

## USE OF DIFFERENTIAL SCANNING CALORIMETRY TO STUDY POLYMER CRYSTALLIZATION KINETICS WITH LONGER HALF TIMES

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### ABSTRACT

A method has been developed to determine polymer crystallization parameters with longer half times using differential scanning calorimetry. This method can be used irrespective of the crystallization temperature, sample weight, nature of the polymer and the sensitivity of the instrument. The results obtained from this method for polyethylene samples are compared with those obtained from dilatometry. Similar values for the kinetic parameters are obtained using both techniques. The calorimetric method has been used for other polymers such as polypropylene and poly(4-methyl-1-pentene).

### INTRODUCTION

A study of the crystallization kinetics can be carried out by following the changes in a property of the sample which is a sensitive function of its degree of crystallinity. Several physical properties such as specific volume, heat of crystallization, intensity of depolarized light, etc., are sensitive to the degree of crystallinity and can therefore be used as its measure. A dilatometer measures the extent of crystallization as a function of time directly in terms of the changes in specific volume. On the other hand, the change in enthalpy during the course of crystallization can be followed by using a differential scanning calorimeter (DSC). The dilatometric method is very convenient and hence most widely used for the study of crystallization kinetics. Measurement of isothermal crystallization rate by calorimetric method has been reported by several authors [1–6]. A DSC measures the rate of evolution of the heat of crystallization ( $dH/dt$ ) as a function of time. At lower degrees of supercooling the development of crystallinity is slow and hence the rate of evolution of the heat of crystallization is also very low. Therefore at these crystallization temperatures, the calorimetric method as developed by earlier workers loses its sensitivity. In the case of polyethylene this limitation restricts the usefulness of this method to crystallization half-times ( $t_{1/2}$ )

ranging from 1.6 to 70 min. These limits would of course vary with the material to be investigated. In the present work we report a new method based on calorimetric measurements which can be used effectively irrespective of the crystallization temperature, sample weight and its nature.

## EXPERIMENTAL

Isothermal crystallization studies were carried out for polyethylene, polypropylene and poly(4-methyl-1-pentene). The bulk properties of these polymers are given in Table 1. Before an isothermal crystallization run, the polymer sample was heated to a temperature a few degrees above its melting temperature and kept at this temperature for about 30 min to erase any previous morphological history. It was then cooled to the crystallization temperature and the development of crystallinity was followed either by dilatometric or calorimetric methods.

The design of the dilatometer used in the present work is described elsewhere [7].

A Perkin-Elmer differential scanning calorimeter model DSC-1B was employed for calorimetric measurements. It was calibrated by using standard reference materials. Samples of 3-15 mg were used for this purpose.

## METHODS

As the name suggests, the dilatometric method consists in following the change in density or the specific volume of the sample as a function of time.

TABLE 1  
Bulk properties of the polymer samples used in the present work

| Polymer sample                              | $M_w$<br>( $\times 10^{-5}$ ) | $M_n$<br>( $\times 10^{-5}$ ) | $\frac{M_w}{M_n}$ | Density<br>( $\text{g cm}^{-3}$ ) | $T_m$<br>(K) | Source                                |
|---|-------------------------------|-------------------------------|-------------------|-----------------------------------|--------------|---------------------------------------|
| Polyethylene<br>(Marlex 6002)               | 1.38                          | 0.113                         | 12.3              | 0.960                             | 405          | Philips<br>Petroleum<br>Co.           |
| Isotactic<br>polypropylene<br>(M6100)       | 2.6                           | 0.183                         | 14.24             | 0.902                             | 436          | Indian<br>Petrochemical<br>Corp. Ltd. |
| Poly (4-<br>methyl-1-<br>pentene)<br>(P4MP) | -                             | 2                             | -                 | 0.834                             | 514.4        | British<br>Petroleum<br>Co.           |

On the other hand, in the calorimetric method, one generally measures [1-6] the rate of evolution of heat during crystallization. The exotherm is recorded as a function of time till it returns to the original baseline position. The area under this curve from the start of crystallization up to a given time becomes a measure of the extent of crystallinity developed in the sample. It is observed that as the crystallization temperature approaches the melting point of the polymer, the exotherm tends to flatten out, thus introducing large uncertainty in the estimation of area under this curve. This fact limits the usefulness of this method to smaller values of  $t_{1/2}$ . For instance, in the case of polyethylene using DSC-1B this method could be applied to  $t_{1/2}$  values ranging between 2 and 30 min [5]. The use of an instrument of higher sensitivity can raise the upper limit of  $t_{1/2}$  to about 70 min. This is one of the reasons why studies of crystallization kinetics using DSC have been restricted to larger degrees of supercooling.

