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ScienceDirect
Polymer 48 (2007) 3925–3929
polymer
www.elsevier.com/locate/polymer

Polymer Communication

Synthesis and fractionated crystallization of organic–inorganic hybrid composite materials from an amphiphilic polyethylene-*block*-poly(ethylene oxide) diblock copolymer

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Received 27 March 2007; received in revised form 8 May 2007; accepted 14 May 2007

Abstract

Mesostructurally ordered inorganic–organic hybrid composite materials were successfully synthesized by utilizing a low-molecular-weight amphiphilic polyethylene-*block*-poly(ethylene oxide) (PE–PEO) diblock copolymer as the directing agent. The hybrid composites were formed via the sol–gel reaction of inorganic precursor tetraethoxysilane (TEOS) in an acidic ethanol/water solution with various amounts of PE–PEO. In these composite materials, the hydrophobic PE block of the PE–PEO copolymer forms separate microphase on the nanoscales within the rigid matrix of silica network. The crystallization of the PE block is strictly restricted within the microphase by the rigid silica matrix and takes place through homogeneous nucleation under the nanoscale confinement environment.

Keywords: Hybrid material; Mesostructure; Crystallization

1. Introduction

Amphiphilic block copolymers have been employed as structure-directing agents to prepare mesoscopically ordered inorganic–organic hybrid composites and the related mesoporous inorganic oxides [1–6]. The richness in morphology of block copolymer renders the possibility of using the self-assembly of block copolymers to direct composite structure formation. Compared with small molecule surfactants [7,8], both new morphologies and larger length scales are feasible with amphiphilic block copolymers. For instance, self-organized organic–inorganic hybrid composites with a range of nanoscale morphologies have been developed by Templin et al. [9] using poly(isoprene-*block*-ethylene oxide) as the structure-directing agent in the sol–gel process of alkoxides. Melosh et al. [10] have reported highly ordered, transparent and crack-free silica/block copolymer monoliths based upon amphiphilic poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block copolymer. However, little attention has been paid to use amphiphilic diblock copolymers with a crystalline hydrophobic block as the directing agents.

We report here some preliminary results on inorganic–organic hybrid composite materials prepared by utilizing a low-molecular-weight amphiphilic polyethylene-*block*-poly(ethylene oxide) (PE–PEO) diblock copolymer as the directing agent. In these mesostructured hybrid composite materials, the hydrophobic PE block of the PE–PEO copolymer forms separate microphase on the nanoscales in the rigid matrix of silica network. Consequently, the crystallization of the PE block can be efficiently restricted within the microphase by the silica matrix. The PE block crystallizes under the nanoscale confinement environment and thus results in fractionated crystallization. To our knowledge, this is the first instance of fractionated crystallization in hybrid composite materials. The microenvironment within a rigid silica matrix is rather

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doi:10.1016/j.polymer.2007.05.021

different from that within an organic polymer matrix; the stiff nature of the silica matrix forces the PE blocks to crystallize strictly within the confined space established by rigid walls of silica.

2. Experimental

The amphiphilic PE–PEO diblock copolymer used was the polyethylene-*block*-poly(ethylene glycol) with 50 wt% ethylene oxide and an average $M_n = 1400$, i.e., (ethylene)$_{25}$(ethylene oxide)$_{16}$, denoted as $E_{25}EO_{16}$ (Aldrich Chemical Co., Inc.). The $E_{25}EO_{16}/SiO_2$ hybrid composites were prepared via the sol–gel reaction according to the procedures described in the literature [11,12]. The amphiphilic $E_{25}EO_{16}$ was first dissolved in an acidic ethanol/water solution (ca. pH 1.5); the hybrid composites were formed in the sol–gel process from $E_{25}EO_{16}$ and various amounts of the inorganic precursor, tetraethoxysilane (TEOS, Aldrich Chemical Co., Inc.). The molar ratio of H_2O to TEOS was held constant at 9:1 to ensure complete hydrolysis of TEOS, as well as to provide the water necessary for the formation of the desired phase with the block copolymer. A series of $E_{25}EO_{16}/SiO_2$ composite samples were obtained with compositions of 0, 10, 25, 40, 50, 57, 62, and 67 wt% $E_{25}EO_{16}$.

