

Nonisothermal Crystallization and Melting Behavior of Poly(ϵ -caprolactone)-*b*-Poly(ethylene glycol)-*b*-Poly(ϵ -caprolactone) by DSC Analysis

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Received 18 December 2008; accepted 29 April 2009

DOI 10.1002/app.30706

Published online 16 June 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Nonisothermal crystallization kinetics and melting behavior of poly(ϵ -caprolactone)-*b*-poly(ethylene glycol)-*b*-poly(ϵ -caprolactone) triblock copolymer (PCL-PEG-PCL), in which the weight fraction of the PCL block is 0.87, has been studied by differential scanning calorimetry (DSC). The nonisothermal crystallization data at various cooling rates are analyzed with the Ozawa, modified Avrami, and Mo models. The modified Avrami and Mo models were found to describe the nonisothermal crystallization processes fairly well. The values of the Avrami exponent n were near three, suggesting the crystallization process with a three-dimensional crystallite growth by het-

erogeneous nucleation mechanism. The crystallization activation energy estimated from the cooling scans using Kissinger's method was 168.9 KJ/mol. The phenomenon of the double melting behavior was observed for the PCL block during melting process after nonisothermal crystallization, being the reflection of a complicated crystallization process and the existence of the amorphous middle PEG block. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 1133–1140, 2009

Key words: PCL-PEG-PCL; nonisothermal crystallization; multiple melting behavior

INTRODUCTION

Poly(ϵ -caprolactone) (PCL) is one of the most attractive and promising biodegradable aliphatic polyesters because of its unique properties such as biodegradability, biocompatibility, miscibility with other polymers, high permeability to a wide range of drugs, and so forth.^{1–3} However, its high crystallinity, hydrophobicity and slow biodegradation rate have considerably limited its medical applications.^{4–6} The hydrophilicity and biodegradability can be improved if hydrophilic poly(ethylene glycol) (PEG) block is attached to PCL backbone. PCL-PEG block copolymers have been prepared by ring-opening polymerization of ϵ -caprolactone (ϵ -CL) using PEG as a macroinitiator.^{7–10} Furthermore, some nontoxic

and restorable catalysts, such as Ca-, Fe-, Zn-, and Mg-based compounds^{11–16} used as the nontoxic and were developed for the synthesis of amphiphilic copolymers containing PEG blocks.

Polymer crystallinity has a great influence on the phys-chemical properties and the biodegradability of aliphatic polyesters. Moreover, the crystallization and melting behaviors of the block copolymers are depended on the copolymer composition and the relative length of each block in copolymers.^{17–25} Gan et al. investigated the crystallization and melting behaviors of PCL/PEO diblock copolymers,^{17,18} the PCL block is crystallizable while the PEG content is lower than 20 wt %. Bogdanov et al. compared the isothermal crystallization behavior of PCL and PEG based copolymer with different structures including diblock, triblock and star block copolymers.^{19,20} Recently, Chen and coworkers studied the composition dependence of the crystallization behavior and morphology of the PEG-PCL diblock copolymer. When the PCL block was longer than the PEG block, the PCL block crystallized first and restricted imperfect crystallization of PEG.^{21,22}

However, the main interest has been focused on the kinetics and morphology of PEG-PCL diblock

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Contract grant sponsor: National Natural Science Foundation of China; contract grant number: 30870633.

Contract grant sponsor: Ph.D. Programs Foundation of Ministry of Education of China; contract grant number: 200801410018.

TABLE I
Molecular Weight and Composition of the PCL-PEG-PCL Triblock Copolymer Obtained with Bu₂Mg

Sample	Wt % (PEG)	n(CL)/n(EG) ^a	M _n (PEG)	M _n (PCL) ^b	M _n (HNMR) ^b	M _n (GPC) ^c	PDI ^c
PCL-PEG-PCL	13	2.5	2000	6500	15,000	16,600	1.96

^a Molar ratio of the CL to EG in the product measured by ¹H NMR.

^b Calculated from ¹H NMR.

^c Measured by GPC using polystyrene standard calibration, THF as eluant at 40°C.

copolymer under isothermal conditions.^{23–25} So far there have been limited reports on nonisothermal crystallization kinetics of the PCL-PEG-PCL triblock copolymer.^{26,27} The study of morphological changes occurring during nonisothermal crystallization from the molten state of absorbable semicrystalline polymers is technologically important, because these conditions are the closest to real industrial processing (e.g. melt spinning, injection molding, extrusion). To reach the optimum condition in an industrial process, it is necessary to have some qualitative evaluations of nonisothermal crystallization process.

