

Poly(ϵ -caprolactone)/Poly(ethylene oxide) Diblock Copolymer II. Nonisothermal Crystallization and Melting Behavior

ZHIHUA GAN,¹ JIE ZHANG,² BINGZHENG JIANG¹

¹Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Academia Sinica, Changchun 130022 People's Republic of China

²College of Sciences, Jilin University of Technology, Changchun 130025, People's Republic of China

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ABSTRACT: The nonisothermal crystallization behavior and melting process of the poly(ϵ -caprolactone) (PCL)/poly(ethylene oxide) (PEO) diblock copolymer in which the weight fraction of the PCL block is 0.80 has been studied by using differential scanning calorimetry (DSC). Only the PCL block is crystallizable, the PEO block with 0.20 weight fraction cannot crystallize. The kinetics of the PCL/PEO diblock copolymer under nonisothermal crystallization conditions has been analyzed by Ozawa's equation. The experimental data shows no agreement with Ozawa's theoretical predictions in the whole crystallization process, especially in the later stage. A parameter, kinetic crystallinity, is used to characterize the crystallizability of the PCL/PEO diblock copolymer. The amorphous and microphase separating PEO block has a great influence on the crystallization of the PCL block. It bonds chemically with the PCL block, reduces crystallization entropy, and provides nucleating sites for the PCL block crystallization. The existence of the PEO block leads to the occurrence of the two melting peaks of the PCL/PEO diblock copolymer during melting process after nonisothermal crystallization. The comparison of nonisothermal crystallization of the PCL/PEO diblock copolymer, PCL/PEO blend, and PCL and PEO homopolymers has been made. It showed a lower crystallinity of the PCL/PEO diblock copolymer than that of others and a faster crystallization rate of the PCL/PEO diblock copolymer than that of the PCL homopolymer, but a slower crystallization rate than that of the PCL/PEO blend. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **63**: 1793-1804, 1997

Key words: nonisothermal crystallization; poly(ϵ -caprolactone); poly(ethylene oxide); PCL/PEO diblock copolymer; crystallinity; crystallization kinetics

INTRODUCTION

Investigations of the kinetics of polymer crystallization are significant both theoretically

and practically. Most frequently, the investigations are conducted under isothermal conditions because of the convenient treatment in the aspect of theory. Many theories have been advanced to describe the isothermal crystallization process such as Avrami's equation¹⁻³ and Turnbull-Fisher's equation.⁴ For practical purposes, polymer crystallinity has a great in-

Correspondence to: Z. Gan.

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fluence on the physical and chemical properties of polymeric material. In practice, production and processing of the polymer are often carried out under nonisothermal conditions, typically the case of the melt-spinning of fibers. Therefore, the investigation of the kinetics of polymer crystallization under nonisothermal conditions is of great significance for the technological optimization and manufacture of high-performance polymeric materials. Some quantitative evaluations of the kinetics of nonisothermal crystallization have been reported.⁵⁻¹¹ However, because of the complication of the nonisothermal crystallization process, the different angle of consideration of the investigators and the different method of mathematical treatment, the applications of their theories are limited. From an experimental point of view, the technique of differential scanning calorimetry (DSC) is a frequently used method to study the nonisothermal crystallization process of polymer. By using DSC, crystallization temperature and enthalpy can be measured conveniently and quickly, and they are related to cooling rate.

The block copolymer with crystallizing blocks has attracted high interest of scientists. However, less work has been reported on the crystallization kinetics of block copolymer, especially the block copolymer with all crystallizing blocks. In a previous article,¹² we have studied the isothermal crystallization behavior and melting process of the poly(ϵ -caprolactone) (PCL)/poly(ethylene oxide) (PEO) diblock copolymer in which corresponding homopolymers of the blocks are crystallizable polymers. The research results of wide-angle x-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) experiments have shown that only the PCL block with 0.80 weight fraction is crystallizable. The PEO block with 0.20 weight fraction cannot crystallize, although its corresponding homopolymer has strong crystallizability. It is shown that the PEO block has a great influence on the crystallization of the PCL block, especially its nucleation; and the extent of this influence depends on the crystallization conditions, particularly temperature.

In this study, we have used DSC to study the nonisothermal crystallization behavior and melting process of the poly(ϵ -caprolactone) (PCL)/poly(ethylene oxide) (PEO) diblock copolymer in which the PCL weight fraction is 0.80. The mutual influence of PEO and PCL blocks has been elucidated, and the crystallization behavior of the

PCL/PEO diblock copolymer, the PCL/PEO blend, and the PCL and the PEO homopolymers have been studied and compared.

