



Thursday 10 September, Session 8, 12:35 – 12:55

Behaviour of semiconducting polymers confined in thin films

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The present concern about sustainability and environmental impact of fossil fuels has increased the necessity to achieve large-scale production of solar energy using photovoltaics at low cost. Semiconducting polymers can potentially be used in numerous applications in the form of thin films, for the production of field effect transistors (FET's), light emitting diodes (LED's) and photovoltaic devices. As their inorganic counterparts present very expensive (especially in term of energy) processing technologies, there is an urgent need to substitute them with organic devices, which have the advantage of solution processibility, whereas conventional silicon-based technologies require expensive ultrahigh vacuum equipment for deposition as a thin layer.

The problem of these materials is that they aren't efficient currently enough and also suitably stable to match the market demands. The efficiency is strongly influenced by the molecular order that controls charge mobility at different lengthscales.

The aim of our study is to understand the states of intermediate order in ultrathin polymer films of the semiconducting polymers poly [N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) and poly(3-hexylthiophene-2,5-diyl) (P3HT). Our hypothesis is that the influence of the surface and interface with the substrate on thin films is strong enough to lead to morphologies, and properties that depend on molecular conformation, which are substantially different from those in the bulk phase diagram.

By the phrase intermediate order we mean states of partial crystallinity and mesomorphic states, which may be stabilised at equilibrium by the presence of surfaces or interfaces, or which may appear transiently in a kinetic pathway which differs from the pathway that is obtained in the bulk. The starting point for understanding the potential importance of these phenomena is a recent rethinking of what had been a long-standing consensus about the kinetics of crystallisation in polymers. There is a body of work [1] summarised by Ströbl [2] which stresses that polymers can be expected to crystallise not by a fully crystalline nucleus growing in an entirely amorphous melt; instead crystallisation proceeds via a state of intermediate order – a metastable mesophase.

In a recent study on the semiconducting polymer PCDTBT we have observed an important interplay of conformational and dynamic anomalies in thin polymer films [3].

- [1] A. Keller, An approach to the formation and growth of new phases with application to polymer crystallization: effect of finite size, metastability, and Ostwald's rule of stages, *J. Mater. Sci.* 29 (1994) 2579–2604.
- [2] G. Strobl, Colloquium: Laws controlling crystallization and melting in bulk polymers, *Rev. Mod. Phys.* 81 (2009)
- [3] T. Wang et al., *Eur. Phys. J. E* 35 129 (2012)