In the previous paper,¹⁶ PCL-PEG-PCL triblock copolymers with various lengths of each block were prepared by the ring opening polymerization of ϵ -CL in the presence of PEG using Bu₂Mg as a catalyst. Among of these copolymers, the PCL-PEG-PCL triblock copolymer with 0.13 weight fraction of the PEG2000 block is particular. Because of the hindrance of the lateral PCL blocks, only the PCL block was crystallized but the PEG block was not crystallized. The aim of the present contribution was to investigate its nonisothermal crystallization kinetics and melting behavior by differential scanning calorimetry (DSC).

EXPERIMENTAL

Materials

ϵ -Caprolactone (ϵ -CL, 99%, purchased from Acros Organics) and 1,4-dioxane were dried over CaH₂ by stirring, distilled under reduced pressure and stored under N₂ before use. Poly(ethylene glycol) (PEG2000) were imported and subpackaged by Tiantai Fine Chemicals Co. Ltd (Tianjin, China) and dried under vacuum before use. Di-*n*-butyl magnesium (Bu₂Mg) solution (1M in heptane) was purchased from Aldrich Chemical Co. Ltd.

The PCL-PEG-PCL triblock copolymer was synthesized as previous method:¹⁶ designed amounts of 1,4-dioxane, PEG2000, and Bu₂Mg were sequentially added to the previously flamed flask and aged for 30 min before the ϵ -CL monomer was injected by a syringe. The reaction vessel was then immersed into a thermostated oil at 70°C under stirring for 24 h. The product was isolated by dissolving in chloroform and precipitating in hydrochloric acidic mixture of hexane and diethyl ether and then dried in vacuum

at room temperature for 24 h. Composition and the average molecular weights of the test sample studied in this work were summarized in Table I.

DSC measurement

The nonisothermal crystallization and melting process of the samples were analyzed by DSC (Mettler-Toledo DSC822^e) according to the following procedure. The samples (ca. 10 mg) were heated to 80°C at a rate of 10°C/min for 5 min to eliminate thermal history, then crystallized at different cooling rates (from 1 to 40°C/min) and the heat flow during crystallization was recorded. After that, the samples were reheated at a rate of 10°C/min to observe the melting behavior. The position and the area of the melting peaks were recorded from each run. The absolute crystallinity was calculated from the fusion heats of the sample and the PCL homopolymer with perfect crystal (139.7 J/g²⁸).

RESULTS AND DISCUSSION

In our previous work,¹⁶ the crystallization and thermal properties of the PCL-PEG-PCL triblock copolymers were investigated by WAXD and DSC. The results illustrated that the crystallization and melting behavior are depended on both the composition and the relative length of each block in the copolymers. Among of these copolymers, the crystallization of the PCL-PEG-PCL triblock copolymer with 0.13 weight fraction of the PEG block is distinctive, and its nonisothermal crystallization process is worthwhile to evaluate qualitatively in the present work.

Nonisothermal crystallization

The crystallization exotherms as a function of temperature for the nonisothermal crystallization of PCL-PEG-PCL triblock copolymer at each cooling rate are shown in Figure 1. The crystallization exotherm becomes broader and shifts towards lower temperatures with increasing cooling rate. Values of some characteristic parameters, such as, the temperature when crystallization begins (T_0), the temperature at maximum crystallization rate (T_{max}), the time ($t_{1/2}$) and temperature ($T_{1/2}$) when the degree of crystallinity reached 50%, and the final value for the heat

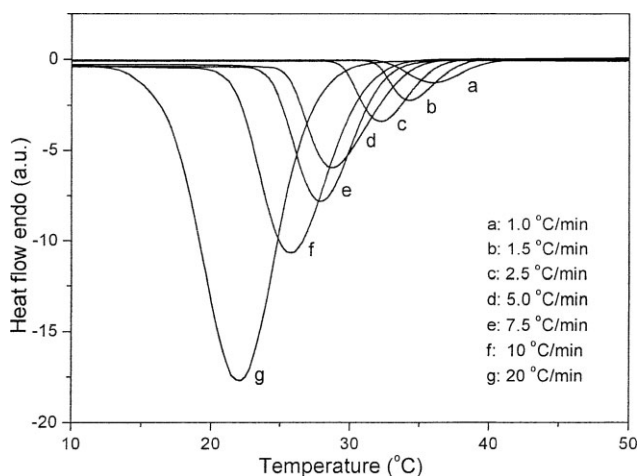


Figure 1 DSC thermograms of nonisothermal crystallization for the PCL-PEG-PCL triblock copolymer at various cooling rates from molten state.

