Crystallization Kinetics of Polyethylene Terephthalate. II. Dynamic Crystallization of PET

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Synopsis

The crystallization behavior of polyethylene terephthalate (PET), was investigated under isothermal and dynamic cooling conditions, as a function of molecular weight, polycondensation catalyst system, and polymerization conditions. Crystallization kinetic parameters were calculated for both cases by utilizing Avrami-type expressions. Analysis of the crystallization kinetic data indicates that the same mechanism is operative under isothermal and dynamic cooling crystallization conditions.

The dynamic cooling crystallization method can establish the minimum cooling rate required to produce PET without detectable crystallinity. The results show that the cooling requirements for producing noncrystalline PET are dependent on the molecular weight of the resin, but more importantly, are dependent on the catalyst system used in the polycondensation step. These results are in good agreement with the results obtained under isothermal conditions.

INTRODUCTION

In Part I of this series,[1] the crystallization kinetics of polyethylene terephthalate (PET) were reported and discussed. The report included also a discussion of the structural and physical factors which control crystallization of PET. In addition, the literature on PET crystallization was reviewed.

Under the conditions of isothermal crystallization from the melt, the previous study[1] led to the following conclusions:

1. The crystallization rates and the mechanism of crystallization are dependent on molecular weight, temperature, and the catalyst system used during polycondensation of PET.
2. The catalyst system can exhibit a greater influence on the rate and mechanism of crystallization than the molecular weight of PET.
3. Among the catalyst systems investigated a titanium-based catalyst exhibited the lowest crystallization rates for PET of equivalent molecular weights.
4. The half-time of crystallization is not a good measure of the rate of crystallization if the mechanism of crystallization is also varying, i.e., the Avrami exponent is also changing.

Isothermal crystallization measurements are usually used for the study of crystallization behavior of materials since they are easier to analyze theoretically. The case of dynamic crystallization, in which the samples are observed

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under a constant rate of cooling, is theoretically more difficult,[2] however, it is a case which more closely simulates the fabrication process.

The present work was undertaken to study the nonisothermal (i.e., under a constant cooling rate) crystallization behavior of PET. Specifically the objectives were: (a) Determine the effects of cooling rates on the crystallization behavior of PET. (b) Compare the results of isothermal and nonisothermal conditions and determine how the various factors (such as the structural and physical) affect each case. (c) Determine the minimum cooling rate required to prevent detectable crystallinity from developing in PET samples of various molecular weights and polycondensation catalysts systems.

EXPERIMENTAL

Materials

The materials used for this study were discussed in Part I[1] and are described here in Table I

Differential Scanning Calorimetry (DSC)

A Perkin-Elmer DSC-2 instrument was used. The samples were weighed in the aluminum sample holder. The calorimeter was operated with a stream of oxygen-free dry nitrogen flowing over the sample and the reference. All samples were previously dried in a vacuum oven to a moisture content of less than 0.005%. The samples were heated at a rate of 10°C/min up to 294°C, then held at that temperature for 15 minutes. The isothermal crystallization temperature was reached by rapidly reducing the temperature; the temperature equilibration at this lower temperature is indicated by the illumination of the control light on the instrument panel. The dynamic crystallization condition was achieved by employing programmed cooling of the sample covering the range of 5–40°C/min.

The calorimeter measures the rate of evolution of heat as a function of time. Crystallization isotherms were constructed by integrating the areas under the

TABLE I
Specifications of PET Resins

	Goodyear 5041	Goodyear 5041 X	Goodyear 5737 A	Celanese 4070 C	Eastman X-14829-93-1
I.V.	1.04	0.83	0.72	0.68	0.81
Monomer	TPA	TPA	TPA	TPA	DMT
Catalyst system	Sb	Sb	Sb	Ti – Mn	Ti – Mn
Stabilizer additives	Phosphorus	Phosphorus	Phosphorus	Phosphorus	Phosphorus
DEG, mol %	1.3	1.7	1.4	1.7	1.7
Polymerization process	Solid-state	Solid-state	Solid-state	Continuous melt-phase	Solid-state

I.V. Measured in 60/40 phenol-tetrachlorethane at 25°C.
Abbreviations: TPA = terephthalic acid; DMT = dimethyl terephthalate; Sb = antimony; Ti = titanium; Mn = manganese; DEG = diethylene glycol.

exothermic peak according to the following equation:

$$X_t = \int_0^t \frac{dH_t}{dt}\, dt \bigg/ \int_0^\infty \frac{dH_t}{dt}\, dt$$

where dH_t/dt is the rate of evolution of heat, t is the time, and X_t is the weight fraction of crystallized material at time t.

