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Crystallization and coalescence of block copolymer micelles in semicrystalline block copolymer/amorphous homopolymer blends

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Abstract

Crystallization of two oxyethylene/oxybutylene block copolymers ($E_{76}B_{38}$ and $E_{155}B_{76}$) from micelles in block copolymer/amorphous homopolymer blends was studied by differential scanning calorimetry (DSC) and time-resolved small angle X-ray scattering (SAXS). Unlike the simultaneous crystallization and formation of superstructure in crystallization from an ordered structure, crystallization of block copolymer from micelles can be divided into two steps. The core of the micelles firstly crystallizes individually, with first-order crystallization kinetics and homogeneous nucleation mechanism. The SAXS revealed that crystallization-induced deformation occurs for the micelles, which strongly depends on microstructure of the block copolymers. For the shorter block copolymer $E_{76}B_{38}$, larger deformation induced by crystallization was observed, leading to coalescence of the micelles after crystallization, while for the longer block copolymer $E_{155}B_{76}$ the micelles show little deformation and the morphology of micelle is retained after crystallization.

Keywords: Crystallization; Micelle; Block copolymer

1. Introduction

Crystallization of block copolymers from the melt with an ordered structure, including lamellae, cylinder and sphere, has been well studied and it has been found that crystallization can be confined either by a glassy wall or by a rubbery wall with strong segregation strength [1–8]. Comparatively, in breakout crystallization coalescence of different micro-domains occurs, which is usually accompanied by the formation of superstructure [9–24]. So far, the structural factors that govern crystallization of block copolymer have been known. The occurrence of confined crystallization in crystalline/rubbery block copolymer is related to the segregation strength and morphology of the block copolymer. The block copolymer with sphere morphology is most likely to exhibit confined crystallization behavior [16,18]. Weakly segregated block copolymers and the block copolymers with the crystalline block as the major component usually exhibit breakout crystallization behavior. However, how coalescence of different micro-domains in breakout crystallization proceeds has not been well understood and some questions remain un-resolved. Firstly, crystallization and coalescence of different micro-domains proceed simultaneously? Usually crystallization and formation of superstructure take place at the same time, but it is not certain that this holds true under all situations. Secondly, coalescence of different micro-domains involves well-separated domains and need to overcomes the unfavorable interaction between the unlike blocks. The effect of kinetic factor such as diffusion on crystallization behavior of block copolymer is still unclear.

In this paper we blended oxyethylene/oxybutylene diblock copolymers (E_mB_n) with large amount of amorphous poly(oxybutylene). Micelles, instead of ordered structure, are formed in the melt of the blends. The aim of the present work is to investigate whether there is any difference in crystallization from the ordered domains and from disordered micelles for the block copolymers. On the other hand, since the distance among crystalline domains in such blends is larger than that in the block copolymers with

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ordered structure, the present study can help us understand whether confined crystallization of crystalline/rubbery block copolymers is kinetically trapped due to diffusion factor. Moreover, we have previously reported the crystallization behavior of oxyethylene/oxybutylene diblock copolymers in *n*-hexane, the selective solvent for the amorphous oxybutylene block, using time-resolved SAXS/WAXS [25]. It was found that spherical micelles are retained after crystallization for longer block copolymer $E_{155}B_{76}$, but macro-aggregation takes place for the shorter block copolymer $E_{76}B_{38}$. Nevertheless, it is inconvenient to study crystallization kinetics using DSC due to the presence of solvent. In this paper, the solvent was replaced by the amorphous component and the crystallization kinetics can be readily studied using DSC. To our best knowledge, following two aspects in the present work are novel and have not been reported in literature: the structural change of the micelles induced by crystallization and crystallization kinetics of block copolymer from micelles.

