Effects of UV-Irradiation on the Nonisothermal Crystallization Kinetics of Polypropylene

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ABSTRACT: The influences of UV-induced photodegradation on the nonisothermal crystallization kinetics of polypropylene (PP) were investigated by differential scanning calorimetry. The Avrami analysis modified by Jeziorny, Ozawa method, and a method modified by Liu were employed to describe the nonisothermal crystallization process of unexposed and photodegraded PP samples. Kinetics studies reveal that the rates of nucleation and growth may be affected differently by photodegradation. A short-term UV-irradiation may accelerate the overall nonisothermal crystallization process of PP, but a long-term UV-irradiation should impede it. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2068–2075, 2006

Key words: UV-irradiation; photodegradation; polypropylene; nonisothermal crystallization kinetics

INTRODUCTION

It is well known that physical and mechanical properties of crystalline polymers depend on the morphology, the crystalline structure, and the degree of crystallinity. The behavior of thermoplastic semicrystallinity polymers during nonisothermal crystallization from the melt is of increasing technological importance. Thus, the crystallization of virgin polypropylene (PP) from the melt has attracted much attention and the factors that control the kinetics have been made well established.[1] However, just a few studies have been made regarding the kinetics of crystallization of degraded PP, even though this has an inherent importance in long-term applications of PP, especially for outdoor use. Chen and Yu had studied the γ-irradiation effect on the isothermal crystallization kinetics of PP with and without some additives.[2] Pospíšil and Rybníkaø had investigated the isothermal crystallization behavior of PP samples of various molecular weights prepared by peroxide melt degradation.[3] As far as we are aware, however, few publications have been dedicated to the studies of nonisothermal crystallization kinetics of photodegraded PP thus far.

This article is mainly devoted to the investigation of the effects of the extent of photodegradation of PP on its nonisothermal crystallization kinetics by using several nonisothermal crystallization kinetic equations. Moreover, the activation energy describing the overall crystallization process under nonisothermal condition was also calculated based on various theoretical propositions.

EXPERIMENTAL

Sample preparation

The injection-molded bars were produced from a commercial grade of isotactic PP (F401. MFR = 3.5, Yangzi Petrochemical Co. Ltd., China) with the dimensions approximately of 75 mm long × 2.5 mm thick and 4.0 mm wide at the narrowest section, using a WK-125 injection-molding machine. The injection pressure was 60 MPa, the barred temperature was 210°C (all zones), and the nozzle temperature was 200°C.

Sample irradiation

The bars were irradiated in a UV-CURE device constructed in our laboratory. The irradiation source was a medium pressure mercury lamp (Philips HPM 15), operated at 2 kW, at a distance of 10 cm from the surface of samples. The irradiation power measured

on the surface of the samples, by means of a radiometer, was of 4.0×10^{-2} W/cm². The exposure was carried out in air at a temperature of about 60°C. The bars were irradiated for different times, and PP0, PP1, PP2, PP3, and PP4 represented the PP samples irradiated for 0, 30, 60, 120, and 240 s, respectively.

Nonisothermal differential scanning calorimetry analysis

A Perkin Elmer differential scanning calorimetry (DSC) 2C was used for measuring nonisothermal crystallization kinetics in the cooling mode from the molten state (melt crystallization). All measurements were carried out in the nitrogen atmosphere. For nonisothermal melt crystallization, the raw sample was heated up rapidly to 200°C and maintained at this temperature for 5 min to remove thermal history. Then, the sample was cooled at constant rates of 5, 10, 20, and 40°C/min, respectively. The exothermic crystallization peak was recorded as a function of temperature.

RESULTS AND DISCUSSION

Crystallization behavior of unexposed and photodegraded PP samples

The crystallization exotherms of unexposed and photodegraded PP samples at various cooling rates are presented in Figure 1. From these curves, some useful parameters, such as the peak temperature (T_p) and relative crystallinity (X_t) as a function of crystallization temperature, can be obtained for describing the nonisothermal crystallization behaviors of unexposed and photodegraded PP samples. First, T_p shifts, as expected, to a low temperature with increasing cooling rate for all unexposed and photodegraded PP samples, which is attributed to the lower time scale that allows the polymer to crystallize as the cooling rate increases; therefore, a higher undercooling was required to initiate crystallization. On the other hand, the motion of PP molecules could not follow the cooling temperature when the specimens were cooled down fast. Second, for a given cooling rate, T_p of photodegraded PP samples is higher than that of unexposed PP as shown in Table I. The noticeable difference of T_p for crystallization of unexposed and photodegraded PP samples is the embodiment of the nucleating effect of impurity groups originating from UV-irradiation, such as carbonyls. It is interesting to note that, when UV-irradiation time exceeds over 60 s, T_p of photodegraded PP samples decreases with increasing UV-irradiation time, but it is still higher than that of pure PP (PP0). This can result from the combined effects of several factors that control crystallization:

1. reduction in molecular weight increases the crystallizability.
2. increase in impurity groups increases the crystallizability.
3. stereo-irregularities decrease the crystallizability.

