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Effect of Melting Conditions on Crystallization Behavior of Poly(trimethylene terephthalate)

Yong Xu,[1*] *Hong-bing Jia*,[1] *Sheng-rong Ye*,[2] *Jian Huang*[3]

[1*] Department of Polymer Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, People's Republic of China; fax +862584317050; e-mail: xuyong@zuaa.zju.edu.cn
[2] Institute of Polymer Science, Zhejiang University, Hangzhou 310027, People's Republic of China; fax +8657187984409; e-mail: yeshr@zju.edu.cn
[3] Department of Chemistry, University of Texas at San Antonio, San Antonio, Texas, 78249-1644; e-mail: Jianhuang@hotmail.com

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Abstract: The effect of melting conditions on the crystallization kinetics of poly(trimethylene terephthalate)(PTT) was presented by means of depolarized light intensity (DLI) technique. The kinetics of PTT crystallization from melt depends on melting conditions and primarily upon the temperature of the melt. Higher melt temperature or longer time of melting may cause a reduction of crystallization rates at the melt temperature range from 506 to 531 K. Crystallization mechanism of PTT crystallizing from various melting conditions has been discussed according to Avrami kinetics parameters and morphology study. The reduction of the rate may result from two reasons: 1) the decrease of regularity such as residual nuclei in the PTT melt which lead to a reduction in the number of heterogeneous nuclei in the crystallization process; 2) the decreased spherulitic growth rate of PTT with higher melt temperature or longer residence time for melting.

Introduction

Poly(trimethylene terephthalate) (PTT) is an odd numbered aromatic polyester in the homologous series of poly(m-alkylene terephthalates) with m=3. Since its development for fibers and engineering thermoplastics in 1990s, PTT has attracted much attention owing to its outstanding characteristics, such as high elastic recovery, chemical resistance and resilience [1-3]. As a typical semicrystalline polymeric material, the applicability and processing condition of PTT are determined by its thermal properties and crystallization behavior. Much study has focused on this topic [4-8]. Recently, we have reported the kinetic analysis of PTT crystallization including the secondary crystallization process using a new mathematical model constructed by us [7] and the crystallization behavior of PTT at high undercooling was also explored[8].

The kinetics of polymer crystallization and morphology are controlled by various factors such as molecular weight, chain flexibility, chain defects, and stereo-regularity, etc., which is different from that of small molecules [9]. The crystallization process is also affected by processing conditions such as temperature, pressure, nucleating agents, stress, etc. Current interest in PTT as moulding materials and fibers has made essential a detailed investigation of crystallization behavior from the molten state [4]. But it is surprising that no attention has been paid to the influence of the melting conditions on the crystallization of PTT in spite of its theoretical and practical importance. In the aforementioned studies on PTT crystallization, samples were heated up to a high temperature (usually 50 K above the melting point of PTT) and kept at that temperature for a period time to erase the thermal history, which means that the thermal history of samples was not taken into account in these investigations. However, the study of polymer crystallization from various melting conditions is of great interest, since industrial processes proceed generally from non-equilibrium melting conditions which usually result in melts with various thermal histories before solidification. Moreover, from a scientific point of view, the study of effect of thermal history on crystallization behavior may expand our general understanding of the crystallization nature of this polymer. In present work, the effect of melting conditions on the crystallization kinetics of PTT is presented and the crystallization mechanism has been discussed herein.

Results and discussion

The isothermal crystallization of PTT samples was investigated at 421, 465 and 475 K. Before the crystallization, all samples were heated to a temperature (*TM*) and held at this temperature for 10 min. Fig. 1 shows typical crystallization isotherms and growths of PTT crystallizing at 465 K with various *TM*s obtained from the depolarized light intensity measurement.

