Crystallization Characteristics of Polypropylene and Low Ethylene Content Polypropylene Copolymer With and Without Nucleating Agents

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SYNOPSIS

In this paper, the crystallization characteristics of polypropylene and low ethylene content polypropylene copolymers with and without nucleating agents were studied by differential scanning calorimetry (DSC) and polarized light microscopy (PLM). In order to determine the nonisothermal crystallization rate of these materials, a new estimation method was introduced. Comparing with the crystallization rate coefficient (CRC), which was proposed by Khanna, we found the new approach is more reasonable. From the analysis of results of DSC and PLM, it can be concluded that nucleating agent is more efficient than it is in PP homopolymer. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Copolymerization of propylene with other α-olefins to improve the impact properties of polypropylene (PP) is a useful method for PP modification. Random or block propylene copolymers with low content ethylene are commercially extremely important since they improve toughness of PP without seriously detracting from other desirable properties.[1-3] Due to the existence of ethylene sequences, the structural regularity of copolymer chain decreases, and their crystallization behavior changes. Usually, the overall crystallization rate of these copolymers is depressed, which may affect their mechanical properties and their cycle time of fabrication processes. For this reason, the addition of nucleating agents to these modified polypropylenes to increase the crystallization rate is necessary.

The kinetics of crystallization in PP with nucleating agents has been thoroughly studied, mainly with regard to isothermal process.[4-6] However, practical processes such as extrusion, injection molding, and film production usually proceed under dynamic nonisothermal crystallization conditions. In order to reach the optimum condition in an industrial process and to obtain products with better properties, it is necessary to estimate the rate of crystallization in the nonisothermal process. For a modified polymer material, monitoring the change of its crystallization rate brought about by a modifier such as comonomers in copolymers or another component in a blend system is particularly important.

There are several attempts reported in the literature to describe nonisothermal crystallization kinetics. Based on the Avrami equation, Ziabicki[7,8] and Ozawa[9] have their theories, respectively, to treat the case where the substances crystallize in the nonisothermal conditions. Recently, Malkin et al.[10] proposed a macrokinetic equation of autocatalytic and Choe et al. proposed another treatment,[11,12] which was derived from Tobin's theory of phase transition kinetics with growth site impingement.[13,14] Both of them were successfully applied to analyze the nonisothermal crystallization behavior of some polymers. However, these treatments described above are too complicated and inconvenient to determine the nonisothermal crystallization rate of polymer materials in practical process. For this reason, the development of a new method to estimate the rate of nonisothermal crystallization is necessary, and some attempts have been made by Khanna[15] and others.[16]

In this work, a method to estimate the noniso-thermal crystallization rate with a crystallization rate coefficient (CRC) parameter proposed by Khanna[15] and another new method proposed by us were employed to study the crystallization characteristics of PP and low ethylene content PP copolymers with and without nucleating agents. Dynamic DSC thermograms supplied the necessary data. Polarized optical microscopic observations on crystallized film of samples were carried out to confirm the nucleation effect of the agents on crystallization.

EXPERIMENTAL

The polymeric materials used are list in Table I. The nucleating agent N1 is sodium benzoate (CP grade) and N2 is talc ($3MgO \cdot 4SiO_2 \cdot H_2O$) obtained from Shandong Jiexian Talc Factory (smaller than 300 mesh). They are two effective nucleating agents of PP homopolymer.[17] The nucleating agents were added to solutions of PP and PP copolymers in hot xylene. The mixtures were then dried in a vacuum oven at 50°C for at least 1 week, dynamic crystallization was carried out in the sample pan of a Perkin-Elmer DSC-2C calorimeter with ~ 10-mg sample. The temperature of DSC was calibrated with indium. The samples were primarily heated to 500 K and kept for 5 min to remove the thermal history. The nonisothermal crystallization thermograms were obtained by cooling the sample at various cooling rates ranging from 5 to 40 K/min. In order to obtain the cooling rate as fast as 20 K/min and 40 K/min, the Intracooler II was used. The polarized optical microscopic observation on the morphology of crystallized samples were carried out using an XPT-7 polarized light microscope (Jiangnan Optical Instrument Factory, China).