of crystallization (ΔH_c) are summarized in Table II. As it is expected with increasing cooling rate all the aforementioned characteristic temperatures and the $t_{1/2}$ values decrease, which means that the crystallization rates increase fast. The data show that the crystallization rate of the PCL-PEG-PCL triblock copolymer is faster than that of the PCL homopolymer,^{29–31} even than that of the PCL-PEG diblock copolymer.¹⁸ Meanwhile, the crystallinity of the samples after nonisothermal crystallization is found to range from 49% to 53%, which is higher than that of PCL homopolymer and PCL-PEG diblock copolymer (ca. 30%–40%).^{29,30} Maybe the amorphous PEG acts as nucleus and significantly increases the crystallinity of PCL block.^{18,27}

From the data for the crystallization exotherms as a function of temperature dH_c/dT the relative crystallinity as a function of temperature $X(T)$ can be calculated as follows³²:

$$X(T) = \frac{\int_{T_0}^T (dH_c/dT)dT}{\int_{T_0}^{T_\infty} (dH_c/dT)dT} \quad (1)$$

where T_0 and T_∞ represent the temperatures at the initial and end of crystallization process, respec-

tively. During the melt nonisothermal crystallization process, the relation between crystallization time t and corresponding temperature T is given by³²

$$t = \frac{T_0 - T}{\Phi} \quad (2)$$

where Φ is cooling rate. According to eq. (2), the temperature-dependent relative crystallinity $X(T)$ can be transformed into the time-dependent relative crystallinity $X(t)$.

The evolution of the relative crystallinity as a function of temperature at all different cooling rates appears in Figure 2. The relative crystallinity data thus obtained $X(t)$, are illustrated in Figure 3 for the different cooling rates. All data give S-type curves, and it shows a slower process during the later crystallization stage. Furthermore, the Ozawa,³³ the modified-Avrami,³⁴ and the combined Avrami-Ozawa method developed by Mo and coworkers³⁵ were tested for the analysis of the experimental results.

Ozawa analysis

Ozawa³³ extended the use of the Avrami macrokinetic model to describe the kinetics of nonisothermal crystallization. In this approach, the nonisothermal crystallization process is the result of an infinite number of small isothermal crystallization steps and the degree of conversion at temperature T , $X(T)$, can be calculated as³³:

$$\ln[1 - X(T)] = -\frac{k_o(T)}{\Phi^m} \quad (3)$$

where Φ is cooling rate, m is the Ozawa exponent that depends on the crystal growth and nucleation mechanism, and $k_o(T)$ is the cooling or heating crystallization function. $k_o(T)$ is related to the overall crystallization rate and indicates how fast crystallization occurs. Taking the double-logarithmic form of eq. (2), it follows:

$$\ln\{-\ln[1 - X(T)]\} = \ln k_o(T) - m \ln \Phi \quad (4)$$

According to the Ozawa analysis, if the relative crystallinities at different cooling rates at a given

TABLE II
Characteristic Parameters of the PCL-PEG-PCL Triblock Copolymer During Nonisothermal Crystallization Process

Cooling rate Φ (°C/min)	T_0 (°C)	T_{max} (°C)	$T_{1/2}$ (°C)	t_{max} (min)	$t_{1/2}$ (min)	$X_{c(max)}$ (%)	ΔH_c (J/g)
1.0	40.68	36.01	36.12	4.67	4.56	52.5	63.3
1.5	39.14	34.28	34.60	3.24	3.03	58.3	64.9
2.5	37.13	32.28	32.48	1.94	1.86	54.9	64.8
5.0	34.28	28.74	29.15	1.11	1.03	58.5	60.5
7.5	33.82	27.87	28.08	0.79	0.76	54.0	60.7
10	32.21	25.73	26.00	0.65	0.62	54.8	61.3
20	29.54	22.13	21.93	0.37	0.38	47.0	61.8

