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Crystallization behavior of partially melting isotactic polypropylene

Xinyuan Zhu, Yongjin Li, Deyue Yan*, Yapeng Fang

College of Chemistry and Chemical Technology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

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Abstract

The crystallization behavior of partially melting isotactic polypropylene (iPP) has been carefully examined by the differential scanning calorimetry (DSC) and polarized light microscopy. The experimental results show that the unmelted material can accelerate the primary nucleation rate and the ordered structure of polymer melt can speed up the linear growth rate of spherulite, so the crystallization of partially melting iPP proceeds very quickly. The Avrami exponent of partially melting iPP sample is about 2, which indicates that the crystallization mechanism of iPP ordered melt after partial melting is different from that of unperturbed equilibrium melt. © 2001 Published by Elsevier Science Ltd.

Keywords: Isotactic polypropylene; Self-nucleation; Crystallization kinetics

1. Introduction

In order to clarify the relationship of molten temperature with crystallization behavior of polymer, Bank, Gordon and Sharples [1] proposed a new kind of crystallization method: the crystallized sample of polymer is partially melted at temperatures below the melting point, and then crystallized in the presence of the unmelted material. Using this technique, they found that the crystallization rate of polyethylene (PE) sample increases greatly. Subsequently, a lot of works on this research field had been performed [2–10], and this method was recommended to name as self-nucleation.[1] In 1984, Carfagna et al. [5] adopted the self-nucleation method to study the recrystallization kinetics of α-iPP by dilatometric technique. The authors observed that the correspondent Avrami exponents (n) are equal to 1.6 for low crystallinity, which is quite distinct from the values obtained from completely molten sample. Recently, the classical self-nucleation procedure, which was mainly based on isothermal experiments and abrupt temperature-jumps, had been extended to dynamic experiments with finite heating or cooling rates by Fillon et al. [6–8]. They investigated the self-nucleation of iPP, and confirmed that the self-nucleation temperature (T_s) has a very important effect on the crystallization behavior and spherulite morphology.

Almost all of works aforementioned attributed the changes of crystallization behavior to the existing crystal fragments generated by incomplete melting. However, our recent findings [11–14] exhibit that the helical structure of individual molecular chain can be well kept in a temperature range after the polymer crystalline of iPP is melted. It is possible that the crystallization mechanism of iPP melt with long helical structure may be different from that of unperturbed equilibrium melt. Until now, no attention has been paid to the relation between crystallization behavior and the ordered structure of polymer melt. In this paper, the crystallization behavior of partially melting iPP sample was carefully studied, and the experimental data show that both residual crystals and the order of polymer melt affect the crystallization of polymer melt.

2. Experimental

The isotactic polypropylene (iPP) used in this study was kindly provided by Shanghai Jinshan Petrochemical Corporation. The material is highly isotactic, being approximately 94.5% insoluble in n-heptane and it has a melt flow index of 3.0 g/10 min. To erase the previous thermo-mechanical history, the film of melted polymer about 300 μm thick was pressed between two glass slides at 210°C for 10 min in a hot stage, and then rapidly transferred to another hot stage which was set at the desired crystallization

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* Corresponding author. Tel.: +86-21-5474-2665; fax: +86-21-5474-1297.

E-mail address: dyyan@mail.sjtu.edu.cn (D. Yan).

[1] Following the recommendation of the IUPAC commission on nomenclature, the term 'self-nucleation' is used throughout rather than 'self-seeding' used in the original papers (see Ref. [6]).

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temperature (T_c). After having crystallized for 27 h at 145°C or for half an hour at 130°C, respectively, the sample was quenched to 0°C.

The calorimetric measurements and some experiments were carried out on a Perkin–Elmer Pyris-1 Series differential scanning calorimeter under a flowing nitrogen atmosphere. The DSC was calibrated using pure indium as a standard. For all experiments, the sample weights were approximately 5 mg and the heating rate was 10°C/min.