The degree of crystallinity in the dynamic crystallization case was calculated from:

$$X = \frac{\Delta H_c}{\Delta H}$$

where ΔH_c is the measured heat of crystallization. ΔH is the heat of crystallization of completely crystalline PET = 20.2 cal/g.[3] The heat of crystallization is calculated from the total area under the exotherm according to the Perkin-Elmer DSC manual.

RESULTS AND DISCUSSION

Dynamic Crystallization

Typical DSC curves obtained in the dynamic crystallization of PET are shown in Figure 1, for cooling rates of 5 and 20°C/minute. It is seen that the crystallization exotherm shifts to lower temperatures with increasing cooling rates.

The area under the exotherm is related to the heat of crystallization, ΔH_c, as discussed above in the experimental section. The amount of crystallinity
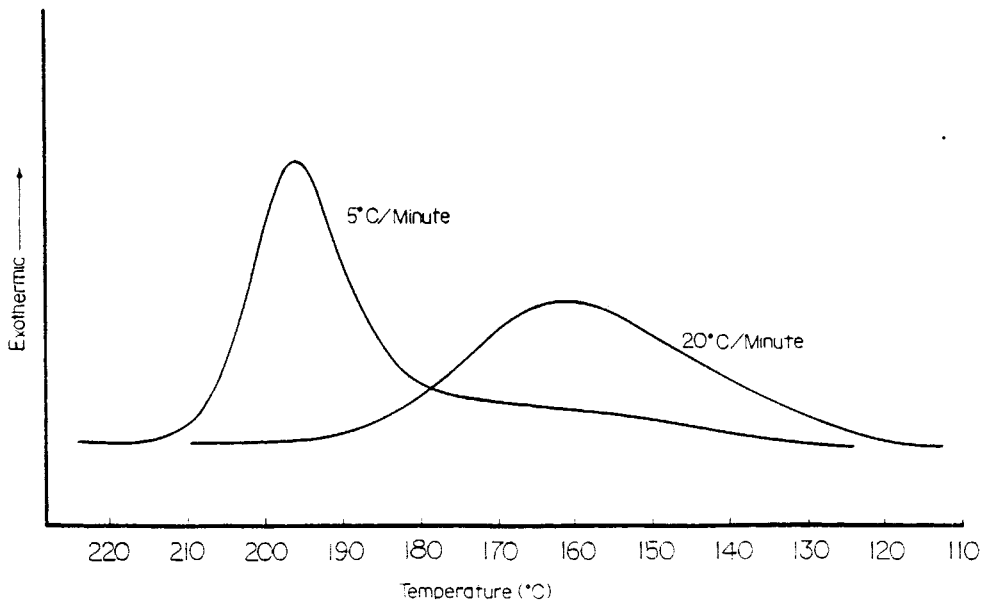

