

Kinetics of non-isothermal crystallization of polyethylene and polypropylene

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Differential scanning calorimetry (d.s.c.) data on non-isothermal crystallization of isotactic polypropylene and high-density polyethylene from the melt at different cooling rates were treated in terms of the Ozawa equation. It was found that the crystallization of polypropylene follows the Ozawa equation but in the case of polyethylene the Ozawa theory is not valid.

Keywords Polyethylene; polypropylene; crystallization; kinetics; Ozawa equation

INTRODUCTION

Numerous studies have been reported of isothermal crystallization of high polymers¹ and the picture used has been that nuclei appear randomly in space in the supercooled melt, and subsequently grow at a constant rate, in one, two, or three dimensions. The Avrami equation^{2,3} has been proposed for these processes and isothermal crystallization was found to follow this kinetic equation.

However, since isothermal crystallization conditions are rarely used in practice, it seemed desirable to study crystallization of polymers under non-isothermal conditions.

Ozawa⁴ has extended the Avrami equation to the non-isothermal situation, assuming that the amorphous polymer is heated or cooled at a constant rate and the mathematical derivation of Evans³ is valid. According to Ozawa theory, the degree of conversion at temperature T amounts to:

$$\ln\left(1 - \frac{x_T}{x_\infty}\right) = \frac{\kappa(T)}{\phi^n} \quad (1)$$

Here x_∞ is crystallinity at the termination of the crystallization process, x_T is crystallinity at temperature T , ϕ is cooling (or heating) rate, $\kappa(T)$ is cooling or heating function. The integer n has a value between 1 and 4 depending on whether nucleation is instantaneous or sporadic, and on the number of dimensions in which growth occurs.

The Ozawa equation has been tested^{4,5} for poly(ethylene terephthalate) and nylon-6 crystallization. In this paper, non-isothermal crystallization of isotactic polypropylene and high-density polyethylene and the effect of varying cooling rates on melt crystallization are studied by differential scanning calorimetry (d.s.c.).

EXPERIMENTAL

The samples used throughout these experiments were Polish commercial isotactic polypropylene and Hostalen

high-density polyethylene. Intrinsic viscosities determined in decalin at 135°C were 2.72 dl g⁻¹ and 2.48 dl g⁻¹ respectively.

Observations of dynamic cooling crystallization of the samples reported here were carried out with a 990 Du Pont differential scanning calorimeter. Each sample was heated from ambient temperature to 458K and annealed in the molten state for 3 min. Then the sample was cooled at a constant rate ϕ (selected in the range from 0.5K min⁻¹ to 10K min⁻¹) and the d.s.c. trace was recorded. Operations were carried out under nitrogen.

RESULTS AND DISCUSSION

Some representative crystallization exotherms of polypropylene at several cooling rates are shown in Figure 1. As can be seen, the baseline is the continuation of straight lines observed on d.s.c. thermograms before and after completion of crystallization heat evolution.

The resistance to heat flow between sample pan and holder, R_0 , results in a lag between the temperature of the sample and the temperature of the pan holder. We have estimated the thermal lag by running a thermogram of the crystallization of very pure indium (see Figure 2a). According to Gray⁶ and O'Neill⁷ the slope of the leading edge of the resulting exotherm is equal to the ratio ϕ/R_0 . Hence, the true temperature at the point A (see Figure 2b) is read off as T , and the area up to AB is measured. The ratio of this area to the total area yields a value for the degree of conversion x_T/x_∞ at temperature T .

The experimental data concerning the temperature dependence of the degree of conversion can be analysed in terms of the Ozawa equation. From equation (1) it follows that:

$$\log\left[-\ln\left(1 - \frac{x_T}{x_\infty}\right)\right] = \log \kappa(T) - n \log \phi \quad (2)$$

If we plot the left side of equation (2) against $\log \phi$ at a given temperature and if the Ozawa theory is valid, we

