

Crystallization Kinetics of Polyethylene Terephthalate. I. Isothermal Crystallization from the Melt

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Synopsis

The crystallization behavior of polyethylene terephthalate (PET) was investigated as a function of molecular weight, temperature of crystallization, and polycondensation catalyst system. A detailed analysis of the crystallization course has been made utilizing the Avrami expression. The crystallization rate constants and the Avrami exponents were calculated. The results show that the rate constant and the mechanism of crystallization are dependent on the molecular weight, temperature, and the polycondensation catalyst system. The catalyst system often exhibits a more significant influence than the molecular weight in controlling the rate of crystallization of PET.

INTRODUCTION

Although polyethylene terephthalate (PET) is a well known commercial polymer manufactured into fibers, films, and recently, into containers, there has been very little reported on the kinetics of crystallization of PET from the melt. This probably is due in part of the fact that a slight modification of the structure, such as a variation of the catalyst system, can significantly alter the crystallization kinetics. The crystallization kinetics determine the final physical state of the fabricated article which in turn controls the physical properties of the manufactured product.

The factors which influence the crystallization rates of PET from the melt can be divided into two classes:

1. The factors which affect the detailed molecular structure of the polymer. These include the molecular weight, which affects the viscosity of the crystallizing polymer and therefore the rate of transporting a crystallizing segment across the liquid-crystal interface. The side reactions are formed during the polymerization (i.e., polycondensation) of PET.¹ Although these side reactions usually occur only to a limited extent, they can cause variation in the polymer structure. Another important factor is the method, that is the catalyst system used during polycondensation. Examples of catalysts used in PET polymerization are given in Table I.¹

2. Physical factors such as the temperature and the environmental surroundings during crystallization, the previous melt history of the polymer, additives such as nucleating agents, and finally the physical conditions of the polymer during crystallization such as strain, orientation, and pressure.

Cobbs and Burton² studied the course of crystallization of a batch of PET in a film form. The crystallization rates were followed by an infrared absorption method. The infrared absorption was correlated with the density of PET

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TABLE I
Examples of Catalysts Used in the Production
of Polyethylene Terephthalate

Catalyst	
PbO	CaH ₂
Sb ₂ O ₃	NaOH
(CH ₃ COO) ₂ Ca	LiAlO ₂
(CH ₃ COO) ₂ Zn 2H ₂ O	NaAlO ₂
LiH	MgO

of varying degrees of crystallinity. The samples used in their study were not characterized in terms of molecular weight or catalyst system; however, the kinetics of crystallization were analyzed in terms of the Avrami equation, and an Avrami exponent, n , was obtained. The Avrami exponent was interpreted in terms of plate-like growth as crystallites formed at crystallization temperatures between 120°C and 180°C.

Morgan and co-workers,^{3,4} using density gradient and density balance methods, studied the crystallization behavior of a series of PET samples of number average molecular weights between 11,000 and 17,000. In this study, they demonstrated the importance of fusion conditions on subsequent crystallization behavior and the necessity of destroying previous thermal history by heat treating the molten polymer. It was found that heating the polymer to 294°C for 10 minutes assured complete melting. The kinetic data were analyzed in the form of Avrami parameters for the highest molecular weight sample. In addition, they found that the rate of crystallization, as measured by the half time, could vary between 15 and 35 minutes at 110°C, when the measurements were made on different samples of PET from different polycondensation methods although the molecular weights were about the same. They attributed the differences in the half times to secondary structural factors (such as side reactions) brought about by the polycondensation step, however, no other characterization (e.g., catalyst system) was given.

Jackson and Longman⁵ studied the effects of molecular weight, certain catalyst residues, and nucleating agent on the rates of crystallization from the melt of PET and related copolymers. The exact natures of the catalyst residues were not given. They found that the rate of crystallization was influenced by the catalyst residue. For polymers with similar molecular weight, soluble polymerization catalyst systems exhibited lower rates of crystallization than insoluble catalysts.

