

# The Complicated Influence of Branching on Crystallization Behavior of Poly(ethylene Terephthalate)

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**ABSTRACT:** The randomly branched poly(ethylene terephthalate) (BPET) was prepared by bulk polycondensation from dimethyl terephthalate (DMT) and ethylene glycol (EG), with 0.4–5.0 mol % (with respect to DMT) of glycerol (GL) as a branching agent. The glass transition and crystallization behavior was studied by differential scanning calorimetry (DSC). It was found that the glass transition temperature of BPET reduced with the increasing content of GL until 1.2 mol %, and then increases a little at high degrees of branching. When compared with a linear PET, the crystallization temperature of BPET from the melt shifted to higher temperature as GL content was smaller than 1.2 mol %, and then became lower while GL load was added. Nonisothermal crystallization kinetics was studied through the modified Avrami analysis. It was revealed that the overall crystallization rate parameter of BPET became larger when the GL content was

less than 1.2 mol %, then turned to lower at higher branching degree. This indicated that low degree of branching could enhance the overall crystallization of poly(ethylene terephthalate) (PET), whereas high degree of branching in the range of 3.5–5.0 mol % would block the development of crystallization. On the basis of Hoffman's secondary crystallization theory, the product  $\sigma\sigma_c$  of the free energy of formation per unit area of the lateral and folding surface was calculated. According to the change of the product  $\sigma\sigma_c$  with the degree of branching, a possible explanation was presented to illuminate this diverse effect of different degrees of branching on crystallization. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 1649–1655, 2008

**Key words:** crystallization; poly(ethylene terephthalate); branched architecture

## INTRODUCTION

Poly(ethylene terephthalate) (PET) is a semi-crystalline polyester widely used in many fields because of its good mechanical and thermal properties, as well as its processability. At the same time there have still been many efforts to modify macromolecular architecture of PET to improve its properties for these decades. For example, modified PET containing ionic groups in polymeric chains exhibited improved cation dye uptake.<sup>1,2</sup> Segmented PET copolymer by incorporation of polyethylene glycol as soft segments showed good toughness.<sup>3,4</sup> Branched and partially crosslinked PET could be expected to show greater melt strength than linear PET, which resulted in better foaming characteristic in extrusion foam processing.<sup>5–7</sup> Furthermore, slightly branched PET (BPET) has also found its application in high-speed spinning fiber formation.<sup>8</sup>

The introduction of branching to PET could cause the imperfection of macromolecular chains, and

might thus lead to the varied crystallization behavior. Jayakannan and Ramakrishnan studied the crystallization behavior of BPET with trifunctional aromatic monomer as a branching agent and found that crystallization temperature from the melt of BPET was lower than that of linear PET. At the same time, they also noticed that the presence of branching, in small concentrations, appeared to enhance the crystallinity.<sup>9</sup> Rose et al. prepared BPET containing trifunctional comonomer glycerol (GL) (2.0–7.0 mol %) and tetrafunctional comonomer pentaerythritol (3.0–5.0 mol %). They reported that branching did not alter the crystallinity, but reduced the rate of crystallization.<sup>10</sup> Righetti and Munari obtained BPET according to the polycondensation starting from dimethyl terephthalate (DMT), butanediol, and 0–1.5 mol % (with respect to DMT) of trifunctional monomer 1,3,5-tricarboxymethylbenzene. A depression in the crystallization rate was observed as the content of branching units increased, and their results suggested that in the presence of branching points the nucleation process was favored. They believed that in the branched samples the reduced chain mobility, because of entanglement, would favor the survival of residual crystalline structure after the melting at 260°C, giving rise to a self-nucleation.<sup>11</sup> In one of the previous works, we

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**TABLE I**  
**Samples Labeled and Their Feed Composition,**  
**Intrinsic Viscosities**

Samples (%)	DMT/mol	EG/mol	GL/mol	Intrinsic viscosity/dL g <sup>-1</sup>
BPET-0	1	1	0	0.66
BPET-0.4	1	0.996	0.004	0.69
BPET-0.8	1	0.992	0.008	0.72
BPET-1.2	1	0.988	0.012	0.74
BPET-3.5	1	0.965	0.035	0.71
BPET-5.0	1	0.950	0.050	0.74

once found that very small degrees of branching (0–1.2 mol % GL over DMT) could make the overall crystallization rate of PET higher during isothermal crystallization, although it also led to a longer induce time.<sup>12</sup> However, by the same small extent of incorporation of GL in the more flexible poly(butylene terephthalate)-polyether chains no enhanced crystallization was observed.<sup>13</sup> Therefore, it was really hard to give a certain conclusion about the influence of branching on crystallization of polyester, especially under the situation that most existing work focused on relatively high degrees of branching.

