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ORIGINAL CONTRIBUTION

Crystallization and melting behavior of low molar weight PEO–PPO–PEO triblock copolymers

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Abstract The crystallization behavior of a series of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) (PEO–PPO–PEO) triblock copolymers (Pluronics) was investigated using time-resolved small-angle X-ray scattering (SAXS), thermal analysis, and polarized optical microscopy. For comparison, a PEO homopolymer, PEO3K, was also included. Time-resolved SAXS during the crystallization of PEO3K shows a typical "two-step" process, i.e., in the initial stage, a metastable crystal with nonintegral folding (NIF) structure forms first, then, it transforms into integral folding (IF) structures, the IF(0) and the IF(1). In contrast with PEO3K, the PEO–PPO–PEO triblock copolymers show a "one-step" crystallization process, i.e., the PEO blocks crystallize directly into the final state and do not change with time. In thermal analysis, only one major solid–melt transition is observed during isothermal crystallization and subsequent melting for triblock copolymers. In the full temperature range, a linear crystal growth is observed. The crystal growth rates monotonously decrease with crystallization temperatures. Notches or breaks due to the NIF–IF transition as clearly seen for PEO3K cannot be recognized for Pluronics. Based on these results, we conclude that the crystallization of PEO–PPO–PEO triblock copolymers follows a "one-step" process; no metastable structure serving as an intermediate state is formed during the crystallization process within the time scale of the current experiments (<120 min).

Keywords PEO–PPO–PEO triblock copolymer · SAXS · Crystallization and melting · Linear growth rate

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Introduction

Poly(ethylene oxide) (PEO) has been used as a model polymer to study polymer crystallization [1–14]. One of the most important conceptions rising from the studies of crystallization of low molecular weight PEO fractions is the integral and nonintegral folding (NIF) structure. Kovacs et al. [3–5] pioneered this issue by pointing out the relationship between linear growth rate, single crystal morphology, and the integral folding (IF) structure. By using time-resolved small-angle X-ray scattering (SAXS), Cheng and coworkers [6–14] first demonstrated the existence of NIF structure. Systematic studies indicated that the NIF crystals form first in the early stage of crystallization as an intermediate stage with respect to the IF crystals. The formation of NIF crystals is due to the lower nucleation barrier [15], i.e., the most favorable kinetics. However, the NIF crystals are thermodynamically less stable than IF crystals, which leads to the subsequent transformation from NIF crystals to the more stable IF crystals by a lamellar thickening or thinning process. This process is schematically presented in Fig. 1a. Further studies on the effect of chain end group and molecular weight indicate that the NIF to IF transition is increasingly hampered upon increasing the size of end group or molecular weight [10, 11, 14].

As far as the molecular architecture is concerned, it is interesting to study the IF or NIF structure in PEO containing block copolymer. As shown in Fig. 1b, the covalent connection with an amorphous segment, e.g., poly(propylene oxide) (PPO), significantly changes the possibility of chain conformation in crystalline state. Intuitively, the formation of NIF crystals as an intermediate stage seems very difficult. This is shown in the middle of Fig. 1b because the junctions must be located at crystalline/amorphous interface. It has been shown that semicrystalline

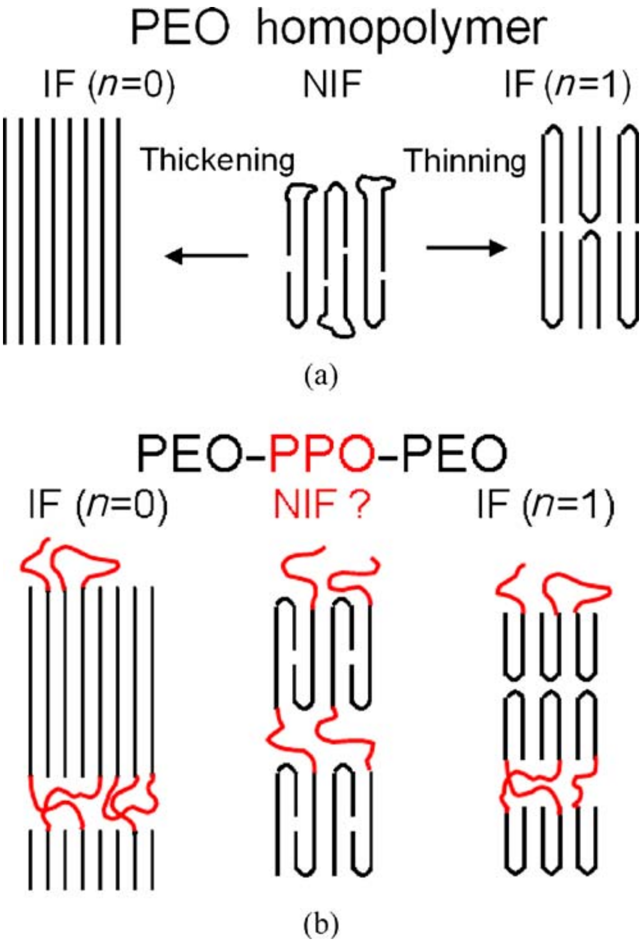


Fig. 1 Schematic drawing of possible folding structure in PEO homopolymer and PEO–PPO–PEO triblock copolymer in their solid state

