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# Study on Crystallization Behaviour of Polypropylene Containing Nano-Calcium Carbonate and Organic Nucleating Agents

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The crystallization behaviour of polypropylene (PP) and PP with additives was investigated by DSC. It was found that the crystallization temperatures and the crystallization rates of PP increased with the addition of nanometer-scale calcium carbonate (nm $CaCO_3$) and with the increasing amount of the organic nucleating agents 1,3; 2,4-di-*p*-chlorobenzylidene sorbitol (CDBS). The crystallization temperature for the PP with CDBS was higher than for non-nucleated PP by 20-25 K when the samples were cooled from molten. The values of Avrami exponent 'n' indicated the addition of nm $CaCO_3$ and CDBS could affect the nucleation process and the crystalline morphology. Three methods are used to deal with the non-isothermal crystallization process for PP and nucleated PP. Ozawa equation could not describe satisfactorily the non-isothermal crystallization behaviour of PP with CDBS in this study, while Mo's method could. The results obtained by modified Avrami equation indicate that the primary crystallization stage for non-isothermal melt crystallization might correspond to a three-dimensional spherical growth with thermal nucleation. The non-isothermal crystallization kinetic parameters revealed that the addition of nm $CaCO_3$ and CDBS increases the crystallization rate of PP from the molten state obviously. The results of DSC and the polarized light microscopy display CDBS is an effective nucleating agent for PP. But more CDBS in samples may affect the crystalline morphology of PP.

**Key Words: Crystallization behaviour, Nucleating agent, Polypropylene, 1,3; 2,4-di-*p*-chlorobenzylidene sorbitol.**

## INTRODUCTION

Polypropylene (PP) is a widely used polymer because of its desirable properties. But it is well known that PP can form large spherulites when it crystallizes from the melt. Polypropylene containing large spherulites

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usually shows unsatisfactory impact strength at low temperatures and its products are opaque. The addition of various fillers is the important method to change the crystalline morphology and physical properties of PP[1-4]. The results obtained by many researchers have indicated that the different additives can result in different improved physical properties of PP[4-6]. When nanometer-scale calcium carbonate (nm $CaCO_3$) particles were added to PP, the higher tensile and flexural strength of PP were obtained[6]. It was reported that 0.8 wt % of an organic phosphorus nucleating agent added in PP increased the nucleation density by six orders of magnitude and the crystallization temperature was enhanced by 12 K[7]. Alkali dehydroabietate added to PP can greatly increase the rate of crystal nucleation in nucleated PP although it hinders PP chains folding on the front of crystals and decreases the rate of crystal growth, since it increases the fold surface energy ($\sigma e$)[8]. Meanwhile, the sorbitol derivatives, which are effective nucleating agents for PP, at concentrations between 0.4 and 1.5 % in PP, increase the rate of crystallization and the temperature at which the maximum rate of crystallization for PP occurs upon cooling from the molten state[9,10]. But few works dealing with the crystallization behaviour of PP have been published when the organic nucleating agents and the nanoparticles are added to PP together[11].

On the other hand, the crystallization behaviour of PP has been carried out under isothermal or non-isothermal conditions reported in many references[12]. Generally, Avrami equation can be used to analyse the overall crystallization rate under isothermal conditions, especially for the early stages of the isothermal crystallization process[13]. But the non-isothermal crystallization of polymers is quite difficult to be modeled, although the study of non-isothermal crystallization of polymers is of great scientific and technological significance. Up to now, the non-isothermal crystallization kinetics of several polymers have been studied and described by several models based on modifications of the Avrami equation[14-16]. However, some model such as Ozawa analysis was thought to be rather inapplicable for PP with $SiO_2$ nanoparticles[17].

In this work, the crystallization behaviour of polypropylene samples in the presence of 1,3; 2,4-di-*p*-chlorobenzylidene sorbitol (CDBS) and nm $CaCO_3$ was investigated under both isothermal and non-isothermal conditions by differential scanning calorimetry (DSC). The isothermal crystallization kinetic parameters of the Avrami equation were obtained. The non-isothermal crystallization kinetics of PP was described by modified Avrami equation[14], Ozawa equation[15] and Mo's method[18], respectively. Finally, polarizing light microscopy (PLM) was used to research the crystallization morphology of PP.

## EXPERIMENTAL

Commercially available PP (supplied by Qilu Petroleum & Chemical Corp., melt flow index 2.86 g/10 min at 503 K and 2.16 kg) was used in this study. PP was characterized by a gel permeation chromatography (GPC V2000, produced by Waters Co.) in 1,2,4-trichlorobenzene at 433 K. The weight average molecular weight (Mw) and the polydispersity of PP were $3.46 \times 10^5$ and 5.9, respectively. The tacticity of PP was characterized by $^{13}$C NMR method recorded at 403 K on an AMX400 Bruker spectrometer in pulse Fourier transform mode. The tacticity of PP was 94.7 %.

