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BULK AND SOLUTION CRYSTALLIZATION KINETICS OF ISOTACTIC POLYBUTENE-1

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Abstract—The crystallization kinetics of an unfractionated sample of isotactic polybutene-1 have been studied from the melt and from dilute solutions in amyl acetate by the dilatometric method. The kinetics of bulk crystallization followed the Avrami equation for most of the transformation with a deviation towards the end of the crystallization process. The Avrami exponent is found to be temperature dependent with the value of $n \approx 3$ at high undercooling (indicating a homogeneous nucleation process) and $n \approx 4$ at lower undercooling (indicating a heterogeneous nucleation process). The temperature coefficients of the rate constants indicate a nucleation controlled process of crystallization.

When amyl acetate is used as a diluent, the crystallization was found to follow the Avrami formulation only at a high undercooling, while at the other temperatures it is applicable only to part of the transformations. The excess interfacial free energy and the lateral free energy have been evaluated for the polymer in amyl acetate.

INTRODUCTION

Isotactic polybutene-1 (PB-1) is found to exist in at least three polymorphic modifications. On crystallization from the melt, the polymer assumes a metastable tetragonal modification (often referred to as Modification II), the more stable modification having a hexagonal unit cell (referred to as Modification I).

Boor and Mitchell(1) have studied the formation and melting of Modifications I and II by different techniques. The kinetics of crystallization of Modification II followed the Avrami equation with the value of the Avrami exponent $n = 4$. However, a dilatometric study by Danusso and Gianotti(2) gives $n = 3 \cdot 1$. A comparative study of the bulk crystallization kinetics of polypropylene and isotactic PB-1 has been made by Gordon and Hillier;(3) they found $n = 3 \cdot 13 \pm 0 \cdot 13$ for isotactic PB-1. Danusso and Gianotti(4) have studied the effect of α-chloronaphthalene and decalin as diluents on the melting point, enthalpy and entropy of fusion of isotactic PB-1.

Thus the existing data gives different values of the Avrami exponent n of $3 \cdot 1$ and 4, and different growth mechanisms have been suggested for the crystallization process from melt. The Avrami exponent is reported to be independent of temperature. Hence a bulk and solution crystallization study of the polymer has been undertaken for a clear understanding of the crystallization process, the temperature dependence of the kinetic parameters and the effect of added diluent on the kinetics of crystallization.

EXPERIMENTAL

Unfractionated isotactic PB-1 was freed from traces of the amorphous form by extraction as reported earlier.(5) The changes in specific volume of the polymer during bulk crystallization were measured by the conventional J-type dilatometer,(6) with a capillary of internal diameter 0·5 mm. About 1 g of the polymer in the form of film was taken in the dilatometer. Distilled mercury was used as the confining liquid. The kinetic studies were made at 95°, 98° 102° and 105°. Prior to crystallization at a predetermined temperature, the dilatometer was heated in an oil bath at 170° for about half an hour to remove all traces of crystallinity. The bath was then allowed to cool to about 140° and the dilatometer was quickly transferred into an oil thermostat held within ± 0·01° of the crystallization temperature. The mercury height in the measuring capillary was recorded using a cathetometer with an accuracy of ± 0·005 cm. The capillary height at the end of the crystallization process was recorded in the usual manner.

Dilatometers used in the study of the crystallization kinetics of dilute solutions were basically of the same design, with a reservoir volume of about 100 ml. The method proposed by Mandelkern(7) was used in the construction and filling of the dilatometers. The capillary had an internal diameter of 1 mm. The same capillary was used throughout the work. The polymer concentrations chosen were 0·05, 1 and 2% (w/v). At each concentration, the undercoolings were chosen to lie slightly below the turbidity temperature. All traces of crystallinity were removed by heating the dilatometer to about 20° above the turbidity temperature and the kinetics of crystallization was followed in the same manner as in the case of bulk crystallization in a thermostat regulated to within ± 0·01° of the crystallization temperature.

RESULTS AND DISCUSSION

Bulk crystallization kinetics

The plots of dilatometric height as a function of log t (time in minutes) were found to be sigmoidal in nature; a typical isotherm is shown in Fig. 1. The relative extent of crystallization, $X(t)$, at time t can be defined as $(h_0 - h_t)/(h_0 - h_\infty)$ where h_0 is the mercury height for the supercooled melt at the crystallization temperature, h_t the height of mercury at time t and h_∞ is the height at the completion of the crystallization process. The experimental results have been analysed according to the Avrami equation;(8,9)

$$(h_t - h_\infty)/(h_0 - h_\infty) = \exp(-zt^n) \qquad (1)$$

where the rate constant z contains geometric factors as well as the growth and nucleation rates.

