Effect of Self-Nucleation on the Crystallization of Segmented Copolymer Poly(Ether Ester)

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ABSTRACT: The effect of self-nucleation on the nonisothermal and isothermal crystallization behaviors of the segmented copolymer poly(ether ester), based on poly(ethylene glycol) as the soft segment and poly(ethylene terephthalate) as the hard segment was investigated by means of differential scanning calorimetry (DSC) and depolarization polarized light (DPL) techniques, respectively. The results demonstrated that self-nucleation could enhance the crystallization rate in both cases. The experimental conditions of the self-nucleation procedure studied by DSC were discussed in detail. The isothermal crystallization was analyzed by the Avrami equation, and the Avrami parameters were dependent on the melting temperature. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 498–504, 2001

Key words: segmented copolymer; poly(ethylene terephthalate); poly(ethylene glycol); self-nucleation; crystallization

INTRODUCTION

The overall crystallization in polymers is a combination of the nucleation and crystal growth. There are three kinds of nucleation: homogeneous nucleation, heterogeneous nucleation, and self-nucleation. The term self-nucleation has been used to describe the nucleation of macromolecular melt or solution by its own crystals grown previously.[1] The self-nucleation technique for growing crystals of macromolecules from solution has been established by Blundell et al.[2] Recently, differential scanning calorimetry (DSC) technique has been applied to study the effect of self-nucleation on the crystallization of polymer.[3] From the research on it, it has been known that self-nucleation has much influence not on the crystallization rate of the polymer,[4] but also on its morphology.[5]

The segmented copolymer poly(ether ester) is a class of materials that exhibit elastomer-like properties at service temperatures, but can be processed as ordinary plastics at elevated temperature. This class of segmented copolymers consists of two types of segments: the "soft" segments are in a rubbery state and give flexibility to the material; the "hard" segments are capable of undergoing intermolecular association or crystallization to form a thermally reversible network structure. The physical crosslinks resulting from crystallization of the hard segments provide for the modulus, strength, and creep resistance of the

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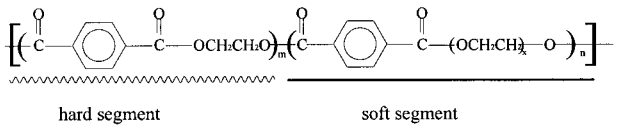
material. The requirement necessary for achieving the ideal morphology is: high crystallization rate of hard segments at temperature higher than the ambient temperature in melt processing to eliminate the deformation-induced orientation prior to the crystallization.[6,7] In the case of melt spinning for the copolymer poly(ether ester), the sluggish crystallization kinetics of the hard segments causes sticking and stretching problems during the processing. Because the crystallization behavior of hard segments crystallization is a key and controlling factor governing the formation of physical crosslinks and subsequent mechanical properties of the copolymer poly(ether ester), it is of importance to study the effect of the self-nucleation process on the crystallization behaviors of the segmented copolymer poly(ether ester).

The present investigation is to study the effect of self-nucleation on the nonisothermal and isothermal crystallization behaviors of the segmented copolymer poly(ethylene terephthalate)-poly(ethylene glycol) by differential scanning calorimetry (DSC) and depolarization polarized light (DPL) techniques, respectively. The experimental variables in the self-nucleation procedure using the DSC technique were discussed in detail. The Avrami equation was used to analyze the isothermal crystallization, and its parameters were obtained and discussed.

EXPERIMENTAL

Sample Preparation and Characterization

The segmented copolymer of poly(ester ether) was prepared by the transesterification and polycondensation reactions. Blends of dimethyl terephthalate, ethylene glycol, and poly(ethylene glycol) (PEG) of average number molecular weight ca. 2000 with a small amount of catalyst, such as zinc acetate and antimony trioxide, were heated to at 180–200°C for about 2 h in a stream of pure nitrogen, then increased to nearly 260°C in a vacuum of 40–60 Pa until the viscosity of reaction system approached a certain degree. The inherent viscosity of the product was measured in 60/40 phenol/tetrachloroethane at 25°C by Schott Gerate CT150 viscometer. The inherent viscosity $[\eta]$ of the sample is 0.81 (dL/g). The composition of the copolymer was analyzed by a JEOL FX-90Q spectrometer and found to be in agreement with the composition expected from the composition of the reaction mixture that the copolymer composed 40 wt % of soft segments (PEG). The products have the chemical units as shown as the following:



The thermal stability of the sample was performed with a Perkin-Elmer TGA-2 instrument in nitrogen atmosphere at flow rate of 40 mL/min.