The nm $CaCO_3$ was commercial product and the particle size was about 50 nm in average. CDBS was synthesized in our laboratory. The melting point for CDBS was 519 K and the crystallization temperature was 475 K.

**Specimen preparation:** Before mechanical mixing, PP was dried in a vacuum oven at 373 K for 4 h and then cooled down to room temperature. CDBS and nm $CaCO_3$ particles were dried at 395 K for 5 h. Homogeneous solid samples of PP with appropriate nucleating agent or nm $CaCO_3$ were prepared in a twin screw Brabender machine under a nitrogen blanket at 475 K. The screw speed was 45 rpm and the mixing time in the extruder was 10 min. The contents of CDBS and nm $CaCO_3$ in PP are shown in Table-1.

TABLE-1
CONTENTS OF ORGANIC NUCLEATING AGENTS AND nm $CaCO_3$ IN 100 g ISOTACTIC POLYPROPYLENE FOR DIFFERENT SAMPLES

| Sample | PP-1 | PP-2 | PP-3 | PP-4 |
|---|---|---|---|---|
| Content of *p*-Cl-DBS (g) | 0 | 0 | 0.2 | 0.4 |
| Content of nm $CaCO_3$ (g) | 0 | 3.0 | 3.0 | 3.0 |

**Apparatus and experimental procedures:** A Perkin-Elmer Pyris-1 DSC was used for calorimetric investigations of crystallization kinetic for all samples. Calibration was performed using pure indium at a heating rate of 10 K/min. About 5 mg of each sample were placed in a DSC pan and heated at a rate of 40 K/min from ambient temperature to 485 K and kept at 485 K for 5 min to remove all memory of previous thermal and mechanical history. Subsequently, the specimens were cooled at a rate of 200 K/min to the selected isothermal crystallization temperatures $T_c$ and held at $T_c$ until no change in the heat flow was recorded in the heat flow *vs.* time plot. After that, the samples were heated again at a rate of 20 K/min to 485 K. For non-isothermal crystallization, each sample was cooled to 323 K at various cooling rate and then kept at 485 K for 5 min. Then, heating at a rate of 40 K/min followed each cooling treatment to 485 K. The constant cooling rates R used were 2.5, 5, 10, 20, 40 and 80 K/min.

Samples containing CDBS or/and nm $CaCO_3$ for morphology observation were prepared by fusion a scrap of samples placed between 2 cover glasses. After melting at 485 K for 3 min under a nitrogen atmosphere, they were kept in a quasi-isothermal state at 398 K for 48 h.

## RESULTS AND DISCUSSION

### Isothermal crystallization analysis

Isothermal crystallization of PP and PP containing nm $CaCO_3$ and CDBS samples was performed at different temperatures. Fig. 1 gives the

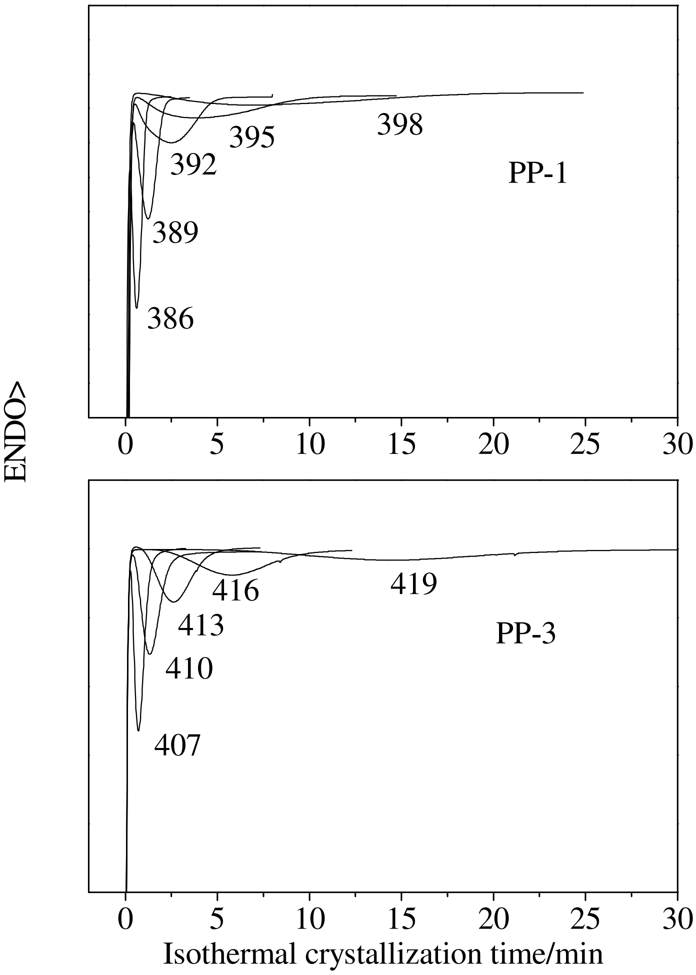


Fig. 1. DSC thermograms of isothermal crystallization for the PP-1 and PP-3 at various temperatures (K)

DSC traces for isothermal crystallization of PP-1 and PP-3. As the crystallization temperature increases, the exothermal peak becomes broader, the time to reach the maximum degree of crystallization increases and the crystallization rate gets slower. It is obvious that PP-3 has higher isothermal crystallization temperatures than PP-1. When the crystallization temperature is below 400 K, it needs 20 min to complete the crystallization for PP-1. PP-3 sample can achieve an overall crystallization process at 416 K only in 15 min. The addition of nm $CaCO_3$ and CDBS can affect the crystallization behaviour of PP evidently.

