Polymer xxx (2014) 1–9

Contents lists available at ScienceDirect

Polymer

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

Nanoribbons with semicrystalline core dispersed in a visible-light photopolymerized epoxy network

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A R T I C L E I N F O

Article history:
Received 13 August 2014
Received in revised form
14 November 2014
Accepted 16 November 2014
Available online xxx

Keywords:
Block copolymers
Epoxy
Self-assembly

A B S T R A C T

It has been well documented that self-assembly of block copolymers (BCP) in selective solvents, where the core-forming block is a crystallizable polymer, results in micelle structures with exceptional aggregation morphologies determined mainly by the crystallization energy from the core. In this contribution, we apply this concept to create ribbon-like nanostructures dispersed in an epoxy network. The selected system was a polyethylene-*b*-poly(ethylene oxide) (PE-*b*-PEO) diblock copolymer in an epoxy monomer based on diglycidyl ether of bisphenol A (DGEBA). This system was selected on the bases that PEO is an epoxy-philic block which is completely miscible with DGEBA before and after curing reaction whereas PE is a crystallizable epoxy-phobic block. Under these conditions, we access to self-assembled nanostructures with semicrystalline core before curing reaction. With the aim of preserving the structural features of these micelles, the epoxy monomers were cured at room temperature (i.e., below the melting transition of the core-forming PE block) by photoinitiated cationic ring-opening polymerization. Long nanoribbons dispersed in the cured epoxy matrix were obtained, as characterized by SAXS patterns and TEM images. These ribbon-like micelles present a tendency to aggregate resulting in the formation of face-to-face stacking of parallel micelles. We demonstrated that while the stacking number decreases with decreasing BCP concentration, the arrangement of the nanoribbons within one stack becomes less organized.

1. Introduction

The design and preparation of structures at the nanometer level is of critical technological importance for future applications in areas such as nanodevices and nanotechnology, sensing, catalysis and drug delivery. Considerable attention has been paid to the bottom-up synthesis of nanomaterials with precisely controlled dimensions. Particularly, the self-assembly of amphiphilic polymers into nanoscale structures is a promising approach. Dendrimers, polysoaps and block copolymers have been used successfully to obtain micelles, nanostructured films and mesophases with different levels of organization [1–3]. Significant recent progress has been made, however the fabrication of complex morphologies with controlled structures by low-cost protocols remains still a challenge.

Block copolymers (BCP) self-assemble in selective solvents to yield a range of micelle morphologies, such as spheres, cylinders, vesicles, and more complex shapes [4,5]. With increasing BCP concentration, different ordered phases can be formed, such as body-centered cubic packed spheres, hexagonally packed cylinders, gyroid, and lamellar [5]. Due to the versatile self-assembly properties of BCP, their use has been explored for the preparation of nanostructured thermosets such as epoxy and novolac resins [6]. Regarding the applications of BCP/epoxy blends, focus has been placed on the role of the BCP as a processing aid [7,8], and as a template for the self-assembly of different type of nanoparticles [9,10]. It has been identified that nanostructures in thermosets can be produced via either initial self-assembly before curing reaction or reaction-induced microphase separation (RIMPS) [11–14]. In the self-assembly approach, the precursors of thermosets act as selective solvents of BCP and micelle structures are formed prior curing [11,12]. The self-organized structures can be fixed via subsequent polymerization reaction. Thus, the self-assembly protocol requires a block that is immiscible with the initial solvent after and before

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http://dx.doi.org/10.1016/j.polymer.2014.11.053
0032-3861/

Please cite this article in press as: Zucchi IA, Schroeder WF, Nanoribbons with semicrystalline core dispersed in a visible-light photopolymerized epoxy network, Polymer (2014), http://dx.doi.org/10.1016/j.polymer.2014.11.053

curing and another block that is miscible throughout the cure (or at least up to high conversion levels). In many instances, both blocks are completely miscible with the initial reactive solvent. Under this circumstance, it has been recently proposed that nanostructured thermosets can be alternatively prepared via the RIMPS approach [13]. In this case, although both blocks are miscible with the initial reactive solvent, one of them phase separates during polymerization while the other one remains miscible up to high conversions. Clearly, knowledge on the miscibility of the subchains of BCP with the thermosets before and after the curing reaction is of critical importance to have control over the formation of nanostructures in thermosetting materials.

There are many examples in the literature on nanostructured epoxy matrices obtained via self-assembly or RIMPS of BCP [6]. In most of these cases, the core-forming block is a noncrystalline polymer, such as poly(dimethylsiloxane) [15], poly(isoprene) [16], poly(butadiene) [17,18], or poly(styrene) [19,20]. Different nanostructures have been prepared, from spherical micelles and vesicles to cylinders, depending on the molecular weight, block length, composition, cure cycle employed, and block–block and block–matrix interaction parameters [11,12,21,22].

