Effect of Branching on the Crystallization Kinetics of Poly(ethylene terephthalate)

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ABSTRACT: The effect of branching on the crystallization behavior of poly(ethylene terephthalate) has been examined by nonisothermal crystallization studies, using DSC. It was found that branching causes a significant change in the crystallization behavior, in that the Avrami exponent *n* lies between 1 and 2, suggesting a rodlike growth process compared to a spherulitic one observed in the case of PET. In addition, the effect of molecular kinks and linear disruptions were also examined; in both these cases, however, the same spherulitic growth, as seen in the case of PET, is observed. Further, the presence of branching, kinks and linear disruptions, in small concentrations, appears to enhance the crystallization process, possibly, by acting to facilitate nucleation. At higher concentrations of such defects, however, the crystallization process is slowed down and the overall crystallinity of the PET copolymers is reduced. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 59–66, 1999

Key words: poly(ethylene terephthalate); nonisothermal crystallization studies

INTRODUCTION

Crystallization kinetics of poly(ethylene terephthalate), PET, has been studied extensively, under both isothermal and nonisothermal conditions, using DSC. The effect of molecular weight,[1–4] presence of catalyst residues,[2,5] addition of nucleating agents,[6,7] etc., on the crystallization behavior of PET has been reported. Recently, the effect of carboxylic chain ends on the crystallization behavior of PET was also reported.[8] Much less attention, however, has been devoted to understand the effect of molecular structural imperfections on the crystallization behavior of PET. It is well known that the presence of random branching drastically changes the crystallization behavior of linear polymers. A few synthetic approaches[9] for the preparation of branched PET, using aliphatic alcohols as branching agents, have indeed been reported; but the effect of branching on their crystallization kinetics has not been investigated. On the other hand, the effect of branching on the crystallization kinetics of polyethylene has been well studied.[10,11] One important observation was that branched polyethylene, LDPE, exhibits a rodlike crystallite growth, unlike the spherelutic growth seen in the case of linear polyethylene, HDPE. Recently, we reported[12] the synthesis and thermal analysis of branched PET, prepared using an aromatic AB_2 monomer as the branching agent. In addition, we also examined the effect of molecular "kinks" and linear disruptions on the thermal properties of PET. It was found that the branching has drastic effect on the melting tran-

sition and percent crystallinity of PET. Herein, we report the results of a detailed investigation of the effect of branching, molecular kinks, and linear disruptions on the crystallization kinetics of PET using DSC.

Theory

The expression that is most often used for the analysis of isothermal crystallization kinetics is the Avrami equation[13]

$$1 - x(t) = \exp(-K(T)t^n) \qquad (1)$$

where $x(t)$ is the weight fraction of the crystallized material at time t, $K(T)$ is a rate constant for the crystallization process, and n is the Avrami exponent that represents the dimensionality of the crystallite growth.[14] The values of n and $K(T)$ are usually obtained from the double logarithmic form of eq. (1).

$$\log[-\ln(1 - x(t))] = \log K(T) + n \log t \qquad (2)$$

Nonisothermal crystallization kinetic studies have gained more importance of late, because most processing of polymers occurs under nonisothermal conditions. The early attempts at understanding the nonisothermal crystallization process by Ziabicki[15] and Harisch et al.[16] were found to be ineffective in retrieving meaningful values of the Avirami exponent. Later, Ozawa[17] derived an expression for nonisothermal kinetics as an extension of Evans' theory,[18] assuming that the crystallization occurs under a constant cooling rate (ϕ)

$$1 - x(T) = \exp(-\chi(T)/\phi^n) \qquad (3)$$

where $\chi(T)$ is the cooling crystallization function and the n represents the Avrami exponent. Ozawa tested this method for PET samples under different cooling rates and found that the Avrami exponent values obtained using his method were in good agreement with those obtained from isothermal experiments. He used the following double logarithmic form of the equation to get the Avrami exponent and cooling crystallization function.
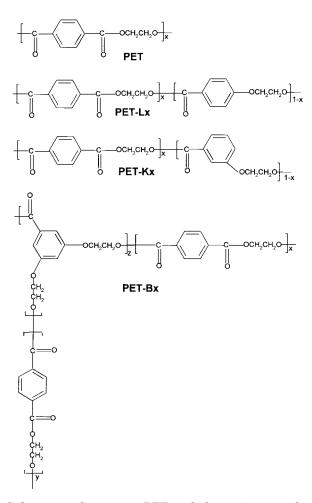
$$\log[-\ln(1 - x(T))] = \log \chi(T) - n \log \phi \qquad (4)$$

