

Crystallization Behavior of Disproportionately High and Low Molecular Weight PEO Blends^{*}

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Abstract The crystallization behavior of PEOs with molecular weight of 10k and 200k as well as their blends was studied in details. The results show that the lower molecular weight PEO crystallizes with faster crystallization rate as judged from a shorter time for completing the crystallization. On the other hand, the higher molecular weight PEO crystallizes at relatively higher temperature, indicating an early start of crystallization compared with the lower molecular weight one. The blends of these two PEOs with different blend ratios always cocrystallize during the cooling processes. It is confirmed that mixing of the 10k PEO with the 200k one is in favor of the crystallization of the system. This is not only demonstrated by the early start of the crystallization at higher crystallization temperature, and also a faster crystal growth of the blend with respect to the 200k PEO. The crystallization of the blends at higher temperature is caused by an early start of nucleation and an increment of nucleus density. This may originate from the density fluctuation of the blend and a reduction in energy barrier for nucleation. Moreover, it is found that the crystallinity of the 10k PEO rich blends increases with increasing concentration of the 10k PEO. This is caused by the solvent effect of the 10k PEO toward the 200k PEO. On the other hand, the crystallinity of the 30/70 (10k/200k) PEO blend is decreased a little bit. This may be a balanced result of the improved crystallization of the 200k PEO at the expense of the high crystallization ability of the 10k PEO.

Keywords: PEO; Molecular weight; Blend; Crystallization; Morphology.

INTRODUCTION

As a biodegradable material, poly(ethylene oxide) (PEO) has attracted much attention in both academic and industrial fields. Also owing to its simple chemical structure and high crystallinity, PEO has been frequently used as model system to study the crystallization and melting behavior of polymers^[1–32]. The most early systematic research work concerning the crystallization and melting of PEO was conducted by Kovacs and co-workers^[1–5]. In the 1990s, Cheng's research group has extremely studied the crystallization behavior of PEOs with different molecular weights^[6–11]. It was found that low molecular weight PEO could grow as extended chain crystals or lamellar crystals with integral folding (IF), depending on the molecular weight and chain end group as well as the crystallization temperature. In some cases, non-integral chain folding (NIF) of PEO crystals has been produced. These crystals can transform into integral folded chain crystals through thickening or/and thinning of the lamellae. This transition process is commonly influenced not only by the molecular weight and chain end group but also by the chain defect and architecture. For example, with increasing molecular weight, the non-

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integral to integral chain folding transformation becomes un conspicuous.

The abovementioned crystallization phenomenon has been observed not only for the PEO homopolymers, but also for the disproportionately high and low molecular weight homogeneous blends, which have been sometimes made for tailoring the mechanical and physical properties of PEO^[12]. Moreover, there are also other particular characteristics such as nucleation and molecular segregation phenomena of the PEO blends. Cheng and his co-workers have done a series of works on the nucleation and molecular segregation of PEOs *via* calorimetric and morphological studies^[13–16]. Through studies on the blends of high molecular weight PEO (molecular weight of 100000) with those having lower molecular weight ranging from 3500 to 20000, they found that the two PEO components with disproportionately high and low molecular weights could cocrystallize into a common crystal lattice at low crystallization temperature, while crystallize separately with dynamically phase splits into its components at high crystallization temperatures. This has also been proved by Schultz and his co-workers through studying the crystallization of PEO mixtures with molecular weights of 5000 and 270000, respectively^[17]. They further identified that the thickness of the cocrystals varies with the blend composition. If the low molecular weight PEO fraction is high, the cocrystalline lamellae are thin, suggesting a folding of the long-chain PEO into the lattice of the low molecular weight PEO crystals. On the other hand, at lower fractions of the low molecular weight PEO, the cocrystalline lamellae are thicker, resembling the crystals of the higher molecular weight PEO.

It should be pointed out that most of the published researches concerning the PEO and its blends have focused on the crystalline structures and morphologies. There are only a few cases with attentions being paid to the crystallization kinetics of PEO^[18, 19]. Moreover, the studies followed mainly the isothermal crystallization processes of single molecular weight PEO samples. A quite recent kinetic study on the PEO blend shows that the crystal growth rate of the PEO blend under isothermal conditions is blend ratio dependant^[19]. Actually, the nonisothermal crystallization kinetics of high and low molecular weight PEO blends is even important because the processing of polymeric materials is most commonly carried out under nonisothermal conditions. Taking this into account, we have studied the nonisothermal crystallization of PEO mixtures with molecular weight of 10000 (10k) and 200000 (200k), respectively, as a function of composition. For this kind of system, cocrystallization of both components during cooling is expected to occur at temperatures below the crystallization temperature of the higher molecular weight component but over the crystallization temperature of the lower molecular weight component^[20]. This is, however, not the case. Therefore, detailed study on the cocrystallization behavior of the PEO blends with disproportionately high and low molecular weights has been performed and possible explanation about the observed unusual behavior is discussed in this paper.

