| | **Experiment title:** Structure of novel rod-coil block copolymers for applications in photovoltaics | **Experiment number:** 26-02-334 |
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| **Beamline:** BM26B | **Date of experiment:** from: 25.09      to:29.09.2006 | **Date of report:** 29.08.2007 |
| **Shifts:** 9 | **Local contact(s):** Kristina Kvashnina Wim Bras | *Received at ESRF: Denis Anokhin Martin Rosenthal Matthieu Defaux Houssam Hamie* |

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## Report:

Semiconducting conjugated polymers are promising materials for the development of low-cost optoelectronic applications.[1] A lot of efforts have in particular been devoted in recent years to the design of polymer materials for solution-processed photovoltaic devices. The long-term stability of such devices is however inherently restricted by the macrophase separation of the blend constituents. Improving the control over the active layer morphology on the nanometer scale is therefore among the present key issues that need to be addressed to further improve the photovoltaic performances. A possible way towards this goal is to use donor-acceptor functionalized diblock copolymers as active layer instead of donor-acceptor blends.[2] By using a semiconducting electron-donor polymer block and a second, electron-accepting block, it is possible to combine the self-assembling ability of diblock copolymers with the functionality of conjugated molecules. Rod-coil diblock copolymers based on poly[(2,5-di(2'-ethyl)hexyloxy)-1,4-phenylene vinylene] (DEH-PPV) as a rod block and P(BA-stat-CMS) as coil block is a good candidate for manufacturing of such self-organized donor-acceptor systems.

In the frame of the present project, we studied the crystalline and liquid crystalline structure of DEH PPV homopolymer and DEH PPV-b- P(BA-stat-CMS) copolymer at different temperatures. The samples were

**Fig.1** Top panel: WAXS diffractogram of DEH-PPV at room temperature (1) and at 65°C (2); DEH-PPV-*b*-P (BA-*stat*-CMS) at room temperature (3); Bottom panel: variable-temperature WAXS for the DEH-PPV sample.

synthesized in the LIPHT Laboratory, Strasbourg, as discribed in previously[3,4]. The degree of polymerization determined by ^{1}H NMR is 9.2 for DEH PPV and 25.2 for P(BA-stat-CMS) block. X-ray measurements were performed in transmission mode on oriented samples (fibers with diameter of 0.7mm) prepared by extrusion
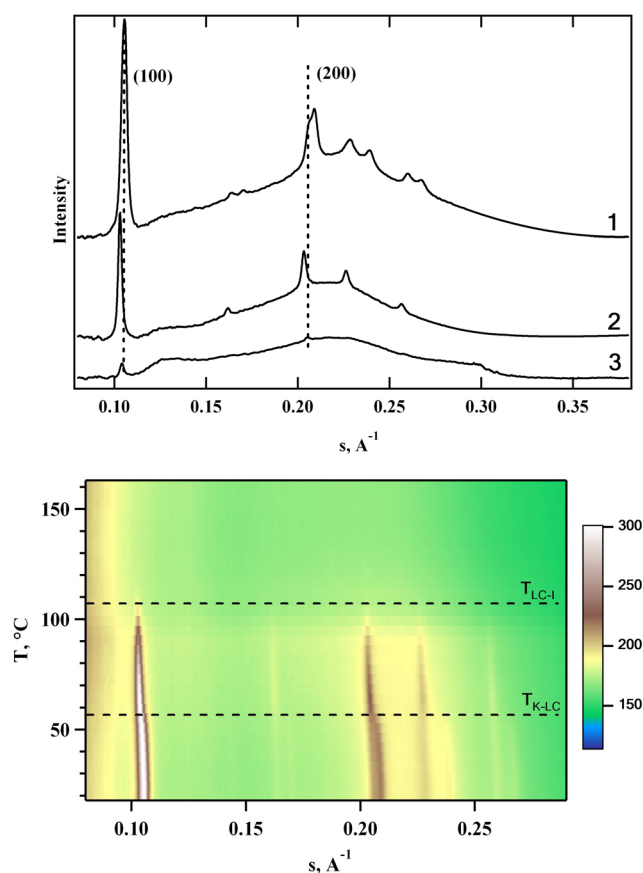
at 80°C using a home-made mini-extruder. The wavelength of 1.24Å was used. Dynamic measurements were carried out during heating in a Linkam heating stage at 10°C/min using an acquisition time of 30 sec.