Therefore, factors 1 and 2 above seem to be predominant for short-term UV-irradiation, whereas for long-term UV-irradiation, the stereo-irregularities effect begins to control the kinetics of crystallization. The hypothesis offered above that the rate of growth and nucleation are influenced differently by the effects of photodegradation will be further confirmed in the following section.

Nonisothermal crystallization kinetics analysis

On the basis of Figure 1, integration of the exothermal peaks during the nonisothermal crystallization process can give the relative degree of crystallinity as a function of the crystallization temperature T:

$$X_t = \int_{T_0}^{T} (dH, dT)dT \left/ \int_{T_0}^{T\infty} (dH_c \, dT)dT \right. \qquad (1)$$

where T_0 and T_α are the onset and end of crystallization temperature, respectively. Figure 2 shows X_t as a function of temperature for unexposed and photodegraded PP samples at various cooling rates. All of these curves have the same sigmoidal shape, indicating that the lag effect of the cooling rate on crystallization was observed only. Using the following equation: $t = (T_0 - T)\phi$ (where T is the temperature at crystallization time t, T_0 is the initial temperature as crystallization begins ($t = 0$), and ϕ is the cooling rate). The value of T on x-axis in Figure 2 can be transformed into crystallization time t as shown in Figure 3. It is clear from the plots that higher the cooling rate, the shorter the time needed for the completion of the crystallization process. An important parameter, which can be taken directly from Figure 3, is the half-time of crystallization $t_{1/2}$, which is the change in time from the onset of crystallization to the time at 50% completion, and the results are summarized in Table I. As expected, the value of $t_{1/2}$ decreases with increasing cooling rates for all unexposed and photodegraded PP samples. However, at a given cooling rate, the value of $t_{1/2}$ decreases with increasing UV-irradiation time within 60 s, but when the UV-irradiation time exceeds over 60 s, the value of $t_{1/2}$ increases with increasing UV-irradiation time, which is attributed to the fact that, at short-term exposures, the heterogeneous nucleation effects of impurity groups originating from photodegradation dominate over their stereo-irregularities effects, but when UV-irradiation time exceeds over 60 s, stereo-irregularities ef-
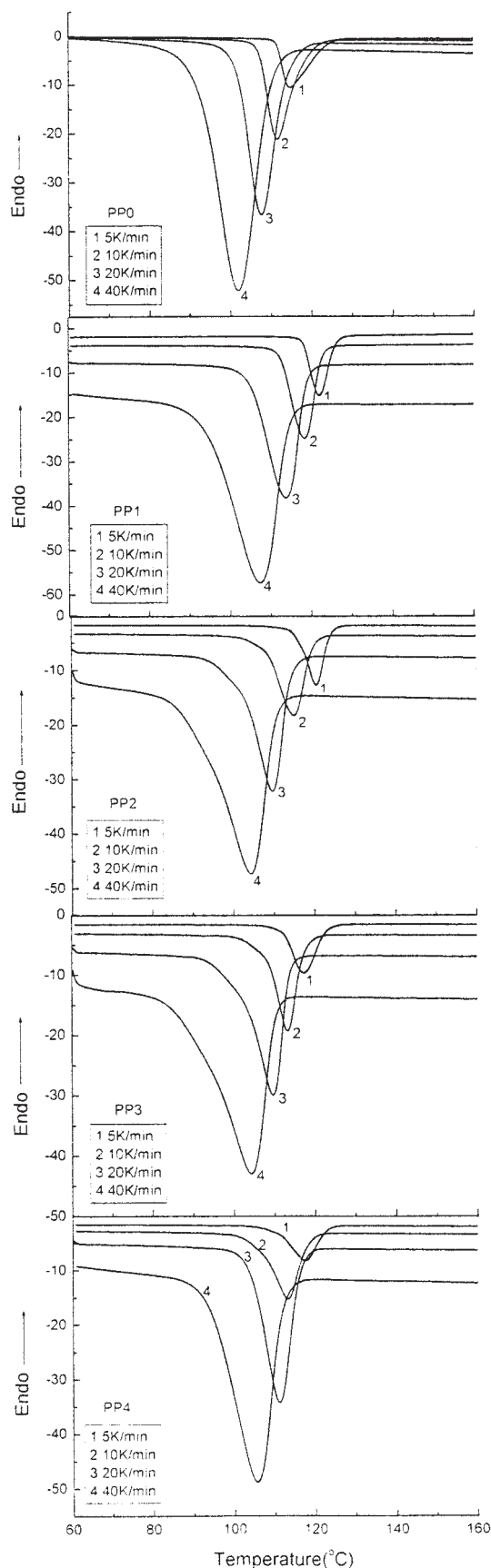
Figure 1 DSC thermograms of nonisothermal crystallization for unexposed and photodegraded PP samples at different cooling rates.

