

Isothermal Crystallization of PP-*g*-GMA Copolymer

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ABSTRACT: The overall isothermal crystallization kinetics for neat polypropylene and grafted polypropylene systems were investigated. The rate constants were corrected assuming the heterogeneous nucleation and three dimensional growth of polypropylene spherulites. A semiempirical equation for the radial growth rate of polypropylene spherulites was developed as a function of temperature, and was used to determine the number of effective nuclei of different temperatures. The number of nuclei in grafted samples was estimated to be 10^2 – 10^3 times larger than that of neat polypropylene.

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INTRODUCTION

As is widely practiced in plastic processing, grafted polyolefins with polar groups alter the properties of the polymers, their crystallization characterization, and morphology. The heterogeneous nucleation takes place generally instantaneously upon cooling a polymer melt, but the number of effective nuclei is strongly temperature-dependent.¹ The temperature dependence of the effect of a nucleating agent on crystallization becomes important since it helps to determine the processing conditions and controls the properties of fabricated articles.

When the number of crystallization centers is relatively small, the effect of a nucleating agent on crystallization can be evaluated visually by polarized optical microscopy. Otherwise, the nucleation effect is estimated by means of a crystallization kinetics analysis, which may be isothermal or nonisothermal. The Avrami equation has been

commonly employed to analyze the isothermal crystallization kinetics of nucleated polypropylene,^{2–7} and the parameters in the equation were evaluated to determine the number of nuclei and the mode of crystal growth. The effect of a nucleating agent has often been estimated by the number of nuclei or the half-time of isothermal crystallization. The Avrami equation was a useful and convenient tool to study crystallization kinetics of a polymer.

In this article isothermal crystallization thermograms of both a neat and a grafted polypropylene (PP), measured by differential scanning calorimetry (DSC), were analyzed with the Avrami equation. Assuming the three-dimensional growth and heterogeneous nucleation of PP spherulites, the rate constants were corrected in the cases where nonintegral values of the Avrami exponent had been determined experimentally. The radial growth of PP spherulites was measured at various temperatures. The relationship between the crystallization temperature and growth rate was used to calculate the number of effective nuclei at different temperatures.

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EXPERIMENTAL

Materials and Methods

PP was supplied by Liao Yang Petrochemical Corp. with a melt flow index of 1.0 g/10 min. Dicumyl peroxide (DCP) and glycidyl methacrylate (GMA) were reagent grade.

Preparation of PP-g-GMA

Composition of the reaction mixture was 40 g of PP, 2–4 wt % of GMA, and 0.05–0.2 wt % of DCP. The reaction mixture was mixed in a XSS-300 internal mixer at 190°C, the rotor rate was 32 rpm, and the mixing time was 15 min. The degree of grafting was determined by the element analysis method.

Differential Scanning Calorimetry

Isothermal crystallization was carried out in the sample pan of a Perkin-Elmer DSC-7 calorimeter with ~ 9 mg of the molded film. The sample was always heated to 200°C and kept for 10 min before cooling to a predetermined crystallization temperature. The cooling rate to the predetermined crystallization temperature was faster than 100°C/min and the crystallization temperature was controlled with an accuracy of 0.05°C.

Polarized Optical Microscopy

The radical growth rate of PP spherulites at various temperatures, which can be used in the crystallization kinetics analysis of the nucleation effect, was determined by the aid of micrographs taken successively with a polarized optical microscope with a 350 mm camera attached; a heating stage with temperature controller was used.

RESULTS AND DISCUSSION

Determination of Isothermal Crystallization Kinetics Parameters Based on the Avrami Equation

The overall crystallization rate can be monitored by thermal analysis through the evaluation of heat of crystallization. DSC can be used to determine the crystallinity as a function of time; the change in crystallinity with time can be expressed by an Avrami equation:

$$1 - X_c = \exp(-kt^n) \quad (1)$$

where X_c is the relative crystallinity at time (t), k is a temperature-dependent constant, and n is the crystal geometry information (Avrami exponent). The Avrami parameters, n and k , are determined by taking the double logarithm of eq. (1) to give a plot of $\ln[-\ln(1 - X_c)]$ versus $\ln t$ where the slope of the plot is equal to n , and k is obtained from the intercept of the plot or from the expression

$$k = \ln 2/t_{1/2}^n \quad (2)$$

where the halftime, $t_{1/2}$, is the time for 50% of the total crystallization to occur. Figure 1 shows the result as a double logarithm form of the Avrami equation with isothermal DSC data obtained at various temperatures for PP and graft copolymer. The kinetics parameters determined by this equation are listed in Tables I–III.

