Colloid Polym Sci 273:317–323 (1995)
© Steinkopff Verlag 1995

ORIGINAL CONTRIBUTION

G.C. Alfonso
A. Ziabicki

Memory effects in isothermal crystallization
II. Isotactic polypropylene

Received: 23 March 1994
Accepted: 17 August 1994

This work and Part I of this research [1] have been supported in part by Research Grant Number PB 1291/52/93/04 from State Committee for Scientific Research (KBN), Poland, and by 40% MURST founds, Italy.

Prof. Dr. G.C. Alfonso (✉)
Institute of Industrial Chemistry
University of Genova
Corso Europa 30
16100 Genova, Italy

A. Ziabicki
Institute of Fundamental Technological Research
Polish Academy of Sciences
21 Swietobrzyska St.
00049 Warszawa, Poland

Abstract The effects of temperature and duration of melting on the rate of isothermal crystallization of isotactic polypropylene were investigated by differential scanning calorimetry (DSC). Crystallization rates were found to decrease with increasing melt temperature and melting time. The results were discussed in the framework of the theoretical model of transient isothermal crystallization developed by the present authors [1]. The results suggest gradual destruction of predetermined nuclei with activation energy $E_a = 89 \pm 7$ kJ/mole as a main mechanism of the observed effects.

Key words Crystallization – crystal nucleation – melting – melting history – thermal history – DSC

Introduction

In the first paper of this series [1], we developed a theoretical model of transient crystallization predicting memory effects related to the distribution of cluster sizes which controls concentration of predetermined crystal nuclei and initial nucleation rate effective in the subsequent isothermal crystallization. Here, we present experimental data obtained on three isotactic polypropylenes. It is evident that gradual destruction of large clusters (crystal aggregates) is the main factor responsible for the effect of melting history on isothermal crystallization.

Our main interest is related to heating well above the melting temperature. In these conditions no large crystalline fragments survive; what remains is small clusters which produce athermal nuclei after cooling below melting temperature.

Experimental

Three isotactic polypropylenes were studied. All samples were provided by Himont Italia (Ferrara, Italy). Their main molecular characteristics are reported in Table 1. Sample SPLLI/103 (labeled "PP1") is a special grade i-PP free of additives and used in the electronic industry. 7073XOP ("PP2") is a typical extrusion grade polymer for injection molding, and 1-142/16 ("PP3") is a polypropylene of the newest generation, characterized by bimodal distribution of molecular mass and very high value of the M_w/M_n ratio.

Films, about 300 μm thick, were prepared from pellets by melting between aluminum foils in a Carver press at 240 °C under slight pressure, and quenched in water at room temperature. This treatment provides a crystalline "standard" state by erasing former thermal history.

K 478

Table 1 Molecular and compositional characteristics of *i*-PP samples

Sample	PP1	PP2	PP3
Manufacturer Code	SPLLI-103	7073XOP	1-142/16
$M_w \times 10^{-3}$	476	520	400
M_w/M_n	6	12	25
Isotacticity index	0.96	0.983	0.98
Residual catalyst, ppm	< 20	90	90
Thermal stabilizers, %	none	0.2	0.2
Nucleating agents, %	none	none	none

To assure constant geometry and good contact between the polymer and pan, DSC holders were loaded with a single flat disk 7.0 ± 0.2 mg, cut from the pressed film. DSC experiments were carried out with a Perkin Elmer DSC7 instrument equipped with Thermal Analysis Data Station model 3600, working in the atmosphere of dry nitrogen. The instrument was calibrated with In, Sn, and Pb standards; constancy of calibration was checked every second or third run. The experiments involved:

a) rapid heating of the "standard" sample at 80 °C/min to the temperature $T_1 \cdot T_1$ is higher than upper limit of the melting endotherm, determined in a slow melting experiment, at 10 °C/min,

b) holding the molten sample at T_1 for the period t_1, ranging from 1 to 500 min,

c) rapid cooling at 100 °C/min from T_1 to crystallization temperature, T_c. Naturally, $T_c < T_m$.

d) isothermal crystallization at $T = T_c$.

The temperature protocol is shown in Fig. 1. Crystallization temperature was chosen so that the crystallization process was completed within 10–40 min. Optimum crystallization conditions corresponded to T_c = 120–130 °C.