fects prevail over heterogeneous nucleation effects, impeding crystallization process of PP, and consequently $t_{1/2}$ rising.

There are several methods to describe the nonisothermal crystallization kinetics. Sometimes, the Avrami equation is directly used to analyze nonisothermal crystallization[4]:

$$1 - X_t = \exp(-Z_t t^n) \qquad (2)$$

where the exponent n is a mechanism constant depending on the type of nucleation and growth rate parameters. Using eq. (2) in double-logarithmic form:

$$\ln(-\ln(1 - X_t)) = \ln Z_t + n\ln t \qquad (3)$$

$\ln(-\ln(1-X_t))$ *vs.* $\ln t$ is plotted to obtain a line from which the corresponding parameters of crystallization kinetics (see Fig. 4) Z_t and n can be determined. However, it should be taken into account that in nonisothermal crystallization Z_t and n does not have the same physical significance as in the isothermal crystallization, because of the fact that during nonisothermal crystallization process the crystallization temperature is lowered continuously. This consequently affects the rates of both nuclei formation and spherulite growth, since they are temperature dependent.

Jeziorny accounted for the nonisothermal character of the process investigated, and the final form of the parameter characterizing the kinetics of nonisothermal crystallization was calculated as[5]:

$$\ln Z_c = \ln Z_t / \phi \qquad (4)$$

The results obtained from Avrami plots and Jeziorny method are listed in Table I. For all unexposed and photodegraded PP samples, as expected, the value of Z_c increases with increase of cooling rates. When UV-irradiation time is within 60 s, the value of Z_c at a given cooling rate increases with increasing UV-irradiation time, but when further prolonging UV-irradiation time, the value of Z_c at a given cooling begins to decrease, implying that short-term exposure can speed crystallization process of PP, whereas long-term exposure impeding it. This result is consistent with the analysis of $t_{1/2}$. The values of the exponent n are not integers but quite scattered, which is different from those of the Avrami exponent obtained from the isothermal crystallization analysis. It is understandable because nonisothermal crystallization is a dynamic process in which the crystallization rate is no longer constant but a function of time and cooling rate. Also, nucleation may be more complicated than that of isothermal crystallization. These factors could make the exponent n fractional and not having a narrow spread. However, the difference of exponent n between unexposed PP and photodegraded PP samples is obvious.

TABLE I
Nonisothermal Crystallization Kinetic Parameters of Unexposed and Photodegraded PP Samples

Samples	ϕ (K/min)	T_{conset}[a] (°C)	T_{end}[b] (°C)	T_p[c] (°C)	n	Z_c	$t_{1/2}$ (min)	ΔH_c (J/g)
PP	5	124.10	111.11	114.58	2.83	0.80	1.06	73.21
	10	119.41	106.02	111.67	2.68	1.01	0.71	68.42
	20	114.73	100.59	107.67	2.54	1.09	0.37	65.30
	40	111.11	91.55	102.00	2.33	1.08	0.24	61.71
PP1	5	125.49	117.60	122.19	2.71	0.98	0.85	78.56
	10	123.11	111.79	118.49	2.55	1.15	0.49	75.72
	20	118.30	104.58	13.13	2.43	1.13	0.30	74.0
	40	113.50	93.26	108.20	2.24	1.08	0.22	67.33
PP2	5	124.46	114.49	120.51	2.50	1.00	0.79	90.42
	10	118.20	107.64	114.88	2.38	1.17	0.44	88.55
	20	114.28	102.16	110.24	2.33	1.14	0.28	76.50
	40	110.00	90.04	105.16	2.25	1.08	0.23	73.33
PP3	5	122.85	110.30	117.46	2.75	0.78	1.14	72.20
	10	117.42	108.02	113.26	2.56	0.99	0.75	69.54
	20	113.50	100.61	110.16	2.45	1.08	0.42	65.40
	40	110.00	90.43	105.00	2.33	1.06	0.27	62.12
PP4	5	123.49	109.69	117.40	2.96	0.72	1.25	62.63
	10	118.39	106.08	113.09	2.74	0.99	0.85	60.62
	20	115.84	104.52	111.65	2.60	1.06	0.54	61.20
	40	111.56	93.96	105.22	2.33	1.05	0.32	60.31

