Bulk Crystallization Behavior of Poly(ε-caprolactone) with a Wide Range of Molecular Weight

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ABSTRACT: Bulk crystallization kinetics and crystallizability of poly(ε-caprolactone) (PCL) with number average molecular weight (M_n) ranging from 1900 to 64700 were investigated. Most PCL samples crystallized rapidly at 30 and 40°C, such that the crystallization started before the equilibration of DSC signal. As a consequence, the relative crystallinity required for Avrami analysis could not be calculated accurately from the recorded DSC exotherms. An alternative method is proposed to evaluate the Avrami crystallization rate constant from the peak time of the isothermal crystallization exotherm. The calculated crystallization rate constants of PCL displayed a maximum in variation with molecular weight (MW). Such behavior was attributed to interplay between the MW effects on the thermodynamic driving force and the segmental mobility associated with crystallization. A kinetic formula proposed by Hoffman was used to obtain the crystal surface free energy product $(\sigma\sigma_e)$. In contrast to the conventional Lauritzen–Hoffman analysis based on crystallization rates measured at different crystallization temperatures (T_c) for a given MW, the present analysis was based on rates measured for different MW at a given T_c. MW variation of degree of crystallinity also displayed a maximum rather than a monotonic drop. Crystallizability was suggested to be controlled by the presence of uncrystallizable short chains and the entanglements in the polymer. The fraction of the uncrystallizable short chains played the main role in controlling the crystallinity for the low MW samples, while entanglement density was the principal factor for the high MW samples.

KEY WORDS   Poly(ε-caprolactone) / Crystallization / Molecular Weight / Crystallization Kinetics / Crystallinity /

Poly(ε-caprolactone) (PCL) is a semicrystalline bio-degradable polymer with a glass transition temperature (T_g) of ca. $-60°C$ and observed melting point around 55°C. Extensive research of PCL and its blends has been reported.[1–9] In a prior study,[10] we prepared PCL with a wide range of molecular weight (MW) (M_n ranging from 1900 to 64700) *via* fractionation by either precipitating PCL/chloroform solutions into different amounts of methanol or adding methanol into PCL/tetrahydrofuran (THF) solutions. The samples thus obtained were used to investigate the MW effects on the spherulite growth rate, equilibrium melting point (T_m^0), nucleation density, and morphology of PCL. The variation of spherulite growth rate with MW was found to exhibit a maximum rather than conventional monotonic drop. A growth kinetics analysis was also devised to extract the crystal surface free energy based on a MW-growth rate relationship proposed by Hoffman. This analysis was conducted using MW as the variable but crystallization temperature (T_c) as a fixed parameter.

In addition to spherulite growth, bulk crystallization behavior such as bulk crystallization kinetics and crystallizability is also a very important aspect of crystalline polymers. The present study extends the previous investigation to discuss the influence of MW on bulk crystallization kinetics and crystallizability of PCL.

EXPERIMENTAL

The fractionation procedures for obtaining PCL with a wide range of MW is described in the previous publication.[10] The absolute molecular weights of all the samples were determined by a Kratos Model Spectraflow 400 Gel Permeation Chromatography (GPC) equipped with Shodex KF-801, KF-802, KF-803, and KE-804 columns and Viscotek Model-100 differential refractometer/viscometer detectors. The average molecular weights (M_n, M_w, and M_z) were obtained through the universal calibration curve using the Viscotek Unical GPC software ver. 4.01. PCL samples with M_n ranging from 1900 to 64700 were used in the present study. The M_n and M_w of some selective samples are listed in Table I. The samples used here had similar polydispersity indices around 1.2 to 1.3. Thus molecular weight distribution was not considered as a principal variable here.