For the analysis of the isothermal crystallization, the most common approach is the so-called Avrami method[13], which can be formulated as:

$$X(t) = 1\text{-}\exp(-Kt^n) \qquad (1)$$

where X(t) is the relative degree of crystallinity as a function of the crystallization time 't', 'n' is the Avrami exponent which is a function of the nucleation process and K is the growth function, which is dependent on nucleation and crystal growth. From a graphic representation of log [-ln(1-X(t))] *vs.* log t, the Avrami exponent n (slope of the straight line) and the crystallization kinetic constant K (intersection with the y-axis) can be obtained. Plots of loglog [-ln(1-X(t))] *vs.* log t are shown in Fig. 2, in which a pretty good linear relationship for the melt crystallization of PP samples appears. Fitting the linear line of log log [-ln(1-X(t))] *vs.* log t allows to determine n and K. The values are listed in Table-2. The values of n for PP are about 2. But the n values found in the case of PP with nm $CaCO_3$ and CDBS are from 2.7 to 3.0 for the crystallization temperatures from 392 to 419 K and they should possibly be related with 3-dimensional growth.

Crystallization half-time, $t_{½}$, is defined as the time at which the extent of crystallization is 50 %. It can be obtained conveniently from the isothermal exotherms of the DSC results and is also regarded as a very important crystallization kinetic parameter. Usually $t_{½}$ can be employed to characterize the rate of crystallization directly. The greater the value of $t_{½}$, the lower the rate of the crystallization. Furthermore, the crystallization rate parameter K can be derived from $t_{½}$ according to eqn. 2:

$$K = \ln 2/(t_{½})^n \qquad (2)$$

As listed in Table-2, the values of $t_{½}$ obtained from eqn. 2 are in agreement with those obtained from Fig. 1, which suggests the Avrami analysis works very well in describing the crystallization from the melt of PP or PP with nm $CaCO_3$ and CDBS. The values of $t_{½}$ indicate that the crystallization rate increases with the addition of nm $CaCO_3$ and CDBS.

## Non-isothermal crystallization kinetics

Fig. 3 gives the DSC traces obtained at cooling rates of 10 K/min (A) and 40 K/min (B) for pure PP and PP with the nucleating agent CDBS and/or nm $CaCO_3$. It is found for PP and nucleated PP that the crystallization

TABLE-2
KINETIC PARAMETERS FOR SAMPLES IN ISOTHERMAL CRYSTALLIZATION PROCESS

| Samples | $T_c$ (K) | $t_{in}$ (min) | $t_{1/2}$ (min)[a] | $t_{1/2}$ (min)[b] | n | log K |
|---|---|---|---|---|---|---|
| PP-1 | 386 | 0.40 | 0.43 | 0.42 | 2.6 | 0.8126 |
| | 389 | 0.48 | 0.80 | 0.82 | 2.3 | 0.0423 |
| | 392 | 0.52 | 2.02 | 1.99 | 2.1 | -0.7845 |
| | 395 | 0.65 | 3.93 | 3.71 | 2.1 | -1.3540 |
| | 398 | 0.82 | 7.79 | 7.74 | 2.2 | -2.1143 |
| PP-2 | 392 | 0.43 | 0.60 | 0.60 | 2.8 | 0.4693 |
| | 395 | 0.58 | 1.29 | 1.29 | 2.7 | -0.4585 |
| | 398 | 0.82 | 2.99 | 3.00 | 2.7 | -1.4465 |
| | 401 | 1.27 | 7.12 | 7.23 | 2.7 | -2.4788 |
| | 404 | 2.78 | 14.84 | 14.58 | 2.6 | -3.1849 |
| PP-3 | 407 | 0.43 | 0.51 | 0.48 | 2.7 | 0.6925 |
| | 410 | 0.57 | 1.00 | 0.98 | 2.8 | -0.1348 |
| | 413 | 0.97 | 1.88 | 1.89 | 2.6 | -0.8774 |
| | 416 | 1.68 | 4.44 | 4.39 | 2.8 | -1.9581 |
| | 419 | 4.32 | 10.66 | 11.23 | 2.7 | -2.9948 |
| PP-4 | 407 | 0.35 | 0.37 | 0.35 | 2.8 | 1.1195 |
| | 410 | 0.48 | 0.67 | 0.66 | 2.9 | 0.3655 |
| | 413 | 0.68 | 1.28 | 1.27 | 3.0 | -0.4723 |
| | 416 | 1.22 | 2.90 | 2.89 | 3.0 | -1.5414 |
| | 419 | 3.60 | 8.08 | 8.41 | 2.7 | -2.6565 |

[a]Obtained from Fig. 1; [b]Obtained from eqn. 2.

temperature $T_P$ decreased with the increase of cooling rate R and increased strongly with addition of CDBS to PP.