2. Experimental

2.1. Materials

The synthesis and characterization of poly(oxyethylene)-*block*-poly(oxybutylene) copolymers, E_mB_n (here E and B represent oxyethylene block and oxybutylene block, and m and n denote the polymerization degrees of the two blocks.), used for blending have been described in previous work [26,27]. Both $E_{76}B_{38}$ and $E_{155}B_{76}$ have narrow molecular weight distributions ($M_w/M_n < 1.05$). The PBO homopolymer (B_h) with $M_n = 2000$ (B_{28}) was purchased from Aldrich and was used without further purification. The other PBO homopolymer with $M_n = 1000$ (B_{14}) was specially synthesized by anionic polymerization. Both PBO homopolymers have narrow molecular weight distributions.

2.2. Preparation of the blends

The blends of E_mB_n with B_h were prepared by a solution blending method employing dicholoromethane as solvent. To ensure that PBO homopolymer was miscible with PBO segments in block copolymers and the condition of 'wet brush' was met [28,29], the molecular weight of PBO homopolymer was smaller than half that of PBO block. As a result, $E_{76}B_{38}$ was blended with B_{14} and $E_{155}B_{76}$ was blended with B_{28}. The blends were dried under vacuum for 24 h at 60 °C after the solvent was evaporated, then were cooled to room temperature slowly and stored below 0 °C for usage.

2.3. Time-resolved small angle X-ray scattering

The simultaneous time-resolved SAXS/DSC experiments were carried out at beamline 16.1 in SRS at the Daresbury, Warrington, UK. For $E_{76}B_{38}/B_{14}$ blends the distance between the sample and the SAXS detector was 3.5 m but it was 5.0 m for $E_{155}B_{76}/B_{28}$ blends. The samples were cooled from 100 °C at a rate of 10 °C/min with a Linkam DSC equipped with liquid N_2 cooling system. The data were collected in 10 s frames separated by a waiting-time of 10 μs. Details of the instrument and data processing are described elsewhere [26,27].

2.4. DSC measurements

Non-isothermal crystallization of the blends was performed on a Perkin–Elmer Pyris-1 calorimeter. Samples of the blends about 10 mg were sealed with aluminum pans and were held at 70 °C for 5 min, and then cooled down to −50 °C at a rate of 10 °C/min. The crystallized samples were heated to 70 °C at a rate of 10 °C/min. The thermal lag was ignored and not corrected.

In isothermal crystallization experiments the blends were held at 70 °C for 5 min, and then cooled down at a nominal rate of 100 °C/min to the crystallization temperatures and held until crystallization was completed. The change of heat flow with time was recorded upon crystallization. The isothermal crystallization kinetics of polymer can be analyzed using Avrami equation: [30]

$$1 - X(t) = \frac{\Delta H^{c}_{t=\infty} - \Delta H^{c}_{t}}{\Delta H^{c}_{t=\infty} - \Delta H^{c}_{t=0}} = \exp(-kt^{n}) \quad (1)$$

where $X(t)$ is the relative crystallinity at time t, $\Delta H^{c}_{t=\infty}$ and ΔH^{c}_{t} are the crystallization enthalpies on complete crystallization and after time t. Therefore, we have:

$$\log[-\ln(1 - X(t))] = \log k + n \log t \quad (2)$$

The crystallization rate constant k and Avrami exponent n can be determined from the interception and the slope, respectively, in the plot of $\log[-\ln(1 - X(t))]$ versus $\log(t)$.

3. Results

3.1. DSC results

The non-isothermal crystallization curves and subsequent melting behavior of $E_{76}B_{38}/B_{14}$ blends beyond the order composition are depicted in Figs. 1 and 2, respectively. It is observed that crystallization peaks appear at both higher temperature and lower temperature in the blends with larger volume fraction of the E block, ϕ_E ($\phi_E = 0.12$, 0.10 and 0.08), which fall into the temperature ranges of heterogeneous nucleation and homogeneous nucleation, respectively [17]. This shows that these three blends exhibit fractionated crystallization behavior [31,32]. Because the number of crystallizable domains is far larger than the number of heterogeneous nuclei, heterogeneous nuclei can