Although it has been mentioned that high degrees (3.5–5.0 mol %) of branching in PET may block the development of crystallization,<sup>13</sup> it was still worth considering the diverse effect of branching with varied degrees of crystallization of PET. In this work, nonisothermal crystallization kinetics of BPET with a wide branching range was investigated to understand the relationship between the branched architecture and crystallization characteristics.

## EXPERIMENTAL

### Preparation of branched poly(ethylene terephthalate)

BPETs were prepared from DMT and EG with 0.4 ~ 5.0% mole ratio of trifunctional GL with respect to DMT as a branching agent by bulk polycondensation via a method just described elsewhere.<sup>10,11</sup> According to the GL content, all these samples, referred to as BPET-0%, BPET-0.4%, etc., were given in Table I.

### Measurements

The chemical composition of BPET was analyzed by means of <sup>1</sup>H NMR analysis (Avance 400 Bruker) with D-trifluoroacetic acid used as solvent. Inherent viscosities were measured at 25°C by using an Ubbelohde viscometer in phenol/1,1,2,2-tetrachloroethane (50 : 50 wt) solvent. Differential scanning calorimetry (DSC, Perkin-Elmer Pyrist) was used to detect the

heat flow from the samples during heating and cooling processes. All the samples were first heated up to 280°C and were kept at this temperature for 3 min to eliminate any thermal history. The exothermic enthalpy in nonisothermal crystallization from the melt during cooling at the rate of 5.0 ~ 15°C/min was recorded. High purity nitrogen atmosphere was supplied during measurement to minimize degradation.

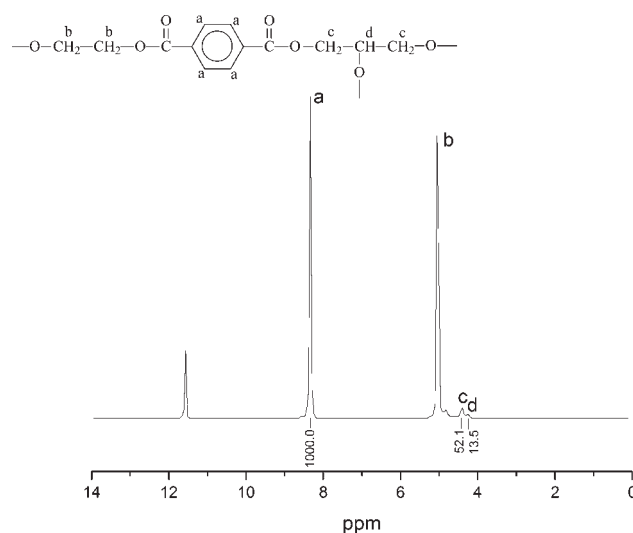
## RESULTS AND DISCUSSIONS

### Chemical composition of BPET

For a typical example, the <sup>1</sup>H NMR spectrum of the BPET-5.0% was given in Figure 1. There were four peaks in the spectrum that correspond to four kinds of protons in the macromolecular structure of BPET. Furthermore, the integral area ratio of proton *c* over proton *a* was about 5 mol %, matching the feed mole ratio of GL over DMT, so it could be concluded that GL was stoichiometrically linked to macromolecular chains of PET. Furthermore, the intrinsic viscosities of each sample were also listed in Table I.