Van Antwerpen and Van Krevelen⁶ studied the influence of crystallization temperature, molecular weight, and additives on the spherulite growth rate, the maximum spherulite radius, and the overall rate of crystallization of PET. It was shown that the maximum spherulite growth rates occur at 180°C for samples of number average molecular weights between 19,000 and 27,000. These results were found to be applicable for crystallization from both the melt and the glassy states. Baranov et al.,⁷ in their study of PET crystallization found that the maximum growth rate of spherulites occurs at 155°C when crystallizing from the melt and it occurs at 190°C when crystallizing from the glassy state.

Gunther and Zachmann⁸ investigated the effects of the amounts and kinds of catalyst systems on the half time of crystallization and orientation of PET. It was found that, under the same drawing conditions, increasing the molar mass of the catalyst system increases the degree of orientation.

In this study, the objective is to examine the crystallization behavior of a variety of commercial and developmental PET materials with known molecular weights, catalyst systems, diethylene glycol (DEG) contents, and polymerization processes. Specifically, the objectives are to: (a) Determine the crystallization rates of different PET resins at various temperatures and relate these results to the processability of PET. (b) Develop an understanding of the crystallization behavior of PET and its dependence on the molecular weight and other factors which influence the polymer structure.

Polymer crystallization kinetics can be studied by a variety of methods including dilatometry, calorimetry, x-ray diffraction, microscopy, light scattering, depolarized light intensity (DLI), and others as discussed by Price.⁹ Methods based on thermodynamic properties are most widely used. These include, the specific volume (or its reciprocal, the density) and the enthalpy. The enthalpy is readily measured by a differential scanning calorimeter (DSC). The DSC method has been shown to be applicable to the study of polymer crystallization.¹⁰⁻¹²

EXPERIMENTAL

Materials

The materials used for this study were PET resins obtained from various manufacturers. The specifications of the materials in terms of inherent viscosity (IV), monomer, catalyst system, stabilizer additive, diethylene glycol (DEG) content, and polymerization process are given in Table II.

The inherent viscosity determinations were made in 60/40 phenol/tetrachloroethane at 25°C using a Cannon-Ubbelohde dilution viscometer. All

TABLE II
Specifications of PET Resins

	Goodyear 5041	Goodyear 5041 X	Goodyear 5737 A	Celanese 4070 C	Eastman X-14829-93-1	Goodyear 3599	ICI B-76
IV ^a	1.04	0.83	0.72	0.68	0.81	1.0	0.68
Monomer	TPA	TPA	TPA	TPA	DMT	DMT	DMT
Catalyst system	Sb	Sb	Sb	Ti-Mn	Ti-Mn	Sb-Mn	Ti-Mn
Stabilizer additives	Phosphorus	Phosphorus	Phosphorus	Phosphorus	Phosphorus	Phosphorus	Phosphorus
DEG, mole %	1.3	1.7	1.4	1.7	1.7	1.3	2.3
				Continuous			
Polymerization process	Solid-state	Solid-state	Solid-state	Melt-phase	Solid-state	Solid-state	Melt-phase

abbreviations: IV Measured in 60/40 phenol-tetrachloroethane at 25°C. TPA = terephthalic acid, DMT = dimethyl terephthalate, Sb = Antimony, Ti = titanium, Mn = manganese, DEG = diethylene glycol.

samples were dried in a vacuum oven at 150°C prior to viscosity measurements. Sample concentrations of 0.25 g/100 mL were used. The relationship between IV and molecular weight using the above condition is.¹³

$$IV = 4.68 \times 10^{-4} (Mw)^{0.68}$$

where Mw = Weight average molecular weight.

Differential Scanning Calorimeter (DSC)

A Perkin-Elmer DSC-2 instrument was used. The samples were weighed in the aluminum sample holder. All samples were dried in a vacuum oven to a moisture content of less than 0.005% prior to measurements. The calorimeter was operated with a stream of oxygen-free, dry nitrogen flowing over the sample and the reference. The samples were heated at a rate of 10°C/min up to 294°C and held for 15 minutes. The isothermal crystallization temperature was reached by rapidly reducing the temperature. Thermal equilibration at this lower temperature was indicated by the illumination of the control light on the instrument panel.

