Study of temperature dependence of crystallisation transitions of a symmetric PEO-PCL diblock copolymer using simultaneous SAXS and WAXS measurements with synchrotron radiation

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Abstract. The reversible transitions of the lamellae of a crystalline-crystalline diblock copolymer from the melt to crystallites were studied using simultaneous small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements with synchrotron radiation. A symmetric poly(ethylene oxide)-poly(ϵ -caprolactone) diblock copolymer was chosen for this study. We showed in the course of the block copolymer crystallisation that the time-resolved integrated intensity I_{int} was proportional to the product of the volume fractions of the PEO and PCL phases and the scattering contrast due to the electron density difference. These results demonstrated that simultaneous SAXS/WAXS measurements could be used to monitor the crystallisation process in two domains of different sizes at the same time.

PACS. 64.70.Nd Structural transitions in nanoscale materials – 64.70.pj Polymers

Introduction

Studies have shown that the crystallites of polymers adopt either an extended or, more often, chain folded conformation. It is important to distinguish the crystallization behaviors between homopolymers and block copolymers. In homopolymers, chain folding leads to metastable structures imposed by crystallisation kinetics. Chain folding in diblocks is influenced by the number of the folds that is controlled by the size of the non-crystallisable block [1,2]. Factors that control different phase transitions of self-organizing polymers have been widely investigated with the objective of developing techniques to fabricate ordered structures at different length scales [3]. It is plausible that multi-scale self-organization of polymers can be achieved by synthesizing a block copolymers with various block structures. For block copolymers that contain crystallisable components, the interplay between crystallisation and microphase separation strongly influences the structural changes, morphology, properties and applications of such materials.

Crystalline-crystalline poly(ethylene oxide)-poly(ϵ -caprolactone) (PEO-PCL) block copolymers were devel-

oped for their unique properties, such as biocompatibility, amphiphilicity, self-assembly, permeability, and controllable biodegradability [4,5]. It is apparent that the crystallinity of these block copolymers has a significant effect on drug permeability and biodegradation behavior. Due to the fact that PEO and PCL have comparable crystallisation temperatures and glass transition temperatures, the crystallisation behavior of the block copolymers containing PEO and PCL blocks is thus far open for investigation since their crystallisation behaviors and mechanisms are not as well understood as those of crystalline-amorphous block copolymers. Small-angle X-ray scattering (SAXS), wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) have been used to investigate the crystallisation of PCL-PEO-PCL triblocks [6]. Both components in these copolymers melted around 40° to 50 °C. During this study, WAXS revealed that the crystals of the PEO and PCL coexisted independently without eutectic or mixed crystals containing both PEO and PCL. In a PEO-PCL binary blend, however, the two components of PEO and PCL were immiscible and crystallised independently [7]. Furthermore, the lamellar spacing and the melting temperature, which did not change with the mixture composition, were close to those of the homopolymers.

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This was a consequence of crystallization-driven segregation observed for most crystalline-crystalline polymer blends. Because of the chain connectivity of the block copolymers, crystalline-crystalline PEO and PCL lamellae occupied the same crystallites when comparable fractions of each component were present. This led to the observed large reduction in lamellar thickness and imperfections within crystals, as evidenced by the melting temperature depression. WAXS patterns also indicated the presence of coexisting crystalline components.

The final solid-state structure in a semicrystalline block copolymer is also a result of the interaction between microphase separation and crystallisation [8–10]. When a crystallisable component is confined within a large number of small isolated microdomains, a substantial decrease in crystallinity, compared to the corresponding homopolymers, can sometimes be observed. This is a result of the fact that stronger supercooling is required for crystallization, as well as topological restrictions caused by the confinement.

The factors that affect the crystallisation properties of PEO-PCL block copolymers have been studied [11–13]. These factors are typically thought to be block length and crystallization temperature. Intuitively, the block with higher molecular weight crystallises first in the melt of PEO-PCL crystalline-crystalline diblock copolymers. However, there are no studies on the crystallisation process of a symmetric diblock copolymer. In this report, we choose to examine the isothermal crystallisation process of a symmetric PEO_{5k}-PCL_{5k} diblock copolymer. Our results show that various crystallisation behaviors are involved in the crystallisation process, depending on the crystallisation temperature. Our results indicate that multi-scale transitions can be detected concurrently using simultaneous SAXS and WAXS measurements with synchrotron radiation.

