

CRYSTALLIZATION OF BLENDS OF AN ASYMMETRIC POLY(OXYETHYLENE)-*b*-POLY(OXYBUTYLENE) BLOCK COPOLYMER WITH POLY(OXYBUTYLENE)*

Jun-ting Xu** and Guo-dong Liang

Department of Polymer Science & Engineering, Zhejiang University, Hangzhou 310027, China

Shao-min Mai and A. J. Ryan

Chemistry Department, The University of Sheffield, Sheffield S3 7HF, UK

Abstract An oxyethylene/oxybutylene block copolymer with asymmetric volume fraction ($E_{115}B_{103}$) was blended with oxybutylene homopolymer (B_h) at different volume fractions of the block (ϕ_E). Crystallization behavior of the blends was studied and was compared with that of the blends from a symmetric block copolymer ($E_{114}B_{56}$). It was found that the crystallization temperature of $E_{115}B_{103}/B_{28}$ blend is lower than that of the blends from symmetric block copolymer. For the blend with $\phi_E = 0.30$ breakout crystallization with an Avrami exponent $n \approx 3.0$ is observed. At $\phi_E = 0.22$ the blend exhibits a variable crystallization behavior: confined crystallization with $n \approx 1.0$ at lower crystallization temperatures but breakout crystallization at high crystallization temperatures. For the blend with $\phi_E = 0.14$ and sphere morphology confined crystallization occurs at all crystallization temperatures studied. When compared with the blends from symmetric block copolymer, confined crystallization occurs more easily in the $E_{115}B_{103}/B_{28}$ blends. The SAXS results agree with the isothermal crystallization kinetics. Deformation of the confined crystalline block is observed in the blend with $\phi_E = 0.14$ and mixed lamellar and cylinder morphologies in the blend with $\phi_E = 0.22$.

Keywords Crystallization, Block copolymer, Blend, Confinement

INTRODUCTION

Recently, crystallization of block copolymers has attracted many researchers. Due to the competition between microphase separation and crystallization, there are numerous possibilities for the crystallization of block copolymers, depending on segregation strength and morphology (or composition)^[1–8]. Using various symmetric oxyethylene/oxybutylene block copolymers (E_mB_n) to blend with amorphous oxybutylene homopolymer (B_h), we have prepared blends with different segregation strength and morphology and observed several types of crystallization behavior^[9]. Breakout crystallization, where the morphology of the melt is destroyed and lamellar structure is formed after crystallization irrespectively of the morphology in the melt, is observed for the weakly segregated block copolymers. Confined crystallization, where the morphology in the melt is retained after crystallization, usually occurs in the block copolymer with sphere morphology and strong segregation strength. The block copolymers with cylinder morphology and intermediate segregation strength can exhibit partially confined crystallization, which refers to the partial preservation of the morphology in the melt. Moreover, weakly confined crystallization in which the size of the confined crystalline domains can vary with temperature is identified as well.

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** Corresponding author: Jun-ting Xu (徐君庭), E-mail: xujt@zju.edu.cn

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It should be noted that the E_mB_n block copolymers used for blending in our previous work have a symmetric volume fraction^[9, 10]. In order to further investigate crystallization behavior of block copolymers, in the present work we use an oxyethylene/oxybutylene block copolymer with asymmetric volume fraction to blend with B_h homopolymer. Crystallization behavior of the blends with different compositions was studied and was compared with that of the blends from symmetric block copolymer.