THE METHODS TO ESTIMATE THE RELATIVE CRYSTALLIZATION RATE

In DSC measurement, the crystallization temperature (T_c) upon cooling from the melted state is a characteristic value of a semicrystalline polymer. In programmed cooling, the crystallization temperature reflects the overall crystallization rate due to the combined effects of nucleation and growth. Thus supercooling ($\Delta T = T_m - T_c$) may be a measurement of a polymer's crystallizability, i.e., the smaller the ΔT, the higher the overall crystallization rate. However, due to the delayed nucleation, there are some exceptions to this approach as indicated by Khanna.[15] In order to alleviate this problem and some other problems in acquiring the desired information from DSC, Khanna introduced a new parameter for characterizing the crystallization rate, i.e., a "crystallization rate coefficient" (CRC), defined as $|\Delta\beta/\Delta T_c|$ (β is cooling rate); it can be obtained from slope of the line of cooling rate plotted against T_c.

Although the CRC parameter can give a direct comparison of crystallization rates of various polymers in some degree, some problems also exist in this approach. For example, two materials crystallize at a cooling rate and attain two crystallization exothermic peaks with the same T_c and without the same half high width, the overall crystallization rate was apparently not identical, and the CRC cannot indicate the difference between these two materials. In this paper, we propose a new approach to determine the relative crystallization rate, which will be described as follows: The DSC thermograms recorded during the cooling of samples from melt with a cooling rate showed a prominent crystallization exothermic peak (Fig. 1). In this peak, we can get some of characteristic temperatures:

1. T_{in}, initial crystallization temperature, which is the temperature where the thermograph initially departs from the base line.
2. T_c, the temperature where the exotherm shows the peak.
3. $T_{1/2}$, the temperature where the 50% area under the peak has been shown in this nonisothermal process.

In terms of the T_{in} and $T_{1/2}$, we can obtain the half crystallization time

Table I   Samples and Their Characteristics

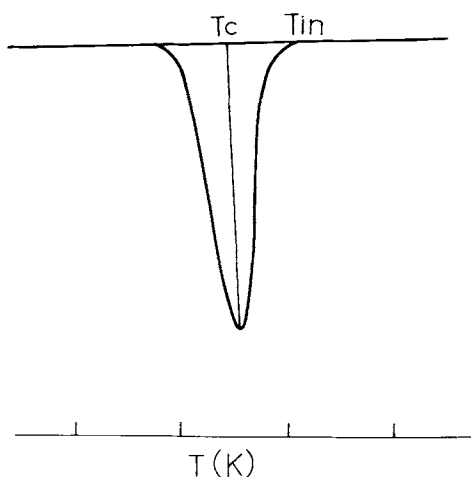| Samples	Description	Ethylene Content (mol %)	MI (G/10 min)
PP	PP homopolymer		2.9
EPR1	PP random copolymer	3.34	1.8
EPB1	PP block copolymer	5.61	3.4

Figure 1 Typical DSC thermogram recorded during the cooling cycle.

$$t_{1/2} = (T_{in} - T_{1/2})/\beta \quad (\beta = \text{cooling rate})$$

When the crystallization exothermic peak is symmetric, the disparity between the $T_{1/2}$ and T_c is negligible and $T_{1/2}$ can be replaced by T_c:

$$t_{1/2} = (T_{in} - T_c)/\beta$$

In our experiment, we only used the cooling rate below 40 K/min (when the cooling rate is higher than 80 K/min, we cannot get a reliable result because of the large deviation between sample and programmed temperature and the thermal gradients across the sample thickness); in this cooling rate range, the supercooling at the crystallization taking place in the nonisothermal process is small, and the crystallization rate is dominated by nucleation rate. In the nonisothermal process, two main factors must be considered between the cooling rate and crystallization exothermic peak. One is the effect of the cooling rate on nucleation rate: The higher the cooling rate, the higher the supercooling of crystallization taking place, and the faster the nucleation. Then a sharper exothermic peak will be exhibited. The other is the mechanical width factor from the cooling rate: The higher the cooling rate, the wider the crystallization exothermic peak. In our treatment, the reciprocal of $t_{1/2}$ is plotted against the cooling rate, and a straight line is obtained. The slope of this line [which may be defined as a crystallization rate parameter (CRP)] corresponds to the crystallization rate of polymer in our measurement range: The faster the crystallization of a polymer, the higher the slope. Thus, the slope can be considered as a parameter to represent the relative crystallization rate.