Bulk crystallization behavior was investigated with a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC). For the crystallization kinetics study, the sample was first annealed at 80°C for 3 min to erase previous thermal history followed by rapid cooling at ca. 120°C min^{-1} to the desired T_c (30 or 40°C) where the isothermal crystallization exotherm was recorded. For crystallizability evaluation, the degree of crystallinity for PCL isothermally crystallized at 25 to 45°C for 11 h was calculated from the enthalpy of melting (Δh_f). The degree of crystallinity was calculated by $\Delta h_f / \Delta h_f^0$ with $\Delta h_f^0 = 117\,\mathrm{J\,g^{-1}}$, the enthalpy of melting of 100% crystalline

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Table I. M_n and M_w of PCL samples in this study

Sample ID	M_n	M_w
1	2700	3200
2	2800	3700
3	4400	5700
4	6300	7300
5	6700	8500
6	19600	26300
7	22400	27600
8	29800	36200
9	44300	55400
10	44700	51700
11	64700	77600

PCL.[11] The DSC scanning rate was $20°C \, min^{-1}$.

RESULTS AND DISCUSSION

The influence of MW on the bulk crystallization kinetics of PCL at 30 and 40°C was investigated. Figure 1 displays the representative isothermal crystallization exotherms of three samples. For samples of $M_n = 2800$ and 22400 the crystallizations were so rapid that they started before the equilibration of DSC signals and hence the initial portions of the exotherms were masked by the equilibration signal. This was observed for most PCL samples under study. Since the whole crystallization exotherm could not be detected intactly, error would be introduced if the observed exotherm was used to calculate the relative crystallinity for performing the conventional Avrami analysis. Although the initial portion of the exotherm was masked by the equilibration signal, the peak time (t_p) of the exotherm was detected without perturbation. t_p of the exotherm is related to the crystallization rate. Shorter t_p would imply a faster crystallization rate. Since t_p can be measured accurately, if a quantitative relationship between crystallization rate constant and t_p is available, the rate constant can be calculated from t_p. Such a quantitative relationship may be formulated easily by considering the Avrami equation:

$$x_c(t) = 1 - \exp(-k_n t^n) \tag{1}$$

where $x_c(t)$ is relative crystallinity, n is the Avrami exponent depending on the nucleation mechanism and growth geometry, k_n is the crystallization rate constant. It is noted that the rate constant is expressed with a subscript n, k_n, to indicate that the unit of the rate constant is $[s]^{-n}$ dependent on the value of n. If the rate constant is written as k, the rate constant is given by $k = k_n^{1/n}$ and has the unit of $[s]^{-1}$. The signal recorded by DSC is proportional to the time derivative of $x_c(t)$, $dx_c(t)/dt$; therefore, t_p corresponds to the maximum of $dx_c(t)/dt$. Then we write,

$$\frac{d}{dt}\left(\frac{dx_c(t)}{dt}\right) = 0$$

at $t = t_p$. Substituting eq 1 for $x_c(t)$ in the above equation, it can be shown that
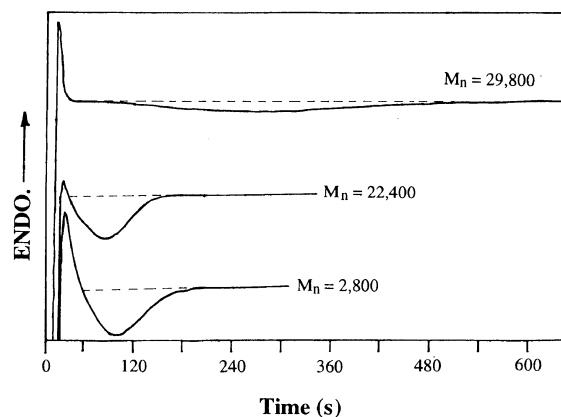
$$k_n = \frac{(n-1)}{n t_p^n} \tag{2}$$

Figure 1. DSC isothermal crystallization exotherms of PCL with $M_n = 2800$, 22400, and 29800. The crystallization temperature was 40°C. The initial portion of the crystallization exotherms was masked by the equilibration signals for $M_n = 2800$ and 22400.