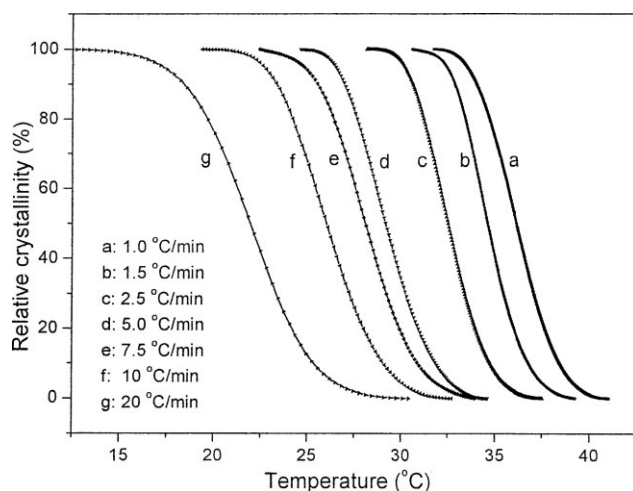


Figure 2 Relative crystallinity as a function of temperature for the PCL-PEG-PCL triblock copolymer during cooling at various cooling rates.

temperature are chosen, the plots of $\ln\{-\ln[1-X(T)]\}$ versus $\ln\Phi$ should give a series of parallel lines. The experimental data of some homopolymers³⁶ and oligo ethylene terephthalate/oligoxy ethylene block copolymers³⁷ showed good agreement with Ozawa's theoretical predictions. However, for some polymer systems, such as poly(*p*-dioxanone)-*b*-poly(ethylene glycol)³⁸ and poly(ϵ -caprolactone)/poly(ethylene oxide) diblock copolymers,¹⁸ their nonisothermal crystallization do not follow Ozawa's equation. These showed that not all the polymers crystallization under nonisothermal condition could be described by using Ozawa's equation.

Indicative Ozawa plots for crystallization of PCL-PEG-PCL are shown in Figure 4. The linearity in the plots is not satisfactory in the range from 26 to 36°C,

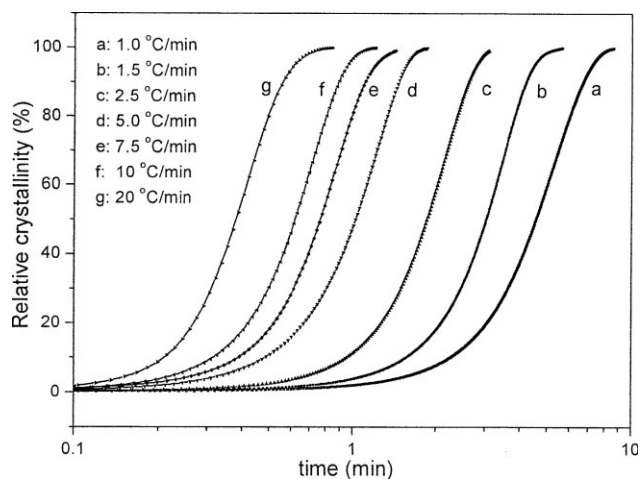


Figure 3 Relative crystallinity as a function of time for the PCL-PEG-PCL triblock copolymer at various cooling rates.

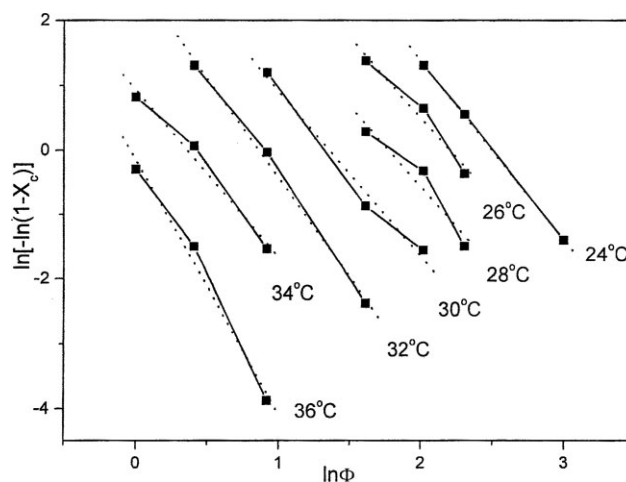


Figure 4 Ozawa-type plots of $\ln[-\ln(1-X_c)]$ versus $\ln\Phi$ for nonisothermal crystallization of the PCL-PEG-PCL triblock copolymer.

which is similar to that in PCL/PEO¹⁸ and PPDO-*b*-PEG.³⁸ The changing of slopes indicates that the Ozawa exponent m is not constant with temperature during the primary crystallization process. The general curvature seen in Figure 4 makes it impossible to determine the cooling function by the Ozawa's method.

