## Hierarchical morphology and confinement in nanostructured polymer blends investigated by Nanofocus X-ray beams and Resonant Soft X-ray Scattering

Álvaro Rodríguez-Rodríguez<sup>1</sup>, Tiberio A. Ezquerra<sup>1</sup>, Esther Rebollar<sup>2</sup>, Jaime J. Hernández<sup>3</sup>, Inés Puente-Orench<sup>4</sup>, <u>Mari-Cruz García-Gutiérrez</u><sup>\*1</sup>,

<sup>1</sup>Institute for the Structure of Matter (IEM-CSIC), Serrano 121, 28006 Madrid, Spain, <sup>2</sup>Rocasolano Institute of Physical Chemistry (IQFR-CSIC), Serrano119, 28006 Madrid, Spain, <sup>3</sup>Institute for Advanced Studies in Nanoscience, Faraday 9, 28049 Madrid, Spain,<sup>4</sup>Institut Laue-Langevin, 71 av. des Martyrs, 38042 Grenoble Cedex 9, France \*maricruz@iem.cfmac.csic.es

Arrays of semiconductor polymer nanostructures exhibit an interesting behavior that makes them candidates for use in organic electronics, photovoltaics, and sensor devices. High aspect ratio (length/diameter) one-dimensional (1D) nanostructures are also appropriate for studying size-dependent processes with length scales comparable to the nanostructures' size [1]. Material properties strongly depend upon molecular order and orientation. Crystallization is one of the simplest molecular-scale self-organization processes capable to control spatially the ordering of molecules and hence to tune the properties of partially crystalline polymer nanostructures, as they will largely depend upon the properties of their crystalline domains. Phase separation and structure confinement are also key factors to take into account in nanostructured polymer blends acting as active layers in organic photovoltaics [2, 3].

This contribution will cover recent research on these phenomena. On one hand, the confinement effects on phase separation, crystal structure and orientation in high aspect ratio (length/diameter) one-dimensional (1D) nanoarrays of the photovoltaic blend poly(2,5-bis(3-hexadecylthiophen-2-yl)thieno[3,2-b]thiophene)/ fullerene have been studied by Nanofocus X-ray Scattering [4]. On the other hand, Resonant Soft X-ray Scattering at the carbon K edge is shown to be an unambiguous approach to evaluate the phase segregation between donor and acceptor phases across the grooves of a laser induced periodic surface nanostructure on a poly(3-hexylthiophene)/fullerene bulk heterojunction. By taking advantage of the use of polarized soft X-rays, the results provide direct evidence that the formation of the nanostructure on the surface of the heterojunction induces not only additional phase separation of the two components but also a preferential directional arrangement of the different phases [5].

*Acknowledgements.* We thank M. Burghammer for assistance during the experiments at ID13 beamline at the ESRF and also thank C. Wang and M. Brady for the scientific support at 11.0.1.2 beamline at the Advanced Light Source. The authors thank the financial support from the MINECO (grant MAT2014-59187-R), Spain.

## References

[1] M. C. García-Gutiérrez, A. Linares, J. J. Hernández, D. R. Rueda, T. A. Ezquerra, P. Poza, R. Davies, *Nano Letters* **10**, 1472–1476 (2010).

[2] A. Rodríguez-Rodríguez, M. Soccio, D. E. Martínez-Tong, T. A. Ezquerra, B. Watts, M. C. García-Gutiérrez, *Polymer* **77**, 70-78 (2015).

[3] A. Rodríguez-Rodríguez, E. Rebollar, T. A. Ezquerra, M. Castillejo, J. V. García-Ramos, M. C. García-Gutiérrez, *Langmuir* **34**, 115-125 (2018).

[4] J. J. Hernández, I. Puente-Orench, T. A. Ezquerra, M. C. García-Gutiérrez , in preparation.

[5] A. Rodríguez-Rodríguez, M. C. García-Gutiérrez, T. A. Ezquerra, M. A. Brady, C. Wang, E. Rebollar, submitted to *Physical Review Materials*.