The morphology of various iPP samples was studied on thin films by using an optical polarizing microscope Leika, with a Leika automatic hot-stage thermal control. The iPP samples, crystallized at 145°C for 27 h or at 130°C for half an hour respectively, were sandwiched between microscope cover glass, heated to different fusion temperature and then rapidly cooled to room temperature (25°C) or to 131°C. The PP spherulitic growth was observed by taking photomicrographs at due intervals of time.

3. Results

It has been well reported that the double melting endotherms appear when the iPP sample isothermally crystallizes at higher crystallization temperature (T_c) for a period of time. A lot of research works [15–17] have corroborated that these double endotherms result from two kinds of lamellae with different thickness. Fig. 1(a) is the melting curve of iPP sample isothermally crystallized at 145°C for 27 h, and two melting peaks at 165 and 175°C, respectively, are observed. Heating the sample crystallized at 145°C for 27 h to 169°C which mediates between two peak temperatures, the thinner lamellae melt while the thicker ones remain. We name this sample after partial melting as 'partially melting iPP' and our recent work [17] has shown that the crystallinity of this sample is less than 5%. Given a supercooling degree, the partially melting iPP sample crystallizes with the presence of thicker lamellae. Fig. 2 is the heat flow change for the isothermal crystallization of partially melting iPP at various temperatures, in which time 0.0 means the time when temperature becomes the crystallization temperature after cooling. As can be seen, the crystallization proceeds too fast and a considerable amount of crystallinity has generated during the cooling from the melt to the crystallization temperature. It demonstrates that the accurate kinetics of isothermal crystallization is difficult to be obtained by calorimetric measurements. So only the nonisothermal crystallization kinetic analysis is accessible, which is just carried out below.

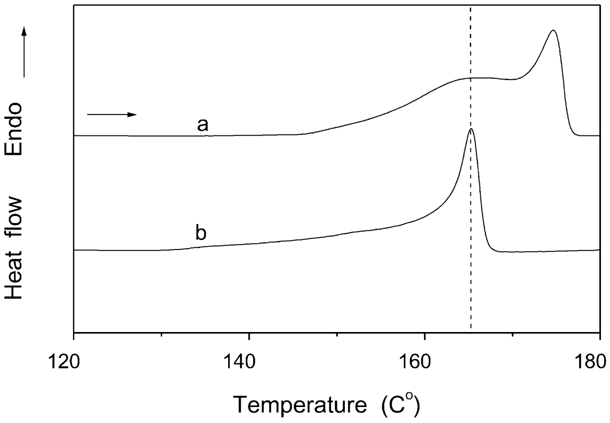

Fig. 1. The melting thermographs of iPP sample which was crystallized: (a) at 145°C for 27 hr; (b): at 130°C for half an hour.

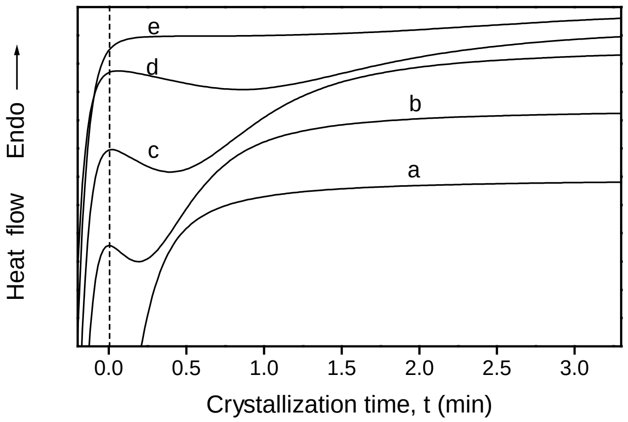

Fig. 2. Time dependence of the heat flow for the isothermal crystallization of partially melting iPP at: (a) 123°C; (b) 125°C; (c) 127°C; (d) 129°C; (e) 131°C.

