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Isothermal crystallization kinetics of poly(ethylene terephthalate)–poly(ethylene oxide) segmented copolymer with two crystallizing blocks

W. Li [a,b,*], Xiaohua Kong [c], Enle Zhou [d], Dezhu Ma [e]

[a] *Department of Mechanical Engineering, Changchun University, Changchun 130022, People's Republic of China*
[b] *Hubei Key Laboratory of Novel Reactor and Green Chemical Technology, Wuhan Institute of Technology, Wuhan 470074, People's Republic of China*
[c] *Department of Agricultural, Food and Nutritional Science, University of Alberta, Edmonton, Canada T6G 2P5*
[d] *Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China*
[e] *Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, People's Republic of China*

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Abstract

The isothermal crystallization kinetics and morphology of poly(ethylene terephthalate)–poly(ethylene oxide) (PET30–PEO6) segmented copolymer, and poly(ethylene terephthalate) (PET) and poly(ethylene oxide) (PEO) homopolymers have been studied by means of differential scanning calorimetry (DSC) and a transmission electron microscope (TEM). It is found that the nucleation mechanism and growth dimension of PEO in the copolymer are different from that in the homopolymer, which is attributed to the effect of the crystallizability of PET-blocks. Furthermore, the crystallization rate of PEO-blocks in the copolymer is slower than that in the homopolymer because the PET-blocks phase is always partially solidified at the temperatures when PEO-blocks begin to crystallize. In contrast, the isothermal crystallization rate of PET-blocks in the copolymer is faster than that in the homopolymer because the lower glass transition temperature of the PEO-blocks (soft blocks) increases the mobility of the PET-blocks in the copolymer.

Keywords: PET–PEO segmented copolymer; PET; PEO

1. Introduction

Block copolymers have long sequences or blocks of one type of repeat unit joined to blocks of a different repeat unit at one or both ends [1–5]. In this class of polymers, the blocks can be diblock, triblock, and multiple-blocks (also termed as segmented) structures, which describe the way the blocks are connected. Block copolymers have been well studied recently in both academic and practical aspects, because it is possible to achieve the combined properties of two completely different polymers without the occurrence of macroscopic phase separation. Due to the chemical link between incompatible polymers, the phase separation is limited to a microscopic scale and is dependent on the volume fraction of the different blocks [6]. Among the great variety of block copolymers, semicrystalline polymers, which have one or two semicrystalline blocks, are particularly interesting because of their wide industrial applications. Studies on these polymers have mainly focused on block copolymers containing one semicrystalline block [7–11]. On one hand, the block copolymers containing two semicrystalline blocks are complex. On the other hand, such complexity also arouses the curiosity to further study various phase behaviors, microstructural evolutions, and crystallization in order to develop novel polymers or to control polymerizations. Of particular interest is the formation and morphology of the semicrystalline/semicrystalline state since it involves the crystallization of two different polymers, each within its specific temperature regime.

It is noted that most of the research on the crystallization behavior so far has focused on block copolymers consisting of an amorphous block and a crystalline and or liquid crystalline block. In the past decades, there have been only a few studies on block copolymers composed of two crystallizable blocks. The first study on this aspect can be traced back to the pioneering work by Perrier and Shiomi [12,13]. They showed that in a triblock copolymer poly(ε-caprolactone)-*block*-poly(ethylene oxide)-*block*-poly(ε-caprolactone) (PCL-*b*-PEO-*b*-PCL), both blocks were able to crystallize. Recently, double crystallizable block copolymers have attracted

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[*] Corresponding author. Address: Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G8.
E-mail address: wenl@ualberta.ca (W. Li).

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increasing interest because more crystalline blocks can increase the complexity and controllability of a copolymer system, which implies further unexpected novel structures and properties [14–17]. For example, Sun et al. [14] studied the crystallization behavior of a polyethylene-*block*-poly(ethylene oxide) (PE-*b*-PEO) diblock copolymer. They demonstrated that when both blocks were crystalline, the PE and PEO blocks formed extended-chain crystals and the PEO chains parallel to the lamellar normal. Shiomi and Takenaka [15] observed a unique morphology of spherulite similar to that of ring-banded spherulites, namely double spherulites like concentric circles, for PCL-*b*-PEO-*b*-PCL triblock copolymer. The central and outer sections in the concentric circles were those of PCL and PEO, respectively. In addition, emphasizing crystalline morphology and dislocation development, Sun et al. [16] investigated a series of diblock copolymers of poly(L-lactide)-*block*-poly(ethylene glycol) (PLLA-*b*-PEG) via differential scanning calorimetry, wide-angle X-ray diffraction, polarized optical microscopy, and atomic force microscopy. In these copolymers, both blocks were crystallizable and biocompatible. It was interesting that these PLLA-*b*-PEG diblock copolymers could form spherulites with banded textures, which was undercooling dependent. Single crystals with an abundance of screw dislocations were also observed. Here it should be pointed out that although various copolymers with two crystallizable blocks have been recently investigated intensively, at present the research on their crystallization behavior is still at an infant state. Considerable issues should be addressed or further studied. For example, the crystallization kinetics of double crystallizable block copolymers is extremely interesting and may be different from that in one crystallizable block copolymers or crystalline homopolymers. However, such crystallization behavior is often complicated due to the concurrent effects of various factors, including nanoconfined geometry, matrix hardness, the glass transition temperature, domain connectivity, morphology, and domain sizes [14,17]. The roles of above factors have not been completely understood. In addition, the PE-*b*-PEO diblock copolymer with double crystalline blocks is ideal for such studies because its high chain regularity, strong immiscibility, and controlled molecular weights. However, the synthesis of high molecular weight linear PE with a PEO block is considerable difficult [14].