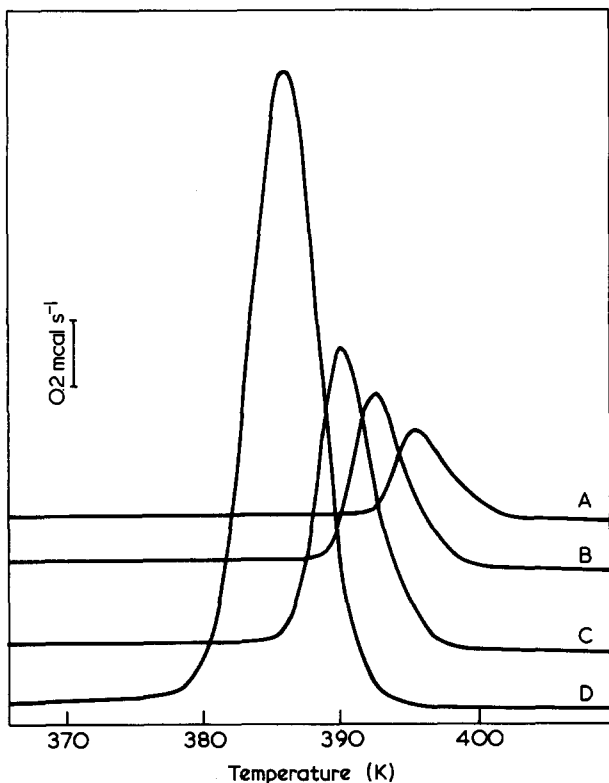


Figure 1 Typical d.s.c. thermograms of non-isothermal crystallization for polypropylene at different cooling rates: curve A, 0.5K min⁻¹; B, 1K min⁻¹; C, 2K min⁻¹; D, 5K min⁻¹

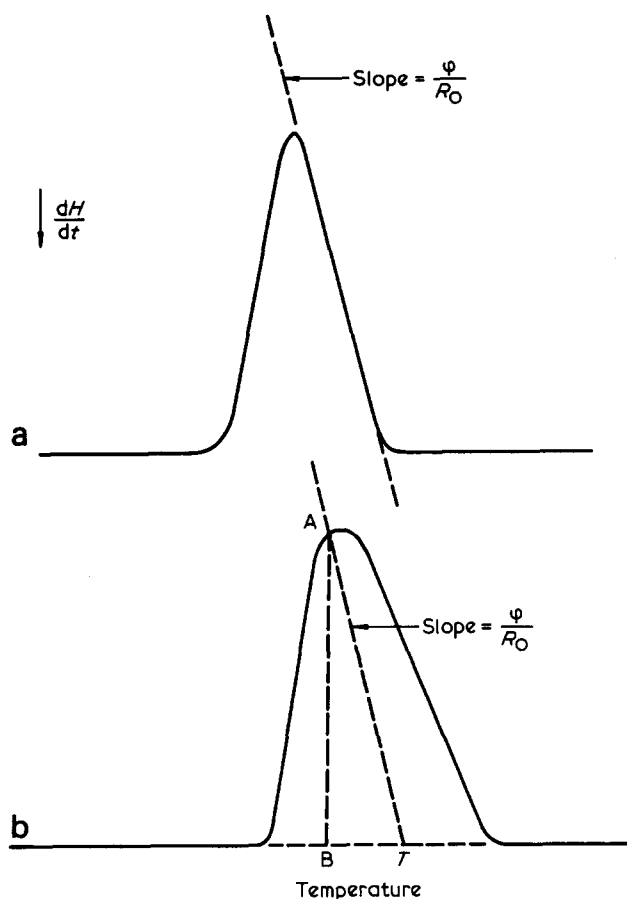


Figure 2 D.s.c. thermograms of crystallization of: (a) very pure indium; (b) polymer

shall obtain a straight line. Parameters n and $\kappa(T)$ can be found from the slope and the intercept of this line.

Figure 3 shows experimental data for non-isothermal crystallization of polypropylene in Ozawa coordinates. It is clear that straight lines may be drawn through the data points. Ozawa exponents n determined by least-squares method, listed in Table 1, suggest that the predetermined nuclei exist before cooling and that the crystallites grow three dimensionally. The cooling function $\kappa(T)$ was found to be an exponential function of temperature (Figure 4). Avrami's exponent n for the same polypropylene derived from isothermal crystallization was equal⁸ to 3, which is in satisfactory accordance with the results of cooling crystallization.