Fig. 3 is the cooling crystallization curve of partially melting iPP sample at various cooling rates. With increasing the cooling rate, the crystallization peak shifts to the low temperature. Integration of the exothermic peak during the nonisothermal scan gives the relative degree of crystallinity as a function of temperature, which is easily transformed into the plot of relative crystallinity vs. time in terms of the different constant-cooling rate. The results are shown in Figs. 4 and 5, respectively. Considering the fact that the free spherulitic growth approximation is valid at low degree of conversion [18], the initial stage of nonisothermal

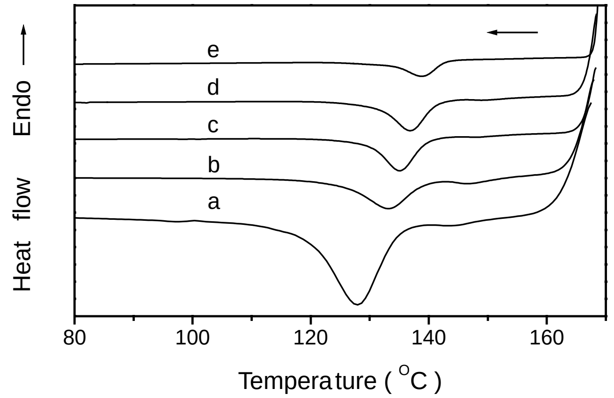

Fig. 3. Heat flow versus temperature during nonisothermal crystallization of partially melting iPP at different cooling rate: (a) 40°C/min; (b) 20°C/min; (c) 15°C/min; (d) 10°C/min; (e) 5°C/min.

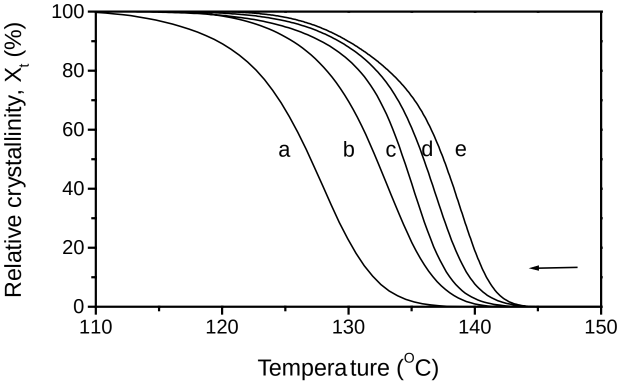

Fig. 4. Relative crystallinity versus temperature during nonisothermal crystallization of partially melting iPP at different cooling rate: (a) 40°C/min; (b) 20°C/min; (c) 15°C/min; (d) 10°C/min; (e) 5°C/min.

crystallization can be described by the Avrami equation [19,20]:

$$X_t = 1 - \exp(-kt^n) \tag{1a}$$

$$or \log[-\ln(1 - X_t)] = \log k + n \log t \tag{1b}$$

where X_t is the relative volume-fraction crystallinity at time t, n is a constant whose value depends on the mechanism of nucleation and on the form of crystal growth, and k is a constant containing the nucleation and growth parameters. However, the DSC measurements only provide the relative mass-fraction crystallinity, which must be converted to relative volume-fraction crystallinity by the following equation [21]:

$$X_t = \frac{\int_0^t \frac{dH}{dt} dt}{\int_0^\infty \frac{dH}{dt} dt} \rho_t \tag{2}$$

where dH/dt is the rate of crystallization heat evolution at time t and ρ_t is the relative mass-fraction crystallinity. The double logarithmic plot of $\log[-\ln(1 - X_t)]$ vs. $\log t$ is shown in Fig. 6. Each curve has an initial linear section and the Avrami parameters of n and k can be determined from the slopes and intercepts of linear portion. Table 1 presents that the Avrami exponent n is ranging from 2.1 to 2.3 with different cooling rate. Generally, $n = 3$ is found for crystallization from unperturbed equilibrium melt and iPP gives a clear-cut example of heterogeneous athermal nucleation followed by a three-dimensional spherulitic crystal growth [21–23]. The lower Avrami exponent ($n = 2$) means that the crystallization mechanism of partially melting iPP is altered. Carfagna et al. [5] had also studied the crystallization kinetics of partially melting iPP by dilatometric technique and found the Avrami exponent is equal to 1.6 for low crystallinity. Since their experiments were performed at lower fusion temperature, the Avrami exponent 1.6 is smaller than that of ours due to the difference in crystallinity. Carfagna et al. [5] attributed the lower Avrami exponent to the presence of unmelted material. But, the detailed analysis in discussion section of this paper shows that both residual crystals and the order of polymer melt affect the crystallization process.