Over the past years, we have conducted a systematic study on the synthesis, characterization, phase transition, and crystallization of segmented copolymers consisting of poly(ethylene oxide) (PEO) and poly(ethylene terephthalate) (PET). In this copolymer, PET segments of relatively high glass transition temperature (T_g) and melting temperature (T_m) are commonly referred to as 'hard' segments, and PEO segments with relatively low T_g and T_m, as 'soft' segments. They may segregate into separate phases in the solid state as other segmented copolymers do due to the incompatibility between soft and hard segments. PET crystal nodes in the network system can prevent the PEO segments from flowing during stretching at a temperature above the T_m of PEO crystals. Such a morphological characteristic in the copolymer enables it to recover from its deformed shape to its original state at a temperature around T_m of PEO crystals, and act as a thermally stimulated shape memory polymer (SMP) [18]. Since this copolymer was first described by Coleman [19] in 1945 in an attempt to reduce the crystallinity of PET and increase its hydrophilicity to improve the dyeability with hydrophilic dyes, practical development of the copolymer has been extended to the modification of copolyester fibers using these segmented copolymers [18]. Recent study [20], has further demonstrated that the copolymer may be widely applied in industries because of its various excellent mechanical and thermal properties (e.g. thermally stimulated shape memory property).

Recently, we have focused on the crystallization behavior of the segmented copolymer. In our previous work [21], we investigated the effect of soft block length on isothermal crystallization kinetics of PEO-blocks in the copolymer in which both blocks are semicrystalline. The crystallizability of PET-blocks exerts strong influences on the crystallization process, crystallinity, as well as the final morphology of soft block. The phase behavior of the copolymer can be summarized as follows: above the melting point of PET, the copolymer forms a fully amorphous state. Decreasing the temperature to lower than T_m (PET), that is, $T < T_m$ (PET), caused the PET blocks to crystallize, which amounts to the transition from the fully amorphous to the amorphous/semicrystalline state. When the temperature is further lowered to $T < T_m$ (PEO), the PEO segments crystallize as well, bringing the system from the amorphous/semicrystalline into the semicrystalline/semicrystalline state.

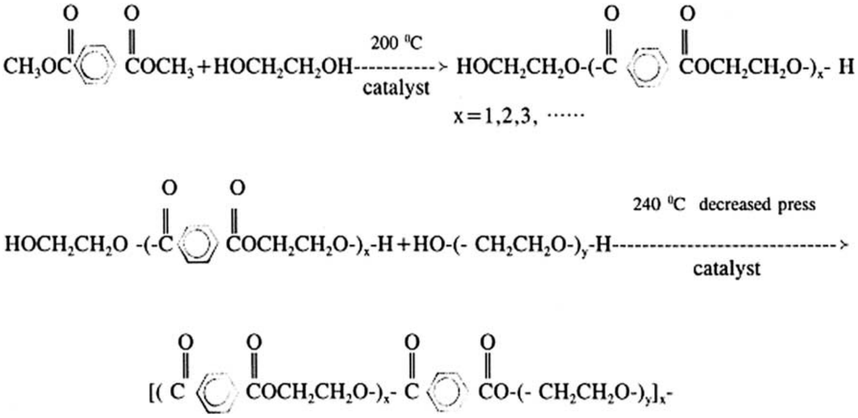
In the present work, we investigate the isothermal crystallization kinetics of PET–PEO in both segmented copolymers and homopolymers. The different behaviors of nucleation and growth of the two blocks are discussed. We focus on the kinetics of both of the above-mentioned polymers through measurement of the overall crystallization kinetics using differential scanning calorimetry (DSC). In addition, to obtain direct evidence for the crystallization behavior we observe the morphology of the segmented copolymer, as well as PET and PEO homopolymers by means of transmission electron microscope (TEM).

2. Experimental

2.1. Materials

The series of poly(ethylene terephthalate)–poly(ethylene oxide) (PEO/PET) segmented copolymers with different lengths of soft segments (PEO) and different hard segments (PET) were synthesized using a two-step reaction method according to the route as follows (Scheme 1).

Further details of the synthetic scheme are published elsewhere [18,21–24]. To characterize the synthetic copolymers, we have used various techniques, including differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR) spectrometer, Fourier transform infrared spectroscopy (FTIR), small angle X-ray scattering (SAXS), dynamic mechanical analysis (DMA), scanning electron microscopy



Scheme 1.

(SEM), and transmission electron microscopy (TEM), to investigate the structure and thermal properties [18,21–24]. In particular, the PET content and the length of hard segments were determined using NMR spectroscopy [23]. In NMR measurements, ^{1}H, ^{1}H–^{1}H and ^{13}C NMR spectra were obtained on a Bruker DMX-500 NMR spectrometer using $CDCl_3$ as a solvent and TMS as an internal standard. ^{13}C chemical shifts were referenced relative to $CDCl_3$ at 77.00 ppm. Moreover, the intrinsic viscosity values $[\eta]$ of the copolymers were determined in $CHCl_2CHCl_2$ solutions at 30 ± 0.1 °C [18]. In addition, we used positron lifetime measurements to investigate the effects of the hard segment content (PET) and the temperatures on free volume properties, structural transition and miscibility behavior of the copolymers [24]. The main results involved in the present work are listed in Table 1. More characteristic data for the copolymers can be found in our previous papers [18,21–24].

Polyethylene terephthalate (PET) homopolymers, with the intrinsic viscosity $[\eta]=0.63$ and 0.5% solution in tetrachloroethane/mesophenol at 25 °C, were used as received from Shanghai Polyester Fiber Co. Inc., China. Polyethylene oxide (PEO) homopolymers, with number-average molecular weight $\bar{M}_n=6000$, were used as received from Shanghai Second Synthetic Detergent Co. Inc., China.

