Crystallization kinetics analysis of poly(trimethylene terephthalate) including the secondary crystallization process

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Since its development for fibers and engineering thermoplastics in the 1990s [1–3], poly(trimethylene terephthalate) (PTT) has attracted much attention due to its outstanding characteristics, such as high elastic recovery, chemical resistance, and resilience [4, 5]. Like poly (ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), PTT is a typical semicrystalline polymer and the investigation of its crystallization kinetics has significant importance both from scientific and technological points of view. PTT crystallizes faster than PET but slower than PBT [6]. Its maximum crystallization rate occurs at 415 K. It has clearly been observed that a primary crystallization process and a secondary crystallization process consecutively occur during isothermal annealing of PTT [7], nevertheless no detailed kinetics analyses of the latter have been reported so far.

Although the nature of the secondary crystallization of polymers is still unclear, several models have been proposed to modify the original Avrami theory to include this process [8–11]. Hillier [8] has proposed a model, which considered that the secondary crystallization of polymers is a first-order process with an Avrami form (i.e., the Avrami exponent is a constant and always equals to 1). Despite this model being a better fit than the Avrami equation to some isotherms analyzed, the imposed invariable Avrami exponent seems quite arbitrary. Velisaris and Seferis [10] have found another way to consider secondary crystallization by describing the time dependence of crystallization degree as a linear combination of two Avrami expressions:

$$X_{\mathrm{t}} = \omega_1(1 - \exp(-k_1 t^{\mathrm{n}_1})) + \omega_2(1 - \exp(-k_2 t^{\mathrm{n}_2}))$$

where $\omega_1 + \omega_2 = 1$. The main limitation of this model is that it assumes that the primary crystallization and the secondary one start at the same time. Verhoyen *et al.* took note of this model and extended it to be a new one

$$X_{\mathrm{t}} = \omega_1(1 - \exp(-k_1(t - t_{0,1})^{\mathrm{n}_1})) + \omega_2(1 - \exp(-k_2(t - t_{0,2})^{\mathrm{n}_2}))$$

Because the induction time of the secondary crystallization, $t_{0,2}$, is longer than the induction time of the primary one, $t_{0,1}$, the secondary crystallization certainly occurs after the primary one [11]. But it is difficult to obtain the kinetics parameters by fitting the experimental data with this model unless the values of n_1 and n_2 are imposed. In this study we first constructed a mathematical model through which the Avrami constant can be obtained from experimental data, then a kinetics analysis for both primary and secondary crystallization of PTT was carried out by means of DSC measurement.

Crystallization of polymers can be divided into two consecutive processes, namely primary crystallization and secondary crystallization [9, 11]. Spherulites grow outward in the primary crystallization process. The secondary process frequently starts at the time when the specimen is completely filled with spherulites [9] and can be treated in isolation from the primary process [12], though there may still be a few spherulites growing at that time. In this study it is assumed that the secondary crystallization process occurs after the primary process is complete. As in the studies by Velisaris *et al.* [10] and Verhoyen *et al.* [11], we presumed that the secondary crystallization is also an Avrami process. Since its kinetics differ greatly from those of the primary one, another essential assumption is that the two processes have independent heat releases. A kind of form of the Avrami equation [13] is

$$X_{\mathrm{t}} = \frac{\int_0^t \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_0^\infty \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t} = 1 - \exp(-kt^{\mathrm{n}}) \quad (1)$$

where dH/dt is the heat flow rate of a DSC exotherm, X_{t} is the weight fraction of crystalline material at

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crystallization time t after the induction time has elapsed, k is the crystallization rate constant, and n is the Avrami exponent which contains information on nucleation and growth geometry. If the above assumptions are considered, the time dependence of crystallinity in the primary and secondary processes are given as:

$$X_{\mathrm{p,t}} = \frac{\int_0^t \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_0^{t_{\mathrm{p,end}}} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t} = 1 - \exp(-k_{\mathrm{p}} t^{\mathrm{n_p}}) \qquad (2)$$