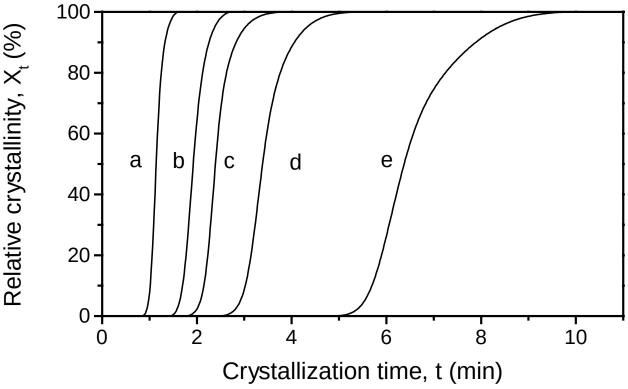

Fig. 5. Relative crystallinity versus crystallization time during nonisothermal crystallization of partially melting iPP at different cooling rate: (a) 40°C/min; (b) 20°C/min; (c) 15°C/min; (d) 10°C/min; (e) 5°C/min.

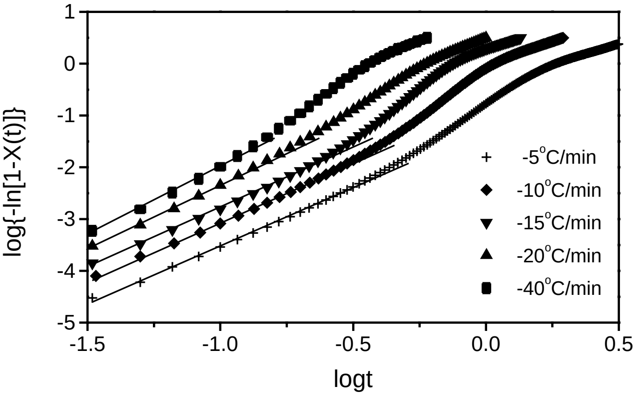

Fig. 6. Plots of $\log[-\ln(1 - X_t)]$ vs. $\log t$ for nonisothermal crystallization of partially melting iPP at different cooling rate: (■) −40°C/min; (▲) −20°C/min; (▼) −15°C/min; (◆) −10°C/min; (+) −5°C/min.

Table 1 shows that the rate constant k increases with decreasing the crystallization temperature. The k value ranges from 0.04 to 1.54 and that is at least several orders of magnitude higher than those in literature [22–28] ($k = 10^{-3}$–10^{-14}), which further confirms that the crystallization

Table 1
Nonisothermal crystallization kinetic parameters for partially melting iPP

Φ (°C/min)	T_p (°C)	n	k (s^{-n})	ΔE^a (kJ/mol)	ΔE^b (kJ/mol)
5	138.8	2.1	0.04		
10	136.8	2.1	0.11		
15	135.0	2.1	0.23	266	261
20	133.0	2.3	1.07		
40	128.0	2.3	1.54		

[a] Determined by Avrami equation.

[b] Determined by Kissinger equation.