EXPERIMENTAL

PEO with $M_w = 200000$ g/mol and $M_w = 10000$ g/mol were purchased from Acros Organic and Alfa Aesar, respectively. The polydispersities of them are 1.1 for the 200k PEO and 1.04 for the 10k PEO. Before use, these two materials were purified by dissolving in chloroform first and then precipitating with *n*-hexane. The resulting samples were dried in a vacuum oven at room temperature for two days. Blends of the different molecular weight PEOs were prepared by dissolving the two components in chloroform and then volatilizing the solvent.

For differential scanning calorimetry study, a Q100TA DSC Instruments was used to record the nonisothermal crystallization and melting processes. The pure and blend samples which weighed ~3–5 mg were melted at 90 °C for 2 min, and cooled to room temperature at a constant rate of 5, 10, or 20 K/min. Melting temperatures and fusion enthalpies of all samples were obtained from the subsequent heating processes with a heating rate of 20 K/min. To estimate the crystallinity of the samples by DSC, the crystallization enthalpy value was used since lamellar thickening of PEO takes place during heating. The enthalpy of fully crystallized 10k and 200k PEOs were taken as 197.8 J/g and 165.5 J/g, respectively^[21–23]. The on-set and end crystallization temperatures of the samples were defined as the point where the DSC curves deviated from and re-join the baselines, respectively.

To measure the crystal growth rate of different samples under different conditions, the crystallization process was monitored by an Axioskop 40 A Pol Optical Microscope (Carl Zeiss). To this purpose, solutions of different molecular weight PEOs and their blends with different ratios were spin-coated onto glass slides with a rotation speed of 2000 r/min at room temperature. To obtain thin films with similar thickness, the solution concentrations of the 10k and 200k PEOs and their 50/50 blend were 300 mg/mL, 50 mg/mL and 100 mg/mL, respectively. The thicknesses of the thus prepared thin films are estimated to be about 22 ± 2 μm . During the optical microscopy observation, the thin films were first heat-treated at 90 °C for 5 min to completely erase the thermal history of the samples and then cooled quickly down to desired temperatures for isothermal crystallization. The crystallization temperatures were set at 38, 40, 43, 45, 48 and 50 °C.

Fine structures on nanometer scale of the thin films were obtained *via* atomic force microscopy (AFM) observation. To this end, an Agilent 5500 AFM operated in tapping mode using silicon cantilevers (spring constant kZ20-30 N/m) with typical resonance frequencies of 140–160 kHz was used. The films for AFM experiments were obtained by spin-coating 10 mg/mL solution of the 50/50 PEO blend in chloroform onto silicon wafers. The obtained films were heat-treated at 90 °C for 5 min to eliminate previous thermal history and then quenched into ice water at 0 °C for crystallization. The structure variation of these thin films during heating process was recorded by in-suit AFM experiments with a heating rate of 2 K/min.

The crystal structure of the PEO samples and their blends were determined by wide angle X-ray diffraction (D/Max 2500 VB2+/PC, Rigaku). The X-ray source was operated with an applied voltage of 45 kV and a filament current of 200 mA and Cu radiation was Ni-filtered in order to select the $K\alpha$ radiation with $\lambda = 0.154$ nm. The scan angle (2θ) ranges from 5° to 50° at a rate of 5 °/min. The films for X-ray diffraction experiments were prepared by solution casting and then melt-crystallization during the cooling process at a rate of 10k/min. The thicknesses of the prepared films are all around 200 μm .

RESULTS AND DISCUSSION

Figure 1(a) shows the DSC scans recorded during the cooling process of pure PEOs with different molecular weights and their 50/50 blend at a cooling rate of 10 K/min. The corresponding characteristic data are summarized in Table 1. From Fig. 1(a) and Table 1, one can see that the 200k PEO crystallizes earlier than the 10k PEO at slightly higher temperature (42.1 versus 41.6 °C). This is expected since that the long-chain polymers have usually a relative higher melting point than the short-chain ones, see the subsequent DSC heating scans shown in Fig. 1(b). Therefore, the body free energy gain of the long-chain fractions will be larger than that of the short-chain fractions, leading to an early start of crystallization of the long-chain fractions at relatively higher temperature with respect to their short-chain counterparts. Moreover, the 10k PEO exhibits clearly a higher crystallinity than the 200k one. This may originate from the fact that diffusion controls the crystallization process of PEO in this molecular weight range. As a consequence, the higher diffusion ability of the low molecular weight PEO is benefit for chain folding as well as packing onto the crystal growth front. By comparing the enthalpies recorded during crystallization and melting processes, one can find that the fusion enthalpies (ΔH_m) are always somewhat larger than the crystallization enthalpies (ΔH_c), *e.g.*, 182.1 J/g versus 175.9 J/g for the 10k PEO and 141.2 J/g versus 138.0 J/g for 200k PEO. This indicates the occurrence of either lamellar thickening or/and further structure perfection of the originally formed crystals during the DSC heating process. AFM observation has unambiguously demonstrated the occurrence of lamellar thickening (see later in Fig. 2). Accordingly, from the increased value of the enthalpy, it is concluded that the thickening of PEO lamellar crystals for the higher molecular weight sample is less evident than its lower molecular weight counterpart. This could be associated to the relatively lower molecular chain mobility of the high molecular weight PEO.