Differential Scanning Calorimetry (DSC)

DSC was performed using a Perkin-Elmer DSC-2 calorimeter equipped with a TADS microcomputer in this investigation to characterize the crystallization of the poly(ether ester). The temperature scale of the DSC instrument was calibrated using the highly purified indium. Unless otherwise stated, the heating and cooling rates of 10 K/min were used in the experiments discussed.

Application of DSC to Study the Effect of Self-Nucleation on the Nonisothermal Crystallization of Poly(ether ester)

The extension of the self-nucleation procedure to the DSC has been described in detail in ref. 3 [also see in Fig. 1(a)]. Four thermal steps are required in the self-nucleation procedure, which are corresponding to (A) erasure of the previous thermal history, (B) creation of a crystalline "standard" state in the sample, (C) partial melting the sample at a temperature, T_s, and (D) crystallization at a temperature, T_{c2}.

Application of DPL to Study the Effect of Self-Nucleation on the Isothermal Crystallization of Poly(ether ester)

The procedure of application the DPL to studying the effect of self-nucleation on the isothermal crystallization was also consistent of four steps [see Fig. 1(b)]. The former three steps, for example, (A), (B), and (C), was the same as the procedure described above. In the final step, D, the partial melted sample was cooled to a predetermined temperature to crystallize isothermally, and the crystallization rate was measured by the DPL apparatus made by the Institute of Chemistry of the Chinese Academy of Sciences. The sample melted at a given temperature in the melting stove for 5 min, then transformed to the crystallization stove immediately. The light transmission through crossed polarizers is

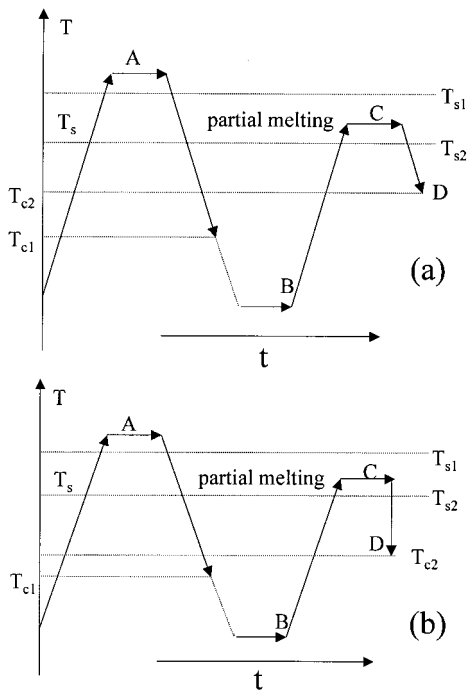


Figure 1 Schematic of self-nucleation study procedure with DSC (a) and DPL (b), respectively.

monitored as a function of time with a photocell and chartrecorder.