Experiment

A PEO-PCL diblock copolymer was synthesized by ring-opening polymerization of ϵ -caprolactone (ϵ -CL) using mPEO_{5k} (monomethoxy poly(ethylene oxide), $M_n = 5000$) as the macroinitiator and Sn(Oct)₂ as the catalyst [14]. mPEO_{5k} was dried by azeotropic distillation with dry toluene.

Proton nuclear magnetic resonance (1H-NMR) spectra of the polymers in deuterated chloroform solutions were recorded by a Bruker 300 MHz spectrometer with tetramethylsilane as internal standard. Gel permeation chromatography (GPC) measurements were carried out using a Waters 515 HPLC pump equipped with a Wyatt interferometer refractometer. GPC columns used chloroform as the eluent at 25 °C. Molecular weights were calibrated with poly(ethylene glycol) standards.

DSC experiments were performed using a Perkin-Elmer DSC-7 differential scanning calorimeter for observations of melting and crystallisation of the PEO-b-PCL diblock copolymer. X-ray scattering experiments were performed using synchrotron radiation with $\lambda = 0.150$ nm

Table 1. Molecular weights of PEO and PCL homopolymers, and the PEO-b-PCL diblock copolymer.

Sample	PEO	PCL ^(a)	M_n ^(b)	M_w/M_n ^(b)
PEO	5000		5000	1.04
PEO-b-PCL	5000	5090	9810	1.16
PCL		5100	5900	1.30

^(a) Evaluated by 1H NMR.

^(b) Determined by GPC (calibrated with PEO standards).

at Beamline A2 of HASYLAB (Hamburg, Germany) and synchrotron radiation with $\lambda = 0.154$ nm at Beamline 4B9A of Beijing Synchrotron Radiation Facility (Beijing, China). Two linear position-sensitive detectors were used simultaneously, one of them covering approximately the 2θ range from 10 to 30° and the other being set at a 230 cm sample-detector distance in the direction of the beam. In this experimental setup, WAXS and SAXS data were collected simultaneously.

Film samples of about 50 mg were covered with aluminum foil to ensure uniform heating or cooling. They were then placed in the temperature controller of the beamline, in a vacuum. Heating and cooling experiments were performed at different heating rates ranging from 1 to 40 °C/min. WAXS data were used to investigate the crystallisation behavior of the samples and SAXS data were used to study the lamellar formation.

Results and discussion

The relative intensities of the characteristic peaks of 1H-NMR (at 2.28–2.33 ppm for PCL and 3.65 ppm for PEO) were used to calculate the PCL weight fraction of the PEO-b-PCL diblock copolymer. The molecular weight of the PCL homopolymer was estimated by comparing the intensity of the PCL characteristic peak at 2.28–2.33 ppm with the intensity of the characteristic peak at 1.24–1.26 ppm for 2-propanol. The molecular weights and polydispersities of all samples were measured using GPC. The molecular weight data, shown in Table 1, reveals that the diblock copolymer has a narrow molecular weight distribution.

Figure 1 shows DSC curves of the PEO_{5k}-b-PCL_{5k} diblock copolymer on heating after isothermal crystallisation at indicated temperatures. The isothermally crystallized samples were heated from the crystallisation temperature to 80 °C with a heating rate of 10 °C/min. A single melting peak was found during the melting process of the PEO-b-PCL block copolymer after isothermal crystallisation. The melting temperatures of PEO and PCL homopolymers are 55.6 and 64.6 °C, respectively [15]. The WAXS results revealed that the crystals of the PEO (monoclinic) and PCL (orthorhombic) in the block copolymer coexisted independently and that there were no eutectic or mixed crystals containing both PEO and PCL, as shown in Figure 2.