[a] Onset temperature of crystallization.
[b] The end temperature of crystallization.
[c] The temperature where the value of the heat flow is maximum.

The exponent n decreases with increasing UV-irradiation time within 60 s, which is due to impurity groups having heterogeneous nucleation effect, leading to the decrease of dimension of space. But when UV-irradiation time exceeds over 60 s, the exponent n begins to increase with increasing UV-irradiation time. It is reasonable because stereo-irregularities effect prevails over heterogeneous nucleation effect of impurity groups, leading to the increase of dimension of time.

Ozawa extended the Avrami equation to be able to describe the nonisothermal case. Assuming that the nonisothermal crystallization process may be composed of infinitesimally small isothermal crystallization steps, the relative crystallinity can be written as a function of cooling rate according to the following equation[6]:

$$1 - X_t = \exp[-K(T)/\phi^m] \quad (5)$$

where $K(T)$ is the cooling rate function, ϕ is the cooling rate, and m is the Ozawa exponent, which is dependent on the dimension of the crystal growth. Taking the double-logarithmic form,

$$\ln(-\ln(1 - X_t)) = \ln K(T) - m\ln\phi \quad (6)$$

and plotting $\ln(-\ln(1-X_t))$ against $\ln\phi$ at a given temperature, a straight line should be obtained if the Ozawa method is valid. Thus, $K(T)$ and m can be determined from the intercept and slope, respectively. Figure 5 illustrates such plots based on the nonisothermal crystallization data of unexposed and photodegraded PP samples according to Ozawa's method. The curvature in Figure 5 prevents an accurate analysis of the nonisothermal crystallization data. This can be explained that at a given temperature, the crystallization process at different cooling rates are at different stages, i.e., at the lower cooling rate, the crystallization process is toward the end of the crystallization process, whereas at the higher cooling rate, the crystallization process is at an early stage. The change in the slope with temperature (Fig. 5) means that the parameter m is not a constant during crystallization, indicating that Ozawa's approach is not a good method to describe the nonistothermal crystallization process of unexposed and photodegraded PP samples.

By combining Ozawa and Avrami equation, Liu et al. developed a method to describe the nonisothermal crystallization process.[7]
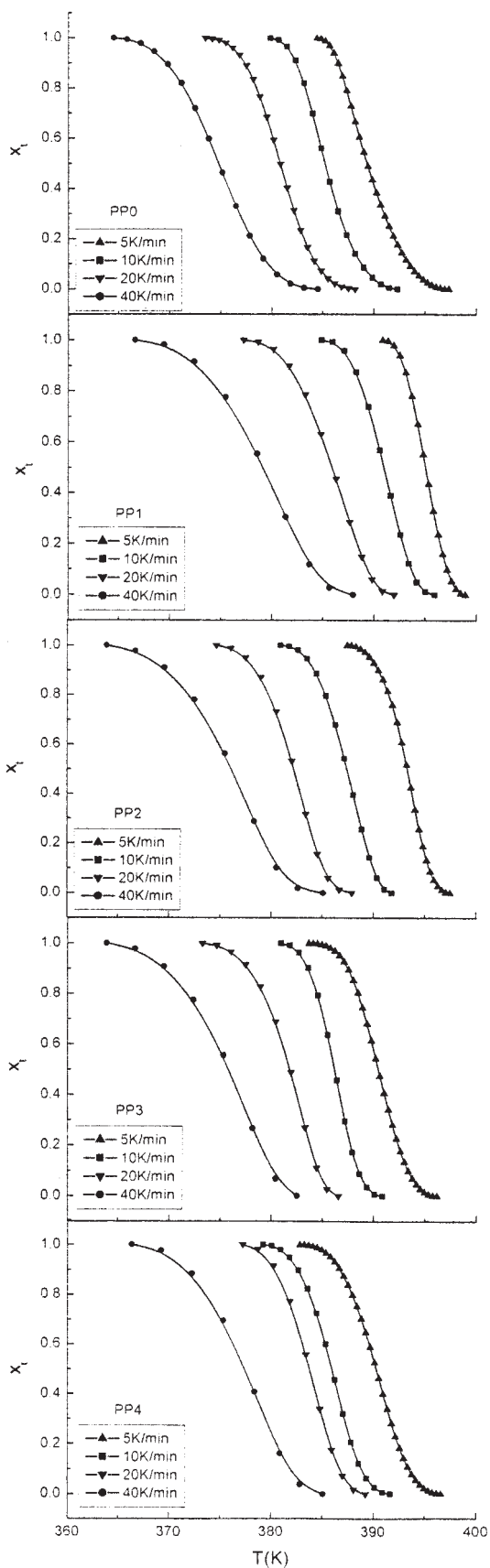
$$\ln\phi = \ln F(T) - a\ln t \quad (7)$$