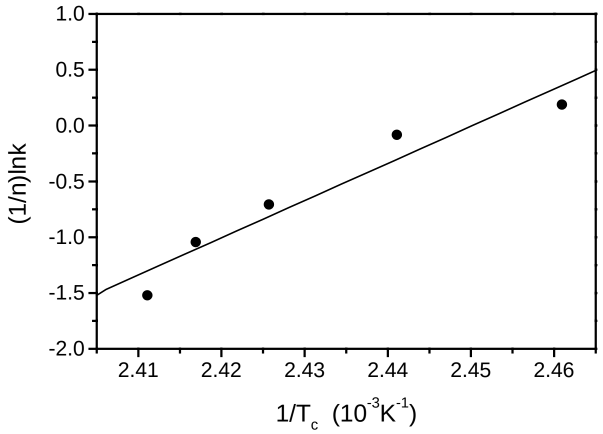

Fig. 7. Plot of $(1/n)\ln k$ vs. $1/T_c$ for the Avrami analysis of nonisothermal crystallization of partially melting iPP.

mechanism of partially melting iPP is changed. If the crystallization process is assumed to be thermally activated, the crystallization activation energy can be obtained by the Arrhenius equation [18]:

$$k^{1/n} = k_0 \exp(-\Delta E/RT_c) \tag{3a}$$

$$\text{or } (1/n)\ln k = \ln k_0 - (\Delta E/RT_c) \tag{3b}$$

where k_0 is a temperature independent preexponential factor, R is the gas constant, T_c is the absolute temperature, and ΔE is the crystallization activation energy. Fig. 7 is the plot of $(1/n)\ln k$ vs. $1/T_c$. From the slope of straight line, the crystallization activation energy is found to be 266 kJ/mol. In addition, the Kissinger method can also be used to determine the activation energy [29]:

$$\mathrm{d}[\ln(\Phi/T_p^2)/\mathrm{d}(1/T_p) = -\Delta E/R \tag{4}$$

where Φ is the cooling rate, T_p is the cooling peak temperature and R is the gas constant. Fig. 8 is the graph of $\ln(\Phi/T_p^2)$ with $1/T_p$. According to the slope of the curve, the activation energy is determined as 261 kJ/mol. The agreement in ΔE values determined by Avrami and Kissinger methods suggests that the Avrami analysis works well in describing the initial stage of nonisothermal crystallization of partially melting iPP sample.

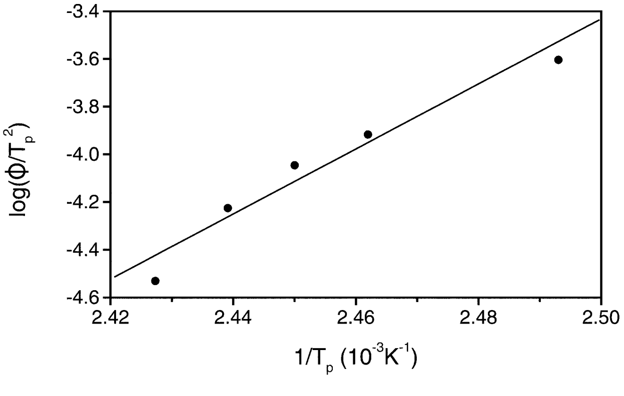

Fig. 8. Kissinger graph for evaluating nonisothermal crystallization activation energy of partially melting iPP.

4. Discussion

Why does the partially melting iPP sample crystallize so quickly at high crystallization temperature? So far, two interpretations have been presented. Bank et al. [1] had investigated the crystallization behavior of partially melting PE sample. They thought that the increase of crystallization rate was due to the seeds of negligible volume in the molten region produced by partial melting, and the unmelted material remained inert. On the contrary, many other researchers [3–10] suggested that the unmelted crystals could serve as nuclei so that the crystallization process was speeded up greatly. In order to check whether the existing crystals have influence on the subsequent crystallization, the iPP samples were isothermally crystallized at 145°C for 27 h and at 130°C for half an hour, respectively. The correspondent melting curves in Fig. 1 show that double melting endotherms with peak temperatures at 165 and 175°C appear when $T_c = 145$°C, while only a single endotherm with peak temperature at 165°C exists when $T_c = 130$°C. Assuming that only the top and bottom surfaces contribute to the free enthalpy of the crystal, the Thomson–Gibbs equation can be simplified to [30]:

$$T_m = T_m^0(1 - 2\sigma_e/l_\Delta h_f) \tag{5}$$

where T_m^0 is the equilibrium melting temperature, σ_e the top and bottom specific surface free energy, l the lamellar thickness, and Δh_f the bulk heat of fusion per volume. Obviously, the identical melting points correspond to the same lamellar

