European Polymer Journal 71 (2015) 164–170

Contents lists available at ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Macromolecular Nanotechnology

The change in the environment of the immiscible block stabilizes an unexpected HPC phase in a cured block copolymer/epoxy blend

Agustina B. Leonardi, Ileana A. Zucchi, Roberto J.J. Williams *

Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), Av. J. B. Justo 4302, 7600 Mar del Plata, Argentina

ARTICLE INFO

Article history:
Received 5 June 2015
Received in revised form 15 July 2015
Accepted 29 July 2015
Available online 30 July 2015

Keywords:
Block copolymer
Block copolymer/epoxy blends
Lamellar to hexagonal transformation
Polymerization-induced self-assembly
PS-*b*-PEO/epoxy
SAXS spectra

ABSTRACT

A conventional SAXS study of ordered phases produced in cured block copolymer (BCP)/epoxy blends with different concentrations, led to the unexpected observation of an HPC (hexagonally-packed cylinders) phase for a blend containing a 55:45 volume ratio of both domains. The BCP was polystyrene (PS, M_n = 28 kDa)-*b*-poly(ethylene oxide) (PEO, M_n = 11 kDa), where PS is the "epoxy-phobic" block and PEO is the "epoxy-philic" block. The epoxy formulation was based on diglycidylether of bisphenol A (DGEBA) and 4,4′-m ethylenebis(2,6-diethylaniline) (MDEA). A fully cured blend containing 60 wt% BCP, equivalent to 45% volume fraction of PS in the blend, exhibited an unexpected HPC morphology as supported by TEM images and SAXS spectra. The same techniques showed that a lamellar (L) phase was generated at low conversions in the same blend. The L to HPC transition was explained by the diffusion of epoxy–amine species out of the PS-rich phase with the increase in conversion. Order-order transitions in BCP/epoxy blends previously reported were explained by the partial phase separation of the *miscible* block from the epoxy solvent. These transitions go always in the sense of decreasing the interface curvature (e.g., from HPC to L). The transition reported in this study goes in the opposite sense (from L to HPC) and was generated by the change in environment of the *immiscible* block during polymerization.

1. Introduction

Block copolymer (BCP)/epoxy blends have been the subject of a large number of recent studies where the focus was placed on the role of the BCP as a processing aid [1,2], as a template for the self-assembly of different type of nanoparticles [3–5], or as a toughening agent [6–19]. The nanostructuration of the BCP in the epoxy matrix requires an immiscible block, either initially [20,21] or during polymerization [22,23], and another block that keeps its miscibility up to high or full conversions. The latter is a necessary condition to avoid macrophase separation.

The morphology initially generated does not remain frozen but can evolve with conversion. Order-order transitions can take place by the fact that the reactive solvent becomes less compatible with the miscible block as conversion increases. Chains of the miscible block can evolve from "wet" brushes swollen by the reactive solvent to partially collapsed "dry"

* Corresponding author.
E-mail address: williams@fi.mdp.edu.ar (R.J.J. Williams).

http://dx.doi.org/10.1016/j.eurpolymj.2015.07.056
0014-3057/

brushes. This can produce order-order transitions that decrease the interfacial curvature. Lipic et al. [21] analyzed the self-assembly of poly(ethylene oxide)-*b*-poly(ethylene-*alt*-propylene) (PEO-*b*-PEP), in an epoxy formulation, where PEO was the "epoxy-philic" block and PEP the "epoxy-phobic" one. For one particular formulation, they reported the transformation of a gyroid (G) to a lamellar (L) phase, just prior to gelation; for another formulation they observed a transition from a cubic packed spherical morphology to a hexagonal phase. These transformations were explained by the decrease of the miscibility of PEO with the epoxy polymer by increasing conversion (the "wet" to "dry" brush concept). In turn, Romeo et al. [24] analyzed the self-assembly of a polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA), in an epoxy formulation, where PMMA was the "epoxy-philic" block and PS the "epoxy-phobic" one. Spherical micelles generated at low conversions were transformed to a cubic packed spherical morphology (S), then to columns of spherical micelles, ending in a hexagonally packed cylinders (HPC) phase. Again, these transitions were explained by the decrease in the solubility of the PMMA block with conversion. It was also shown that by a particular selection of the cure cycle these transformations could be reverted. By increasing temperature at an intermediate conversion, the solubility of PMMA in the epoxy was increased (PMMA exhibits an upper-critical-solution-temperature in epoxy formulations). This produced a reversion of the HPC phase to columns of spherical micelles ("dry" brushes became "wet" again by the temperature increase). This morphology was frozen at complete conversion.