block copolymers may possess an equilibrium chain-folding lamellar structure [16] resulting from the balance between an enthalpic driving force to minimize the fold surface energy and the entropic term from stretching of the amorphous blocks. If a disorder to order transition occurs before the crystallization, crystal growth may be confined within the nanoscaled domains. Such confined crystallization affects the size, orientation, and folding structure in crystalline domains [17–25]. Early studies [26, 27] on PEO/PPO di- or triblock copolymers indicate that the Flory–Huggins interaction parameter, χ, only shows a weak temperature dependence. Combined with the fact of low molecular weight, it has been predicted that the Pluronic copolymers will not exhibit microphase separation even if they were pure samples [27]. Our previous studies support this prediction. We observed crystallization at temperatures being up to 10° higher than the spinodal phase separation temperature predicted by mean-field theory [28]. However, whether a kinetically favored intermediate stage could exist in the early stage of crystallization of semicrystalline copolymers is still not known.

Several studies on the structure and thermal behavior of the final crystalline state of PEO/PPO di- or triblock copolymers have been reported [29–36]. In our previous work [28], we have studied a series of PEO–PPO–PEO (EPE) triblock copolymers (Pluronics) in their melt and solid state mainly using SAXS. In the solid state, crystallization of PEO blocks induces phase separation resulting in an alternating crystalline/amorphous lamellar structure. Samples with short PEO block form a simple lamellar structure with extended-chain conformation. The domain spacing increases with crystallization temperature. Samples with long PEO block form a mixed lamellar structure. Structures with once-folded and extended PEO block coexist in a large temperature range, and their relative fractions change with crystallization temperature. This mixed structure is reduced to a simple lamellar structure with once-folded crystalline structure at low crystallization temperatures.

In the present work, we continue our study on the crystallization and melting behavior of PEO–PPO–PEO triblock copolymers. We now focus on the whole crystallization process by using time-resolved SAXS, differential scanning calorimetry (DSC), and polarized optical microscopy (POM) to answer the question: does an intermediate stage of NIF crystals exist in the PEO–PPO–PEO triblock copolymer systems?

Experimental section

Materials

The PEO homopolymer, PEO3K (M_w=3,000 g/mol, M_w/M_n=1.01) was obtained from Polymer Standard Services (Mainz, Germany). Symmetric PEO–PPO–PEO triblock copolymers (Pluronics) were kindly supplied by BASF. To remove the low molecular weight fractions, the copolymers were precipitated from dilute solution in benzene by addition of isooctane [33]. The precipitates were freeze-dried from benzene and then in vacuum oven for 1 day. The basic parameters of Pluronic samples are listed in Table 1.

Time-resolved small-angle X-ray scattering

Two-dimensional SAXS was carried out with a Molecular Metrology System. Detailed information concerning the configurations of the instrument and the related calibrations has been described in previous publication [28]. The X-ray source is a sealed X-ray tube with copper anode and nickel filter working at 40 kV and 55 mA. The wavelength of $Cu\,K_\alpha$ is λ=1.54 Å. The accessible q-range is from 0.008 to 0.26 Å^{-1}.

Table 1 Molecular characters of samples used in this work

Sample	Total molar mass	PEO block f (wt%)	T_c (°C)[a]	T_m (°C)[a]	ΔH_{fus}(J/g)	Crystallinity X (%)[b]
PE6800/$E_{80}P_{30}E_{80}$[c]	8,750	80	18.3/22	51.0	114.6	72.9
PE9400/$E_{21}P_{47}E_{21}$	4,600	40	1.45	36.42	66.6	84.7
PE10400/$E_{25}P_{56}E_{25}$	5,420	40	7.90	38.24	55.2	70.2
PE10500/$E_{37}P_{56}E_{37}$	6,500	50	18.01	46.03	87.4	88.9
PEO3K/E_{68}	3,000	100	29.6	56.6	–	–

[a] Crystallization (T_c) and melting (T_m) were obtained from standard DSC measurements, i.e., cooling and second heating scan with scanning rate of 10 °C/min.

[b] Degree of crystallinity was calculated by $X = \Delta H_{fus} \Big/ \left(f \Delta H_{fus}^0 \right)$, where ΔH_{fus}^0=196.6 J/g is the equilibrium heat of fusion of PEO [37]. The final crystallinity is normalized by PEO weight fraction.

[c] In the notations, e.g., $E_{80}P_{30}E_{80}$, the E and P are denoted to PEO and PPO, respectively, and the subscripts indicate the degree of polymerization or the number of the repeat unit.

Samples in solid or liquid state with high viscosity were put in the sample cell and closed by two mica windows with two Kalrez gaskets. Temperature was controlled in the range of −10 to 90 °C by a Thermostat (HAAKE Phoenix II P1, Germany) with the coolants glycerol and water. Time-resolved measurements were carried out at various temperatures after a quench from the melt state. Samples were first melted on a hot stage at 60 °C for several minutes, and then rapidly transferred to the sample holder which was kept at the preset T_c. The temperature jump needed less than 240 s, and the measurements started 300 s later.

In data collection, two methods were used to collect the data: (1) differential mode: Each measurement takes 200 s, and the time interval between measurements is 5 s. Measurements for a given temperature were extended up to 10,000 s. (2) Integral mode: the exposure time was set as 10,000 s, but the scattering data were saved at any intermediate times during a measurement. In most cases, an intermediate saving of data was done every 200 s.