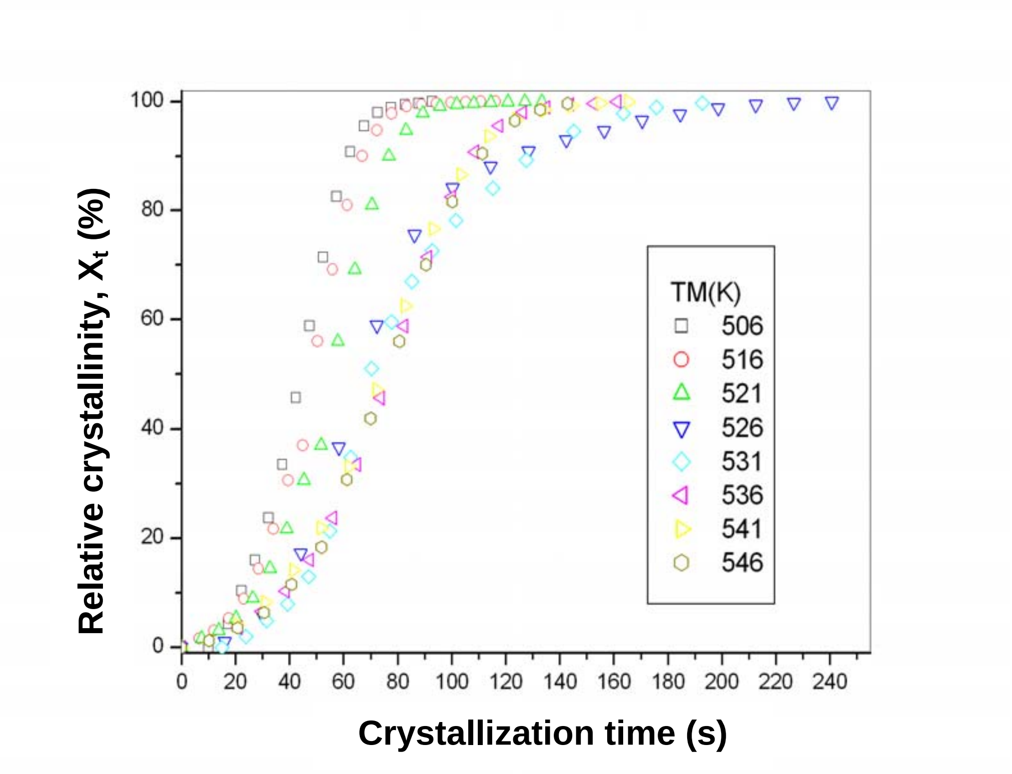


Fig. 1. Relative crystallinity as a function of time for crystallization at 465 K with various melt temperatures.

Development of relative crystallinity was analyzed according to the Avrami equation [10–12] and the rate constant *k* and Avrami exponent *n* have been obtained from the intercept and the slope of the straight line of $\log[-\ln(1-X_t)]$ versus $\log t$, respectively. The results that summarized the variation of rate constant *k* with crystallization temperature under various *TM*s are shown in Fig. 2. 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. Fig. 2 also shows the corresponding changes in $t_{1/2}$.