For the 50/50 blend, several aspects should be addressed here. First of all, the appearance of only one crystallization peak in the cooling scan and the single melting peak in the subsequent heating scan indicate the occurrence of cocrystallization of the high and low molecular weight PEOs without segregation. This is expected since the quick cooling process leads to the crystallization of the blend at relatively low temperature^[20].

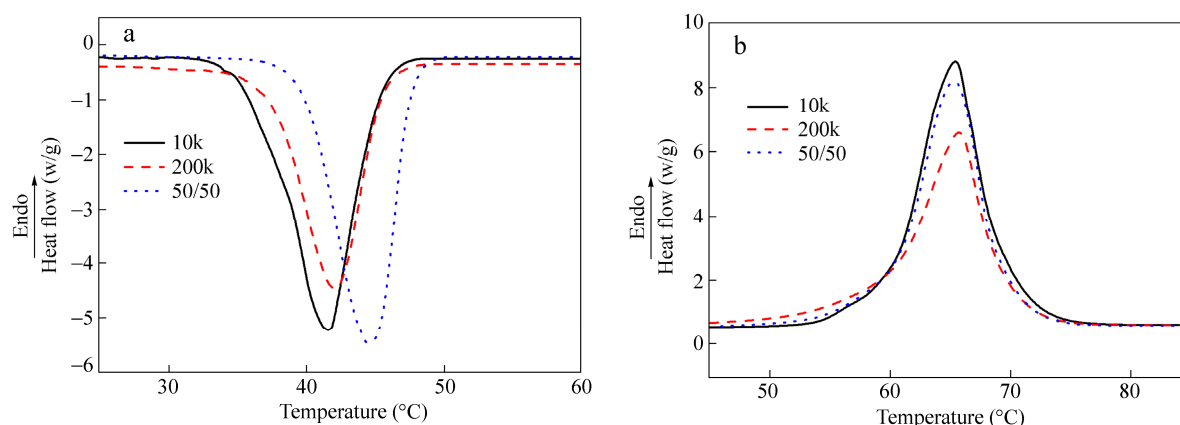


Fig. 1 DSC thermograms of PEOs with different molecular weights and their 50/50 blend taken during the cooling (a) and the subsequent heating (b) processes
The cooling rate was 10 K/min while the heating rate was 20 K/min.

Table 1. Characteristic data concerning the crystallization temperature (T_c), crystallization enthalpy (ΔH_c), melting temperature (T_m), fusion enthalpy (ΔH_m) and crystallinity (X_c) measured from the DSC scans as shown in Fig. 1

Sample	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)	X_c (%)
10k	41.6	175.9	65.4	182.1	88.9
200k	42.1	138.0	65.7	141.2	83.4
50/50	44.5	164.8	65.3	168.7	—

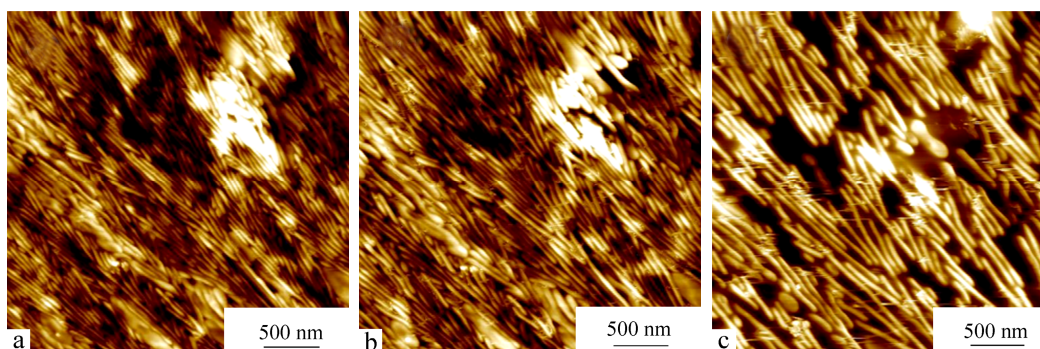


Fig. 2 AFM height images of a 50/50 PEO blend, prepared by quenching the melt into ice water at 0 °C, in a heating process at (a) 25 °C, (b) 62 °C and (c) 64 °C (The heating rate was 2 K/min.)