The incorporation of crystallizable polymers as the immiscible core-forming block provides opportunities toward nanostructures with additional structural features. Reported studies on self-assembled nanostructures with semicrystalline cores in organic solvents have shown that the crystallization energy from the core may result in unique aggregation behaviour [23–32]. Thin lamellae and elongated structures are the predominant morphologies observed. For example, Richter et al. reported elongated thin platelets from PEP-*b*-PE (coil-crystalline) diblock copolymers (PEP: poly(ethylene-*alt*-propylene)) in decane, a selective solvent for PEP [28]. The self-assembly was driven by the crystallization of PE, which resulted in lamellar sheets of several nanometers in thickness surrounded on both sides by PEP brushes. Winnik, Manners and co-workers have studied the formation of elongated micelles with polyferrocenyldimethylsilane (PFS) core blocks. These polymers undergo crystallization-driven self-assembly in selective solvents for the non-PFS block, giving place to cylindrical micelles [23–30] or elongated tapelike nanostructures [31]. The detailed morphology of these structures is governed by a competition between crystallization of the PFS core, which favours extended platelike crystalline lamellae, and the stretching of the corona block, which limits the extent of the plates [31].

Only a limited number of studies have been focused on nanostructures formed in thermosets with semicrystalline thermoset-phobic interiors [33–35]. In all these cases, the blend of the thermoset precursors with the BCP was thermally cured above the melting temperature of the semicrystalline core. Under such conditions, the structural features of the nanophases formed before curing, by crystallization-driven self-assembly at room temperature, cannot survive. In fact, spherical nanophases were commonly obtained in these cases. The possibility of retaining the morphology of micelles with semicrystalline cores by carrying out the curing reaction at low temperature (i.e., below the melting temperature of the core-forming block) can result in a unique approach to produce nanostructured thermosets with a variety of micelle morphologies. Such an investigation remains still unexplored.

In this study, we describe the formation of self-assembled nanostructures with semicrystalline core in a thermosetting matrix. The selected system was a polyethylene-*block*-poly(ethylene oxide) (PE-*b*-PEO) diblock copolymer in an epoxy monomer based on diglycidyl ether of bisphenol A (DGEBA). This system was selected on the bases that PEO is an epoxy-philic block which is completely miscible with DGEBA before and after curing reaction [35–38] whereas PE is a crystallizable epoxy-phobic block [33,34]. Under these conditions, we access to micellar nanostructures with semicrystalline core before curing reaction. With the aim of preserving the structural features of these micelles, the epoxy monomers were photocured at room temperature, i.e., below the melting transition of the core-forming PE block. In this way, long nanoribbons dispersed into the cured epoxy matrix were obtained. We demonstrate that this strategy provides access to morphologies that were previously unattainable in nanostructured epoxy thermosets.

2. Experimental section

2.1. Materials

The selected BCP was a low-molecular-weight polyethylene-*block*-poly(ethylene oxide) (PE-*b*-PEO) purchased from Aldrich Chemical Co. It had an average $M_n = 1400$ and 50 wt% ethylene oxide content. The epoxy monomer was based on diglycidyl ether of bisphenol A (DGEBA, DER 332 Aldrich Chemical Co.) with an epoxy equivalent weight of 174.3 g/eq and an average number of hydroxyl groups per two epoxy groups of $n = 0.03$. *p*-(octyloxyphenyl) phenyliodonium hexafluoroantimonate (Ph_2ISbF_6) was supplied by Gelest Inc. (Philadelphia, USA). Camphorquinone (CQ) and ethyl-4-dimethyl aminobenzoate (EDMAB) were purchased from Aldrich Chem. Co. All materials were used as received.

2.2. Sample preparation

Proper amounts of PE-*b*-PEO were blended with DGEBA to prepare samples containing 1, 5, 10 and 20 wt% BCP. The resin was activated for visible light polymerization by the addition of a three-component photoinitiating system based on Ph_2ISbF_6 (2 wt%), CQ (1 wt%) and EDMAB (1 wt%) [39]. Samples were prepared in the following way. The PE-*b*-PEO was transferred to a glass vial containing one-half of the total mass of DGEBA. This mixture was first nitrogen purged at room temperature for 30 min, and then stirred and heated in a 100 °C oil bath to disperse the BCP into the epoxy resin. After that, the vial was removed from the oil bath and allowed to cool to room temperature, then the three components of the initiating system dissolved in the remaining DGEBA were added. The resulting mixture was nitrogen purged at room temperature for 15 min, and subsequently stirred and heated in the 150 °C oil bath until a homogeneous mixture was obtained. The sample was then immediately cast onto an aluminium substrate in order to obtain a photocurable film of ca. 1 mm in thickness.

The obtained film was continuously irradiated at room temperature with the polychromatic light of a Xenon lamp (Hamamatsu, L8253, 150 W, irradiance $I \sim 60$ mW/cm^2 in the wavelength range 390–800 nm). Additionally, irradiations with a light-emitting diode (LED) unit (Valo, Ultradent, USA, irradiance $I = 600$ mW/cm^2 in the wavelength range 410–530 nm) for 40 s, once each day, were also carried out. Under these conditions, between three and four irradiation days were required to reach a high enough conversion level.

2.3. Characterization techniques

2.3.1. Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy was employed to determine conversion versus irradiation time curves for the different studied formulations. The FTIR measurements were conducted on a Nicolet 6700 Thermo Scientific spectrometer at room temperature. Near-infrared (NIR) spectra were acquired over the range 4000–7000 cm^{-1} from 32 co-added scans at 4 cm^{-1} resolution. The uncured sample was sandwiched between two glass plates

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