Interpretation of DSC measurements

The DSC signal recorded during crystallization (heat flux, $\dot{Q}$) is proportional to sample weight, w, crystallization enthalpy, ΔH_c, and overall crystallization rate, $\dot{x} = dx/dt$ expressed in terms of relative degree of crystallinity normalized to unity, $0 \le x \le 1$

$$\dot{Q} \propto w \cdot \Delta H_c \cdot \dot{x}(t) \tag{1}$$

ΔH_c is smaller than melting enthalpy of a perfect crystal; it depends on crystallization conditions and maximum degree of crystallinity which can be attained in given temperature.

According to the Kolmogoroff–Avrami model of transformation kinetics [2–4] the relative degree of transformation (crystallinity) at time t is given by:

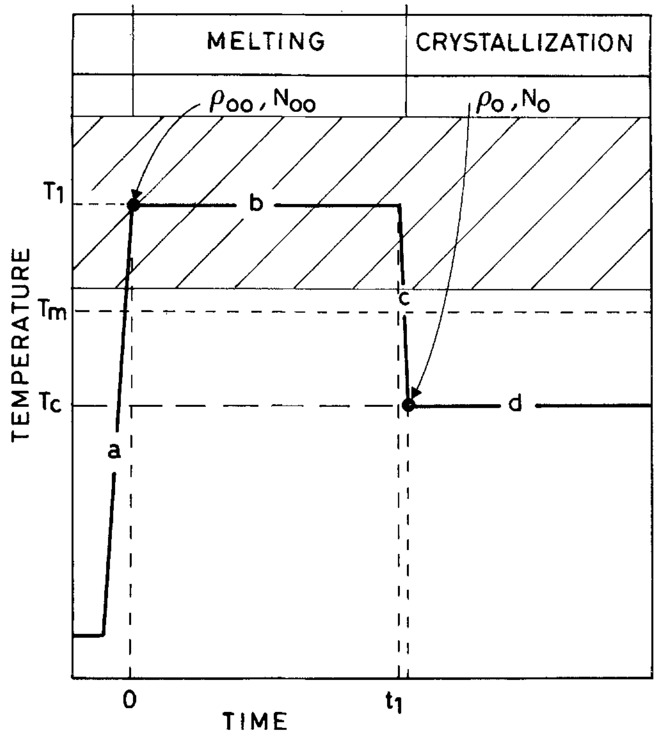


Fig. 1 Schematic representation of the standardized thermal history, $T(t)$, used in the experiments

$$x(t) = 1 - \exp[-E(t)] \tag{2}$$

$E(t)$ denotes volume fraction of phantom crystals grown up to time t. Differentiation of Eq. (2) yields

$$\dot{x}(t) = dx/dt = \dot{E}(t)\exp[-E(t)]\ , \tag{3}$$

$$\ddot{x}(t) = d^2x/dt^2 = \{\ddot{E}(t) - \dot{E}^2(t)\}\exp[-E(t)]\ . \tag{4}$$

For n-dimensional growth, $E(t)$ is given by:

$$E(t) = N_0 \cdot v(0, t) + \int_0^t \dot{N}_{th}(s) \cdot v(s, t)\, ds\ , \tag{5}$$

where N_0 is the number of predetermined nuclei present in unit volume at the instant $t = 0$, $\dot{N}_{th}$ is nucleation rate, and $v(s, t)$ is volume of a phantom crystal nucleated at the instant s and grown up to the instant t. If the growth is isotropic and proceeds independently in n dimensions, $v(s, t)$ can be expressed through linear growth rate, G

$$v(s, t) = C_n \cdot \left[\int_s^t G(z)\, dz\right]^n ; \tag{6}$$

C_n denotes shape factor.