In the new method, a sample is crystallized isothermally at the temperature of interest for a predetermined time and then the process is terminated by rapid cooling. In this procedure the fraction of the sample which could not become crystallized isothermally, crystallizes during cooling. The crystallization peak is recorded. The area under this peak is proportional to the fraction of the sample which remained uncrystallized after the crystallization was terminated. The time dependence of this parameter is then used to derive the desired information about the crystallization kinetics.

#### ANALYSIS OF THE CRYSTALLIZATION ISOTHERMS

The time dependence of crystallization can be represented by the Avrami equation [8]

$$1 - v_c = \exp[-zt^n] \quad (1)$$

where  $v_c$  is the crystalline fraction at any time  $t$ ,  $z$  is the rate constant and  $n$  is the Avrami exponent. If  $X_t$  and  $X_\infty$  are the weight fractions of the crystallized material at any time  $t$  and at infinitely long time, eqn. (1) can then be written as

$$1 - \frac{X_t}{X_\infty} = \exp[-zt^n]$$

or

$$\log \left[ -\ln \left( 1 - \frac{X_t}{X_\infty} \right) \right] = n \log t + \log z \quad (2)$$

Equation (2) can be used to determine the Avrami exponent  $n$ . The rate constant  $z$  can then be obtained from the relation

$$z = \frac{0.693}{t_{1/2}^n} \quad (3)$$

In dilatometric measurements the changes in volume are measured in terms of the height of the mercury column. Therefore, for the dilatometric method eqn. (2) takes the form

$$\log \left[ -\ln \left( \frac{h_t - h_\infty}{h_0 - h_\infty} \right) \right] = n \log t + \log z \quad (4)$$

where  $h_0$ ,  $h_t$  and  $h_\infty$  are the heights of the mercury column at times equal to zero,  $t$  and  $\infty$ , respectively.

In the conventional calorimetric method, as the DSC measures the rate of evolution of heat, ( $dH_t/dt$ ), during crystallization, it follows that

$$\frac{X_t}{X_\infty} = \frac{\int_0^t \left( \frac{dH_t}{dt} \right) dt}{\int_0^\infty \left( \frac{dH_t}{dt} \right) dt} \quad (5)$$

The data obtained in this type of measurement can, therefore, be analyzed by using eqns. (2) and (5).

If the isothermal crystallization is terminated after a time  $t$  and the crystallization peak recorded during rapid cooling as stated earlier, the area under this peak is proportional to the fraction of the sample which remained uncrystallized at time  $t$ . Therefore, it follows that

$$A_t = K(1 - X_t) \quad (6)$$

where  $A_t$  is the area under the crystallization peak obtained on termination of the isothermal crystallization after a time  $t$  and  $K$  is a constant. Hence

$$1 - \frac{X_t}{X_\infty} = \frac{A_t - A_\infty}{A_0 - A_\infty} \quad (7)$$

where  $A_0$  and  $A_\infty$  are the areas under the crystallization peaks corresponding to zero and infinite crystallization times, respectively. Thus for this method eqn. (2) can be written as

$$\log \left[ -\ln \left( \frac{A_t - A_\infty}{A_0 - A_\infty} \right) \right] = n \log t + \log z \quad (8)$$

The data obtained by the calorimetric method can therefore be analyzed making use of eqn. (8).

## RESULTS AND DISCUSSION

In all the three polymer samples investigated, the progress of crystallization was followed by dilatometric and calorimetric methods. Some typical results obtained by the new calorimetric method in polyethylene are shown

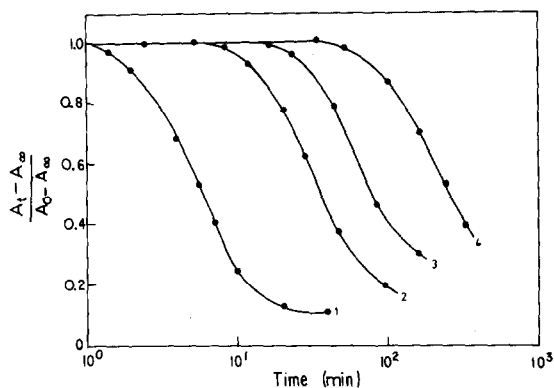


Fig. 1. Crystallization isotherms at different crystallization temperatures for polyethylene (Marlex 6002) as obtained from the calorimetric method based on the area under the crystallization peak: curves 1, 2, 3 and 4 are for  $T_c = 396, 398.7, 399.5$  and  $400$  K, respectively.