The values of the crystallization temperatures $T_P$, the half-life $\theta_{1/2}$ and the degree of crystallinity ($C_r$) for all specimens are listed in Table-3. Here, the crystallization temperatures ($T_P$) are those corresponding to the exothermic peak maxima, the half-life $\theta_{1/2}$ is the time taken for 50 % of the total crystallization to occur. The degree of crystallinity ($C_r$) has been calculated from the enthalpy of crystallization, using the value of 237 J/g for the enthalpy of fusion of 100 % crystalline PP[19]. The results in Table-3 indicate that the crystallization temperatures of PP change with the cooling rates and the addition of nucleating agents and nm $CaCO_3$. When the cooling rate decreases from 80 K/min to 2.5 K/min, the crystallization temperatures of PP increase about 20 K. Comparison to the PP-1, the addition of nm $CaCO_3$ increases the $T_P$ of PP about 6 K only. When CDBS and nm $CaCO_3$ are added to PP together, the difference of TP between nucleated PP and pure PP increases from 20 to 25 K with increase of CDBS in

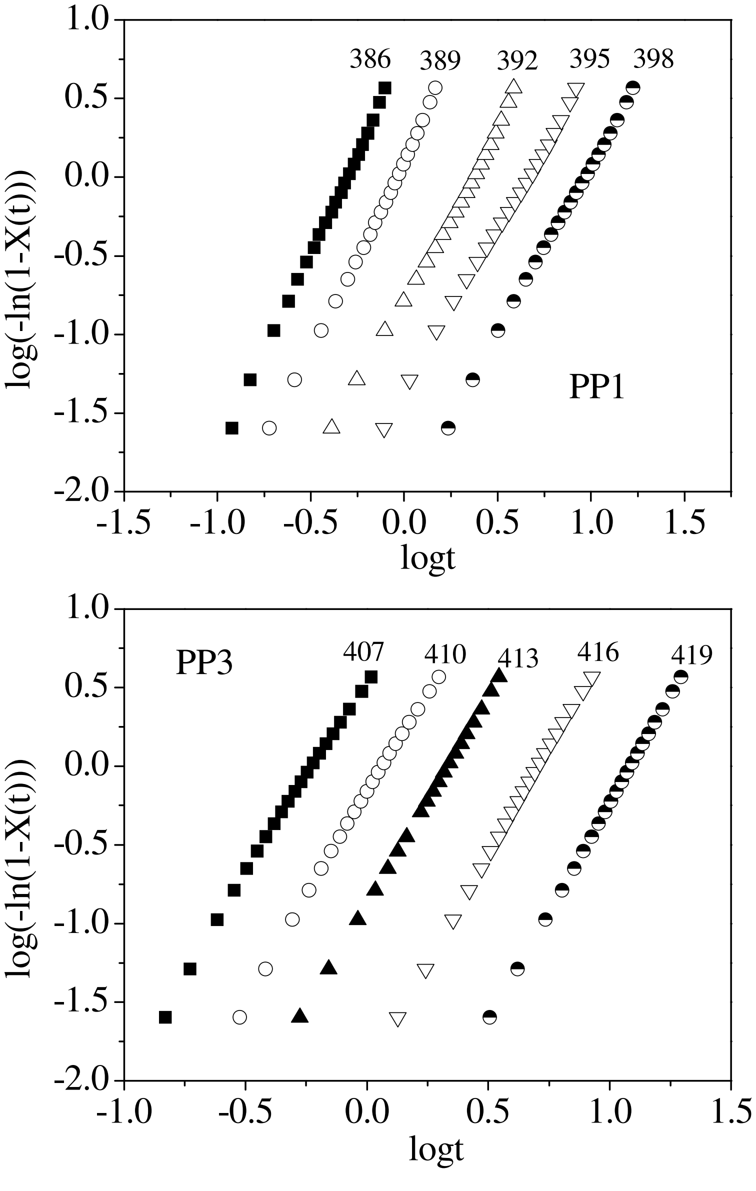


Fig. 2. Avrami plots of log [-ln(1-X(t))] *vs.* log t for isothermal crystallization of the samples PP-1 and PP-3

specimens. The CDBS as nucleating agent of PP can change the crystallization temperatures obviously. The values of $\theta_{½}$ reveal that the addition of nm $CaCO_3$ and CDBS can increase the crystallization rate of PP. When the cooling rates are low (2.5 and 5 K/min), PP-4, which contains more CDBS, has the lowest half-life $\theta_{½}$. The sharpness of the crystallization peaks, also can be observed in Fig. 3, is considerably higher for the addition of nm $CaCO_3$ and/or CDBS than for pure polypropylene. From the degree of crystallinity $C_r$, it can be found that the addition of CDBS increases the crystallinity of polypropylene slightly, while the addition of nm $CaCO_3$ decreases the $C_r$ of polypropylene imperceptibly.