For simple isothermal and steady-state conditions, in which both $G(t)$ and $N_{th}(t)$ are constants throughout the crystallization process, Eq. (5) reduces to:

$$E(t) = C_n G^n [N_0 t^n + \dot{N}_{th} t^{n+1}/(n+1)] \qquad (7)$$

Equations (5) and (7) include two crystallization regimes: growth of predetermined nuclei and sporadic thermal nucleation followed by growth. In extreme conditions one or the other mechanism is dominating. In the first part of this study [1], we have shown that strong memory effects can be expected when the dominating regime is growth of predetermined nuclei (first term on the right-hand side of Eqs. (5) and (7). In the conditions dominated by sporadic nucleation, thermal history effects are suppressed. Therefore, we will try to interpret our observations using reduced Eq. (7) in the form

$$E(t) = C_n G^n N_0 t^n = K_n t^n , \qquad (8)$$

corresponding to the asymptotic regime 2.1 described in ref. [1], i.e., long relaxation times and not too small undercooling. K_n is the co-called Avrami rate constant. Using the kinetic equation (8), we obtain from Eq. (4) the condition for *maximum crystallization rate*

$$dx/dt = \text{maximum};\ t = t_p$$

$$\{n(n-1)Kt^{n-2} - n^2K^2t^{2n-2}\}\exp[-K\cdot t^n] = 0 \Rightarrow$$

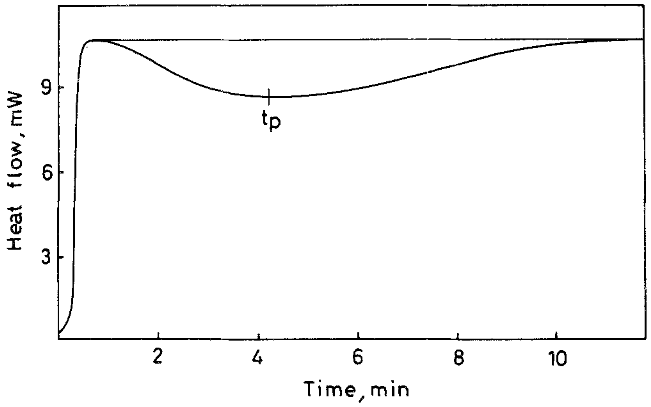
$$\Rightarrow t_p^n = [(n-1)/n]K_n = [(n-1)/n]C_n G^n N_0 . \qquad (9)$$

It is evident that the time required for reaching maximum crystallization rate, t_p (cf. Fig. 2) depends on the number of predetermined nuclei. Assuming three-dimensional growth ($n = 3$), we obtain

$$t_p = \frac{2}{3} G^{-1} C_3^{-1/3} N_0^{-1/3} . \qquad (10)$$

It is assumed that linear growth rate is insensitive to melting history. In the *growth of spherulites* linear growth rates are constants [5]. This does not guarantee the same behavior of the *growth of crystals*, but speaks in favor of our assumption of negligible effects of thermal history, i.e.,

Fig. 2 DSC trace of isothermal crystallization of isotactic polypropylene PP2. Crystallization temperature, $T_c = 127\,°C$. Thermal history: $T_1 = 200\,°C$, $t_1 = 10$ min



$$\partial G/\partial T_1 = \partial G/\partial t_1 = 0 \qquad (11)$$

If the above assumption holds true, variation of crystallization rate (and maximum crystallization rate time, t_p) should reflect changes of the number of predetermined nuclei, N_0, present in the system at the start of crystallization and controlled by melting conditions $\{T_1, t_1\}$. From Eq. (10) with constant growth rate it follows

$$t_p = \text{const.}\, N_0^{-1/3} . \qquad (12)$$

The time of maximum crystallization rate is measured in DSC diagrams as time required to reach the peak of exothermal heat flux (minimum in Fig. 2).

With the above assumptions, t_p is related to the number of predetermined nuclei, N_0. The total number of growing nuclei at any instant t, consists of the following contributions

$$N_{tot}(t) = N_0 + \int_0^t \dot{N}_{th}(s)\,ds = N_{het} + N_{ath} + \int_0^t \dot{N}_{th}(s)\,ds . \qquad (13)$$

Nuclei present in the system at the start of crystallization include *heterogeneous*, and *athermal homogeneous*, nuclei. Heterogeneous nuclei are formed by particles chemically different from the crystallizing polymer, like catalyst, pigments, or impurities. The role of heterogeneous nuclei can also be played by surface defects. Sensitivity of heterogeneous nuclei to thermal history is small, if any. On the other hand, concentration of athermal nuclei strongly varies with melt temperature, T_1, and melting time, t_1. Memory effects can be measured only when heterogeneous nuclei do not dominate in crystallization. We will try to find such conditions of thermal treatment that the number of heterogeneous nuclei, N_{het}, is small compared to the number of athermal nuclei, N_{ath}.