or

$$k = \left[\frac{(n-1)}{n}\right]^{1/n} t_p^{-1} \tag{3}$$

The rate constants can be calculated by eq 2 and 3 once t_p and n are known. Equations 2 and 3 prescribe that a larger value of t_p corresponds to a smaller k. Since Avrami equation does not consider the contribution of secondary crystallization to $x_c(t)$, the rate constants calculated by eq 2 and 3 are only associated with the primary crystallization. Therefore, when the observed t_p is used to calculate the rate constants by eq 2 and 3, it has tacitly assumed that the occurrence of secondary crystallization did not shift the location of t_p associated with the primary crystallization exotherm. This is probably a sound assumption, since secondary crystallization normally accounts for less than 35% of the total crystallinity and only becomes important at the late stage of crystallization where primary crystallization is close to the end.[12] Calculations of rate constants by eq 2 and 3 also assume that the equilibration of the DSC signal does not perturb the actual position of t_p.

In addition to t_p, the value of n is also necessary for calculating the rate constants by eq 2 and 3. The value of n can be evaluated from the slope of the Avrami plot ($\ln[-\ln(1-x_c(t))]$ *vs.* $\ln t$) for some samples whose crystallization exotherms can be detected without overlapping with the equilibration signal. $n = 3$ is the typical value which signifies a thermodynamically controlled crystallization with instantaneous nucleation and spherulitic growth geometry. The Avrami plots of two PCL samples whose crystallization exotherms were recorded intactly are shown in Figure 2. The slopes of the plots are about 2.5 ± 0.5. The value of $n = 2.5$ would imply a diffusion-controlled crystallization with homogeneous nucleation and spherical growth geometry. However, crystallization kinetics of PCL at the temperatures under investigation (*i.e.*, 30 and 40°C) is controlled by the thermodynamic driving force of crystallization rather than mobility of the molecules. This was evidence by the observation that crystallization rate decreased with increasing temperature (or decreasing degree of supercooling) within this temperature range.[10] Since the uncertainty associated with the determination of n was 0.5,
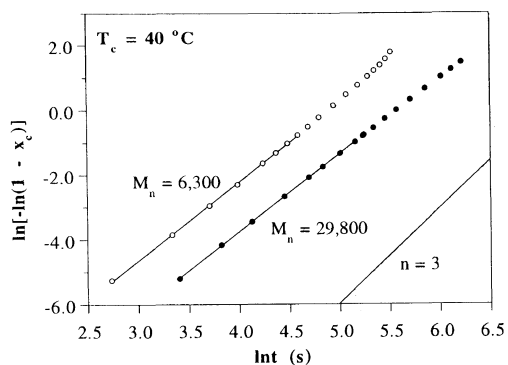
890

Figure 2. Avrami plots of PCL samples whose crystallization exotherms could be recorded intactly without overlapping with the equilibration signals.
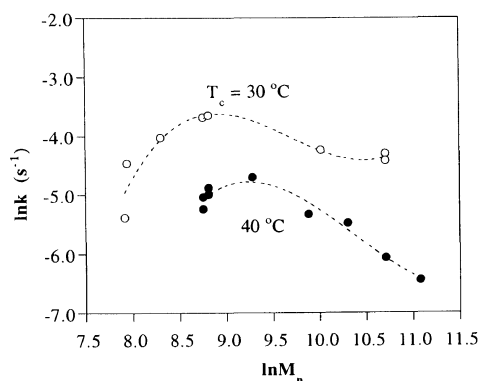

Figure 3. Variation of crystallization rate with MW for PCL. The variation displayed a maximum rather than a monotonic drop.

we adopted the value of 3 as the Avrami exponent to calculate the rate constants by eq 3. The value of $n = 3$ appears more reasonable because it stands for a thermodynamically-controlled crystallization with spherulitic growth geometry. The spherulitic morphology has been confirmed for all PCL samples in the prior study.[10]