2.2. DSC measurements

Isothermal crystallization was carried out in a sample pan of Perkin–Elmer DSC-2 calorimeter. A scanning rate of 10 °C/min was chosen for DSC measurements and a nitrogen purge was used throughout. The investigations of the copolymer were performed as follows: the copolymer was heated to 280 °C and held at this temperature for 5 min, before quenching the molten samples to the crystallization temperature of PEO-blocks. The samples were cooled to a predetermined crystallization temperature of PET-blocks and crystallized isothermally until DSC could not examine any heat flow. The homopolymer was heated to a molten state and held 5 min, then quenched to the predetermined crystallization temperature. Finally, all the polymer samples above were heated to their molten states at 10 °C/min. We assume that the extent of crystallinity, which developed at time t, X_t, was

$$X_t=\frac{\int_0^t (\mathrm{d}H_c/\mathrm{d}t)\mathrm{d}t}{\int_0^\infty (\mathrm{d}H_t/\mathrm{d}t)\mathrm{d}t} \qquad (1)$$

where $\mathrm{d}H_c/\mathrm{d}t$ is the heat evolution rate at time t, owing to crystallization, $\int_0^\infty (\mathrm{d}H_t/\mathrm{d}t)\mathrm{d}t$ is the total area under the crystallization exotherm at the crystallization temperature T_c.

2.3. TEM observations

A JEOL TEM 2010 EXII transmission electron microscope (TEM) was used to examine morphology at 200 kV. Droplets of 0.1 wt% 1.1.2.2-tetrachloroethane solution of PET30–PEO6 copolymer, 0.1 wt% chloroform solution of PEO homopolymer and 0.2 wt% 1.1.2.2-tetrachloroethane/mesophenol(1/1) solution of PET homopolymer were placed onto carbon-coated cleaved mica, respectively. First the solvent was allowed to evaporate at room temperature for about 3 days to form films. Then the films were held under vacuum for 24 h. After post-annealing (T_m was 280 °C, the annealing temperature for the PET-blocks was 200 °C, and the annealing temperature for the PEO-blocks was 35 °C, which was the same as that used for

Table 1
Parameters of PET–PEO segmented copolymer

Sample	PEO $\bar{M}_w$	Hard segment (%)		Number of PET units		$[\eta]$ (dL/g)	T_{g1} (°C)	T_{g2} (°C)
		Theory	By NMR	Theory	By NMR			
PET30–PEO6	6000	30	31.5	13.4	14.4	0.70	−68	37

T_{g1} is the glass transition temperature of PEO-blocks determined by positron annihilation lifetime spectroscopy; T_{g2} is the glass transition temperature of PET-blocks determined by positron annihilation lifetime spectroscopy.

the DSC experiments), pieces of the carbon and polymer film were next floated onto water and picked up with 400-mesh copper grids. Prior to observation by TEM, some of the copolymer specimens were exposed to vapors of hydrazine solution for 5 h. After the unsaturated bonds linked to the phenethyl of PET segments, they were then transferred to vapors of an aqueous solution of osmium tetroxide for 8 h. OsO_4 preferentially stains the unsaturated bonds of PET segments. The samples thus obtained were obliquely shadowed with Pt in a vacuum evaporator.

3. Results and discussion

The isothermal crystallization of PEO and PET blocks of PET30–PEO6 segmented copolymer are shown in Fig. 1(a) and (b). According to Eq. (1), the relative crystallinities at different temperature can be obtained. The Avrami plot $\log[-\ln(1-X_t)]$ against $\log(t)$ is shown in Fig. 2. The Avrami plot of PEO and PET homopolymer is shown in Fig. 3(a) and (b), respectively. It is evident that the Avrami equation fails to describe the overall crystallization process.

As known, the early stage of overall crystallization of bulk polymer obeys the Avrami equation very well. However, because of the different mechanism of crystallization, our experimental data cannot be described very well using the Avrami equation. Fractional values of the Avrami exponent (n) and large deviations to experimental results at later stage are obtained. These discrepancies are generally attributed to the simplified assumptions made in the Avrami model such as: constant radial growth rate, constant density and shape of the growing nuclei, uniqueness of the nucleation; no secondary crystallization, and no volume change during phase transformation/crystallization.

The kinetics parameters of the primary stage of PEO-blocks in PET30–PEO6 segmented copolymer and PEO-6000 homopolymer are summarized in Table 2; those of PET-blocks in the copolymer and the PET homopolymer are summarized in Table 3. From Table 2, it is found that for PEO-blocks in PET30–PEO6 segmented copolymer, the average values of the Avrami exponent n is 2.1, which implies either disklike (lamellar) growth from heterogeneous nuclei or rodlike growth from homogeneous nuclei. For PEO-6000 homopolymer, n is 3.9, which corresponds to the three-dimensional spherulitic growth from homogeneous nuclei. For PET-blocks in PET30–PEO6 segmented copolymer, as listed in Table 3, the average value of n is 4, which also implies three-dimensional spherulitic growth from homogeneous nuclei. For the PET homopolymer, n is 3.1 which implies either a three-dimensional spherulitic growth from heterogeneous nuclei or a disklike growth from homogeneous nuclei. It is evident that the mechanism of nucleation and growth dimension of the soft and hard blocks in the segmented copolymer are different from those of the homopolymers.