Fig. 1. DSC heating curve (heating rate of 10 °C/min) for the PEO-*b*-PCL block copolymer after isothermal crystallisation at 40 and 50 °C.

Fig. 2. WAXS patterns of PEO, PCL and the PEO-*b*-PCL block copolymer.

Fig. 3. Simultaneous (a) SAXS and (b) WAXS profiles collected during isothermal crystallisation of PEO-PCL at 40 °C.

To clarify the nature of the single melting peak of the symmetric double crystalline blocks of the PEO-*b*-PCL copolymer, the structure and the structure transition behavior of the copolymer were investigated using time-resolved simultaneous WAXS/SAXS measurements with synchrotron radiation. The scattering patterns were collected in time frames of 10 and 60 s at isothermal crystallisation temperatures of 40 and 50 °C, respectively. The spacings for the different detectors and positions were calibrated using the diffraction peaks of a crystalline poly(ethylene terephthalate) sample for the WAXS detector and the different orders of the long spacing of the rat tendon tail ($L = 65$ nm) for the SAXS detector.

Typical time-resolved SAXS and WAXS profiles obtained during isothermal crystallisation of PEO_{5k}-PCL_{5k} at 40 °C are shown in Figures 3a and b. The relatively low supercooling used for the PEO-PCL block copolymer crystallisation resulted in a low crystallisation rate, allowing for the possibility of a detailed examination of the simultaneously collected SAXS and WAXS profiles. A detectable scattering shoulder first appeared in the raw SAXS profile almost at the same time as the crystalline reflections first became identifiable in the WAXS data

Fig. 4. The integrated intensity I_{int} as a function of time obtained from SAXS and WAXS measurements during isothermal crystallisation of PEO-PCL at 40 °C.

(cf., Fig. 3). This was confirmed by comparing the time evolution of the integrated intensity from the scattering maximum ($s = 0.048 \text{ nm}^{-1}$) of the SAXS profiles and the strong reflections of WAXS (as shown in Fig. 2 (120) of PEO and (110) of PCL at $2\theta = 19.09$ and 21.05 , respectively). These comparisons are shown in Figure 4. The SAXS results in Figure 3a imply that the long spacing was almost constant during isothermal crystallization and the results in Figure 4 indicate that the PEO block crystallised first. This is further illustrated in a schematic diagram shown in Figure 7a.

SAXS peaks corresponding to a lamellar thickness were present in the supercooled melt prior to the WAXS observation of three-dimensional crystal ordering. The lag time, ($t_{\text{WAXS}} - t_{\text{SAXS}}$), decreased as crystallisation temperature decreased or as the degree of supercooling increased. Wang *et al.* [16] reported that the lag was attributed to the detection limits of SAXS and WAXS. They argued that the detection limits of SAXS and WAXS differ and the attempt to detect the presence of the initial crystalline phase by comparing the first appearance of SAXS and

Fig. 5. The integrated intensity I_{int} as a function of time obtained from SAXS and WAXS measurements during isothermal crystallisation of PEO-PCL at 50 °C.

WAXS intensities may not provide any meaningful results. It was thought that the WAXS technique may not be able to detect the low crystallinity in the early stage. By contrast, the low crystallinity fraction can be easily detected by SAXS as long as the contrast between the constituting phases is sufficiently large and the length scale is within the detectable range. However, this is not the case for the PEO-PCL block copolymer (as shown in Figs. 4 and 5).

The time-resolved SAXS and WAXS profiles were also investigated during isothermal crystallisation of PEO_{5k}-PCL_{5k} at 50 °C. Time evolutions of the integrated intensity of the SAXS scattering peak ($s = 0.046 \text{ nm}^{-1}$) and of the strong WAXS reflections ((120) of PEO and (110) of PCL at $2\theta = 19.09$ and 21.05 , respectively) are shown in Figures 5a and b. It is worth noting that the PCL block crystallized first upon PEO_{5k}-PCL_{5k} crystallisation at 50 °C as shown in Figure 5 and also illustrated in Figure 7b. It was found that all of the transitions of the PEO-PCL crystallisation process at 50 °C took place at the same time as detected by both SAXS and WAXS. This indicates that both the nano- and micro-scale structure transformations are related to the PEO and PCL block

crystallisation behavior and the block copolymer condensate structures.