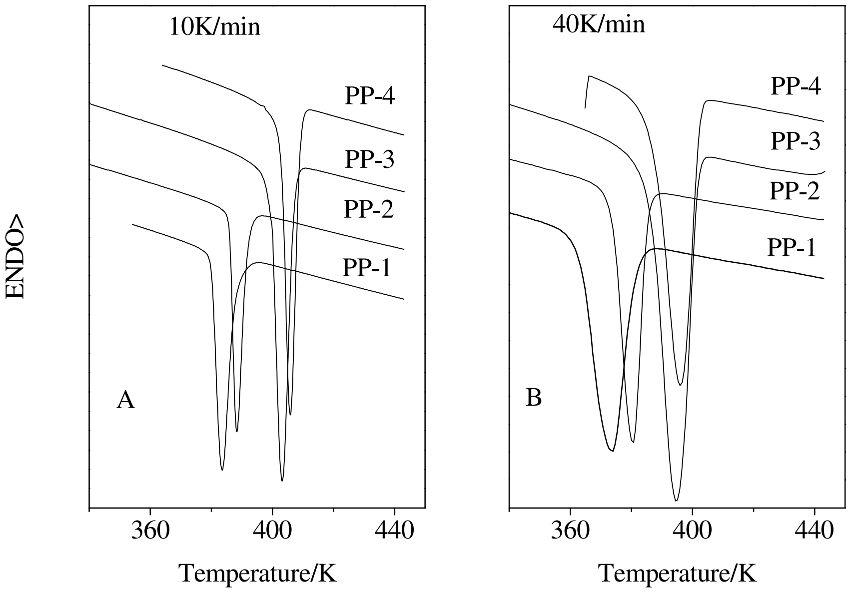


Fig. 3. DSC cooling traces of all samples recorded at the cooling rates 10 K/min (A) and 40 K/min (B)

In order to discuss the crystallization behaviour of PP further, some methods that can be used to describe the non-isothermal crystallization of polymers are employed. Generally, isothermal crystallization of polymers can be described by Avrami equation[13]. But for the non-isothermal crystallization with constant cooling rate R, Jeziorny[14] pointed out that the value of rate parameter $K_t$ should be adequately corrected as follows:

$$\log K_c = (\log K_t)/R \tag{3}$$

by using Avrami equation, the plots of $\log [-\ln(1-X_t)]$ *vs.* log t for PP-1 (A) and PP-3 (B) are shown in Fig. 4. Each curve shows an initial linear portion, subsequently tending to level off. Comparison to the curves in Fig. 2, the linearity of the curves for all samples in Fig. 4 is lower obviously. Usually, the linear portion is considered to be due to the primary crystallization and the deviation to be due to the secondary crystallization. It is suggested that there is the secondary crystallization occurring in all samples. The values of 'n' and $\log K_c$, determined from the slope and intercept of the initial linear portion in Fig. 4. The average values of the Avrami exponent for PP-1 to PP-4 were 4.0, 4.6, 4.8 and 4.9, respectively.

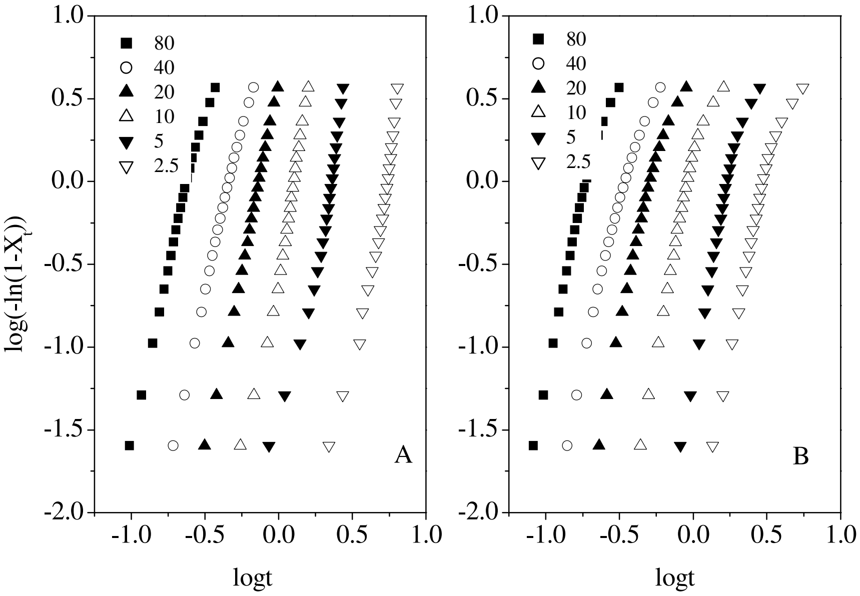


Fig. 4. Avrami plots of log [-ln (1-$X_t$)] *vs.* log t for non-isothermal crystallization of PP-1(A) and PP-3 (B) at various cooling rates