Figure 2 Plots of X_t *vs.* T for unexposed and photode-graded PP samples during nonisothermal crystallization process.
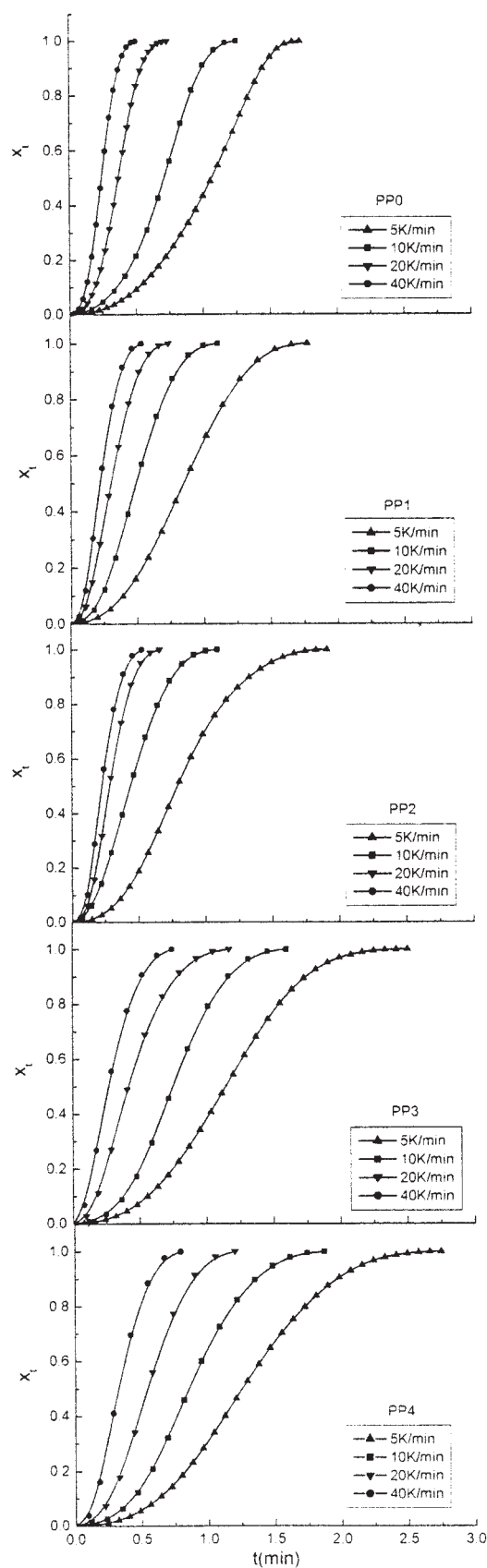
Figure 3 Plots of X_t *vs.* t for unexposed and photodegraded PP samples during nonisothermal crystallization process.