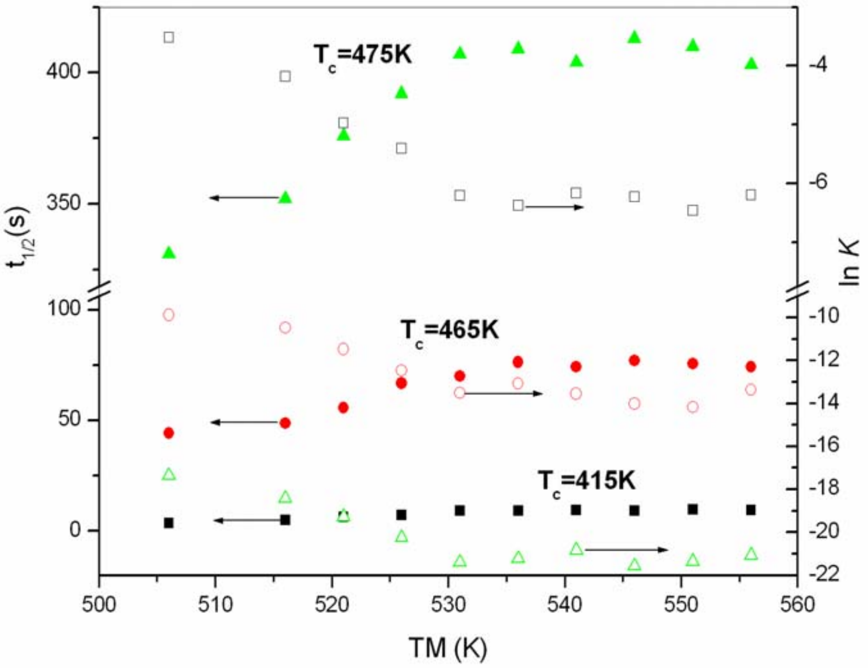


Fig. 2. Variation of logarithm of rate constant *k*, and crystallization half time, $t_{1/2}$ as a function of melt temperature (*TM*); Residence time for melting is 10 min.

A strong correlation between the value of parameter *K* and crystallization half time is observed as expected. Crystallization half time decreases with increasing values of *K* and slower crystallization rates are observed as crystallization temperature increases. This is consistent with our previous study and other authors' results on kinetic investigation of PTT crystallization in the same temperature range [5, 7-8]. Moreover, it can be seen that the crystallization rates fall sharply when *TM* is increased from 506 to about 530 K and then the crystallization kinetics is independent of the melting temperature for all T_cs. It is important to note that the Avrami exponent is in the range of 2.4-3.5 at all the melting temperatures (Table 1 lists the kinetics parameter of PTT crystallization from melts with various *TM*s) and meanwhile, observations in polarized light microscopy indicated the formation of spherulitic textures in all these crystallized samples (Fig. 3 gives the representative crystallization morphology for PTT crystallized at 465 and 475 K with various *TM*s). So we can conclude that the mechanism of PTT crystallization from melt with all *TM*s should be the growth of spherulites from heterogeneous nuclei.

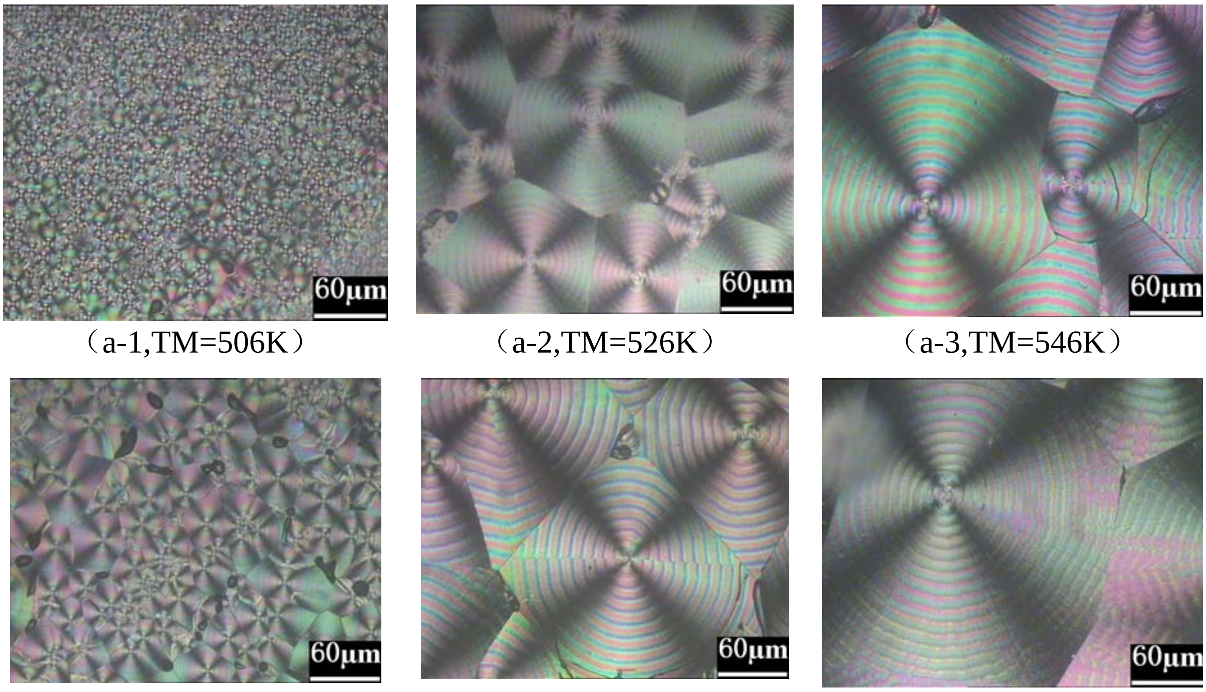
Tab. 1. Values of the rate constant *k* and Avrami exponent *n* for PTT crystallizing from melts with various temperatures.