EXPERIMENTAL

Materials

The synthesis and characterization of oxyethylene/oxybutylene block copolymer ($E_{115}B_{103}$, the subscripts denote the average degree of polymerization) were described elsewhere^[11, 12]. This block copolymer has a narrow molecular weight distributions ($M_w/M_n < 1.05$) measured by GPC. The volume fraction of the E block in $E_{115}B_{103}$ is 0.371, the morphology in the melt is cylindrical and the order-disorder transition temperature is 225 °C^[13]. The oxybutylene homopolymer (B_h) with a reported $M_n \approx 2000$ g/mol (B_{28}) was purchased from Aldrich and was used without further purification. The blends were prepared by mixing $E_{115}B_{103}$ and B_{28} in chloroform at various volume fractions of the E block (ϕ_E). The calculation of ϕ_E at 70 °C in the blends is based on Eq. (1):

$$\phi_E = \frac{w_{EB} \times 0.406 / 0.923}{w_{EB} \times 0.406 / 0.923 + w_{EB} \times 0.594 / 1.067 + w_B / 1.067} \quad (1)$$

Where w_{EB} and w_B are the weight of $E_{115}B_{103}$ and B_h , respectively. The densities of poly(oxyethylene) and poly(oxybutylene) at 70 °C are 0.923 g/cm³ and 1.067 g/cm³^[14] and the weight percentages of the E block and the B block in $E_{115}B_{103}$ are 0.406 and 0.694, respectively.

The blends were dried under vacuum for 24 h at 60 °C after solvent evaporation and then cooled to room temperature slowly and stored below 0 °C prior to use. The blends are designated as EB-XX, where the hyphenated numbers are the volume fraction of E block in the blends.

Differential Scanning Calorimetry (DSC)

The non-isothermal and isothermal crystallization experiments were carried out on a Perkin-Elmer Pyris-1 calorimeter. The copolymer samples (about 5–10 mg, depending on B volume fraction in the blends) were enclosed in aluminum pans and were heated to 70 °C, and held for 5 min. In non-isothermal crystallization the melts of the blends were cooled down to crystallization at prescribed rates. In isothermal crystallization the melts were cooled to crystallization temperature at a rate of 100 K/min and held until crystallization was complete. The change of heat flow with time was recorded upon crystallization. The isothermal crystallization kinetics of polymer was analyzed using the Avrami equation^[15]:

$$1 - X(t) = \frac{\Delta H_{t=\infty}^c - \Delta H_t^c}{\Delta H_{t=\infty}^c - \Delta H_{t=0}^c} = \exp(-kt^n) \quad (2)$$

Where $X(t)$ is the relative crystallinity at time t , $\Delta H_{t=\infty}^c$ and ΔH_t^c are the crystallization enthalpies for complete crystallization and after time t . Therefore, we have:

$$\lg[-\ln(1 - X(t))] = \lg k + n \lg t \quad (3)$$

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

Time-Resolved Small Angle X-ray Scattering (SAXS)

The simultaneous time-resolved SAXS/DSC experiments were carried out on a beamline 8.2 of the SRS at Daresbury, Warrington, UK. The blends were cooled from the melt (70 °C) at a rate of 10 K/min to complete crystallization and then were re-heated at a rate of 10 K/min until the order-disorder transition was observed. The data were collected in 10 s frames separated by a waiting-time of 10 μ s. Details of the instrument and data processing are described elsewhere^[11, 12].

RESULTS AND DISCUSSION

Non-Isothermal Crystallization

Figure 1 shows the DSC curves of some blends cooled from the melt at a rate of 2 K/min. It was found that EB-30 (cylinder morphology) exhibits a crystallization peak at high temperature, not far from that of the neat block copolymer, whereas the other three blends, EB-26 (cylinder morphology), EB-22 (cylinder morphology) and EB-14 (sphere morphology), crystallize at very low temperatures, which have dropped into the temperature range of homogeneous nucleation^[10]. At higher cooling rate (10 K/min), the crystallization temperatures of EB-14, EB-22 and EB-26 are slightly decreased (Fig. 2). For EB-30, a crystallization peak appears at low temperature region well apart from the high temperature crystallization peak. This shows that crystallization of EB-30 is strongly influenced by cooling rate. At slower cooling rate, heterogeneous nucleation occurs and EB-30 has a higher crystallization temperature, while at a faster cooling rate only a minor part of crystallization of EB-30 is initiated by heterogeneous nucleation and the major part of crystallization of EB-30 is initiated by homogeneous nucleation, leading to a drastic shift of the crystallization temperature to lower temperatures. The crystallization temperatures of $E_{115}B_{103}/B_{28}$ blends at various volume fractions are shown in Fig. 3. For the purpose of comparison, the crystallization temperatures of the blends prepared from a symmetric block copolymer $E_{114}B_{56}$ are also shown in Fig. 3^[10]. It is observed that the neat block copolymer $E_{115}B_{103}$ has a crystallization temperature comparable to that of the $E_{114}B_{56}/B_{28}$ blend with the same composition. For the $E_{115}B_{103}/B_{28}$ blends with cylinder morphology the crystallization temperature decreases gradually as the volume fraction of the E block decreases.