Another method, Ozawa's theory is also adopted to describe the non-isothermal crystallization[15]. In the present work, the overall non-isothermal crystallization kinetics of PP and nucleated PP is studied using the Ozawa formalism. This is based on the equation:

$$\log [-\ln (1-X(T))] = \log K(T) - m \log R \qquad (4)$$

where X(T) is the volume fraction of material crystallized at temperature T, m is Owaza exponent that depends on the dimension of crystal growth and nucleation mechanism and K(T) is the cooling crystallization function. K(T) is related to the overall crystallization rate and indicates how fast crystallization occurs. Fig. 5 (A) shows the results of Ozawa analysis for specimen PP-1. A series of lines are obtained for different temperatures and it indicates the Ozawa equation describes satisfactorily the nonisothermal crystallization behaviour of pure PP. However, Ozawa analysis for the non-isothermal crystallization of PP-3 and PP-4, which contain CDBS and nm $CaCO_3$, is not appropriate, as shown in Fig. 5 (B). Obviously, the Ozawa equation doesn't describe satisfactorily the non-isothermal crystallization behaviour of all specimens in present studies. In fact, the Ozawa equation failed to describe the non-isothermal crystallization kinetics for some polymers, such as PE, PEEK, Nylon-11, for which a large part of crystallinity is attributed to secondary crystallization[12,20]. The linear deviation in Fig. 4 confirmed the further perfection of crystal occurs in PP with CDBS.

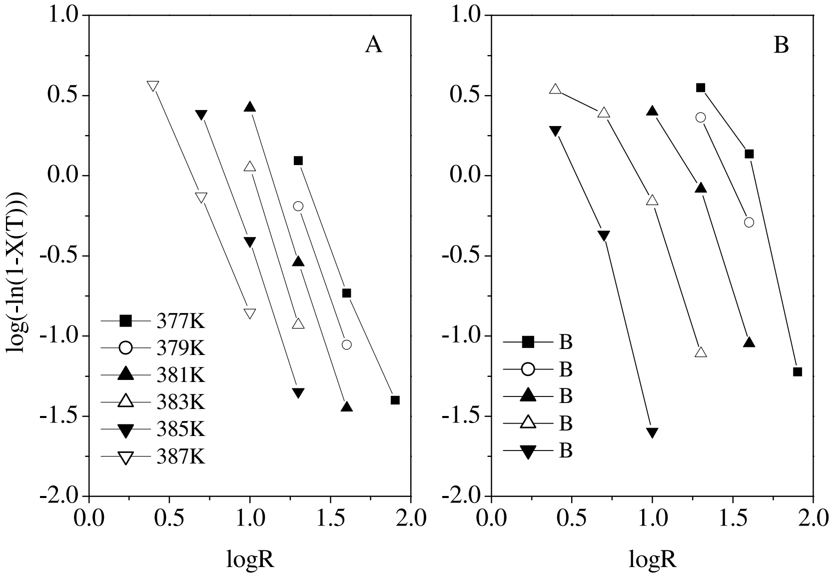


Fig. 5. Ozawa plots of log [-ln (1-X(T))] *vs.* log R for non-isothermal crystallization of PP-1 (A) and PP-3 (B)

In order to analyse the non-isothermal crystallization for all specimens better, another method is adopted to deal with non-isothermal data by combining the Avrami equation with the Ozawa equation, as follows[17]:

$$\ln R = \ln F(T) - \alpha \ln t \qquad (5)$$

where the parameter $F(T) = [K(T)/K_t]^{1/m}$ refers to the value of cooling rate chosen at unit crystallization time when the measured system amounts to a certain degree of crystallinity; $\alpha$ is the ratio of the Avrami exponent n to the Ozawa exponent m, *i.e.* $\alpha = n/m$. Fig. 6 shows a series of straight lines of ln R *vs.* ln t for PP-1 (A) and PP-3 (B). The kinetic parameter F(T) and $\alpha$ for specimens are listed in Table-4. For each specimen, the values of degree of crystallinity ($\alpha$) change slightly with the relative degree of the crystallinity and contents of CDBS and nm $CaCO_3$ in PP. F(T) for each specimen increases as increasing the relative crystallinity. It is interesting that the values of F(T) for PP-4 is the lowest in all samples at same relative crystallinity. It indicates that it has shortest time for PP-4 when the measured system arrives to a certain degree of crystallinity.