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

RESULTS AND DISCUSSION

Experimental Results

In work on polymer crystallization, it is customary to represent the experimental results in terms of the fraction of uncrystallized material, θ_a , as a

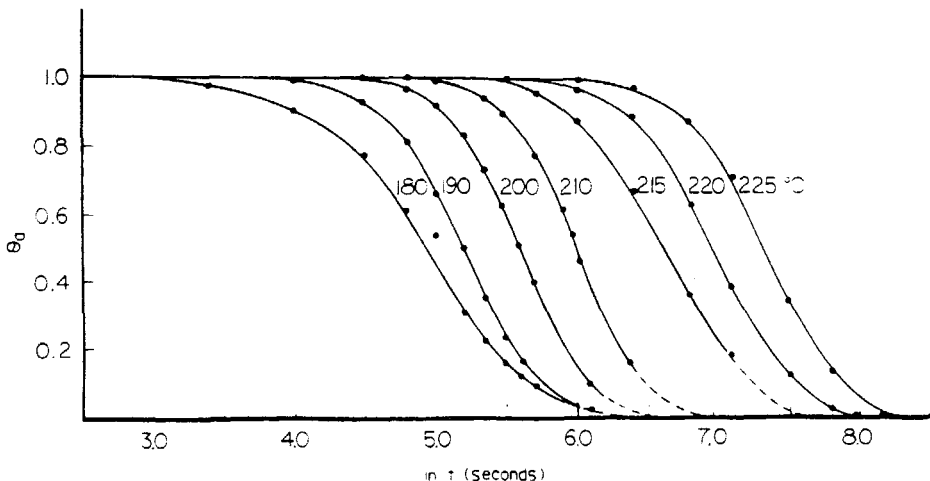


Fig. 1. Crystallization isotherms of Goodyear 5041 PET at 180, 190, 200, 210, 215, and 225°C.

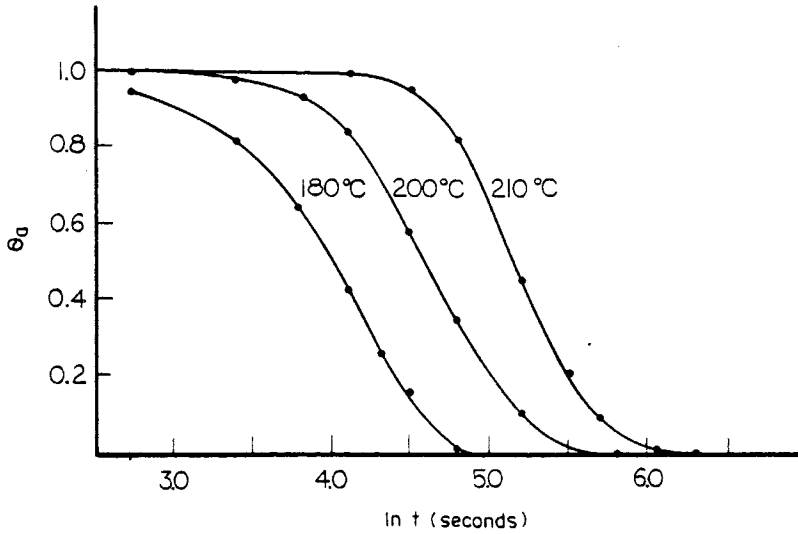


Fig. 2. Crystallization isotherm of Goodyear 3599 PET at 180, 200, and 210°C.