$$X_{\mathrm{s,t}} = \frac{\int_{t_{\mathrm{p,end}}}^{t-t_{\mathrm{p,end}}} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_{t_{\mathrm{p,end}}}^{\infty} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t} = 1 - \exp(-k_{\mathrm{s}}(t - t_{\mathrm{p,end}})^{\mathrm{n}_s}) \qquad (3)$$

where $t_{\mathrm{p.end}}$ is the time at which the primary process finishes and the secondary one starts. k_{p}, n_{p} and k_{s}, n_{s} are Avrami constants in the two consecutive processes, respectively. $X_{\mathrm{p,end}}$, the crystallinity at the end of the primary process, and X_{s}, the total crystallinity developed in the secondary one can be expressed as

$$X_{\mathrm{p,end,}} = \frac{\int_0^{t_{\mathrm{p,end}}} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_0^{\infty} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t} \qquad (4)$$

$$X_{\mathrm{s}} = \frac{\int_{t_{\mathrm{p,end}}}^{t-t_{\mathrm{p,end}}} \left(\frac{\mathrm{d}H}{\mathrm{d}t}\right)\mathrm{d}t}{\int_0^{\infty} (\frac{\mathrm{d}H}{\mathrm{d}t})\mathrm{d}t} \qquad (5)$$

thus, Equations 2 and 3 are reduced to

$$X_{\mathrm{p,t}} = \frac{X_{\mathrm{t}}}{X_{\mathrm{p,end}}} = 1 - \exp(-k_{\mathrm{p}} t^{\mathrm{n_p}}) \qquad \text{(primary crystallization)} \quad (6)$$

$$X_{\mathrm{s,t}} = \frac{X_{\mathrm{t}} - X_{\mathrm{p,end}}}{X_{\mathrm{s}}} = 1 - \exp(-k_{\mathrm{s}}(t - t_{\mathrm{p,end}})^{n_{\mathrm{s}}}) \qquad \text{(secondary crystallization)} \quad (7)$$

when $X_{\mathrm{p,end}} = 1$, Equation 6 is equivalent to Equations 1 and 7 has no relevance because the secondary process would not take place. Utilizing this model, one can directly obtain the Avrami kinetic parameters of the primary and secondary crystallization processes of polymers from the crystallinity data. The model also gives the crystallinity X_{t} at actual crystallization time t developed from the two consecutive crystallization processes. The half-times of crystallization of the primary process and of the secondary one can be obtained from the equations $t_{1/2,\mathrm{p}} = (\frac{\ln 2}{k_{\mathrm{p}}})^{\frac{1}{n_{\mathrm{p}}}}$ and $t_{1/2,\mathrm{s}} = (\frac{\ln 2}{k_{\mathrm{s}}})^{\frac{1}{\mathrm{n}_s}}$, respectively.

PTT sample ($[\eta] = 0.0795$ m^3/kg at 298 K) prepared using terephthalic acid and 1,3-propanediol only contains tetrabutyl titanate (used as polymerization catalyst) and triphenylphosphite(used as polymerization stabilizer). DSC measurements were performed on a Perkin Elmer DSC-7 instrument with samples about 5 mg. Temperature calibration was carried out using In, Pb and Zn standards. After being completely dried, the samples were first heated to 553 K for 5 min to remove the thermal history, then were cooled rapidly from the melt to different desired crystallization temperatures. An XP-201 polarized light microscopy (Jiangnan Optics and Electronics Co. Ltd., Nanjing, China) was used to observe the morphology of sample films (thickness of about 70 μ) at different crystallization times, and the microstructures were recorded by a CCD camera.