### Glass transition and crystallization of BPET

The glass transitions of BPETs with different extents of branching were given in Figure 2. The glass transition temperature (*T<sub>g</sub>*) firstly decreased with increasing branching till GL addition reached to 1.2 mol %, and then increased slightly when more GL (3.5–5.0 mol %) was added; however, the *T<sub>g</sub>* of each BPET sample was lower than that of BPET-0%, i.e., the linear PET (Table II). It was well known that branched macromolecule possessed a smaller mean square radius of gyration compared with a linear



**Figure 1** Chemical composition and <sup>1</sup>H NMR spectrum of BPET-5.0%.

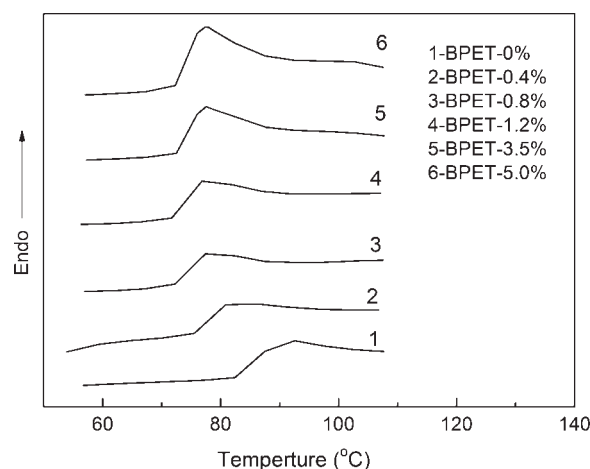


Figure 2 Glass transitions of BPET.

macromolecule with the same molecular weight. Therefore, there would be less entanglements and more free volume in BPETs, resulting in a lower  $T_g$ . The increment  $T_g$  under a relatively high-GL content (3.5–5.0 mol %) should be attributed to the partial crosslink, which could limit the mobility of polymer segments.<sup>14,15</sup>

The lowering of  $T_g$  would promote crystallization.<sup>16,17</sup> Actually, the crystallization temperatures ( $T_{ch}$ ) in the low-temperature region from the glass state decreased with increasing content of GL, as shown in Figure 3(a). Moreover, the crystallization of BPET-3.5% and BPET-5.0% showed double peaks, one was lower whereas the other was higher than the  $T_{ch}$  of BPET-0%, implying a diverse effect of branching at high degrees. The crystallization temperatures ( $T_{cc}$ ) in the high-temperature region from the melt of BPETs were also given in Figure 3(b), and the corresponding exothermic enthalpies ( $\Delta H_{cc}$ ) were listed in Table II. When compared with BPET-0%, the crystallization of BPET developed at relatively higher temperature region as the GL content was less than 1.2 mol %, and then the  $T_{cc}$  decreased considerably with addition of 3.5–5.0 mol % of GL. The crystallization exothermic curves from the melt at different cooling rates such as 5, 10, and 15°C/min also indicated that BPETs with the low-branching degree (1.2 mol % GL) could accomplish crystallization under each cooling rate; but highly BPETs (3.5

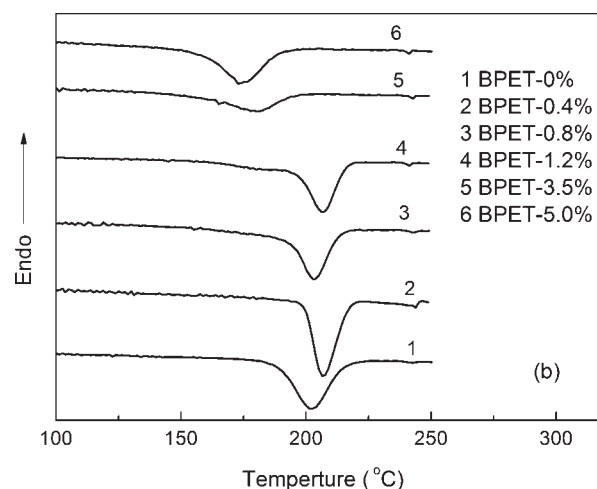
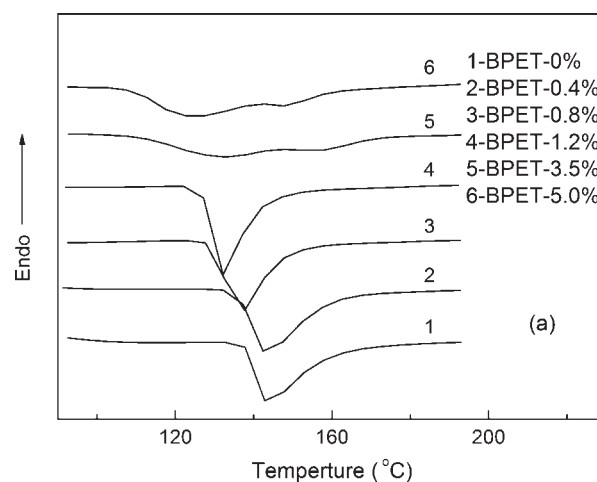


