

# Recrystallization kinetics of isotactic polypropylene ( $\alpha$ -form)

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The recrystallization kinetics of isotactic polypropylene (i-PP) ( $\alpha$ -form) in the usual melting temperature region (155°–170°C) has been studied by calorimetric and dilatometric techniques. The recrystallization is possible over a large range of temperatures also when the residual crystallinity is very low ( $\approx 1\%$ ). Low values of the Avrami exponents independent of  $T_r$  ( $n \leq 1.6$ ), have been found, although the residual crystallinity shows a large variation (1–35%).

(Keywords: isotactic polypropylene ( $\alpha$ -form); recrystallization kinetics; Avrami analysis; dilatometry; calorimetry)

## INTRODUCTION

In some recent studies<sup>1,2</sup>, a process of ordering, relative to the 'up' and 'down' positioning of chains, as a consequence of thermal treatment has been shown for the  $\alpha$ -form of isotactic polypropylene (i-PP).

More recently we have pointed out that a 'continuum' of different structures may exist for the  $\alpha$ -form, starting from a limiting disordered modification to a limiting ordered modification, and that in the transition from a disordered to a more ordered modification one goes through a recrystallization<sup>3</sup>. Evidence for crystal transformations in the partially melted state of i-PP samples have already been presented in the literature<sup>4-6</sup>. We have pointed out that these recrystallizations imply an up/down ordering process, the degree of ordering being greater the higher the fraction of melted polymer at the beginning of the recrystallization process<sup>3</sup>.

These recrystallizations are responsible for the large increase in the melting temperature after high temperature annealing procedures<sup>3,5,6</sup> and this explains the double peak shape of the melting d.s.c. endotherms at low heating rates for i-PP samples<sup>3,7</sup>.

In this paper the kinetics of such recrystallization processes in the usual melting temperature region of i-PP (155°–170°C) studied by calorimetric and dilatometric techniques, are described.

## EXPERIMENTAL

The isotactic polypropylene samples were supplied by Montepolimeri S.p.A. The material is highly isotactic, being approximately 97.5% insoluble in n-heptane and it has an intrinsic viscosity of 2.5 dl/g.

To erase the previous thermomechanical history, the as-received powder was melted at 470 K and then cooled at a rate of 10 K/min to room temperature.

Calorimetric measurements were carried out on a Perkin-Elmer differential scanning calorimeter (DSC-2) in a nitrogen atmosphere.

Dilatometric experiments were carried out using dilatometers as described by Danusso *et al.*<sup>8</sup>. After calibration and sample introduction, the apparatus was filled with mercury by suction at a pressure of  $10^{-3}$  mm Hg.

The dilatometric crystallinity ( $X_d$ ) has been evaluated as

$$X_d = \frac{V_0 - V}{V_0 - V_c}$$

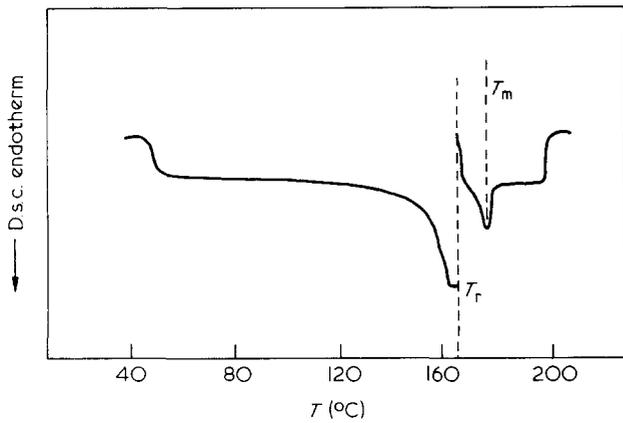
where  $V$  and  $V_0$  are the measured specific volumes of the recrystallizing sample and of the undercooled melted polymer respectively;  $V_c$  is the specific volume of the completely crystalline sample assumed to be equal to  $1.068 \text{ cm}^3 \text{ g}^{-1}$ , (ref 9).