Second, the crystallization of the blend finished at a temperature higher than both of the individual component (see Fig. 1a). This is acceptable under the following consideration. It is generally accepted that the crystallization of a polymer follows a typical nucleation and crystal growth mechanism. Nucleation is a key process, which initiates the crystallization of the polymer from supercooled melt. It was well demonstrated that the nucleation rate and nucleation temperature depend on the chain length, *i.e.* the molecular weight. For polydispersed polymers, it is believed that the long-chain fractions, *i.e.*, the higher molecular weight fractions, initiate the crystallization and lead to the formation of thicker dominant lamellae. The short-chain fractions grow then later, originating the formation of subsidiary thinner lamellae^[20, 24]. During the crystallization process of long-chain fraction, the short-chain fraction serves as solvent, which enhances the diffusion ability of the molecular chain segments and promotes the crystallization^[25]. In other words, the high molecular weight component promotes the nucleation of the system, while the lower molecular weight component enhances the diffusion ability of the blend and is therefore benefit for the crystal growth. Taking this into account, the 50/50

blend can be regarded as a polymer with bimodal distribution of 200k and 10k. In this case, the 200k PEO acts as the long-chain fraction and initiates the crystallization of the system, while the 10k PEO acts as the short-chain fraction and accelerates the crystal growth of the blend. As a consequence, the crystallization of the blend completes in a narrow temperature window and at relatively higher temperature.

Third, the fusion enthalpy (ΔH_m) of the blend is also larger than the crystallization enthalpy (ΔH_c). This is caused by the occurrence of lamellar thickening as illustrated by AFM observation. As shown in Fig. 2, at room temperature edge-on oriented PEO lamellae of about 20 nm can be observed. When the film is heated to 62 °C (Fig. 2b), the PEO lamellae are relatively thicker than those shown in Fig. 2(a). With further increase of the temperature, *e.g.* see Fig. 2(c) at 64 °C, the thickness of the PEO edge-on lamellae changes from 20 nm to about 40 nm. This confirms that the increase of fusion enthalpy compared with crystallization enthalpy is related mainly to the lamellar thickening, which is frequently encountered also for many other semicrystalline polymers. Moreover, one may notice that both the ΔH_m and ΔH_c of the 50/50 blend are larger than half the sum of the enthalpies for the two components, *e.g.* $(175.9 + 138.0)/2 = 156.95$ J/g versus 164.8 J/g for the crystallization enthalpy and $(182.1 + 141.2)/2 = 161.65$ J/g versus 168.7 J/g for the fusion enthalpy. This unambiguously indicates an increment in crystallinity of the blend. It may be expected under the consideration that the short-chain molecules enhance the chain segment diffusion ability of the blend system and promote the crystallization ability of the blend. The crystallinity of the blend can, however, not be exactly calculated since we do not know the crystallized portions of the low and high molecular weight fractions in the blend, respectively. In generally speaking, the addition of lower molecular weight component, which serves as solvent, would most likely enhance the crystallization of the high molecular weight component. Taking this into account, the crystallinity increase of the 200k PEO may be larger than that of the 10k PEO.

Forth, one can clearly see from Fig. 1(a) that the on-set crystallization temperature of the blend (~50 °C) is evidently higher than that of both components. This is somewhat hard to be understood when the 200k PEO component is thought to be a long-chain fraction that initiates the crystallization of the blend.

Figure 3 shows the DSC thermograms of PEOs with different molecular weights and their 50/50 blend taken during the cooling processes with different cooling rates. The characteristic data obtained from the DSC scans including the on-set and peak crystallization temperatures, melting temperature, crystallization enthalpy, fusion enthalpy as well as crystallinity are listed in Table 2. The melting temperatures and fusion enthalpies of these samples were obtained during the subsequent heating processes at a rate of 20 K/min, which is not shown here in the text. From Fig. 3 and the data listed in Table 2, one can find that the crystallization of all samples during the slow cooling process at a rate of 5 K/min (Fig. 3a) takes place at higher temperature than that during the 20 K/min cooling process (Fig. 3b). This is caused first by an early start of the crystallization as demonstrated by the difference in on-set crystallization temperatures, *e.g.*, 48.6 °C versus 46.1 °C and 50.7 °C versus 47.0 °C for the 10k and 200k PEOs, respectively. A detailed comparison of the peak and on-set crystallization temperatures of all samples is presented in Fig. 4. From left part of Fig. 4, one can see that the peak crystallization temperature of 200k PEO sample is mostly affected by increasing the cooling rate from 5 K/min to 10k/min, while the peak crystallization temperature of 10k PEO sample decreases more evidently when the cooling rate is increased from 10 K/min to 20 K/min. Comparing with the cooling rate dependence of the on-set crystallization temperatures, we concluded that the tremendous peak crystallization temperature decrease of the 200k PEO by increasing the cooling rate from 5 K/min to 10 K/min is mainly contributed by the significant decrease of on-set crystallization temperature, *i.e.*, the reduced nucleation ability of the 200k PEO. On the other hand, the quick decrease of the peak crystallization temperature of the 10k PEO by increasing the cooling rate from 10 K/min to 20 K/min originates from the reduced nucleation ability as well as the reduced crystal growth rate, since the decreases in on-set crystallization temperature of the 10k and the 200k PEOs are essentially the same in this cooling rate range. For the 50/50 blend, it can be clearly seen that both the peak and the on-set crystallization temperatures decrease almost linearly with increasing cooling rate. This may imply that the cooling rate effect on the crystallization of the PEO blend has averaged the effect of cooling rate on the 10k and 200k PEO materials. Nevertheless, one can easily find from Fig. 4 that the on-set as well as the peak