RESULTS AND DISCUSSION

Erasure of the Previous Thermal History

It is known from the self-nucleation from solution that the number of surviving nuclei was depended on the temperature and time of original crystallization, and the time spent at temperatures above the original crystallization temperature.[1] The effect of self-nucleation on the polymer crystallization from melt also demonstrates that the temperature to which the molten polymer is raised prior to crystallization may be an important factor in determining subsequent behavior.[8–10] So the step of erasure the former thermal history is a critical factor in this procedure. Normally, to erase of the former thermal history polymer is often heated to the temperature 20–40 K above its melting temperature (T_m) or equilibrium melting point (T_m^0), but whether the aim is reached has not been discussed in detail.[3] The DSC thermogram of sample used was show in Figure 2. It shows that a wide endotherm appears in the temperature range from 427 to 532 K. Therefore, to affirm the effect of removal the former thermal history of the sample, the sample of poly(ether ester) was heated to the temperature near the end of melting range to those higher than it, and held for 5 min, then cooled to room temperature. The peak temperature of the exotherm was used to characterize the effect. As shown in Figure 3 the peak temperature of the exotherm drops significantly to lower temperature as the T_m increased up to 543 K. The phenomena indicated that the number of nuclei decreased with the increase of T_m. The remains seem to be foreign, and temperature-resistant heterogeneous nuclei present in the melt. However, the peak temperature shifts to higher temperature at higher melting temperature instead, which may be caused by the posttransesterification of the polymer resulted in the sequential reordering of the hard sequences[11] or the thermal degradation.[12] Although the curve from the thermogravimetric analysis for the sample (see in Fig. 4) shows that the onset thermal degradation of the copolymer is about 654 K. Therefore, to avoid the variations in the hard segments a temperature of 543 K was chosen as the temperature to erase the former thermal history in our experiments. And further, Figure 5 shows that the melting time has little effect on the peak temper-

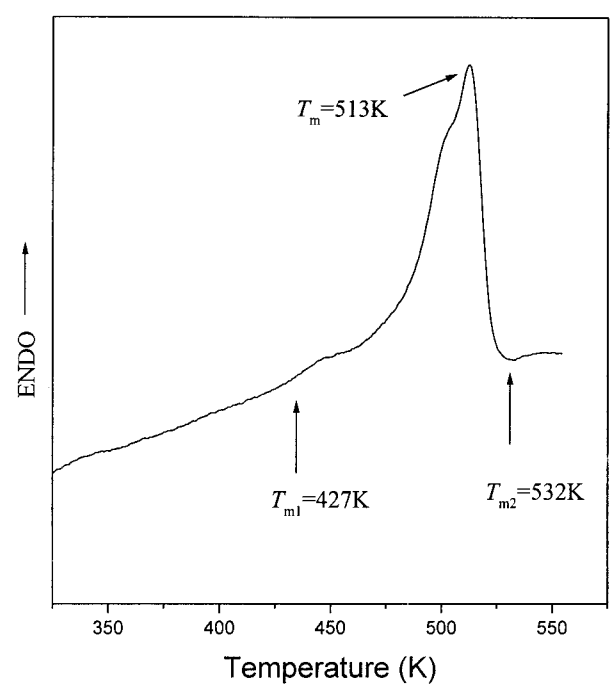


Figure 2 DSC heating curve of the copolymer poly(ether ester).

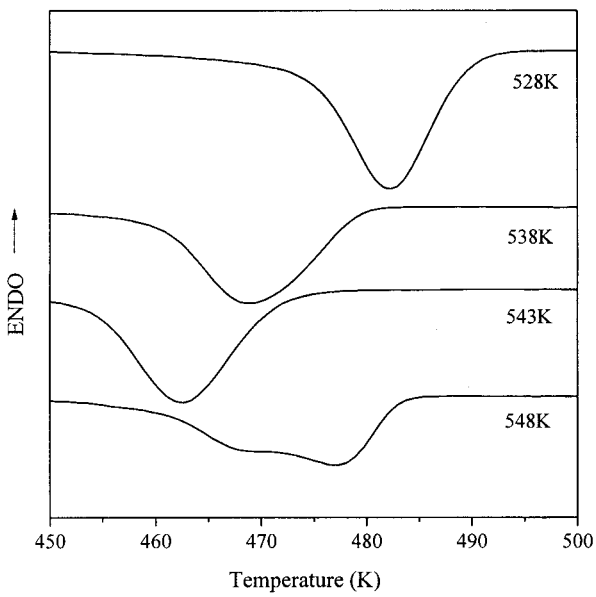


Figure 3 The crystallization exotherms of the poly(ether ester) melted at the temperature as indicated for 5 min.

ature, which was also in line with the results of Keller[13] and Wittmann.[5] So samples of the poly(ether ester) were held at 543 K for 5 min to erase the previous thermal history.