Jabarin studied the crystallization kinetics of various commercial PET samples, of different in molecular weights, both under isothermal[3] and nonisothermal[4] conditions using DSC. He again found that the Avrami exponent obtained from eqs. (1) and (3) were in good agreement. Using the same formalism, studies by Wilkes et al. on poly-(*p*-phenylene sulfide), PPS, of different molecular weights also demonstrated good agreement between isothermal[19] and nonisothermal[20] crystallization kinetics. The Ozawa approach has thus been able to successfully retrive the Avrami exponent from nonisothermal crystallization experiments, although the exact physical significance of the cooling cystallization function $\chi(T)$ is yet to be clearly exemplified. In an effort to examine the effect of branching on the crystallization behavior of PET, we have used the Ozawa equation for our kinetic analysis.

Materials and Experimental Methods

Poly(ethylene terephthalate) (PET) was synthesized by self-condensation of bis-(2-hydroxyethyl) terephthalate (BHET). Copolymerization of BHET with an AB_2 monomer, ethyl, bis-3,5-(2-hydroxyethoxy) benzoate (EBHEB) and ethyl, 3-(2-hydroxyethoxy) benzoate (E3HEB) yielded copolymers that contain varying amounts of branching and kinks, respectively. Copolymerization of BHET with ethyl, 4-(2-hydroxyethoxy) benzoate (E4HEB), on the other hand, yielded copolymers in which only the backbone symmetry is broken without disruption of the linearity. Details of the synthetic methods, the molecular weight determination, and structural characterization of the copolymers were reported earlier.[12]

Differential Scanning Calorimetric studies were carried out using a Rheometric Scientific DSC Plus instrument. The instrument was calibrated using indium, tin, and lead standards. All the polymer samples were first heated to 30° above their melting temperatures and held at that temperature for 3 min to destroy any residual crystallites. The samples were then cooled at different cooling rates of 10, 8, 6, 4, and 2°/min. Fresh polymer samples (~10 mg) were used for each experiment to preclude the possibility of thermal degradation. All the scans were recorded under a 5 mL/min purge of dry nitrogen to prevent any possible oxidative degradation.

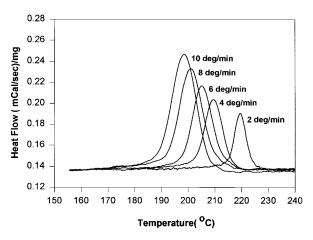**Scheme 1** Structures PET and the various copolymers.

Figure 1 Representative DSC thermograms of PET showing the crystallization exotherms recorded at different cooling rates.

expected, with decrease in cooling rate T_c is seen to increase.

All the DSC exotherms were normalized with respect to their weights and baseline corrected prior to the kinetic calculations. The crystalline weight fraction of the polymer, $x(T)$ was calculated from the fractional partial areas under the crystallization exotherms, as was done previously.[1,3] The calculated $x(T)$ values were plotted versus temperature; representative plots for PET, and one for each of the copolymers, PET-$B_{3.7}$, PET-$K_{15.3}$, and PET-L_{11}, are shown in Figure 3(a)–(d). In most cases, as expected, the shape of the curves is essentially similar at different cooling rates, suggesting that the mechanism for crystallization is invariant. To determine

RESULTS AND DISCUSSIONS

The structure of PET and its various copolymers are shown in Scheme 1. The copolymers PET-Lx, PET-Kx, and PET-Bx represent those having linear, kink, and branching comonomers, respectively, and x represents the extent of comonomer incorporation, as determined by ^{1}H-NMR spectroscopy.[12] The crystallization kinetics of copolymers PET-$L_{20.3}$ and PET-$K_{25.5}$ were very slow, and hence, were not used for the dynamic analysis. Typical DSC thermograms for PET and PET-$B_{3.7}$, at different cooling rates, are shown in the Figures 1 and 2, respectively; all the other copolymers exhibited essentially similar variations with cooling rates. The values of crystallization temperature (T_c) of PET and the various copolymers are summarized in the Table I. In all cases, as
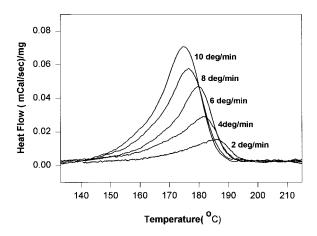

Figure 2 Representative DSC thermograms of PET-$B_{3.7}$, showing the crystallization exotherms recorded at different cooling rates.