The calculated crystallization rate constants for $T_c = 30$ and $40°C$ are plotted against $\ln M_n$ in Figure 3. The calculated rate constants for the two samples in Figure 2 were $\ln k(s^{-1}) = -5.24$ and -5.48 for $M_n = 6300$ and 29800 respectively, which agrees quite well with the rate constants, -5.56 and -5.01, obtained from the intercepts of the Avrami plots. It can be seen in Figure 3 that the variation of rate constants with MW displayed a maximum rather than a monotonic drop. The existence of such a maximum was attributed to the dependence of crystallization rate on T_m^0 and segmental mobility. Increasing MW exerted two opposing effects on the crystallization rate of a polymer; one to reduce the segmental mobility which would result in retardation of crystallization rate, while the other, to increase T_m^0 and hence the degree of supercooling which would promote the crystallization rate. Interplay between these two will determine the observed crystallization rate and may generate a maximum observed in Figure 3. At low MW, the effect of T_m^0 increase was more pronounced than reduction in segmental mobility, and the crystallization rate increased with MW; the opposite was true at high MW.

The dependence of crystallization rate on MW can be

described by the following equation[13]

$$k = \left(\frac{k_0}{\xi}\right)\exp\left(-\frac{Q_D^*}{RT_c}\right)\exp\left[-\frac{\alpha b_0 \sigma \sigma_e T_m^0(\xi)}{k_B \Delta h_f^0 T_c[T_m^0(\xi) - T_c]}\right] \quad (4)$$

where k_0 is a constant, ξ is the average number of units in a polymer chain, Q_D^* is the activation energy for the reptation process, σ and σ_e are the side and fold surface free energy, respectively, b_0 is the monomolecular thickness, Δh_f^0 is the bulk enthalpy of melting per unit volume of crystal, and α is a constant depending on the growth regime. If the fold structure of the crystal surface does not vary with MW (although tie chains may increase with MW, their contribution to the crystal surface is considered to be much smaller than chain folds; therefore, the crystal surface is assumed to be unaffected by MW), σ_e can be assumed independent of MW. The logarithmic form of eq 4 can thus be rearranged to give

$$\ln k + \ln \xi = \ln W(T_c) - \psi(T_c)\frac{T_m^0(\xi)}{T_m^0(\xi) - T_c} \quad (5)$$

where

$$\ln W(T_c) = \ln k_0 - \frac{Q_D^*}{RT_c} \quad (6)$$

and

$$\psi(T_c) = \frac{\alpha b_0 \sigma \sigma_e}{k_B \Delta h_f^0 T_c} \quad (7)$$

Equation 5 shows that a plot of $\ln k + \ln \xi$ vs. $T_m^0(\xi)/[T_m^0(\xi) - T_c]$ for a given T_c yields a straight line with the slope of $-\psi(T_c)$. Once $\psi(T_c)$ is obtained the surface free energy product $\sigma \sigma_e$ can be calculated. This appears to be an alternative method to obtain the crystal surface free energy based on the crystallization kinetic study, while $\sigma \sigma_e$ has typically been obtained by studying the crystallization rate at various T_cs for a fixed MW.

The above analysis was performed for $T_c = 30$ and $40°C$ using the calculated crystallization rate constants. ξ was calculated by $\xi = M_n/M_u$ with M_u the MW of a unit. M_u was taken as $114 \div 7\,\text{g}\,\text{mol}^{-1}$ here because a caprolactone unit $-(CH_2)_5COO-$ has a molecular weight of 114 and is considered to contain seven units. T_m^0 of PCL corresponding to different MW was extrapolated by a Hoffman–Weeks plot, previously.[10] The dependence of T_m^0 on MW was expressed as