TM (K)	T_c					
	421K		465K		475K	
	$K\times10^{-n}$	n	$K\times10^{-n}$	n	$K\times10^{-n}$	n
506	2.96×10^{-2}	2.41	5.11×10^{-5}	2.51	2.87×10^{-8}	2.93
516	1.53×10^{-2}	2.40	2.84×10^{-5}	2.60	9.94×10^{-9}	3.08
521	6.94×10^{-3}	2.48	1.04×10^{-5}	2.76	4.23×10^{-9}	3.19
526	4.51×10^{-3}	2.55	3.85×10^{-6}	2.88	1.60×10^{-9}	3.33
531	2.01×10^{-3}	2.62	1.37×10^{-6}	3.09	5.10×10^{-10}	3.50
536	1.69×10^{-3}	2.71	2.11×10^{-6}	2.93	6.00×10^{-10}	3.47
541	2.09×10^{-3}	2.59	1.30×10^{-6}	3.06	8.98×10^{-10}	3.41
546	1.97×10^{-3}	2.63	8.20×10^{-7}	3.14	4.29×10^{-10}	3.52
551	1.56×10^{-3}	2.66	7.05×10^{-7}	3.19	5.27×10^{-10}	3.49
556	2.04×10^{-3}	2.60	1.55×10^{-6}	3.02	7.12×10^{-10}	3.45

Note: TM is the temperature of PTT melt before crystallization.

In the polymerization process, tetrabutyl titanate was added into the reaction mixture as catalyst and finally existed in the resultant polyester as a solid residue, which may act as heterogeneous nucleating agent in the crystallization process. Some authors have presented similar point of view on PTT crystallization [13]. However, the decreasing of the crystallization rate at melt temperature range from 506 to 531 K allow us to propose that there may be another mechanism of heterogeneous nucleation in PTT with various melting conditions, aside from the usual effect of purely foreign inclusions such as nucleation agent, catalyst, pigment etc. This mechanism may be possible because of the presence of unmelted or partially melted crystalline chains acting as nucleants. Numerous indirect and direct experiments [14-16] indicate such regularity in the polymer melt. In this view, the following explanation may be given for the particular dependence of PTT crystallization kinetics on melting conditions: The decreasing of the crystallization rate is mainly the result of disappearance of regularity such as residual nuclei in the PTT melt. After the decrease of the crystallization rate all the regularities from the molecular chains were destroyed but a certain heterogeneous nucleation factor (mainly come from catalyst) in the melt is retained, which lead to a relatively invariable crystallization rate.

So the decrease of the crystallization rate of PTT whose *TM*s increased from 506 to 531K is in part due to decrease in the number of the heterogeneous nuclei which come from the reserved regularity in the melt. This was confirmed by the morphology study as shown in Fig. 3. It can be seen from Fig. 3 that, a reduction in the number of nucleation sites and consequently a reduction in the number of spherulites formed were observed when the melt temperature was raised. All the spherulites formed in the isothermal crystallization had impinged on one another with more or less straight boundaries, which resulted from the secondary crystallization of PTT and has been illustrated in one of our previous papers [7]. It is clearly revealed that the spherulite size increased with the melt temperature increasing because of the reduction of the number of spherulites formed.



（a-1,TM=506K） （a-2,TM=526K） （a-3,TM=546K）

（b-1, TM=506K） （b-2, TM=526K） （b-3, TM=546K）

Fig. 3. PLM images of PTT crystallized at 465K(a) and 475K(b) with various melt temperatures (*TM*s).