Differential scanning calorimetry

DSC measurements were conducted on a computerized Perkin-Elmer differential scanning calorimeter, Model DSC-7. Sample mass was in the range of 2–5 mg. During the measurement, dried N_2 gas was purged at a constant flow rate. Crystallization and melting temperature and the degree of crystallinity were measured with a scanning rate of 10 °C/min. For the case of isothermal crystallization, the sample was heated at a rate of 20 °C/min to 80 °C and held for a period of 1 min to remove residual crystals which may provide seeds for crystallization. Then, it was cooled rapidly to the predetermined crystallization temperature T_c at a rate of 80 °C/min, and the temperature was held constant until the crystallization was completed. Thereafter, the specimens were heated again without prior cooling to obtain the DSC endotherms at a rate of 10 °C/min. The temperature reading and caloric measurement were calibrated by using standard indium.

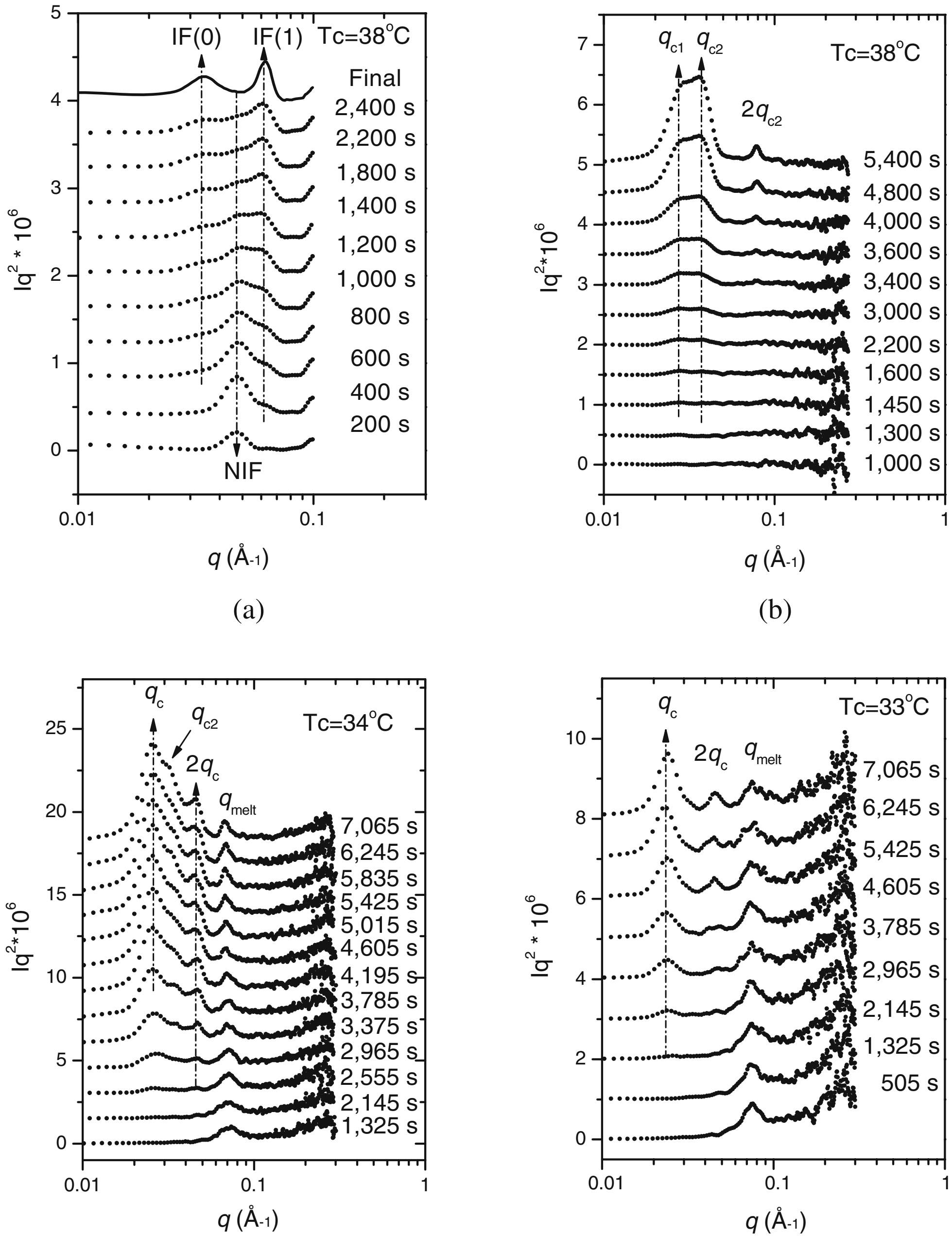
Polarized optical microscopy

An Olympus BX40 optical microscope equipped with THMS600 hot stage (Linkam) was used to follow the growth of spherulites or hedrites at various crystallization temperatures and to determine the lateral growth rate. Temperature was controlled by Eurotherm heating and LNP cooling systems. Samples were sandwiched between two glass slides separated by a 10-μm glass fiber spacer. At high T_c, the self-seeding technique was used to initiate the primary crystallization [3–5]. All the pictures were captured with an Olympus DP10 digital camera.