Turning our attention now to the non-isothermal crystallization of polyethylene (Figure 5) we may notice that in this case the disappearance of the liquid phase cannot be related to the temperature by the equation developed by Ozawa. Figure 5 shows the non-linear dependence of

$$\log \left[-\ln \left(1 - \frac{x_T}{x_\infty} \right) \right]$$

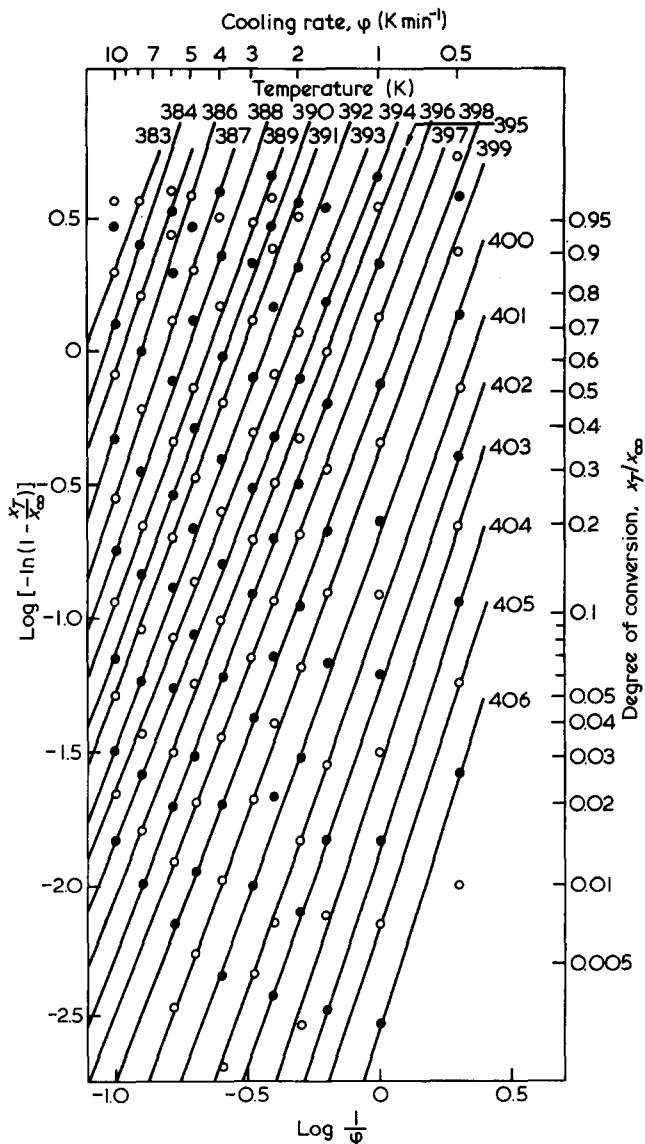
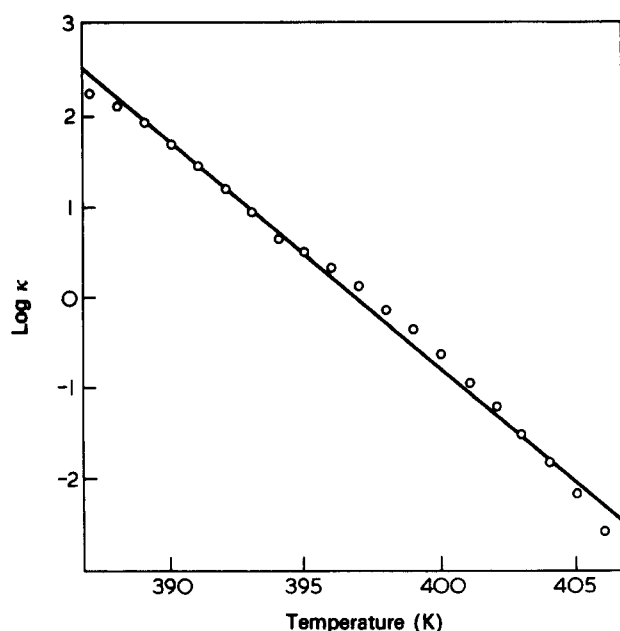


Figure 3 Test of Ozawa equation for polypropylene

Table 1 Ozawa exponent n as a function of temperature for polypropylene

Temperature (K)	Ozawa exponent, n
406	3.29
405	3.13
404	2.96
403	2.97
402	2.90
401	2.77
400	2.74
399	2.60
398	2.55
397	2.60
396	2.55
395	2.57
394	2.66
393	2.59
392	2.71
391	2.74
390	2.78
389	2.80
388	2.82
387	2.80

Figure 4 Cooling functions κ for polypropylene versus temperature

upon $\log \phi$. With polyethylene the crystallization is complicated by an additional slow process, referred to as secondary crystallization¹, which is considered to involve improvement of the degree of the crystalline order.