A remarkable property of block copolymers is their ability to self-assemble within the melt into a variety of ordered structures with nanoscale periodicities via the process of microphase separation. These structures can be controlled by varying the composition of the block copolymer or the degree of segregation between blocks via changes in the temperature and/or degree of polymerisation. Microphase separation is driven by the enthalpy of demixing of the constituent components of block copolymers, whilst macrophase separation is prevented by the chemical connectivity of the blocks. For a diblock copolymer, the volume fraction of one component controls which ordered structures can be accessed in an order-disorder transition. Symmetric block copolymers form a lamellar phase with alternating layers of constituent blocks. Following the crystallisation kinetics and the temperature dependence of the long spacing, there is a tendency to assume that the crystallized morphology of PEO_{5k}-PCL_{5k} block copolymers is overall lamellar, as other studies have suggested [17,18].

The integrated intensity can be calculated using the following equation [19]:

$$I_{\text{int}} = \int_{q_2}^{q_1} I(q) q^2 dq \propto \phi_a \phi_c (\rho_a - \rho_c)^2, \quad (1)$$

where q is the momentum transfer vector. ϕ_c and ϕ_a are the volume fractions of the crystalline and amorphous phases, respectively. ρ_c and ρ_a are the electron densities of the crystalline and amorphous phases, respectively. In equation (1), the integrated intensity I_{int} is proportional to the product of the volume fractions of the crystalline and amorphous phases and the scattering contrast due to the electron density difference between the crystalline and amorphous phases. From the results shown in Figures 4a and 5a, it can be seen that the integrated intensity I_{int} obtained from the SAXS analysis does not always increase with time in a crystallisation process. According to equation (1), I_{int} should increase with time when the specimen crystallizes from the melt. However, from the results obtained on the PEO_{5k}-PCL_{5k} block copolymer, I_{int} was controlled by the crystallisation behavior of the PEO and PCL blocks rather than the crystalline and amorphous phases. For PEO_{5k}-PCL_{5k} crystalline-crystalline symmetric diblock copolymers, there is a layer structure within the melt due to the microphase separation. There are four known phases in this system, including crystal PEO, crystal PCL, amorphous PEO and amorphous PCL. However, the density difference between the PEO and PCL melts and the electron density difference between the PEO and PCL melts are almost the same. The electron density difference between the amorphous and crystalline PEO phases as well as that between the amorphous and crystalline PCL phases are also too small to be detected [18]. Hence the following relations can be obtained:

$$\rho_{\text{PEO},m} \approx \rho_{\text{PCL},m}, \quad (2)$$

$$\rho_{\text{PEO},ed} \approx \rho_{\text{PCL},ed}, \quad (3)$$

where $\rho_{\text{PEO},m}$ and $\rho_{\text{PCL},m}$ are the melting densities of PEO and PCL, $\rho_{\text{PEO},ed}$ and $\rho_{\text{PCL},ed}$ are the electron densities of the PEO and PCL phases. This is a special case for crystalline-crystalline diblock copolymers in which the block crystallizes one after the other. From the SAXS results in Figure 4a, it can be deduced that the maximum SAXS intensity is attributed to the domains induced by the microphase separation during the crystallisation process. It is well known that the size of the crystalline lamellae is of the same magnitude (nanoscale) as that of the microphase in the block copolymer and the long spacing, including the PEO and PCL layers. The results in Figure 4a indicate that the electron density difference increases as one of the blocks crystallises, but decreases when the other block also crystallises. According to equations (2) and (3) the electron density difference during the crystallisation of the crystalline-crystalline diblock copolymer may written as

$$(\rho_c - \rho_a)^2 \approx (\rho_{\text{PEO},ed} - \rho_{\text{PCL},ed})^2. \quad (4)$$