Table II CRC and CRP Values of Various Samples

Samples	(a) PP Homopolymer with and without Nucleating Agents		
	PP	PP + N1	PP + N2
CRC	2.995	2.993	2.295
CRP	0.0570	0.0886	0.0769

Samples	(b) PP Random Copolymer with and without Nucleating Agents		
	EPR1	EPR1 + N1	EPR1 + N2
CRC	2.027	2.960	2.095
CRP	0.0439	0.0949	0.0881

Samples	(c) PP Block Opolymer with and without Nucleating Agents		
	EPB1	EPB1 + N1	EPB1 + N2
CRC	1.390	2.733	2.071
CRP	0.0337	0.1067	0.0857

RESULTS AND DISCUSSION

The results obtained from DSC are summarized in Table II. According to the method proposed by us, CRP is obtained from the line of the reciprocal of $t_{1/2}$ plotted against the cooling rate as shown in Figures 2–4 (the lines were best fit statistically). From the results of CRP, we can find the CRP value of PP with nucleating agents is higher than the values
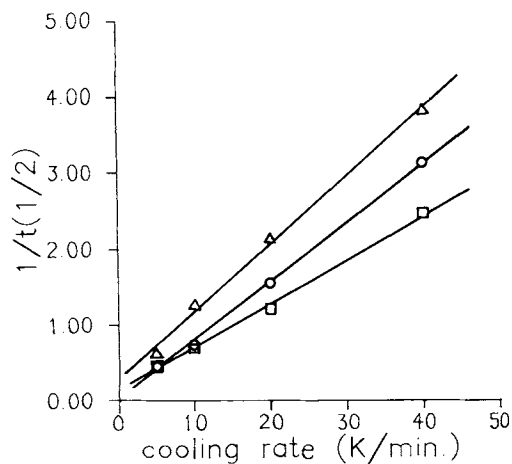

Figure 2 Plot of $1/t_{1/2}$ against the cooling rate of PP with and without nucleating agents: (□) PP; (△) PP + N1; (○) PP + N2.
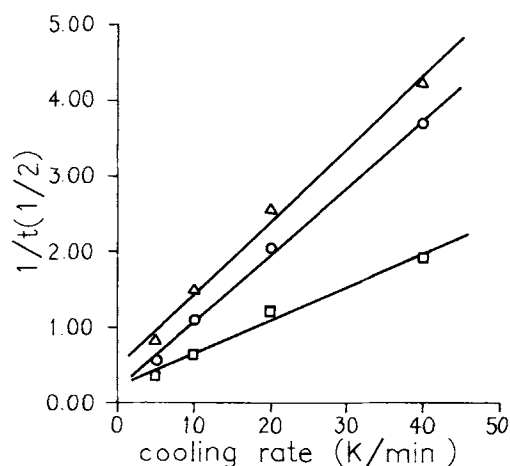
Figure 3 Plot of $1/t_{1/2}$ against the cooling rate of EPR1 with and without nucleating agents: ($\square$) EPR1; ($\triangle$) EPR1 + N1; ($\bigcirc$) EPR1 + N2.

of PP without nucleating agents. In PP homopolymer, the nucleating agents used in our experiment were approved to be a high efficient,[17] and they will increase the crystallization rate. The higher CRP values in PP with nucleating agents confirm the expected trend. Thus, using CRP to characterize the crystallization behavior of PP copolymers may be reasonable.

For polymer with nucleating agents, epitaxial crystallization of polymer onto various particle surface was reported by some authors.[18-21] The nucleating agent N1 (sodium benzoate), having a structure layered with alternating polar and apolar parts, will make the PP crystal nucleate onto the apolar part through epitaxial crystallization. Lotz and

Wittmann[21] proposed an explanation of epitaxial crystallization of a helical chain polymer on a salt model compound substrate. A helical chain polymer such as PP interacts with the substrate surface through its methyl groups, which are aligned in rows at the interacting surface of the polymer crystal. The nucleating agent N2 (talc) also has a alternating layer structure, which may be the factor which makes the PP crystal nucleate on its particle surface in a manner similar to PP with N1.