$$T_m^0(\xi) = 353.0\frac{(118.9 + \xi)}{(132.3 + \xi)} \quad (8)$$

where the unit of $T_m^0(\xi)$ described by the above equation is K. Substituting eq 8 for $T_m^0(\xi)$ in eq 5, the plot of $\ln k + \ln \xi$ vs. $T_m^0(\xi)/[T_m^0(\xi) - T_c]$ was constructed as shown in Figure 4. It appears that the slopes or $-\psi(T_c)$ of the two linear lines are not the same. The value of $-\psi(T_c)$ for $T_c = 30°C$ is -1.23 which is 2.2 times that for $T_c = 40°C$. This is in agreement with the observation using spherulite growth rate for the analysis.[10] Equation 7 shows that $\psi(T_c)$ is proportional to α whose value is determined by the growth regime; $\alpha = 4$ for regimes I and III while $\alpha = 2$ for regime II. The difference in $\psi(T_c)$ between the two T_cs is hence due to different
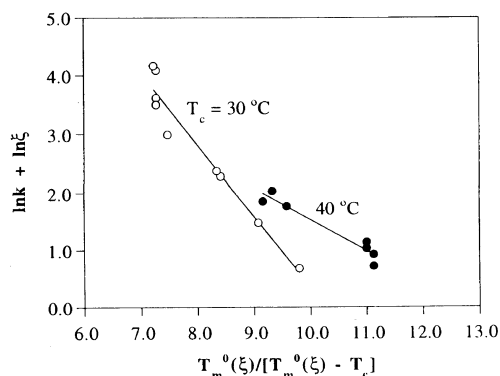
Figure 4. $\ln k + \ln \xi$ vs. $T_m^0(\xi)/[T_m^0(\xi) - T_c]$ plot for PCL. The slopes of the linear line for $T_c = 30°C$ was about two times that for $T_c = 40°C$.
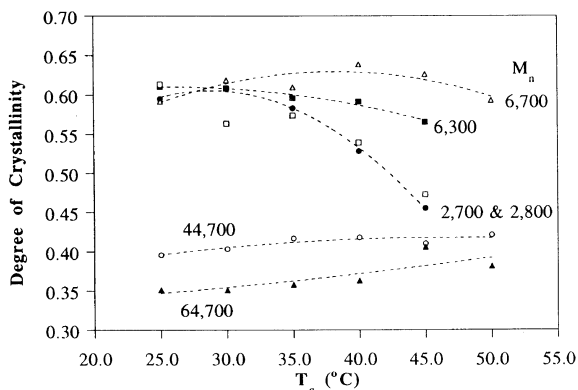

Figure 5. Degree of crystallinity of PCL crystallized at different T_cs. The crystallinity decreased with increasing T_c for the samples with $M_n < 10000$, while the opposite was observed for the two samples with $M_n = 44700$ and 64700.

Figure 6. Variation of crystallinity with MW for PCL. The variation displayed a maximum rather than monotonic drop.

regimes the crystal growth is associated. Crystal growth of PCL took place in regime II at 40°C but in regime III at 30°C; consequently, $\psi(30°C)$ was about two times $\psi(40°C)$. Using the values of $b_0 = 4.13\,\text{Å}$ and $\Delta h_f^0 = 1.48 \times 10^9\,\text{erg cm}^{-3}$,[6] $\sigma\sigma_e$ was calculated as $460\,\text{erg}^2\,\text{cm}^{-4}$ and $432\,\text{erg}^2\,\text{cm}^{-4}$ using $\psi(30°C)$ and $\psi(40°C)$, respectively. These values were about 21% lower than obtained from the crystallization rate at various T_cs (conventional Lauritzen–Hoffman analysis).[1] Determination of $\sigma\sigma_e$ using the conventional method needs to assume the values of the activation energy of mobility (U^*) and temperature at which the segmental transport is prohibited ($T_\infty = T_g - C$). $U^* = 1500\,\text{cal mol}^{-1}$ and $T_\infty = T_g - 30$ were adopted for PCL in the previous study.[1] The method proposed here does not require such assumptions because all the parameters (such as ξ and $T_m^0(\xi)$) can be obtained experimentally.