Table I   Crystallization Data of the Various PET Copolymers

Polymer		10°C/min	8°C/min	6°C/min	4°C/min	2°C/min
PET	T_c (°C)	198.55	201.06	205.15	209.25	219.52
	% Crystallinity	0.270	0.282	0.290	0.304	0.320
B-1.4	T_c (°C)	187.64	189.56	190.11	193.60	193.98
	% Crystallinity	0.314	0.320	0.326	0.327	0.320
B-3.7	T_c (°C)	174.68	176.46	179.85	181.45	186.03
	% Crystallinity	0.259	0.263	0.267	0.271	0.265
B-5	T_c (°C)	165.74	170.32	171.81	176.26	179.63
	Crystallinity	0.258	0.265	0.269	0.268	0.241
K-3.3	T_c (°C)	191.83	193.62	198.54	202.39	208.31
	% Crystallinity	0.280	0.294	0.302	0.307	0.313
K-9.6	T_c (°C)	186.14	194.03	196.26	200.84	206.71
	% Crystallinity	0.255	0.261	0.282	0.307	0.311
K-15.3	T_c (°C)	154.28	158.20	165.07	172.32	177.12
	% Crystallinity	0.178	0.188	0.195	0.198	0.197
L-2.7	T_c (°C)	206.76	210.23	211.94	216.08	221.05
	% Crystallinity	0.295	0.301	0.304	0.318	0.333
L-7.3	T_c (°C)	170.48	178.97	181.87	186.87	195.10
	% Crystallinity	0.265	0.272	0.279	0.288	0.301
L-11	T_c (°C)	169.21	172.59	178.45	184.18	192.17
	% Crystallinity	0.192	0.202	0.206	0.219	0.243

the values of $x(T)$ corresponding to different cooling rates, isothermal lines were drawn on these plots [as shown for PET-B$_{3.7}$ in plot 3(b)] and the $x(T)$ values are taken as the points corresponding to the intersection of these isothermal lines with the appropriate curves. In general, only curves corresponding to those cooling rates that were closely spaced were used for calculating the $x(T)$ values. Thus, for instance, in the case of PET, the curve corresponding to the 2°/min cooling rate was not used (see Fig. 1). Similarly, in some other cases also, neither the 2°/min or the 10°/min curves were used for calculating the $x(T)$ values. But in the case of branched copolymers, all the curves were used for the calculations because all the exotherms were closely spaced (see Fig. 2). Using these $x(T)$ values, $\log[-\ln(1-x(T))]$ was plotted versus $\log \phi$, according to the double logarithmic form of the Ozawa equation . As was suggested previously by Wilkes and coworkers,[20] to preclude the effects of impingement and truncation of spherulities, only values of $x(T)$ that were less than 0.6 were used. Representative plots of $\log[-\ln(1-x(T))]$ versus $\log \phi$ for PET, PET-B$_{3.5}$, PET-K$_{15.3}$, and PET-L$_{11.0}$ are shown in Figure 4(a)–(d); the straight lines represent the least square fit of the data points. The values of the Avrami exponent (n) and the cooling crystallization function, $[\chi(T)]$, are obtained from the slope and

intercept of such plots, respectively. The values of Avrami exponent are summarized in Table II.

It is clear from Table II that the Avrami exponents for PET (ranging from 3.0 to 3.6) correspond to the spherulitic growth and are in accordance with those reported earlier by Ozawa[17] and Jabarin,[4] thus validating the experimental procedure used for this study. All the linear and kinked copolymers exhibit values of n that lie in the same range, averaging about 3. This suggests that, as in the case of PET, in both the kinked and linear copolymers crystallization occurs by spherulitic growth. All the branched PETs, on the other hand, exhibit a much lower value for the Avrami exponent, which lies between 1 and 2. This significantly smaller value of the exponent suggests a rodlike growth[14] of crystallites in branched PETs. Interestingly, while the variation in branching content changes the crystallization temperatures, T_c, drastically (see Table I), it does not affect the crystallization mechanism significantly, as seen by invariance of the Avrami exponent.