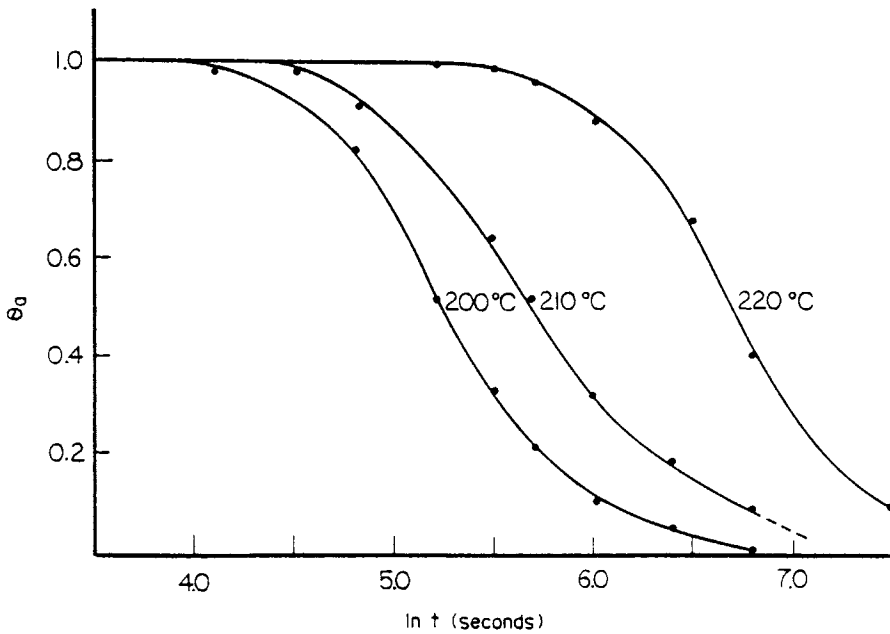


Fig. 3. Crystallization isotherms of Goodyear 5041X PET at 200, 210, and 220°C.

function of time ($\ln t$). These plots are called crystallization isotherms. Figures 1-7 give the variation of θ_a with time at various crystallization temperatures for the PET samples.

All of the isotherms have a sigmoidal shape typical of polymer crystallization behavior. In many cases, the curves for different crystallization temperatures may be exactly superposed by shifting horizontally along the axis of $\ln t$, indicating that similar crystallization mechanism is occurring.

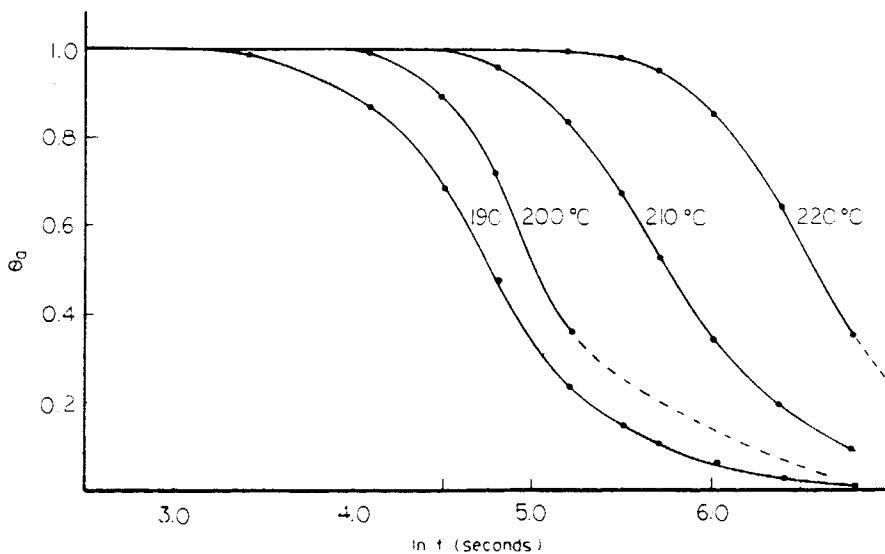


Fig. 4. Crystallization isotherms of Goodyear 5737A PET at 190, 200, 210, and 220°C.