The reason for nonisothermal crystallization of the PCL segment of the copolymers does not follow the Ozawa equation is probably, that the crystallization processes with different cooling rates are at different stages at a given temperature. In other words, the lower cooling rate process takes place toward the end of the crystallization process, whereas at the higher cooling rate, the crystallization process is at an earlier stage. In addition, the secondary crystallization of later stage could not be neglected; therefore, the Ozawa approach could not describe the nonisothermal crystallization process of the tested PCL-PEG-PCL triblock copolymer.

Modified Avrami method

According to the modified Avrami method, the relative degree of crystallinity, $X(t)$, can be calculated from³⁴:

$$X(t) = 1 - \exp(-Z_t t^n) = 1 - \exp[-(K_{\text{Avrami}} t)^n] \quad (5)$$

where Z_t and n denote the growth rate constant and the Avrami exponent, respectively. Again the composite-Avrami method can be used with $K_{\text{Avrami}} = Z_t^{1/n}$.

According to the eq. (5), Z_t and n can be obtained from the intercept and slope of the straight lines by plotting $\ln[-\ln(1-X(t))]$ against $\ln t$ (Fig. 5). In the fitting, only the relative crystallinity data between 10%

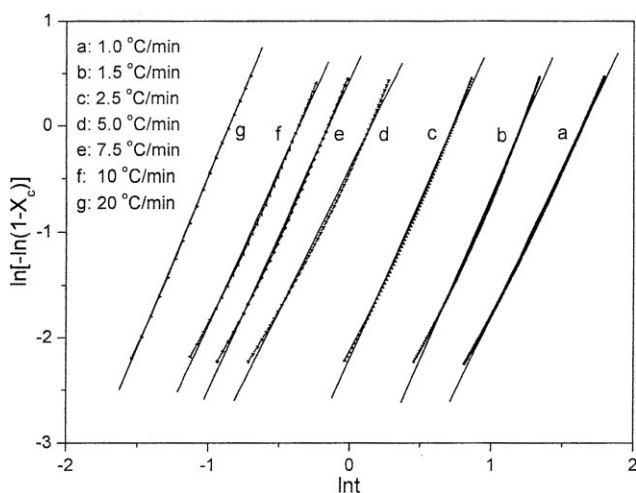


Figure 5 Plots of $\ln[-\ln(1-X_c)]$ versus $\ln t$ for nonisothermal crystallization of the PCL-PEG-PCL triblock copolymer by Modified Avrami method.

and 80% were used. It is obvious that the modified Avrami method described the experimental data very well for each cooling rate used.

However, it is inadequate to extract Z_t in this way, due to the influence of the cooling rate for nonisothermal crystallization. In considering this factor, Jeziorny³⁴ assumed that the nonisothermal crystallization comprises many infinitesimal isothermal crystallization steps, and applied the following equation to arrive at the nonisothermal crystallization kinetics parameter Z_c ³⁴:

$$\ln Z_c = \frac{\ln Z_t}{\Phi} \quad (6)$$

Table III summarizes the values of the Avrami parameters n , Z_t , K_{Avrami} , and Z_c calculated using eq. (6) for PCL-PEG-PCL at each cooling rate. The crystallization constant, Z_t , increases with increasing cooling rate, while the exponent n does not seem to follow any trend. This is reasonable, since Z_t measures the crystallization rate, which gets faster with supercooling. The values of Z_c become constant at high cooling rates (greater than 10°C/min). The values of n for all the test samples are near 3, indicating

TABLE III
Results of the Avrami Analysis for Nonisothermal Crystallization of the PCL-PEG-PCL Triblock Copolymer

Cooling rate Φ (°C/min)	n	Z_t (min ⁻¹)	K_{Avrami} (min ⁻ⁿ)	Z_c
1.0	2.81	0.01	0.19	0.01
1.5	3.08	0.02	0.30	0.08
2.5	3.01	0.11	0.48	0.41
5.0	2.70	0.67	0.86	0.92
7.5	2.95	1.55	1.16	1.06
10	2.94	2.87	1.43	1.11
20	3.24	15.78	2.35	1.15

the crystallization process is a three-dimensional crystallite, which can be elucidated by the heterogeneous nucleation mechanism. In contrast, the larger value of n (near 4) for the PCL homopolymer suggests a three-dimensional crystallization growth by homogeneous nucleation mechanism.²⁹