Previous studies, comparing the behavior of linear polyethylene (HDPE) and branched polyethylene (LDPE), have also arrived at similar conclusions; linear polyethylene[21] exhibits spherulitic growth with the exponent values in the range of 3–4, while branched polyethylene[10] has rodlike
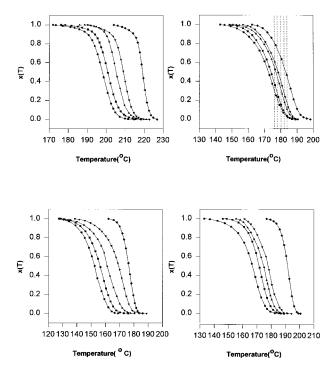
Figure 3   Representative plots of $x(T)$ versus temperature for PET (a), PET-B$_{3.7}$ (b), PET-K$_{15.3}$ (c), and PET-L$_{11.0}$ (d), at different cooling rates of 10°/min (●), 8°/min (■), 6°/min (▲), 4°/min (▼), and 2°/min (◆).

growth with n values between 1 and 2. In the case of polyethylene, this difference has been attributed to the inherent branched nature of the polymer, which causes a difference in the mechanism of growth by impeding the diffusion process. Although other factors such as polydispersity were initially implicated, it was later conclusively dismissed using detailed small-angle X-ray–scattering studies.[11] Thus, the lower values of the Avrami exponent in the case of branched PET may also be suggestive of an inherent difference in the growth mechanism, although in this case the other factors such as polydispersity cannot be unequivocally excluded.

In an effort to examine the role of the various kinds of structural modifications on the crystallization kinetics, we have plotted the cooling crystallization function, [$\chi(T)$], obtained from the intercept of lines in plots 4(a)–(d), versus temperature for the different copolymers, and these are shown in Figure 5. The measured $\chi(T)$ values for PET are in good agreement with those reported by Ozawa[17] and Jabarin.[4] The general trend of a decrease in the $\chi(T)$ values with an increase in temperature in such nonisothermal studies has also been noted by several others.[4,20] Just as in

the case of the Avrami exponent, the $\chi(T)$ values for both linear and kinked copolymers are in the same range as for PET. All the branched copolymers, on the other hand, have much lower $\chi(T)$ values than PET, suggesting a significantly slower crystallization of branched copolymers. A similar behavior was observed in branched poly-(p-phenylene sulfide).[20] Although these trends indicate qualitative changes in the crystallization rate, quantitative analysis using $\chi(T)$ values is difficult, as the exact physical meaning of the cooling crystallization function is yet unclear.

The percent crystallinity of the copolymers at different cooling rates was calculated using the formula,[4]

$$\% \text{ crystallinity} = \Delta H_\phi / \Delta H$$

where ΔH_ϕ is the heat of crystallization of polymer at the particular cooling rate ϕ, and ΔH is the heat of crystallization corresponding to the 100% crystalline PET, which is taken as 120 J/g.[1,22] These calculated values were summarized in Table I.

A plot of the % crystallinity (at a cooling rate of 10°/min) versus the comonomer concentration for all copolymers is shown in Figure 6. Similar trends are also observed for other cooling rates. It is apparent from the plot that at very low concentrations of comonomer, the % crystallinity increases slightly before it begins to fall, suggesting a distinct difference in behavior at very low concentrations of the comonomer. At higher concentrations of comonomer, however, a drastic reduction in the crystallinity of the copolymers is observed; the effect being most pronounced in the case of branching. Similar behavior was also observed previously,[12] in the plots of the enthalpy of melting transitions (during heating runs) versus the comonomer concentration. In addition, it was noticed that when prequenched (amorphous) polymer samples were reheated at 10°/min, the crystallization temperatures (peak values of the crystallization exotherms) in all the copolymers decreased at first with comonomer concentration before increasing to higher values.[12] This suggested that at very low concentrations of the comonomer, the propensity of PET toward crystallization may, indeed, be enhanced.

