Experimental report

15/09/2016

Proposal: 9-11-1744 **Council:** 4/2015

Title: TEMPERATURE DEPENDENCE OF THE MOLECULAR DYNAMICS OF THE LOW BAND GAP CONJUGATED POLYMER PCPDTBT

Research area: Materials

This proposal is a new proposal

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Samples: PCPDTBT

Instrument	Requested days	Allocated days	From	To
IN16B	3	3	17/11/2015	20/11/2015

Abstract:

Conjugated polymers have been developed since the past 30 years, but only recently, applications to optoelectronic devices such as thin film transistors, light emitting diodes, organic lasers and organic solar cells have become close to commercial applications. Regarding solar cells, a new class of low band gap polymers are showing promising results in power conversion efficiency. After our initial experiments and SANS measurements, we have chosen PCPDTBT as the best candidate for quasielastic experiments.
The importance of temperature processing on the control of the molecular dynamics (and final structure) of the polymer and its impact on the optoelectronic performance is the driving force for the proposed experiment. Our aim is to explore the molecular motions of PCPDTBT on a broad range of temperatures, from 10K to 450K, which are tipically used in annealing cycles during processing of the active layer of organic solar cells. We expect to characterize the molecular motions (activation energy, characteristic times), and in detail: Debye-Waller, alpha and beta relaxations, and eventually, methyl group rotations (at the end of side chains).

PRELIMINARY EXPERIMENTAL REPORT

EXPERIMENT: 9-11-1744

Instrument: IN16B

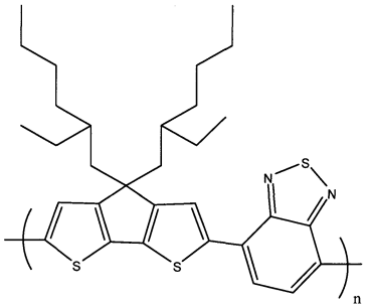
Title: Temperature dependence of the molecular dynamics of the low band gap conjugated polymer PCPDTBT

Dates of experiment: 17-20 Nov 2015

1. Introduction

Conjugated polymers have been developed since the past 30 years, but only recently, applications to optoelectronic devices such as thin film transistors, light emitting diodes, organic lasers and organic solar cells have become close to commercial applications. After previous small angle neutron scattering and quasielastic neutron scattering measurements of the benchmark polymer P3HT [2,3], we proposed a quasielastic experiment for a representative of a new class of conjugated polymers: PCPDTBT, which has a lower band gap than P3HT. This modification of band gap is aimed to improve light absorption globally but also to absorb in bands that are complementary to P3HT and therefore make the optimum partner for a tandem solar cell with better power conversion efficiency.

The molecular structure of PCPDTBT is complex compared to P3HT: backbone combines two conjugated units and side-chains are branched, structure and dynamics are expected to present significant variations with respect to was previously reported for P3HT. The experimental proposal was accepted and the experiment performed during November 2015 (three days, 17th to 20th) on a bulk sample contained in flat Al sample holder ("Copenhagen" model) with average M_w~20,000 (PDI<2) [Molecular formula: $(C_{31}H_{38}N_2S_3)_n$].



2. Summary of results

Efficient use of beamtime allowed us to perform the following experiments: Quasielastic neutron scattering scans at various temperatures: (5K, 20K, 150K, 200K, 250K, 300K, 350K and 400K) and an additional set of fixed window scans for a broad temperature range between 20K and 400K (elastic line plus three fixed energy transfers: 3, 4.5 and 6μeV).

The sample probed to be a good scatterer and 5h per quasielastic scan provided enough signal to noise ratio and a significant quasielastic broadening for intermediate temperatures (see for example, Fig 1 and Fig. 2 for a comparison between low and high temperatures for two momentum transfer values), also the fixed window scans demonstrated good sample thermal stability and reproducibility (in Fig 3 the superposition of scans performed at different times showed good matching, this scans were performed in temperature ramps between quasielastic scans, i.e. after several hours there is no sign of uncontrolled sample ageing effects).

Figure 1 shows two QENS spectra at low momentum transfer, the difference between 5K and 300K is not significant, contrary to what is clearly seen at intermediate momentum transfer in Figure 2. This is a clear indication of the importance of Q-dependence of the motions at different temperatures. In Figure 3, the fixed window scan experiment confirms that interesting activation of motions are occurring at the energy (time) window of IN16B, in particular for the three selected energy transfers

for the experiments. The fixed window scans demonstrated the reliability and interest of this measurements but did not allowed to analyse the momentum transfer dependence (in Figure 3 all Q´s are added in a single line for each energy transfer).