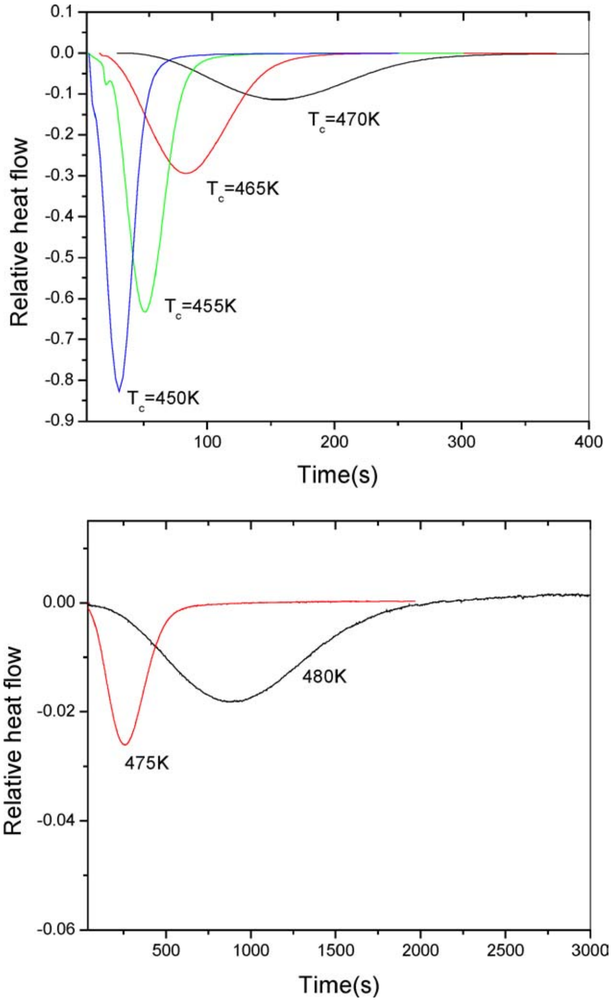


Figure 1 Dsc exotherms of isothermal crystallization of PTT at T_{c} indicated on each curve.

Fig. 1 shows the isothermal crystallization exotherms of PTT from 450 to 480 K. The development of the weight fraction crystallinity with time, X_{t}, which is the fractional area bounded by the exothermic curve and the base line at time t, is shown in Fig. 2. The conventional Avrami plot of $\log(-\ln(1 - X_{\mathrm{t}}))$ versus $\log t$ (from Equation 4) did not yield a single straight line, as shown in Fig. 3. In fact, each curve has an inflection and this was attributed to the presence of secondary crystallization, which can usually be identified by deviation of an Avrami plot at the later stage [14]. For distinguishing and analyzing the primary and the secondary processes, it is very important to determine a critical crystallinity, $X_{\mathrm{p,end}}$, which marks the completion of the primary crystallization. In this work, $X_{\mathrm{p,end}}$ was obtained from a critical value of $L_{\mathrm{p,end}}$ ($L_{\mathrm{p,end}} = \log[-\ln(1 - X_{\mathrm{t,end}})]$). Fig. 4 gives an example to help understand how to determine $L_{\mathrm{p,end}}$. The resulting values of $L_{\mathrm{p,end}}$, $X_{\mathrm{p,end}}$ and $t_{\mathrm{p,end}}$ at different crystallization temperatures are listed in Table I. The results indicated that the starting time of PTT secondary crystallization had no obvious temperature dependence, but all the secondary processes