The X-ray diffraction pattern of the homopolymer shown in Figure 1 (top, curve 1) reveals the presence of a large number of diffraction peaks, which, with the exception of the peak at 4.84Å, can be indexed to a monoclinic unit cell with following parameters: **a**=9.53A, **b**=8.1A, $\gamma$ =88° (the **c**-parameter cannot be identified due to the absence of non-equatorial peaks).The SAXS curves of DEH PPV (Figure 2, top, curve 1) are featureless even after annealing at 105°C. We therefore hypothesize that, in the solid state, the homopolymer organizes into a lamellar-type crystalline structure (K-phase) characterized by a significant inter-lamellar disorder. The thermal behaviour of the sample was studied with temperature resolved X-ray scattering. The evolution of the WAXS intensity during sample heating is shown in Figure 1 (bottom). At 55°C, several diffraction peaks disappear, while others are slightly shifted to smaller values of the scattering vector (i.e., to larger distances). We attribute this behaviour to a phase transition from a crystalline state to a smectic-like mesophase (LC-phase). Above 105°C, the amplitude reduction of all diffraction peaks indicates that the material undergoes another transition into a disordered isotropic state. In the WAXS diffraction pattern of the copolymer only low-order diffraction peaks can be observed (Figure 1, top, curve 3). The corresponding d-spacings are close to the values observed for the homopolymer in the LC
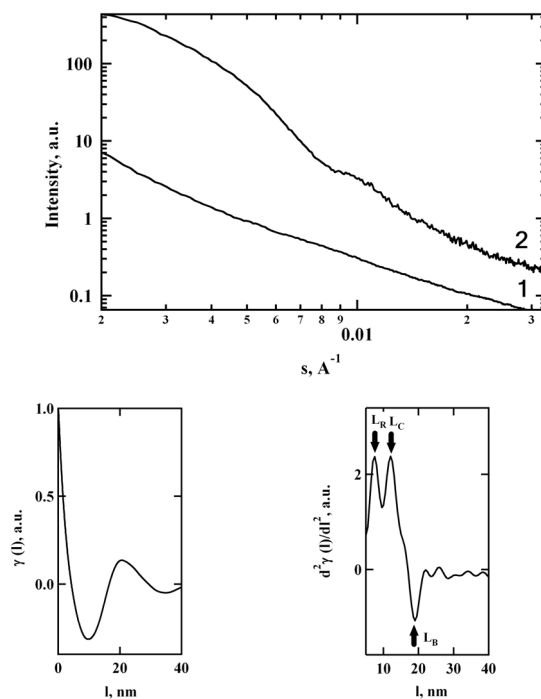


**Fig.2** Top panel: SAXS curves corresponding to DEH-PPV (1) and DEH-PPV-*b*-P (BA-*stat*-CMS) (2) at room temperature; Bottom panel: correlation (left) and interface distribution functions (right) of DEH-PPV-*b*-P (BA-*stat*-CMS).

state. The WAXS clearing temperature is 90°C, which is significantly lower than that of DEH PPV and illustrates the weakening of the rod-rod interactions by the presence of the coil block. The copolymer SAXS profile, shown in Figure 2 (top, curve 2), clearly displays ripples that are absent in the spectra of DEH PPV (curve 1)**.** The SAXS signal remains visible up to temperatures as high as 166°C, well above the WAXS clearing temperature, where rod-rod interactions are considerably weakened. These results point out that microphase separation enhances the inter-lamellar ordering and remains active even when the rod block is in its isotropic state. Analyzing the curves with the classical approach of one-dimensional SAXS correlation (CF), $\gamma(l)$, and interface distribution functions[5] (IDF), $d^2\gamma/dl^2$, two characteristic sizes of the structure can be deduced (Figure 2, bottom): $L_R$=7.5nm, $L_c$=12nm and $L_B$=$L_c$+$L_R$=19nm, where $L_c$ and $L_R$ stand for the "lamellar core" and "lamellar shell" thickness, respectively and $L_B$ for the lamellar stacking period. It should be noted that the found $L_R$ value is close to the contour length of the DEH PPV block in the stretched conformation - 6.7nm.

In conclusion, the rod-block DEH PPV homopolymer crystallises at room temperature in a monoclinic unit cell, which at higher temperature transforms to a liquid-cryslalline smectic phase. The presence of a coil block considerably destabilizes the rod-rod interactions and leads to the formation of a lamellar phase with the rod-block being in a LC state at room temperature. On the other hand, the microphase separation enhances the inter-lamellar ordering and results in stacks of parallel lamellae, as observed by SAXS. Hence, DEH PPV-b- P(BA-stat-CMS) forms a phase-separated system and can be a potential candidate for organic photovoltaic devices.

**References**

1   A.J Heeger,  *J. of Phys. Chem.B*  2001, *105*, 8475-8491.
2   U. Stalmach, B. de Boer, C. Videlot, P. F. van Hutten, G. Hadziioannou,*J. Am. Chem. Soc.,* 2000, *122*, 5464.
3   U. Stalmach, B. de Boer, A. D. Post, P. F. van Hutten and G. Hadziioannou, *Angew. Chem. Int. Ed.* 2001, *40*, 428.
4   M. H. van der Veen, B. de Boer, U. Stalmach, K. I. van de Wetering and G. Hadziioannou, *Macromolecules* 2004, *37*, 3673.
5   W. Ruland, *Colloid Polym. Sci..* 1977, *255*, 417; F. J. Balta-Calleja, C. G. Vonk, *X-ray Scattering of Synthetic Polymers*; Elsevier: Amsterdam, 1989.