Mo analysis

Nonisothermal crystallization is difficult to describe with a single equation since there are a lot of parameters that have to be taken into account simultaneously. Liu et al.³⁵ proposed a different kinetic model by combining the Ozawa and Avrami equations. The importance of this method is that it correlates the cooling rate to temperature, time, and morphology. As the degree of crystallinity was related to the cooling rate (Φ), and the crystallization time (t) or temperature (T), the relation between Φ and t could be defined for a given degree of crystallinity. Consequently, combining eq. (3) and (5) derived a new kinetic model for nonisothermal crystallization:

$$\ln Z_t + n \ln t = \ln k_o(T) - m \ln \Phi \quad (7)$$

By rearrangement at a given crystallinity and solving for the cooling rate, eq. (7) becomes:

$$\ln \Phi = \ln F(T) - b \ln t \quad (8)$$

where $F(T) = [k_o(T)/Z_t]^{1/m}$ refers to the value of the cooling rate chosen at unit crystallization time, when the system has a certain degree of crystallinity, b is the ratio of the Avrami exponent to Ozawa exponents, i.e., $b = n/m$. According to eq. (8) at a given degree of crystallinity the plot of $\ln \Phi$ against $\ln t$ will give a straight line with an intercept of $\ln F(T)$ and a slope of $-b$. As it is shown in Figure 6, plotting $\ln \Phi$

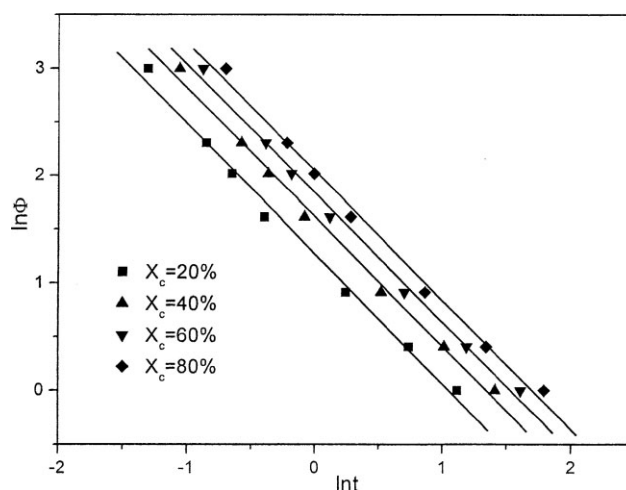


Figure 6 Plots of $\ln \Phi$ versus $\ln t$ for nonisothermal crystallization of the PCL-PEG-PCL triblock copolymer using Mo's analysis by combining Avrami and Ozawa equations.

versus $\ln t$, at a given degree of crystallinity, a series of good straight lines is observed. The values of $F(T)$ and the slope b are listed in Table IV. The $F(T)$ values increase with the relative degree of crystallinity while b values keep constant. Obviously, these equations successfully described the nonisothermal crystallization process of some polymer system, such as, PP/MMT³⁹ and PP/silica nanocomposites⁴⁰ and PBsu.⁴¹

Crystallization activation energy (ΔE)

The crystallization activation energy (ΔE) is the activation energy required to transport molecular segments to the crystallization surfaces. The activation energy of the nonisothermal crystallization can be derived from the combination of cooling rate (Φ) and crystallization peak temperature (T_{\max}), and Kissinger suggested a method for calculating the activation energy of the nonisothermal crystallization as follows^{42,43}:

$$\frac{d(\ln \frac{\Phi}{T_{\max}^2})}{d(\frac{1}{T_{\max}})} = -\frac{\Delta E}{R} \quad (9)$$

where R is the universal gas constant, the rest parameters have as above mentioned meanings.

Accordingly, in the light of the results in Tables II, the slope of $\ln(\Phi/T_{\max}^2)$ versus $1/T_{\max}$ plot will give the crystallization activation energy; $\Delta E = R \times \text{slope}$ (Fig. 7). The value of ΔE , being estimated as 168.9 kJ/mol for the PCL-PEG-PCL triblock copolymer, is higher than that of ca.116.8 kJ/mol for PCL homopolymer,^{29,30} indicating that the PCL segment crystallize more difficultly in the copolymer than that of in the homopolymer. It showed that the middle PEG block restricts the movement of the lateral PCL chains and the development of crystallinity in the PCL block,⁴⁴ resulting in the PCL chains in the triblock copolymer require more energy to rearrange in comparison with the PCL homopolymer. Consequently, we presumed that the amorphous PEG block has double effects on the nonisothermal crystallization of the PCL-PEG-PCL triblock copolymer. On the one hand, it acts as nucleating agents for the

TABLE IV
Values of b and $F(T)$ Versus Degree of Crystallinity Based on Mo's Treatment for the PCL-PEG-PCL Triblock Copolymer