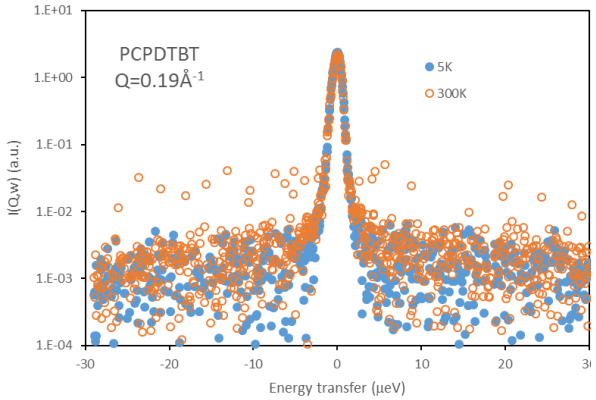


Figure 1. QENS spectra of PCPDTBT at two different temperatures and low momentum transfer.

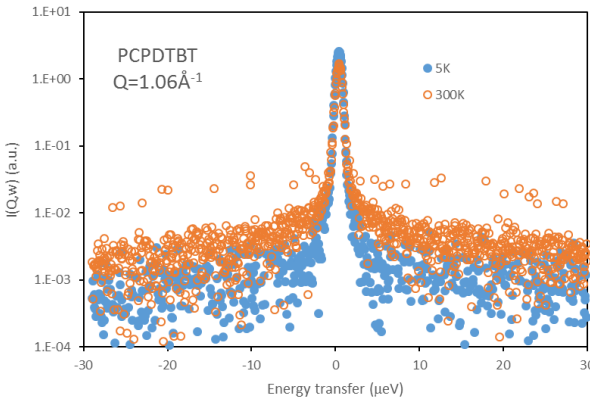


Figure 2. QENS spectra of PCPDTBT at two different temperatures and intermediate momentum transfer.

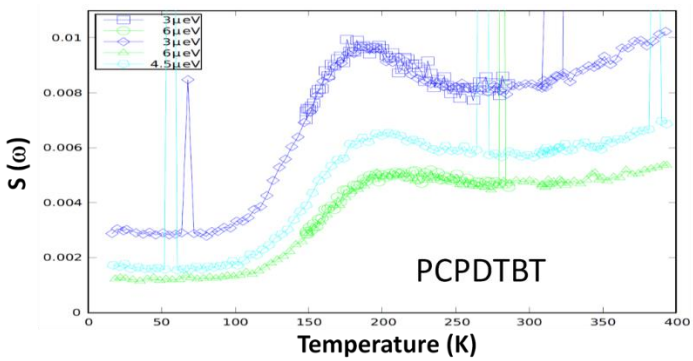


Figure 3. Fixed window scans at three different energy transfers on a PCPDTBT sample

3. Discussion

Preliminary analysis on the data demonstrates that the following properties can be quantitatively measured on PCPDTBT samples by neutron scattering: i) Debye-Waller contribution of motions using the lower temperature part of the scans; ii) the onset of side-chain motions at intermediate temperatures has been demonstrated, further Q-dependence analysis is required to fit with models of diffusion within a cage for this motion ; iii) the expected contribution of methyl groups at the end of side-chains could not be stablished (the 20K spectra had comparatively less time of data acquisition). Further studies using molecular dynamics modelling will be performed. Also further measurements to provide more scans at lower temperatures (range 10K to 50K) to confirm (or discard) the models for methyl group motions and to obtain a Q-dependence in the fixed window scans are desirable.

References:
[1] J. Burroughes et al. *Nature*, 347, 539 (1990); C.J. Brabec, et al., *Advanced Functional Materials*, 11, 15 (2001); H. Sirringhaus et al., *Advanced Materials*, 17, 2411 (2005); I. D. W. Samuel et al., *Chemical Review*, 107, 1272 (2007).
[2] C. Díaz Paniagua et al. Journal of Chemical Physics, 427, 129 (2013).
[3] Guilbert A. A. Y et al, Chemistry of Materials, 27, 7652 (2015).