However, no attention has been paid to the consequences of the partition of the reactive solvent between both phases. When phase separation (nanostructuration) takes place, thermodynamics predicts that a fraction of the reactive solvent enriched in monomers and short oligomers must segregate together with the immiscible block [25–29]. As polymerization continues in the phase rich in the immiscible block, the largest oligomers are no longer miscible and diffuse out of this phase. This has two different consequences. The obvious one is the continuous variation of the volume ratio between both phases that might convey the system to cross the stability limit between different ordered phases. This is analogous to the order-order transitions observed in solutions of a BCP when adding increasing amounts of a highly selective solvent for one of the blocks [30]. The second less obvious consequence derives from the fact that the reactive solvent species segregated with the immiscible block behave as a poor solvent that turns into a no-solvent as polymerization continues in this phase. Conformation of coils of the immiscible block must gradually change from an initial collapsed state to a more extended theta state as the reactive solvent species diffuse out of this phase. This might produce an unexpected order-order transition, generating an ordered phase outside the stability limits corresponding to its volume fraction in the blend. In this study, we report experimental evidence of such a transition for a particular BCP/epoxy blend.

2. Experimental section

2.1. Materials

The epoxy monomer was based on diglycidylether of bisphenol A (DGEBA), with an epoxy equivalent of 179 g/mol, determined by chemical titration. The hardener was 4,4′-methylenebis(2,6-diethylaniline) (MDEA, Aldrich), used in an almost stoichiometric proportion (stoichiometric epoxy/amine ratio equal to 0.974 in equivalents of both monomers). The BCP was a commercial polystyrene (PS)-*b*-poly(ethylene oxide) (PEO) (Polymer Source), with M_n (PS) = 28 kDa and M_n (PEO) = 11 kDa, and a polydispersity index, *PI* = 1.11.

2.2. Synthesis and cure of blends

First, DGEBA was blended with the BCP, in proportions giving 40–60 wt% BCP in the final cured material. The dissolution was performed in a silicon mold adding a small amount of toluene to facilitate the process. Toluene was then removed at 60 °C during several hours until a constant weight was obtained. Then, temperature was increased to 80 °C and MDEA added with continuous stirring. The polymerization was carried out at 135 °C during 4 h. The nanostructures generated were analyzed at this stage (partial conversion) and after a thermal treatment at 190 °C for another 4 h under nitrogen (full conversion).

2.3. Characterization techniques

Near-infrared spectroscopy was used to follow the conversion of epoxy groups during polymerization at 135 °C, determined by measuring the height of the absorption band of epoxy groups at about 4525 cm^{-1} with respect to the height of a reference band at about 4615 cm^{-1}. A Nicolet 6700 FTIR device, equipped with a heated transmission cell (HT-32, Spectra Tech) with glass windows (32 mm diameter, 1.4 mm rubber spacer), and a programmable temperature controller (Omega, Spectra Tech, DTZG1 8C), was employed.

Transmission Electron Microscopy (TEM) images were recorded at room temperature using a JEOL 100CX device. Thin sections were obtained employing an LKB ultramicrotome. PS blocks appeared black in the images and therefore no staining procedure was necessary.