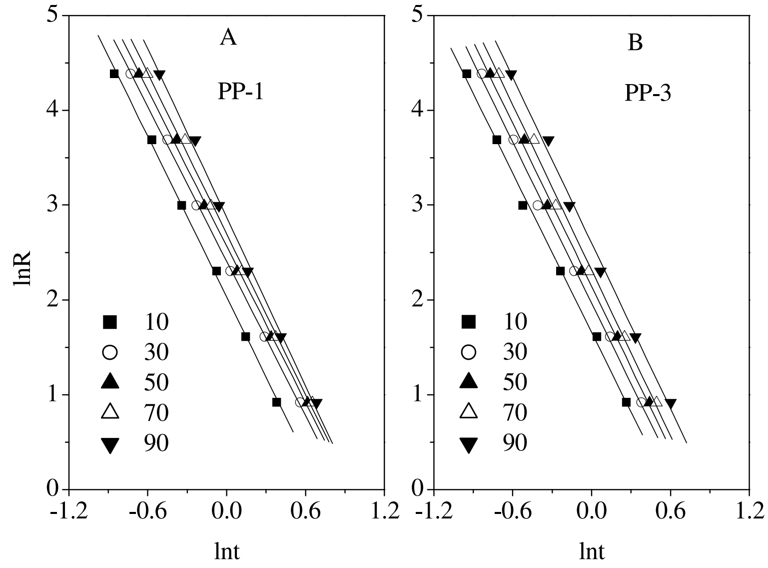


Fig. 6. ln R *vs.* ln t from the combined Avrami and Ozawa equation for non-isothermal crystallization of PP-1 and PP-3

TABLE-3

CRYSTALLIZATION TEMPERATURE ($T_P$), $\theta_{½}$ AND CRYSTALLINITY FOR ALL SAMPLES AT DIFFERENT COOLING RATES

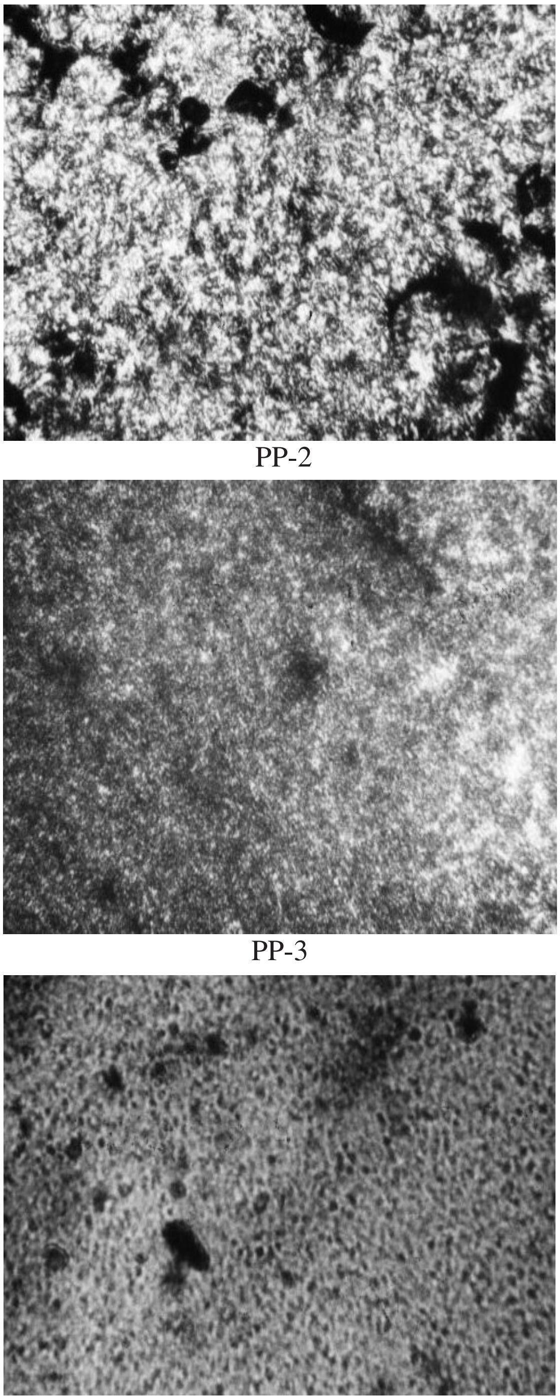
| Specimens | | PP-1 | PP-2 | PP-3 | PP-4 |
|---|---|---|---|---|---|
| 80 K (min) | $T_p$ (K) | 368.80 | 375.20 | 385.90 | 393.60 |
| | $\theta_{½}$ (min) | 0.22 | 0.15 | 0.17 | 0.17 |
| | $C_r$ (%) | 34.90 | 33.70 | 35.10 | 36.30 |
| 40 K (min) | $T_p$ (K) | 374.60 | 381.20 | 394.50 | 396.00 |
| | $\theta_{½}$ (min) | 0.42 | 0.29 | 0.31 | 0.29 |
| | $C_r$ (%) | 36.20 | 35.20 | 36.30 | 37.40 |
| 20 K (min) | $T_p$ (K) | 379.20 | 385.20 | 399.60 | 402.00 |
| | $\theta_{½}$ (min) | 0.68 | 0.42 | 0.46 | 0.43 |
| | $C_r$ (%) | 36.70 | 35.60 | 36.70 | 37.80 |
| 10 K (min) | $T_p$ (K) | 384.10 | 388.90 | 403.10 | 405.90 |
| | $\theta_{½}$ (min) | 1.20 | 0.83 | 0.84 | 0.66 |
| | $C_r$ (%) | 37.60 | 36.10 | 37.70 | 37.90 |
| 5 K (min) | $T_{cp}$ (K) | 386.90 | 392.00 | 406.30 | 408.70 |
| | $\theta_{½}$ (min) | 2.18 | 1.50 | 1.58 | 1.12 |
| | $C_r$ (%) | 37.80 | 36.30 | 37.90 | 37.90 |
| 2.5 K (min) | $T_p$ (K) | 389.20 | 395.10 | 409.40 | 411.20 |
| | $\theta_{½}$ (min) | 5.20 | 2.92 | 2.76 | 2.33 |
| | $C_r$ (%) | 38.80 | 36.40 | 39.10 | 40.20 |