in Figs. 1 and 2. The values of the kinetic parameters  $n$ ,  $z$  and  $t_{1/2}$  as obtained by three different methods for various polymers are given in Tables 2–4. It is seen that the values of the kinetic parameters obtained by these methods compare well with each other. In the case of polyethylene the Avrami exponent  $n$  is found to be independent of the temperature of crystallization and has an average value of 2.3. However, the data constant  $z$  and the half crystallization time  $t_{1/2}$  are found to depend on the crystallization temperature. In this case the agreement between the results from the three methods is better seen in Fig. 3 which is a plot of  $t_{1/2}$  vs. temperature

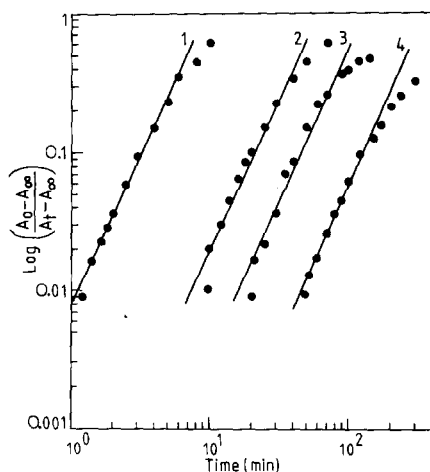


Fig. 2. Avrami plots at different crystallization temperatures for polyethylene (Marlex 6002) as obtained from the data shown in Fig. 1. The curves 1, 2, 3 and 4 are for  $T_c = 396, 398.7, 399.5$  and  $400$  K, respectively.

TABLE 2

Values of the kinetic parameters  $n$ ,  $z$  and  $t_{1/2}$  for polyethylene obtained from three different methods

| $T_c$<br>(K)  | $n$ | $z$<br>( $\text{min}^{-n}$ ) | $t_{1/2}$<br>(min) |
|---|-----|------------------------------|--------------------|
| <i>(a) Dilatometric method</i>                                      |     |                              |                    |
| 396   | 2.2 | $1.62 \times 10^{-2}$        | 5.5                |
| 398   | 2.3 | $7.05 \times 10^{-4}$        | 20                 |
| 399.7   | 2.3 | $1.95 \times 10^{-5}$        | 95                 |
| 401   | 2.5 | $1.61 \times 10^{-7}$        | 450                |
| <i>(b) Calorimetric method (conventional)</i>                       |     |                              |                    |
| 396   | 2.2 | $1.6 \times 10^{-2}$         | 5.5                |
| 396.5   | 2.2 | $6.2 \times 10^{-3}$         | 8.5                |
| 397.2   | 2.3 | $8.98 \times 10^{-4}$        | 18                 |
| 398.7   | 2.3 | $1.94 \times 10^{-4}$        | 35                 |
| <i>(c) Calorimetric method (based on crystallization peak area)</i> |     |                              |                    |
| 396   | 2.2 | $1.6 \times 10^{-2}$         | 5.5                |
| 398.7   | 2.2 | $2.96 \times 10^{-4}$        | 34                 |
| 399.5   | 2.3 | $2.95 \times 10^{-5}$        | 70                 |
| 400.5   | 2.3 | $3.53 \times 10^{-6}$        | 200                |
| 401.0   | 2.3 | $4.95 \times 10^{-7}$        | 470                |

of crystallization of a polyethylene sample as obtained from the three different methods. Similar plots for polypropylene and P4MP are shown in Figs. 4 and 5, respectively. It is again seen that the results obtained from the

TABLE 3

Values of the kinetic parameters  $n$ ,  $z$  and  $t_{1/2}$  for isotactic polypropylene as obtained from different methods

| $T_c$<br>(K)  | $n$ | $z$<br>( $\text{min}^{-n}$ ) | $t_{1/2}$<br>(min) |
|---|-----|------------------------------|--------------------|
| <i>(a) Dilatometric method</i>                                      |     |                              |                    |
| 397   | 2.6 | $1.4 \times 10^{-2}$         | 5                  |
| 402   | 2.5 | $1.82 \times 10^{-3}$        | 12                 |
| 407   | 2.4 | $7.76 \times 10^{-5}$        | 45                 |
| 411.5   | 2.1 | $3.23 \times 10^{-6}$        | 170                |
| <i>(b) Calorimetric method (based on crystallization peak area)</i> |     |                              |                    |
| 396   | 2.6 | $3.77 \times 10^{-2}$        | 3                  |
| 400   | 2.6 | $3.67 \times 10^{-3}$        | 7.5                |
| 404   | 2.4 | $2.44 \times 10^{-4}$        | 26                 |
| 411   | 2.5 | $2.14 \times 10^{-6}$        | 160                |