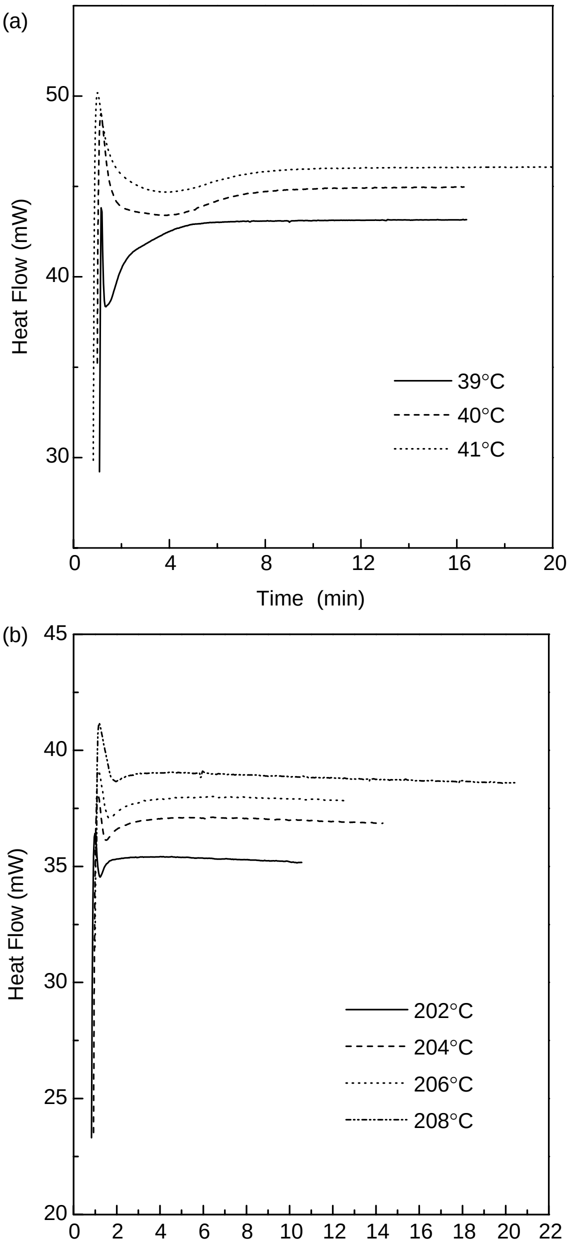


Fig. 1. DSC crystallization curves of PEO (a) and PET (b) of PET30–PEO6 segmented copolymer crystallizing at different temperatures.

Fig. 4 shows TEM micrographs of PET30–PEO6 segmented copolymer, PET, and PEO homopolymers with the same thermal history as that for the isothermal crystallization kinetics study. Fig. 4(a) shows a lamellar structure. The inset gives the selected electron diffraction, indicating two concentric rings. After Au calibration, the d values from the center are 0.463 nm corresponding to (120) reflection of PEO, and 0.338 nm corresponding to (100) reflection of PET. Fig. 4(b) shows the morphology of PET30–PEO6 segmented copolymer stained by OsO_4, in which the morphology of PET distributed in the lamellar of PEO is observed. Fig. 4(c) shows the morphology of the PET homopolymer, indicating a characteristic feature of spherulitic morphology consisting of edge-on lamellae. Fig. 4(d) shows the morphology of the PEO homopolymer. A complete spherulitic texture with an 'eye-like' morphology near the spherulitic center is observed for most spherulites during crystallization. The different mechanism of PEO crystallization between copolymer and

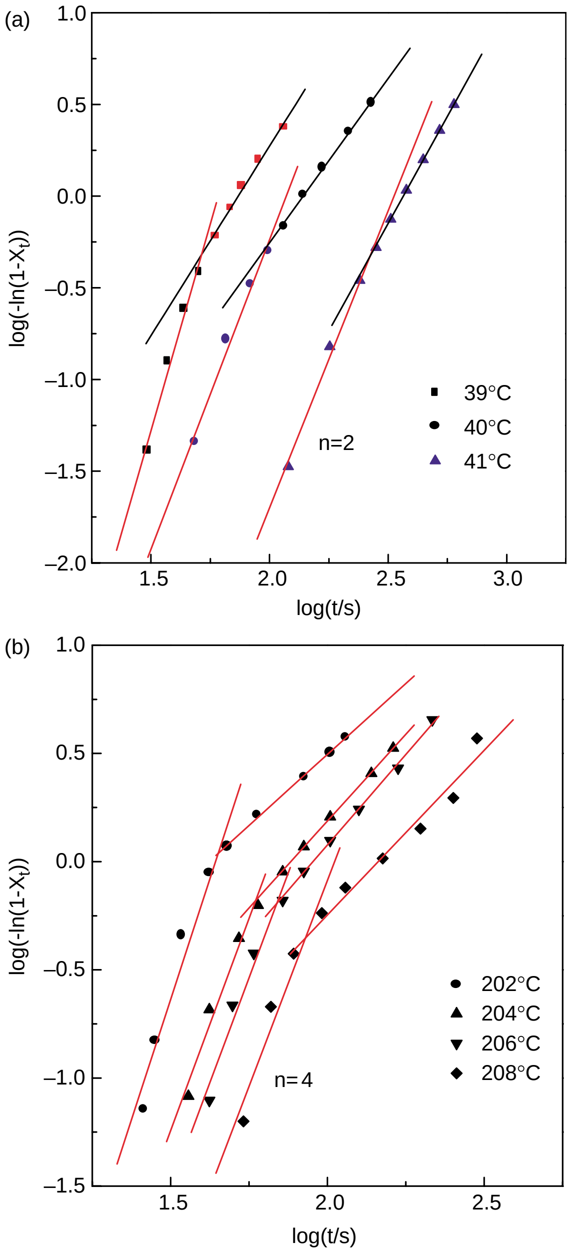


Fig. 2. Avrami plot of $\log[-\ln(1-X_t)]$ versus $\log(t/s)$ of PEO-blocks (a) and PET-blocks (b) in PET30–PEO6 segmented copolymer crystallizing at different temperatures.