Fig. 1. Crystallization exotherms of PET at various cooling rates.
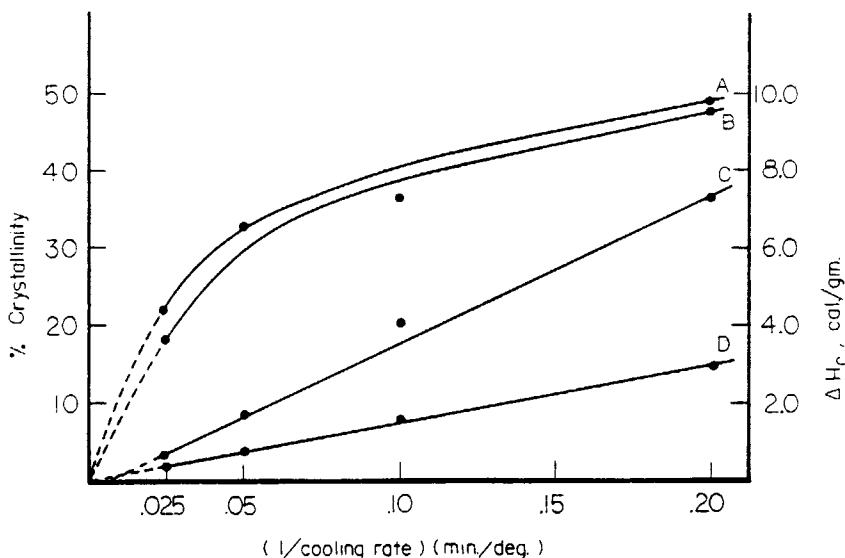
Fig. 2.   Percent crystallinity, and heat of crystallization as a function of reciprocal of cooling rate for various PET samples. A = Celanese 4070C, 0.7 I.V. B = Goodyear 5737A, 0.7 I.V. & 5041X, 0.8 I.V. C = Goodyear 5041, 1.0 I.V. D = Eastman X-14829-93-1, 0.8 I.V.

can be calculated from the heat of crystallization. Figure 2 gives the variation of ΔH_c and the corresponding percent crystallinity of various PET samples as a function of cooling rates. These results show dramatic differences in the crystallization behavior of the various PET resins. The sample D (Eastman 0.8 I.V.) exhibits slower crystallization rates than Sample C (Goodyear 1.0 I.V.) although it is of lower molecular weight. This is attributed to the different catalyst systems used. The effect of the catalyst system is more clearly demonstrated by comparing Curve B (Goodyear 0.8 I.V.) with curve D (Eastman 0.8 I.V.) These samples are of about the same molecular weight but are made by different polycondensation processes employing different catalysts.

The results in Figure 2 are important in relation to the cooling requirement to produce clear parts of PET. Zero percent crystallinity can be achieved when cooling at about 130°C/min for the resins (D) and (C). At this cooling rate, however, resins represented by curves (B) and (A) exhibit 6 and 9% crystallinity. According to these results, resins represented by curves (A) and (B) require a cooling rate of more than 400°C/min to produce crystallinity levels of less than 1%.

Kinetics of Dynamic Crystallization

The Avrami equation describing the isothermal crystallization has been extended by Ozawa[2] for the nonisothermal kinetic process. The modified Avrami equation is given by:

$$1 - a(T) = e^{-K(T)/R^n} \tag{1}$$

where $a(T)$ is the amount of transformed material at temperature T, $K(T)$ is

the rate, R is the cooling rate, and n is the Avrami exponent which describes qualitatively the mechanisms of crystallization.

Equation (1) can be used to obtain the kinetic parameters if one observes the crystallization process at different cooling rates, since Eq. (1) can be represented as:

$$\log[-\ln(1-a)] = \log K - n \log R \qquad (2)$$

A plot of $\log[-\ln(1-a)]$ against $\log R$ at a given temperature should yield a straight line with a slope of $(-n)$ and intercept of $\log K$.
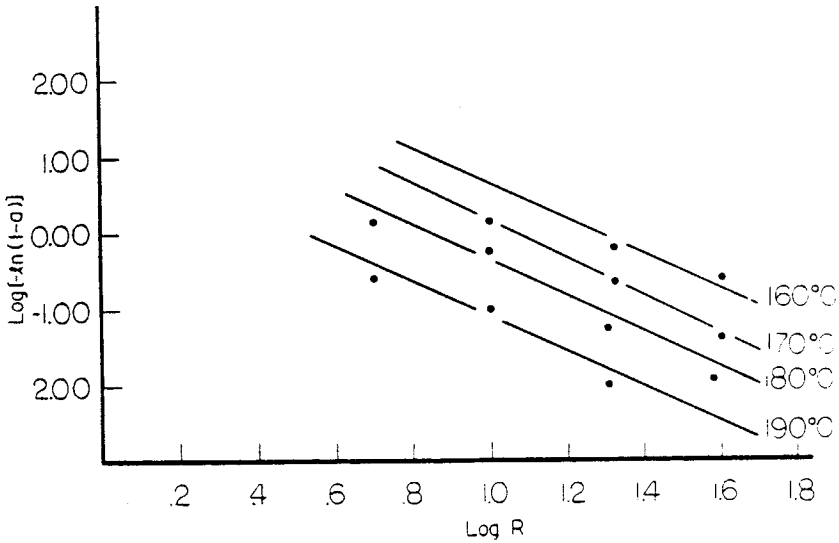

