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LETTER

Isothermal crystallization behavior of poly(trimethylene terephthalate) at high undercoolings

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After successfully being commercialized in the 1990s, poly(trimethylene terephthalate) (PTT) has drawn more and more attention due to its superior characteristics, such as elastic recovery, chemical resistance and resilience in comparison with poly (ethylene terephthalate) (PET) and poly (butylene terephthalate) (PBT) [1, 2]. PTT is a typical semicrystalline polymer material and many reports were focused on its crystallization behaviors recently. Huang and Chang [3] investigated the crystallization behavior for PTT from the melt and analyzed the kinetics in the temperature range from 451 K to 483 K, some important parameters for crystallization such as equilibrium melting temperature($T_m^0 = 521$ K), lateral surface-free energy (σ),work of chain folding (q) were also reported. Crystallization kinetics parameters of PET, PTT and PBT were compared by Chuah [4], it could be concluded that PTT crystallized faster than PET but slower than PBT at the same degree of undercooling. Hong and his coworkers [5] took note of the inaccuracy of Chang and Huang in determining the work of chain folding (q) and gave a more reasonable value of 27.2 kJ mol^{-1}, they also investigated the regime behaviors of PTT crystallization using the secondary crystallization theory [6] and found the boundaries between the classical regime I → II and regime II → III are located at 488 and 468 K, respectively. We also carried out the kinetics analysis of PTT crystallization including the secondary crystallization process using a new mathematical model constructed by us [7].

Much of the above work has concentrated on the measurement of overall rate of crystallization or the measurement of spherulitic growth rate of PTT crystallization from melt at low and moderate degrees of undercooling ($\Delta T = T_m^0 - T_c$, T_c is crystallization temperature), yet a detailed overall kinetics analysis at high undercoolings ($\Delta T > 70$ K), especially in the temperature range where the fastest crystallization rate would occur is still lacking. However, study of the behavior of a semicrystalline polymer crystallizing in this temperature range is of great importance from both theoretical and practical view points. Of theoretical importance is the mechanism of nucleation, the growth geometry of crystals and the formation of polymer fine structure during crystallization. The practical importance is that such crystallization data may be very useful to polymer processing such as fiber spinning and injection molding, because most polymer shaping processes need a very fast crystallization rate to shorten the solidifying time. The importance also arises from the effect of final crystallinity on the physical and chemical properties of polymers. In this study, we present the isothermal crystallization behavior of PTT from 356 K to 465 K, the overall crystallization kinetics data in the temperature range 356–450 K was reported for the first time.

Poly(trimethylene terephthalate) samples with different molecular weights were obtained by the polycondensation of terephthalic acid in the melt phase with 1,3-propandediol using different reaction time

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under the same reaction conditions. The intrinsic viscosity (IV) was measured in a 1:1(w/w)1,1,2,2-tetrachloroethane/phenol solution at 298 K. The number-average molecular weights (M_n) of 61,190, 55,030 and 18,130 corresponding to the IV values of 0.085, 0.0795 and 0.0395 m^3/kg were calculated from the equation [8] IV = 8.2×10^{-4}Mn$^{0.63}$. The samples were denoted as PTT61190, PTT55030 and PTT18130, respectively.

The depolarized light intensity (DLI) technique was used to follow the crystallization of samples. A detailed description of this technique has been published [9, 10]. Isothermal crystallization in the present work was carried out with a JJY-1A Instrument (designed by Institute of Chemistry, Chinese Academy of Science). The sample that had been made into thin film (thickness of about 150 μm) between two glass cover slips, was first heated at 553 K for 100 s in the melting oven and then immediately shot into the crystallization bath whose temperature (T_c) had already been selected. The intensity of depolarized transmittance I_t which was proportional to the fraction of crystal phase formed at time t, was recorded during the crystallization process. The relative crystallinity X_t can be expressed as:

$$X_t = (I_t - I_0)/(I_\infty - I_0) \qquad (1)$$

where I_0, I_∞ are the intensity values of depolarized light before and after the crystallization transformation, respectively.

The films of PTT55030 and PTT18130 that had been crystallized at various temperatures for 30 min in the crystallization bath of the JJY-1A instrument were used for a wide-angle X-ray diffraction (WAXD) analysis. The analysis was carried out with a Rigaku D/max-ra diffractometer using graphite monochromatized Cu K$_\alpha$ radiation (λ = 0.1542 nm; 40 kV; 80 mA). The maximum electron count rate recorded by the radiation detector is 2000 counts per second (2 K cps).