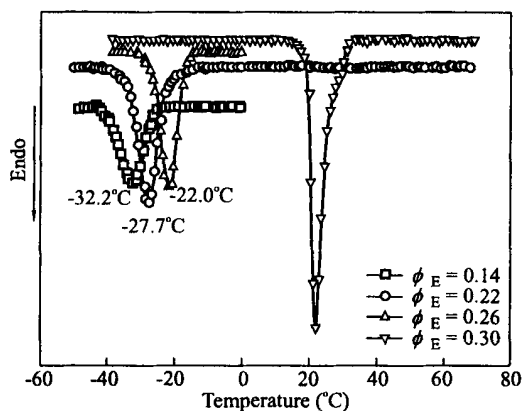


Fig. 1 DSC crystallization traces of $E_{115}B_{103}/B_{28}$ blends cooled from the melt at a rate of 2 K/min

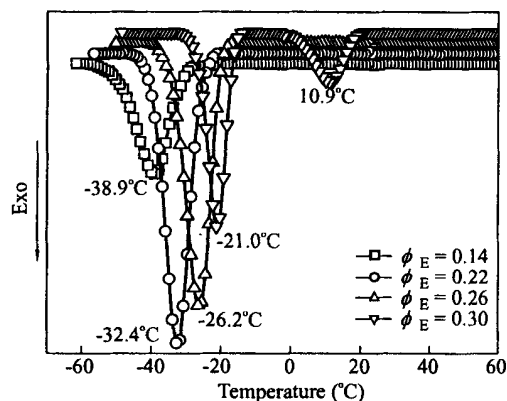


Fig. 2 DSC crystallization traces of $E_{115}B_{103}/B_{28}$ blends cooled from the melt at a rate of 10 K/min

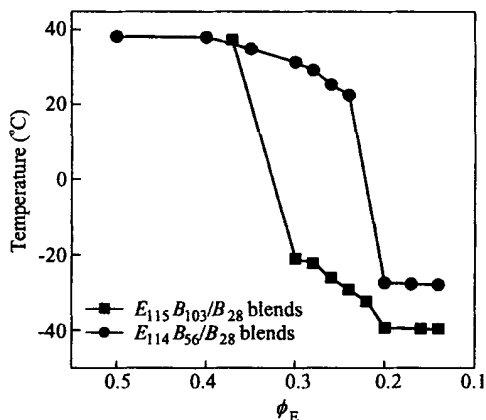


Fig. 3 Crystallization peak temperatures of $E_{115}B_{103}/B_{28}$ blends and $E_{114}B_{56}/B_{28}$ blends. The cooling rate is 10 K/min.

The $E_{114}B_{56}/B_{28}$ blends show a similar tendency, but their crystallization temperatures are remarkably higher than those of the $E_{114}B_{56}/B_{28}$ blends with the same composition. The crystallization temperatures of both $E_{115}B_{103}/B_{28}$ blends and $E_{114}B_{56}/B_{28}$ blends with sphere morphology hardly change with volume fraction of the E block, but the $E_{115}B_{103}/B_{28}$ blends still have lower crystallization temperatures. The non-isothermal crystallization experiments reveal that the blends prepared from asymmetric block copolymer with minor crystalline block systematically have lower crystallization temperature than the blends from symmetric block copolymer.

