Influence of the order of polymer melt on the crystallization behavior: II. Crystallization kinetics of isotactic polypropylene

Received: 16 June 2000
Accepted: 16 October 2000

X. Zhu · D. Yan (✉)
College of Chemistry
and Chemical Technology
Shanghai Jiao Tong University
800 Dongchuan Road
Shanghai 200240
People’s Republic of China
e-mail: dyyan@mail.sjtu.edu.cn
Tel.: +86-21-5474-2665
Fax: +86-21-5474-1297

Abstract The crystallization behavior of isotactic polypropylene (iPP) melts with a high order has been carefully examined by differential scanning calorimetry (DSC) and polarized light microscopy (PLM). The experimental results show that the helically ordered iPP melt crystallizes by heterogeneous nucleation with two-dimensional diffusion controlled growth and the Avrami exponent is about 2. The data available both from our DSC and PLM experiments and from the literature indicate that the order of a polymer melt can speed up the crystallization process. When some unmelted materials exist in the ordered melt, the crystallization will become more rapid.

Keywords Isotactic polypropylene · Polymer melt · Crystallization kinetics · Avrami analysis

Introduction

Considerable attention has been focused on the crystallization kinetics of isotactic polypropylene (iPP) because of its importance in both mechanism studies and the processing of polymers [1–30]. In 1959, Marker [1], Griffith [2], and Falkai et al. [3] adopted the dilatometry and optical microscopy methods, respectively, to examine the crystallization behavior of iPP at different temperatures. They found that the crystallization follows the kinetics of a nucleation-controlled process according to the Avrami equation and that the corresponding Avrami exponent is 3. Since then, many other methods such as light depolarization microscopy (LDM) [4, 10], infrared microscopy (IR) [13], differential scanning calorimetry (DSC) [9–10, 14–17], and differential thermal analysis (DTA) [6] have also been used in this field of research. Generally, the crystallization of isotactic polypropylene is heterogeneous, athermal nucleation followed by a three-dimensional spherulitic crystal growth and the Avrami exponent is equal to 3.

Griffith et al. [2] found that an iPP sample with a lower molecular weight has a more rapid crystallization. Subsequently, Parrini and Corrieri [5] observed that, compared with a polydisperse sample, the narrow distribution sample has a lower crystallization rate. Based on the observations of optical microscopy and X-ray diffraction, Hoshino et al. [8] proposed that the crystallization of iPP consists of two stages: primary crystallization and secondary crystallization. Both primary and secondary crystallization can be well described by the Avrami equation, while the Avrami exponent of the former is larger than that of the latter. However, Martuscelli and Avella [15–17] pointed out that the secondary crystallization occurs only in a lower degree of stereoregularity, which suggests that the secondary crystallization results from the presence of some configurational irregularity in the iPP chains. These authors [15–17] have systematically investigated the influence of the degree of stereoregularity on the overall rate of crystallization, and concluded that at constant crystallization temperature the overall rate constant of crystallization decreases with the increase of configurational chain defects. Moreover, the recrystallization kinetics of partially melting iPP reveal that the crystallization process can be accelerated by the existence of unmelted materials [18, 30]. Recently, many studies have been focused upon the relationship of nucleating agents or additives with crystallization behavior [14, 19, 21–26]. It is found that the addition of nucleating agents or
additives will increase the nucleation density and crystallization rate.

Even though the crystallization kinetics of iPP have been extensively studied during the past decades of years, no attention has been paid to the relation between the order of the polymer melt and the crystallization behavior. The main aim of the present research is to study the crystallization kinetics of a helically ordered melt, in order to analyze the influence of the order of the polymer melt on the kinetic parameters controlling the crystallization process of the iPP sample.

Materials and methods

The isotactic polypropylene (iPP) used in this study was kindly provided by Shanghai Jinshan Petrochemical Corp. (Shanghai, P. R. China). The material is highly isotactic, being approximately 94.5% insoluble in n-heptane and has a melt flow index of 3.0 g/10 min. To erase the previous thermomechanical history, a film of melted polymer about 300 µm thick was pressed between two glass slides at 210 ºC for 10 min in a hot stage, and then rapidly transferred to another hot stage that was set at 130 ºC. After having crystallized for half an hour, the sample was quenched to 0 ºC.

The crystallization kinetics study was carried out on a Perkin-Elmer Pyris-1 Series differential scanning calorimeter under a flowing nitrogen atmosphere. The iPP sample, crystallized at 130 ºC for half an hour, was heated to 169 ºC or 210 ºC, respectively, and then quickly cooled to different crystallization temperatures (Tc) for isothermal crystallization or cooled to 20 ºC at different cooling rates. The DSC was calibrated using In and Zn as standards. For all experiments, the sample weights were approximately 5 mg and the heating rate was 10 ºC/min.

The morphological studies were performed on an optical polarized Leica microscope, with a Leica hot-stage thermal control. The iPP sample, crystallized at 130 ºC for half an hour, was sandwiched between two microscope cover glasses, heated to 169 ºC or 210 ºC, respectively, and then rapidly cooled to 131 ºC for isothermal crystallization.

Results

Our recent findings [30–33] have pointed out that when the iPP sample, isothermally crystallized at 130 ºC for half an hour, is heated to 169 ºC, the polymer crystalline material is melted while the helical structure of the individual macromolecular chain can be well retained. The multiple melting behaviors observed in the first part of this series further confirm the existence of a helically ordered melt [34]. Given an appropriate supercooling degree, these helically ordered iPP melts would crystallize. Fig. 1 shows the heat flow change for the isothermal crystallization at various temperatures. It can be seen that the iPP melt crystallizes very quickly and there is no induction period for every curve. When Tc ≤ 123 ºC, the crystallization proceeds so rapidly that a considerable amount of crystallinity is produced during the cooling process. Therefore, the isothermal analysis is performed at every 2 ºC in the temperature interval 123–131 ºC.

![Fig. 1](image1.png)  
**Fig. 1** Time dependence of the heat flow for the isothermal crystallization of a helically ordered iPP melt at: (a) 131 ºC; (b) 129 ºC; (c) 127 ºC; (d) 125 ºC; (e) 123 ºC

The relative amount of crystallinity has been plotted as a function of time for five different crystallization temperatures (see Fig. 2). The development of the relative crystallinity during the isothermal process can be analyzed by the Avrami equation (Eq. 1) [35–36]:

\[ X_t = 1 - \exp(-kt^n) \]  

(1a)

or

\[ \log[-\ln(1 - X_t)] = \log k + n \log t \]  

(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. The double logarithmic plot of \( \log[-\ln(1 - X_t)] \) versus \( \log t \) is shown in Fig. 3 and each

![Fig. 2](image2.png)  
**Fig. 2** Relative crystallinity versus time during isothermal crystallization of a helically ordered iPP melt at different temperatures: (a) 131 ºC; (b) 129 ºC; (c) 127 ºC; (d) 125 ºC; (e) 123 ºC