crystallization temperatures of the blend are always higher than those of the homopolymers in all cases. From Table 2, it is further concluded that i) lamellar thickening takes place during the heating processes of all samples as judged from the increase of fusion enthalpy with respect to the corresponding crystallization enthalpy and ii) an increment in crystallinity is identified after mixing the lower molecular weight PEO into its higher molecular weight component. All the above mentioned results indicate that the enhanced crystallization ability of the blend compared with its individual homopolymer is not affected by the cooling rate.

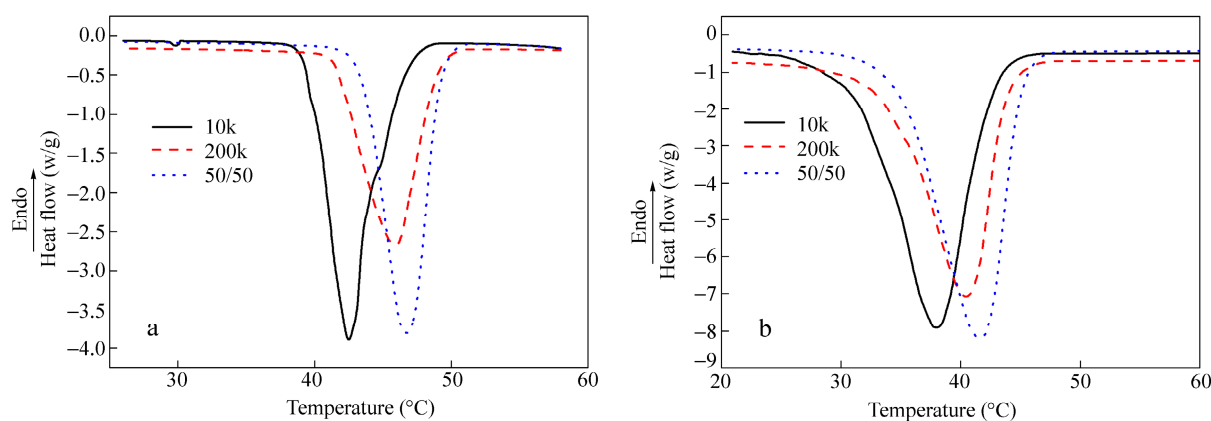


Fig. 3 DSC thermograms of PEOs with different molecular weights and their 50/50 blend taken during the cooling process. The samples were heated to 90 °C for 2 min and then cooled at a rate of (a) 5 K/min and (b) 20 K/min to room temperature.

Table 2. Characteristic data concerning the on-set ($T_{\text{on-set}}$) and peak (T_c) crystallization temperatures, melting temperature (T_m), crystallization enthalpy (ΔH_c), fusion enthalpy (ΔH_m) and crystallinity (X_c) measured from the DSC scans as shown in Fig. 2

Cooling rate	Sample	$T_{\text{on-set}}$ (°C)	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X_c (%)
5 K/min	10k	48.6	42.5	65.5	178.1	187.5	90.0
	200k	50.7	45.9	66.0	137.1	147.6	82.8
	50/50	51.1	46.8	65.7	165.3	171.8	—
20 K/min	10k	46.1	38.0	65.4	171.6	181.2	86.1
	200k	47.0	40.5	65.3	132.5	145.3	80.1
	50/50	48.2	41.7	65.1	163.2	166.2	—

