Isothermal Crystallization Behavior of Polypropylene Catalloys

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ABSTRACT: The isothermal crystallization behavior of polypropylene (PP) catalloys and neat PP were studied with differential scanning calorimetry and polarized optical microscopy (POM). The crystallization kinetics of the samples were described with the well-known Avrami equation. The crystallization rate depended remarkably on the content of the ethylene component in the PP catalloys. The crystallization half-time increased obviously with the increase of the ethylene component in the PP catalloys. We also observed by POM that in isothermal crystallization, there were many more nuclei in the PP catalloys than that in neat PP and with an increase of the ethylene component, the average size of the spherulites decreased obviously. Even when ethylene content was as high as 27%, the crystallization rate still increased apparently, and this was quite different from common PP melting blends, in which the crystallization rate decreased when the ethylene content was relatively high because of the obstruction effect of dispersed droplets to the spherulite growth of the PP matrix. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 93: 877–882, 2004

Key words: crystallization; poly(propylene) (PP); differential scanning calorimetry (DSC); blends

INTRODUCTION

As one of the most widely used polymers, polypropylene (PP) has found applications in extensive areas in industry. Its commercial growth and popularity are not fortuitous but are based on its favorable cost/property/performance balance.[1] However, as sufficiently illuminated by many researchers, plain PP has some apparent disadvantages, including relatively poor impact resistance, large contractility, poor chromaticity, and poor climatic resistance, that restrict its application to some extent. The relatively large size of PP spherulites results in crack expansion along the spherulite interface, which causes brittleness in applications, especially under impact.

To overcome the disadvantages of PP, the modification of the structure and properties of PP has attracted great interest in researchers in the past several decades. Various kinds of block, random, and graft copolymers of PP with polyolefins, polyesters, and so on; polymer blends or alloys; and PP filled with various kinds of inorganic fillers have been produced through physical or chemical methods. As the physical properties of polymeric materials strongly depend on their microstructure and crystallinity, studies on the crystallization behavior and morphology and their relations with the mechanical properties of modified PP have been carried out extensively by many researchers.[2–18]

Short glass fibers, poly(ethylene terephthalate) fibers, polyamide fibers, and some other fibers have been introduced into the PP matrix and have brought about improved mechanical properties and enhanced crystallization rates because of the nucleation effect of the fibers toward the PP matrix.[3–6] Through the incorporation of polyethylene (PE), the impact behavior of PP was obviously improved. Also, the crystallization rate of PP was markedly reduced by the presence of PE domains, which contributed to improved impact resistance.[7–9] However, the crystallization behavior of PP/elastomer blends has been studied with different methods.[10–17] The incorporation of elastomers altered the superstructure of the PP matrix by decreasing the average size of the spherulites. The impact modifiers acted as nucleating agents for the PP monoclinic phase, and they seemed to decrease the undercooling degree for PP.

Recently, Montell Co. developed a so-called catalloy technology, in other words, in-reactor blending technology, which has opened a new horizon for the synthesis of polyolefin materials. This technique involves the bulk polymerization of propylene followed by the gas-phase copolymerization of ethylene and propylene driven by spherical superactive $TiCl_4/MgCl_2$-

TABLE I
Characteristics of PP and PP Catalloy Samples

Sample	Description	Ethylene content (mol %)	Ethylene–propylene content (wt %)	MI (g/10 min)
PP	PP homopolymer	0	0	3.00
PEP20	PP catalloy	2.87	17.8	1.54
PEP30	PP catalloy	3.10	19.9	1.38
PEP40	PP catalloy	11.80	23.2	1.27
PEP60	PP catalloy	27.10	34.2	0.56

based catalyst systems. This technique allows the production of innovative polyolefin materials and multiphase blends directly in the reactor, so its development has been regarded as a great progress in the field of polyolefin preparation. It has made possible a growing range of new products including soft, flexible PP materials produced without the use of plasticizers and has enabled the production of high-stiffness materials with excellent mechanical strengths comparable to engineering plastics.[18]