The mesostructures and crystallization of the composite materials were investigated using transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and differential scanning calorimetry (DSC). The specimens for TEM observation were microtomed at room temperature with a Leica EMFCS instrument equipped with a diamond knife. The resulting ultrathin sections of 80 nm thickness were picked up on copper grids and imaged in a LEO Omega 912 TEM with an accelerating voltage of 120 kV. TEM images were taken from the unstained ultrathin sections and the experiments relied on the natural contrast of the organic component versus inorganic silica. The SAXS experiments were performed with a Kratky compact camera (Anton Paar K.G., Graz, Austria) at room temperature (25 °C) as described previously [13,14]. The calorimetric measurements were made on a Perkin–Elmer Pyris 1 DSC in a dry nitrogen atmosphere.

3. Results and discussion

The TEM study revealed appreciable mesoscopic structural order from lamellar to hexagonal mesostructures and disordered wormlike aggregates for the $E_{25}EO_{16}/SiO_2$ composites with decreasing block copolymer concentration from 67 to 25 wt%. The TEM image in Fig. 1a shows a well-organized lamellar mesostructure in the 67 wt% $E_{25}EO_{16}$ copolymer sample. The light areas represent the PE microphase, whereas the dark areas correspond to the PEO microphase swollen by the inorganic silica, i.e., the PEO block and the inorganic silica form a single phase (the dark areas). De Paul et al. have shown by solid-state NMR that the PEO block of polyisoprene (PI)-*block*-PEO diblock copolymer mixed with the inorganic phase on a molecular level in organic–inorganic hybrid composites [15]. Similar mesostructural features were observed for the $E_{25}EO_{16}/SiO_2$ composite with 62 wt% $E_{25}EO_{16}$. The composite with 57 wt% $E_{25}EO_{16}$ also displayed lamellar mesostructure, co-existed with hexagonal mesostructure. Hexagonal mesostructure became the dominated one in the composite with 50 wt% $E_{25}EO_{16}$ and remained to appear for the composite with 40 wt% $E_{25}EO_{16}$. Fig. 1b clearly shows a hexagonal array of cylinders of PE microphase (the light areas) in a continuous phase (the dark areas) composed of the inorganic silica and the PEO block in the composite with 40 wt% $E_{25}EO_{16}$. However, disordered wormlike aggregates were also observed for the composite with 40 wt% $E_{25}EO_{16}$ as shown in the same image (Fig. 1b). Further reduction of the $E_{25}EO_{16}$ copolymer concentration to 25 wt% resulted in a mesostructure composed exclusively of disordered wormlike aggregates (Fig. 1c). The composite with 10 wt% $E_{25}EO_{16}$ displayed no discernible mesoscopic features of any kind in the TEM images (not shown here).

Fig. 2 shows desmeared SAXS patterns of the $E_{25}EO_{16}/SiO_2$ composites. The peaks become narrower and more intense with the concentration of $E_{25}EO_{16}$ block copolymer, reflecting increased long-range mesostructural ordering in these materials. For the composites with 10 and 25 wt% $E_{25}EO_{16}$ copolymer, no discernible X-ray scattering peaks were observed. For the composites with 40 and 50 wt% $E_{25}EO_{16}$, the SAXS patterns give a shoulder or peak