Results

Isothermal crystallization studied by time-resolved SAXS

Typical time-resolved SAXS profiles of PEO–PPO–PEO triblock copolymers and PEO3K during isothermal crystallization are presented in Fig. 2. The data in Fig. 2a, b were collected in integral model. The data were saved at the time labeled at the right side of the figures. As a comparison, Fig. 2a shows the Lorentz corrected SAXS profiles for the crystallization of PEO3K at 38 °C. It is obvious that in the initial stages of crystallization, a major scattering peak (q=0.047 Å^{-1}) appears. It corresponds to a fold length of 134 Å, an NIF structure. With increasing time, one finds that two additional scattering peaks develop gradually from both sides of the original peak q=0.032 and 0.062 Å^{-1} corresponding to fold length of 196 and 101 Å, respectively. These are IF(0) and IF(1) crystals, respectively. In contrast with the increase of intensity of IF(0) and IF(1), the scattering intensity of original NIF peak decreases gradu-



(a) (b)

(c) (d)

Fig. 2 Time-resolved 1D SAXS profiles of PEO–PPO–PEO triblock copolymers and PEO homopolymer during isothermal crystallization. **a** PEO3K crystallized at 38 °C; **b** PE6800 at 38 °C; **c** PE10500 at 34 °C; and **d** PE10400 at 33 °C. For clarity only, every tenth data point is shown

ally. After a complete crystallization, the sample was measured again, and these scattering data are shown at the top portion of Fig. 2a in a solid line style. It is clear that the NIF peak in the final state has completely disappeared. Very similar results have been reported by Cheng et al. [6–11], and this result successfully demonstrated the existence of NIF and the transition between NIF and IF by thinning or thickening process during crystallization.

Figure 2b shows the SAXS profile of PE6800 during isothermal crystallization at 38 °C. From our previous study [28], we know that PE6800 crystallization at 38 °C results in two types of lamellar structure with different thicknesses. The time-resolved SAXS results of Fig. 2b indicate that two lamellar structures with q=0.028 Å^{-1} (q_{c1}) and 0.038 Å^{-1} (q_{c2}) formed almost at the same time around 1,600 s. Once they are formed, the q values do not change with time. The third peak appears after 3,600 s at q=0.078 Å^{-1}. Its position corresponds to the second order of the $2q_{c2}$, which means that the lamellar structure of q_{c2} has a much more regularly packed domains in which the lamellae oriented parallel to each other and the interference contribute to the second order of $2q_{c2}$. Similar results at T_c=35 °C are observed (results not shown in this study).

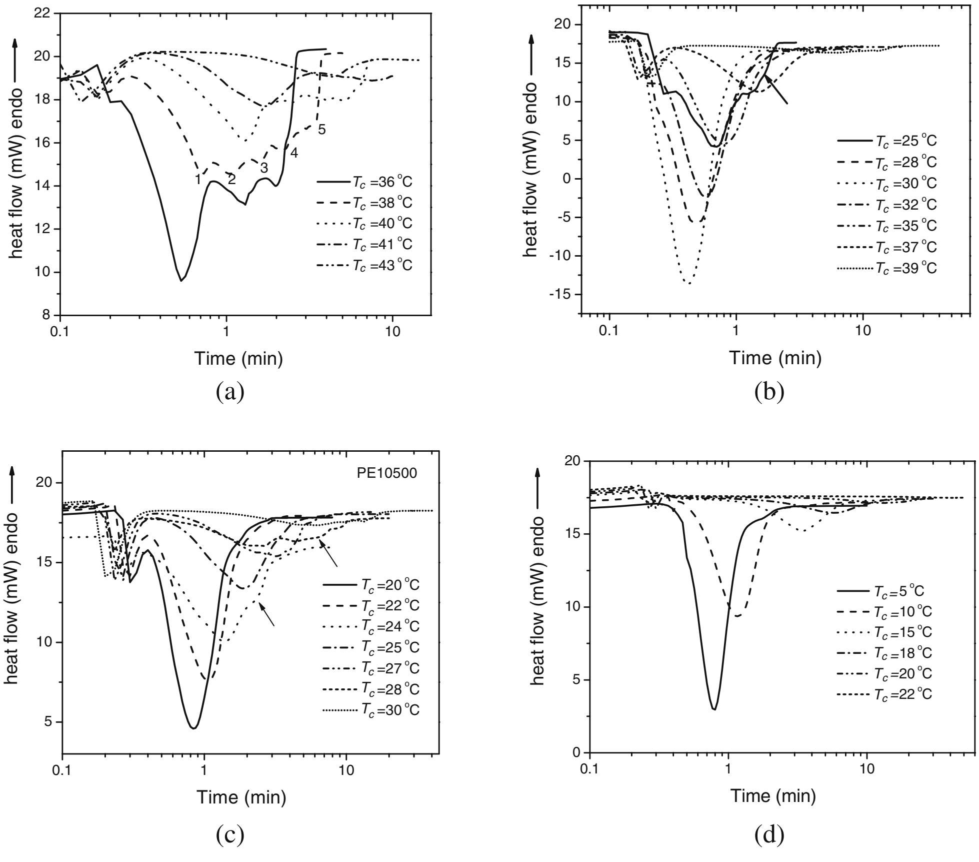
Figure 2c presents the SAXS profiles for PE10500 crystallization at 34 °C. In the initial state, only one major intensity maximum at q=0.07 Å^{-1} is observed, which corresponds to the composition fluctuation in melt state, q_{melt}, and it could be observed from the start in the whole crystallization process. Scattering maxima at q=0.024 Å^{-1} (q_{c}) and q=0.047 Å^{-1} ($2q_{\mathrm{c}}$) correspond to the Bragg scattering of a dominant lamellar structure, and the shoulder at q=0.032 Å^{-1} indicates the coexistence of another lamellar structure. A mixed lamellar structure for PE10500 at T_{c}>28 °C has been shown in our previous study [28]. It should be noted that the data in Fig. 2c, d are collected in differential mode, i.e., each profile takes 200 s with a 5-s interval. Not all profiles are presented in the figures.