Nonisothermal Crystallization Behavior

It is reported that the determinant variable in the self-nucleation procedure is the self-nucleation

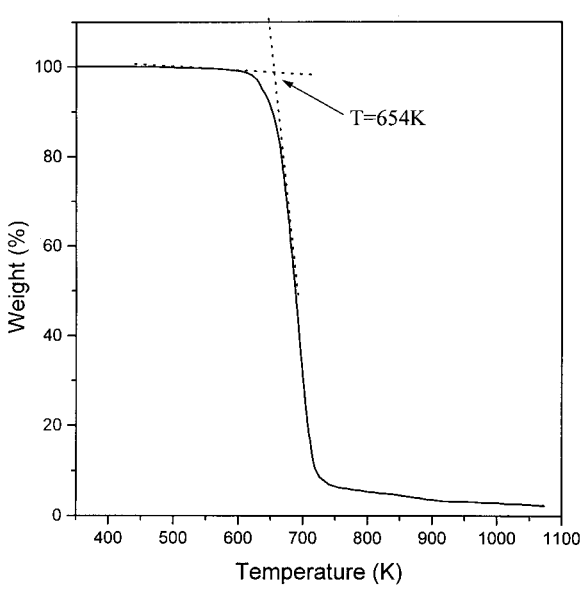


Figure 4 TGA curve for copolymer Poly(ether ester) heated in nitrogen atmosphere at 10 K/min.

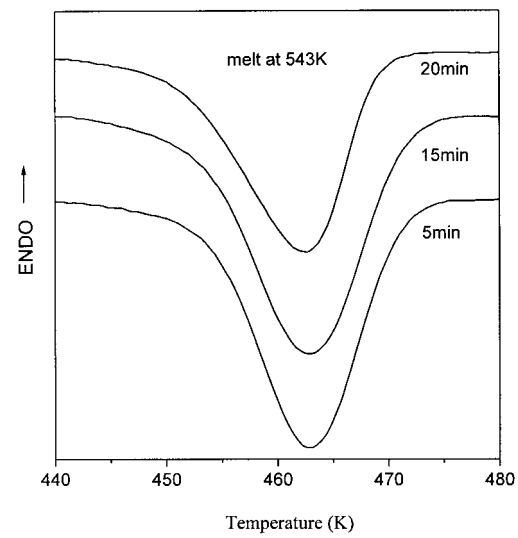


Figure 5 Crystallization exotherms of the poly(ether ester) melt at 543 K for different times.

temperature, T_s, and it also affected the crystallization behaviors of the polymer.[3] Figure 6 demonstrates that the crystallization behaviors of the poly(ether ester) after melting at various T_s. The crystallization temperature T_{c2} significantly shifts to a lower temperature as T_s increased. The dependence of T_{c2} on T_s indicated that more crystal fragments sustained with decreasing T_s, and they acted as nucleus in the subsequent process of crystallization, so self-nucleation enhanced the crystallization rate of poly(ether ester) significantly. Figure 6 also indicated that two temperature domains for self-nucleation could be determined: domain I, $T_s < 524$ K, in which poly(ether ester) melted incompletely, and recrystallized rapidly on subsequent cooling, and domain II, 524 K $< T_s <$ 543 K, in which the concentration of remaining crystal fragments varies dramatically with T_s. A small variation in T_s results in a significant shift of T_{c2} in the subsequent cooling. Thus, domain II was an effective temperature domain to study the effect of self-nucleation on the crystallization behavior for the poly(ether ester).

It was worthy to note that the other experimental variables in the procedure may affect the effect of self-nucleation. It is shown from Figure 7 that T_{c2} shifts to lower temperature with only increasing the cooling rate in the step to create a "standard" crystalline state. It assumed that more crystal fractions were present and in a more perfect form in the case of lower cooling rate so that more nuclei remained after partial melting.