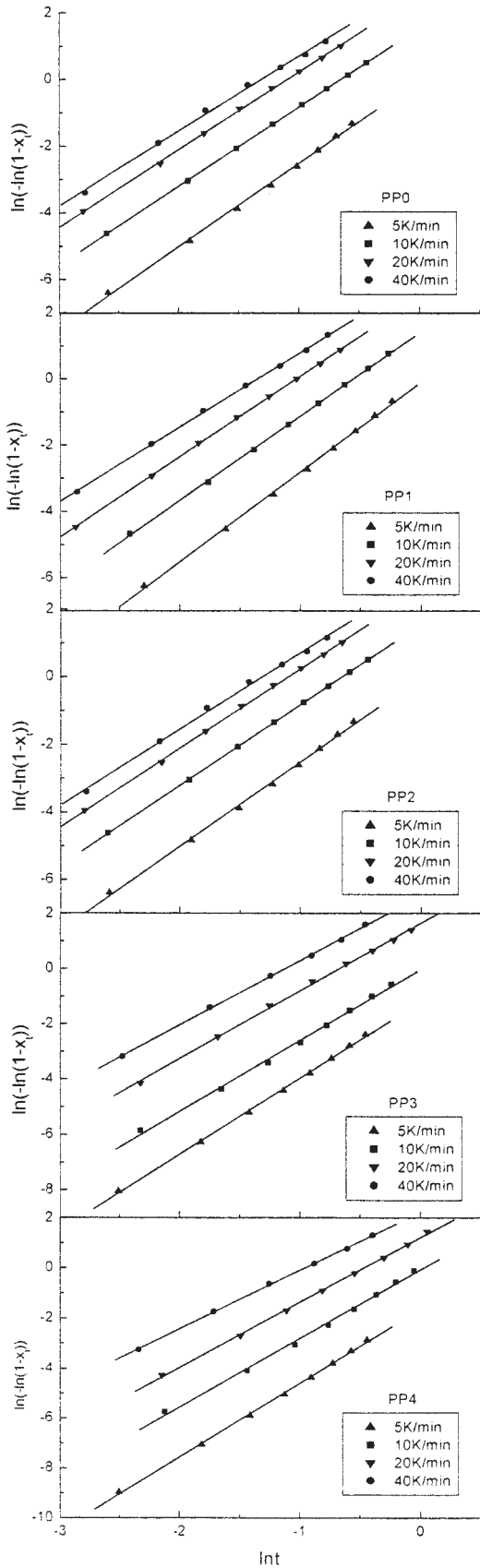**Figure 4** Plots of $\ln(-\ln(1-X_t))$ *vs.* lnt for unexposed and photodegraded PP samples during nonisothermal crystallization process.
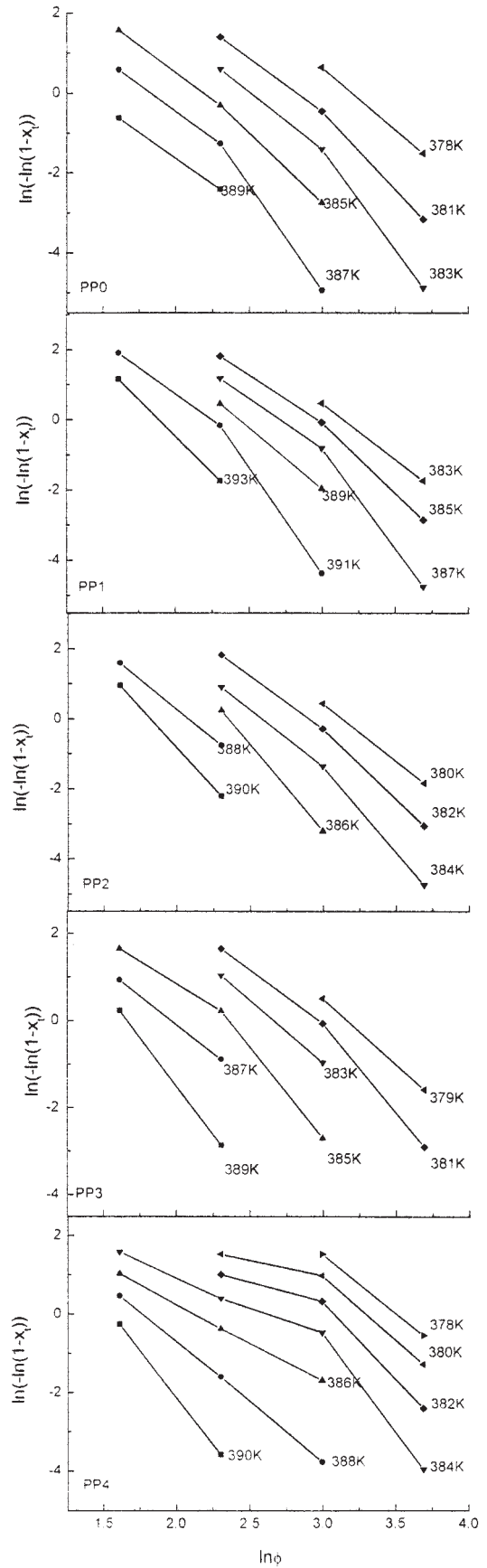
Figure 5 Ozawa plots of $\ln(-\ln(1-X_t))$ *vs.* $\ln\phi$ for unexposed and photodegraded PP samples during nonisothermal crystallization process.
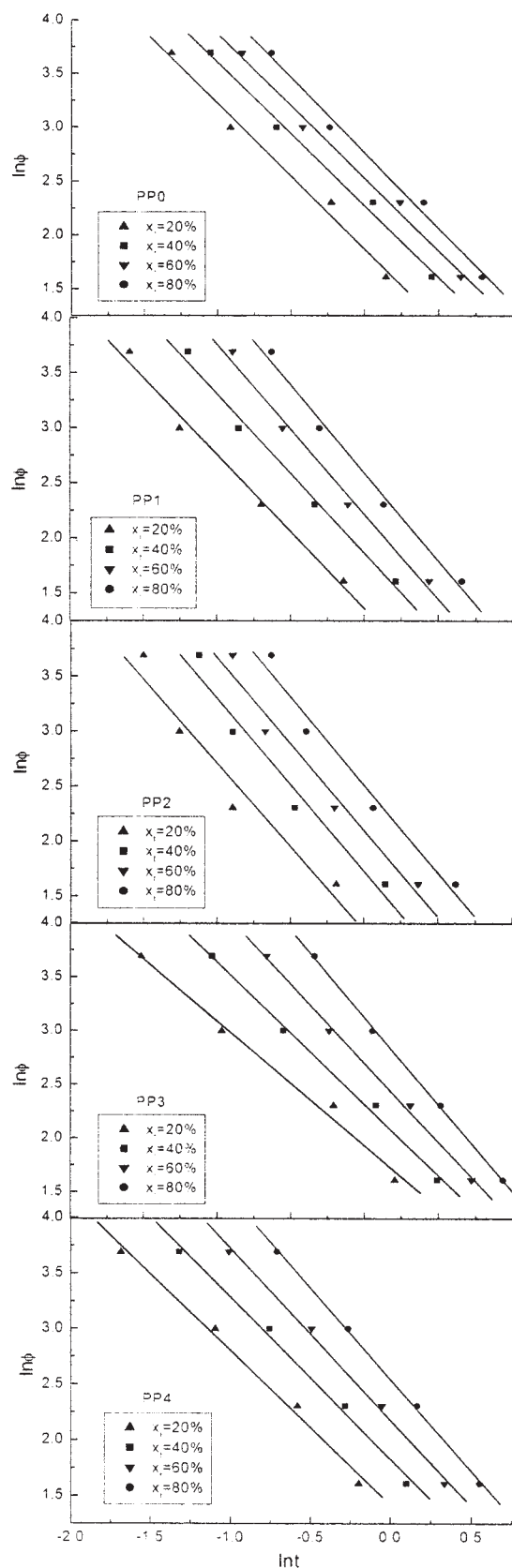
Figure 6 Liu plots of $\ln\phi$ *vs*. $\ln t$ for unexposed and photodegraded PP samples during nonisothermal crystallization process.