The overall kinetics of polymer crystallization is usually studied in a differential scanning calorimeter (DSC) by following the crystallization exotherms. But high speed of crystallization would cause problems when PTT is investigated at high undercoolings. Figure 1 shows some isothermal crystallization curves of PTT55030 in the DLI analysis. The ultrashort induction times imply that no reliable data could be gathered in a DSC analysis in the region of fast crystallization rates due to the start of crystallization during the cooling phase (the most rapid cooling rate of a DSC instrument is usually 200 K/min). However, we have found that methods based on DLI can determine the polymer crystallization process precisely, although this polymer displays a high crystallization rate [11]. In the present study all samples in DLI

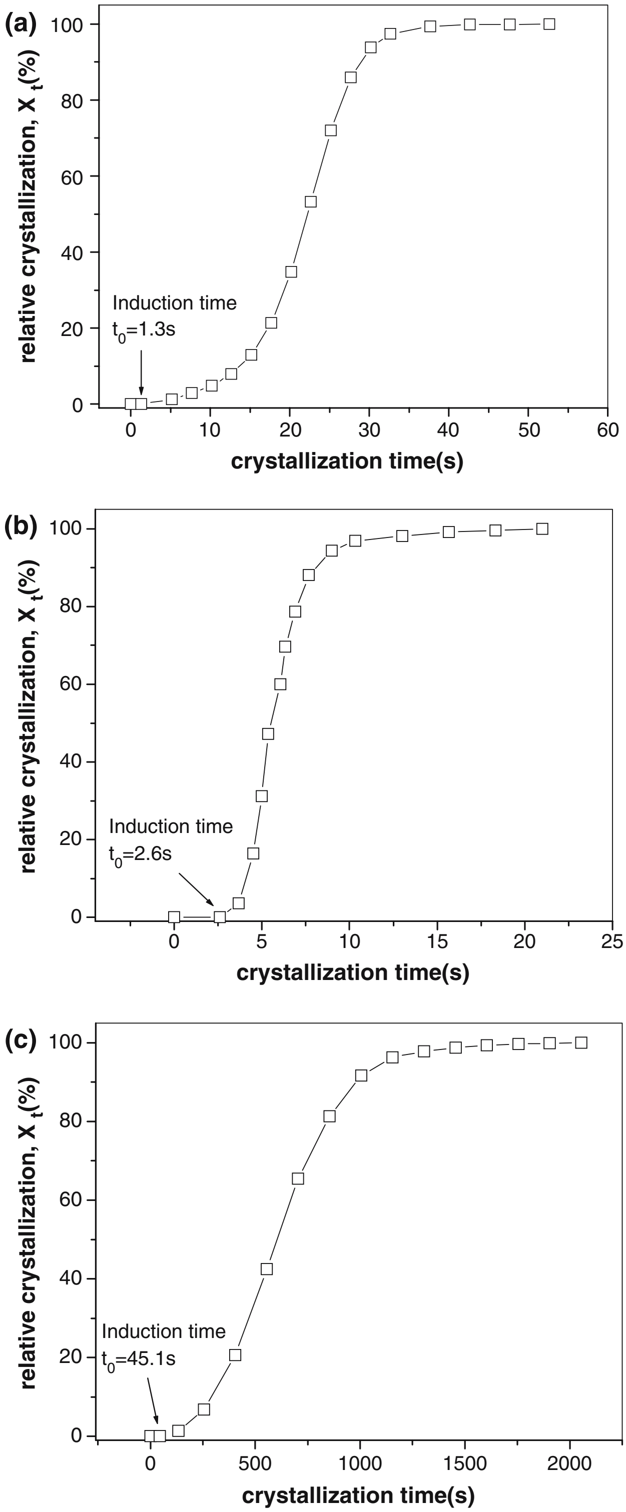

Fig. 1 Relative crystallinity as a function of time at different crystallization temperatures: (**a**) 356 K; (**b**) 401 K; (**c**) 465 K

analysis passed through an induction time (t_0). Development of relative crystallinity was analyzed according to the Avrami equation [12–14] and the plots of log [–*ln* (1–X_t)] versus log (t–t_0) are presented in Fig. 2 . The rate constant K and Avrami exponent n were obtained from the intercept and the slope of the straight line, respectively.