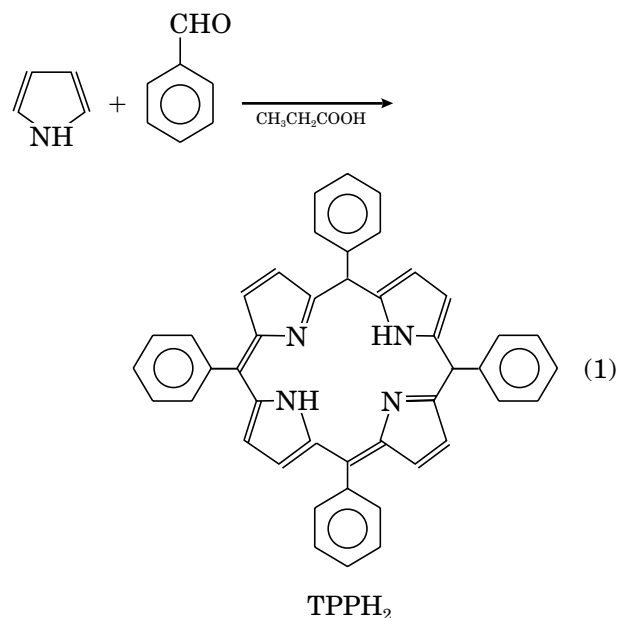
EXPERIMENTAL

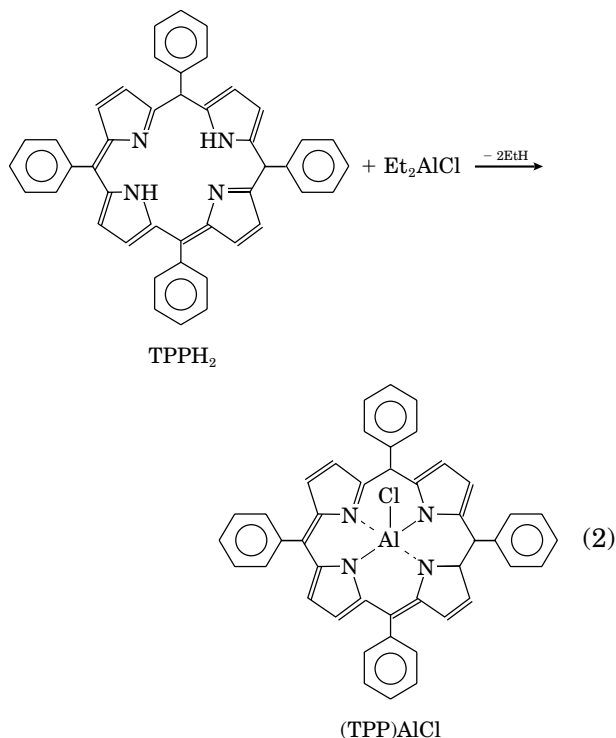
Materials

ϵ -Caprolactone (CL) (Aldrich) was dried with calcium hydride CaH_2 over two days and then distilled at reduced pressure under protection of nitrogen atmosphere. Ethylene oxide (EO) was also dried with CaH_2 , then distilled over the mixture of CaH_2 and potassium hydroxide KOH in a nitrogen atmosphere, and finally collected in an ampoule cooled with liquid nitrogen. 5,10,15,20-tetraphenylporphine (TPPH₂) was prepared via the reaction of pyrrole and benzaldehyde in propionic acid.¹³ Dichloromethane CH_2Cl_2 was washed with concentrated sulfuric acid, neutralized with an aqueous solution of sodium bicarbonate, dried over calcium chloride CaCl_2 , and then distilled over CaH_2 in a nitrogen atmosphere. Diethylaluminum chloride Et_2AlCl (Fluka) was used without further purification.

Preparation of Catalyst

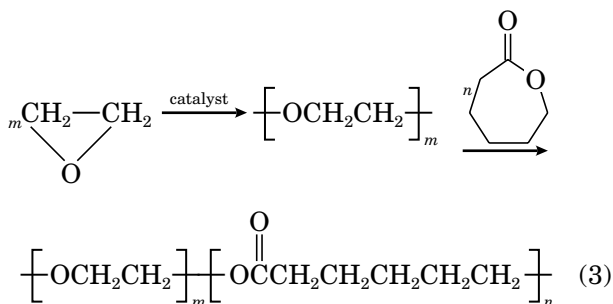
(5,10,15,20-tetraphenylporphinato) aluminum chloride (TPP) AlCl was used as catalyst. It was prepared by the reaction of Et_2AlCl with TPPH₂ in the solution of CH_2Cl_2 , as described by Aida and Inoue¹⁴:





Polymerization

The PCL/PEO diblock copolymer was synthesized in a flask under the protection of nitrogen atmosphere by sequential ring-opening polymerization.¹⁵ The prepolymer of ethylene oxide was prepared first. When copolymerization reaction was completed, the residual catalyst and homopolymers were removed; in the end, the pure PCL/PEO diblock copolymer was a white or light yellow powder.



Characterization of the PCL/PEO Diblock Copolymer

The structure, molecular weight, and distribution of the PCL/PEO diblock copolymer were determined by nuclear magnetic resonance (NMR) spectra and gel permeation chromatography

(GPC). The analysis results were as follows. The PEO block has a number-average molar mass, $M_n = 7900$; the dispersion of molar mass $M_w/M_n = 1.36$; the PCL/PEO diblock copolymer has an $M_n = 17,000$; $M_w/M_n = 1.65$. The weight fraction of the PCL block in the PCL/PEO diblock copolymer is 0.80; that of the PEO block is 0.20.

Preparation of the PCL/PEO Blend, and PCL and PEO Homopolymers

PEO was the prepolymer of the PCL/PEO diblock copolymer, with $M_n = 7900$ and $M_w/M_n = 1.36$. PCL was purchased from PolyScience Company, and its M_n and M_w/M_n were 50,600 and 2.0, respectively. The sample of the PCL/PEO blend, in which the PEO weight fraction is 0.20, the same as that of the PEO block in the PCL/PEO diblock copolymer, was prepared by solution casting from dichloromethane at room temperature. The residual solvent was removed under vacuum.

DSC Measurements

The nonisothermal crystallization behavior and melting process of the sample were analyzed by DSC (Perkin-Elmer DSC-7).

The nonisothermal crystallization process was studied according to the following procedure. The samples (ca. 10 mg) were heated to 80°C at rate of 10°C/min (ca. 20°C above the melting temperature of PEO and PCL homopolymers) for 5 min. The samples were then crystallized at different cooling rates (from 2 to 80°C/min), and the heat flow during crystallization was recorded. The relative crystallinity X_T as a function of temperature T is calculated according to the following equation:

$$X_T = \frac{\int_{T_o}^T H(T) dT}{\int_{T_o}^{T_\infty} H(T) dT} \quad (4)$$

where T_o and T_∞ are the temperature at which crystallization starts and ends, respectively. After nonisothermal crystallization, the polymer samples were heated at a rate of 5°C/min to the molten state (80°C). The position and the area of the melting peaks were recorded from each run. The absolute crystallinity is calculated from the fusion heats of the sample and the sample with perfect crystal. The fusion heats of the perfect crystals