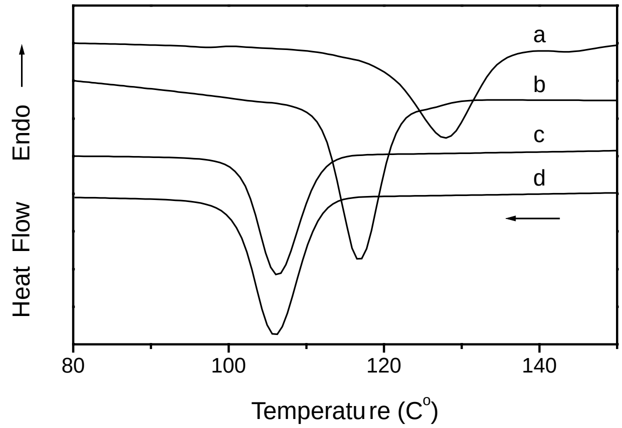

Fig. 9. The cooling thermographs of iPP sample: (a) isothermally crystallized at 145°C for 27 h, quenched to 0°C, heated to 169°C and then cooled to 50°C at 40°C/min; (b) isothermally crystallized at 130°C for half an hour, quenched to 0°C, heated to 169°C and then cooled to 50°C at 40°C/min; (c) isothermally crystallized at 145°C for 27 h, quenched to 0°C, heated to 210°C and kept for 10min, finally cooled to 50°C at 40°C/min; (d) isothermally crystallized at 130°C for half an hour, quenched to 0°C, heated to 210°C and kept for 10 min, finally cooled to 50°C at 40°C/min.

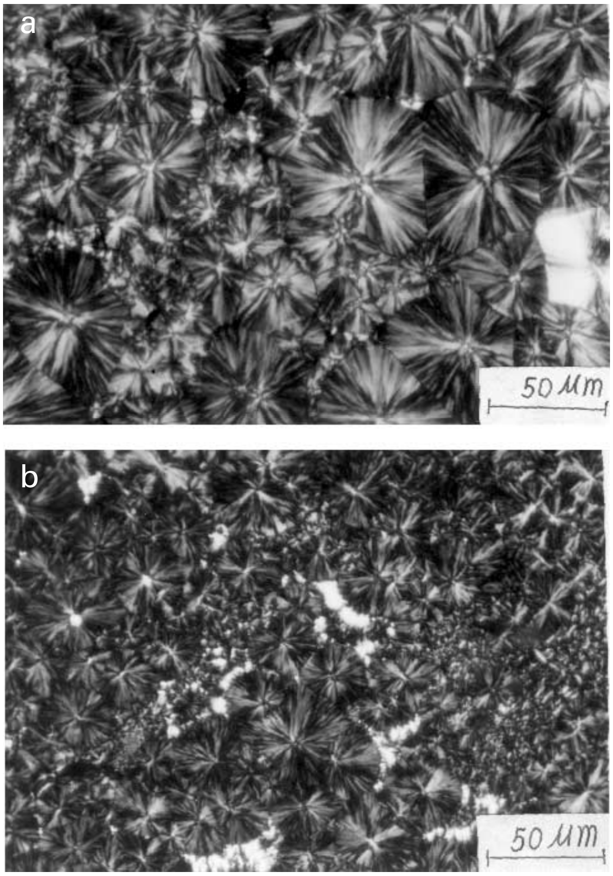

Fig. 10. Micrographs for iPP sample: (a) crystallized at 145°C for 27 h, quenched to 0°C, heated to 169°C and then cooled to 25°C at 20°C/min; (b) crystallized at 130°C for half an hour, quenched to 0°C, heated to 169°C and then cooled to 25°C at 20°C/min.