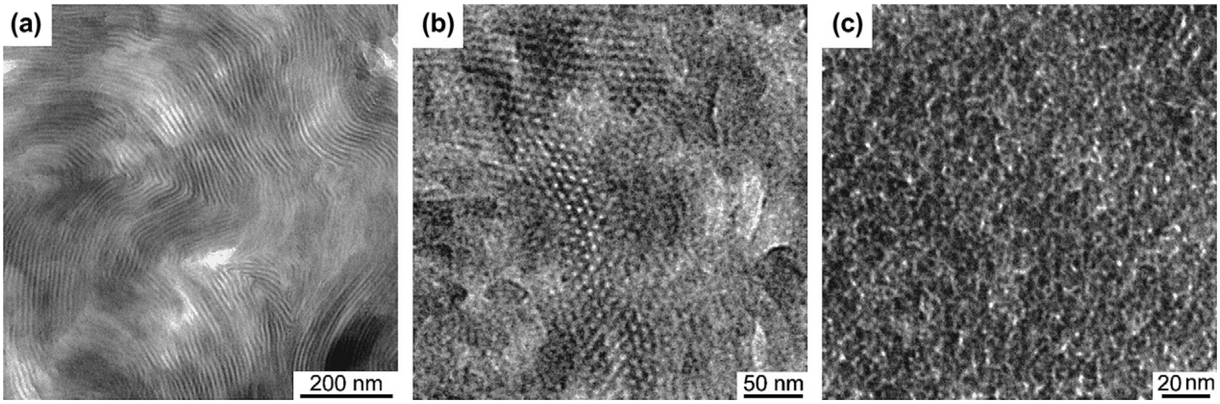

Fig. 1. TEM micrographs of (a) 67:33, (b) 40:60, and (c) 25:75 $E_{25}EO_{16}/SiO_2$ hybrid composite materials. Note that the scale bars are different for the three images. The light areas represent the PE microphase, whereas the dark areas correspond to the PEO microphase swollen by the inorganic silica.

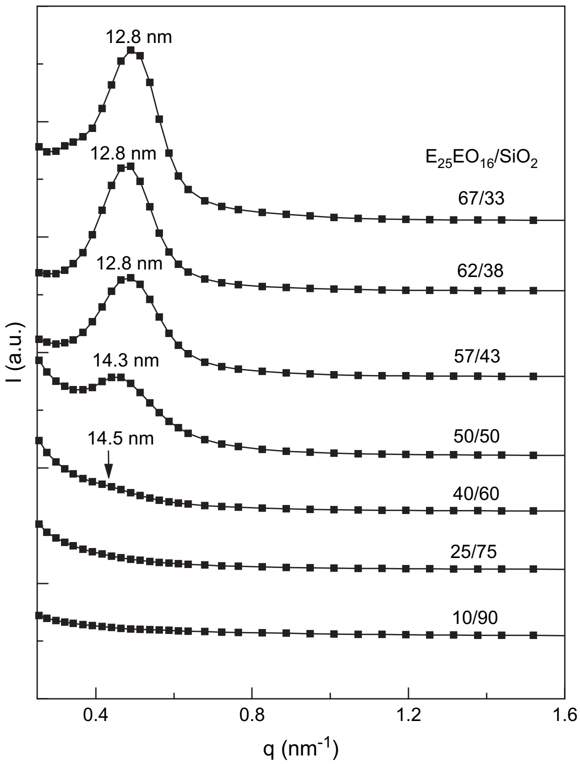

Fig. 2. Desmeared SAXS patterns of $E_{25}EO_{16}/SiO_2$ hybrid composite materials at room temperature (25 °C). The scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, where $\lambda = 0.154$ nm is the wavelength and θ the scattering angle.