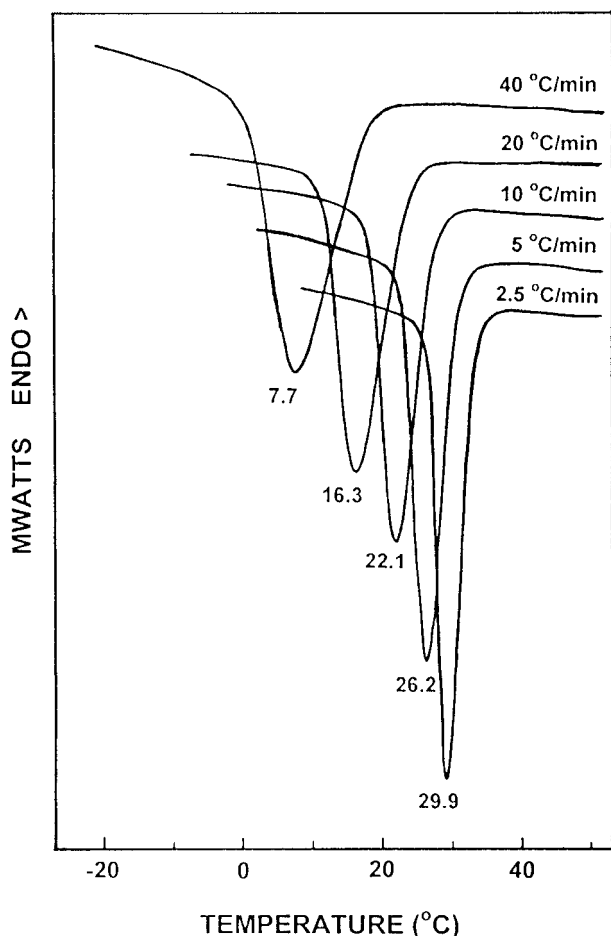


Figure 1 DSC crystallization curves of the PCL/PEO diblock copolymer cooling from molten state (80°C) at different rates.

of the PCL/PEO diblock copolymer (0.20 weight fraction of the PEO block), the PCL/PEO blend (0.20 weight fraction of the PEO component), and the PCL and PEO are 150.4, 153.0, 142, and 197 J/g, respectively.¹⁵

RESULTS AND DISCUSSION

Nonisothermal Crystallization of the PCL/PEO Diblock Copolymer

Although PCL and PEO homopolymers have a strong tendency to crystallize, when the PCL/PEO diblock copolymer with 0.20 weight fraction of the PEO block crystallizes, either under isothermal or nonisothermal conditions, only the PCL block can crystallize; the PEO block cannot crystallize.¹⁵

The results of the nonisothermal crystallization behavior of the PCL/PEO diblock copolymer are shown in Figure 1. The exothermic peak wid-

Table I Characteristic Parameters of the PCL/PEO Diblock Copolymer During Nonisothermal Crystallization Process

Cooling Rate (°C/min)	T_{\max} (°C)	t_{\max} (min)	X_{\max} (%)
80	-25.4	0.32	56.3
40	7.8	0.38	56.0
20	16.4	0.65	56.4
10	22.2	0.99	56.1
5	26.3	2.13	57.6
2.5	29.3	3.46	55.8

ens and shifts to lower temperature region as the cooling rate increases. Table I presents a summary of the temperature T_{\max} , relative crystallinity X_{\max} at the maximum crystallization rate, and the time t_{\max} to reach this rate at different cooling rates.

If the reciprocal value of t_{\max} , $1/t_{\max}$, is used to describe the nonisothermal crystallization rate of the PCL/PEO diblock copolymer, it is found that with the increase of cooling rate, the crystallization rate increases fast but slow after 40°C/min of the cooling rate (Fig. 2).

Kinetic Analysis of Nonisothermal Crystallization of the PCL/PEO Diblock Copolymer

Integration of the exothermic peaks during the nonisothermal crystallization process of the PCL/PEO diblock copolymer could give the relative crystallinity X_T as a function of temperature.

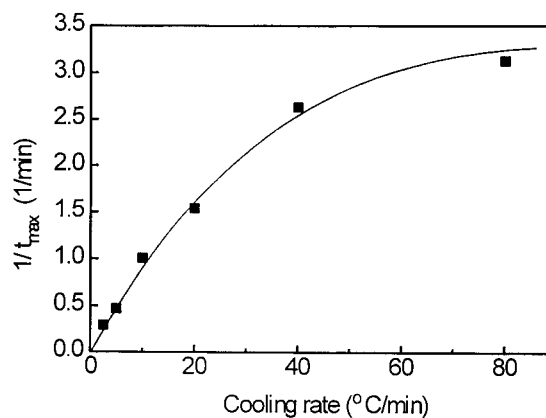


Figure 2 Crystallization rates of the PCL/PEO diblock copolymer at different cooling rates.

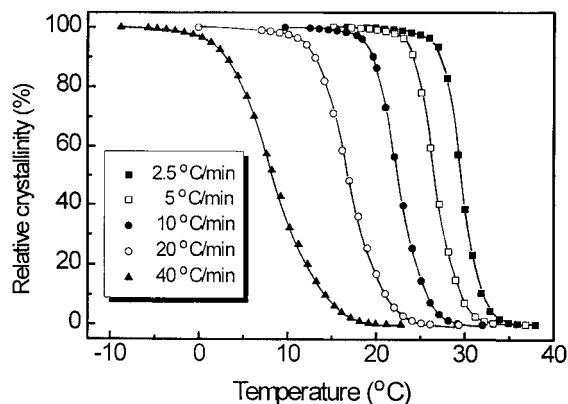


Figure 3 Relative crystallinity versus temperature of the PCL/PEO diblock copolymer during nonisothermal crystallization process at different cooling rates.

These results are shown in Figure 3. The development of relative crystallinity with temperature gives an S-shape curve, and it shows a slower process during the later crystallization stage.

Kinetics of nonisothermal crystallization of polymers are generally analyzed using Ozawa's equation.⁵ The equation is a modification of the Avrami's equation which considers the effect of cooling rate on crystallization from the melt and replaces the crystallization time under isothermal conditions with cooling rate R , as follows:

$$X_T = 1 - e^{-\Phi(T)/R^n} \quad (5)$$

where R is cooling rate, X_T is relative crystallinity at temperature T , and $\Phi(T)$ is called the cooling function of the process.