TABLE II
Nonisothermal Crystallization Kinetic Parameters at Different Degrees of Crystallinity

Samples	X_t (%)	$F(T)$	a	R
PP0	20	3.28	1.35	0.99306
	40	5.01	1.33	0.99567
	60	6.36	1.34	0.99511
	80	7.85	1.40	0.99489
PP1	20	1.94	1.40	0.99403
	40	3.13	1.44	0.99479
	60	4.24	1.54	0.99426
	80	6.01	1.60	0.99455
PP2	20	1.54	1.52	0.97109
	40	2.57	1.57	0.97941
	60	3.72	1.57	0.98344
	80	5.54	1.60	0.98561
PP3	20	3.87	1.16	0.99448
	40	5.22	1.32	0.99711
	60	7.12	1.47	0.99831
	80	10.07	1.62	0.99963
PP4	20	4.14	1.38	0.99566
	40	6.22	1.45	0.99635
	60	8.83	1.55	0.99787
	80	12.72	1.65	0.99944

where $F(T) = [K(T)/Z_t]^{1/m}$, and a is the ratio between the Avrami and Ozawa exponents. Here, $F(T)$ has a specific physical meaning that refers to the value of cooling rate required to reach a defined degree of crystallinity at unit crystallization time. According to eq. (7), at a given degree of crystallinity, the plot of $\ln\phi$ *vs*. $\ln t$ gives a straight line (shown in Fig. 6) with $\ln F(T)$ as the intercept and $-a$ as the slope. The values of $F(T)$ and a are listed in Table II. It can be seen from Table II that $F(T)$ systematically increases with increasing the relative degree of crystallinity for all virgin and photodegraded PP samples. The change characteristic of $F(T)$ is the same as that of Z_c. It is clear that this approach is successful in describing the nonisothermal crystallization process of virgin and photodegraded PP samples.