Large clusters, originating from crystal fragments left from previous structures, are gradually destroyed by heating; some of them may reappear as athermal nuclei when temperature is reduced below the melting point.

The last (integral) term in Eq. (13) describes the number of thermal nuclei produced during crystallization. This term does not appear in our analysis because, at the beginning of crystallization it is small compared with the first two terms.

As shown in our previous paper [1], the number of athermal nuclei can be calculated from cluster size density function, $\varrho_0(g)$, resulting from thermal history of the melt $\{T_1, t_1\}$, and is controlled by crystallization temperature, T_c, which determines critical cluster size, g^*.

$$N_{ath}(T_1, t_1) = \int_{g^*(T_c)}^{\infty} \varrho_0(g;\, T_1, t_1)\,dg \qquad (14)$$

Using approximate solution for cluster distribution function after a single heating step $\{T_1, t_1\}$, we obtain [1]

$$\varrho_0(g; T_1, t_1) = \varrho_{eq}(g; T_1) + [\varrho_{00} - \varrho_{eq}] \times \exp[-t_1/\tau(T_1)] \qquad (15)$$

$\varrho_{00}(g)$, and N_{00} (appearing in Eqs. (17), (18) below) denote, respectively, cluster size distribution and number of potential predetermined athermal nuclei at the instant of time when the sample reaches the treatment temperature T_1. $\varrho_{eq}(g; T_1)$ denotes equilibrium distribution at the temperature $T_1 > T_m$. We have shown in ref. [1] that for organic polymers $\varrho_{eq}(g)$ in the range of cluster sizes which can produce athermal nuclei is small and can be neglected. Consequently, Eq. (15) reduces to

$$\varrho_0(g; T_1, t_1) \simeq \varrho_{00} \exp[-t_1/\tau(T_1)] \;, \qquad (16)$$

and the concentration of athermal nuclei at the start of crystallization

$$N_{ath}(T_1, t_1) \cong N_{00} \exp[-t_1/\tau(T_1)] \;. \qquad (17)$$

The total number of predetermined nuclei, related to maximum crystallization-rate time t_p (Eq. (12)) reads

$$\begin{aligned} N_0(T_1, t_1) &= N_{ath}(T_1, t_1) + N_{het} \\ &\cong N_{00} \exp[-t_1/\tau(T_1)] + N_{het} \\ &= \text{const.}\, t_p^{-3}(T_1, t_1) \end{aligned} \qquad (18)$$

Equation (18) provides the basis for interpretation of experimental (DSC) data. By extrapolation to infinite melting time, the concentration of infusible heterogeneous nuclei is obtained

$$N_{het} = \text{const.}\, t_p^{-3}(T_1, \infty) \;. \qquad (19)$$

The plot of $\ln[t_p^{-3}(T_1, t_1) - t_p^{-3}(T_1, \infty)]$ vs. t_1 at constant temperature T_1 yields relaxation time

$$1/\tau = -\partial \ln[t_p^{-3}(T_1, t_1) - t_p^{-3}(T_1, \infty)]/\partial t_1 \;. \qquad (20)$$

Results and discussion

Effect of crystallization temperature, T_c

Preliminary experiments were carried out in order to find crystallization temperatures most suitable for the study of memory effects. Melt treatment for these experiments was chosen in the range typical for crystallization studies of polypropylene: $T_1 = 220$ °C and $t_1 = 10$ min. As shown in Fig. 3, time required to reach the exothermal DSC peak (identified with maximum crystallization rate), for all samples monotonically increases with crystallization temperature, in agreement with the common behavior of crystallization rates at moderate undercooling. At any T_c, crystallization times (reciprocal crystallization rates) for the studied polypropylenes increased in the order:

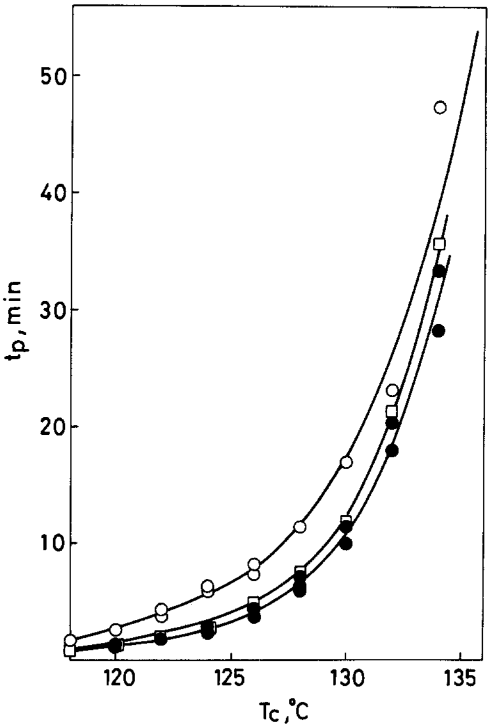


Fig. 3 Dependence of the time-to-peak, t_p, on crystallization temperature, T_c. Temperature of the melt, $T_1 = 220$ °C, melting time, $t_1 = 10$ min. ○: PP1; □: PP2; ●: PP3

$$t_p(\text{PP1}) > t_p(\text{PP2}) > t_p(\text{PP3}) \;.$$

Slow crystallization of sample PP1 can be attributed to reduced content of residual catalyst (acting as heterogeneous nucleating agent) and reduced tacticity. Low molecular weight of sample PP3 may account for enhanced crystallization rate of the latter.

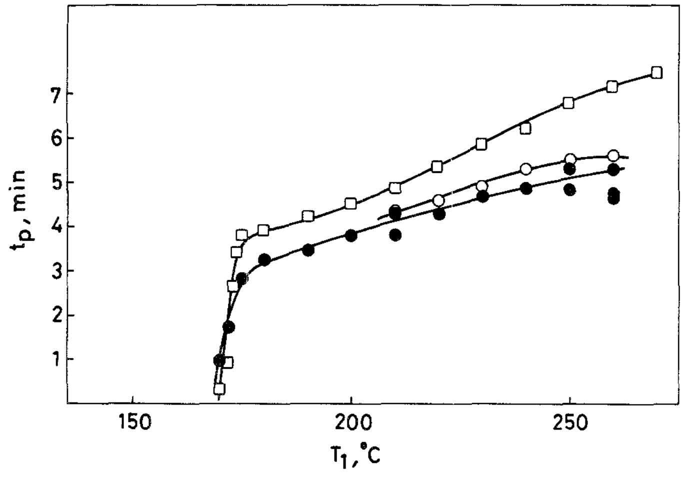
Crystallization below 120 °C was too fast and would produce a considerable amount of crystallinity already during cooling from T_1 to T_c. This was particularly evident when studying samples with mild melt treatment (low T_1 and short t_1). On the other hand, for T_c higher than 130 °C, the time needed for complete crystallization became very long, and low signal-to-noise ratio made precise determination of t_p impossible. In the range of T_c between 120 and 130 °C, crystallization temperatures giving t_p values in the range of 4 to 6 minutes provided a good compromise between the precision of measurements and time required for transformation. In these conditions a good reproducibility of t_p was obtained, provided that the instrument was calibrated and operated in strictly standardized conditions. Repeated runs using the same polymer and the same thermal history yielded t_p values differing less than 5% from each other.

Effect of melt temperature, T_1

In Fig. 4, the time-to-peak values, t_p, were measured on samples heated for 10 min at various temperatures, T_1. A common feature of all three polypropylenes is steep dependence of t_p on melt temperature, T_1, in the range just above melting temperature, T_m. When T_1 was changed from 170 °C (ca 5 degrees above melting temperature) to 180 °C, time-to-peak increased by a factor of 10. Similar effects were observed by Carfagna et al. [6] in the range of 160–170 °C. The authors [6] found that the heating rate used to reach T_1 provides an additional experimental parameter that must be controlled to get reproducible results: the faster the heating, the greater the reduction of residual crystallinity. Our results obtained in the range of 170–180 °C are also comparable to observations of Fillon et al. [7–9] at lower temperatures. Higher tacticity and higher molecular weight of our polypropylenes make our experiments equivalent to lower temperature range when conventional polypropylenes are used [10].