Similar SAXS profiles are observed for PE10400 at 33 °C in Fig. 2d. In the initial state, only one major intensity maximum at q_{melt}=0.074 Å^{-1} is observed. After 2,000 s, as a consequence of the onset of crystallization, a new scattering maximum at q=0.023 Å^{-1} appears. The intensity of the new peak increases with time, but its position does not change. At around 3,000 s, a second peak with q=0.046 Å^{-1} is observed. The intensity values of the two peaks related to the crystalline mesostructure have a ratio around 8 at t=7065 s, and the q values have the ratio of 1/2. Therefore, these two peaks may be assigned to the first and second orders of a lamellar structure. The degree of crystallinity increases with time, but the lamellar thickness or lamellar structure does not change with time. Previous study on the solid state of PE10400 indicates that the PEO block always crystallizes in a chain-extended crystal [28]. The time-resolved measurements shown in Fig. 2d further demonstrate that the crystalline mesostructure formed in the initial state is the same as in the final state. Similar results are observed at T_{c}=30 °C (results not shown in the figure).

Isothermal crystallization and melting behavior studied by DSC

DSC crystallization profiles at different temperature are shown in Fig. 3. For comparison, the crystallization of PEO3K is also studied, and the results are presented in Fig. 3a. The crystallization curves show three or more peaks or shoulders at various temperatures. For example, at T_{c}=38 °C, five peaks could be discriminated as labeled in Fig. 3a. Cheng et al. [6–8] studied the crystallization behavior of a comparable PEO homopolymer in a large temperature range. They found that three exothermal peaks or shoulders could be observed, and their fractions change with crystallization temperature. Combined with the results of time-resolved SAXS measurements, they explained the three exotherms from short to long time as the formation of NIF, IF(1), and IF(0) structures [6–8]. The multiple exothermal peaks or shoulders observed in our experiments (Fig. 3a) may be explained as the result of the overlapping

Fig. 3 DSC curves of isothermal crystallization at various temperatures for **a** PEO3K, **b** PE6800, **c** PE10500, and **d** PE10400



(a) (b)

(c) (d)

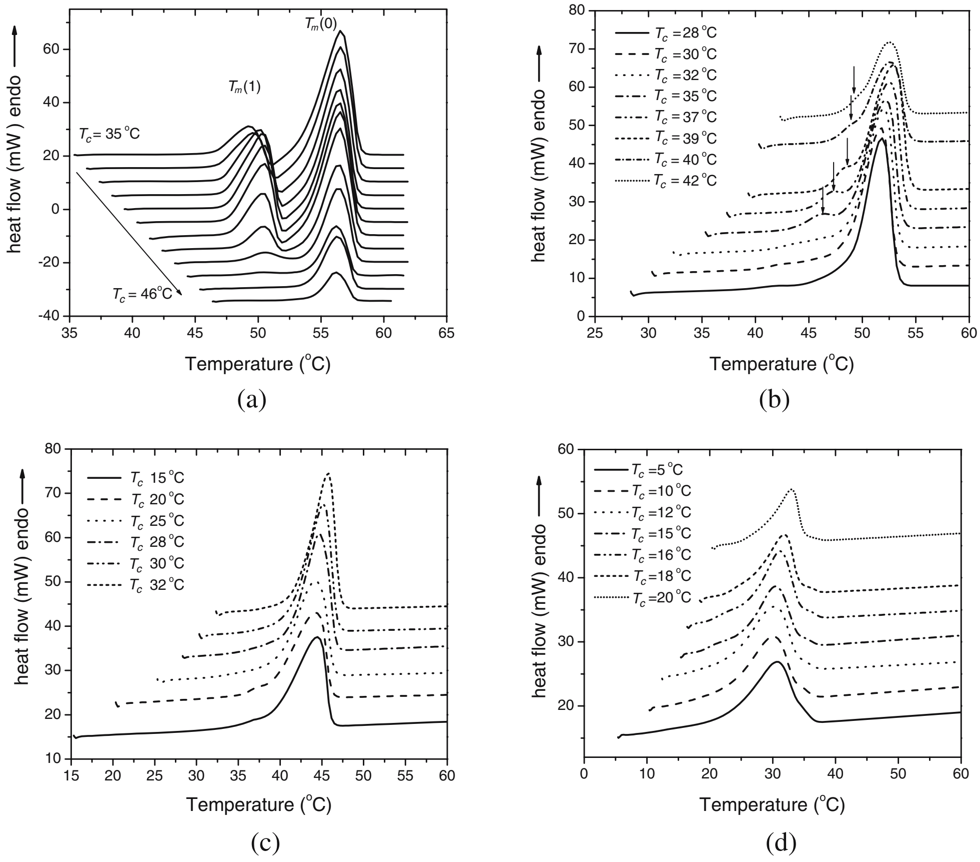
of the triple exotherms of the time-dependent nucleation and crystal growth process. Compared with PEO3K, the crystallization behavior of Pluronics (Fig. 3b–d) is relatively simple: usually, only one main exothermal peak is observed. In some measurements, as indicated by the arrows in Fig. 3b, c, a shoulder appears at longer times. It may be attributed to the polydispersity of the length of PEO block and the existence of PEO–PPO diblock copolymer in the sample (see below).