From the polymer processing standpoint, more useful information is the crystallization half-time, $t_{1/2}$, which is the time needed for half of isothermal crystallization to occur. In this study, Avrami analyses of PTT hot crystallization from 376 K to 465 K were carried out and thus $t_{1/2}$s were obtained not only from the isothermal crystallization curves but also calculated from the following relation:

$$t_{1/2} = (\frac{\ln 2}{K})^{1/n} \tag{2}$$

Figure 3(a) shows a plot of $t_{1/2}$ of PTT55030 as a function of crystallization temperature. It can be seen that the $t_{1/2}$s obtained with the two methods compare very favorably. The maximum crystallization rate locates at about 401 K and all the $t_{1/2}$s are < 50 s when the samples crystallize at very high degrees of undercooling ($\Delta T > 76$ K, $T_c < 445$ K). $t_{1/2}$s of samples with different molecular weight are presented in Fig. 3(b). Slower crystallization rates are observed as molecular weight increases. This is reasonable since increasingly longer chains need more cooperative displacements to go from the melt to the crystal growth faces. Therefore, the time necessary to crystallize increases and the crystallization rate deceases.

At an undercooling of 100 K, the crystallization half-time increased by a factor of 1.5 as the molecular weight of PTT increased from 18,130 to 61,190. It is of interest to compare such factors to those corresponding to PET in view of their similar window for crystallization. Van Antwerpen and Van Krevelen [15] studied the effect of molecular weight on the crystallization kinetics of PET in a range of M_n from 19,000 to 35,400. They observed that at an undercooling of 100 K, the overall rate of crystallization as measured by $t_{1/2}$ decreased by a factor of 2.2 as the M_n increased from 19,000 to 35,400. Therefore,the effect of molecular weight on the overall rate of bulk crystallization seems to be less important in PTT than in PET.

The Avrami exponents obtained in all cases vary from 2.5 to 3.1, as shown in Fig. 4. This implies a three-dimensional spherulite growth with heterogeneous nucleation mechanism or a homogeneous nucleation accompanied by two-dimensional growth. However, observations in polarized light microscopy indicated the formation of spherulitic textures in all these crystallized samples (the morphology study will be reported in a separate paper). So the mechanism of