Correction of the Rate Constant

In a spherulitic crystallization process controlled by heterogeneous nucleation, where the Avrami exponent n is 3, the rate constant is expressed as

$$k_3 = \frac{3}{4}\pi NG^3 \quad (3)$$

where N and G are the number of effective nuclei per unit volume and the spherulite growth rate, respectively. The subscript 3 attached to k in the equation suggests that the relationship is valid only for the crystallization condition mentioned above. However, it is usually assumed that nonintegral values of n are caused by such factors as mixed nucleation modes, secondary crystallization, or intermediate dimensionality of crystal growth.⁵ It has been also pointed out that experimental factors such as erroneous determinations of the zero time and the heat of crystallization at a given time or at the end of crystallization can cause nonintegrality of n .⁸ Then a strong correlation among k , t , and n ⁹ may result in large deviations in k . The values of k might be corrected if the true values of the exponent n are known. Assuming that the nucleation is purely instantaneous (true value of $n = 3$), Kowalewski and Galeski⁵ made an approximation for the corrected value of the rate constant, k' , as

$$k' = \frac{3}{4}\pi NG^3 \approx (k \exp)^{3/n} \quad (4)$$

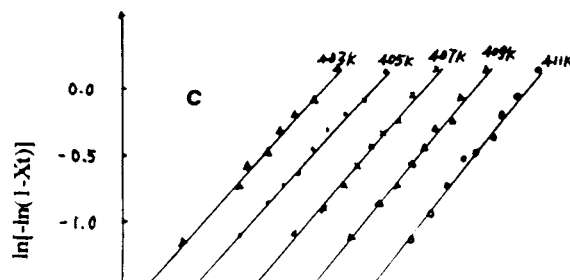
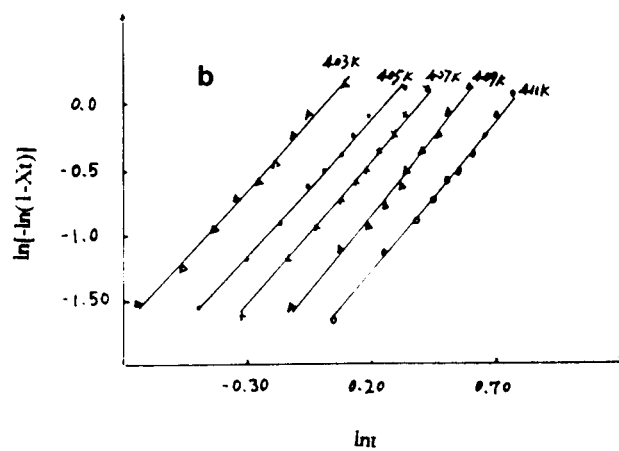
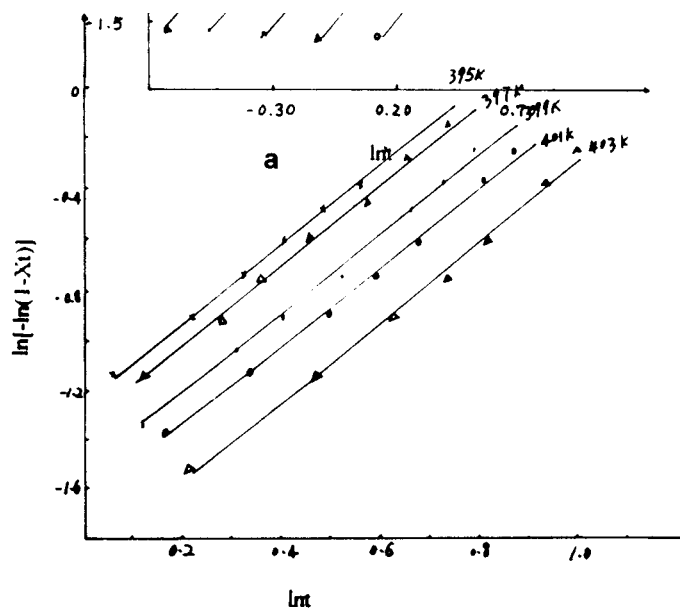


Figure 1 Avrami curves of PP and PP-g-GMA copolymers. (a) PP; (b) PP-g-GMA (0.28 wt % GMA content); (c) PP-g-GMA (0.59 wt % content).

Table I Crystallization Kinetics Parameters of PP

Temp. (K)	Rate Constant (k)	Avrami Exponent (n)	Corrected Rate Constant (k')	Spherulite Growth Rate ($\mu\text{m}/\text{min}$)	Number of Effective Nuclei (per cm^3)
395	1.55×10^{-2}	2.45	6.06×10^{-3}	8.77	1.14×10^7
397	2.30×10^{-3}	2.56	8.26×10^{-4}	6.12	1.50×10^6
399	1.42×10^{-3}	2.42	2.96×10^{-4}	4.40	1.36×10^6
401	3.03×10^{-4}	2.59	8.40×10^{-5}	2.89	1.47×10^6
403	7.46×10^{-5}	2.45	8.80×10^{-6}	1.96	1.10×10^6

where k exp denotes the rate constant obtained experimentally. Values of k' corrected by eq. (4) are listed in Tables I–III.