The following equation can also be obtained derived from eq. (5):

$$\begin{aligned} \text{Log}[-\text{Ln}(1 - X_T)] \\ = \text{Log}[\Phi(T)] - n \text{Log} R \quad (6) \end{aligned}$$

According to the Ozawa analysis, if the relative crystallinities at different cooling rates at a given temperature are chosen, the plot of $\text{Log}[-\text{Ln}(1 - X_T)]$ versus $\text{Log} R$ should give a series of parallel lines. The experimental data of some homopolymers and oligoethyleneterephthalate/oligoxyethylene block copolymers¹⁶ show good agreement with Ozawa's theoretical predictions. However, for some polymer systems, such as poly(ether-ether-ketone) (PEEK)¹⁷ and poly(ethylene oxide)/poly(methyl methacrylate) blends,¹⁸ their nonisothermal crystallization do not follow Oza-

wa's equation. These show that not all the polymer crystallization under nonisothermal conditions could be described by using Ozawa's equation.

In the present paper, the nonisothermal crystallization of the PCL/PEO diblock copolymer were also studied by using Ozawa's theory. The results are shown in Figure 4. In the first stage (ca. $X_T < 85\%$, $\text{Log}[-\text{Ln}(1 - X_T)] < 0.25$), a series parallel lines are observed by using the Ozawa's equation to analyze the nonisothermal crystallization process of the PCL/PEO diblock copolymer. However, in the later stage (ca. $X_T > 85\%$, $\text{Log}[-\text{Ln}(1 - X_T)] > 0.25$), the plot of $\text{Log}[-\text{Ln}(1 - X_T)]$ vs. $\text{Log} R$ gives a series of curves.

Generally, the crystallization of polymer consists of the following two processes: the primary crystallization, and secondary crystallization that followed. When he established his theory, Ozawa thought that the secondary crystallization occurred in the later period and the temperature went down in the cooling crystallization process. Because of the lower temperature and slower crystallization rate, the secondary crystallization could be neglected.

Although it takes place in the later stage, the secondary crystallization is influenced greatly by the outside factors such as the cooling rate, and the effect could not be neglected for the nonisothermal crystallization of some polymer systems.

As mentioned previously,¹² when the PCL/PEO diblock copolymer crystallized under isothermal conditions, only the PCL block with 0.80 weight fraction could crystallize. The amorphous

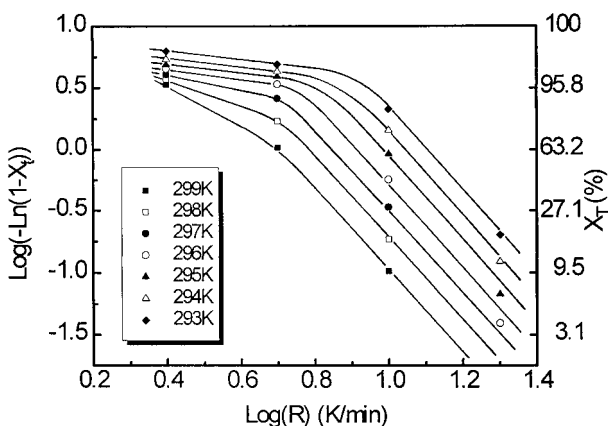


Figure 4 Plot of $\text{Log}[-\text{Ln}(1 - X_T)]$ versus $\text{Log} R$ for the cooling crystallization of the PCL/PEO diblock copolymer.

Table II Relative Crystallinity of the PCL/PEO Diblock Copolymer During Nonisothermal Crystallization Process at Different Temperatures and Cooling Rates

Temperature (K)	Cooling Rate (K/min)			
	2.5	5.0	10	20
296	0.989	0.967	0.435	0.039
295	0.992	0.980	0.603	0.065
294	0.995	0.986	0.763	0.116
293	0.998	0.993	0.883	0.183

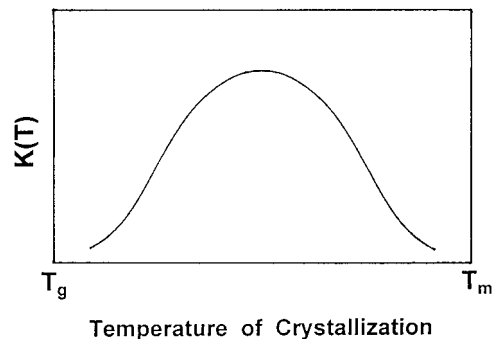
PEO block had a great influence on the crystallization of the PCL block, so is it in nonisothermal crystallization for the PCL/PEO diblock copolymer. At different cooling rates, the PEO block also has a great influence on the PCL block crystallization (it will be discussed later) even in the second crystallization period. The curves of $\text{Log}[-\text{Ln}(1 - X_T)]$ versus $\text{Log } R$ in the later crystallization process are the reflection of this effect.

The range of the temperature of nonisothermal crystallization is different at different cooling rates. From Table II it is found that when the cooling rates are 2.5 and 5 K/min and the temperature is 296 K, the relative crystallinities selected are 98.9 and 96.7%, respectively, all in the second stage of crystallization. However, when the cooling rates are 10 and 20 K/min, the selected relative crystallinities are 43.5 and 3.9%, respectively; they are in the first stage. Because the relative crystallinities selected at a fixed temperature are in the different stage of crystallization, and the secondary crystallization of later stage could not be neglected, Ozawa's analysis fails to describe the whole crystallization process of the PCL/PEO diblock copolymer. It is adequate, however, to describe the first stage (i.e., to approximately $X_T \approx 50\%$) for the current system.

Kinetic Crystallinity of the PCL/PEO Diblock Copolymer

In order to characterize the kinetics of nonisothermal crystallization of polymer, a new physical parameter was advanced by Ziabicki.⁷⁻⁹ He first assumed that the crystallization could be described by the following first equation:

$$\frac{dX_t}{dt} = (1 - X_t)K(T) \quad (7)$$

**Figure 5** The schematic temperature dependence of crystallization rate constant $K(T)$.

where X_t is the relative crystallinity at time t , and $K(T)$ is the rate constant and dependent only on temperature.

Because the crystallization temperature of polymer is in the range of temperatures between glass transition T_g and melting T_m , a corresponding value of $K(T)$ can be determined at a temperature T . (Fig. 5).