Figure 3 Crystallization curves from the glass state (a) and the melt (b).

mol % GL) could not complete the crystallization under high rates (10 and 15°C/min). So the exothermic peaks were observed at about 160°C on the second heating of BPET-3.5%, which correspond to the compensatory crystallization from glass state (Figs. 4 and 5). Thus it could be inferred that weakly BPET could crystallize easier than highly BPET. The melting temperatures ( $T_m$ ) of BPETs became low, which was similar as reported in other literature.<sup>10,11,18</sup> However, the  $T_m$  and the melting enthalpy ( $\Delta H_m$ ) of BPETs at 0.4–1.2 mol % kept almost unchanged with respect to the degree of branching (Table II).

### Nonisothermal crystallization kinetics

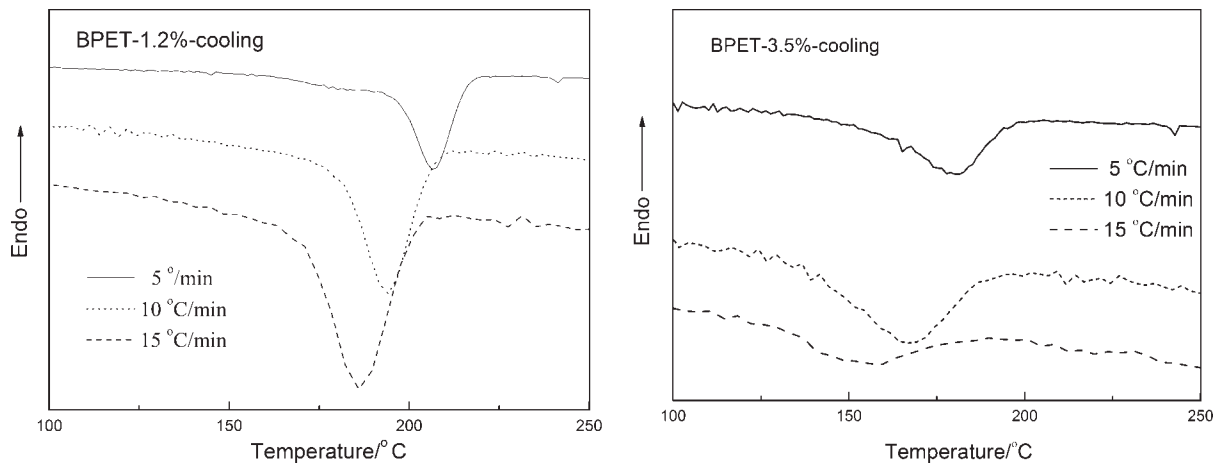
The Avrami analysis can be extended for nonisothermal crystallization just as described previously in the literature.<sup>19–22</sup>

$$X(t) = 1 - \exp(-Z_t t^n) \quad (1)$$

Where,  $Z_t$  is the crystallization rate parameter associated with the rate of nucleation and Avrami

TABLE II  
The Data from DSC for BPETs (10°C/min)

Samples (%)	$T_g/^\circ\text{C}$	$T_m/^\circ\text{C}$	$\Delta H_{cc}/\text{J g}^{-1}$	$\Delta H_m/\text{J g}^{-1}$
BPET-0	86.4	264.2	39.3	39.2
BPET-0.4	78.6	255.7	41.1	39.5
BPET-0.8	75.1	255.6	41.6	41.4
BPET-1.2	74.3	254.8	34.4	38.7
BPET-3.5	75.1	246.6	17.6	33.2
BPET-5.0	74.9	237.3	21.2	32.9



**Figure 4** Crystallization exothermic peaks on cooling from the melt.

exponent  $n$ ,  $X(t)$  the relative crystallinity developed after time  $t$ .

According to the results of DSC analysis, for nonisothermal crystallization at a chosen cooling rate the relative crystallinity  $X(T_c)$  can be formulated as:<sup>19–22</sup>

$$X(T_c) = \frac{\int_{T_0}^{T_c} (dH_c/dT)dT}{\int_{T_0}^{T_\infty} (dH_c/dT)dT} \quad (2)$$

where  $T_c$  is the crystallization temperature,  $T_0$  and  $T_\infty$  represent the onset and end temperature of crystallization, respectively, and  $dH_c$  is the enthalpy of crystallization released during an infinitesimal temperature range  $dT$ .