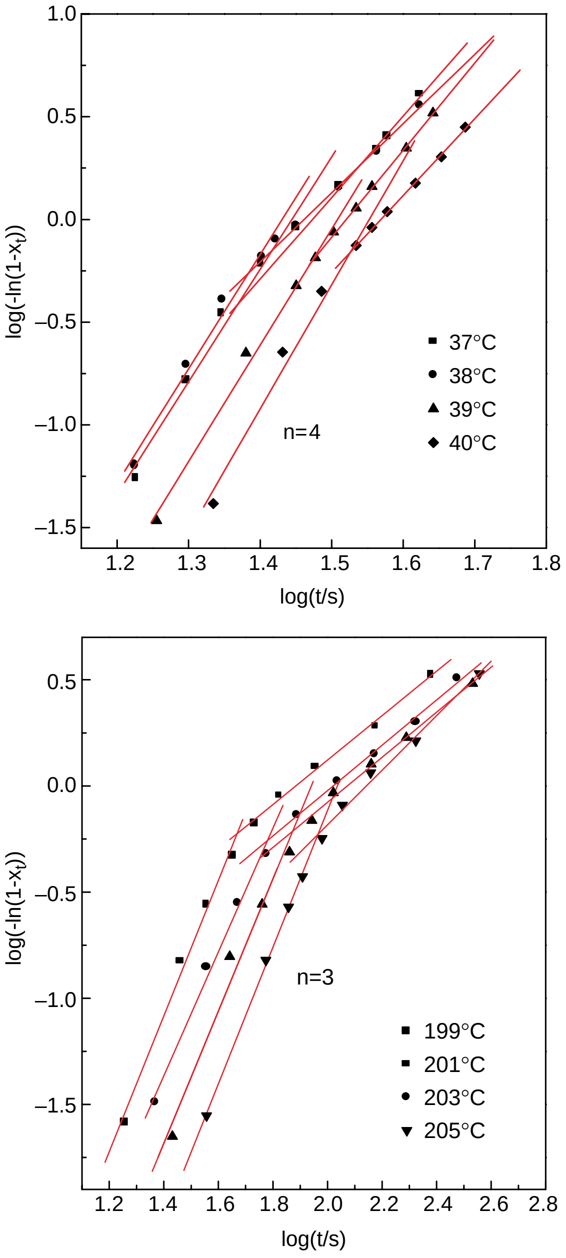


Fig. 3. Avrami plot of $\log[-\ln(1-X_t)]$ versus $\log(t/s)$ of PEO homopolymer (a) and PET homopolymer (b) crystallizing at different temperatures.

homopolymer may be attributed to the different phase states of the system existing when PEO begins to crystallize. For PET30–PEO6 segmented copolymer, crystallization of PEO-blocks takes place at temperatures well below the crystallization temperature of PET-blocks. This means that the two polymers crystallize in well-separated temperature regimes. When the copolymer was quenched from higher temperature to the predetermined crystallization temperature, PEO-blocks were mainly incorporated between the PET crystalline phases, and PEO-blocks started to crystallize after the completion of crystallization of the PET-blocks. Hence, the crystallization of PEO-blocks is physically constrained by the microstructure of the PET crystalline phase, i.e. the PET-blocks will always be partially solidified when PEO-blocks starts to crystallize. As a result, the system has been in a semicrystalline-amorphous state when PEO-blocks begin to crystallize. However, crystallization of PEO homopolymer always occurs in a homogeneous state, which results in a complete spherulitic structure shown in Fig. 4(d). In comparison, the growth dimension of PET has not been influenced by copolymerization; only the type of nucleation changed.

In addition, the different crystallization morphologies between the copolymers and the homopolymers may be attributed to the effects of the PET composition and the PEO length in copolymers [21]. As indicated earlier, the crystallized PET in the copolymer may confine the crystallization growth of PEO since the crystallization temperature of PET is much higher that that of

Table 2
Crystallization kinetics parameters of PEO-blocks of PET30–PEO6 segmented copolymer and PEO homopolymer

T_c (°C)	PET30–PEO6			PEO-6000		
	$t_{1/2}$ (min)	n	$-\log k$	$t_{1/2}$ (min)	n	$-\log k$
37	–	–	–	0.43	4.47	7.90
38	0.71	–	–	0.45	3.56	7.95
39	1.31	1.88	3.22	0.51	3.66	8.57
40	1.33	2.07	4.26	0.54	4.04	9.38
41	3.85	2.39	5.34	–	–	–

Table 3
Crystallization kinetics parameters of PET-blocks of PET30–PEO6 segmented copolymer

T_c (°C)	PET30–PEO6			T_c (°C)	PET homopolymer		
	$t_{1/2}$ (min)	n	$-\log k$		$t_{1/2}$ (min)	n	$-\log k$
202	0.65	4.45	7.31	199	0.92	3.19	5.55
204	1.06	3.92	7.12	201	1.01	2.91	5.44
206	1.23	3.88	7.32	203	1.27	3.11	6.04
208	1.81	3.81	7.70	205	1.70	3.22	6.56

PEO (Tables 2 and 3). It is therefore speculated that the larger the composition of PET, the more effective is the confinement. Moreover, such a confinement in the PEO growth in the copolymer may depend strongly on the length of the PEO blocks (i.e. the molecular weight of the PEO blocks), which is related to the compositional heterogeneity that can stimulate heterogeneous or non-spherulitic growth of crystallization [2]. In other words, the smaller the composition of PET in the copolymer and the shorter the PEO, the less obvious lamellar (i.e. smaller n value) or the more visible spherulitic (i.e. larger n value) the morphology. To verify the above speculation, the observations of crystallization morphology have been extended to various samples with different compositions of PET and lengths of PEO in segmented copolymers. As shown in Figs. 5 and 6, the small composition of PET and short PEO blocks do lead to a near-spherulitic morphology, which experimentally supports the above speculation. Here it should be indicated that the above conclusion may not be adequate because it is based only on the TEM observations. Detailed data on crystallization kinetics, in particular, further studies on the effect of the composition of PET, are required to provide more convictable evidence. At present, theoretical and experimental work focused on the crystallization kinetic analysis for PET10–PEO6, PET20–PEO6, and PET30–PEO6 is on the way and will be submitted for publication shortly.