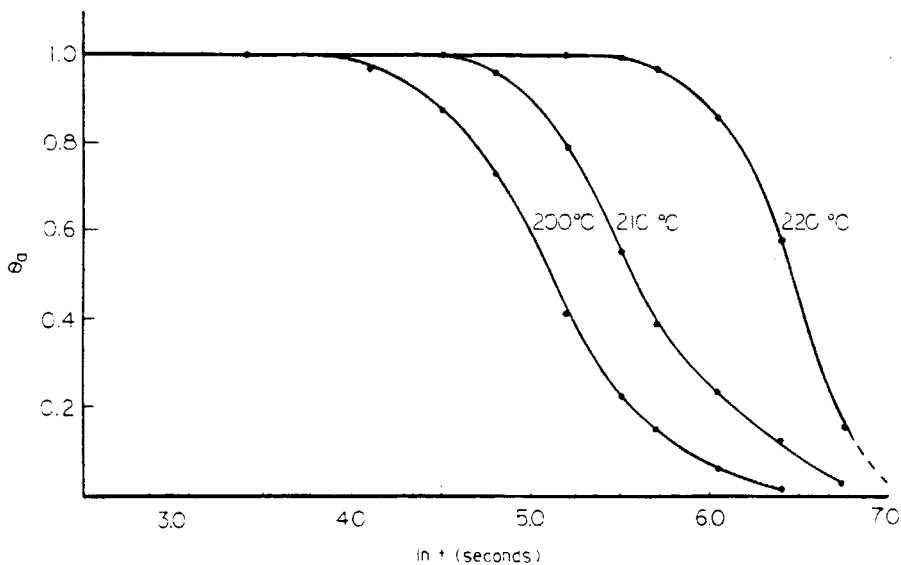


Fig. 5. Crystallization isotherms of Celanese 4070C at 200, 210, and 220°C.

Analysis of Results

The crystallization kinetics of polymers is analyzed in terms of the Avrami expression given in eq. (1).

$$\theta a = e^{-kt^n} \quad (1)$$

Where θa is the fraction of uncrystallized material, k is the kinetic rate constant, t is the time, and n is the Avrami exponent describing the mechanism of crystallization.

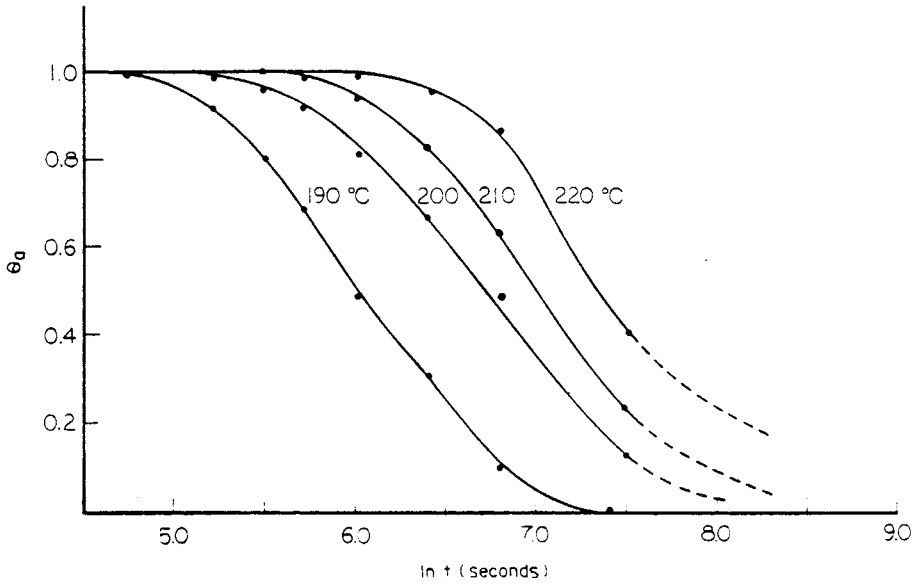


Fig. 6. Crystallization isotherms of Eastman X-14829-93-1 PET at 190, 200, 210, and 220°C.