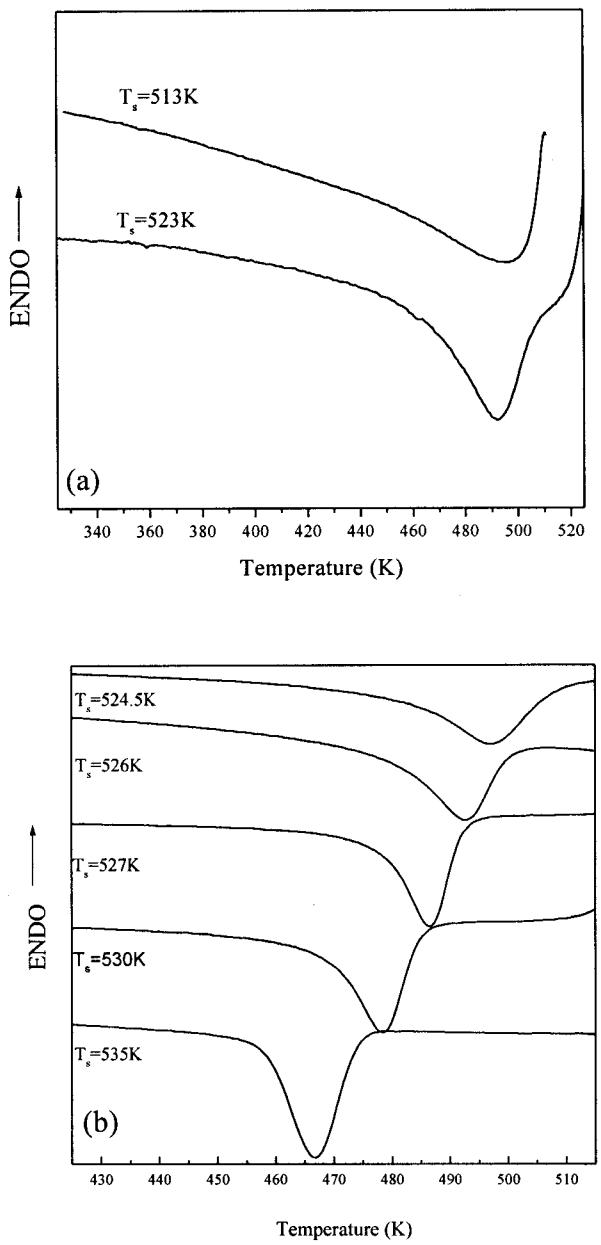


Figure 6 Crystallization exotherms of poly(ether ester) after partial melt at different temperatures, as indicated.

It was needed to note that to get to the self-nucleation temperature at the heating rate of 10 K/min, the sample examined at the highest annealing temperature spends 4 extra minutes at an elevated temperature compared to the sample that was evaluated at the lowest annealing temperature. Therefore, the effects of the heating rate from the step B to step C and the partial melting time t_s on T_{c2} were shown in Figures 8 and 9, respectively. Both figures show that T_{c2} is independent of the two experimental parameters.

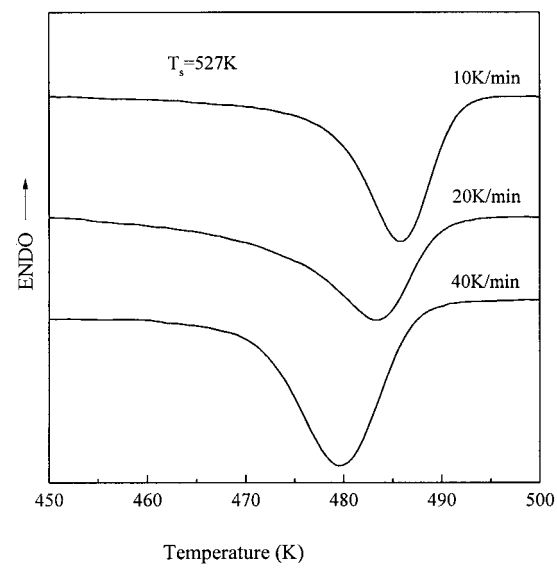


Figure 7 Effect of the cooling rate as indicated in the step to create a "standard" crystalline state on the recrystallization temperature T_{c2}.