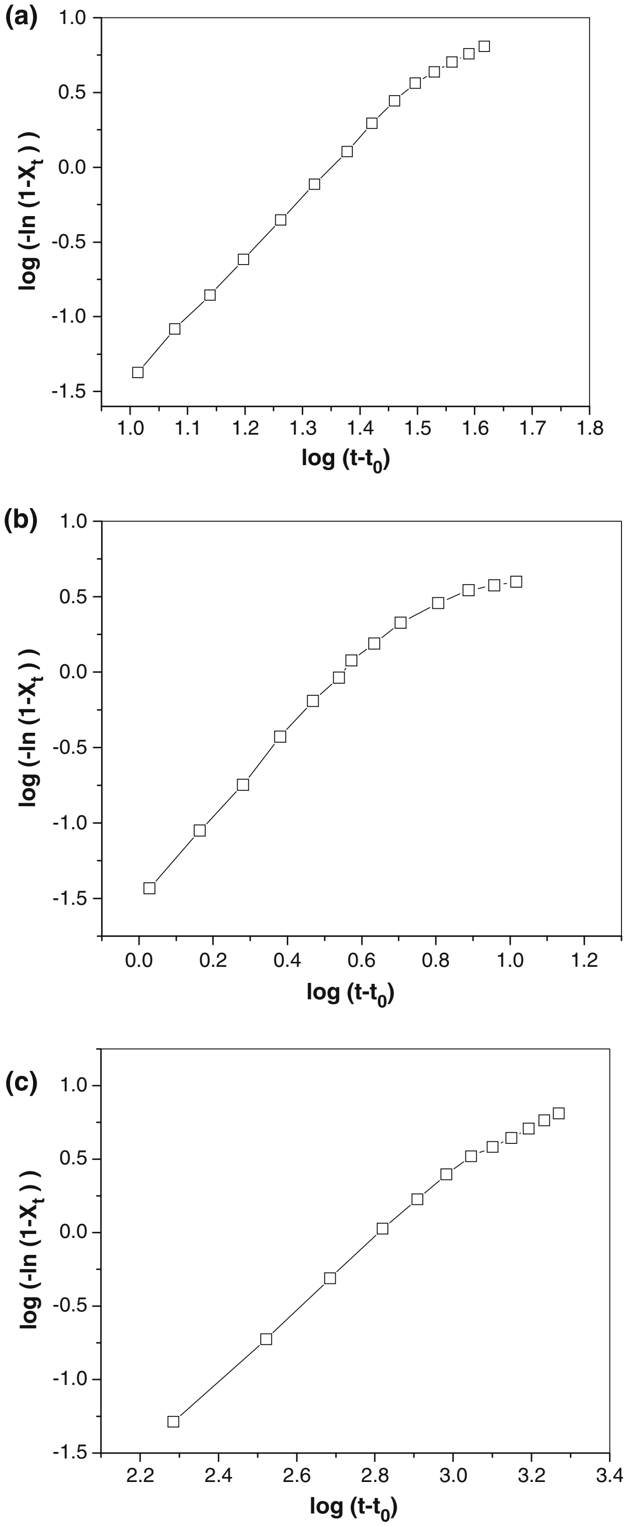

Fig. 2 Typical Avrami plots for PTT isothermal crsytallization at different temperatures: (**a**) 356 K; (**b**) 401 K; (**c**) 465 K

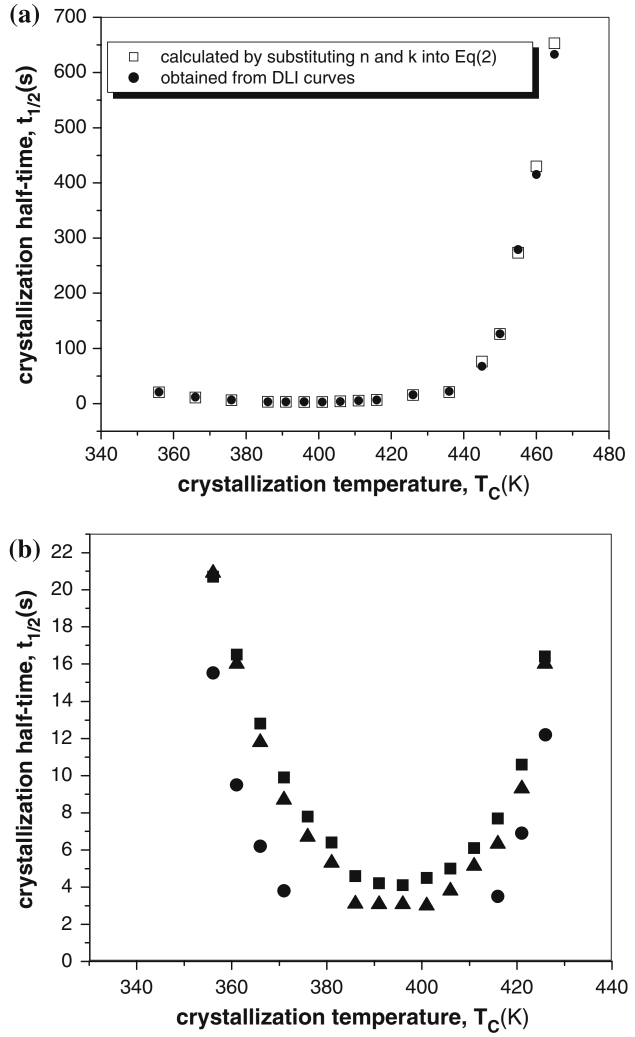

Fig. 3 (**a**) Relationship between $t_{1/2}$ and crystallization temperature of PTT55030; (**b**) Effect of molecular weight on $t_{1/2}$, M_n:\$, 61190; ▲, 55030; •,18130. $t_{1/2}$s in (**b**) are calculated from Eq. 2

PTT crystallizing from the melt at high undercoolings should be the growth of spherulites from heterogeneous nuclei.

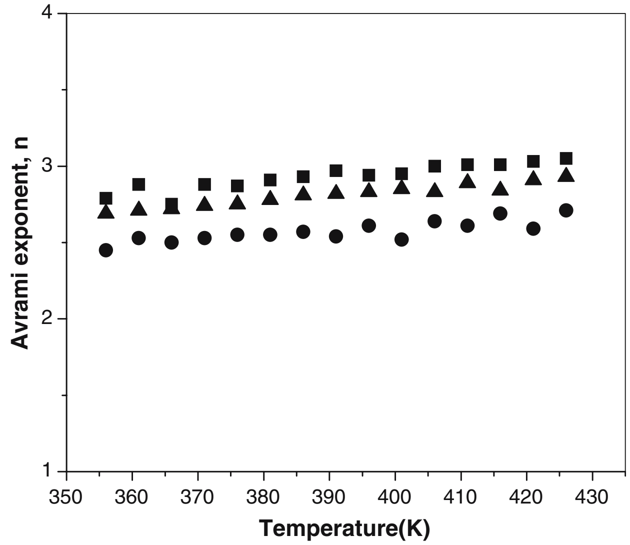

Fig. 4 Avrami exponent as a function of crystallization temperature, M_n: ■, 61190; ▲,55030; •,18130