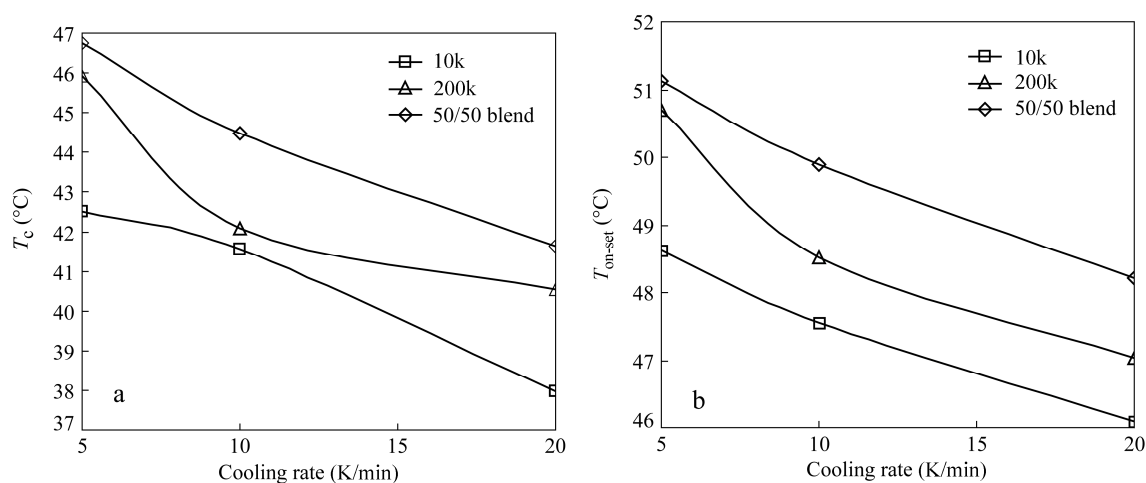


Fig. 4 Dependence of peak (left part) and on-set (right part) crystallization temperatures on the cooling rate

Presented in Fig. 5 are the DSC thermograms of 10k/200k PEO blends with different blend ratios. The characteristic data including the on-set and peak crystallization temperatures, melting temperature, crystallization enthalpy, fusion enthalpy as well as crystallinity are listed in Table 3. The melting temperatures and fusion enthalpies of these samples were also obtained from the subsequent heating processes at a rate of 20 K/min. The DSC heating scans are also not shown here in the text. From Fig. 5 and Table 3, we can see that all of the blends with different blend ratios crystallize always at higher crystallization temperature comparing with the individual component. Especially for the 10k/200k PEO blend with blend ratio of 70/30, the crystallization started and finished much earlier than all of the other samples. This means that a small amount high molecular weight PEO can promotes the crystallization of the low molecular weight PEO significantly. This may illustrate on the one hand the effect of the long PEO chains on initiating the crystallization of the blend and on the other hand the effect of short PEO chains on enhancing the crystal growth of the blend.

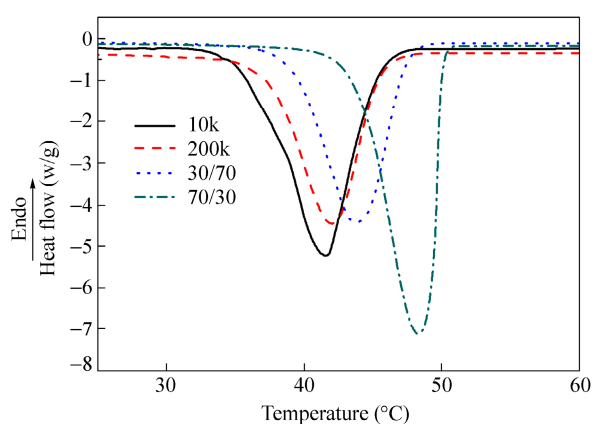


Fig. 5 DSC thermograms of 10k/200k PEO blends with different blend ratios recorded during the cooling processes at a rate of 10 K/min

Table 3. Characteristic data of the 10k/200k PEO blends including the on-set ($T_{\text{on-set}}$) and peak (T_c) crystallization temperatures, melting temperature (T_m), crystallization enthalpy (ΔH_c), fusion enthalpy (ΔH_m) and crystallinity (X_c) measured from the DSC scans as shown in Fig. 5

Blend ratios	$T_{\text{on-set}}$ (°C)	T_c (°C)	T_m (°C)	ΔH_c (J/g)	ΔH_m (J/g)	X_c (%)
100/0	47.6	41.6	65.4	175.9	182.1	88.9
70/30	51.1	48.3	66.0	187.4	192.1	—
30/70	49.9	43.8	66.6	144.1	147.2	—
0/100	48.5	42.1	65.7	138.0	141.2	83.4

Another thing which should be addressed is about the enthalpies of the blends. The increase of fusion enthalpies compared with the corresponding crystallization enthalpies demonstrates unambiguously the occurrence of lamellar thickening of all samples during the DSC heating processes. Moreover, when estimating the crystallization enthalpies according to the following equation: $\Delta H_{\text{blend}} = \Delta H_{10k} \Phi_{10k} + \Delta H_{200k} (1 - \Phi_{10k})$, where the ΔH_{10k} and ΔH_{200k} are the respective crystallization enthalpies of the 10k and 200k PEOs, while the Φ_{10k} is the concentration of 10k PEO in the blend. We can get the crystallization enthalpies of the 70/30, 50/50 and 30/70 blends as 164.5, 157.0 and 149.4, respectively. Comparing these data with those listed in Table 1 and 3, one can easily find that the calculated enthalpy values of the 70/30 and 50/50 blends are smaller than the experimentally obtained enthalpies, indicating an increase in crystallinity of the blends. On the other hand, the calculated value for the 30/70 blend is larger than the experimental datum, *i.e.* 149.4 versus 144.1, which indicates a decrease in crystallinity of the blend. One may attribute the blend ratio dependant crystallinity change to the different crystalline modifications since it was reported that the PEO can crystallize in monoclinic or triclinic forms^[26, 27]. To find out whether the PEOs and their blends with different compositions crystallize in different crystal phases

or not, wide angle X-ray diffraction experiments were conducted. The wide angle X-ray diffraction profiles with the main diffraction being indexed are shown in Fig. 6. As seen from Fig. 6, the X-ray diffraction profiles are essentially the same with the main reflections located at $2\theta = 19.1^\circ$ and 23.2° , which can be accounted for by the monoclinic unit cell as the (120) and (112)/(032) reflections. The difference in intensity reflects the different crystallinity since all the films used here have a similar thickness. Clearly, the (120) reflection peak of the 70/30 blend has the highest intensity, which may imply a highest crystallinity. This is in good agreement with the DSC results.