Isothermal Crystallization Kinetics

Three $E_{115}B_{103}/B_{28}$ blends, EB-30, EB-22 and EB-14, were subjected to isothermal crystallization experiments. Figure 4 shows the Avrami plots of EB-30 (cylinder morphology). It is observed that this blend has an Avrami exponent $n \approx 3.0$, indicating typical breakout crystallization with the formation of spherulite and heterogeneous nucleation. The Avrami plots of EB-22 (cylinder morphology) at various crystallization temperatures are illustrated in Fig. 5. The obtained Avrami exponents and logarithmic crystallization rate constants are shown in Fig. 6. It was found that the Avrami exponent of EB-22 gradually increases with crystallization temperature, ranging from -1.0 to 3.0 . The Avrami exponent $n = 1.0$ is one of the characteristics of confined crystallization with homogeneous nucleation. The non-isothermal crystallization also shows that the crystallization temperature of EB-22 falls into the temperature range of homogeneous nucleation. As a result, we can judge that the crystallization behavior of EB-22 varies with crystallization temperature. This blend exhibits confined crystallization at lower temperatures, but breakout crystallization at higher crystallization temperatures. By contrast, we observed variable crystallization behavior only in $E_{114}B_{56}/B_{28}$ blends with sphere morphology, *i.e.* at lower volume fraction of the E block^[10]. All the $E_{114}B_{56}/B_{28}$ blends with cylinder morphology exhibit breakout crystallization behavior and have an Avrami exponent larger than 1.0 . The Avrami plots of EB-14 with sphere morphology are shown in Fig. 7 and the variation of Avrami exponent and crystallization rate constant with crystallization temperature are depicted in Fig. 8. It is noted that the Avrami exponents of EB-14 range from $n \approx 0.5$ to $n \approx 1.0$, which are quite different from the Avrami exponents of $E_{114}B_{56}/B_{28}$ blends with the same ϕ_E .

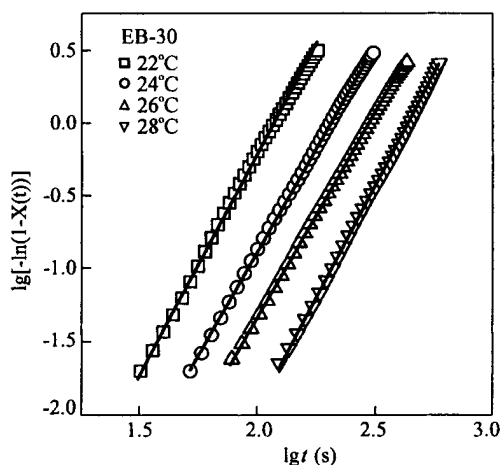


Fig. 4 Avrami plots of EB-30 at various crystallization temperatures

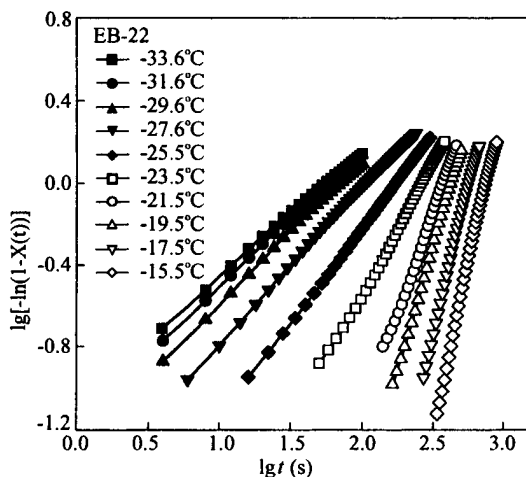


Fig. 5 Avrami plots of EB-22 at various crystallization temperatures

The Avrami exponent $n = 0.5$ may arise from diffusion-controlled confined crystallization at extremely low crystallization temperature^[16, 17]. Therefore, EB-14 exhibits confined crystallization at all crystallization temperatures studied. The results of isothermal crystallization kinetics indicate that confined crystallization occurs more easily in the blends prepared from an asymmetric block copolymer with minor crystalline block than in the blends from a symmetric block copolymer.