Fig. 3. Avrami plot of dynamic crystallization of PET (I.V. = 1.0) at various crystallization temperatures.
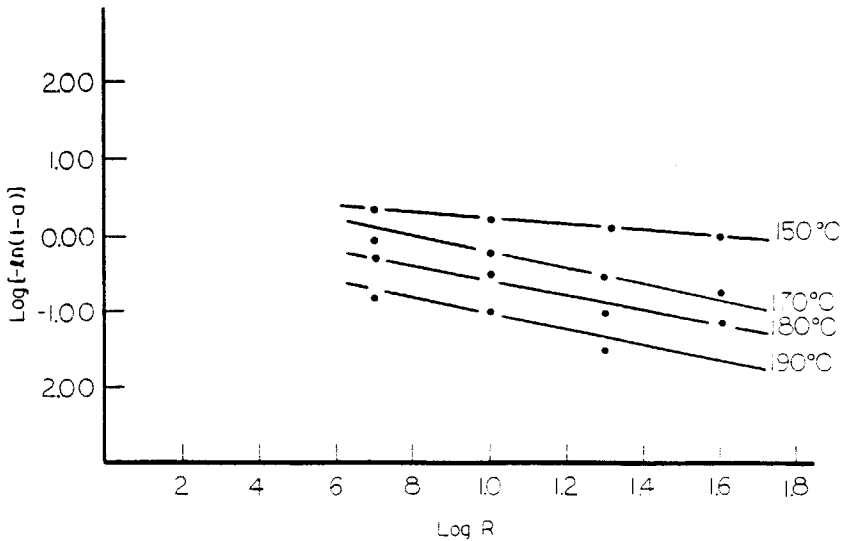

Fig. 4. Avrami plot of dynamic crystallization of PET (I.V. = 0.8) at various crystallization temperatures.

TABLE II
Analysis of the Course of Dynamic Crystallization of PET Samples

Temp. °C.	Goodyear resins						Celanese		Eastman	
	5737A		5041X		5041		4070C		X-14829 93-1	
	0.72		0.83		1.04		0.68		0.81	
	K	n	K	n	K	n	K	n	K	n
190	229	2.6	159	2.6	100	2.8	501	2.5	1	1.0
180	1380	2.6	1047	2.6	626	2.8	1995	2.5	2.5	1.0
170	6309	2.6	3630	2.6	1980	2.8	7943	2.5	6.3	1.0
160	—	—	—	—	6250	2.8	25119	2.5	—	—

$n = X \pm 0.2$.
$K = (\text{min/deg})^3$ for Goodyear and Celanese resins.
$K = (\text{min/deg})$ for Eastman resin.

Typical plots of the above equation for the dynamic crystallization behavior of various PET resins are given in Figures 3 and 4 for Goodyear 5041 and Eastman PET, respectively. A summary of the dynamic crystallization kinetic data is given in Table II. The Avrami exponent n for the Goodyear and the Celanese resins is close to 3. Therefore, the rate constant is calculated with $n = 3$. In the case of the Eastman resin, the results are surprising in that the n value is close to unity. Therefore, a direct comparison of the rates between Eastman resin and the other resins is not possible. The agreement in the Avrami exponent for the case of dynamic and the isothermal crystallization is quite good.[1]

CONCLUSIONS

1. The minimum cooling rate required to produce noncrystalline PET is dependent on molecular weight and the polycondensation catalyst system.

2. A method has been developed to predict the minimum cooling rate required to produce noncrystalline and thus optically clear PET articles. For high I.V. polymer this cooling rate is about 130°C/min, while for low I.V., the cooling rate is above 400°C/min.

3. The crystallization rate parameters calculated from the dynamic cooling experiment are in agreement with those calculated from isothermal experiments. This indicates that the mechanism of crystallization is similar in both cases.

A modified Avrami expression can be used to analyze dynamic cooling crystallization data.

References

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