The structure and properties of PP catalloys are quite different from those of conventional PP blends or alloys obtained from melt blending, and they are also different from those of copolymers. However, the characterization of the structure and crystallization behavior of PP catalloys has seldom been reported in the literature to date. Fan et al.[18] systematically studied the microstructure of PP catalloys with temperature-gradient extraction fractionation combined with ^{13}C-NMR, Fourier transform infrared spectroscopy, differential scanning calorimetry (DSC), and wide-angle X-ray diffraction. They found that the in-reactor PP blends were mainly composed of propylene homopolymer, ethylene–propylene random copolymer, and ethylene–propylene segmented copolymer with various PE and PP segmental lengths. The heterogeneous chain structure played an important role in the improved impact strength of the PP catalloys. However, the superstructures of PP catalloys, which are also critical to their mechanical properties, especially impact resistance, have not been paid enough attention. Therefore, in this study, we further investigated the isothermal crystallization behavior and crystal morphology of PP catalloys with various ethylene contents with DSC and polarized optical microscopy (POM) and compared them with those of plain PP. Results of this study may help us to better understand the influence of the incorporation of second component, ethylene, on the structure and properties of PP catalloys and the reason for their improved impact resistance.

EXPERIMENTAL

Materials

The PP used here was a commercial product (T300) with a number-average molecular weight (M_n) of 80,643, a weight-average molecular weight (M_w) of 333,465, a M_w/M_n value of 4.14, and a melting index (MI) of 3.0 g/10 min from Sinopec Shanghai Petrochemical Co., Shanghai, China. The poly(propylene–ethylene) catalloy samples were supplied by Z. Q. Fan's group of the Institute of Polymer Science of Zhejiang University, China. The catalloy synthesis included two steps: propylene homopolymerization in liquid propylene and then the gas-phase copolymerization of ethylene and propylene. The details of the catalloy preparation are available in the literature.[18] The PP catalloy samples were designated PEP20, PEP30, PEP40, and PEP60, respectively, in which the figures represent the percentage of ethylene used in the gas-phase copolymerization in the third stage. The ethylene contents in the final catalloys and the MI values for the various catalloy samples are listed in Table I.

DSC analysis

A PerkinElmer Pyris 1 DSC apparatus with nitrogen purge was used. The samples were heated to 200°C and isothermally treated for 5 min to eliminate any previous thermal histories. Then, the samples were rapidly cooled to the isothermal crystallization temperature (T_c) and maintained at that temperature for a certain time until crystallization was accomplished. The T_c values selected were between 120 and 130°C because of appropriate crystallization rates in this regime. The relative degree of crystallinity during isothermal crystallization (X_t) is the ratio of heat generated at time t (Q_t) against the entire heat generated during crystallization (Q_∞), as given in the following equation:

$$X_t = Q_t/Q_\infty = \int_0^t (dH/dt)\, dt \bigg/ \int_0^\infty (dH/dt)\, dt \qquad (1)$$

where dH/dt is the rate of heat evolution.

The isothermal crystallization was analyzed on basis of the Avrami equation

$$X_t/X_\infty = 1 - exp(-kt^n) \qquad (2)$$
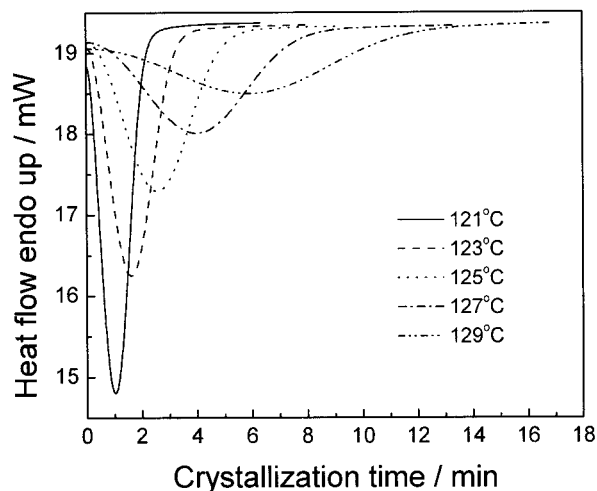
Figure 1 Heat flow curves during the isothermal crystallization of PEP40.