On the other hand, our results seem to be in opposition to those reported by Janimak et al. [11] who failed to observe any melting history effects in isothermal crystallization of PP fractions. Janimak's conclusions, however, were based on direct comparison of the Avrami, *log(log)* plots. Low sensitivity of such plots, as well as arbitrariness of selecting the base line, the start, and the end of crystallization, may have hidden effects of melting history.

Fig. 4 Dependence of the time-to-peak, t_p, on melt temperature, T_1, at constant melting time, t_1 = 10 min. ○: PP1, T_c = 124 °C; □: PP2, T_c = 127 °C; ●: PP3, T_c = 126 °C



There is still some uncertainty as to the value of equilibrium melting temperature of isotactic polypropylene. Some results suggest T_m^0 = 180°–190 °C, while others point to higher range, 200°–220 °C. According to Wunderlich [12] the most probable value is 187.5 °C, while Monasse and Haudin [13] obtained by extrapolation T_m^0 = 208 °C. The T_1 range where strong effect of heating temperature on t_p was observed, lies below the lower bound for T_m^0; therefore it seems reasonable to expect that, similarly to what happens in self-nucleation procedure [14], microscopic and submicroscopic fragments of previous crystals resist mild thermal treatment and strongly speed-up crystallization when the sample is cooled down to T_c.

Further increase of T_1 causes t_p to increase steadily, but less steeply, up to the point when thermal degradation contributes to chain scission (and causes slight increase in crystallization rate). In order to find the highest T_1 which does not cause degradation, the following experiments were performed. After prolonged treatment of the melt at highest temperatures (250°–300 °C), samples were quenched to room temperature, submitted to standard thermal cycle, and t_p was measured after heating for 10 min at 220 °C. Reproducible t_p values were obtained for T_1 up to 260 °C for PP1 and PP3, and up to 290 °C for PP2.

The effect of T_1 on crystallization kinetics should be attributed to physical, rather than chemical processes in the molten state. Increase of melt treatment temperature is expected to affect the concentration of athermal nuclei through the reduced relaxation time, τ (cf. Eq. (17). Higher heating temperatures should result in slower crystallization after cooling to $T = T_c$.

Effect of melting time, t_1

The effect of melting time, t_1, on the overall crystallization kinetics is shown in Fig. 5. The data refer to sample PP2, but are representative for the other two polypropylenes. Increasing duration of melting at constant temperature, one observes gradual increase of crystallization time t_p, suggesting gradual reduction of the number of predetermined athermal nuclei, N_{ath}. At high heating temperatures, an asymptotic value of t_p is observed. Heating for periods longer than 100 min does not affect subsequent crystallization. Usually, 20 min of heating is sufficient to bring the sample close to the asymptotic t_p value. When heat treatment is performed slightly above the melting temperature, t_p continues to increase for many hours and no asymptotic level is reached.

The data obtained in higher melt temperatures indicate that the asymptotic level of t_p does not depend on temperature. This confirms suggested interpretation of t_p as a

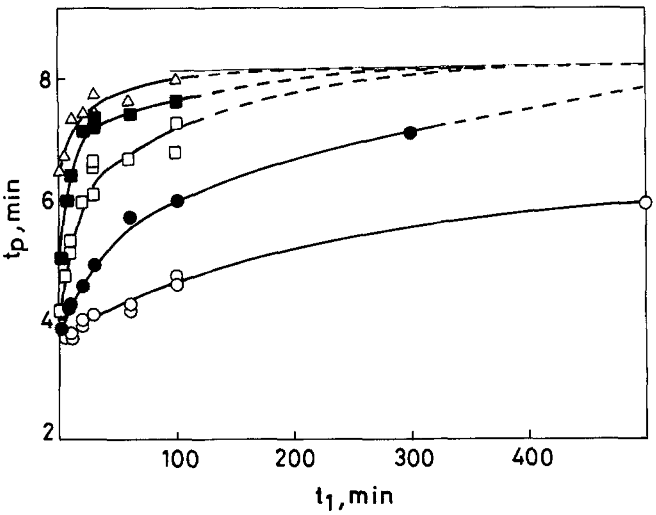


Fig. 5 Time-to-peak for isothermal crystallization of sample PP2 at $T_c = 127\,°C$ as a function of melting time, t_1. ○: $T_1 = 180\,°C$; ●: $T_1 = 200\,°C$; □: $T_1 = 220\,°C$; ■: $T_1 = 240\,°C$; △: $T_1 = 260\,°C$

result of two kinds of predetermined nuclei: melting-history-dependent *athermal* nuclei (which disappear after prolonger heating), and insensitive to heating *heterogeneous* nuclei which contribute to the observed asymptotic behavior (cf. eqs. 18, 19).