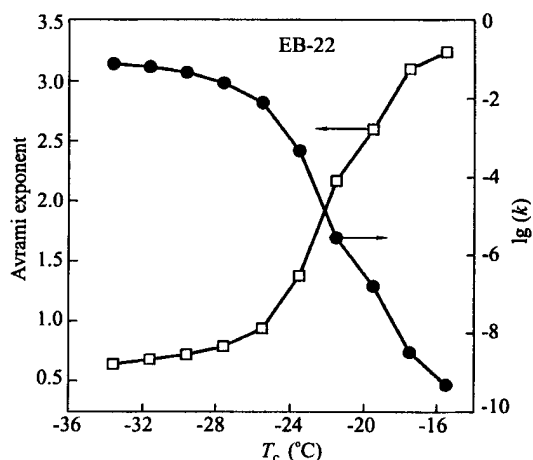


Fig. 6 Avrami exponents (n) and logarithmic crystallization constants ($\lg k$) of EB-22 at various crystallization temperatures

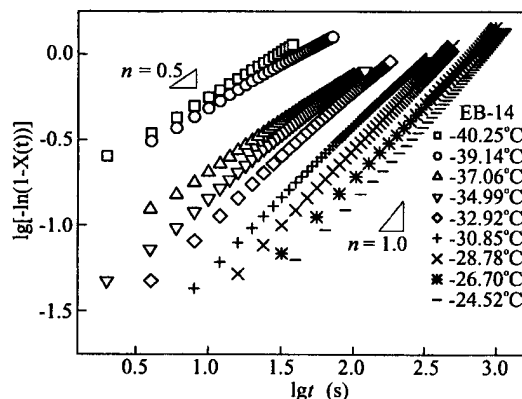


Fig. 7 Avrami plots of EB-14 at various crystallization temperatures

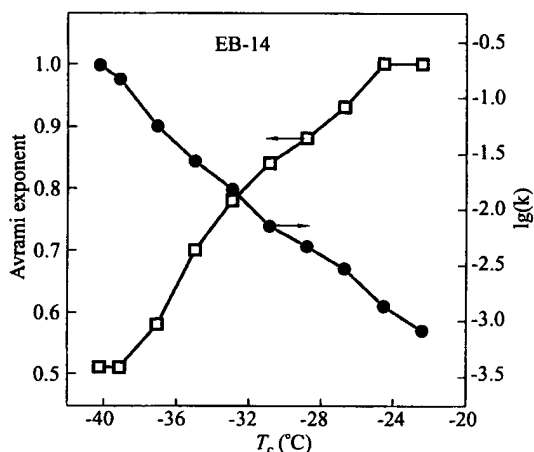


Fig. 8 Avrami exponents (n) and logarithmic crystallization constants ($\lg k$) of EB-14 at various crystallization temperatures

SAXS Results

Figure 9 shows the three-dimensional SAXS profiles ($\lg(I(q))$ versus q versus T) of EB-30 when cooled from the melt at a rate of 10 K/min. The SAXS patterns confirm that the morphology in the melt of this blend is cylinder, since the higher order peaks appear at $q = 3^{1/2}q^*$ and $q = 2q^*$ (q^* is the position of the first order SAXS peak). After crystallization we found that a lamellar structure is formed, as revealed by the higher order peaks at $q = 2q^*$ and $q = 3q^*$. There is also evident displacement of the position of the first order SAXS peak after crystallization. These facts show that the morphology in the melt is destroyed after crystallization and agree well with its breakout crystallization behavior deduced from isothermal crystallization kinetics and non-isothermal crystallization. The SAXS profiles of the blends EB-22 and EB-14, which have cylinder morphology and sphere morphology in the melt, respectively, are illustrated in Fig. 10 and Fig. 11. No obvious displacement is observed for the first order peaks after crystallization in these two blends, but the SAXS peaks become broader due to crystallization, as indicated by arrows. There are two possible reasons for the broadening of the SAXS peak: deformation of the confined crystalline domains induced by crystallization and/or the existence of mixed morphologies (partially retained morphology of the melt and lamellar structure)^[8, 9–18]. In the isothermal crystallization experiments we found that the crystallization behavior of EB-22 is variable with temperature, but

EB-14 always shows confined crystallization. As a result, the broadening of the SAXS peak of EB-14 is attributed to the deformation of the confined crystalline domains, while the broadening of the SAXS peak of EB-22 may result from the mixed lamellar and cylinder morphologies in the solid.