Isothermal Crystallization Behavior

The recording of the depolarization of linearly polarized light vs. time has developed into a useful technique for studying the kinetics of isothermal crystallization of polymer.[14,15] Crystallization half-times can be interpolated directly from

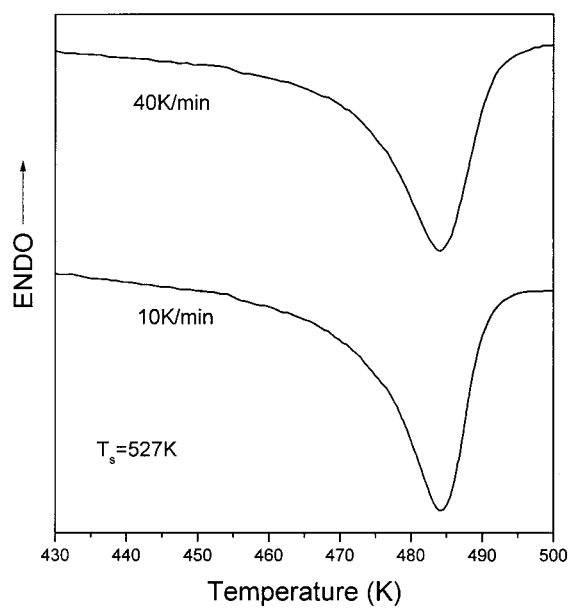


Figure 8 Effect of heating rate as indicated from state B to state C on the self-nucleation of poly(ether ester).

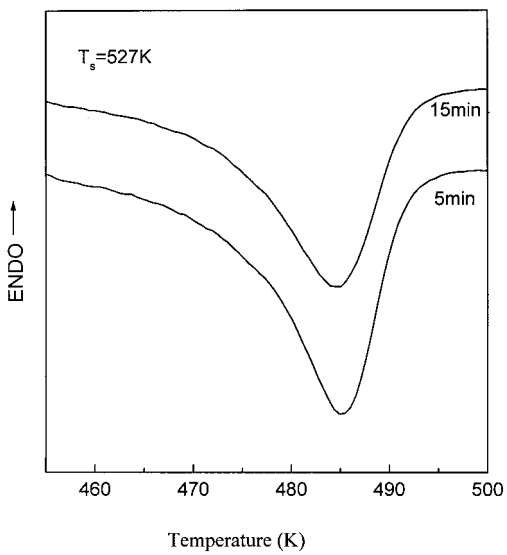


Figure 9 Crystallization exotherms of poly(ether ester) partial melting at 527 K for different times, as indicated.

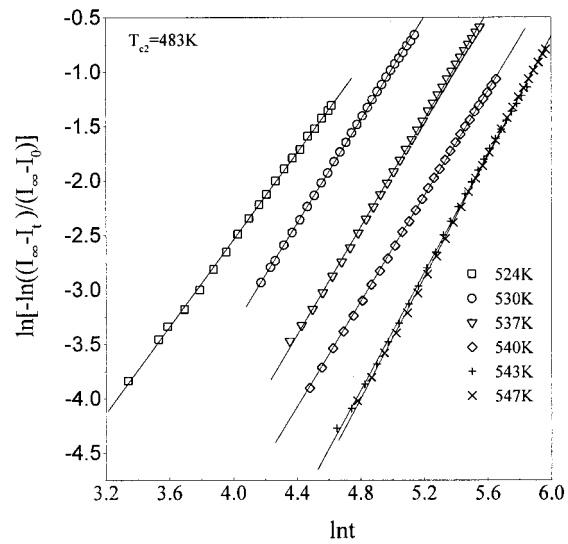


Figure 10 Avrami plot of isothermal crystallization behavior of poly(ether ester) at 483 K after melt at different temperatures.

normalized light transmission/time plots of the form $(I_\infty - I_t)/(I_\infty - I_0)$ vs. log t, where I_0 and I_∞ are initial and final intensities, and I_t the intensity at time t. Rate constants can be calculated from the Avrami equation:

$$\theta_t = \exp(-Kt^n) \tag{1}$$

where θ_t is the fraction of uncrystallized polymer at the time t; the exponent, n, depends on the type of nucleation and the crystal growth geometry. The parameter K is also a function of nucleation and growth. The Avrami parameters, n and K, can be determined by plotting

$$\ln\left[-\ln\left(\frac{I_\infty - I_0}{I_\infty - I_t}\right)\right]$$

vs. ln t (see Fig. 10). The crystallization half-time, $t_{1/2}$, characterized as the crystallization rate, can also be obtained from the expression:

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

The results of the Avrami parameters, n, and $t_{1/2}$ were listed in Table I.