In order to further understand the different crystallization behavior of the copolymer and the homopolymers, the crystallization kinetics of PET30–PEO6 segmented copolymer, and the PEO and PET homopolymers are investigated. The overall crystallization rates for the homopolymers and the copolymer are evaluated by the half-crystallization time ($t_{1/2}$), at which 50 wt% of crystallinity is reached during an isothermal crystallization. Fig. 7 shows the relationship between the $1/t_{1/2}$ and crystallization temperature (T_c) for the PEO-blocks in the copolymer and the PEO homopolymer (Fig. 7(a)) and the PET-blocks in the copolymer and the PET homopolymer (Fig. 7(b)). From Fig. 7, the crystallization rate for PEO in the copolymer is much slower than that for the PEO homopolymer, while the crystallization rate for PET in the copolymer is much faster than that for the PET homopolymer at the same T_c. As mentioned earlier, structures and properties of copolymers are extremely complex compared with those of hompolymers. In particular, the crystallization behavior of copolymers depends on various physical and/or thermodynamic parameters [25]. Such a complicated dependence of the crystallization behavior on multiple factors makes it considerably difficult to understand the physical mechanisms responsible for crystallization kinetics of copolymers, such as crystallization rate. For example, it is found that the hardness and glass transition temperature (T_g) of the amorphous blocks may result in slow crystallization kinetics for the PEO blocks in polystyrene-*b*-PEO/polystyrene (PS-*b*-PEO/PS) blends [26]. However, it is not certain whether the mobility of the chains at the junction points between the two blocks can also affect the crystallization kinetics [17]. As suggested by Zhu et al. [26], phase morphology and/or Avrami exponent n-values play a crucial role in determining the crystallization rate. Based on the present TEM observations and the Avrami exponent calculations, here we try to give a simple interpretation for the different crystallization rates between the investigated copolymer and homopolymers. In the case of PEO, it is clear that the remarkable decrease on crystallization rate of PEO-blocks in its copolymer is because the PET phase is always partially solidified at temperatures where crystallization of PEO-blocks occurs. It was mentioned earlier that the bulk crystallization of PEO-blocks proceeds with homogeneous nucleation. In the copolymer, however, the solid PET phase provides a foreign surface where heterogeneous nucleation can take place, indicating a much higher nucleation rate for PEO. Such an increase in nucleation rate was indeed observed by TEM (Fig. 4). Furthermore, the addition of PET will result in not only an increase of nucleation rate but also a decrease of the linear growth rate of PEO crystals due to the dilution effect which reduces the number of crystallization units at the crystal growth front. Thus, the decrease of the overall crystallization