The crystallization process follows the Avrami equation for most of the crystallization, as indicated by the linearity of the plots of log $[\ln\{(h_0 - h_\infty)/(h_t - h_\infty)\}]$ against log t. A slight deviation was observed in all cases towards the end of the crystallization process when simultaneous secondary crystallization sets in.(10) Such plots

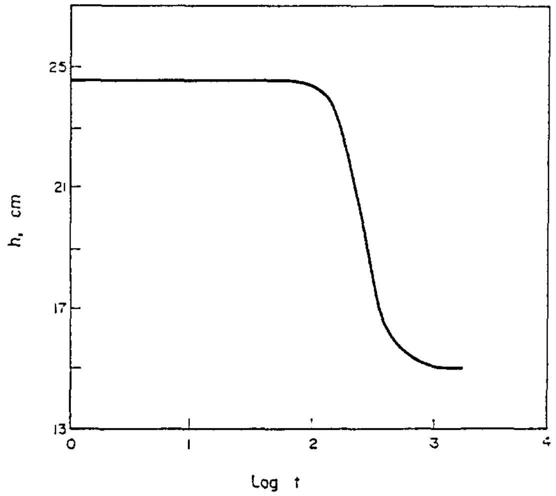

FIG. 1. Plot of dilatometric height as a function of log t for the bulk crystallization of isotactic PB-1 at 98°.

are shown in Fig. 2. The Avrami exponent n and the rate constant z have been evaluated from the slope and intercept of the linear portions of these plots and are reported in Table 1. The times required for the completion of half of the crystallization process $(t_{0\cdot 5})$ are also included in Table 1.

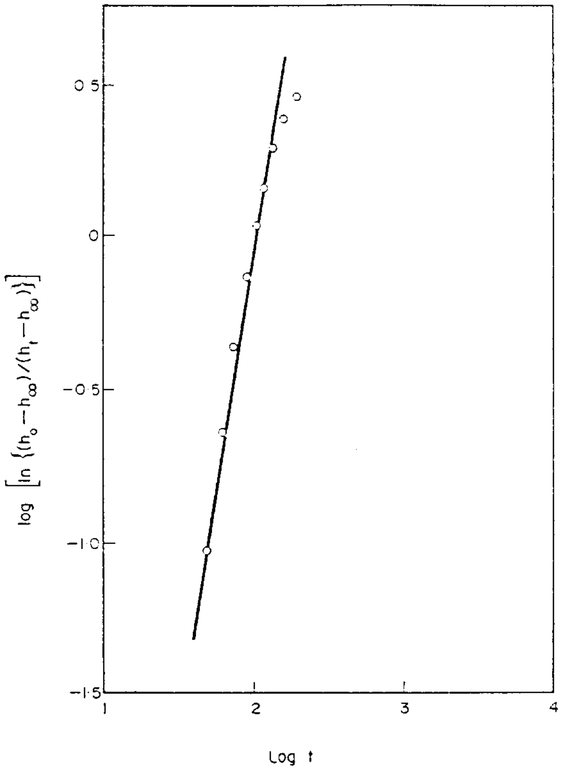

FIG. 2. Plot of log [ln $\{(h_0 - h_\infty)/(H_t - h_\infty)\}$] against log t at 95°.

TABLE 1.

T_c(°C)	n	z	$t_{0\cdot 5}$ (min)
95	3·05	$1{\cdot}59 \times 10^{-6}$	125
98	3·10	$2{\cdot}98 \times 10^{-7}$	250
102	3·43	$2{\cdot}51 \times 10^{-9}$	1000
105	3·80	$2{\cdot}00 \times 10^{-13}$	3160

It is observed that the value of n increases from 3·05 to 3·80 as the crystallization temperature is raised from 95° to 105°. The value of 3·05 and 3·10 at 95° and 98° are in good agreement with those reported by Danusso and Gianotti.(2) They have taken an average value of n assuming that the exponent is independent of the temperature over the range studied. However, from their data also it can be seen that the value of n increases with an increase in T_c. The values of the exponent at 95° and 98° indicate that the crystallization starts from a heterogenous nucleation process followed by three-dimensional growth. But the values of n at 102° and 105° indicate that the crystallization process starts from homogeneous nucleation followed by three-dimensional growth. However, there is no clear line of demarcation between the two types of nucleation as far as temperature dependence is concerned.