In diblock copolymers, the crystallisation begins by microphase separation of the PEO and PCL phases. If the volume fractions of PEO and PCL are ϕ_{PEO} and ϕ_{PCL} , respectively, then equation (1) can be re-written as

$$I_{\text{int}} \propto \phi_{\text{PEO}} \phi_{\text{PCL}} (\rho_{\text{PEO}} - \rho_{\text{PCL}})^2. \quad (5)$$

The integrated intensity I_{int} is shown to be proportional to the product of the volume fractions of the PEO and PCL phases and the scattering contrast due to the electron density difference $(\rho_{\text{PEO}} - \rho_{\text{PCL}})^2$. During the crystallization of PEO-PCL at 40 °C, the PEO blocks crystallised first, followed by the PCL blocks. Consequently, the electron density difference $(\rho_{\text{PEO}} - \rho_{\text{PCL}})^2$ increased, then subsequently decreased. This is consistent with the data shown in Figure 4a. The interrelated transitions seen in Figures 4a and 5a may be interpreted using equation (5). I_{int} can be determined from the crystallisation rates of PCL and PEO.

Our results in this study have shown that simultaneous SAXS and WAXS measurements are useful in the study of crystallization of block copolymers [20,21]. The SAXS peak resulted from the density fluctuations ranging between 5 and 100 nm, while WAXS crystalline peaks were brought about by the three-dimensional crystal ordering in the range of 0.2 to 1 nm. The appearance of the SAXS peak before the WAXS crystalline peaks suggests that density fluctuation occurred prior to the crystallisation. The results shown in Figures 4 and 5 demonstrated that simultaneous SAXS/WAXS measurements could be used to monitor the crystallisation process in domains of two different sizes at the same time.

More information about the structural parameters such as the average lamellar thickness and the long spacing can be gained from the one-dimensional electron intensity correlation function, $K(Z)$, which was defined by Strobl, and can be derived from the Fourier transformation of a scattering curve [22]

$$K(Z) = \frac{1}{2\pi} \int_0^\infty I(s) s^2 \cos(sZ) ds, \quad (6)$$

Fig. 6. Curves of experimental correlation function $K(Z)$ obtained for (a) PEO and (b) $\text{PEO}_{5k}\text{-PCL}_{5k}$.

Fig. 7. Schematic diagrams of the isothermal crystallisation of $\text{PEO}_{5k}\text{-PCL}_{5k}$ (a) at 40 °C and (b) at 50 °C.

where $s = 2 \sin \theta / \lambda = q / 2\pi$ and 2θ is the scattering angle. For example, the $K(Z)$ of the lamellar structures of PEO and $\text{PEO}_{5k}\text{-PCL}_{5k}$ is shown in Figure 6. From the well-known “self-correlation triangle” which reflects the electron density correction within a lamella, one can directly estimate various solid-state structural parameters of PEO and $\text{PEO}_{5k}\text{-PCL}_{5k}$ by making use of some general properties

Table 2. Lamellae parameters: long period (L), lamellar thickness ($\bar{d}$) for homopolymers and the diblock copolymer after isothermal crystallisation at (a) 40 °C and (b) 50 °C.

Sample	Temperature (°C)	L (nm)	$\bar{d}$ (nm)
PEO	40	16.2	7.0
	50	17.3	7.4
PCL	40	13.6	5.8
	50	15.7	6.0
PEO-PCL	40	20.5	9.1
	50	22.9	9.9

of $K(Z)$. The invariant, Q , is the value of $K(Z)$ at $Z = 0$ which is determined by the interception of the extrapolation of the straight-line section of the self-correlation function with the $K(Z)$ axis (see Fig. 6). Physically, it represents the mean-square electron density fluctuation. According to Strobl, the thickness of the transition zone, d_{tr} , can be obtained directly from the curvature of $K(Z)$. The long period L can be determined from the position of the first maximum in the correlation function. The average lamellar thickness $\bar{d}$ can be obtained from the crossing point of the baseline with the sloping line of the “self-correlation triangle”. The calculated long period and lamellar thickness for PEO, PCL and $\text{PEO}_{5k}\text{-PCL}_{5k}$ are listed in Table 2.