It can be seen that $t_{1/2}$ increased with increasing T_s up to 543 K. It indicated that less crystal fragments remained with increasing T_s, so the number of nucleus formed by them decreased in the following isothermal crystallization. Similar to the trend shown in Figure 3 $t_{1/2}$ decreased instead as T_s increased further. It maybe result from the increase in the regularity of the hard sequences induced by the posttranseterization,[11] which made the crystallization rate accelerated. Table I also shows that the Avrami exponent, n, tends to increase with the increase on the melting temperature except for the sample melted at 540 K. Similar results about the dependence of it on melting temperature have been reported for isotactic polypropylene[4] and polyethylene.[13] The dependence of it on T_s indicated the physical aggregation of the remain nuclei and the change of crystal growth geometry from circular lamellar to spherical crystals.

It is generally known that two effects can cause residual structures to be capable of self-nucle-

Table I Parameters of Isothermal Crystallization at 483 K Melted at Different Temperatures

Melt Temperature (K)	Avrami Exponent N	Half Time $t_{1/2}$ (s)	Induction Time τ (s)
524	2.0	152	30
530	2.37	173	45
537	2.47	267	70
540	2.43	382	78
543	2.69	464	93
547	2.77	455	92

ation.[16,17] Small crystals grown at low temperatures in a crack of a foreign substance may survive temperatures higher than its own melting point; and the nucleus in subcritical size (embryo) created by steady state fluctuations at the higher temperature might become supercritical or stable on quenching to a lower crystallization temperature. The time to reach steady state is frequently called the induction time τ. It is the time need to establish the steady state distribution after cooling from a higher temperature. The induction time, τ_i, can be obtained in the curve of intensity of depolarized light I vs. crystallization time t by means of DPL. In fact τ_i obtained from the curve including actual induction time τ and the time needed to reach thermal equilibrium, t_e. The thermal equilibrium time is a function of supercooling ΔT ($\Delta T = T_s - T_c$).[18] Thus, the actual induction time τ could be obtained by subtracting t_e from τ_i, and the results were also listed in Table I. The variation of the induction time τ with T_s was also similar to that of $t_{1/2}$. This demonstrated that the decrease in melting temperature could shorten the time needed to reach critical nucleus size so as to accelerate crystallization rate. It also may be assumed that the self-nucleation in the poly(ether ester) was induced by the nucleus, which was created by steady-state fluctuations at the higher temperature, then became supercritical or stable on quenching to a lower crystallization temperature, and finally acted as nucleus in the process of crystallization.

It is also needed to consider the effects of homogeneous and heterogeneous nucleation on the nonisothermal and isothermal crystallization behaviors of the poly(ether ester) melted at different temperatures. In our studies the temperature range or the spent time cooling the sample from the melting temperature to the onset temperature of crystallization decreased with decreasing T_s in the both cases, so it can be imagined that the effect of homogeneous nucleation decreased with decreasing T_s. Although the contribution of heterogeneous nucleation that resulted from the nucleation at the surface of the foreign substance such as the residuals of the catalysts and antioxidant to the crystallization in the both cases could be considered as the same. Therefore, the dependence of the crystallization rate on the melting temperature in the studies cases was actually ascribed to the effect of self-nucleation.

So on the condition of the processability for the poly(ether ester) we could choose proper melting temperature as low as possible to apply the effect of self-nucleation to increase the crystallization rate of it on the melt spinning line.

CONCLUSION

The effect of self-nucleation on the nonisothermal and isothermal crystallization behaviors of the segmented copolymer poly(ethylene terephthalate)-poly(ethylene glycol) were investigated by DSC and DPL, respectively. It was found that the crystallization rate increased with the decrease of T_s, which indicated that the self-nucleation could increase the crystallization rate. The experimental conditions for nonisothermal crystallization were discussed in detail. It was found that the melting temperature to erase the prethermal history and the cooling rate to create a standard crystal state greatly influenced the effect of self-nucleation. The isothermal crystallization kinetics for poly(ether ester) melted at different temperatures was studied by the Avrami equation.

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