where X_∞ is the relative degree of crystallinity when isothermal crystallization occurs, which is equal to 1; therefore, Eq. (2) can be written as

$$\log[-\ln(1 - X_t)] = \log k + n\log t \qquad (3)$$

where n is the Avrami exponent, a parameter dealing with the nucleation mechanism and crystal growth geometry. The crystallization rate coefficient (k) is a parameter of crystallization growth rate relating to the nucleation crystal growth geometry and T_c.

From the correlation between $\log[-\ln(1 - X_t)]$ and $\log t$, n and k can be obtained from the slope of the straight line and its intersection with the y axis, respectively. On the basis of these values, the crystallization half-time ($t_{1/2}$) can be obtained from the following equation

$$t_{1/2} = \frac{\ln 2}{k^{1/2}} \qquad (4)$$

POM observation

A XPT-7 polarized optical microscope (Jiangnan Optics and Electronics Co., Ltd., Nanjing, China) with a hot stage (1000 W) was used to study the crystallization morphology of neat PP and PP catalloys. The temperature fluctuation of the hot stage was less than ±1°C, which was more than enough for these experiments. The samples films were first sandwiched between two microscope cover slides, then heated to 200°C and maintained at the molten state for 5 min in a separate hot stage, and then were rapidly moved to the hot stage assembled to the microscope that had been set to the T_c values in advance for observation.

RESULTS AND DISCUSSION

Isothermal crystallization

The isothermal crystallization behaviors of the neat PP and PP catalloys with different compositions (PEP20, PEP30, PEP40, and PEP60) were investigated with DSC. The isothermal crystallization curves for PEP40 at T_c values from 121 to 129°C are plotted in Figure 1. The corresponding evolution of relative crystallinity with time was then obtained with eq. (1) and the data in Figure 1, as is shown in Figure 2. It could be readily seen that the crystallization kinetics was strongly temperature-dependent, and the crystallization rate obviously decreased with increasing T_c within the experimental regime. In addition, the crystallization rate of neat PP and all of the other PP catalloys also showed similar sensitivity to temperature. This is a phenomenon that commonly exists in almost all semicrystalline homopolymers and polymer blends or mixtures.