Based on Figure 5, a new concept of kinetic crystallinity was given by Ziabicki, as follows:

$$G = \int_{T_g}^{T_m} K(T)dT \quad (8)$$

From Figure 5 and eq. (8), it is found that the value of G characterizes the crystallizability in the entire temperature range ($T_g \sim T_m$) and it depends only on the polymer structure. Table III gives the kinetic crystallinities of some polymers.

According to Ziabicki's theory, Jeziorny derived a simple equation, as follows, to calculate the kinetic crystallinity by means of the data of nonisothermal crystallization¹⁹:

$$G = \int_{T_g}^{T_m} K(T)dT = \left(\frac{\pi}{\ln 2}\right)^{1/2} K_{\max} \frac{D}{2} \quad (9)$$

Table III Kinetic Crystallinities of Some Polymers

Polymer	Kinetic Crystallinity G
Rubber	0.003
Polypropylene (isotactic)	33
Poly(ethylene terephthalate)	1.0
Nylon-6	6.4
Nylon-6,6	133
Polystyrene (isotactic)	0.15

Table IV Kinetic Crystallinity of the PCL/PEO Diblock Copolymer Calculated from the Data of Nonisothermal Crystallization

Cooling Rate (K)	D (K)	X_{\max} (%)	dX_{\max}/dt (1/min)	G	G_c
2.5	4.4	55.8	0.485	5.19	2.07
5	5.1	57.6	0.852	10.87	2.17
10	5.8	56.1	1.535	21.40	2.14
20	7.3	56.4	2.424	42.86	2.14
40	9.6	56.0	3.585	83.56	2.09
80	18.9	56.3	4.032	185.66	2.32

where K_{\max} is the value of $K(T)$ at the maximum crystallization rate, and D is the half-width of the crystallization peak. Because of the effect of cooling rate R , G must be corrected properly, and its final form is as follows:

$$G_c = \frac{G}{R} \quad (10)$$

where G_c means the kinetic crystallinity at unit cooling rate.

By means of Ziabicki's theory and the Jeziorny method, we calculated the value of kinetic crystallinity of the PCL/PEO diblock copolymer from the data of nonisothermal crystallization. The results are shown in Table IV.

It is found that kinetic crystallinities are different when they are calculated from the data at different cooling rate; however, after eliminating the effect of cooling rate, the values of kinetic crystallinities are the same and about 2.1, related only with the intrinsic structure of the PCL/PEO diblock copolymer; the value also indicates the strong crystallizability of this particular PCL/PEO diblock copolymer.

Comparison of Nonisothermal Crystallization Process of the PCL/PEO Diblock Copolymer, PCL/PEO Blend, and PCL and PEO Homopolymers

If the crystallization rates of the PCL/PEO diblock copolymer, PCL/PEO blend, and PCL and PEO homopolymers under nonisothermal conditions are expressed by the reciprocal value of the time t_{\max} , which is the time to reach the maximum crystallization rate, the crystallization rates at different cooling rates are shown in Figure 6.

The crystallization rates of the PCL/PEO diblock copolymer and blend, in which the weight fractions of the PCL block and component are both 0.80, are faster than that of the PCL homopolymer but slower than that of PEO homopolymer.

It has been reported that the PEO in the PCL/PEO blend crystallizes difficultly when the weight fraction of PEO was 0.20.²⁰ The PEO block could not crystallize when its weight fraction is 0.20 in the PCL/PEO diblock copolymer. Thus, though not important for the PCL/PEO diblock copolymer or the blend, the PEO block or component plays a role of nucleus for crystallization and makes the crystallization rates of them faster than that of PCL homopolymer.

It is also found from Figure 6 that the crystallization rate of the PCL/PEO diblock copolymer is always slower than that of the blend. It is due to the chemical bond between the PCL and PEO blocks, so the movability of the PCL block chain is restricted. Meanwhile, such restriction does not exist in the PCL/PEO blend.

Crystallinities of the PCL/PEO Diblock Copolymer, PCL/PEO Blend, and PCL and PEO Homopolymers

The absolute crystallinities of the polymer samples were calculated from the fusion heats and that of the perfect crystals.

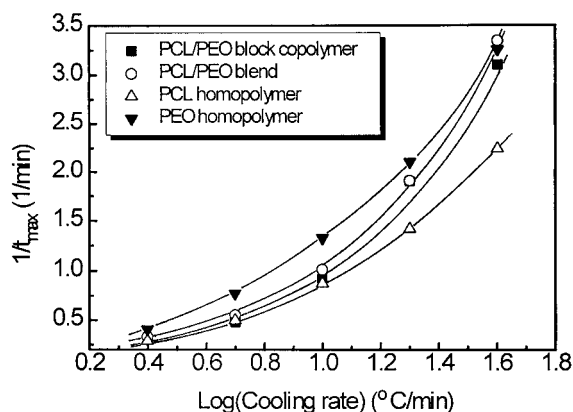


Figure 6 The relationship between crystallization rate and cooling rate during the nonisothermal crystallization process of the PCL/PEO diblock copolymer, PCL/PEO blend, and PCL and PEO homopolymers.

From Figure 7, we find that the crystallinity of the PEO homopolymer could reach ca. 83%; that of PCL homopolymer is lower, about 55%. The crystallinity of the PCL/PEO blend is lower than that of the PCL homopolymer, ca. 50%, due to the existence of the PEO component. For the PCL/PEO diblock copolymer, the amorphous PEO block bonds chemically with the crystalline PCL block, limits the motion of the PCL block chains, and makes it difficult to form crystalline structure with high regularity. Thus, the crystallinity of the PCL/PEO diblock copolymer is much lower than that of the PCL/PEO blend, approximately 35%.

Melting Behavior of the PCL/PEO Diblock Copolymer

After crystallizing from the molten state at 80°C at different cooling rates, the PCL/PEO diblock copolymer was heated again to the molten state at a rate of 5°C/min. The DSC melting curves are shown in Figure 8.

The outstanding characteristics during the melting process after nonisothermal crystallization are the two melting peaks. This phenomenon is the same as that after isothermal crystallization. The previous investigations¹² have shown that for the PCL/PEO diblock copolymer, only the PCL block with 0.80 weight fraction could crystallize; the PEO block with 0.20 weight fraction is amorphous. Thus, the double melting peak is the reflection of a complicated crystallization process for the PCL/PEO diblock copolymer and certainly related to the PEO block.