From the results of CRP, we can find the nucleating agents N1 and N2 are efficient not only for the PP homopolymer, but also for the random and block propylene copolymers with low ethylene contents. That means some nucleating agents of PP homopolymer can also be used as nucleating agents for PP copolymers.

Comparing the variation of the values of CRP of the PP with and without nucleating agents with that of PP copolymers with and without nucleating agents, we can find the change of CRP values inducing by nucleating agent in PP copolymer systems are greater than that in PP homopolymer systems. This means the heterogeneous nucleation effect on PP copolymer is greater than PP homopolymer. In PP copolymer, the structure of molecular chain is affected by the existence of the secondary monomer. The relative irregular molecular chain in the copolymer will increase active energy of the homogeneous nucleation and give a slower crystallization nucleation rate of the copolymer than that of the homopolymer. After addition of a effective nucleating agent in the copolymer, the heterogeneous nucleation dominated the nucleation rate, the low ac-
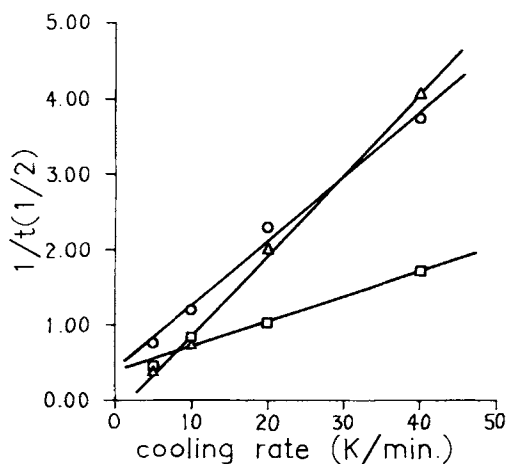