The crystallization temperature  $T_c$  in eq. (2) can be converted to crystallization time  $t$  according to eq. (3), where  $\phi$  is the cooling rate.

$$t = \frac{|T_0 - T_c|}{\phi} \quad (3)$$

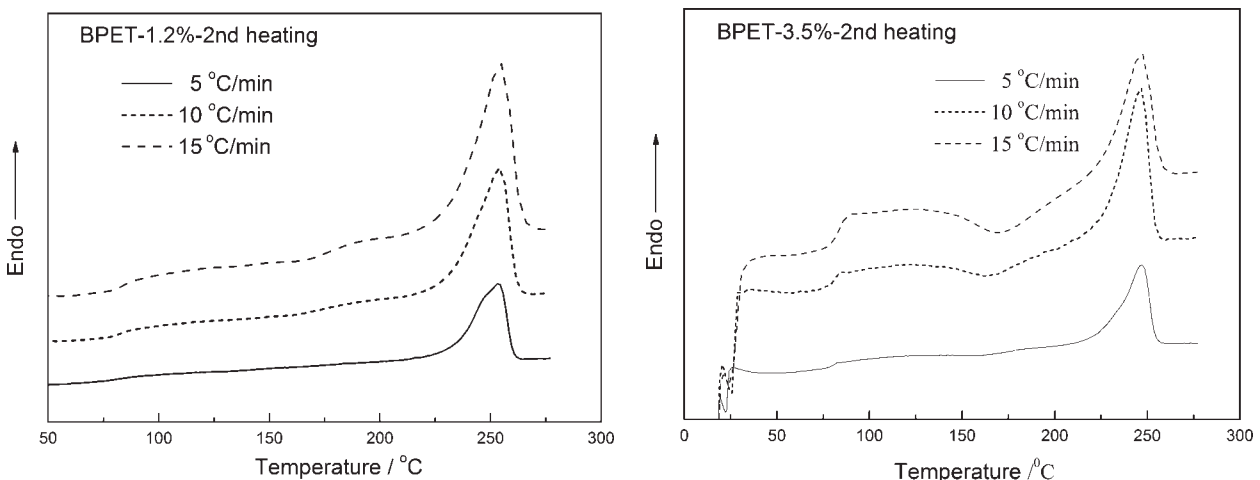
After the double logarithmic form of eq. (1), we can obtain:

$$\log [-\ln(1 - X(t))] = \log Z_t + n \log t \quad (4)$$

In a nonisothermal crystallization process,  $Z_t$  can be further modified by the cooling rate  $\phi$  as eq. (5), where  $Z_c$  is the kinetic rate parameter of nonisothermal crystallization.

$$\log Z_c = (\log Z_t)/\phi \quad (5)$$

According to eq. (4), the Avrami parameter  $n$  and the crystallization rate parameter  $Z_t$  for each BPET sample could be obtained from the linear regression



**Figure 5** The second heating curves from DSC.

TABLE III  
Kinetics Crystallization Rate Parameter and Avrami Exponent of BPETs on Nonisothermal Crystallization based on the Modified Avrami Analysis

Samples (%)	$Z_c/\text{min}^{-1}$			$n$			$t_{1/2}/\text{min}$ (exp)
	5°C	10°C	15°C	5°C	10°C	15°C	10°C
BPET-0	0.317	0.655	0.862	3.6	3.5	3.6	2.74
BPET-0.4	0.459	0.771	0.911	3.6	3.5	3.6	1.95
BPET-0.8	0.476	0.778	0.917	3.2	3.4	3.1	1.91
BPET-1.2	0.527	0.778	0.936	3.5	3.5	3.0	1.79
BPET-3.5	0.289	0.627	0.797	3.1	3.1	3.1	2.79
BPET-5.0	0.304	0.628	0.801	3.5	3.4	3.2	2.76

analysis of DSC data, and the results were shown in Table III.