thickness. If the samples are heated to 169°C, the iPP melt is formed. For the sample crystallized at 145°C, some thicker lamellae exist in melt; for the sample crystallized at 130°C, there is little unmelted material in the melt. Cooling both samples to 50°C at the rate of 40°C/min, the melt crystallizes. The comparison of Fig. 9(a) with Fig. 9(b) indicates that the peak temperature (128°C) of the iPP sample crystallized at 145°C is higher than that (117°C) of the sample crystallized at 130°C by 11°C, which reveals that the crystallization rate of the former is faster than that of the latter. The correspondent crystalline morphologies of these two samples after quickly cooling are shown in Fig. 10. From a comparison of Fig. 10(a) and (b) it clearly emerges that the unmelted crystals determine a strong nucleating effect. If the iPP samples crystallized at 145 and 130°C, respectively are heated to 210°C, kept for 10 min and then cooled them to 50°C at 40°C/min, the correspondent crystallization curves in Fig. 9(c) and (d) are similar and both crystallization peak temperatures are 106°C, which is much lower than those of Fig. 9(a) and (b). It is evident that all memory of previous crystallization is effectively removed at 210°C, i.e. the residual small crystallites that are not able to be detected by DSC are completely melted at 210°C. In our another work [14], the iPP sample crystallized at 130°C for half an hour was heated to 169 and 210°C, respectively, and then cooled to 131°C for isothermal crystallization. The micrographs show that the spherulite number corresponding to lower fusion temperature is much more than that corresponding to higher fusion temperature [14]. All these experimental results seem to suggest that the presence of unmelted material accelerates the primary nucleation rate.

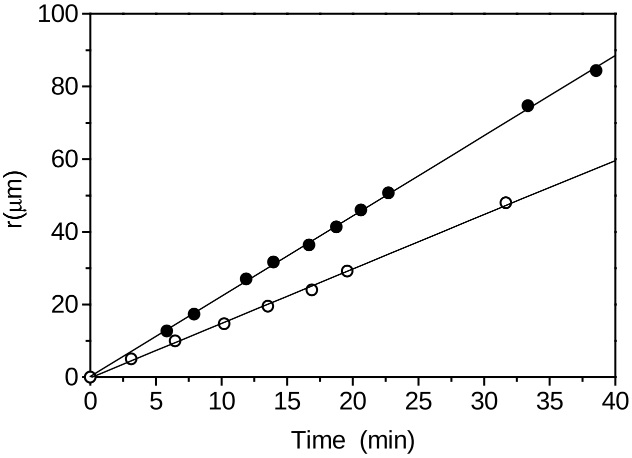

Fig. 11. Time dependence of radii of spherulites for ordered melt (●) and unperturbed equilibrium melt (○) generated by heating the iPP sample crystallized at 145°C to 169 or 210°C, respectively. The temperature of isothermal crystallization is 131°C.

Now, another problem appears. Apart from the existence of unmelted crystals, is there any other factor to affect the crystallization behavior of partially melting iPP? Recently, we [11–14] have studied the melting process of crystallized iPP sample and found that the helical structure of individual molecular chain can be well kept at a lower fusion temperature. The crystallization behavior of ordered melt may be different from that of unperturbed equilibrium melt, which has been confirmed by the fact that the Avrami exponent of partially melting iPP sample is about 2. In order to clarify the crystallization mechanism more precisely and directly, the microscopy observation has been performed. Cooling the partially melting iPP sample to 131°C for isothermal crystallization, the spherulites are observed and the radius of the spherulites increases linearly with time. Fig. 11 shows the time dependence of radii of spherulites for ordered melt and unperturbed equilibrium melt generated by heating the iPP sample crystallized at 145°C to 169 or 210°C, respectively, and the difference of linear growth rate of spherulites can be determined by the slopes of lines. Because of the existence of the ordered melt, the linear growth rate of spherulite increases. Consequently, the overall crystallization rate of partially melting iPP sample is speeded up.