Parameter	Relative crystallinity			
	20%	40%	60%	80%
b	1.21	1.20	1.20	1.20
$\ln F(T)$	1.27	1.61	1.83	2.04
$F(T)$	3.55	5.00	6.25	7.65

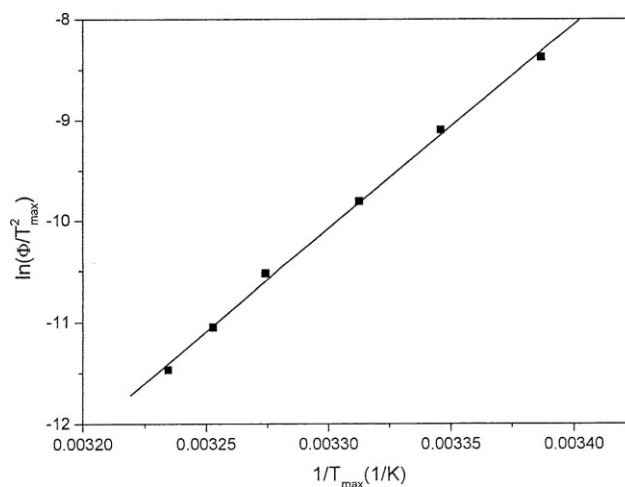


Figure 7 Plot of $\ln(\Phi/T_{\max}^2)$ versus $1/T_{\max}$ to determine the activation energy for nonisothermal crystallization of the PCL-PEG-PCL triblock copolymer.

PCL block crystallization and quickens the crystallization rate, on the other hand it increases the activation energy for nonisothermal crystallization, due to its covalent bond with the PCL block.

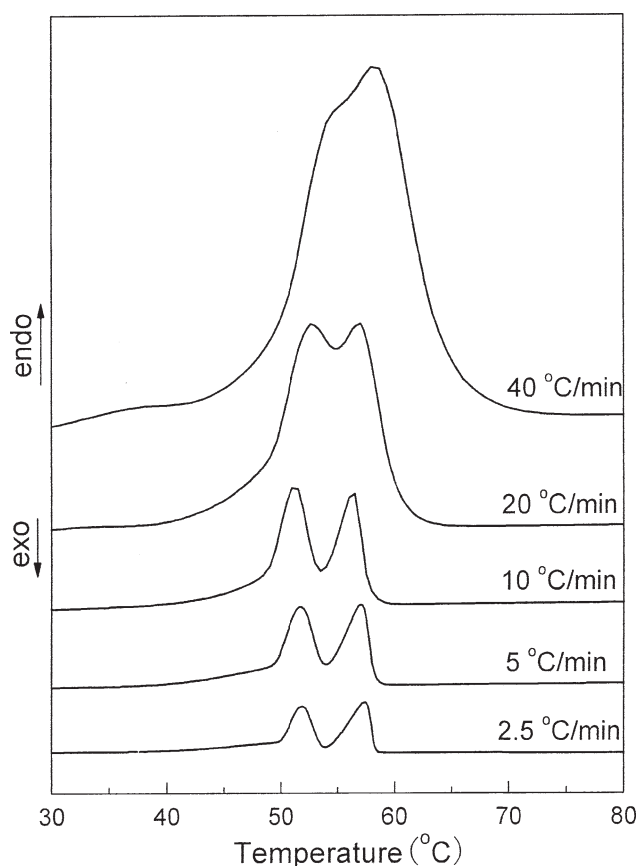


Figure 8 DSC melting curves of the PCL-PEG-PCL triblock copolymer after nonisothermal crystallization from the melt at the cooling rate of 10°C/min. The heating rate is indicated above the curve.

Melting behavior

After nonisothermal crystallization from the molten state at different cooling rates, the samples were heated again to the molten state at a rate of $10^{\circ}\text{C}/\text{min}$. The outstanding characteristics during the melting process after nonisothermal crystallization are the two melting peaks, which is similar to the previous studies on PCL/PEG di and triblock copolymers.^{18,27} Because the previous results have shown that for the test sample, only the PCL block is crystalline and the PEG block is amorphous, the double melting peaks are attributed to the PCL block. Considerable research attentions have been attracted to make clear the origin of the multiple melting peaks in certain semicrystalline polymers.^{17,18,27,41} One possible explanation for the origin of multiple melting behavior is attributed to a successive melting, recrystallization, and remelting process by many researchers.⁴¹ If this process is followed, when the heating rate is increased, the lower melting peak will be magnified and the higher melting peak will finally disappear. To elucidate the nature of the double melting peaks of the PCL-PEG-PCL triblock copolymer, the samples were heated at different rates after nonisothermal crystallization fixed the same cooling rate ($10^{\circ}\text{C}/\text{min}$). However, with the increasing heating rates, as shown in Figure 8, both peaks widen and increasingly overlap, but none of the two melting peaks disappear. Therefore, the double melting behavior is not originated from the recrystallization during the heating process.