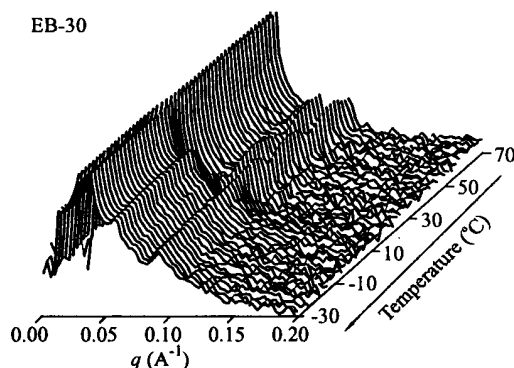


Fig. 9 Three-dimensional SAXS profiles ($\lg(I(q))$ versus q versus T) of EB-30 cooled from the melt at a rate of 10 K/min

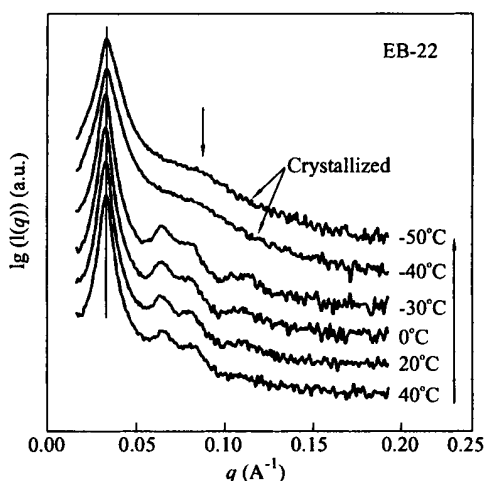


Fig. 10 SAXS profiles of EB-22 at different temperatures when cooled from the melt at a rate of 10 K/min

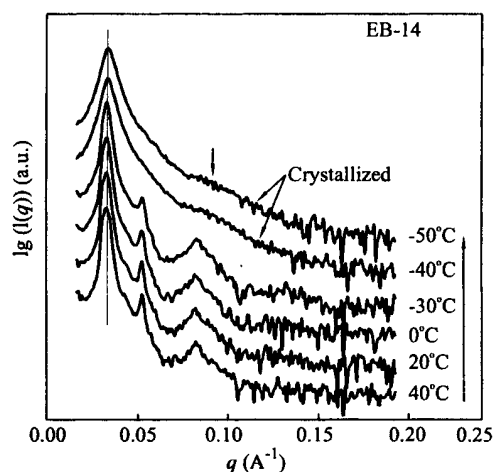


Fig. 11 SAXS profiles of EB-14 at different temperatures when cooled from the melt at a rate of 10 K/min

CONCLUSION

The non-isothermal crystallization shows that the blends prepared from an asymmetric block copolymer with minor crystalline block systematically have lower crystallization temperature when compared with the blends from a symmetric block copolymer with similar length of the E block. In isothermal crystallization experiments, breakout crystallization, confined crystallization and variable crystallization behaviors can be observed in the $E_{115}B_{103}/B_{28}$ blends, depending on volume fraction of the E block and crystallization temperature. When compared with $E_{114}B_{56}/B_{28}$ blends, confined crystallization occurs more easily in $E_{115}B_{103}/B_{28}$ blends. The SAXS results are in accord with the isothermal crystallization kinetics. After crystallization deformation of the confined crystalline domains is found in the blend with sphere morphology and mixed lamellar and cylinder morphologies is observed in the blend with cylinder morphology in the melt.

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