5. Conclusions

The study of crystallization kinetics of partially melting iPP sample has been carried out by differential scanning calorimetry (DSC). It is found that the partially melting iPP can crystallize very quickly at high temperature and the Avrami equation describes the initial stage of non-isothermal crystallization very well. Interestingly, the Avrami exponent of partially melting iPP sample is about 2, which seems to suggest that the crystallization mechanism of partially melting iPP is different from that of completely melting sample. With decreasing the crystallization temperature, the rate constant *k* increases. The activation energy is 266 kJ/mol or 261 kJ/mol determined by Avrami and Kissinger methods, respectively.

The microscopy observation demonstrates that the unmelted crystals can serve as nuclei so as to accelerate the primary nucleation rate. On the other hand, because of the existence of the ordered melt after partial melting, the linear growth rate of spherulite is also speeded up. Therefore, the crystallization of partially melting iPP sample proceeds very quickly. Moreover, the results of Avrami analysis and microscopy observation suggest that the crystallization mechanism of partially melting iPP sample is different from that of unperturbed equilibrium melt.

Acknowledgements

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References

[1] Bank W, Gordon M, Sharples A. Polymer 1963;4:289.
[2] Holland VF. J Appl Phys 1964;35:59.
[3] Blundell DJ, Keller A, Kovacs AJ. J Polym Sci, Polym Lett 1966;4:481.
[4] Chivers RA, Barham PJ, Martinez-Salazar J, Keller A. J Polym Sci, Polym Phys Ed 1982;20:1717.
[5] Carfagna C, Rosa CD, Guerra G, Petraccone V. Polymer 1984;25:1462.
[6] Fillon B, Wittmann JC, Lotz B, Thierry A. J Polym Sci, Polym Phys Ed 1993;31:1383.
[7] Fillon B, Lotz B, Thierry A, Wittmann JC. J Polym Sci, Polym Phys Ed 1993;31:1395.
[8] Fillon B, Thierry A, Wittmann JC, Lotz B. J Polym Sci, Polym Phys Ed 1993;31:1407.
[9] Tan S, Su A, Li W, Zhou E. Macromol Rapid Commun 1998; 19:11.
[10] Tan S, Su A, Luo J, Zhou E. Polymer 1999;40:1223.
[11] Zhu XY, Yan DY, Yao HX, Zhu PF. Macromol Rapid Commun 2000;21:354.
[12] Zhu XY, Yan DY. Macromol Chem Phys 2001;202:1109.
[13] Zhu XY, Li YJ, Yan DY, Zhu PF, Lu QH. Colloid Polym Sci 2001;279:292.
[14] Zhu XY, Yan DY. Colloid Polym Sci 2001;279:546.
[15] Kim YC, Ahn W, Kim CY. Polym Eng Sci 1997;7:309.
[16] Al-Raheil IA, Qudah AM, Al-Share M. J Appl Polym Sci 1998;67:1267.
[17] Zhu XY, Yan DY, Tan S, Wang T, Yan DH, Zhou E. J Appl Polym Sci 2000;77:163.
[18] Cebe P, Hong SD. Polymer 1986;27:1183.
[19] Avrami M. J Chem Phys 1939;7:1103.
[20] Avrami M. J Chem Phys 1940;8:212.
[21] Wunderlich B. Macromolecular physics, vol. III. New York: Academic Press, 1980.
[22] Pratt CF, Hobbs SY. Polymer 1976;17:13.
[23] Martuscelli E, Pracella M, Crispino L. Polymer 1983;24:693.
[24] Marker L, Hay PM, Toilley GP, Early RM, Sweeting O, J. J Polym Sci 1959;38:33.
[25] Griffith JH, Ranby BG. J Polym Sci 1959;38:107.
[26] Magill JH. Polymer 1962;3:35.
[27] Parrini P, Corrieri G. Makromol Chem 1963;62:83.
[28] Bogoeva-Gaceva G, Janevski A, Grozdanov A. J Appl Polym Sci 1998;67:395.
[29] Kissinger HE. J Res Natl Stds 1956;57:217.
[30] Wunderlich B. Macromolecular physics, vol. III. New York: Academic Press, 1980.