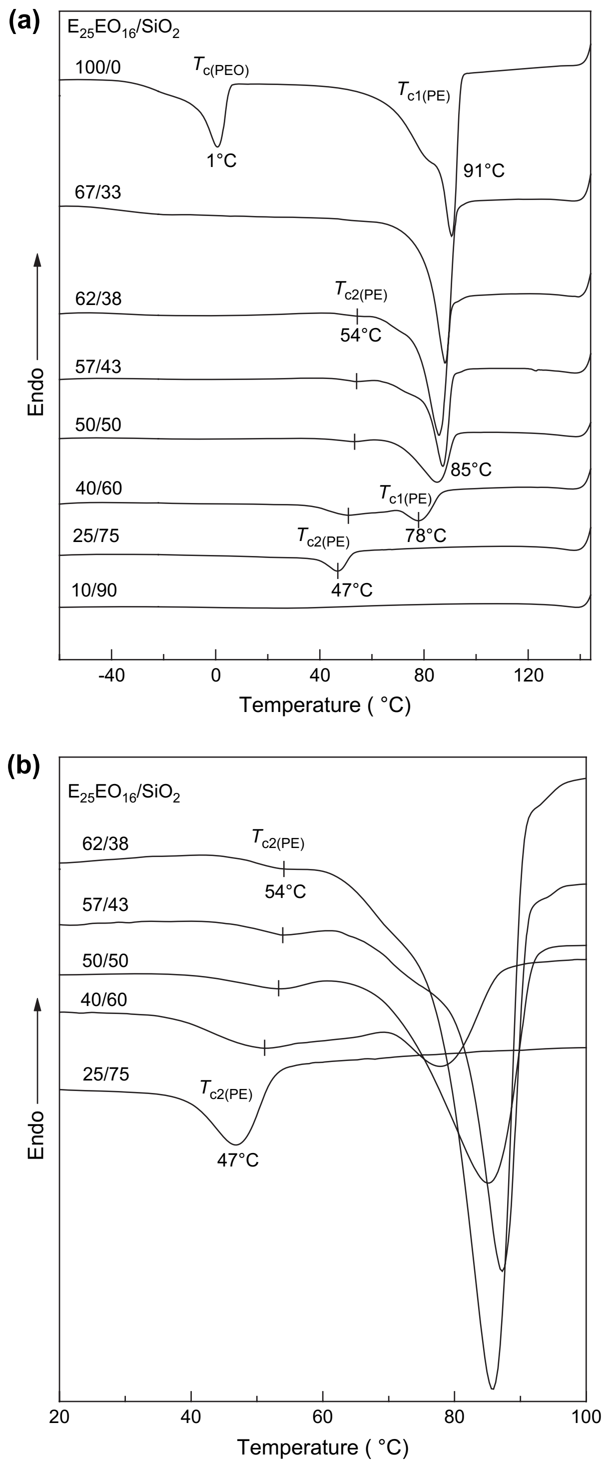

Fig. 3. DSC crystallization curves during the cooling at −20 °C/min: (a) all $E_{25}EO_{16}/SiO_2$ hybrid composite materials; (b) magnified region in the vicinity of the small crystallization exotherm, $T_{c2(PE)}$. All samples were first heated to 150 °C and kept at that temperature for 2 min to remove the thermal history.

corresponding to the long spacing of the hexagonal mesostructure at 14.5 and 14.3 nm, respectively. A scattering peak is observed for the composites containing 57, 62, and 67 wt% $E_{25}EO_{16}$ copolymer, corresponding to a distance of 12.8 nm in real space which is the long spacing of the lamellar mesostructure.

Fig. 3a shows DSC thermograms of the cooling scan for the $E_{25}EO_{16}/SiO_2$ hybrid composites at a cooling rate of −20 °C/min from 150 °C. Prior to the cooling scan, all samples were first heated to 150 °C at a rate of 20 °C/min and kept at that temperature for 2 min to remove the thermal history. The plain $E_{25}EO_{16}$ displays a crystallization peak, $T_{c(PEO)}$, at 1 °C, attributable to the crystallization of the PEO block. This crystallization peak, $T_{c(PEO)}$, was not observed in the hybrid composites with 10–67 wt% $E_{25}EO_{16}$ under the experimental conditions. These results imply that the PEO microphase and the inorganic silica were intimately mixed and the crystallization of PEO block was depressed. This is in agreement with the result that the inorganic and PEO phases were mixed on a molecular level in organic–inorganic hybrid composites from amphiphilic PI–PEO diblock copolymers [15].

The plain $E_{25}EO_{16}$ displays a major crystallization peak for the PE block, $T_{c1(PE)}$, at 91 °C, which does not significantly shift to lower temperatures in the hybrid composites with $E_{25}EO_{16}$ concentration down to 50 wt%, then remarkably drops to a lower temperature (78 °C) at 40 wt% $E_{25}EO_{16}$ composition. The relative intensity of this crystallization peak substantially decreases with decreasing $E_{25}EO_{16}$ content. Finally, this major crystallization peak disappears when the $E_{25}EO_{16}$ content is further down to 25 wt%. It is also noted that a small crystallization exotherm, $T_{c2(PE)}$, begins to appear on the low temperature side (54 °C) in the hybrid composite with $E_{25}EO_{16}$ content down to 62 wt%. Fig. 3b shows a magnified region of the crystallization curves in the vicinity of

$T_{c2(PE)}$, so that it can be more clearly seen. This observation indicates that the crystallization of a small amount of the PE block was performed at a greatly reduced rate in the hybrid composite. This crystallization peak only slightly varies between 54 and 47 °C in the hybrid composites with $E_{25}EO_{16}$ content further down to 25 wt%. However, its relative intensity gradually increases with decreasing $E_{25}EO_{16}$ content. Finally, this crystallization peak becomes the exclusive one at 25 wt% $E_{25}EO_{16}$ concentration. No crystallization peak appears for the hybrid composite at 10 wt% $E_{25}EO_{16}$ concentration.