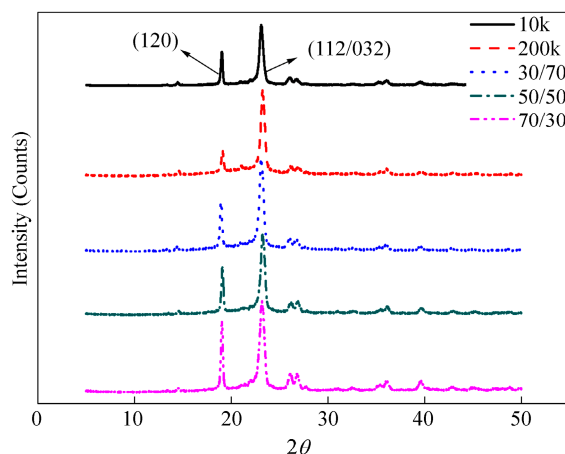


Fig. 6 X-ray diffractions of the pure PEOs and their corresponding blends crystallized during the cooling process at a rate of 10 K/min

The above experimental results clearly indicate that the blends of PEOs with different molecular weights crystallize always earlier than the pure PEOs. It is cooling rate and blend ratio independent, even though the blend ratio influences the crystallization kinetics and crystallinity of the blends. Hereafter, we will try to explain the accelerated crystallization of the blends and the effect of blend ratio on the crystallization kinetics and crystallinity of the blends. To this end, several aspects will be discussed in the following section.

First of all, the crystal growth rate has been concerned. The crystal growth rate of PEO with molecular weight ranging from $M_w = 10^4$ to $M_w = 10^6$ has been reported^[28, 29]. Here, the appearance of single crystallization and melting peaks of the PEO blends with different blend ratios indicates the cocrystallization of the PEOs with different molecular weights. Consequently, the crystal growth rate of both PEOs and their blends can be determined. We have measured the growth rates of the PEOs and their 50/50 blend under different temperatures by using the polarized optical microscope. Through recording the images of the spherulites during the growth processes under different isothermal crystallization temperatures, the linear relationship between the spherulite radius and the time can be obtained and the spherulite growth rate can be calculated from the slope of the radius versus time plot. As shown in Fig. 7, the crystal growth rates of all samples are temperature dependant. Nevertheless, the spherulite of the 10k PEO grows always faster than that of the 200k PEO in the measured temperature region. This implies that the higher diffusion ability of the lower molecular weight PEO is indeed in favor of the propagation of its crystals. Taking into account that the solvent effect of the lower molecular weight PEO towards its higher molecular weight counterpart, the spherulites of the 50/50 blend grow quicker than the 200k PEO ones but slower than the 10k ones. This should result in a shorter time for completing the crystallization of the blend than the 200k PEO and lead to therefore an increase of peak crystallization temperature.

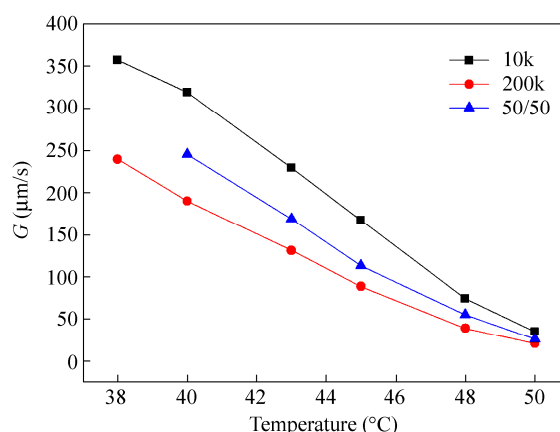


Fig. 7 Plots of crystal growth rate versus isothermal crystallization temperature of the PEOs and their 50/50 blend