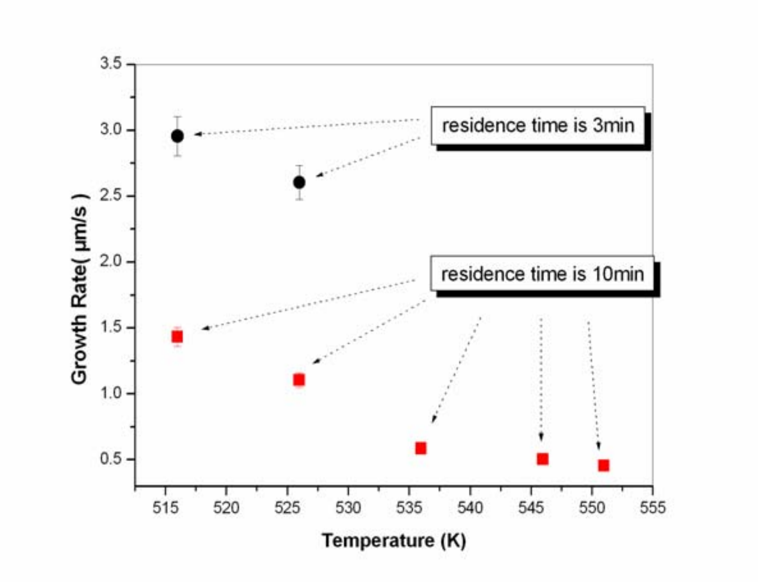


Fig. 4. Spherulitic growth rates at 465 K after various initial melt conditions.

Moreover, the slower crystallization response for harsher melt may have resulted from the decreased spherulitic growth rates. To evaluate this effect, thin PTT films sandwiched between two glass slides were quenched to 465 K after melt at 516-551 K and the growth rate of PTT crystallization with various melt history was measured by following the development of radius with time. The results are summarized in Fig. 4. It can be seen that melt temperature and melt residence time have a strong effect on the subsequent spherulitic growth rate. Higher melt temperature or longer residence time results in significantly reduced growth rates. For a residence time of

10 min, the spherulitic growth rates show a sharp decrease if the melt temperatures are raised from 516 to 536 K. Growth rate data was also collected after a 3 min residence at 516 and 526 K although the high nucleation density encountered and the data were an average of several repetitions of this experiment. The growth rate after 3 min and 10 min residence times at 516 K were found to be 2.956 µm/s and 1.432 µm/s respectively. Similar results were obtained for a melt temperature of 526 K. According to the study by Kelsey and Kiibler [17], PTT chains cleaved easily during thermal degradation and this led to the decrease of its molecular weight. With high temperatures, such as 551 K used in the present work, and long melt residence time, PTT samples are ought to be highly degraded which caused much lower melting points of the samples than those of the starting PTTs. At the same crystallization temperature, the degree of undercooling of the degraded PTT should be much smaller than that of the undegraded PTT and thus the crystallization rate decreases accordingly. However, there is relatively a smaller drop in growth rate if the temperature is raised from 536 to 551 K. This indicates that the extent of degradation reactions is somewhat similar at 536 and 551 . Detailed investigations of the influence of thermal history on PTT crystallization are in progress and will be published shortly.

Experimental part

PTT ([η] =0.0795 m^3/kg at 298 K) used in this study was synthesized by meltcondensation of 1,3-propandiol (PDO) with terephthalic acid (TPA) using tetrabutyl titanate as a catalyst [7]. Samples were dried in a vacuum oven at 408 K for 12 h prior to further use. The depolarized light intensity (DLI) technique was used to follow the crystallization of samples. 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 a melting temperature (TM) for a period of time 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:

$$X_t = (I_t - I_0)/(I_\infty - I_0) \tag{1}$$

where I_0 , I_∞ are the intensity values of depolarized light before and after the crystallization transformation, respectively. A BM-11 polarized light microscopy (PLM) (Jiangnan Optics and Electronics Co. Ltd., Nanjing, China) was used to observe the morphology of crystallizing and crystallized sample films and the microstructures were recorded by a CCD camera.

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