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CRYSTALLIZATION OF BLOCK COPOLYMERS MICRODOMAINS

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Recently, the interest generated by the crystallization of block copolymers microdomains has greatly increased (see for instance ref. 1). One of the reasons could be that they provide excellent model systems to study the effect of morphological confinement on the crystallization behaviour of polymers and another, the promising future applications in for instance nanotechnology[2]. In this work, a review will be presented of recent and on going efforts[3,4] that have been done in our laboratory to analyze the nucleation and crystallization behavior of several types of block copolymers using DSC, TEM and polarized optical microscopy. We have used AB diblock copolymers and ABC triblock copolymers that incorporate amorphous blocks such as polybutadiene and polystyrene and crystallisable blocks like poly(ε-caprolactone), poly(ethylene oxide) and polyethylene.

In strongly segregated systems, a crystallisable component can be confined in isolated microdomains (such as cylinders or spheres) where fractionated crystallization takes place or even crystallization initiated in exclusive homogeneous nuclei. The fractionated crystallization process arises when the number of dispersed crystallizable microdomains is much greater than the number of heterogeneities that usually nucleate this phase when it conforms the matrix or when it is the parent homopolymer in the bulk. In the case of block copolymers, the confinement of crystallizable blocks in the nanoscopic scale, into microphases where no percolation path exists between them, enables the clear observation in some cases of exclusive crystallization from homogeneous nuclei. The technique of self-nucleation was found to be an excellent tool to explore the nucleation behavior of the block copolymer components and can be vital to ascertain the origin of coincident crystallization phenomena and crystallization at lower temperatures than in the parent homopolymer. The isothermal crystallization behavior and the effects of confinement on the Avrami index will also be discussed.

(1) Various authors, *Macromolecules*, Vol. **34**, pp. 671, 1244, 1258, 2398, 2876, 6649, 6936, 7009, 7336, 7973, 8968 (2001). (2) Reiter G., Castelein G., Sommer J.-U., Röttele A., Thurn-Albrecht T., *Phys. Rev. Lett*., **87**, 226101 (2001). (3) Arnal M.L., Balsamo V., López-Carrasquero F., Contreras J., Carrillo M., Schmalz H., Abetz V., Laredo E., Müller A.J., 2001, *Macromolecules*, **34**, 7973-7982. (4) A.J. Müller, V. Balsamo, M.L. Arnal, T. Jakob, H. Schmalz, V. Abetz, 2002, *Macromolecules*, 35, 3048-3058.