To analyze the influence of the composition of the PP catalloys on crystallization kinetics, the time evolution of relative crystallinity for the neat PP and PP catalloys with various ethylene contents isothermally crystallized at $T_c = 121$°C was obtained with eq. (2) and is represented in Figure 3. The PP catalloys exhibited much rapid crystallization rates than neat PP. Furthermore, it was apparent that with increasing ethylene content in the PP catalloys, the PP crystallization accelerated obviously. To illustrate the influence of ethylene on the crystallization kinetics of the PP catalloys more clearly, the values of $t_{1/2}$, defined as the time at which the normalized crystallization content reached 0.5 and commonly used as quantitative parameter for describing crystallization kinetics, are presented in Figure 4. Obviously, the $t_{1/2}$ values of the PP catalloys were much lower than that of neat PP, and with increasing ethylene content, the $t_{1/2}$ values decreased obviously.
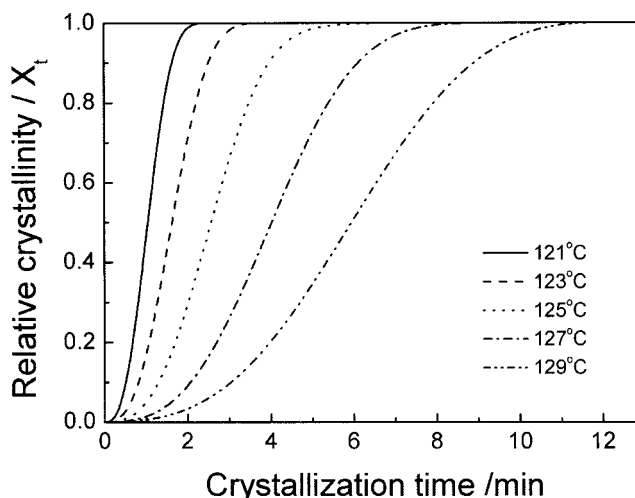
Figure 2 Dependence of the relative crystallinity on time for the isothermal crystallization of PEP40.
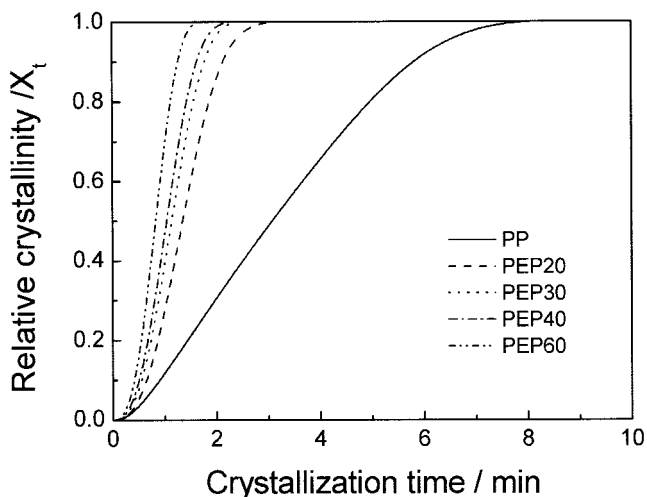
Figure 3 Dependence of the relative crystallinity on time for the isothermal crystallization of PP and PP catalloys at 121°C .

In the study of the effect of a small addition of low-density polyethylene (LDPE) on the crystallization kinetics of PP, Avalos et al.[19] found that the $t_{1/2}$ values were only slightly affected when the LDPE percentage was lower than 10%, whereas when the LDPE percentage was larger than 10%, the $t_{1/2}$ values increased markedly because LDPE aggregates were located in PP spherulites and obstructed the spherulite growth of PP. As mentioned previously, Fan et al. found that catalloys in their study were mainly composed of propylene homopolymer, ethylene–propylene random copolymer, and ethylene–propylene segmented copolymer with various PE and PP segmental lengths, but no ethylene homopolymers were observed. Therefore, the ethylene-rich domains in PP catalloys should be much smaller than those in PP/LDPE melting blends and should work as nucleating agents. Therefore, even when the ethylene content was as high as 27.1% (PEP60), the $t_{1/2}$ values continued to decrease.

PP/ethylene–propylene–diene terpolymer (EPDM) blends are another system whose crystallization behavior has been studied extensively with DSC analysis. It has been found that when the concentration of EPDM was low, the crystallization rate of PP increased markedly, which was ascribed to the increased nucleation area in the samples. PP containing 25% EPDM exhibited a fast crystallization rate. However, when the concentration of EPDM was larger than 25%, the crystallization rate started decreasing gradually, which resulted from the impingement effect of the rubber phase on the spherulite growth.[14,15,20] The ethylene content in EPDM used in that study was about 68%, so the ethylene content in the 75/25 PP/EPDM blends was about 17%, which was about 10% lower than that in PEP60. Therefore, it was reasonable to suppose that the ethylene copolymer domains in the PP catalloys dispersed more ho-

mogeneously with smaller size than those in the PP/ EPDM blends and worked as nucleating agents that accelerated the crystallization rate of PP.