After having determined the asymptotic value of t_p for each sample, the data were processed according to the procedure described in Eqs. (19)–(20). The results presented in Fig. 6 concern sample PP2. Similar results were obtained for samples PP1 and PP3.

Linear dependence between $\ln[t_p^{-3}(T_1, t_1) - t_p^{-3}(T_1, \infty)]$ and melting time, t_1 was found for low melt temperatures. At higher T_1, upward curvature of the relation was noted, indicating, slower than linear, reduction of crystallization rate. With increased temperature T_1, the deviation from linearity was shifted to shorter heating times, t_1.

Non-linear behavior at higher melt temperatures can be explained on the basis of combined, predetermined *and* sporadic nucleation at $T = T_c$. Mild, or moderate thermal treatment (i.e., low temperature and/or short heating time) leave behind a considerable amount of clusters which are converted into athermal nuclei. Crystallization kinetics at $T = T_c$ are controlled by predetermined nuclei (Eq. (8)), and the relation between t_p and melting time, t_1, is as predicted by Eq. (18). Stronger heating regimes leave only low concentration of large homogeneous clusters. Subsequent crystallization at $T = T_c$ is controlled by heterogeneous nuclei and sporadic nucleation. Consequently, crystallization rate is higher (t_p is smaller) than that predicted for a pure predetermined mechanism (cf. Eqs. (7) and (8)).

The higher the melt temperature, T_1, the steeper the reduction of crystallization rate (and t_p^{-3}) with heating time. Initial slopes of the plot

$$\ln[t_p^{-3}(T_1, t_1) - t_p^{-3}(T_1, \infty)] \text{ vs. } t_1$$

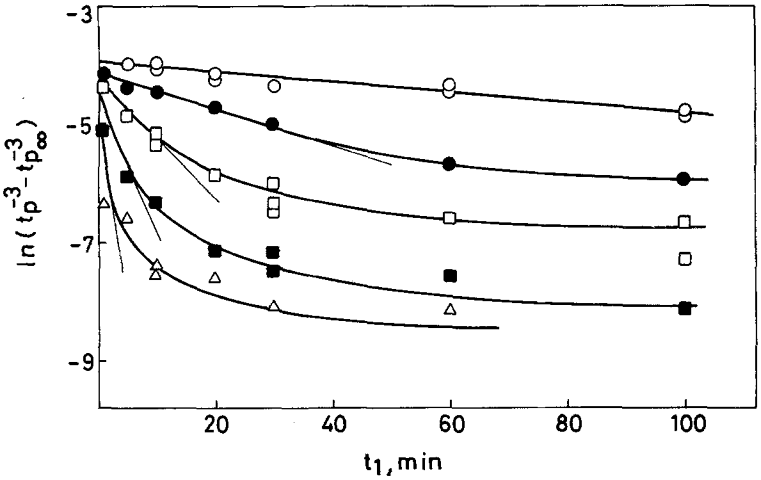
determine relaxation times involved in the process of thermal restructuring cluster distribution function, $\rho_0(g)$.

Relaxation times calculated for all three polypropylenes and various melt temperatures are shown in Fig. 7. Logarithms of relaxation times form straight lines when plotted vs. reciprocal absolute temperature, suggesting the Arrhenius relation

$$\tau(T_1) = \tau_0 \exp[E_a/kT_1] \tag{21}$$

Activation energies, E_a, pre-exponential factors, τ_0, and example relaxation times for the three polypropylenes are given in Table 2.