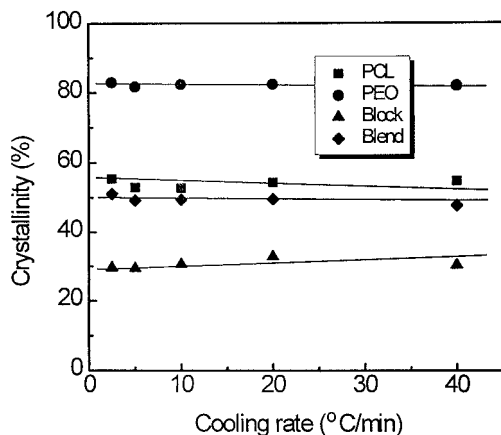


Figure 7 The crystallinities of the PCL/PEO diblock copolymer, PCL/PEO blend, and PCL and PEO homopolymers cooling from the molten state at different rates. Heating rate = 5°C/min.

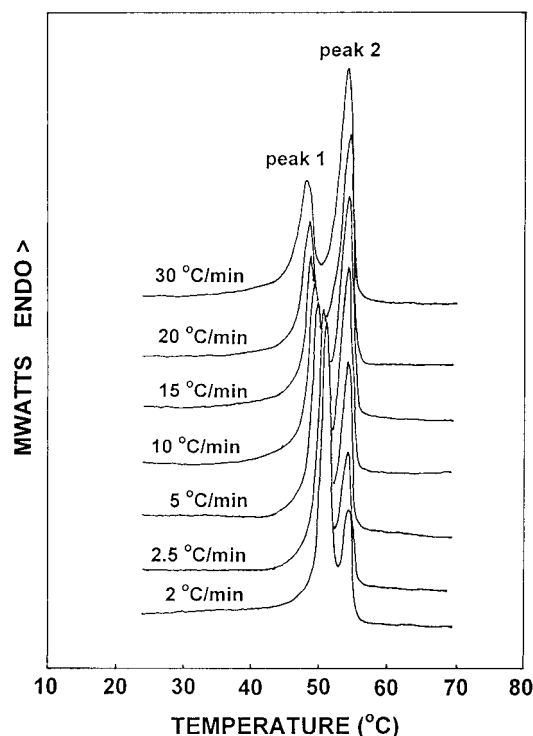


Figure 8 DSC melting curves of the PCL/PEO diblock copolymer crystallizes from the melt at different cooling rates. Heating rate = 5°C/min.

If the temperature T_0 at which the two melting peaks overlap is used as the boundary of the two peaks (Fig. 9), the percent areas of the two melting peaks could be calculated.

With the increase of cooling rate, the position of peak 2 with higher temperature does not change; however, the position of peak 1 with lower temperature shifts from higher temperature region to lower temperature region (see Figs. 8 and 10). The area of peak 1 increases linearly with the reciprocal value of cooling rate (see Fig. 11); however, the slope is different when the cooling rate is greater or smaller than 10°C/min, and it is this cooling rate of 10°C/min at which the area of peak 2 comes to exceed that of peak 1 with the reduce of cooling rate.

Origins of the Double Melting Peaks

The above investigation shows that the crystallization rate of the PCL/PEO diblock copolymer is faster than that of the PCL homopolymer, and this is because the amorphous PEO block acts as a nucleus during the crystallization of the PCL/PEO diblock copolymer.

The PEO block, of which the weight fraction is

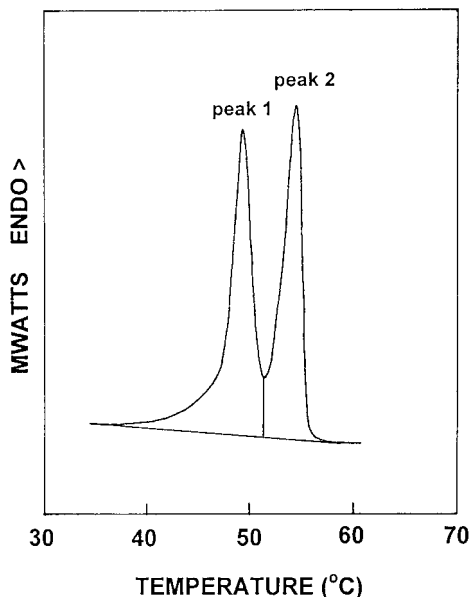


Figure 9 DSC melting curve of the PCL/PEO diblock copolymer crystallizes from the molten state at $10^{\circ}\text{C}/\text{min}$. Heating rate = $5^{\circ}\text{C}/\text{min}$.

0.20, separates in microphase but bonds chemically with the PCL block. So the PEO block microdomain reduces the crystallization entropy of the PCL block and provides nuclei for the crystallization of the PCL block. The melting peak with lower temperature (peak 1) in DSC thermogram is the reflection of this crystallization (see Fig. 8). The melting peak with higher temperature (peak 2) arises from a more perfect crystal of the PCL block under the nonisothermal conditions, and its position does not shift with the crystallization conditions.

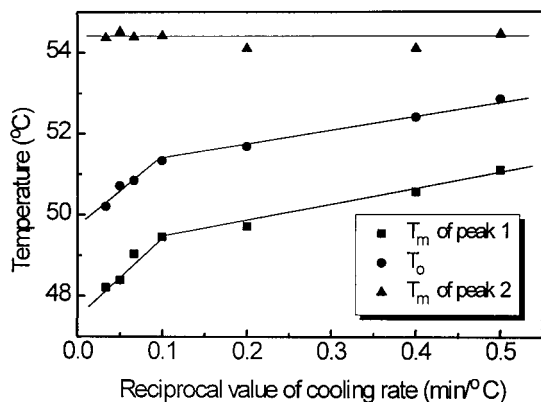


Figure 10 The effect of cooling rate on the temperatures of the two melting peaks and temperature T_0 at which the two peaks overlap. Heating rate = $5^{\circ}\text{C}/\text{min}$.