TABLE-4
KINETICS PARAMETERS OF NON-ISOTHERMAL CRYSTALLIZATION FOR iPP AND NUCLEATED iPP AT DIFFERENT RELATIVE CRYSTALLINITY BY THE COMBINATION OF THE AVRAMI-OZAWA EQUATION

| Samples | Relative crystallinity (%) | $\alpha$ | lnF(T) |
|---|---|---|---|
| PP-1 | 10 | 2.8 | 2.03 |
| | 30 | 2.7 | 2.41 |
| | 50 | 2.7 | 2.57 |
| | 70 | 2.8 | 2.70 |
| | 90 | 2.9 | 2.87 |
| PP-2 | 10 | 2.7 | 1.66 |
| | 30 | 2.7 | 1.98 |
| | 50 | 2.7 | 2.13 |
| | 70 | 2.8 | 2.26 |
| | 90 | 2.9 | 2.44 |
| PP-3 | 10 | 2.8 | 1.66 |
| | 30 | 2.8 | 1.97 |
| | 50 | 2.9 | 2.15 |
| | 70 | 2.9 | 2.31 |
| | 90 | 2.9 | 2.60 |
| PP-4 | 10 | 3.3 | 1.20 |
| | 30 | 3.4 | 1.55 |
| | 50 | 3.5 | 1.75 |
| | 70 | 3.6 | 1.96 |
| | 90 | 3.6 | 2.34 |

## Crystallization morphology

Fig. 7 shows the optical micrographs viewed with cross polars for some specimens obtained at 398 K for 48 h after cooling from the molten state. The larger spherulitic dimensions of the order of about 20 μm have been observed for PP-2, which contains nm $CaCO_3$ only. In fact, the largest spherulits about 100 μm in diameters can be observed for pure PP (not shown in Fig. 7). Much smaller spherulitic dimensions appear in PP-3 that contains either CDBS or nm $CaCO_3$. In the micrograph of this sample, one can see large numbers of spots no more than 5 μm in diameters. Optical micrographs in Fig. 7 reveal that PP crystallites are birefringent but not spherulitic when nucleation is induced by more CDBS in PP-4, although an increase in the nucleation density can be observed in this sample. It indicates that CDBS is an effective nucleating agent for PP but it may affect the crystallization morphology of PP.



PP-2

PP-3

PP-4

Fig. 7. Polarized light micrographs for iPP with CDBS and/or nm $CaCO_3$ obtained at 393 K for 48 h

## Conclusion

It can be seen from the above analysis that the crystallization temperatures for PP with nm $CaCO_3$ or/and CDBS were higher than those for pure PP. Isothermal crystallization rates of samples increased with the addition of nm $CaCO_3$ and with the increasing amount of CDBS. The values of Avrami exponent 'n' indicated the addition of nm $CaCO_3$ and CDBS can affect the nucleation process and the crystalline morphology. Three methods are used to deal with the non-isothermal crystallization process for PP and nucleated PP. Ozawa equation can't describe satisfactorily the non-isothermal crystallization behaviour of PP with CDBS in this studies, while Mo's method can explain satisfactory. For pure PP and PP containing nm $CaCO_3$ only, three methods are appropriate. According to the results obtained by modified Avrami equation, the primary crystallization stage for non-isothermal melt crystallization might correspond to a three-dimensional spherical growth with thermal nucleation. The results of DSC and the polarized light microscopy display CDBS can increases the crystallization temperatures of PP and CDBS is an effective nucleating agent for PP. But more CDBS in samples may affect the crystalline morphology of PP. When CDBS and nm $CaCO_3$ are added to PP together, the crystallization rate and crystallization temperature ($T_P$) increase with the increasing amount of CDBS.

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