Such a difference in the crystallization behavior at low defect concentration is reminiscent of some recent studies that were carried out in polymer blends. Lin et al.[23] observed that in blends of PET
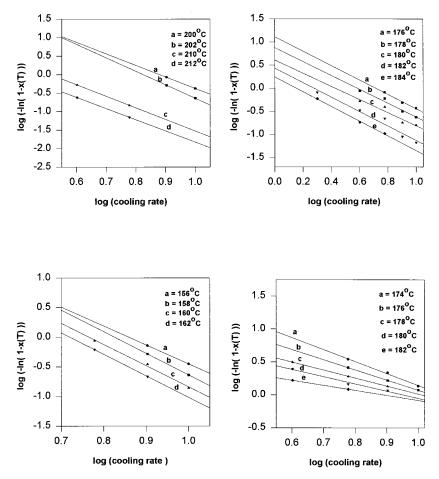
Figure 4 Representative plots of $\log[-\ln(1-x(T))]$ versus $\log \phi$ for PET (a), PET-B$_{3.7}$ (b), PET-K$_{15.3}$ (c), and PET-L$_{11.0}$ (d).

with a liquid crystalline polyester, [poly(p-oxyben-zoate-coethyleneterephthalate)], (POB/PET), the rate of crystallization is enhanced in the presence of

small amounts of the copolymer. In a similar study, Gopakumar et al.[24] showed by nonisothermal kinetic studies that small amounts of such LCP copol-

Table II   Avrami Exponents of the Various PET Copolymers at Different Temperatures

Polymer	Avrami Exponent (n), (Temperature)[a]				
PET	3.12 (200)	3.64 (202)	3.13 (210)	3.03 (212)	—
B-1.4	1.0 (188)	1.25 (190)	1.51 (192)	1.21 (194)	0.93 (196)
B-3.7	1.56 (176)	1.50 (178)	1.41 (180)	1.56 (182)	1.59 (184)
B-5	1.51 (172)	1.76 (174)	2.11 (176)	1.72 (180)	2.06 (182)
K-3.3	2.52 (192)	3.26 (194)	3.07 (203)	2.84 (208)	—
K-9.6	2.74 (195)	2.93 (197)	3.06 (199)	—	—
K-15.3	3.21 (156)	3.65 (158)	3.57 (160)	3.63 (162)	—
L-2.7	3.35 (210)	2.53 (212)	2.99 (214)	3.00 (220)	—
L-7.3	3.52 (182)	3.79 (184)	2.53 (186)	2.75 (188)	2.52 (190)
L-11	3.24 (174)	3.80 (176)	2.26 (178)	2.82 (180)	2.54 (182)

[a] Number in parentheses corresponds to the temperature of the isothermal lines drawn.

ymers increase the crystallization rate of PPS. Both these authors concluded that these LCP units were acting as nucleating agents for the crystallization process. Thus, in these copolymers of PET also it appears that, when a comonomer is present in very small concentrations, the propensity of the system to nucleate is enhanced, leading to an increase in the crystallinity. Further detailed microscopic studies are essential to confirm this hypothesis.

CONCLUSION

The effect of linear, kink, and branching imperfections on the crystallization process of poly(ethylene terephthalate) was analyzed by nonisothermal DSC studies. The branched PET copolymers appear to promote a rodlike growth process, much like in the case of branched polyethylene. The growth process in both linear and kinked copolymers, however, does not appear to be affected by the presence of defects; all of which exhibit a three-dimensional spherulitic growth, as in PET. Further, it appears that at very low concentrations of the comonomer nucleation is facilitated, and this leads to a slight increase in the crystallinity. Further polarized light microscopic investigations are, of course, essential to confirm this hypothesis.
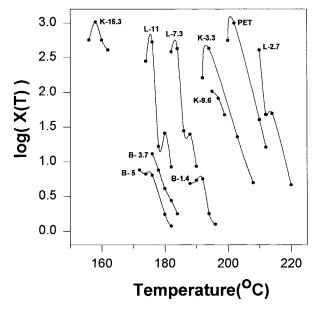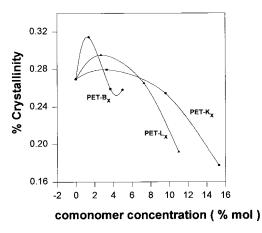
Figure 6 Plot of percent crystallinity versus comonomer concentration for PET copolymers, at a cooling rate of 10 deg/min.

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Figure 5 Plot of cooling crystallization function, $\chi(T)$, versus temperature for PET and the various copolymers.

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