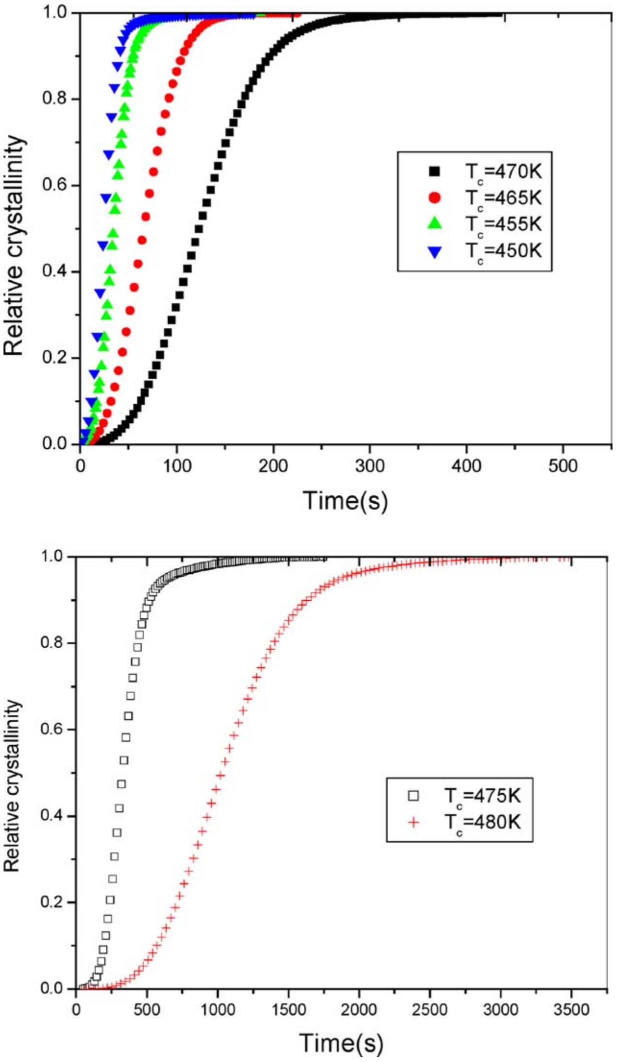


Figure 2 Development of crystallinity with time during isothermal crystallization.

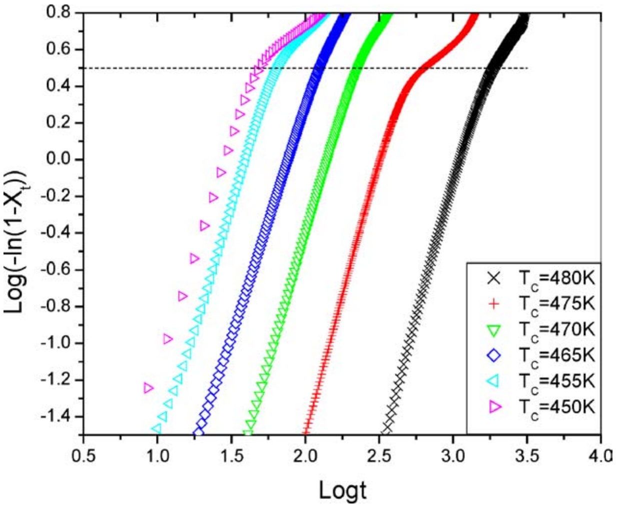


Figure 3 Avrami curves for PTT at different T_c.

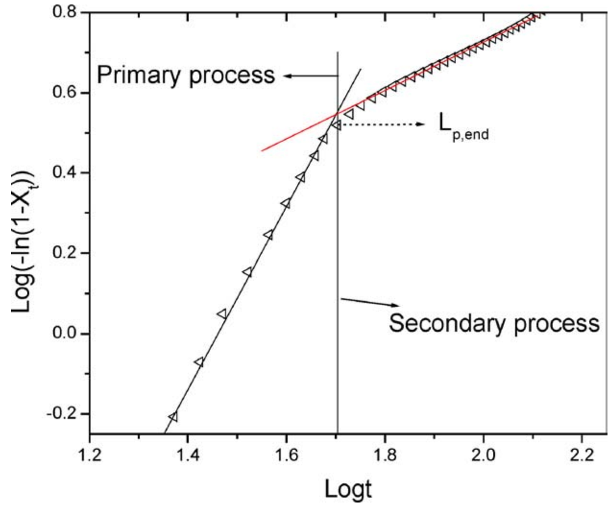
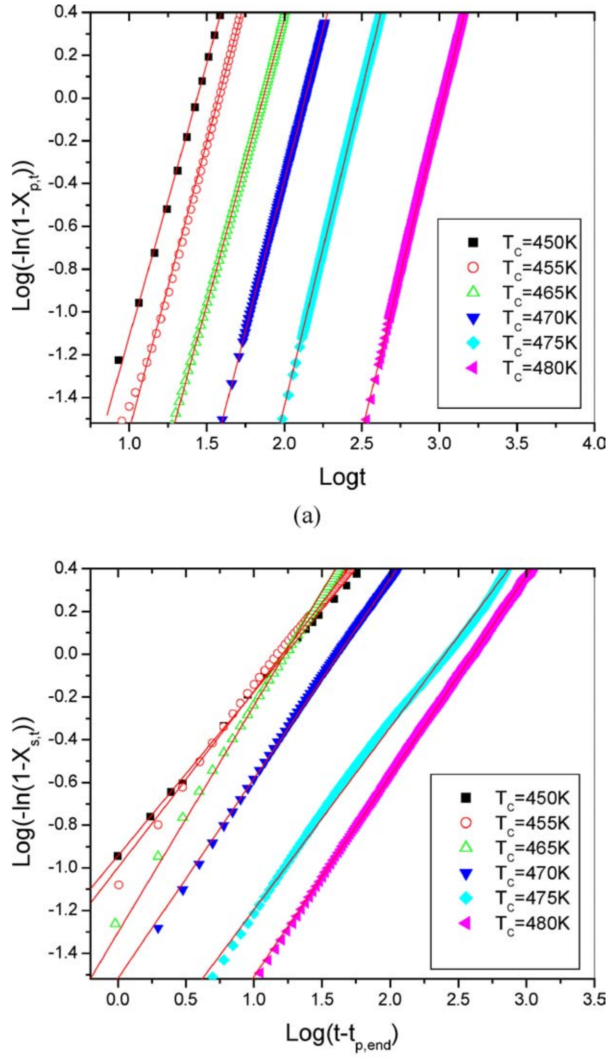