The effect of MW on the crystallizability of PCL was investigated. The degree of crystallinity normally decreased with increasing MW,[14,15] probably due to the higher entanglement density associated with the polymer of higher MW polymer. Figure 5 displays the degree of crystallinity calculated from the enthalpy of melting for PCL crystallized at different T_cs for 11 h. The crystallinity is seen to depend on MW and T_c. For the four samples with M_n less than 10000, the crystallinity decreased with increasing T_c and the drop was more obvious for lower MW samples. The opposite was observed
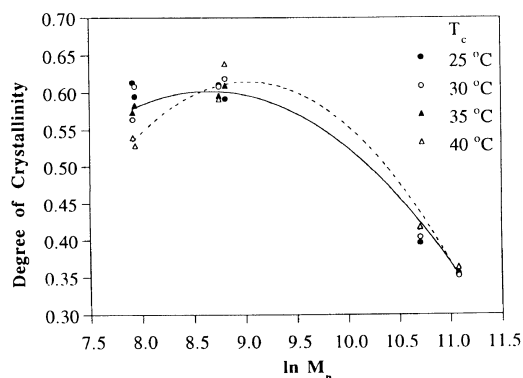
for the samples with high M_n of 44700 and 64700. Figure 6 plots the degree of crystallinity against $\ln M_n$. Just like the crystallization rate, the variation of crystallinity with MW also displayed a maximum. For the lower MW polymer, there existed a portion of short chains whose T_m^0 were close or even lower than T_c; as a result, they were not able to crystallize at T_c. As T_c increased, the fraction of these uncrystallizable short chains increased, and hence the crystallinity dropped with increasing T_c. For higher MW samples, the amounts of short chains whose T_m^0 were close or lower than T_c was low, and crystallizability was predominantly controlled by the entanglement density. As T_c increased, the polymer chains had higher mobility and hence they could release the restraints imposed by entanglements more easily. As a consequence, the crystallinity increased with T_c. The above interpretation suggests that for a given type of polymer with various MW, the crystallizability is controlled by the fraction of short chains with low T_m^0 and the entanglement density. For the low MW polymer, the crystallizability is predominantly controlled by the fraction of short chains such that the crystallinity increases with increasing MW but decreases with increasing T_c. The crystallizability is predominantly controlled by the entanglement density for the high MW sample, the crystallinity thus decreases with increasing MW but increases with T_c.

CONCLUSIONS

The bulk crystallization kinetics and crystallizability of PCL with a wide range of MW have been investigated. A method was devised to obtain the Avrami crystallization rate constants from the peak time of the isothermal crystallization exotherm. This method should be useful as the crystallization rate is so fast such that the entire crystallization exotherm cannot be recorded by DSC. Just like the spherulite growth rate, the variation of crystallization rate constants with MW displayed a maximum for PCL. This observation was attributable to interplay between the MW effects on T_m^0 and segmental mobility associated with crystallization.

A new method is proposed to obtain the crystal surface free energy product ($\sigma\sigma_e$). This analysis is based on the rates measured for different MW at a given T_c. Determination of $\sigma\sigma_e$ using the conventional Lauritzen–

892

Hoffman analysis needs to assume the values of the activation energy of mobility (U^*) and the temperature at which segmental transport is prohibited $(T_\infty = T_g - C)$. The method proposed here does not require such assumptions as all the parameters used can be obtained experimentally.

MW variation of degree of crystallinity also displayed a maximum in contrast to a conventional monotonic drop. The presence of uncrystallizable short chains and entanglement density were suggested to control the crystallizability of the polymer. For low MW samples, the presence of uncrystallizable short chains was more important and hence the crystallinity decreased with decreasing MW and increasing T_c. For high MW samples, the entanglement density played the major role such that the crystallinity decreased with increasing MW and decreasing T_c.

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