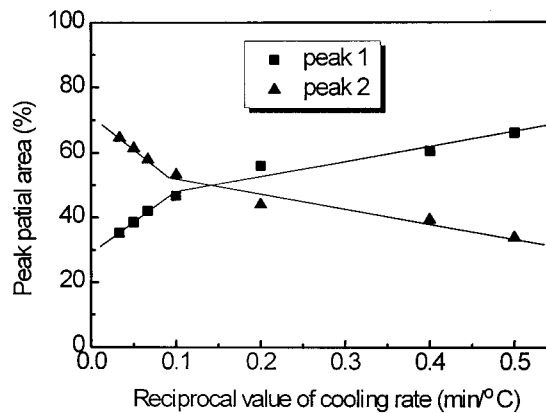


Figure 11 The effect of cooling rate on the percent areas of two melting peaks of the PCL/PEO diblock copolymer. Heating rate = $5^{\circ}\text{C}/\text{min}$.

When the PCL/PEO diblock copolymer crystallizes nonisothermally at slower cooling rates, because of the small degree of undercooling, the key of crystallization lies in the formation of nuclei. Under this condition, the amorphous and microphase separating PEO block provides nucleating sites for the crystallization of the PCL block. Thus, many PCL block chains crystallize with the PEO microdomain as nuclei. After completion of the crystallization, when the PCL/PEO diblock copolymer is heated to the molten state, the area of peak 1 is much large.

Meanwhile, when the PCL/PEO diblock copolymer crystallizes at faster cooling rates, the crystallization rates are faster. The influence of microphase-separating PEO block on the crystallization of the PCL block is much smaller. Less PCL block chains crystallize with the PEO microdomain as nucleating sites. Therefore, the area of peak 1 is small.

On the other hand, the multiple peak endotherms arise usually from recrystallization during DSC measurement. To elucidate the nature of the double melting peaks of the PCL/PEO diblock copolymer, the copolymer was crystallized at a fixed cooling rate ($10^{\circ}\text{C}/\text{min}$) and was then heated at different rates. The DSC melting curves are shown in Figure 12.

With the increasing heating rates, none of the two melting peaks disappear. Both peaks widen and increasingly overlap. Therefore, these results show that the occurrence of the two melting peaks of the PCL/PEO diblock copolymer does not result from recrystallization when heating in the course of a DSC run.

To summarize, the origin of the two melting

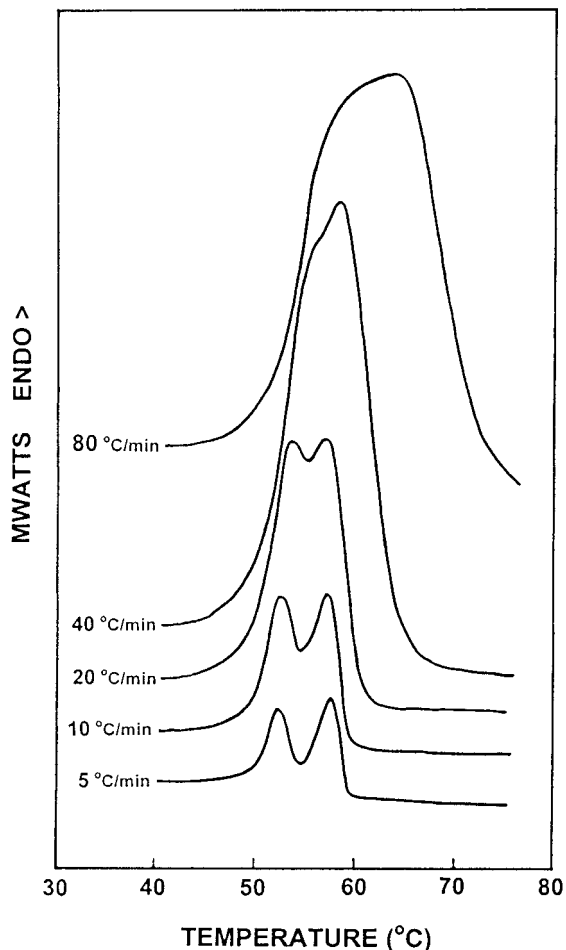


Figure 12 DSC melting curves of the PCL/PEO diblock copolymer after nonisothermal crystallization from the melt at the cooling rate of 10°C/min. The heating rate is indicated above the curve.

peaks of the PCL/PEO diblock copolymer after nonisothermal crystallization is related mainly to the amorphous PEO block bonding chemically with the PCL block. Combined with the melting curves after isothermal crystallization (Fig. 13),¹² we can notice that when the PCL/PEO diblock copolymer crystallizes at a small degree of undercooling (i.e., higher temperature of isothermal crystallization and slower cooling rate of nonisothermal crystallization), the crux of crystallization lies in the nucleation. At this moment, the microphase-separating PEO block domain plays a great role. It provides nuclei for the crystallization of the PCL block; thus, the area of the melting peak with lower temperature is larger (see Figs. 8 and 13). However, when the copolymer crystallizes at a larger degree of undercooling (i.e., lower temperature of isothermal crystalliza-

tion or faster cooling rate of nonisothermal crystallization), the influence of the PEO block is small. Therefore, the area of the melting peak with lower temperature is smaller. All of these results, including isothermal and nonisothermal crystallizations, have been proven to influence the PEO block on the crystallization of the PCL block in the PCL/PEO diblock copolymer.