The corresponding heating scans after isothermal crystallization shown in Fig. 3 are presented in Fig. 4. For PEO3K, two endothermic peaks related to the melting of IF (1) and IF(0) crystals are clearly observed at T_c<44 °C. For PE10500, our previous SAXS studies in solid state indicate a mixed lamellar structure [28]. However, the DSC melting curves show only one endothermic peak. The lamellar structure in SAXS studies includes both the crystalline and the amorphous domains, whereas in DSC measurements, only the crystalline domains contribute to the endothermic peak. It has been pointed out that the commercial products of Pluronics contain a certain amount of PEO–PPO diblock copolymers [24]. Therefore, compared with the lamellar structure formed by triblock copolymers, the diblock copolymers with the same length of PEO block will form a lamellar structure having the same melting point but different lamellar thickness.

For all Pluronics except PE6800, in the full range of T_c, one main melting peak is observed, and the melting point increases slightly with T_c. The data of melting points of all the samples are collected in Fig. 5. Both the crystallization and melting temperatures decrease with the decrease in the length of PEO block.

For PE6800, the shoulders shown in the melting curves of PE6800 may correspond to the multilamellar structure observed by SAXS (Fig. 4b). Two questions are to be clarified. First, are they related to the melting of two kinds of primary crystals? Second, is there any transition relation between them? To answer these questions, crystallization time and heating rate dependence experiments are performed. Heating rate dependence of the shape of DSC heating curves has been widely used to study the multiple melting behaviors of crystalline polymers [37–40]. If reorganization or recrystallization occurs during the DSC scan, with increasing scan rate, the high-temperature peak should decrease its intensity or even disappear at high scan rate, while the low-temperature shoulder should increase its intensity. Figure 6a shows the subsequent heating curves with different scan rate after complete crystallization at 37 °C. For T_c=37 °C, in all heating scans, both the shoulder and the peak coexist with proportional intensities. Although the reorganization process might be very fast [40], regarding our SAXS observations (Fig. 1b and in the paper

Fig. 4 Subsequent DSC heating curves after isothermal crystallization at various temperatures for **a** PEO3K, **b** PE6800, **c** PE10500, and **d** PE10400



(a) (b)

(c) (d)

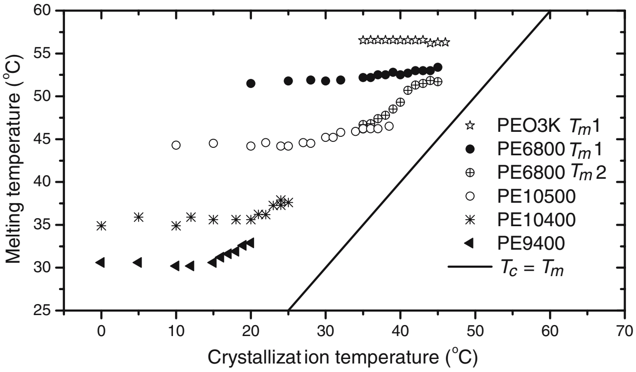
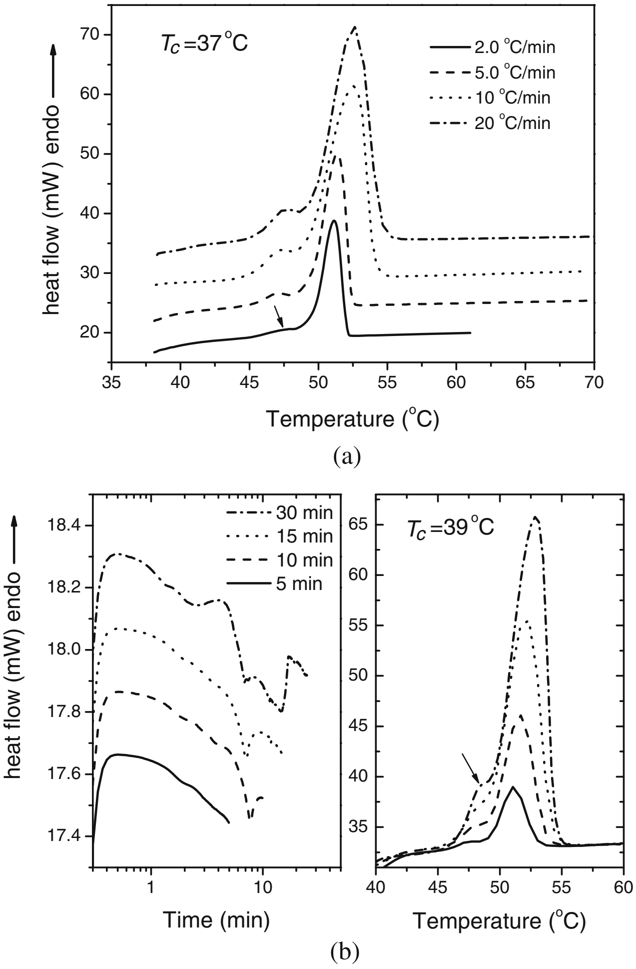


