

CONFINED NUCLEATION AND CRYSTALLIZATION OF POLYMERS AND DIBLOCK COPOLYMERS WITHIN ALUMINA NANOPOROUS TEMPLATES

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ABSTRACT

Ordered alumina (AAO) templates have been prepared by two-step electrochemical anodization of aluminum with 20, 35 and 60 nm cylindrical pores. They were subsequently infiltrated with poly(ethylene oxide), PEO, polyethylene, PE, and polyethylene-*block*-polystyrene diblock copolymers, PE-*b*-PS, of various compositions prepared by anionic polymerization. The crystallization within the nanocylinders of the AAO templates was studied by Differential Scanning Calorimetry (DSC) and Wide Angle X-ray Diffraction (WAXD). In the case of PEO, a clear change from heterogeneous to homogeneous bulk nucleation was detected before and after infiltration within a 20 nm template respectively. The homogeneously nucleated nanocylinders needed extreme supercooling in order to crystallize¹, and their low crystallization temperature was successfully correlated with the volume of the crystallizing phase. Furthermore, 2D-WAXD measurements demonstrated that the PEO chains within the crystals formed inside the nanocylinders, preferentially orient perpendicular to the cylinder axis.² For the infiltrated model PE the nucleation is probably originated at the surface of the nanocylinders and cannot be considered homogeneous bulk nucleation².

Strongly segregated PE-*b*-PS diblock copolymers were infiltrated into AAO templates for the first time, thereby creating a nanostructured hybrid material where the PE block phase experienced ***double confinement*** for some compositions (i.e, the phase segregated confinement within a vitreous PS matrix and the physical confinement within the nanopores), see Figure 1 and reference 2. A first order crystallization kinetics has been found for the polymeric components within the nanopores.

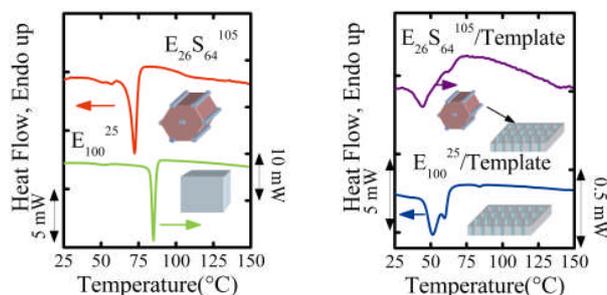


Figure 1. A comparison between uninfiltred (bulk) PE and cylinder forming PE-*b*-PS (left) and infiltrated within 60 nm AAO templates (right). See details in ref. 2.

References

1. Müller, A. J.; Balsamo, V.; Arnal, M. L. *Adv. Polym. Sci.*, **2005**, *190*, 1-63.
2. Michell, R. M.; Blaszczyk-Lezak, I.; Lorenzo, A. T.; Martín, J.; Müller, A. J.; Mijangos, C.; Ming-Champ, L.; Hsin-Lung, C. *Macromolecules*, **2012**, *45*, 1517–1528