Fig. 6 Representation of experimental data according to Eq. (18). Symbols and conditions as in Fig. 5



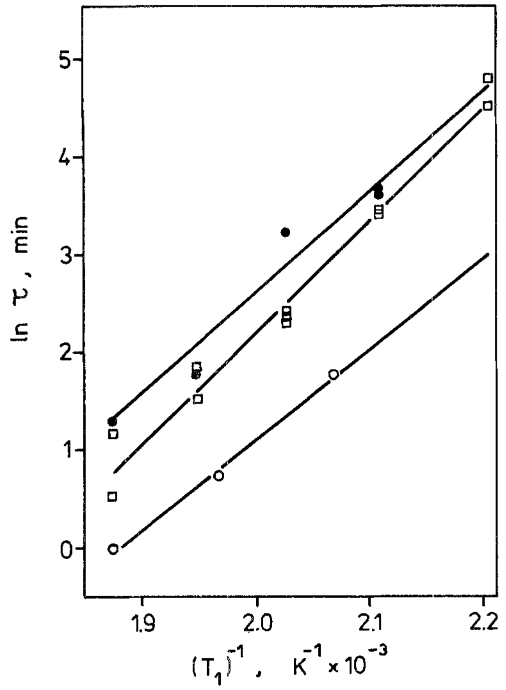


Fig. 7 Temperature dependence of relaxation time, τ. ○: PP1; □: PP2; ●: PP3

The data in Table 2 do not show any correlation of activation energy or pre-exponential factor with molecular weight or polydispersity. Considering activation energy as a constant within the range of experimental error, one obtains the value 89 ± 7 kJ/mole. This result corresponds well with the value 88 kJ/mole found by Billingham et al. [15] for activation energy of self diffusion of atactic polypropylene.

Table 2 Relaxation times and activation energy

Sample	PP1	PP2	PP3
$M_w \times 10^{-3}$	476	520	400
M_w/M_n	6	12	25
τ (200 °C), min	8.47	32.7	43.5
τ (260 °C), min	0.94	2.15	3.82
E_a, kJ/mole	76.8	95.1	84.9
τ_0, (min × 10^{-8})	2.87	0.11	1.86
average E_a, kJ/mole		89 ± 7	

In the range of temperatures analyzed, relaxation times change is in the order

$$\tau(\mathrm{PP3}) > \tau(\mathrm{PP2}) > \tau(\mathrm{PP1}) ,$$

which may suggest molecular weight distribution (characterized by the ratio M_w/M_n) as the main molecular characteristic. Consistency of activation energy with the data for self-diffusion suggests that relaxation in the thermal transformation of cluster distribution function is diffusion-controlled.

Acknowledgements The help of Prof. Yan Deyue, of the Jiao Tong University (Shanghai, China) who has performed the great part of the experimental work, is greatly appreciated. We thank also Dr. T. Simonazzi (Himont Italia, Ferrara) for providing high purity polypropylene samples and for his continuing interest in this research.

References

1. Ziabicki A, Alfonso GC (1994) Colloid Polym Sci 272:1027
2. Kolmogoroff AN (1937) Izvestiya Akad Nauk SSSR, Ser Math 3:335
3. Avrami M (1939) J Chem Phys 7:1103
4. Evans UR (1945) Trans Faraday Soc 41:365
5. Barham PJ (1993) in: "Crystallization of Polymers". Dosière M, Ed., NATO ASI Series, C-405, p. 153, Kluwer Academic Press, Dordrecht
6. Carfagna C, De Rosa C, Guerra G, Petraccone V (1984) Polymer 25:1462
7. Fillon B, Wittmann JC, Lotz B, Thierry A (1993) J Polym Sci B Polym Phys 31:1383
8. Fillon B, Lotz B, Wittmann JC, Thierry A (1993) J Polym Sci B Polym Phys 31:1395
9. Fillon B, Thierry A, Wittmann JC, Lotz B (1993) J Polym Sci B Polym Phys 31:1407
10. Janimak JJ, Cheng SZD, Giusti PA, Hsieh ET (1991) Macromolecules 24:2253
11. Janimak JJ, Cheng SZD, Zhang A, Hsieh ET (1992) Polymer 33:728
12. Wunderlich B (1980) "Macromolecular Physics", Vol. 3, Academic Press, New York
13. Monasse B, Haudin JM (1986) Colloid Polym Sci 264:117
14. Blundell DJ, Keller A, Kovacs AJ (1966) J Polymer Sci Ser B 4:481
15. Billingham NC, Calvert PD, Uzuner A (1990) Polymer 31:258