Figure 4 Plot of $1/t_{1/2}$ against the cooling rate of EPB1 with and without nucleating agents: ($\square$) EPB1; ($\triangle$) EPB1 + N1; ($\bigcirc$) EPB1 + N2.
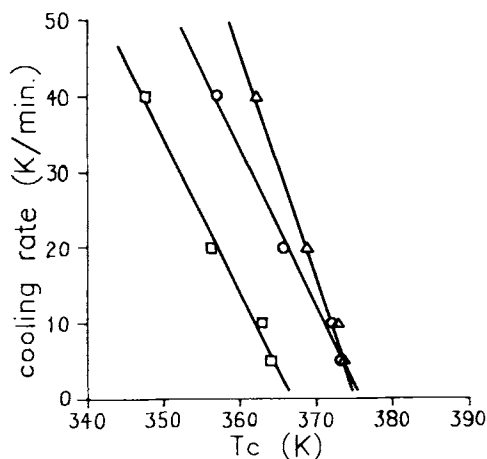
Figure 5 Plot of the cooling rate against T_c of EPR1 with and without nucleating agents: ($\square$) EPR1; ($\triangle$) EPR1 + N1; ($\bigcirc$) EPR1 + N2.
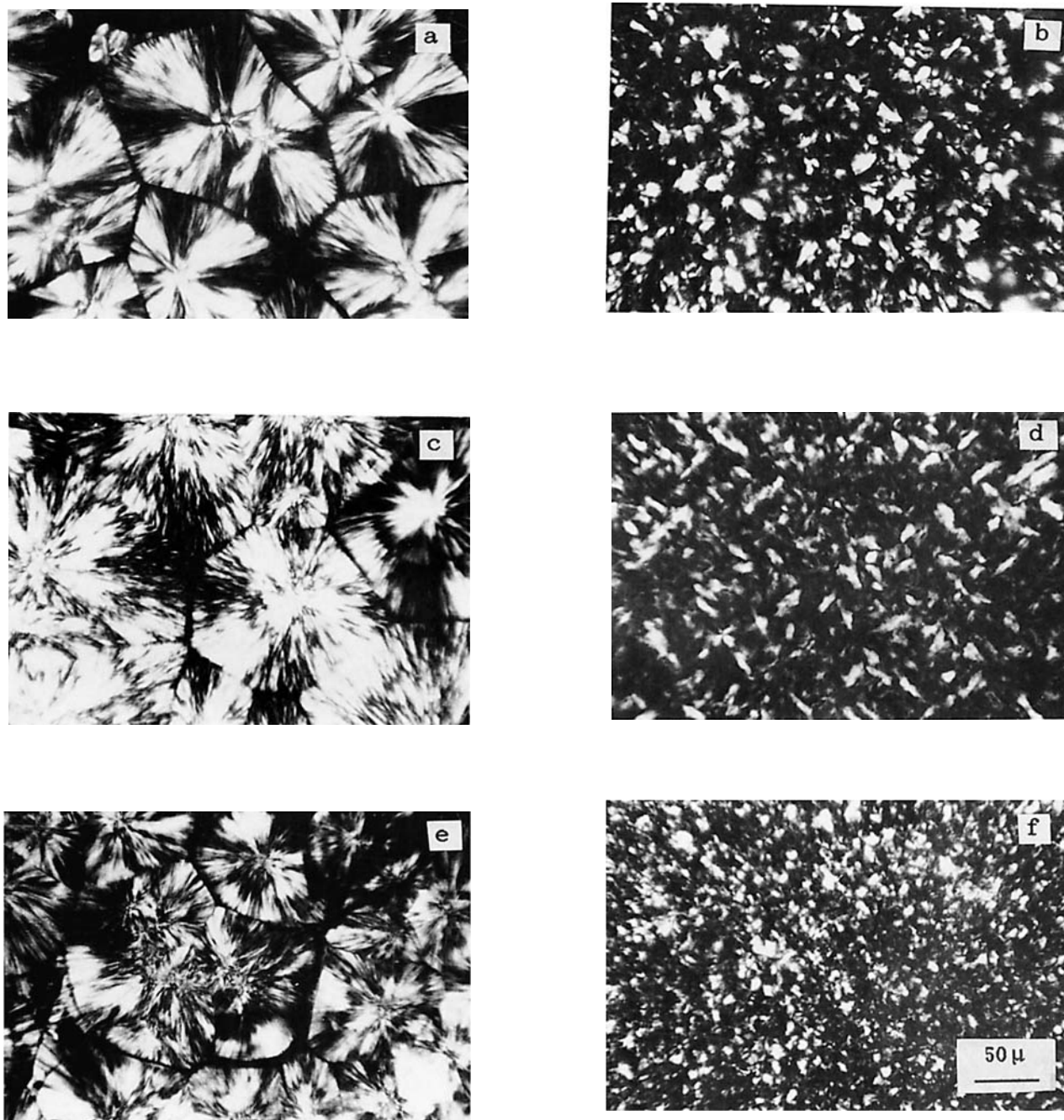
Figure 6 Polarized light micrographs of samples: (a) virgin PP; (b) PP + N1; (c) virgin EPR1; (d) EPR1 + N1; (e) virgin EPB1; (f) EPB1 + N1. All samples were crystallized at 125°C for 3 h.

tive energy of the heterogeneous nucleation will make the nucleation rate increase. For a nucleating agent, the active energy of the heterogeneous nucleation in copolymer and homopolymer of PP may be nearly equal; thus, the effect of the nucleating agents on those copolymers of PP turns out to be more notable than that on PP homopolymer.

According to the treatment proposed by Khanna,[15] the cooling rate is plotted against T_c as shown in Figure 5, and the slope of the line, CRC, can be given (Table II). From the results, we find that the CRC value of PP with nucleating agents is lower than the CRC value of PP without nucleating agents. As indicated by Khanna,[15] the higher the

value of CRC, the higher the crystallization rate. Therefore, in this polymer, the variation of CRC values was not consistent with the result of a higher crystallization rate derived from the existence of nucleating agent. However, for the PP copolymers, the higher CRC values of copolymers with nucleating agents were consistent with the higher crystallization rate. Thus, using CRC to characterize the crystallization behavior of polymers in our case is unreasonable.

Figure 6 shows polarized optical micrographs of PP and PP copolymers with and without nucleating agents at isothermal crystallization conditions. The spherulites of the PP and PP copolymers with nucleating agents were much smaller than the spherulites of pure polymers, thus confirming that the nucleating agents were highly efficient and the crystallization rates of the polymers increased in these systems with the existence of nucleating agents.

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