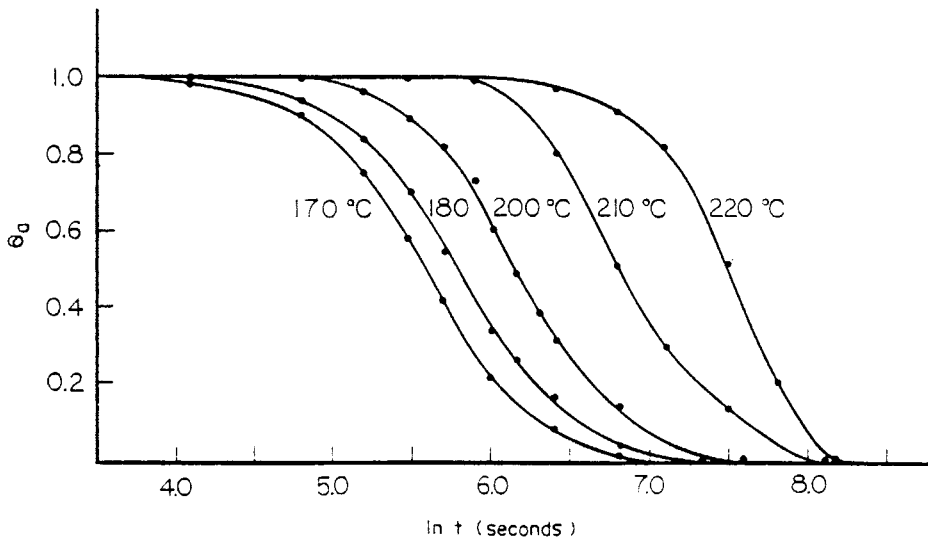


Fig. 7. Crystallization isotherms of ICI B-76 PET at 170, 180, 200, 210, and 220°C.

The mathematical formulation of the kinetic phase change and the derivation of the Avrami equation can be found in many sources.¹⁴⁻¹⁶ In the Avrami expression, the kinetic rate constant, k , is a function of the nucleation and the growth rates. The Avrami exponent provides qualitative information on the nature of nucleation and the growth processes. The various values which can be obtained for n are listed in Table III. However, it is often found that n is not an integer. This behavior has been discussed by Mandelkern.¹⁴

TABLE III
Values of the Avrami Exponent, for Various Types
of Nucleation and Growth¹⁵

n	Mechanism
4	Spherulitic growth from sporadic nuclei
3	Spherulitic growth from instantaneous nuclei
3	Disc-like growth from sporadic nuclei
2	Disc-like growth from instantaneous nuclei
2	Rod-like growth from sporadic nuclei
1	Rod-like growth from instantaneous nuclei

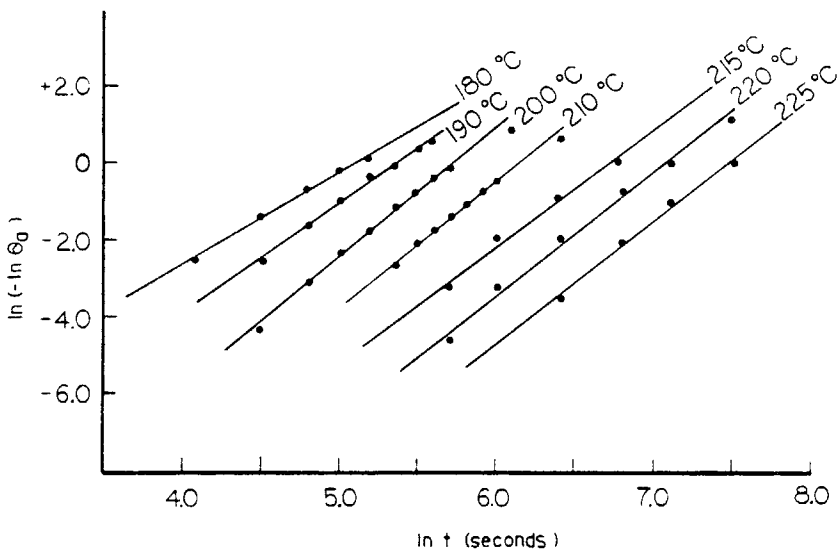


Fig. 8. Avrami plot of crystallization behavior of Goodyear 5041 PET at various temperatures.