A plot of $t_{0.5}$ as a function of the crystallization temperature gives a curve characteristic of the rapid increase of $t_{0.5}$ with rise in T_c. Assuming that the secondary crystallization involved in spherulitic growth is three-dimensional in character and that the critical free energy required to form a secondary nucleus is less by a factor $\bar{a}$ than that for the primary nucleus, Mandelkern$^{(11)}$ has derived the equation:

$$\ln z = \ln z_0 - \frac{nE_D}{RT} - \frac{[1 + (n-1)\,\bar{a}]\,kT_m^2}{T_c\,(\Delta T)^2} \tag{2}$$

where E_D is the free energy of activation for transport across the liquid–nucleus interface at the steady state, k is a constant involving the excess interfacial free energy per repeating unit σ_e, the lateral interfacial free energy σ_u and heat of fusion ΔH_u of the polymer, z is the rate constant and z_0 is a constant independent of temperature. If the rate constant is expressed in terms of $t_{0.5}$, Eqn. (2) reduces to

$$\ln\,(1/t_{0.5}) = \frac{1}{n(\ln k_0 + \ln \ln 2)} - \frac{E_D}{RT} - \frac{[1 + (n-1)\,\bar{a}]\,kT_m^2}{n\,T_c(\Delta T)^2}. \tag{3}$$

In Eqns. (2) and (3), the last term dominates at low undercoolings and a plot of $\ln(1/t_{0.5})$ against $T_m^2/T(\Delta T^2)$ should be linear. Experimental data shows that such a plot is linear as shown in Fig. 3, from which it can be concluded that secondary nucleation in the bulk crystallization of isotactic PB-1 is three-dimensional in character. The temperature dependence of the Avrami rate constant, z, is shown in Fig. 4. It is observed that log z varies linearly with $1/(\Delta T)^2$ corresponding to growth by a process of three-dimensional secondary nucleation. Gordon and Hillier$^{(3)}$ have observed a break in such a plot at low undercoolings for isotactic PB-1. However, such a break has not been observed in the present case.

The large negative temperature coefficient of the crystallization rate in the vicinity of the melting temperature involves a transformation which is nucleation controlled. Mandelkern$^{(11)}$ has expressed the steady state rate of nucleation N, in the pure melt of a polymeric system under these conditions in terms of the equations:

$$N = N_0 \exp\,(-E_D/RT_c) \exp\,(-\Delta F_2^*/RT_c) \tag{4}$$

$$N = N_0\,T_c \exp\,(-E_D/RT_c) \exp\,(-\Delta F_2^*/RT_c) \tag{5}$$

$$N = N_0 \exp\,(-E_D/RT_c) \exp\,(-\Delta F_3^*/RT_c) \tag{6}$$

$$N = N_0\,T_0 \exp\,(-E_D/RT_c) \exp\,(-\Delta F_3^*/RT_c). \tag{7}$$

Here ΔF^* is the critical free energy of nucleus formation. The subscripts 2 and 3 differentiate between the two-dimensional and three-dimensional nucleation processes. Mandelkern *et al.*,$^{(12)}$ have given equations for ΔF_2^* and ΔF_3^* in the range of infinite molecular weight as

$$\Delta F_2^* = 4\,\sigma_u\,\sigma_e/\Delta f_u \tag{8}$$

$$\Delta F_3^* = D\,\sigma_u^2\,\sigma_e/(\Delta f_u)^2 \tag{9}$$

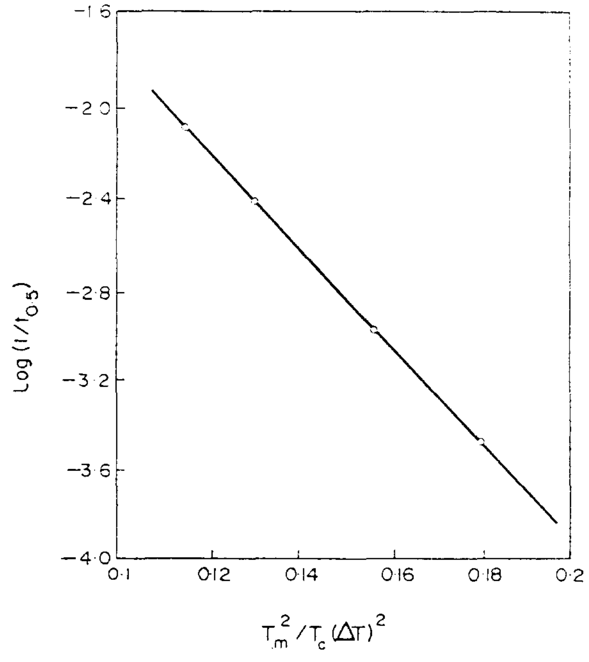

FIG. 3. Variation of log ($1/t_{0.5}$) as a function $T_m^2/T_c(\Delta T)^2$.