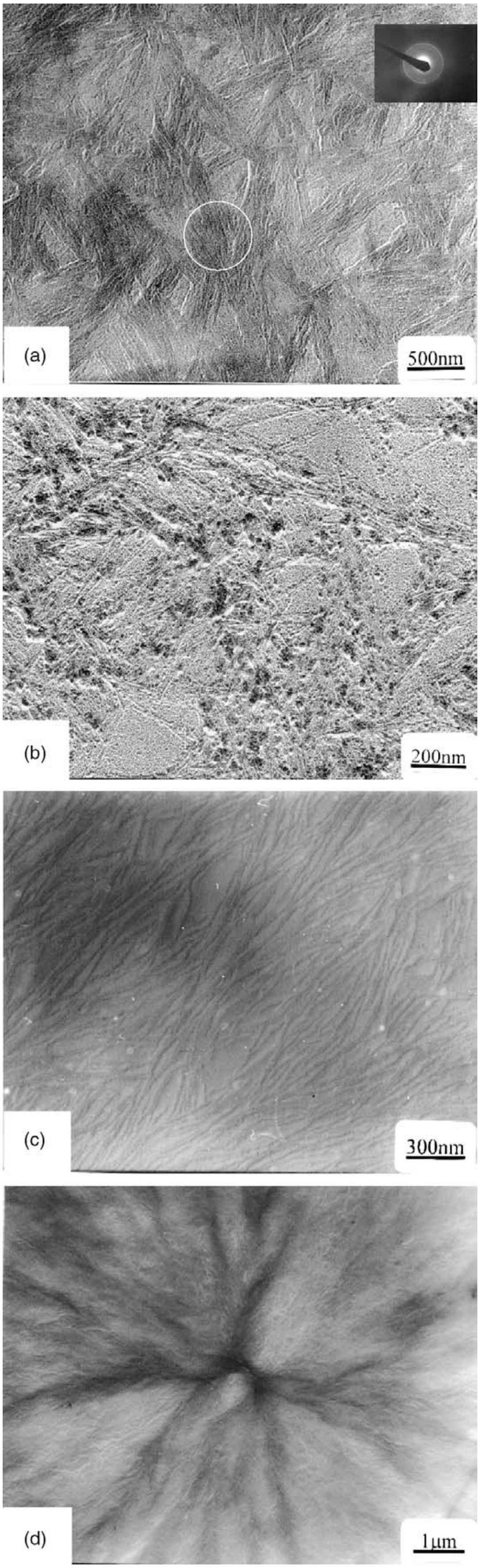


Fig. 4. TEM images of PET30–PEO6 segmented copolymer with the

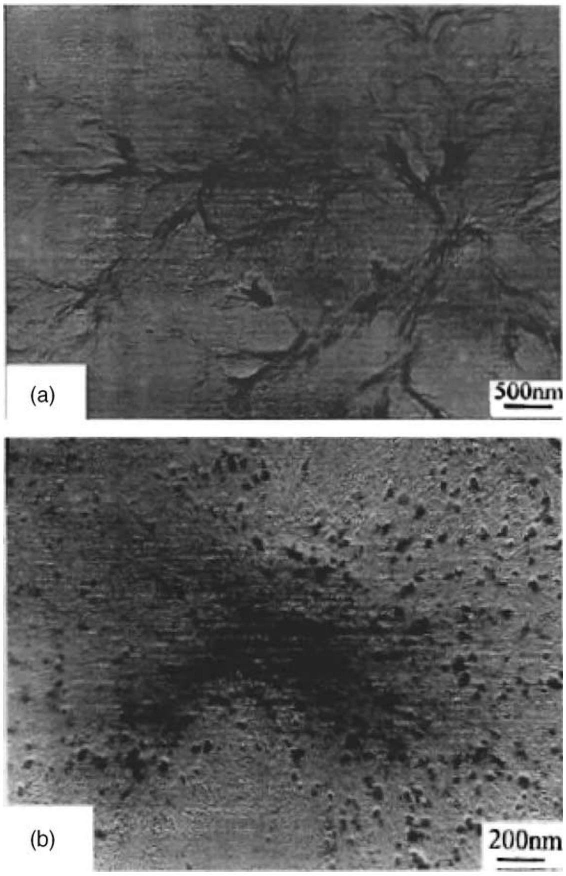


Fig. 5. TEM images of the PET20–PEO6 segmented copolymer (a); after stained by OsO_4 (b).

rate of PEO-blocks most likely arises from the combined effects of enhanced nucleation and lowered crystal growth rates. On the other hand, the decrease in the n value from 4 to 2 for PEO-blocks in its copolymer indicate a decease in the crystal growth dimension, which is also due to the effect of solidified PET phase, i.e. hard confinement environment during PEO-blocks crystallization. In this case, the PEO-block crystals are exclusively constrained inside the domain surrounded by crystallized PET matrix.

In the case of PET, the lower T_g blocks increase the mobility of PET-blocks in the copolymer, i.e. the crystallizability of the PET-blocks in the copolymer is larger than that of the pure PET homopolymer due to the lower T_g of the soft blocks and hence an increased mobility of the PET in the copolymer. The faster crystallization of PET-blocks in the copolymer, as shown in Fig. 7(b), may be attributed to the high mobility of PET-blocks in the copolymer.

Finally, it should be pointed out that the copolymer and the hompolymers used in the present study have different molecular weights. The molecular weight of blocks can play an important role in the crystallization kinetics of the copolymer. This has been well demonstrated in term of block length in detail in our previous work [21]. For example,

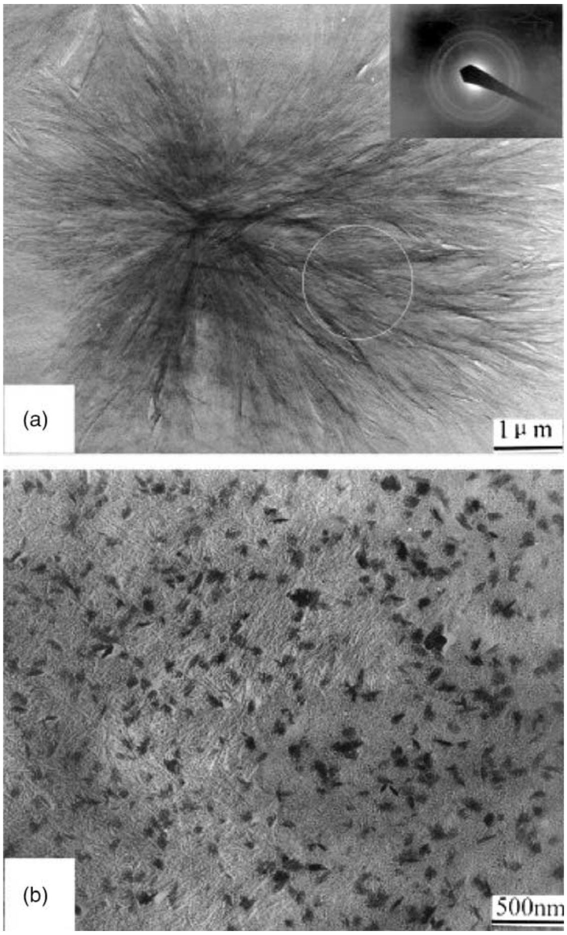


Fig. 6. TEM images of the PET30–PEO4 segmented copolymer with the corresponding selected electron diffraction patterns (a); after stained by OsO_4 (b).

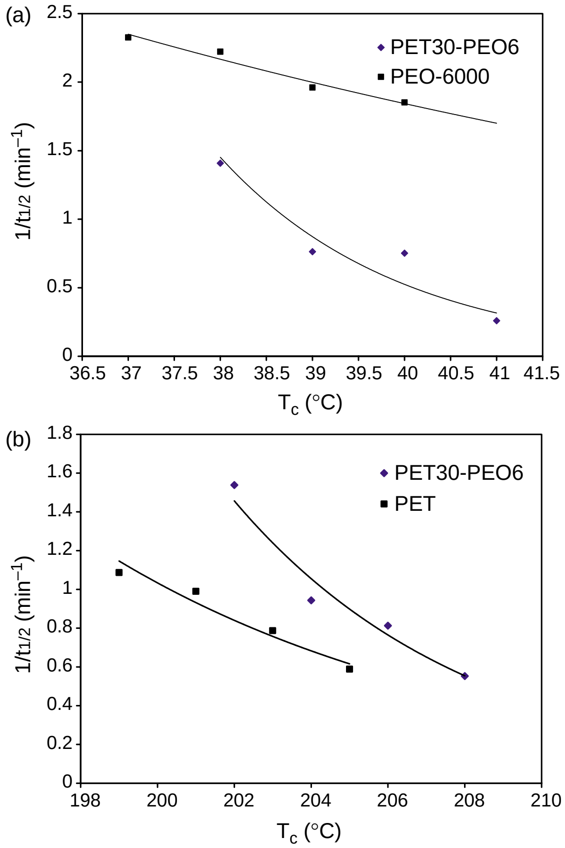


Fig. 7. Variations in crystallization rate with respect to crystallization temperature. (a) PEO-blocks in PET30–PEO6 and the PEO homopolymer; (b) PET-blocks in PET30-PEO6 segmented copolymer and the PET homopolymer.