Figure 5 shows WAXD powder patterns of PTT55030 crystallized at different isothermal temperatures. There are seven characteristic peaks exhibited in each profile which correspond to the reflection planes (010), $(0\bar{1}2)$, (012), $(10\bar{2})$, (102), $(1\bar{1}3)$ and $(10\bar{4})$, respectively [16]. The peak of the $(1\bar{1}3)$ reflection separates from the (102) reflection, and the separation increases with temperature. Except for this change, the fundamental profile of the diffraction pattern does not change over the whole temperature range. PTT18130 gave the same results. This fact indicates that the crystal structure of PTT crystallized at high undercoolings does not change with varying crystallization temperatures. The unit cell of PTT (based on WAXD results) has been determined to be triclinic ($P\bar{1}$ space group) with dimensions a = 0.453 nm, b = 0.620 nm, c = 1.870 nm, α = 97.6°, $\beta = 93.2$, and $\gamma = 110.1$ [17].

The apparent degrees of crystallinity were calculated from the following relation:

$$X_c^{\mathrm{WAXD}} = \frac{A_c}{A_c + A_s} \tag{3}$$

where A_c and A_s are the sum of the areas under the crystalline and amorphous peaks of a WAXD powder pattern and are measured after the application of a

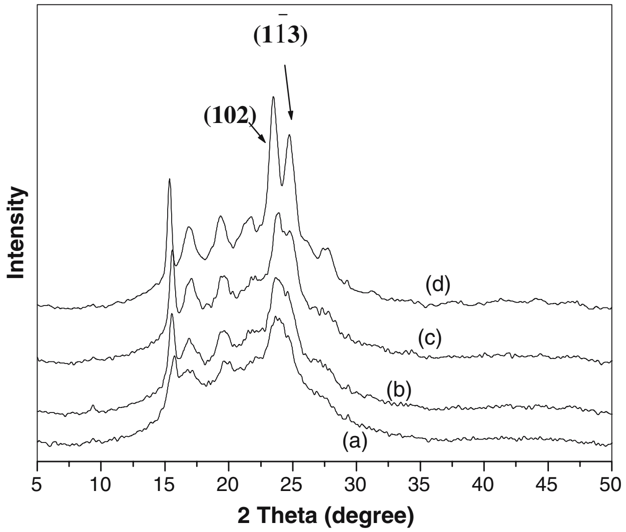

Fig. 5 Wide-angle X-ray diffractograms for PTT55030 isothermally crystallized from the melt at different crystallization temperatures: (**a**) 356 K, (**b**) 403 K, (**c**) 436 K, (**d**) 465 K

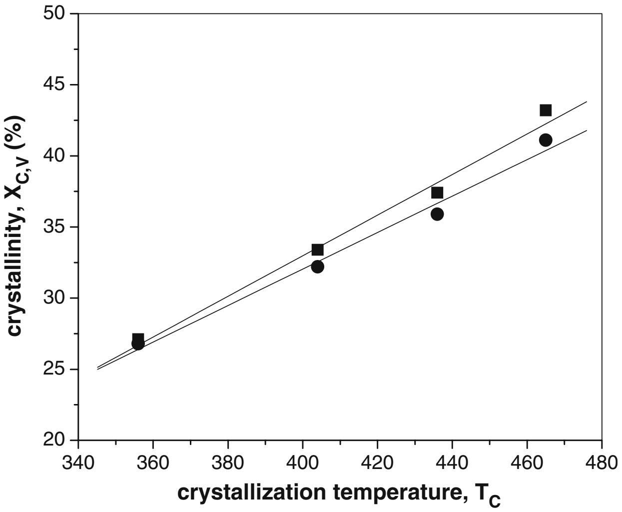

Fig. 6 Crystallinity as a function of crystallization temperature for PTT samples: ■,PTT18130; •, PTT61190

standard Gaussian curve-fitting routine to the peaks. The development of final apparent degrees of crystallinity as a function of T_c is given in Fig. 6. Although there is a peak in crystallization rate of PTT crystallized at the temperature range investigated (as shown in Fig. 3), it is clearly observed that the degree of crystallinity of PTT55030 continuously increases in the range 26.8–41.1% with increasing T_c. The crystallinity also increases as molecular weight is decreased. When T_c is below 468 K, regime III kinetics are operational [6]. The surface spreading process governs the crystallization, lowering the molecular weight increases the molecular mobility and hence obtains more favorable perfection of crystals.

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