## RESULTS

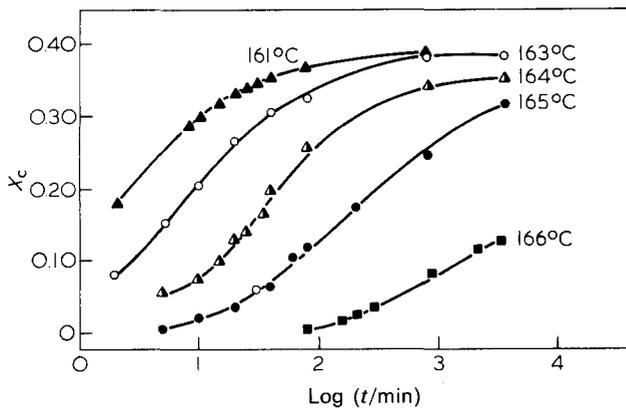
A typical d.s.c. scan for our recrystallization kinetic studies is reported in *Figure 1*: the temperature is increased at a given heating rate until a value  $T_r$ , at which a partial melting of the sample occurs. The temperature is then maintained constant for a time  $t_r$ , at which the sample partially or totally recrystallizes; finally the sample is completely melted at 10 K/min without previous cooling to room temperature. The area of this melting peak allows us to evaluate the crystalline polymer fraction ( $X_c$ ) after the time  $t_r$  at the recrystallization temperature  $T_r$ , (the melting enthalpy variation for completely crystalline samples has been assumed to be equal to 50 cal/g (ref. 10).

The so evaluated calorimetric crystallinity, when the temperature  $T_r$  is reached at the rate of 10 K/min, is reported in *Figure 2* for various  $T_r$  values. The peak temperature values ( $T_m$ ) of the endotherms of the type shown in *Figure 1*, are reported in *Figure 3* versus the recrystallization time, for various  $T_r$  values.

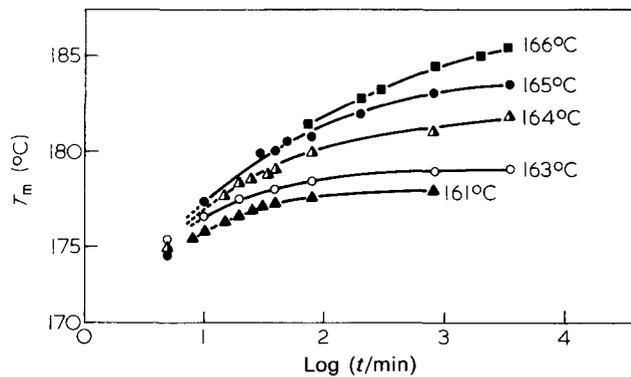
The described calorimetric technique allows us to obtain accurate peak area values only for  $t_r > 2$  min;



**Figure 1** Typical d.s.c. scan for our recrystallization kinetics;  $T_r$  is the partial melting temperature,  $T_m$  is the melting peak temperature after the recrystallization process at  $T_r$



**Figure 2** Calorimetric crystallinity ( $X_c$ ) at various recrystallization temperatures as a function of time. The recrystallization temperature is reached at a rate of 10 K/min



**Figure 3** Plots of the peak temperatures ( $T_m$ ) versus the recrystallization time, for various  $T_r$  values

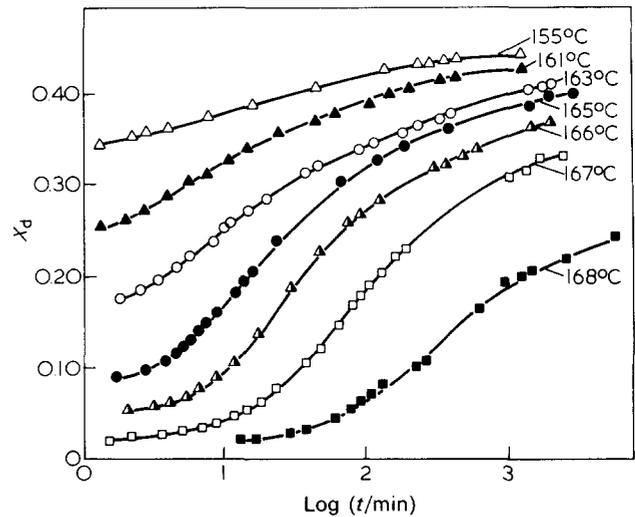
therefore, by using this technique it is impossible to obtain accurate kinetics for the low  $T_r$  values, for which the recrystallization is too fast; moreover it is impossible to evaluate the seed crystallinity ( $X_s$ ), that is the residual crystallinity at the beginning of the crystallization process, which is necessary to draw Avrami's plots. For these reasons the recrystallization kinetics have also been followed by dilatometric measurements.

The dilatometric crystallinity versus the recrystallization time is reported in Figure 4 for a heating rate, in reaching  $T_r$ , equal to 3.8 K/min. The seed crystallinities, for the recrystallization kinetics of Figure 4, are reported versus  $T_r$  in Figure 5.