In addition, as shown in Figure 4, the $t_{1/2}$ values of neat PP increased by 700 s when T_c increased from 121 to 129°C, whereas the $t_{1/2}$ values of PEP20, PEP30, PEP40, and PEP60 increased by 387, 303, 292, and 261 s, respectively. Hence, with increasing ethylene content, the crystallization kinetics of the PP catalloys exhibited less temperature dependence than neat PP. This was related to the different heterogeneous nucleating behaviors in the two systems. The nucleating effect of the ethylene copolymer could occur at relatively high temperatures, which brought about an obvious increase in the crystallization rate of the PP catalloys. The heterogeneous nucleating rate of the ethylene copolymer in the PP catalloys was less temperature dependent than that of neat PP. The quantitative investigation of the temperature dependence of the nucleating rate of the PP catalloys during isothermal crystallization process is still under investigation and will be reported in the future.

Figure 5(a,b) presents the plots of $\log[-\ln(1 - X_t)]$ against $\log t$ for neat PP and PEP40, respectively. It was obvious that for both samples, $\log[-\ln(1 - X_t)]$ linearly depended on $\log t$ at lower T_c values and at the early or middle stage of crystallization. The values of n, k, and $t_{1/2}$, as calculated from the Avrami plots, are summarized in Table II. In all cases, fractional values of n were obtained and could be explained in terms of a partial overlapping of primary nucleation and crystal growth.[21] The n values of both the PP catalloys and neat PP were located between the integers 2 and 3 over the T_c range studied. The results imply that they shared the same nucleation and growth mechanism. According to the values of n, the spherulitic development arose from an athermal, in-
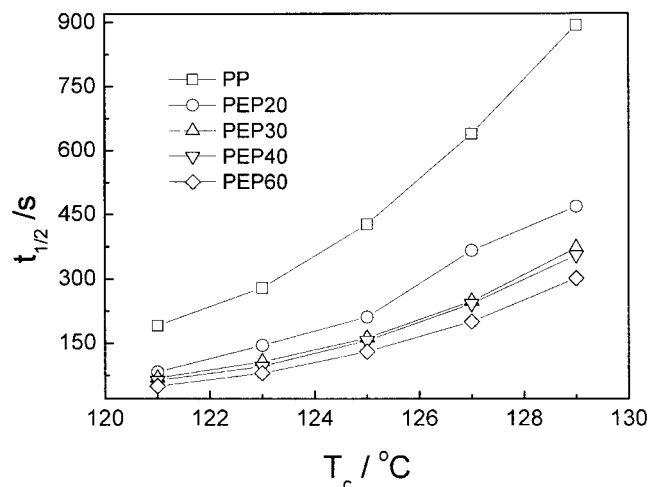
Figure 4 Temperature dependence of $t_{1/2}$ for PP and PP catalloys.
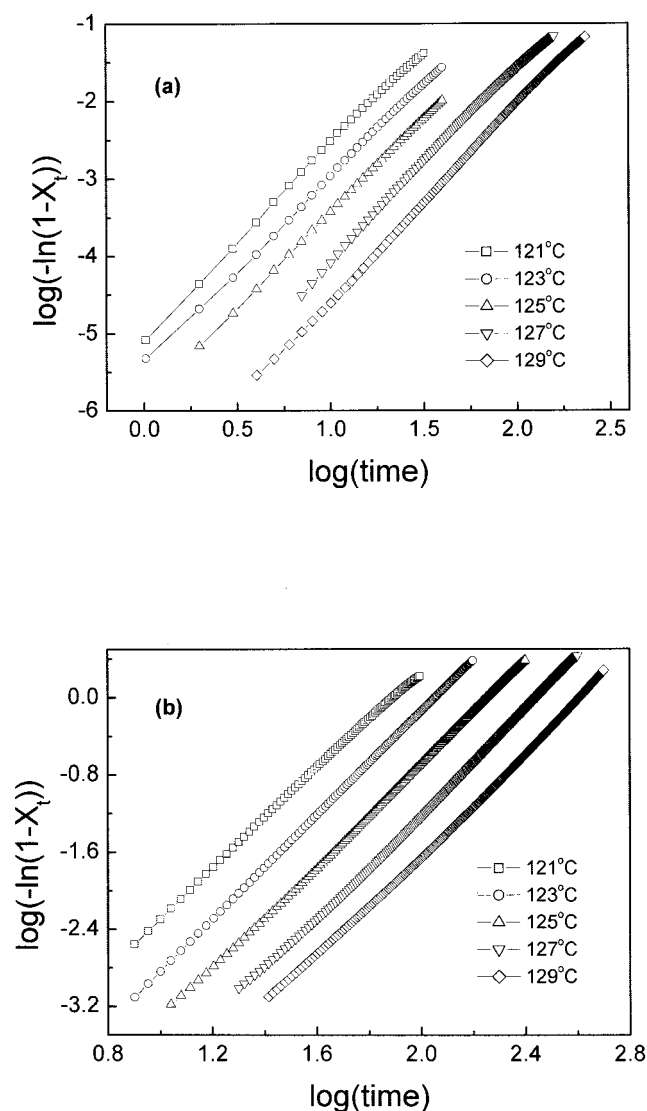
Figure 5 Relationship of log[$-\ln(1 - X_t)$] with log t for the isothermal crystallization at various temperatures of (a) PP and (b) PEP40.