The symmetric block copolymer was annealed for 5 minutes in a vacuum at 90 °C. *In situ* SAXS monitoring was performed with the aid of a small- and wide-angle X-ray scattering twin camera produced by Hecus-Braun Co., Freiburg, Germany. The SAXS results of the annealed sample indicated no scattering peaks. The SAXS intensity patterns of the $\text{PEO}_{5k}\text{-PCL}_{5k}$ block copolymer during isothermal crystallisation at 40 and 50 °C showed no transitions before the onset of crystallisation. It is possible that the microphase separation might not be visible in SAXS before crystallisation because the density contrast between amorphous PEO and amorphous PCL phases is too small [15]. However, the structural parameters of the homopolymers and the block copolymer shown in Table 2 and the DSC results imply a layer structure and confined crystallisation behavior. On the basis of these investigations, we can construct a full picture of the crystallisation behavior of the $\text{PEO}_{5k}\text{-PCL}_{5k}$ block copolymer, which is schematically presented in Figure 7. The PEO blocks crystallise first from the block copolymer melt at 40 °C and then the PCL blocks crystallise (Fig. 7a), the PCL blocks crystallise first from the block copolymer melt at 50 °C and then the PEO blocks crystallise (Fig. 7b), as supported by WAXS measurements. Accompanying the crystallisation of the PEO or PCL block, microphase separation occurs between the PEO and PCL blocks. This is evidenced by the simultaneous SAXS and WAXS results.

The calculated long period, lamellar thickness and transition layer for $\text{PEO}_{5k}\text{-PCL}_{5k}$ crystallised at 40 and 50 °C over a long period of time are shown in Figure 8. It can be found that there is not as much change in the

Fig. 8. Lamellar parameters: long period (L), lamellar thickness ($\bar{d}$) and transition layer (d_{tr}) obtained from SAXS data of PEO_{5k}-PCL_{5k} during isothermal crystallisation at (a) 40 °C and (b) 50 °C.

long period, lamellar thickness and transition layer for PEO_{5k}-PCL_{5k} as there is in the integrated intensity I_{int} obtained from SAXS during the crystallisation. The reduction in long period and lamellar thickness is thought to be due to the volume difference between the amorphous and the crystalline block copolymer.

From the calculated long period, lamellar thickness and the transition layer of the symmetry diblock copolymer as shown in Figure 8, the following relation can be found:

$$L = 2\bar{d} + d_{tr} \quad (7)$$

and

$$2\bar{d} = \bar{d}_{PEO} + \bar{d}_{PCL}. \quad (8)$$

The final structure in a semicrystalline block copolymer is a result of a complex interplay between microphase separation and crystallisation. The glass transition temperatures of PEO and PCL are lower than crystallisation temperatures (40 and 50 °C). For the symmetric PEO-PCL block copolymer, a weakly segregated system with soft confinement has been described, where the order-disorder transition temperature is higher than the crys-

tallisation temperatures and the crystallisation temperatures are higher than the glass transition temperatures of both blocks. In this case, crystallisation can provoke a “break-out” from the ordered melt morphology and overwrite the morphological pattern of the melt. There is the possibility of formation of a lamellar structure, regardless of composition [23–25]. The melt morphology of symmetric block copolymers is lamellar driven by microphase separation. The results shown in Table 2 reveal the soft-confined crystallisation behavior of the crystalline-crystalline diblock copolymer. For each lamella, the crystalline and amorphous components of one block are included and the transition layer includes both PEO and PCL.

In summary, the transition of PEO-PCL block copolymer at different crystallisation temperatures was investigated. Temperature-dependent reversible crystallisation behavior was found. The transitions of the PEO-PCL diblock copolymer during melt crystallisation can be detected in different length scales by SAXS and WAXS at the same time. The time-resolved I_{int} is proportional to the product of the volume fractions of the PEO and PCL phases and the scattering contrast due to the electron density difference.

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