For the primary crystallization of linear PET and BPET, Avrami exponent  $n$  is estimated to be 3.5–3.6 and 3.0–3.6, respectively, depending upon the cooling rate. The  $n$  values of linear PET here is slightly higher than that reported previously.<sup>19,23</sup> Phillips and Manson suggested that for the PET homopolymer the nonisothermal crystallization in the early stage followed either three-dimensional growth with heterogeneous nucleation or two-dimensional growth with homogeneous nucleation.<sup>23</sup> In this study, it is believed that both PET and BPET crystallize according to three-dimensional or truncated spherical growth of crystallization with either homogeneous or heterogeneous nucleation.

It is important to note that  $Z_c$  values increase firstly with increasing content of GL until 1.2 mol %, and then decrease at high degrees of branching (3.5–5.0 mol %). The half-time of crystallization ( $t_{1/2}$ ) shows the same trend. This result is agreement with the change of  $T_{cc}$  observed on cooling from DSC mentioned earlier.

Actually, it has been widely reported that the branching retarded crystallization.<sup>9,14,18</sup> Concerning the crystallization of polyester, the small degrees of branching (lower than 1% mol ratio) were usually neglected by most researchers. According to the analysis results of both the isothermal crystallization<sup>12</sup> and the nonisothermal crystallization mentioned in this study, we suggest that the small degrees of branching (less than 1.0–1.2 mol %) could enhance whereas high degrees of branching would block the crystallization of PET.

#### Analysis of the influencing of branching on crystallization based on Lauritzen-Hoffman expression

Bulk crystallization initiates with a primary nucleation and is followed by crystal growth on the primary nucleation. It should be emphasized that overall crystallization rate is the combination of nucleation and crystal growth. The crystal growth is

strictly a process controlled by the secondary nucleation. The temperature dependent linear growth rate ( $G$ ) could be analyzed according to Lauritzen-Hoffman (HF) expression,<sup>11,24–26</sup>

$$G = G_0 \exp\left[\frac{-U^*}{R(T_c - T_\infty)}\right] \exp\left[\frac{-K_g}{fT_c(\Delta T)}\right] \quad (6)$$

where the first term represents a contribution due to diffusion of the polymeric segments and the second concerns the thermodynamic driving force. In the HF expression,  $G_0$  is a temperature independent pre-exponential term,  $U^*$  is the transport activation energy of crystallizable polymer segments at liquid–solid interface,  $T_\infty$  is the hypothetical temperature below which all viscous flow ceases,  $f(f = 2T_c/(T_m^0 + T_c))$  is a correction factor to accounts for the change of enthalpy of fusion ( $H_f^0$ ) of the perfect crystal,  $\Delta T$  is the degree of undercooling  $\Delta T = T_m^0 - T_c$ ,  $R$  is the gas constant, and  $K_g$  is the nucleation constant, which can be expressed as:

$$K_g = \frac{mb\sigma\sigma_e T_m^0}{kd\Delta H_f^0} \quad (7)$$

where  $m$  is a parameter which depends on the regime of crystallization,  $b$  is the distance between two adjacent fold planes,  $\sigma$  and  $\sigma_e$  are the free energy of formation per unit area of the lateral and folding surface, respectively,  $d$  is the density while  $k$  is the Boltzmann constant, and  $T_m^0$  is the equilibrium melting point of crystalline polymer.

The overall crystallization growth rate of the crystallization gives a better correlation of theory and experimental observation than the rate of spherulitic radial growth.<sup>11,25,26</sup> Assuming that the three-dimensional crystal growth is linear with time, the overall kinetic parameter  $k_3$  ( $k_3$  equivalent to  $Z_c$  obtained from Avrami analysis in this study) can be written as:

$$k_3 = (4\pi/3)G^3N \quad (8)$$

where  $N$  is nucleation density.



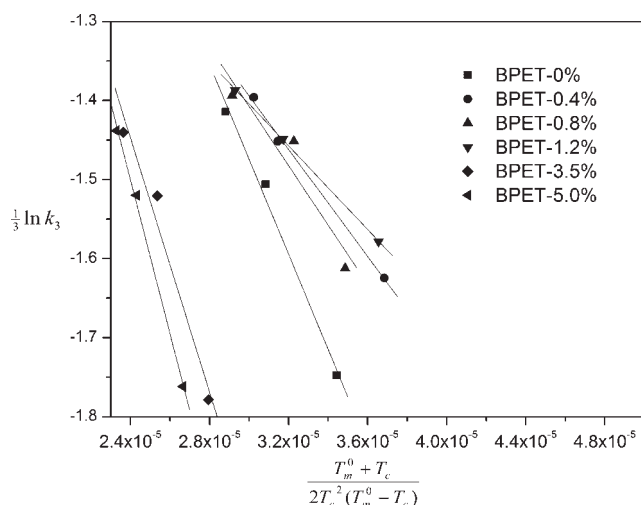
From eqs. (6) and (8), the following relationship can be obtained:

$$\frac{\ln k_3}{3} = C_0 - \frac{U^*}{R(T_c - T_\infty)} - \frac{K_g}{fT_c\Delta T} \quad (9)$$

with  $C_0 = \ln G_0 - \frac{1}{3} \ln \frac{3}{4\pi N}$ . Assuming that the transport term is constant, the slope of linear plot of  $\ln k_3$  versus  $\frac{1}{fT_c\Delta T}$  gives the nucleation constant ( $K_g$ ), which could be used to calculate the product  $\sigma\sigma_e$  according to eq. (7).

Assuming the PET folding along (010) plane,<sup>11,25</sup> the layer thickness  $b$  is estimated to be 5.94 Å and the density  $d$  of perfectly crystalline phase is equal to 1.455 g/cm<sup>3</sup>, using the value  $T_m^0$  and  $\Delta H_f^0$  as 267°C and 117.6 J/g respectively,<sup>27</sup> the lines for all samples were plotted in Figure 6, from which the product  $\sigma\sigma_e$  was obtained and presented in Table IV.

The product  $\sigma\sigma_e$  decreased firstly with the increasing degree of branching till 1.2 mol % of GL, then became larger with the more addition of GL. The similar change of the product  $\sigma\sigma_e$  was reported by Kalkar and Deshpande for PBT/Vectra A950 (VA) blends.<sup>26</sup> That is, the product  $\sigma\sigma_e$  decreases with increasing VA content as the load of VA is smaller than 40 wt %, then becomes larger when the content of VA exceeds 50 wt %. Concerning BPETs in this study, low degrees of branching provided more free volume and less intermolecule interactions, whereas relative high degrees of branching led to partially crosslinked structures, which could restrict the polymer chains motion. In this way low degrees of branching could depress the chain folding energy barrier and be in favor of chain folding, whereas high degrees of branching would increase the chain folding energy and retard polymer chains mobility.



**Figure 6** Kinetic analyses of the overall crystallization growth rate data for BPETs.

**TABLE IV**  
Values of  $\sigma\sigma_e$  for BPETs with Different Degrees of Branching

Samples (%)	$\sigma\sigma_e$ (erg <sup>2</sup> /cm <sup>4</sup> )
BPET-0.0	305.62
BPET-0.4	171.99
BPET-0.8	171.48
BPET-1.2	134.54
BPET-3.5	409.64
BPET-5.0	523.33

The melting enthalpy ( $\Delta H_m$ ) shows a little increase and the  $T_m$  is almost the same as GL addition is in a small amount (0.4–1.2 mol %), but they all decrease as more GL is added (Table II), which could also result from the same reason mentioned earlier.

## CONCLUSIONS

The glass transition temperature of BPET decreases with increasing content of GL ranged from 0 to 1.2 mol % with respect to DMT, then increases a little at high content of GL (3.5–5.0%), implying the varied mobility of PET chains at different degrees of branching. The crystallization temperatures of these BPETs from the glass state generally fall with increasing content of GL, whereas the crystallization temperatures from the melt firstly shift to higher temperature as the addition of GL is low, and then move to lower temperature when the branching is high compared with that of linear PET. The study on nonisothermal crystallization kinetics explains that a small degree of branching (smaller than 1.2 mol %) could enhance the overall crystallization of poly(ethylene terephthalate), but a higher degree (3.5–5.0 mol %) of branching would block the development of crystallization. The product  $\sigma\sigma_e$  was found to decrease with increasing degree of branching until 1.2 mol %, and then increase at high extents of branching (3.5–5.0%). It could be concluded that the observed complicated effect of branching on crystallization behavior is the result of competition between two sides: one is in favor of crystallization growth resulting from more motion of polymer chains; the other is to depress the crystallization rate owing to more disorder and/or partial crosslink from branching architecture.

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