The kinetic parameters are obtained from Eq. (1) by plotting the data according to Eq. (2).

$$\ln(-\ln \theta_a) = \ln k + n \ln t \quad (2)$$

Therefore, a plot of $\ln(-\ln \theta_a)$ vs. $\ln t$ yields a straight line; the slope is equal to n and the intercept is equal to $\ln k$.

Typical Avrami plots for the crystallization behavior of Goodyear 5041 and ICI PET are given in Figures 8 and 9, respectively. Similar plots were constructed for the other PET samples. A summary of the n and k values for the crystallization behavior of the various PET samples is given in Table IV.

Discussion and Interpretations

The rate constant, k , in Eq. (1) determines the rates of the nucleation and the growth processes which control the crystallization. It is extremely sensitive to temperature. As seen in Table III, a change of 10^4 is obtained for a change of crystallization temperature of 45°C in the case of Goodyear (5041) PET and 10^3 for a change of 50°C in the case of ICI PET samples.

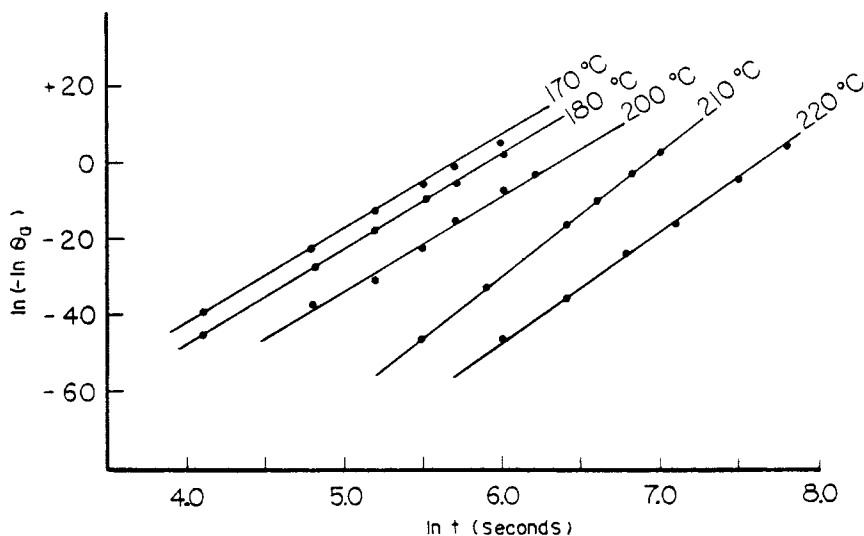


Fig. 9. Avrami plot of crystallization behavior of ICI PET at various temperatures.

The results given above indicate a very important feature of PET crystallization. The values of n are different for different PET samples. This indicates that the crystallization mechanism (as shown in Table III) is different for different PET samples. Although the two kinds of Goodyear PET (5041 and 3599) have virtually the same molecular weight ($IV = 1.0$), the n and k values are significantly different. This is partly due to the secondary molecular structure brought about by the use of different polycondensation catalyst systems. The same point can be illustrated by comparing the results of Goodyear 3599 and ICI PET samples. Although the Goodyear 3599 PET is of higher molecular weight ($IV = 1.0$) than the ICI PET ($IV = 0.68$), the crystallization rates of ICI, PET are significantly lower than those of Goodyear (3599) PET. The difference can also be accounted for by the secondary molecular structure due to the polycondensation catalyst systems. Similarly, although the Eastman and Goodyear 5041X exhibit similar IV , the rate of crystallization of Eastman is significantly lower.

The results given in Table IV show that the n value changes from $n = 3$ to $n = 2$ at lower crystallization temperatures for the ICI and the Goodyear (3599) PET samples. This kind of behavior has been observed by other workers,^{2,4} and it indicates a transition in the mechanism of crystallization as shown in Table II. In order to elucidate the differences in growth mechanism or differences between nucleation course, another independent technique such as microscopy or light scattering is needed. However, the application of these techniques requires the use of thin films.