Fig. 5 Plots of melting point as a function of crystallization temperature for several Pluronics. The melting points of IF(0) crystal of PEO3K are also presented for comparison

of Zhang and Stühn [28]), the shoulder and the peak should be related to different primary crystals. The formation of two kinds of crystals with different melting points for a given crystallization temperature may be due to the polydispersity of the length of PEO block. Similar results have been observed in branched polyethylene system. The multiple melting behaviors have been explained as the polydispersity of the length of ethylene sequences [39].



(a)

(b)

Fig. 6 Time and heating rate dependence of DSC melting curves of PE6800. **a** Heating rate dependence at T_c=37 °C; **b** crystallization time dependence: (*left*) heat flow curves for isothermal crystallization at T_c=39 °C for 5, 10, 15, and 30 min. The curves were shifted upward by the same unit for clarity; (*right*) subsequent heating curves

Figure 6b shows the time-dependent heat flow during crystallization at 39 °C for different time and subsequent heating scans. It is worth noting that the multiple exothermal peaks shown in heat flow curve for 30 min cannot contribute to the formation of NIF or IF crystalline structure; rather, it is due to time-dependent nucleation and crystal growth process. By using the same sample and performing the experiments continuously, we see that the crystallization curves for different times are almost following the same history. The most important observation in the subsequent heating curves is that the shoulder could be observed in all experiments even for the longest crystallization times. This result further confirms that both components of the mixed lamellar structure form at the same time during crystallization. The DSC results are therefore fully consistent with our time-resolved SAXS observations (Fig. 2b).

Linear growth rate and morphology studied by POM

POM is used to follow the crystal growth of Pluronics at different temperatures. Due to the low rate of nucleation events, self-seeding technique is used for relatively high T_c [3–5]. For all the samples used and in the whole T_c range, a linear growth rate is observed. The temperature dependence of growth rate is displayed in Fig. 7 in semilogarithmic scale. The result of PEO3K is also shown in Fig. 7 for comparison. The notched appearance of the growth rate curve for PEO3K has been reported in the literature [3–5, 7, 8]. It results from the juxtaposition of independent hyperbolic branches having different maxima. Three regimes may be discriminated. From high T_c to low, they are attributed to IF(0) for T_c>49 °C, a mixture of IF(0) and IF(1) for 49 °C>T_c>44.5 °C, and a mixture of IF(1) and NIF for T_c<44.5 °C [7, 8]. In contrast with PEO3K, the T_c dependence of crystal growth rate in PE6800 and PE10500

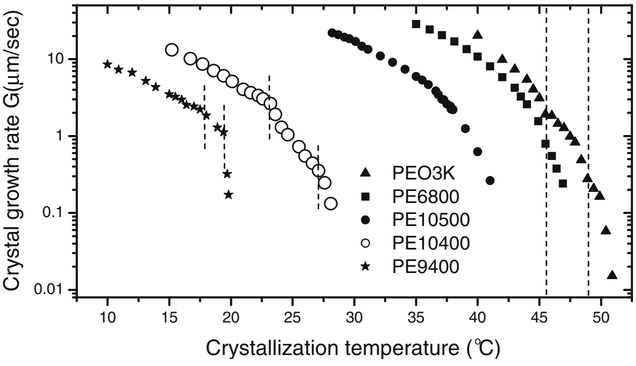


Fig. 7 Crystal growth rates as a function of crystallization temperature

is very simple. It smoothly decreases with T_c; no obvious discontinuous can be recognized. Even for PE6800 with the length of PEO block similar to that of PEO3K, no break can be observed. This means that the folding structure in this system changes step by step, in agreement with the SAXS study in our previous publication [28]. A similar result is obtained for PE10500. It is interesting to note that for the Pluronics with short PEO blocks, i.e., PE9400 at T_c=17.5 and 19.4 °C and PE10400 at T_c=23.2 and 27.1 °C, the T_c dependence of growth rate shows three regimes as indicated by dashed lines in Fig. 7. At temperatures slightly higher than the boundary temperatures, the growth rate decreases dramatically as shown in the figure. This is a clear difference to PEO3K. For NIF to IF transition of low molecular weight PEO homopolymers, the driving force for crystallization in the corresponding lamellar structure is very small at temperatures slightly higher than the transition temperature. Thus, the crystal growth rate varies slightly with temperature. SAXS results of these samples indicate that they are always in the extended-chain structure [28]. Thus, the regimes observed for PE9400 and PE10400 do not originate from the change of crystal structure. From POM observations, the regimes correspond to different morphologies as shown in Fig. 8. At low T_c, or high supercooling, e.g., 10 °C for PE9400, crystallization results in well-developed spherulites with clear Maltese cross-extinction pattern, in the medium T_c, e.g., 24.2 °C for PE10400, the spherulites lose the extinction pattern and finally, at high T_c, e.g., 28.1 °C for PE10400, crystallization results in hedrites.