TABLE 4

Values of the kinetic parameters  $n$ ,  $z$  and  $t_{1/2}$  for poly(4-methyl-1-pentene) as obtained from different methods

| $T_c$<br>(K)  | $n$ | $z$<br>( $\text{min}^{-n}$ ) | $t_{1/2}$<br>(min) |
|---|-----|------------------------------|--------------------|
| <i>(a) Dilatometric method</i>                                      |     |                              |                    |
| 497   | 2.5 | $7.80 \times 10^{-2}$        | 2.2                |
| 500   | 2.6 | $4.84 \times 10^{-3}$        | 6                  |
| 502   | 2.7 | $9.83 \times 10^{-4}$        | 11                 |
| 504.2   | 2.7 | $3.96 \times 10^{-5}$        | 34                 |
| 506   | 3.1 | $4.43 \times 10^{-6}$        | 75                 |
| 508   | 2.9 | $9.35 \times 10^{-8}$        | 320                |
| <i>(b) Calorimetric method (based on crystallization peak area)</i> |     |                              |                    |
| 497   | 2.6 | $7.37 \times 10^{-2}$        | 2.4                |
| 499   | 2.7 | $1.45 \times 10^{-2}$        | 4.2                |
| 501   | 2.7 | $1.79 \times 10^{-3}$        | 9                  |
| 504   | 2.8 | $1.48 \times 10^{-4}$        | 20                 |
| 506.5   | 2.8 | $1.74 \times 10^{-6}$        | 100                |
| 507.7   | 2.6 | $3.64 \times 10^{-7}$        | 260                |

dilatometric method and the calorimetric method based on the area under the crystallization peak yield identical results.

The above results demonstrate the validity of the new method. It has been mentioned earlier that the conventional calorimetric method, due to the limited sensitivity of DSC, cannot be used for crystallization half-times larger than about 70 min in the case of polyethylene. It has, however, been shown that the new calorimetric method is applicable even for crystallization

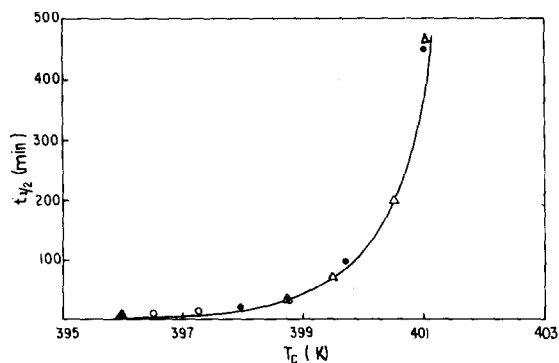


Fig. 3. Variation of  $t_{1/2}$  with the crystallization temperature for polyethylene: ●, dilatometry; ○, conventional calorimetric method; △, calorimetric method based on the area under the crystallization peak.

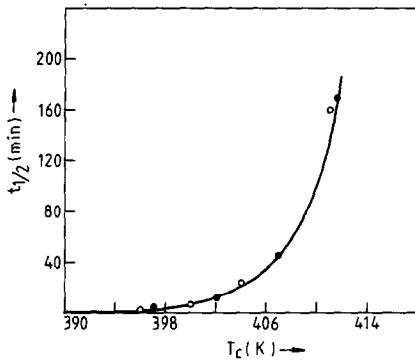


Fig. 4. Variation of  $t_{1/2}$  with the crystallization temperature for polypropylene: ●, dilatometry; ○, calorimetric method based on the area under the crystallization peak.

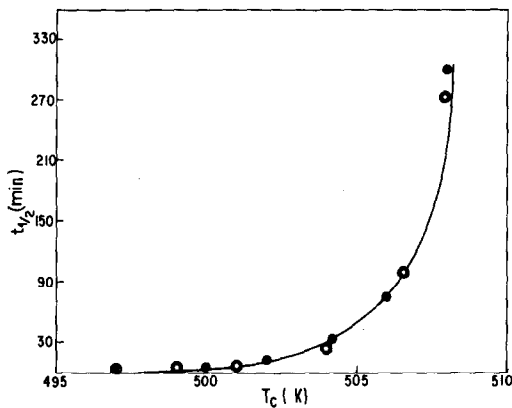


Fig. 5. Variation of  $t_{1/2}$  with the crystallization temperature for P4MP: ●, dilatometry; ○, calorimetric method based on the area under the crystallization peak.

half-times as large as 470 min. Thus it may be concluded that the new method is as sensitive as the dilatometric method. This method, however, has an advantage over the dilatometric method of being simpler and easier to perform.

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