Radial Growth Rate of PP Spherulites

The isothermal radial growth of polymer spherulites usually has been observed to be linear. With the aid of successively taken polarized light micrographs, the radial growth of PP spherulites was measured as a function of isothermal crystallization temperature. The isothermal growth of PP spherulites was linear and the growth rate decreased with increasing crystallization temperature. According to Keith and Padden,^{10,11} the radial growth rate of polymer spherulites, G is described as

$$G = G_0 \exp(\Delta E/RT) \times \exp(-\Delta F/RT) \quad (5)$$

where ΔF is the free energy of formation of a surface nucleus of critical size, ΔE the diffusion activation energy of crystallizing segments across the phase boundary, R the gas constant, and T

the crystallization temperature in K . The logarithm of eq. (5) gives

$$\ln G = \ln G_0 + (\Delta E - \Delta F)/RT \quad (6)$$

The plot of $\ln G$ against $1/T$ gave a straight line, as shown in Figure 2. By the least square method, $\ln G_0$ and $(\Delta E - \Delta F)/R$ were obtained from the intercept and the slope, respectively. The radial growth rate of PP spherulites is expressed as a function of crystallization temperature:

$$\begin{aligned} \ln G (\mu\text{m}/\text{min}) \\ = -73.77 + 3.001 \times 10^4 \times 1/T \end{aligned} \quad (7)$$

The radial growth rate of PP-*g*-GMA (0.28 wt % GMA content) spherulites is expressed as a function of crystallization temperature:

$$\begin{aligned} \ln G (\mu\text{m}/\text{min}) \\ = -69.91 + 2.858 \times 10^4 \times 1/T \end{aligned} \quad (8)$$

The radial growth rate of PP-*g*-GMA (0.59 wt %

Table II Crystallization Kinetics Parameters of PP-*g*-GMA (0.28 wt % GMA Content)

Temp. (K)	Rate Constant (k)	Avrami Exponent (n)	Corrected Rate Constant (k')	Spherulite Growth Rate ($\mu\text{m}/\text{min}$)	Number of Effective Nuclei (per cm^3)
403	1.94×10^{-2}	2.87	1.62×10^{-2}	2.72	1.03×10^9
405	1.86×10^{-3}	3.06	2.11×10^{-3}	2.04	1.06×10^8
407	1.15×10^{-4}	3.35	2.96×10^{-4}	1.32	5.46×10^7
409	5.96×10^{-5}	2.89	4.12×10^{-5}	1.00	1.70×10^7
411	5.21×10^{-5}	2.40	4.43×10^{-6}	0.69	5.73×10^6

Table III Crystallization Kinetics Parameters of PP-g-GMA (0.59 wt % GMA content)

Temp. (K)	Rate Constant (k)	Avrami Exponent (n)	Corrected Rate Constant (k')	Spherulite Growth Rate ($\mu\text{m}/\text{min}$)	Number of Effective Nuclei (per cm^3)
403	2.24×10^{-1}	3.05	2.29×10^{-1}	1.46	3.12×10^{10}
405	3.54×10^{-2}	3.15	4.15×10^{-2}	0.99	1.81×10^{10}
407	1.05×10^{-2}	2.94	9.59×10^{-3}	0.72	1.09×10^{10}
409	1.59×10^{-3}	2.74	8.62×10^{-4}	0.49	3.11×10^9
411	3.73×10^{-4}	2.82	2.26×10^{-4}	0.34	2.44×10^9

GMA content) spherulites is expressed as a function of crystallization temperature:

$$\ln G (\mu\text{m}/\text{min}) = -74.04 + 2.999 \times 10^4 \times 1/T \quad (9)$$

Estimation of the Number of Effective Nuclei

With the corrected values of the rate constant k' , and the radial growth rate of PP calculated by eq. (7), the number of effective nuclei of the PP and the graft copolymer was estimated by eq. (4) at different crystallization temperatures as listed in Tables I through III. The numbers of effective nuclei in the graft copolymer were 10^2 – 10^3 times larger than those in PP.

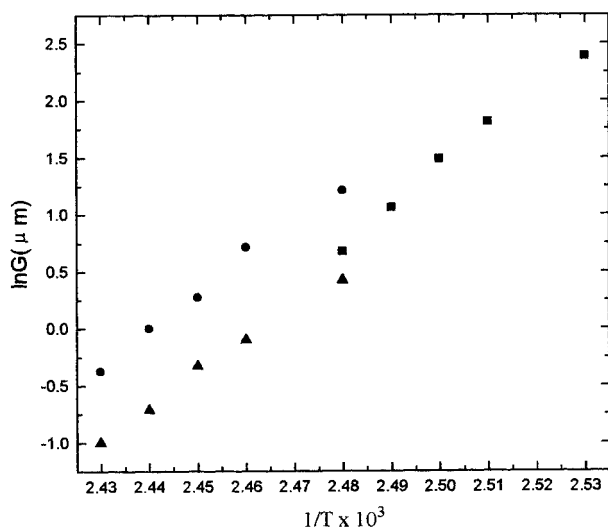


Figure 2 The plot of $\ln G$ versus $1/T$ of PP and PP-g-GMA copolymers. (■), PP; (●), PP-g-GMA (0.28 wt % GMA content); (▲) PP-g-GMA (0.59 wt % GMA content).

CONCLUSIONS

The number of effective nuclei in grafted samples was estimated to be 10^2 – 10^3 times larger than that in PP. The overall crystallization rate of PP is smaller than that of grafted samples: it showed that the grafted monomer onto PP acts as a heterogeneous nucleating agent in the polymer crystallization process.

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