Conclusions

We have studied the crystallization behavior of a series of PEO–PPO–PEO triblock copolymers (Pluronics) and a PEO homopolymer, PEO3K, by using time-resolved SAXS, DSC, and POM. For PEO3K, SAXS measurements show the formation of NIF crystal in the early stage of crystallization and subsequently transform into IF(0) and IF (1) during crystallization. DSC thermal analysis shows multiple exothermal or endothermic peaks during crystallization or melting scan. The plot of logarithmic crystal growth rate obtained from POM as a function of crystallization temperature shows the typical notched appearance characterized as the NIF to IF transition. All experimental results support a "two-step" crystallization model for PEO3K, i.e., in the initial stage, a metastable crystal with NIF structure forms first as an intermediate stage, then, it transforms into integral folding (IF) structures. In contrast with PEO3K, the SAXS measurements indicate that the lamellae formed in the early stage reversed until the end of crystallization for the PEO–PPO–PEO triblock copolymers

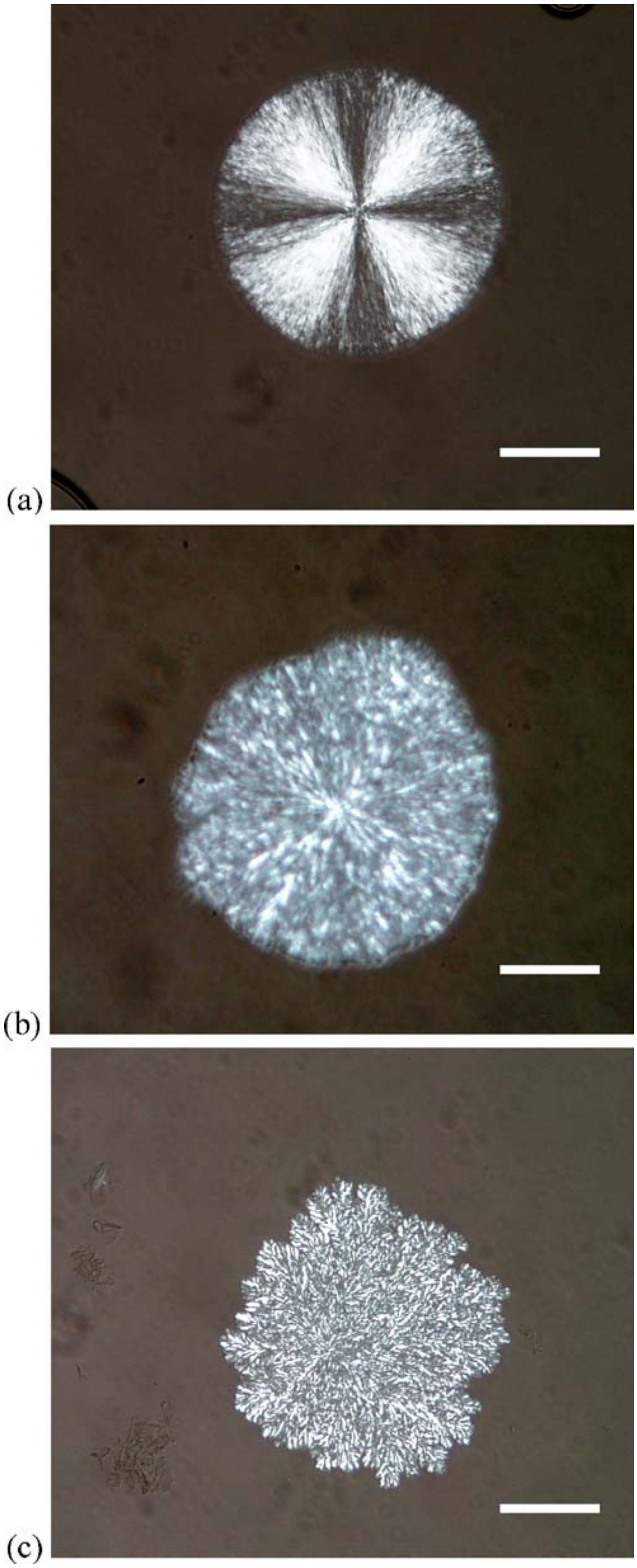


Fig. 8 POM images of Pluronics with short PEO blocks crystallized at different regimes. **a** PE9400, T_c=10 °C. **b** PE10400, T_c=24.2 °C. **c** PE10400, T_c=28.1 °C. *Scale bar* is 100 μm

no matter if the final state shows a single or mixed lamellar structure. In thermal analysis, only one solid–melt transition is observed during isothermal crystallization and subsequent melting for triblock copolymers. The mixed lamellar structure in the final crystalline state is due to the polydispersity of the length of PEO block or the existence of PEO–PPO diblock copolymer in the material. In the full temperature range, a linear crystal growth rate is observed. The logarithmic plot of crystal growth rates shows a monotonous and continuous decrease with crystallization temperature. Notches or breaks due to the NIF–IF transition as clearly observed for PEO3K cannot be recognized for Pluronics. The anomalous observation for PE10400 and PE9400 on crystal growth rate is due to the morphological change from spherulite to hedrite. Therefore, the crystallization of PEO–PPO–PEO triblock copolymers (Pluronics) may be described by a “one-step” crystallization process in the experimental time scale, i.e., the PEO blocks crystallize directly into the final state and do not change with time.

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