stantaneous, and heterogeneous nucleation followed by two-directional diffusion controlling spherulitic crystallization growth.[14] The relatively narrow interval of n ($2 < n < 3$) was similar to that previously observed in various kinds of PP melting blends.[2,14] Hence, there was no difference in the nucleation mechanism between the PP catalloys and melting blends. However, at the same T_c, n of the PP catalloys was slightly higher than that of neat PP, which was ascribed to a change from instantaneous to sporadic nucleation.

The intercept value log k decreased with increasing T_c, indicating that both the nucleation rate constant and the growth rate constant of the PP catalloys decreased. It is well known that the overall crystallization rate of polymers is determined by both the rate of nucleation and the rate of crystal growth. According to

the values of log k, as shown in Table II, we observed that in the experimental temperature range, the kinetic constant of the PP catalloys was higher than that of neat PP. Although the kinetic constant did not always increase with the increase of the ethylene component, which may have been a result of experimental error, as shown in Table II, it was still reliable enough to conclude that the kinetics constant increased with increasing ethylene component content. Namely, PP catalloys had faster crystallization rates than neat PP, which could be attributed to the nucleating effect of the ethylene component in the PP catalloys. These values confirmed the conclusion from the analysis of $t_{1/2}$; that is, the crystallization rate of the PP catalloys was higher than that of PP because of the existence of the second component.

POM

The morphology of the isothermally crystallized PP, PEP30, PEP40, and PEP60 samples were observed through POM and were recorded with an optical camera. Figure 6 shows the polarized optical micrographs for PP and PEP40 isothermally crystallized at $T_c = 129°C$ for 45 min. Large crystalline spherulites with average diameter of 75 μm were observed in the neat PP sample. For the PP catalloys, the average size of the spherulites was smaller than that of neat PP and with increasing ethylene content in the PP catalloys, the size decreased dramatically and the number of