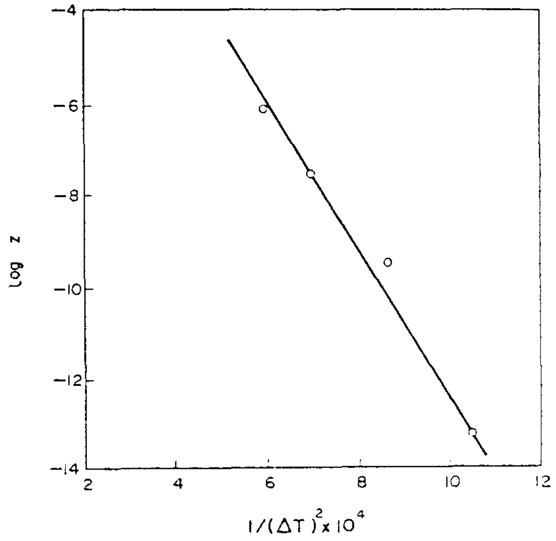

FIG. 4. Plot of log z against $1/\Delta T^2$.

where Δf_u is the free energy of fusion per repeating unit and D is a constant determined by the geometrical shape of the nucleus formed. The rate at which crystallinity develops from the melt for the phase transformation can be written in the general form

$$1 - \lambda(t) = 1 - \lambda(\infty)\,\{1 - \exp(-zt^n/1 - \lambda(\infty))\} \tag{10}$$

where $1-\lambda(t)$ and $1-\lambda(\infty)$ refer to the weight fractions of the polymer that is crystalline at time t and at the termination of the process respectively. Combining Eqns. (4)–(7) with (10), four corresponding equations for the crystallization rate in terms of the time, $t_{0\cdot1}$, for one tenth of the transformation to occur have been derived.[11]

$$\ln\left(\frac{1}{t_{0\cdot1}}\right) = \ln\left(\frac{1}{t}\right)_0 - \frac{E_D}{RT_c} - \frac{k_2 T_m}{nRT_c\Delta T} \tag{11}$$

$$\ln\left(\frac{1}{t_{0\cdot1}}\Big/T_c^{1/n}\right) = \ln\left(\frac{1}{t}\right)_0 - \frac{E_D}{RT_c} - \frac{k_2 T_m}{nRT_c\Delta T} \tag{12}$$

$$\ln\left(\frac{1}{t_{0\cdot1}}\right) = \ln\left(\frac{1}{t}\right)_0 - \frac{E_D}{RT_c} - \frac{[1 + (n-1)\,\bar{a}]}{n}\cdot\frac{k_3 T_m^2}{RT_c(\Delta T)^2} \tag{13}$$

$$\ln\left(\frac{1}{t_{0\cdot1}}\Big/T_c^{1/n}\right) = \ln\left(\frac{1}{t}\right)_0 - \frac{E_D}{RT_c} - \frac{[1 + (n-1)\,\bar{a}]}{n}\cdot\frac{k_3 T_m^2}{RT_c(\Delta T)^2}. \tag{14}$$

Here k_2 and k_3 are the constants for two-dimensional and three-dimensional nucleation. In the above equation Δf_u has been approximated by $\Delta f_u = \Delta H_u\ \Delta T/T_m$. In deriving Eqns. (11)–(14), it has been assumed that the thermodynamic contribution to the nucleation process is rate determining and the contribution of transport process, as embodied in E_D has been neglected. According to Eqns. (11) and (13) plots of $\ln(1/t_{0\cdot1})$ against $T_m/T_c(\Delta T)$ and $T_m^2/T_c\ (\Delta T)^2$ must be linear. Similarly equations (12) and (14) require plots of $\ln(1/t_{0\cdot1}/T_c^{1/n})$ against $T_m/T_c\ (\Delta T)$ and $T_m^2/T_c\ (\Delta T)^2$ to