Figure 4 Determination of $L_{p,\mathrm{end}}$ at $T_c = 450$ K.



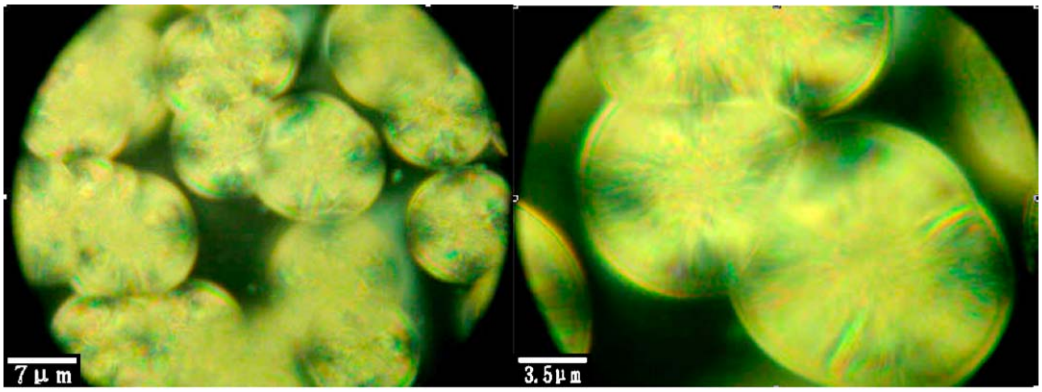
(a)

(b)

Figure 5 Avrami analysis for crystallization of PTT: (a) primary process and (b) secondary process.

started after most of the total crystallization (including the primary crystallization process and the secondary crystallization process) had taken place.

The Avrami kinetics analyses of the primary (using Equation 6) and the secondary (using Equation 7) crystallization processes are shown in Fig. 5. Good linear dependences were obtained with each curve in both processes. The Avrami constants for primary and secondary crystallization processes, and the linear correlation coefficients R (denoted as R_p for the primary crystallization and R_s for the secondary crystallization) of data in each curve are listed in Tables II and III. The



(a) (b)

Figure 6 Polarized light micrographs of PTT spherulite crystallized at 455 K (crystallization time is 70 s): (a) general view and (b) higher magnification image of part of (a).

values of R in the secondary process are slightly lower than those in the primary process, but all the values of R are > 0.997. This indicates that the experimental data fits the model very well.

The n_p values of the primary process were in the range between 2.5 and 3.0 but not integeral. Generally, an Avrami exponent close to 3 indicates a three-dimensional spherulite growth with athermal nucleation mechanism. The results are consistent with other studies on PTT crystallization [6, 7].