the longer the block length, the higher the required crystallization temperature and the smaller the $t_{1/2}$. Therefore, from a physical point of view, it is not sufficiently significant to compare the quantitative results, in particular, the crystallization rates, of the copolymer with those of the homopolymers. One strategy to remedy this deficit and to reveal the essential difference in crystallization kinetics between copolymers and hompolymers is to employ diblock copolymers that can be well defined, as demonstrated by Zhu et al. in their recent studies [26]. Nevertheless, as demonstrated in the present study, even if using the results of homopolymers as qualitative references, we could reveal the essential crystallization behavior of the copolymer, which is considerably different from that of the homopolymers. Furthermore, as mentioned in the introduction section, one of the most important reasons to study the segmented copolymers is because their molecular design may be tailored to a specific application by controlling the number of blocks (i.e. diblock, triblock, or multiblock) and their crystallization kinetics, as well as the block length and composition of the respective blocks. As fundamental data, the present results could be helpful for the development of new copolymers with unique properties or the modification of homopolymers with special properties. For example, it is considerably difficult and complicated to synthesize a pure and well-crystallized copolymer. In particular, the synthesis of block copolymers with high molecular weight has been inefficient in terms of time. Toward this aim of improving efficiency, the present study could provide an approach to improve the synthesis time of copolymers. This can be realized by manipulating crystallization rate (e.g. adjusting composition and length of blocks), since the crystallization rate of PET-blocks in the copolymer becomes fast, whereas that of PEO-blocks in the copolymer becomes slow.

4. Conclusion

We have studied the isothermal crystallization kinetics and morphology of PET–PEO segmented copolymer, and PET, PEO homopolymer as well. The nucleation mechanism and growth dimension of PEO in the copolymer are different from that in the homopolymers, which is attributed to the different phase states of the system existing when PEO-blocks begins to crystallize. At the same T_c, the crystallization rate of PEO-blocks in copolymer is slower than that of PEO homopolymer, because the PET phase of the copolymer is always partially solidified at the temperatures where PEO-blocks crystallization takes places. The isothermal crystallization rate of PET-blocks in the copolymer is faster than that of the pure PET homopolymer due to the lower glass transition temperature of the soft blocks, which increases the mobility of the PET-blocks in the copolymer.

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References

[1] Hong S, Yang LZ, MacKnight WJ, Gido SP. Macromolecules 2001;34:7009.
[2] Balsamo V, de Navarro CU, Gil G. Macromolecules 2003;36:4507.
[3] Zhu L, Huang P, Chen WY, Ge Q, Quirk RP, Chen SZD, et al. Macromolecules 2002;35:3553.
[4] Zhu L, Cheng SZD, Huang P, Ge Q, Quirk RP, Thoma SEL, et al. Adv Mater 2002;14:31.
[5] Zhu L, Huang P, Cheng SZD, Ge Q, Quirk RP, Thoma SEL, et al. Phys Rev Lett 2001;86:6030.
[6] Fischer H. Polymer 1994;35:3786.
[7] Lotz B, Kovacs A, Bassett GA, Keller A, Kolloid ZZ. Polymer 1966;209:115.
[8] (a) Gervais M, Gallot B. Makromol Chem 1973;171:157.
(b) Gervais M, Gallot B. Makromol Chem 1973;174:193.
(c) Gervais M, Gallot B. Makromol Chem 1977;178:1577.
(d) Gervais M, Gallot B. Makromol Chem 1977;178:2071.
(e) Gervais M, Gallot B. Makromol Chem 1979;180:2041.
[9] Gervais M, Gallot B. Polymer 1981;22:1124.
[10] Nojima S, Kato K, Yamamoto S, Ashida T. Macromolecules 1992;25:2237.
[11] Richardson PH, Richards RW, Blundell DJ, MacDonald WA, Mills P. Polymer 1995;36:3059.
[12] Perret R, Skoulious A. Makromol Chem 1972;162:147.
[13] Perret R, Skoulious A. Makromol Chem 1972;162:163.
[14] Sun L, Liu YX, Zhu L, Hsiao BS, Avila-Orta CA. Polymer 2004;45:8181.
[15] Shiomi T, Imai K, Takenaka K. Polymer 2001;42:3233.
[16] Sun JR, Hong ZK, Yang LX, Tang ZH, Chen XS, Jing XB. Polymer 2004;45:5969.
[17] Sun L, Zhu L, Ge Q, Quirk RP, Xue CC, Cheng SZD. Polymer 2004;45:2931.
[18] Wang MT, Zhang LD, Ma DZ. Eur Polym J 1999;35:1335.
[19] Coleman D. J Polym Sci 1954;14:15.
[20] Luo XL, Zhang XY, Ma DZ. J Appl Polym Sci 1998;34:1.
[21] Kong XH, Tan SS, Yang XN, Li G, Zhou EL, Ma DZ. J Polym Sci, Part B: Polym Phys 2000;38:3230.
[22] Luo XL, Zhang XY, Wang MT, Ma DZ. Chem J Chin Uni 1997;18:642.
[23] Zhang ZP, Luo XL, Lu YC, Ma DZ. Eur Polym J 2001;37:99.
[24] Wang B, Zhang M, Zhang JM, He CQ, Dai YQ, Wang SJ, et al. Phys Lett A 1999;262:195.
[25] Hong S, Yang LZ, MacKnight WJ, Gido SP. Macromolecules 2001;34:7009.
[26] Zhu L, Mimnaugh BR, Ge Q, Quirk RP, Cheng SZD, Thomas EL, et al. Polymer 2001;42:9121.