TABLE II
Avrami Values of n log k and $t_{1/2}$

Sample	T_c (°C)	n	log k	$t_{1/2}$ (s)
PP	121	2.47	−5.8	191
	123	2.40	−6.0	279
	125	2.44	−6.6	427
	127	2.41	−6.9	639
	129	2.51	−7.6	893
PEP20	121	2.54	−5.0	83
	123	2.72	−6.0	145
	125	2.80	−6.5	211
	127	2.71	−7.1	366
	129	2.67	−7.3	470
PEP30	121	2.53	−4.8	69
	123	2.55	−5.3	107
	125	2.52	−5.7	162
	127	2.46	−6.1	248
	129	—	—	372
PEP40	121	2.54	−4.8	63
	123	2.69	−5.5	96
	125	2.68	−6.0	156
	127	2.74	−6.7	242
	129	2.68	−7.0	355
PEP60	121	2.59	−4.6	50
	123	2.55	−5.0	80
	125	2.50	−5.4	130
	127	2.74	−6.5	200
	129	—	—	301
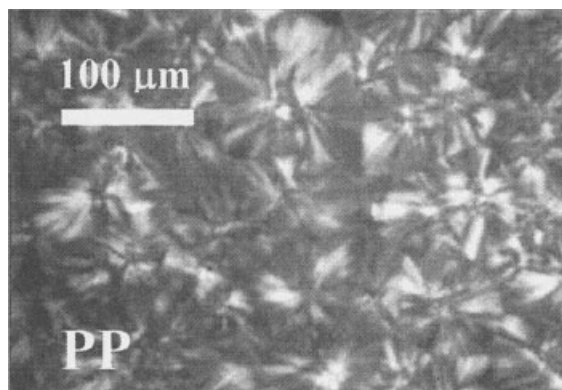
(a)
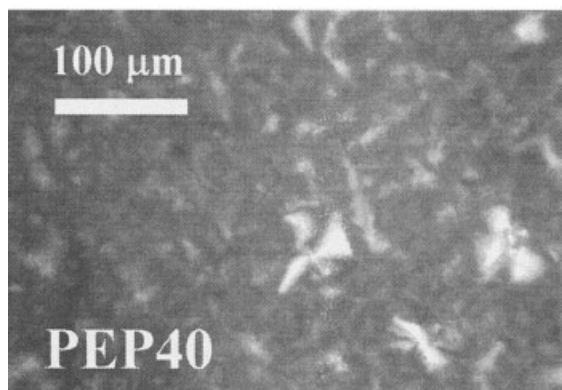
(b)

Figure 6 Polarized optical micrographs of (a) PP and (b) PEP40 isothermally crystallized at 129°C for 45 min showing PP droplets.

spherulites within a certain visual field increased greatly. This was direct evidence that the second component ethylene worked as a heterogeneous nucleation agent and increased the nucleation rate in the PP catalloys and, therefore, caused a great increase in the crystallization rate of the PP catalloys, which was consistent with the DSC measurements. In case of PEP20 and PEP30, distinct spherulites were still observed, and their size was only a bit smaller than that of neat PP. However, for PEP40, the spherulites size was much smaller than that of neat PP, as shown in Figure 6(b). In addition, most of its spherulites were so imperfect and had such irregular shape that it was hard to measure their actual size; therefore, average spherulites for this sample were not available. For PEP50 and PEP60, the spherulites were much smaller and more irregular-shaped, and no spherulites with distinguishable Maltese-crosses were observed in the micrographs. The smaller size of the PP spherulites with increasing ethylene content was a good explanation for the improved mechanical properties, especially impact resistance, of the PP catalloys with in-

creasing ethylene content. Fan et al. confirmed that an increase in the content of the ethylene copolymer, no matter random or block copolymers, has positive effect on their impact resistance. However, their investigations did not include the crystalline superstructure of PP catalloys;[18] therefore, our aforementioned observations are a good supplement to their studies.

CONCLUSIONS

We investigated the crystallization behavior of PP catalloys with DSC analysis and polarized optical microscopy and compared it with that of neat PP. The incorporation of the second component, ethylene, into PP greatly influenced its crystallization behavior and the superstructure of its spherulites. During isothermal crystallization, the ethylene component in the PP catalloys acted as a nucleation agent and caused an increase in the crystallization rate and a decrease in the crystallinity and spherulite size. When the ethylene content in the PP catalloys was as high as 27%, the crystallization rate of the PP catalloys still increased. This was different from common PP blends obtained from melt blending, in which the crystallization rate decreased because of the obstruction effect of dispersed droplets to the spherulite growth when the ethylene content is high.

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