin-incoherent* (i.e. due to the spin-dependent nuclear scattering length) and not *isotope-incoherent* (i.e. due to randomly positioned nuclear isotopes). This is a valid assumption for incoherent scattering for most H-containing materials. We used D7 with an incident wavelength of 5.7 Å which covers a similar Q-range to that measured on IRIS (0.3–1.8 $Å^{-1}$) [1]. We measured both in diffraction mode, to determine the structure factor of the pure polymer and P3HT:PCBM blends, and in inelastic mode to measure the QENS signal of the incoherent/coherent scattering using the Fermi chopper option. D7 is equipped with a supermirror analyser detector bank with an angular range of 132°. We measured the spin-flip and non-spin-flip scattering with the polarisation axis normal to the scattering plane, with the axis preserved by means of a magnetic guide field (~10 G) that extended along the path of incident and scattered beams. The polarisation

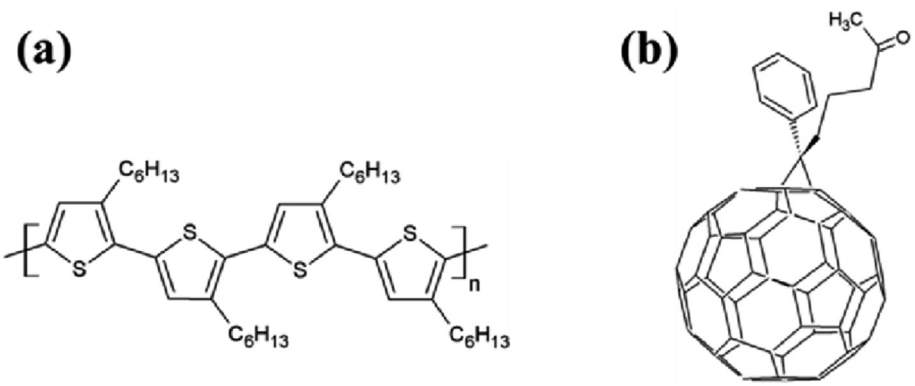

Fig. 1. Molecular structure for P3HT (a) and PCBM (b). P3HT and PCBM are the electron-donor and electron-acceptor of choice in bulk heterojunction organic solar cells.

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