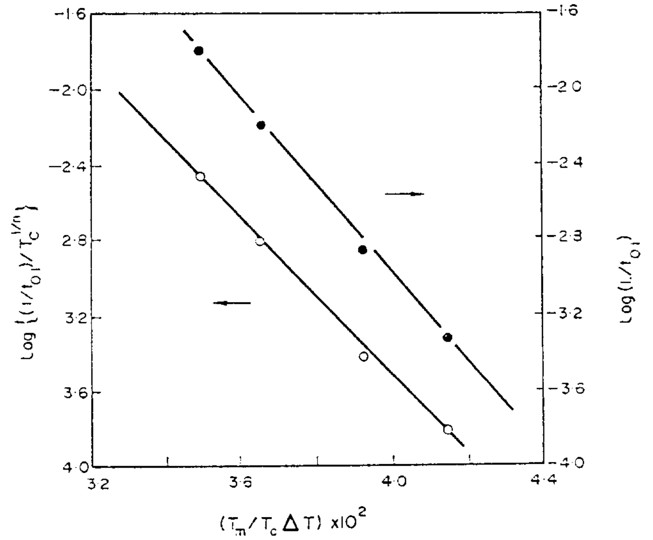

FIG. 5. Plots of $\log(1/t_{0\cdot1}/T_c^{1/n})$ and $\log(1/t_{0\cdot1})$ against $T_m/T_c(\Delta T)$.

be linear. Analysis of the present data in terms of Eqns. (11)–(14) indicate that such plots are linear as shown in Figs. (5) and (6). Kim and Mandelkern⁽¹³⁾ have shown that, even if E_D is not neglected, the nature of the relationships is not altered.

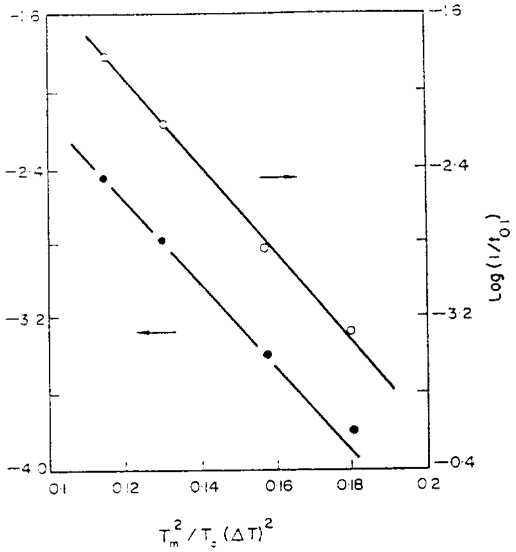

FIG. 6. Variation of log $(1/t_{0\cdot1}/T_c^{1/n})$ and log $(1/t_{0\cdot1})$ against $T_m^2/T_c\,(\Delta T)^2$.

From this, it can be concluded that the data for the overall crystallization kinetics can fit equally well into any of the Eqns. (11)–(14) by the appropriate choice of parameters. Universal parameters for the overall crystallization rates for many polymers have been deduced by Kim and Mandelkern.⁽¹³⁾

Solution Dilatometry

The isotherm shapes and consequently the kinetic processes that determine the isotherms depend to a large extent on the concentration of polymer in polymer–diluent mixtures. It has been established⁽¹¹,¹⁴⁾ that for polymer–diluent mixtures containing small amounts of diluents, and for very dilute solutions, the experimental curves compare favourably with those for homopolymers, although the crystallization mechanisms are not the same.

The shape of the individual isotherms obtained for the crystallization of isotactic PB-1 in amyl acetate at low undercoolings, by plotting dilatometric height as a function of log t, are similar to those observed in the bulk crystallization kinetics. A typical plot is shown in Fig. 7. Partial linearity is observed in the plots of log [ln $\{(h_0 - h_\infty)/(h_t - h_\infty)\}$] against log t. In most cases, a break in the linearity is observed showing two distinct rate constants for the crystallization process, as shown in Fig. 8. In morphological studies⁽¹⁵⁾ it has been found that both hexagonal and orthorhombic modifications of isotactic PB-1 crystallize at the turbidity temperature from solutions in amyl acetate. The two distinct rate constants may be due to the two morphologies growing at different rates due to different chain packing in the crystals. The value of the rate constant, z, and the Avrami exponent n, for the portions of the crystallization process to which the Avrami equation is applicable, have been calculated from the slope and intercept of the above plots. It is observed that n remains constant only during small fractions of crystallization and increases as crystallization progresses. The value of n and z are reported in Table 2.

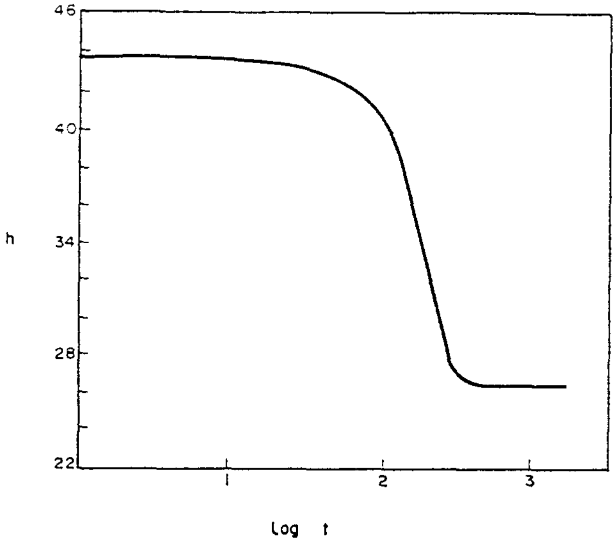

FIG. 7. Plot of h vs. log t for 2% solution of isotactic PB-1 in amyl acetate at 58°.