Effective activation energy describing the overall crystallization process

In the case of a nonisothermal crystallization experiment using DSC, the effective activation energy ΔE can be evaluated from methods such as those proposed by Kissinger or Takhor.[8,9] Considering the variation of the peak temperature T_p with the cooling rate ϕ, the effective activation energy ΔE can be evaluated based on plots of the following forms:

(1) Kissinger method.

$$\frac{d[\ln(\phi T_p^2)]}{d(1T_p)} = \frac{\Delta E}{R} \quad (8)$$

and (2) Takhor method.

$$\frac{d(\ln\phi)}{d(1/T_p)} = -\frac{\Delta E}{R} \tag{9}$$

where R is the universal gas constant, and ΔE is the activation energy of crystallization. Figures 7(a) and 7(b) illustrate plots based on the Kissinger method and the Takhor method, respectively. The slope of the curve determines $\Delta E/R$; thus, the effective activation energy ΔE can be calculated accordingly. The calcu-

TABLE III
Crystallization Activation Energy of Unexposed and Photodegraded PP Samples

Samples	ΔE_1 (kJ/mol)	ΔE_2 (KJ/mol)
PP	−202.40	−182.35
PP1	−188.91	−156.74
PP2	−175.77	−150.98
PP3	−214.58	−194.96
PP4	−221.25	−205.37

lated values of ΔE are listed in Table III. It is obvious that, ΔE decreases with increasing UV-irradiation time within 60 s, but when UV-irradiation time amounts to 120 s, ΔE is higher than that of unexposed PP. Accordingly, a short-term UV-irradiation may accelerate the overall nonisothermal crystallization process of PP, but long-term UV-irradiation should impede it, which confirms with the analyses of T_p, $t_{1/2}$, and Z_c.

CONCLUSIONS

1. The Avrami analysis modified by Jeziorny and the method modified by Liu were successful for describing the nonisothermal crystallization process of unexposed and photodegraded PP samples.
2. Kinetics studies revealed that the rates of nucleation and growth might be affected differently by photodegradation. A short-term UV-irradiation may accelerate the overall nonisothermal crystallization process of PP, but long-term UV-irradiation should impede it.
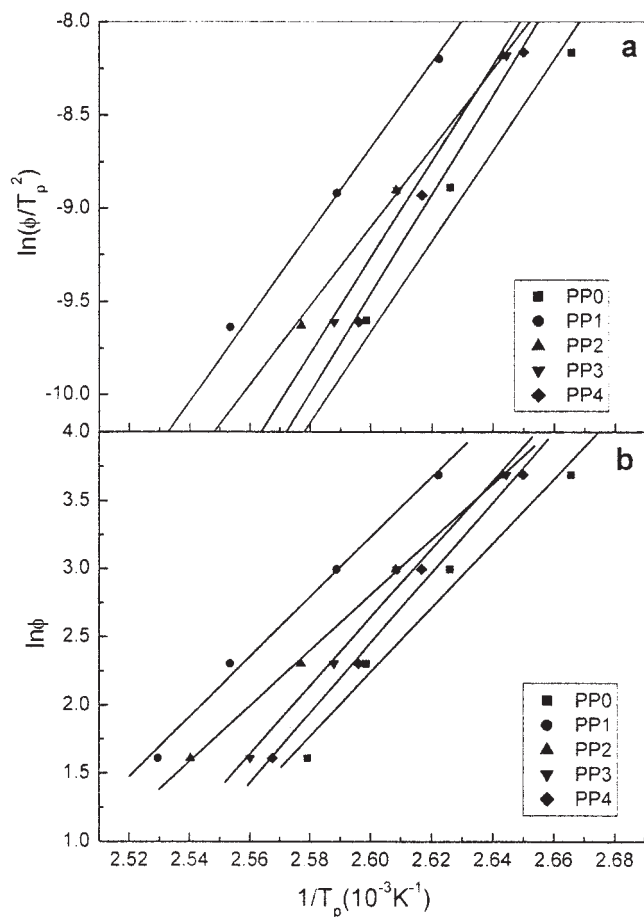

Figure 7 Determination of the effective activation energy ΔE describing the overall crystallization process for unexposed and photodegraded PP samples. (a) The Kissinger method; (b) the Takhor method.

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