From Table III it can be seen that the n_s values of the secondary process were limited from 0.8 to 1.1, suggesting that the growth mechanisms are the same in the crystallization temperature range investigated. The mechanism of the secondary crystallization has not been found. It could be interpreted in terms of an increase of lamellar thickness [9, 15, 16], perfection of the crystals [15, 16], or formation of lamellar stacks [16]. The secondary crystallization process of polymers involves the attachment of chain segments to preexisting crystal growth faces, but the way in which this attachment proceeds has not been documented so far. This may be an interesting topic for the further study of secondary crystallization of polymers. According to the Avrami theory, the changing of Avrami exponent from about 3 to about 1 indicates that the crystallization mode might shift to one-dimensional crystal growth caused probably by spherulite impingement [14]. Indeed, by the time secondary crystallization started, the spherulites had impinged on one another with more or less straight boundaries (see Fig. 6). Besides, this phenomenon became more obvious with increasing crystallization time.

TABLE I $L_{p,end}$, $X_{p,end}$ and $t_{p,end}$ for PTT isothermal crystallization

T_c (K)	450	455	465	470	475	480
$L_{p,end}$	0.519	0.481	0.463	0.488	0.410	0.441
$X_{p,end}$	0.96	0.95	0.95	0.95	0.92	0.94
$t_{p,end}$/s	50.5	63.0	117.0	225.0	507.0	1.723×10^3

The crystallization rates in the secondary process are observably dependent on temperature and change in the same way as those in the primary one i.e., decreased with increasing T_c. In general, the rate of crystallization increases as the temperature decreases within the temperature range between the melting temperature of

TABLE II The Avrami parameters for PTT in primary crystallization

T_c (K)	450	455	465	470	475	480
n_p	2.6	2.7	2.5	2.8	2.9	3.0
k_p	2.14×10^{-4}	5.62×10^{-5}	2.19×10^{-5}	1.17×10^{-6}	6.61×10^{-8}	1.02×10^{-9}
$t_{p,1/2}$/s	22.4	32.7	63.1	115	263	877.6
R_p	0.9990	0.9976	0.9986	0.9999	0.9988	0.9993

Note: n_p, k_p and $t_{p,1/2}$ are Avrami exponent, crystallization rate constant, and half-time of crystallization in primary crystallization, respectively. R_p is linear correlation coefficient for data in Fig. 5a.

TABLE III The Avrami parameters for PTT in secondary crystallization

T_c (K)	450	455	465	470	475	480
n_s	0.8	0.8	1.1	0.9	0.9	1.0
k_s	1.15×10^{-1}	1.0×10^{-1}	4.27×10^{-2}	3.02×10^{-2}	8.91×10^{-3}	2.69×10^{-3}
$t_{s,1/2}$/s	9.5	11.2	12.6	32.4	125.5	257.5
R_s	0.9980	0.9982	0.9985	0.9996	0.9976	0.9967

Note: n_s, k_s and $t_{s,1/2}$ are Avrami exponent, crystallization rate constant, and half-time of crystallization in secondary crystallization, respectively. R_s is linear correlation coefficient for data in Fig. 5b.

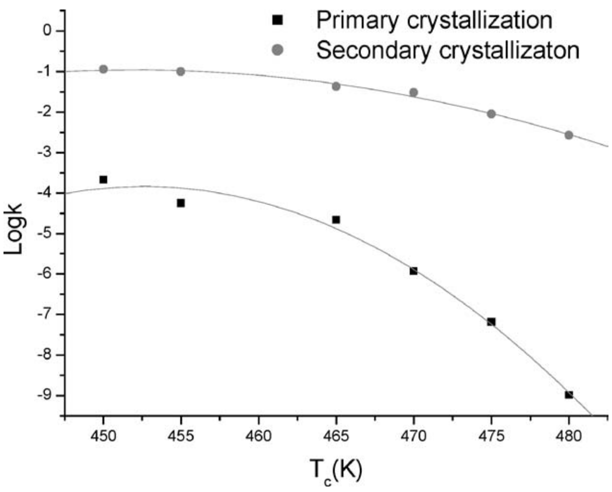


Figure 7 The variation of log k with T_c for the primary and secondary processes.

the polymer and the temperature at its maximum crystallization rate. This follows the fact that the driving force increases as the sample is supercooled. Our results indicate that both the primary and the secondary crystallization processes obey this rule. It should be noted that a nonlinear curve of log k versus T_c was obtained (Fig. 7). Thus one could not directly obtain the crystallization activation energy by the usual method from the slope of a linear Arrhenius plot.

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