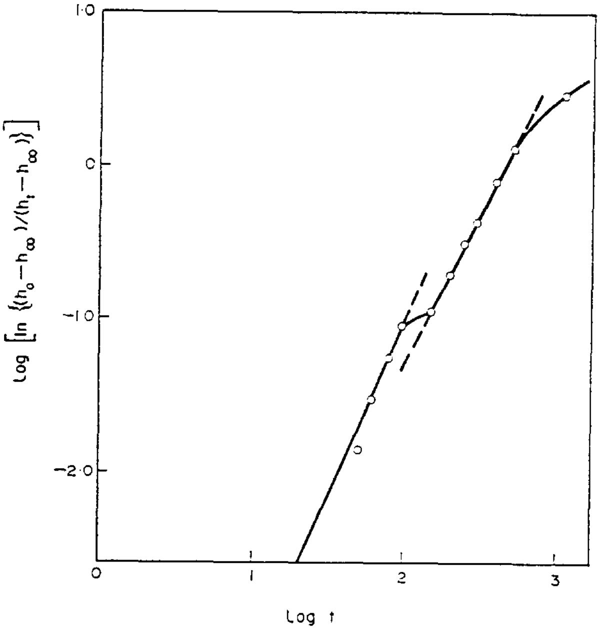

FIG. 8. Plot of log $[\ln\{(h_0 - h_\infty)/(h_t - h_\infty)\}]$ against log t for solution dilatometry.

TABLE 2. KINETIC PARAMETERS OF THE CRYSTALLIZATION OF ISOTACTIC PB-1 FROM SOLUTIONS IN AMYL ACETATE AT 58°

Conc. (g/dl)	z		n		$t_{0\cdot5}$ (min)
	I	II	I	II	
0·5	$1\cdot79 \times 10^{-6}$	$9\cdot17 \times 10^{-6}$	2·41	1·67	450
1·0	$3\cdot16 \times 10^{-6}$	$7\cdot65 \times 10^{-5}$	2·40	1·56	210
2·0	$7\cdot94 \times 10^{-7}$	$1\cdot42 \times 10^{-3}$	2·44	1·00	160

I—Initial part of the crystallization.
II—Final part of the crystallization.

Although the Avrami equation appears to be applicable, the very low values of n observed for the crystallization process can only be explained as due to the limitation of applicability of the equation. A similar discrepancy has been observed in the bulk crystallization of poly(ethylene oxide) by Banks and Sharples.(16)

According to the theory of phase changes of the solute species from a binary mixture proposed by Turnbull(17)

$$\ln (1 - X) = -\frac{4}{3} v^2 (C_0 - C_\infty)^2 n_i G^3 t^3 \tag{15}$$

for small amounts of transformation, where v is the molar volume of the solution, C_0 and C_∞ are the initial concentration of the crystallizing species, and the final concentration of the supernatant fluid at the end of the transformation respectively, n_i is the number of particles at time $t = 0$ and G is the growth rate. Many workers(9,18,19) have shown that the growth rate is nucleation controlled in bulk as well as in solution crystallization. Avrami(20,21) has shown that irrespective of whether or not the nuclei are formed homogeneously at the onset of crystallization, the initial rate at which the centres are formed and consequently their number will directly depend on the free energy of forming a primary nucleus of critical size, ΔF^*.

The steady state nucleation theory for condensed systems proposed by Turnbull and Fischer(22) leads to the equation proposed by Mandelkern,(23)

$$\log (1/\tau_{0\cdot9}) = \frac{1}{n} [\log k_0(v_2) + \log \log (1/0\cdot9)] \cdot \frac{E_D(v_2)}{2\cdot3RT_c} - \frac{(1 + n\bar{a})}{n} (\Delta F^* v_2/2\cdot3RT_c) \tag{16}$$

where v_2 is the volume fraction of the polymer and $\tau_{0\cdot9}$ is defined as the time when $(1 - X) = 0\cdot9$. The major contribution to the temperature dependence of the rate will be embodied in the last term of Eqn. (16) because of the restricted temperature range for the experiments in the present study. ΔF^* is defined(24) as