Influence of Undercooling Degree on the Crystallinity of the PCL/PEO Diblock Copolymer

Generally, the larger the degree of undercooling, the faster the crystallization rate of polymer, and the weaker the mobility of polymer chains. So the

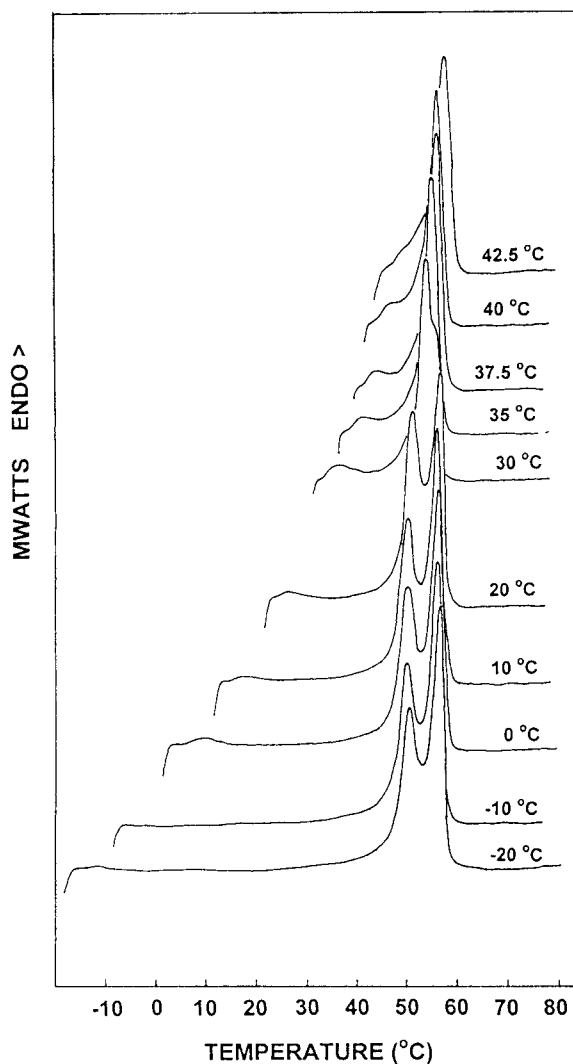


Figure 13 DSC melting curves of the PCL/PEO diblock copolymer after isothermal crystallization at different temperatures. Heating rate = 10°C/min.

larger undercooling degree does not favor the regular arrangement of polymer chains and leads to lower crystallinity of polymer.

For the PCL/PEO diblock copolymer, the crystallinity can be calculated from the fusion heat after crystallization. With the increase of undercooling degree, i.e., the drop of temperature of isothermal crystallization and the increase of cooling rate of nonisothermal crystallization, the crystallinity does not decrease; on the contrary, it increases slightly (Figs. 14 and 15).

As discussed above, when the PCL/PEO diblock copolymer crystallizes at small undercooling degree, the key to the crystallization lies in the formation of the nuclei. The microphase-separating PEO block reduces the entropy of the PCL crystallization. However, the linkage of chemical bonds between the PCL and PEO blocks limits the movement of the PCL block chain and makes it difficult to arrange sufficiently and regularly. Thus, the crystallinity is lower. On the other hand, when the PCL/PEO diblock copolymer crystallizes at large undercooling degree, the influence of the PEO block is small; therefore, the crystallinity is slightly higher.

CONCLUSIONS

In the PCL/PEO diblock copolymer at the weight fractions studied, only the PCL block is crystallizable; the PEO block with 0.20 weight fraction cannot crystallize, although its corresponding homo-

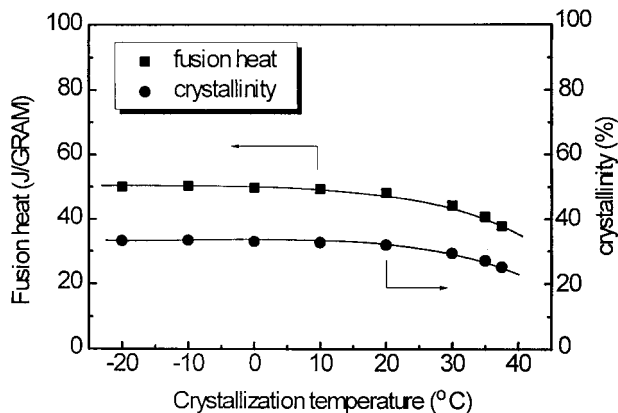


Figure 14 Crystallinity and fusion heat of the PCL/PEO diblock copolymer after isothermal crystallization at different temperatures. Heating rate = 5°C/min.

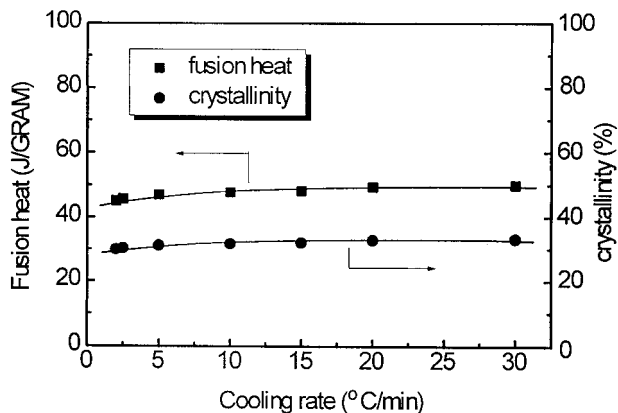


Figure 15 Crystallinity and fusion heat of the PCL/PEO diblock copolymer after nonisothermal crystallization at different cooling rates. Heating rate = 5°C/min.

polymer has strong tendency to crystallize. The PEO block bonding chemically with the PCL block has a great influence on the crystallization of the PCL, particularly the nucleation of the PCL block; and the extent of influence depends on the crystallization conditions, such as cooling rates of nonisothermal crystallization and temperature of isothermal crystallization. Ozawa's equation fails to describe the whole crystallization process of the PCL/PEO diblock copolymer because the secondary crystallization in the later stage cannot be neglected. The kinetic crystallinity of the PCL/PEO diblock copolymer is about 2.1, not varying with crystallization conditions. The occurrence of the two melting peaks of the PCL/PEO diblock copolymer is due to the influence of the PEO block and does not result from the recrystallization when heating in the course of DSC. The variation of the position and area of the two melting peaks depends on the extent of the influence of the PEO block. Because the amorphous PEO block and component provide nucleating sites for the copolymer and blend, the crystallization rates of the PCL/PEO diblock copolymer and PCL/PEO blend are faster than that of the PCL homopolymer, but the degrees of crystallinity are lower than that of the PCL homopolymer. The crystallinity of the PCL/PEO diblock copolymer is much lower than that of the PCL/PEO blend due to the linkage of the chemical bonds between the PCL and PEO blocks.

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