The presence of more than one crystallization exotherm is known as fractionated crystallization [16,17]. It has been observed that fractionated crystallization can occur in dispersed domains of crystallizable polymers in low-molecular-weight media [16,17], in polymer blends [17–22], and in block copolymers [23–32]. However, to our knowledge, this is the first example of fractionated crystallization observed in organic–inorganic hybrid composite materials. In the present case, the inorganic matrix which is a combination of silica and PEO is rather different from organic matrices such as vitrified polymers [23–32] and rigid thermosets [13]. For fractionated crystallization to take place, the number of dispersed domains should be significantly greater than the number of active heterogeneities at low supercoolings that crystallization of dispersed domains will occur by homogeneous nucleation [16]. It has been shown that crystallization of crystallizable blocks for crystalline–amorphous diblock copolymers can be efficiently confined within nanoenvironments and the crystallization process occurs through homogeneous nucleation when the amorphous blocks vitrify prior to the crystallization [23–26]. Analysis of the homogeneous nucleation rate in crystalline–amorphous diblock copolymers at a given temperature has been addressed by Loo et al. [24] using the first-order kinetics. In the present case, the appearance of fractionated crystallization, i.e., the presence of two crystallization exotherms can be ascribed to the crystallization of the PE block in two different nanoenvironments in the $E_{25}EO_{16}/SiO_2$ hybrid composites. $T_{c1(PE)}$, the major crystallization peak in the proximity of 91 °C, is attributable to the crystallization of the PE block within the lamellar and hexagonal mesostructures in the composites. The crystallization is highly cooperative among the lamellar and hexagonal microdomains of the PE block of the $E_{25}EO_{16}$ copolymer and induced by heterogeneous nucleation. $T_{c2(PE)}$, the lower one intermediate between 47 and 54 °C, is related to the disordered wormlike aggregates of the PE block. The crystallization of the PE block is largely confined at nanoscales within the wormlike aggregates and takes place by homogeneous nucleation. The appearance of small $T_{c2(PE)}$ peak indicates that there exists some disordered wormlike aggregates in the composites with 62, 57 and 50 wt% $E_{25}EO_{16}$, apart from the dominated lamellar and hexagonal mesostructures. However, only a single melting endotherm for the PE block was observed in the subsequent heating DSC thermogram (not shown here), which is as expected for fractionated crystallization. From the subsequent heating scan, the melting point of the PE block, $T_{m(PE)}$, was determined to be 109 °C for the plain $E_{25}EO_{16}$ and its values only slightly varied between 108 and 111 °C for the composites with $E_{25}EO_{16}$ content down to 40 wt%. However, $T_{m(PE)}$ drastically dropped down to 72 °C for the composite with 25 wt% $E_{25}EO_{16}$, indicating that the crystallization of the PE block was highly restricted and spatial confinement reduced the crystallite size of the PE block. The heat of fusion of the PE block, $\Delta H_{f(PE)}$, was measured to be 105 J/g for the plain $E_{25}EO_{16}$. The $\Delta H_{f(PE)}$ values proportionately decreased in the composites with $E_{25}EO_{16}$ content down to 50 wt%, only slightly below those predicted by simple additivity. However, the $\Delta H_{f(PE)}$ values were dramatically decreased, i.e., much lower than those predicted by simple additivity in the composites with 40 wt% and less $E_{25}EO_{16}$; no melting endotherm was observed for the composite with 10 wt% $E_{25}EO_{16}$. The crystallization process of the PE block was remarkably influenced in the composites with 40 wt% and less $E_{25}EO_{16}$.

4. Conclusion

In conclusion, we have successfully prepared mesostructurally ordered inorganic–organic hybrid composite materials by utilizing a low-molecular-weight amphiphilic diblock copolymer $E_{25}EO_{16}$ as the directing agent. Fractionated crystallization is revealed in hybrid composite materials for the first time. Crystallization of the PE block of $E_{25}EO_{16}$ copolymer in the composites can be efficiently confined within the wormlike aggregates at nanoscales by the rigid silica matrix. The PE block crystallizes within the wormlike aggregates through homogeneous nucleation.

Acknowledgments

One of us (Q.G.) would like to express his gratitude to the Australian Research Council for financial support under the Queen Elizabeth II Fellowship and Discovery Project Schemes and to the Alexander von Humboldt Foundation for awarding a Research Fellowship.

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