$$\Delta F^* = (8\pi \sigma_u^2 \sigma_e/\Delta f_u'^2) - (4\pi RT \sigma_u^2 \ln v_2/\Delta f_u'^2) \tag{17}$$

where $\Delta f_u'$, the free energy of fusion of a polymer unit from the pure crystalline phase to the melt at the specified composition is approximated to

$$\Delta f_u'^2 = \Delta H_u (T_m - T_c)/T_m. \tag{18}$$

From the above considerations, the data of the crystallization kinetics of the polymer–diluent mixtures can be analysed by plotting $\log (1/\tau_{0\cdot 9})$ against $T_m^2/T_c\,(\Delta T)^2$ and the relation must be linear for a temperature range in the vicinity of the melting temperature. The slope, S, of such plots depends on the polymer concentration according to the relation:

$$S = -\left(\frac{1+n\bar{a}}{n}\right)\frac{8\pi\,\sigma_u^2\,\sigma_e}{2\cdot 3R\Delta H_u^2} - \frac{4\pi\,\sigma_u\,T_c \ln v_2}{\Delta H_u^2}. \tag{19}$$

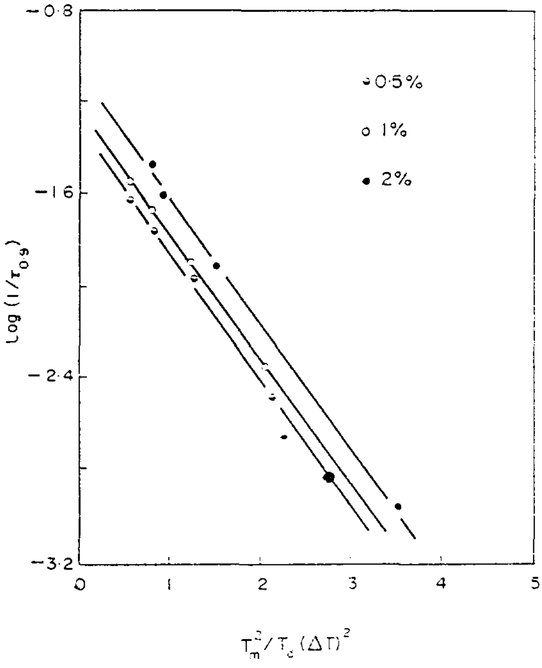

FIG. 9. Plots of $\log (1/\tau_{0\cdot 9})$ vs. $T_m^2/T_c\,(\Delta T)^2$ at three different concentrations of isotactic PB-1 in amyl acetate.

Such plots of $\log (1/\tau_{0\cdot 9})$ vs. $T_m^2/T_c\,(\Delta T)^2$, where T_m is the turbidity temperature of the polymer–diluent mixtures, are shown in Fig. 9 for the three concentrations of isotactic PB-1 in amyl acetate. The plots are linear. In the case of polyethylene, Mandelkern(23) has observed that the slope is invariant from 0·1 to 1% solutions in α-chloronaphthalene. In the present case, however, the slopes of the plots are found to decrease with increase in polymer concentration.

The slope of these plots, defined by Eqn. (19), must vary linearly with $-\ln v_2$. A plot of S against $-\log v_2$ is shown in Fig. 10. The ratio of the slope at a concentration v_2 to that of the pure polymer ($v_2 = 1$) is given by

$$\frac{\text{slope } (v_2)}{\text{slope } (v_2 = 1)} = K = 1 - \frac{2\cdot 3RT_c \log v_2}{2\Delta H_u\,(\sigma_e/\Delta H_u)}. \tag{20}$$

Hence, K must also be a linear function of $-\log v_2$. Such a plot is also included in Fig. 10 and the relation is observed to be linear.

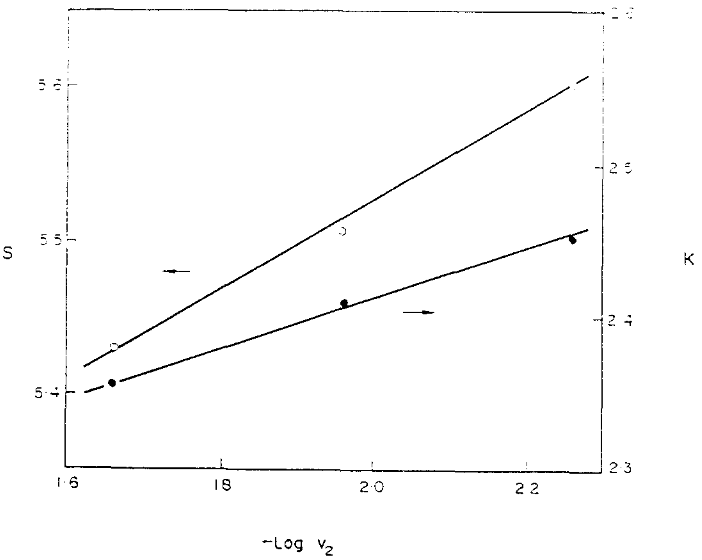

FIG. 10. Plots of S and K vs. $-\log v_2$ for solution dilatometry.