Another possible explanation could be caused by the competition of crystallization and phase separation.^{17,18,27} During the cooling process, the crystallization of PCL and the phase separation are competing with each other. At fast cooling rate, the crystallization of PCL blocks dominates resulting in more perfect crystals with higher melting temperature. While at slow cooling rate, the phase separation becomes more complete. In the block copolymers, the phase separated domains are very small due to its typical micro-phase separation resulting in imperfect crystal structure with lower melting temperature. Figure 9 shows that a different cooling history is applied to the test sample, with the decrease of cooling rate, the position of peak at higher temperature does not change but its area decreases; however, the position of peak at lower temperature shifts from lower temperature region to higher temperature region but its area increases. Consequently, the double melting behavior in Figure 9 follows the above mentioned pattern. It is worthwhile to note that the two peaks converge into a single one at very lower cooling rates (lower than $1.5^{\circ}\text{C}/\text{min}$). This may be attributed to the perfection of the crystal structure by the destruction of the micro-phase separated morphology.²⁷

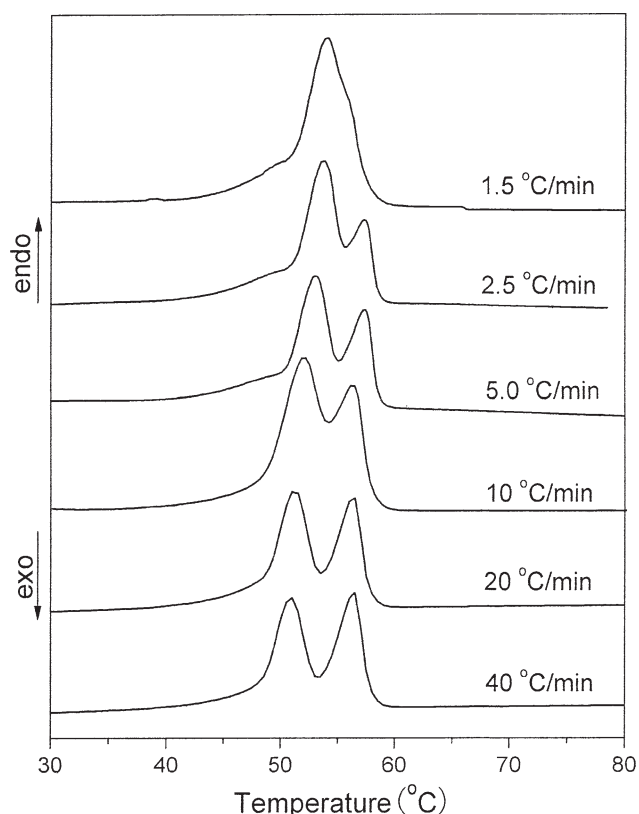


Figure 9 DSC melting curves at $10^{\circ}\text{C}/\text{min}$ of the PCL-PEG-PCL triblock copolymer crystallized from the melt at various cooling rates indicated.

Based on the above analyses, the double melting peak is the reflection of a complicated crystallization process for the PCL-PEG-PCL triblock copolymer and mainly related to the PEG BLOCK. To elucidate the relationship in more detail, more elaborated experiments, such as direction observation of morphology using POM, SAXS, and AFM,⁴⁵ should be conducted.

CONCLUSIONS

Nonisothermal crystallization and subsequent melting behavior of PCL-PEG-PCL triblock copolymer have been investigated by DSC. The kinetics analysis of nonisothermal crystallization shows that both the modified Avrami and Mo methods could describe this system fairly well, but the Ozawa analysis failed. The values of the Avrami exponent n were near 3, suggesting the crystallization process with a three-dimensional crystallite growth by heterogeneous nucleation mechanism. The crystallization activation energy was estimated using the Kissinger method as $168.9\text{ KJ}/\text{mol}$. The double melting behavior of the PCL block could not be interpreted by sequential melting-recrystallization-remelting mechanism. It is assumed that the double melting peaks

are caused by a complicated competing crystallization process, which strongly related with the existence of the amorphous middle PEG block.

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