



# Functional rod-coil block copolymers for opto-electronic applications

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MA-434

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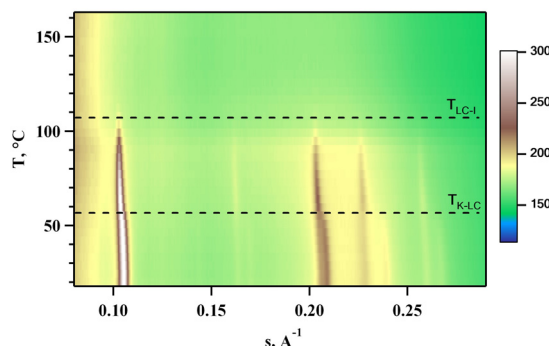
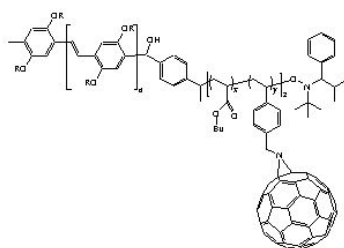
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## Report:

For polymer-based photovoltaic systems, the nanoscale structure (e.g., the perfectness of  $\pi$ - $\pi$  stacking) of the active layer is crucial for the device performance. A possible way toward this goal is to use functionalized rod-coil block copolymers as active layers.



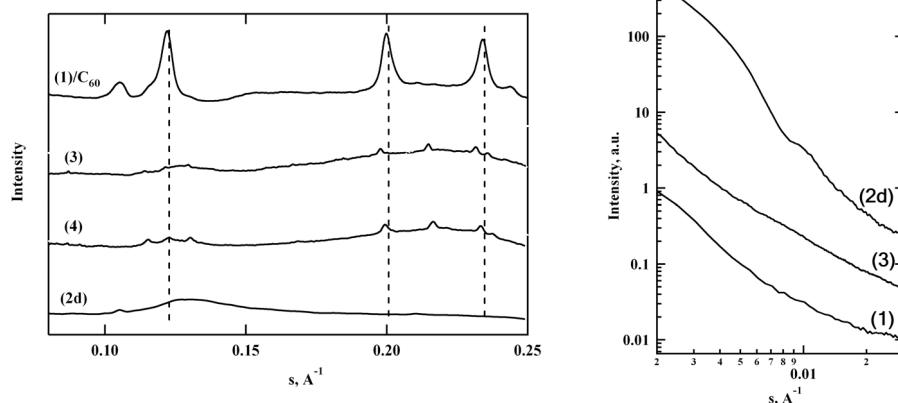
**Fig.1:** Chemical structure of sample 3 (left), WAXS pattern of sample 1 during heating from 20 to 160°C (right)

This gives the opportunity to form

thermodynamically stable, nanostructured donor-acceptor films with optimized morphology [1]. Consequently, it is important to understand the influence of the coil block functionalization on the self-assembling process to find the experimental conditions, which lead to an appropriate thin film nanostructure. In our project we focused on comparative study of the structure of semiconductive rodlike homopolymer poly[(2,5-di(2'-ethyl)hexyloxy)-1,4-phenylene vinylene] (DEH-PPV, sample 1), coil block of poly(butyl acrylate-stat-C<sub>60</sub>MS) with grafted C<sub>60</sub> (sample 4), rod-coil diblock copolymer without grafted fullerene molecules (sample 2d), and rod-coil diblock copolymers with a fixed amount of grafted C<sub>60</sub> (sample 3, Figure 1, left).

The thermal behavior of homopolymer 1 was studied with temperature- resolved WAXS during heating at

10 °C/min (Figure 1, right). A large number of diffraction peaks are found, which can be indexed to a monoclinic unit cell with the following parameters:  $a=9.53\text{\AA}$ ,  $b=8.1\text{\AA}$ , and  $\gamma=88^\circ$  (c-parameter can not be identified). It is noteworthy that no diffraction peak induced by the molecular  $\pi$ - $\pi$  stacking ( $s = 0.3\text{ \AA}^{-1}$ ) was



**Fig.2** WAXS (left) and SAXS (right) patterns of the studied samples at room temperature. The numbers correspond to the sample notations.

observed. It can be seen that at 65 °C several diffraction peaks disappear, while others are slightly shifted to smaller values of the scattering vector. We attribute this behavior to a phase transition from a crystalline state to a smectic-like liquid crystalline phase (TK-LC). Above 105 °C the material undergoes a transition to a disordered isotropic state. The positions of the peaks in the WAXS curve of copolymer 2d are close to the values observed for homopolymer 1 in the LC phase (Figure 2, left). In contrast, the WAXS pattern of the fullerene-grafted copolymer 3 differs significantly from that of sample 2d (Figure 2, left). The results obtained on sample 3 show several broad diffraction peaks as well as a number of smaller relatively narrow peaks. The peak positions are close to those found on copolymer 4 and on the blend of homopolymer 1 and free C<sub>60</sub>. The three major peaks observed in the blend coincide with those expected for pure C<sub>60</sub> crystals except for the peak at  $0.106\text{ \AA}^{-1}$  which corresponds to the homopolymer crystalline structure [2]. Indexation of the diffraction peaks of 3 and 4 to a monoclinic structure similar to that of PCBM strongly suggests that distorted C<sub>60</sub> nanocrystals are formed in these materials where the fullerenes are covalently bonded to the polymer backbone. The formation of the C<sub>60</sub> crystals hinders the lamellar organization of the DEH-PPV block. In contrast to featureless SAXS patterns of homopolymer 1, the SAXS profile of block-copolymer 2d displays a ripple at about  $s = 0.08\text{ \AA}^{-1}$  corresponding to the form factor of the lamella with a thickness of 12.6 nm (Figure 2, right). Importantly, the stacking period is not well-defined indicating that there is a broad distribution of the interlamellar distances. On the SAXS curve of block-copolymer 3 the intensity of the ripple is significantly decreased due to the described disturbance of the lamellar morphology.

In the conclusion, we have shown that in the novel rod-coil copolymers lamellar structure is formed, similar to the that on rod homopolymer. The grafting of the fullerene molecules disturbs the LC phase formation and C<sub>60</sub> nanocrystals appear in the samples which impedes the lamellar organization. More details on these results can be found in our recent publication [3].

## References:

1. J.Y. Kim, K. Lee, N.E. Coates, D. Moses, T.Q. Nguyen, M. Dante, A.J. Heeger, *Science* **2007**, 317, 222.
2. W.I.F. David, R.M. Ibberson, J.C. Matthewman, K. Prassides, T.J.S. Dennis, J.P. Hare, H.W. Kroto, R. Taylor, D. R. M. Walton, *Nature* **1991**, 353, 147.
3. S. Barrau, T. Heiser, F. Richard, C. Brochon, C. Ngoy, K. van de Wetering, G. Hadziioannou, D.V. Anokhin, D.A. Ivanov, *Macromolecules* **2008** 41, 2701.