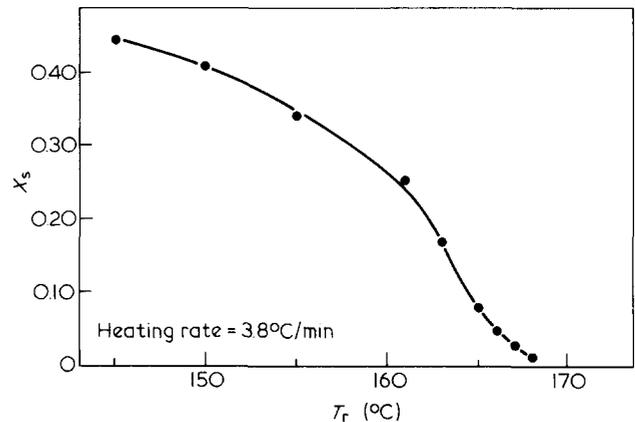
The influence of the heating rate on the recrystallization kinetics is highlighted in Figure 6, where the dilatometric crystallization kinetics are reported for  $T_r = 167^\circ\text{C}$ , for three different heating rates.

The analysis of the kinetics of crystallization, for each  $T_r$  has been carried out on the basis of Avrami's equation:

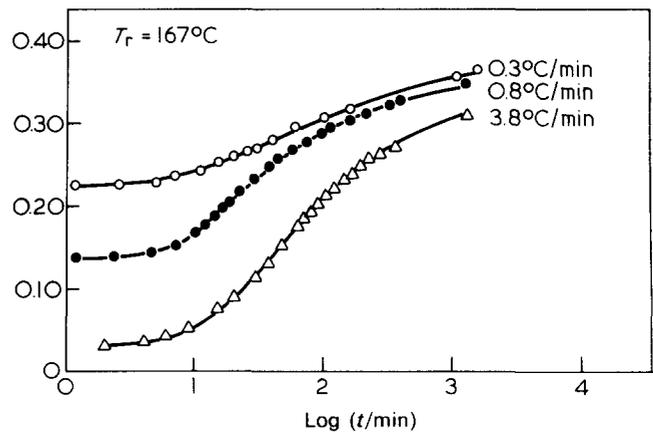
$$(1 - X_t) = \left( \frac{V_\infty - V}{V_\infty - V_s} \right) = \exp(-Kt^n)$$



**Figure 4** Dilatometric crystallinity ( $X_d$ ) at various recrystallization temperatures as a function of time. The temperature is reached at a rate of 3.8 K/min



**Figure 5** Seed crystallinity ( $X_s$ ) versus the recrystallization temperature for the kinetics in Figure 4



**Figure 6** Dilatometric kinetics relative to a fixed  $T_r$  value, reached at different heating rates

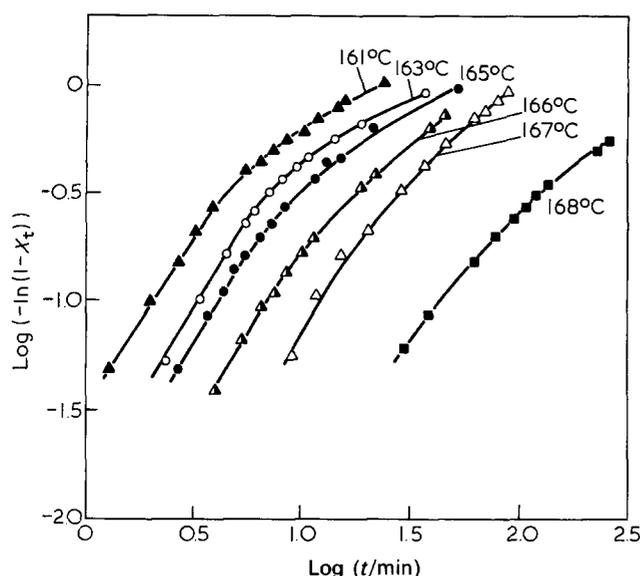


Figure 7 Avrami plots for the dilatometric kinetics of Figure 4

where  $X_t$  is the polymer fraction crystallized at time  $t$ ,  $K$  is the overall kinetic rate constant and  $n$  is a parameter dependent on the nucleation process and on the geometry of growth of the crystals;  $V_\infty$  and  $V_s$  are the specific volumes at the end and at the beginning of the crystallization process, respectively. ( $V_s$  is lower than the specific volume of the undercooled polymer melt, previously defined as  $V_0$ )<sup>11,12</sup>.

The quantity  $\log[-\ln(1-X_t)]$  is reported in Figure 7 against  $\log t$ , for the data of Figure 4. A linear dependence with  $n \approx 1.6$ , for low degrees of conversion ( $< 30\%$ ), is obtained in all the cases; a change in the slope of the curves is observed for higher degrees of conversion especially for the lowest recrystallization temperatures,  $n$  ranging between 1.6–0.5 (until 70% of conversion).

No difference was observed between the Avrami kinetic plots at different heating rates in Figure 6.