Estimates of σ_u and σ_e can be made from the above plots corresponding to Eqns. (19) and (20) if the factor $(1 + n\bar{a})/n$ is taken to be of the order of unity. The slope of the S vs. $-\log v_2$ plot leads to the calculation of σ_u, σ_e can be evaluated from the slope of the K vs. $-\log v_2$ plot. Taking the value of the heat of fusion, ΔH_u, as 1650 cal/monomer,(25) σ_u and σ_e have been calculated. Their values have been found to be 90 cal/monomer and 1390 cal/monomer respectively, taking the average of T over the temperature range studied. The values of $\sigma_u/\Delta H_u = 1 \cdot 83 \times 10^{-2}$ and $\sigma_e/\Delta H_u = 0 \cdot 84$ obtained for isotactic PB-1 are comparable to those of 1×10^{-2} and $0 \cdot 75$ respectively obtained for polyethylene.(21) According to Mandelkern *et al.*,(14) for a polymer of infinite molecular weight in an infinitely dilute solution, a unimolecular crystallization process is to be expected. This condition, however, is not achieved in the present case indicating that the mechanism of crystallization involves the participation of more than one molecule in the rate-determining step.

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Résumé—On a étudié par dilatométrie la cinétique de cristallisation d'un échantillon non fractionné de polybutène-1 isotactique à l'état fondu et en solution diluée dans l'acétate d'amyle. La cinétique de la cristallisation en masse obéit à l'équation d'Avrami pour la plupart des transformations avec une déviation vers la fin du processus de cristallisation. On a troué que l'exposent d'Avrami dépend de la température avec une valeur de $n \simeq 3$ pour une surfusion importante (ce qui indique un processus de nucléation homogène) et $n \simeq 4$ pour une faible surfusion (ce qui indique un processus de nucléation hétérogène). Les coefficients de température des constantes de vitesse indiquent que le processus de cristallisation est controlé par la nucléation.

Sommario—Mediante il metodo dilatometrico, si è studiata la cinetica di cristallizzazione di un campione di polibutene-1 isotattico non sottoposto alla distillazione frazionata, a partire dallo stato di fusione e in soluzioni diluite di amilacetato. La cinetica della cristallizzazione in massa segue l'equazione di Avrami per la maggior parte della trasformazione con una deviazione verso la fine del processo di cristallizzazione. Si è trovato che l'esponente di Avrami dipende dalla temperatura con il valore di $n \approx 3$ con elevata soprafusione (indicando così una germinazione omogenea) e di $n \approx 4$ con soprafusione bassa (indicando così una germinazione eterogenea). I coefficienti di temperatura delle costanti di velocità indicano che il processo della cristallizzazione è controllato dalla germinazione.

Con impiego di amilacetato come diluente, si è trovato che la cristallizzazione segue la formula di Avrami solamente con soprafusione elevata, mentre ad altre temperature la formula è valida solo per parte delle trasformazioni. Per il polimero in amilacetato, si sono stimate l'energia libera d'interfaccia in eccesso e quella laterale.

Zusammenfassung—Die Kinetik der Kristallisation einer unfraktionierten Probe von isotaktischem Polybuten-1 aus Schmelze und aus verdünnten Lösungen in Amylacetat wurde mit Hilfe der dilatometrischen Methode untersucht. Die Kinetik der Kristallisation aus der Schmelze folgte für den überwiegenden Teil der Umwandlung der Avrami-Gleichung mit einer Abweichung gegen Ende des Kristallisationsprozesses. Der Avrami Exponent ist temperaturabhängig und hat den Wert $n = 3$ bei starker Unterkühlung (was einen homogenen Keimbildungsprozess anzeigt) und einen Wert $n = 4$ für geringere Unterkühlung (was einen heterogenen Keimbildungsprozess anzeigt). Die Temperaturkoeffizienten der Geschwindigkeitskonstanten weisen auf einen durch Keimbildung kontrollierten Kristallisationsprozess hin.