Second, we discuss the early start of the crystallization of the blend. All of the experimental results indicate that the 10k/200k PEO blends crystallize always earlier than both homopolymers. This means that mixing the 10k PEO into the 200k one affects not only the crystal growth but also the nucleation of the blends, which leads to an early on-set of the crystallization, *i.e.*, a higher on-set crystallization temperature of the blends compared to the homopolymers. The influence on nucleation of the blend may be two folds. One is the amount of the nucleus formed at a certain temperature and the other one is the temperature at which the nucleation started, or most likely a combination of both. For the first case, assuming that a certain number of nuclei is required to give the DSC signal, different amounts of the nuclei will give different DSC results. In this case, even if the nucleation of the blends and the 200k PEO takes place at the same temperature, an increment in nucleus number of the blends compared with the 200k PEO will lead to an early change of the enthalpy in the DSC scan, which illustrates an early start of the crystallization as manifested by a higher on-set crystallization temperature. A comparison with the times for completing the crystallization of different samples seems to support this explanation. The time for completing the crystallization is defined as the tenth of the temperature difference between the on-set and end crystallization temperatures determined during the 10 K/min cooling process. It is found that the time for completing the crystallization of the 10k PEO (~1.64 min) is shorter than that of the 200k PEO (~2.15 min). This is reasonable since the crystal growth rate of the 10k PEO is higher than that of the 200k PEO. The time for completing the crystallization of the 50/50 blend is 1.56 min, which is about the same or even shorter than the time used for the 10k PEO. This is hard to be understood when only crystal growth rate is considered. Therefore, it is concluded that an increment in nucleus number leads to a further reduction of the crystallization time of the blend. It should be pointed out that the increase of nucleus number of the blend itself can, however, not well explain the blend ratio dependence of the on-set crystallization temperature. In this sense, an early start of nucleation in the blends is also highly possible. The exact reason for the early start of nucleation in the PEO blends is not clear at moment. One possibility may rest on the density fluctuation of the blends with different molecular weights, which will most likely increase the amount of the nucleation density. This has been found for many other systems^[33–35]. Another possible explanation is the reduction in energy barrier for nucleation by adding the 10k PEO into the 200k PEO, which initiates an early start of nucleation at relatively higher temperature. For a better understanding of this issue, further detailed studies are clearly needed.

Third, we talk about the crystallinity of the blend systems. As mentioned above, the estimated crystallization enthalpies of the 70/30, 50/50 and 30/70 blends are 164.5, 157.0 and 149.4 J/g, respectively, while the corresponding experimental data are 187.4, 164.8 and 144.1 J/g. A comparison indicates a crystallinity increase for the 70/30 and 50/50 blends while decrease for the 30/70 blend. It may be understood in the following way. The experimental results indicate that the crystallization of 10k PEO gives a higher enthalpy

value than the crystallization of 200k PEO. This implies a higher crystallization ability of the 10k PEO compared with the 200k PEO. Taking this into account, for the 70/30 blend, the 10k PEO with high crystallization ability is the main component. The crystallization ability of the minor 200k PEO can be improved due to the solvent effect of the 10k PEO part. Therefore, an overall increment in crystallinity is seen. On the other hand, for the 30/70 blend, the 200k PEO with lower crystallization ability is the rich phase. This leads to an overall small crystallization enthalpy value as compared with 70/30 and 50/50 blends. Moreover, the minor 10k PEO component may crystallize in this case mainly with 200k PEO. This will to some extent improve the crystallization ability of the 200k PEO at the expense of the 10k PEO's higher crystallization ability. This results in an overall crystallinity decrease of the blend.

Finally, we recall the previous work of Schultz and his co-workers^[17]. Through studying the cocrystallization behavior of the 5k/27k PEO mixtures, they found that the thickness of the cocrystals varies with the blend composition. In the low molecular weight PEO rich blend, the cocrystalline lamellae are thin. It is therefore concluded a folding of the long-chain PEO into the lattice of the low molecular weight PEO crystals. This may imply that the cocrystallization of the system is initiated by the low molecular weight PEO. In this case, a much early start of the crystallization of the 70/30 (10k/200k) PEO blend is hard to be understood. On the other hand, if the thinner cocrystalline lamellae are initiated by the long chain PEO (200k PEO), it is then expected an early nucleation at relative higher temperature owing to the reduced critical nucleus size corresponding the long chain of 200k PEO.

CONCLUSIONS

In conclusion, the crystallization behavior of 10k and 200k PEOs as well as their blends with different blend ratios was studied in details. The results show that, compared with the 200k PEO, the 10k PEO crystallizes at relatively lower temperature with faster crystallization rate as judged from a shorter time for completing the crystallization. The blends of the two PEOs always cocrystallize under the crystallization condition used in this work. Mixing of the 10k PEO with the 200k one is in favor of the crystallization of the system. This is demonstrated by the early start of the crystallization at higher crystallization temperature and a faster crystal growth of blend with respect to the 200k PEO. The accelerated crystallization of 10k/200k PEO blends is caused by an early start of nucleation and an increment of nucleus number. This may originate from the density fluctuation of the blend system and a reduction in energy barrier for nucleation. Moreover, it is found that the crystallinity of the 10k PEO enrich blends increases with increasing concentration of the 10k PEO. This is caused by the solvent effect of the 10k PEO toward the 200k PEO. On the other hand, the crystallinity of the 30/70 (10k/200k) PEO blend is decreased a little bit. This may be a balance result of the improved crystallization of the 200k PEO at the expense of the high crystallization ability of the 10k PEO.

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