## DISCUSSION

The calorimetric and dilatometric data summarized in Figures 2, 4 and 6 show the presence of a recrystallization phenomenon over a large range of temperatures. The strong dependence of the position of the melting peak on the temperature and the time of recrystallization is displayed in Figure 3; in fact  $T_m$  increases from 164°C (for samples annealed below the melting temperature region<sup>3</sup>) to greater than 180°C. Such recrystallization processes, and the associated large shifts of the melting peak temperatures, are possible for polypropylene samples since their usual melting temperature regions (155–170°C) are far from the limiting melting temperature (187.5°C) found for the  $\alpha$ -form<sup>13</sup>. This behaviour is not generally observed for all the polymers; for instance, by annealing polyethylene samples in the melting temperature region, no recrystallization and no increase of  $T_m$  is observed<sup>6</sup>.

The seed crystallinity depends not only on the temperature of partial melting (Figure 5), but also strongly on the heating rate in reaching  $T_r$  (Figure 6). This behaviour is due to a recrystallization process which is relevant on heating at low heating rates, as previously

shown in the d.s.c. analysis<sup>5,7</sup>. In turn the increase in seed crystallinity, for low heating rates, makes higher recrystallization temperatures accessible and accounts for the differences between the kinetics in Figures 2 and 4.

For all such kinetics, in the presence of unmelted material, the  $n$  values for the Avrami plots are nearly independent of the  $T_r$  values although the seed crystallinity varies over a large range (at least for  $0.01 < X_s < 0.35$ ); the  $n$  values, in the range 1.6–0.5 are quite distinct from the values obtained for crystallization from completely molten samples. Generally  $n = 3$  is found, and i-PP gives a clear-cut example of heterogeneous athermal nucleation followed by a three-dimensional spherulitic crystal growth<sup>14–16</sup>. When the melt is initially heated to 200°C and above, for suitable crystallization temperatures, the Avrami exponent increases to  $n = 4$ , indicating a change from athermal to thermal nucleation<sup>17,12</sup>.

Low  $n$  values were found also in the case of the crystallization of polyethylene in the presence of unmelted material. In such cases, to have crystallization, the recrystallization temperature must be lower than the partial melting temperature<sup>11,18</sup>. When the seed crystallinity percentage is higher, the Avrami exponent  $n$  decreases from values in the range 4–3, to values in the range 1.6–1.2. These low  $n$  values have been assumed to be an indication of a crystallization phenomenon which involve sub-units formed from a large number of seeds left within the outlined of the original spherulites<sup>11</sup>.

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## REFERENCES

- Hikosaka, M. and Seto, T. *Polym. J.* 1973, **5**, 111
- Corradini, P., Giunchi, G., Petraccone, V., Pirozzi, B. and Vidal, H. M. *Gazz. Chim. Ital.* 1980, **110**, 413
- Guerra, G., Petraccone, V., Corradini, P., De Rosa, C., Napolitano, R., Pirozzi, B. and Giunchi, G. *J. Polym. Sci., Polym. Phys. Edn.* 1984, **22**, 1029
- Padden, F. J., Keith, H. D. *J. Appl. Phys.* 1959, **30**, 1479
- Cox, W. W. and Duswalt, A. A. *Polym. Eng. Sci.* 1967, **7**, 309
- Kamide, K. and Yamaguchi, K. *Makromol. Chem.* 1972, **162**, 205
- Corradini, P., Napolitano, R., Oliva, L., Petraccone, V., Pirozzi, B. and Guerra, G. *Makromol. Chem., Rapid Commun.* 1982, **3**, 753
- Danusso, F., Moraglio, G., Ghiglia, W., Motta, L. and Talamini, G. *Chim. Ind.* 1958, **41**, 748
- Natta, G. and Corradini, P. *Nuovo Cimento, Suppl.* 1960, **15**, 40
- Wunderlich, B. in 'Macromolecular Physics', Academic Press, Vol. I, 1973, p 388
- Banks, W., Gordon, M. and Sharples, A. *Polymer* 1963, **4**, 289
- Parrini, P. and Corrieri, G. *Chim. Ind.* 1967, **49**, 1172
- Wunderlich, B. in 'Macromolecular Physics', Academic Press, Vol. III, 1980, p. 63
- Wunderlich, B. in 'Macromolecular Physics', Academic Press, Vol. II, 1976, p 235
- Pratt, C. F. and Hobbs, S. Y. *Polymer* 1976, **17**, 13
- Martuscelli, E., Pracella, M. and Crispino, L. *Polymer* 1983, **24**, 693
- Majer, J. M. *Kunststoffe* 1960, **50**, 565
- Vidotto, G., Lévy, D. and Kovacs, A. J. *Kolloid Z. Z. Polym.* 1969, **230**, 289
- Banks, W., Sharples, A. and Thomson, G. *Eur. Polym. J.* 1966, **2**, 309