Some workers use the half time of crystallization as a measure of the rate. This can be misleading and results in gross errors. The explanation is as follows:

$$\text{At } t = t_{1/2} \quad \text{then } \theta_a = 1/2$$

TABLE IV
Analysis of the Course of Crystallization of Various PET Samples^a

Temp. °C	Goodyear 6041		Goodyear 5041 X		Goodyear 5737 A		Celanese 4070 C		Eastman X-14829-93-1		Goodyear 3599		ICI B-76	
	n	k, sec ⁻ⁿ	n	k, sec ⁻ⁿ	n	k, sec ⁻ⁿ	n	k, sec ⁻ⁿ	n	k, sec ⁻ⁿ	n	k, sec ⁻ⁿ	n	k, sec ⁻ⁿ
170	—	—	—	—	—	—	—	—	—	—	—	—	—	—
180	3	5.0×10^{-6}	—	—	—	—	—	—	—	—	—	—	—	—
190	3	2.5×10^{-7}	—	—	3	31.7×10^{-7}	—	—	—	—	—	—	—	—
200	3	3.0×10^{-8}	3	10.2×10^{-8}	3	45.6×10^{-8}	3	1.86×10^{-8}	3	0.63×10^{-7}	2	22.5×10^{-5}	2	6.8×10^{-7}
210	3	9.2×10^{-9}	3	16.8×10^{-9}	3	44.4×10^{-9}	3	9.3×10^{-9}	3	1.43×10^{-10}	2	45.5×10^{-6}	2	1.4×10^{-7}
215	3	1.8×10^{-9}	—	—	—	—	3	4.87×10^{-9}	3	4.87×10^{-9}	3	1.1×10^{-7}	3	8.4×10^{-10}
220	3	5.3×10^{-10}	3	8.3×10^{-10}	3	20.6×10^{-10}	3	21.0×10^{-10}	—	—	—	—	—	—
225	3	1.9×10^{-10}	—	—	—	—	—	—	—	—	—	—	—	—

^a n = x ± 0.1.

From Eq. (1), it follows that

$$k = \frac{0.69}{t_{1/2}n}$$

In other words, the rate constant, k , is a combined function of $t_{1/2}$ and n , and hence $t_{1/2}$ values alone do not provide a direct means for comparing the rates for the two different processes if n is also changing. The application of $t_{1/2}$ for determining the rate of crystallization would require a prior knowledge of n .

If the objective is to produce transparent injection-molded parts, then the early stages of crystallization are very important, since the development of haze or turbidity will be noticed at a small fraction of crystallinity.¹⁷ The haze in PET is a function of the number and volume of the spherulites and the refractive index difference between the spherulites and the amorphous surroundings. Therefore, even at very small percent crystallinity, the haze level can be very large. It is clear from Table IV and from Eq. (1), that in the case of large values of k and small values of n , the early fraction of crystallized material will be larger than in the case of smaller k and larger n .

In summary, this work has shown that the crystallization behavior of PET is dependent on the molecular weight, temperature, and the polycondensation catalyst system. The catalyst system can exhibit a greater influence than the molecular weight in controlling the rate of crystallization of PET. This may be partly due to the secondary molecular structure introduced by the use of different polycondensation catalysts. Another possible explanation is that residual catalyst can act as nucleating agents and thus enhance crystallization rates.^{5, 18}

CONCLUSIONS

The crystallization behavior of various polyethylene terephthalate, PET, resins varying in molecular weight and in the polycondensation catalyst systems has been investigated. The results lead to the following conclusions.

The crystallization rates and the mechanism of crystallization are dependent on molecular weights, temperature, and the catalyst system used during polycondensation of PET.

The catalyst system can exhibit a greater influence in controlling the rate and mechanism of crystallization than the molecular weight of PET.

Among the catalyst systems investigated, a titanium-base catalyst exhibits the lowest crystallization rates, for PET of equivalent molecular weight.

The half time of crystallization may not be a good measure of the rate of crystallization as often believed if the mechanism of crystallization is also varying, that is, the Avrami exponent n is also changing.

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