The secondary effect for polyethylene crystallization is sometimes greater than 40% of the total⁹ and maybe for this reason the Ozawa equation is not fulfilled.

The theory of Ozawa neglects several other factors affecting the rate of non-isothermal crystallization.

Since the lamellar thickness is a function of crystallization temperature the fold-length should be taken into account. Moreover, both sporadic and predetermined nucleation have been observed for some polymers, each in different temperature ranges. The above-mentioned factors probably result in the inadequacy of the Ozawa equation for polyethylene and variation of the Ozawa exponent with temperature in the case of non-isothermal crystallization of polypropylene (Table 1).

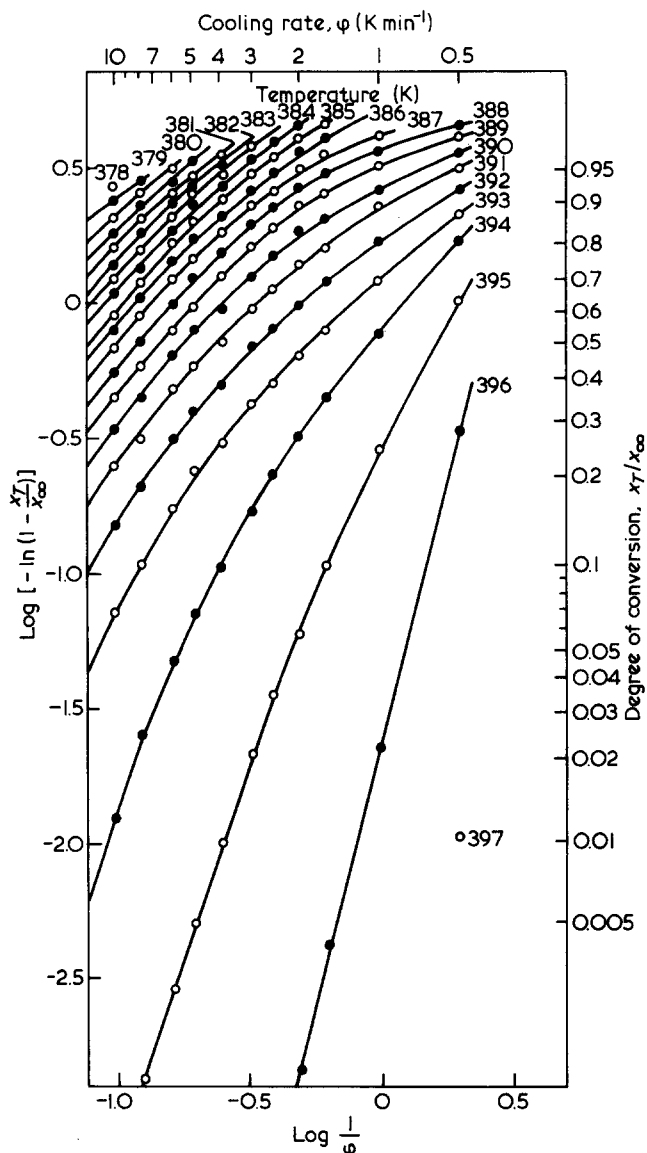


Figure 5 Test of Ozawa equation for polyethylene

CONCLUSIONS

Non-isothermal crystallization of isotactic polypropylene can be described by the Ozawa equation. Ozawa exponent n ranging from 3.3 to 2.6 suggests predetermined nucleation and three-dimensional growth of the crystallites.

Cooling crystallization of polyethylene does not follow the Ozawa equation, probably because of factors neglected in the theory of Ozawa, such as secondary crystallization, dependence of lamellar thickness on crystallization temperature and variation of Avrami's exponent with crystallization temperature.

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