PE/PE-*g*-MAH/Org-MMT Nanocomposites. II. Nonisothermal Crystallization Kinetics

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ABSTRACT: The nonisothermal crystallization kinetics of high-density polyethylene (HDPE) and polyethylene (PE)/PE-grafted maleic anhydride (PE-*g*-MAH)/organic-montmorillonite (Org-MMT) nanocomposite were investigated by differential scanning calorimetry (DSC) at various cooling rates. Avrami analysis modified by Jeziorny, Ozawa analysis, and a method developed by Liu well described the nonisothermal crystallization process of these samples. The difference in the exponent *n*, *m*, and *a* between HDPE and the nanocomposite indicated that nucleation mechanism and dimension of spherulite growth of the nanocomposite were different from that of HDPE to some extent. The values of half-time ($t_{1/2}$), $K(T)$, and $F(T)$ showed that the crystallization rate increased with the increase of cooling rates for HDPE and composite, but the crystallization rate of composite was faster than that of HDPE at a given cooling rate. Moreover, the method proposed by Kissinger was used to evaluate the activation energy of the mentioned samples. It was 223.7 kJ/mol for composite, which was much smaller than that for HDPE (304.6 kJ/mol). Overall, the results indicated that the addition of Org-MMT and PE-*g*-MAH could accelerate the overall nonisothermal crystallization process of PE. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 3054–3059, 2004

Key words: high-density polyethylene (HDPE); nanocomposites; crystallization; kinetics

INTRODUCTION

Crystallization is one of the most important behaviors of crystallizable polymer. The final properties of composites based on polymer in an engineering application are critically dependent on extent of crystallinity and the nature of crystalline morphology of polymer, which in turn depend on the processing conditions. It is, therefore, necessary to understand the relationship between processing conditions and the development, nature, and degree of crystallinity of composites based on polymer.

Crystallization process of polymers can be studied under either isothermal condition or nonisothermal condition. Isothermal experiments are generally carried out[1–3] because the theoretical analysis is easy to handle and problems associated with cooling rates and thermal gradients within specimens are avoided. In practice, however, crystallization in a thermal environment being continuously changing is of great interest because industrial processes generally proceed under nonisothermal conditions. Therefore, more and more attention has been paid to the nonisothermal crystallization process of polymers.[4–9]

Polyethylene (PE) is a typical crystallizable polymer and is widely used because of its high strength, cheap cost, and excellent processibility. Crystallization behavior of PE has been well studied because of its great significance in academic and engineering aspects.[10–14]

Because the Toyota group developed a montmorillonite/nylon nanocomposite with excellent mechanical properties, the use of a clay mineral as a reinforcement material for polymer nanocomposites has aroused great interest.[15–17] Nanocomposites based on PE were also prepared because of prospect.[18,19] However, most of the reports concentrated on the physical and mechanic properties of nanocomposites. In our previous work, we successfully prepared PE/PE-grafted maleic anhydride/organic-montmorillonite (PE/PE-*g*-MAH/Org-MMT) via direct melt intercalation. In this article, nonisothermal crystallization kinetics were investigated and data obtained were analyzed with several modified Avrami equations. The crystallization activation energies of high-density polyethylene (HDPE) and PE/PE-*g*-MAH/Org-MMT were also calculated by an evaluation proposed by Kissinger.[20]

EXPERIMENTAL

Materials

HDPE used was purchased from Yanshan Petrochemical Co. Ltd. (Beijing, China) and used without any
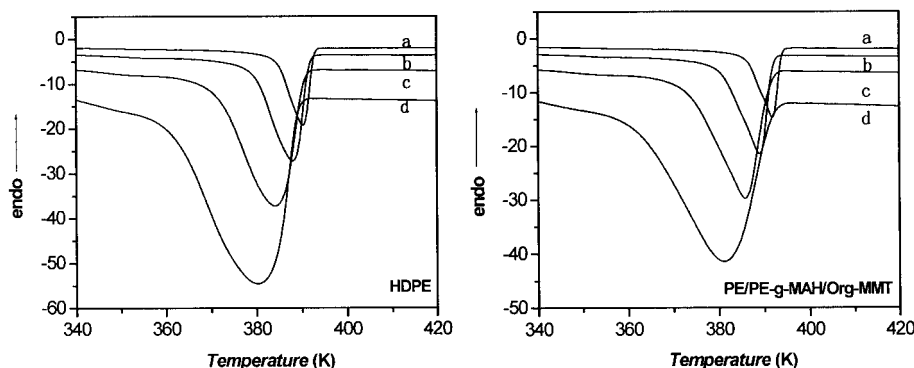
Figure 1 DSC patterns for HDPE and PE/PE-g-MAH/Org-MMT (88 : 9 : 3) during the nonisothermal crystallization process at the following cooling rates: (a) 5 K/min, (b) 10 K/min, (c) 20 K/min, (d) 40 K/min.

treatment (the brand was 5000s). Montmorillonite was available from Lin'an Chemistry Agent Factory (Zhejiang, China). Surfactants used were purchased from Shanghai Cleansing Agent Factory (Shanghai, China). PE-g-MAH (with 1.09 wt % maleic anhydride grafted level) and organic montmorillonite (300 mules) were synthesized by our laboratory.

Preparation of PE/PE-MAH/Org-MMT

PE-g-MAH and Org-MMT were melt mixed in a roller mill at 145–150°C for 15 min at a certain prescription (3 : 1) to make a master batch; then the master batch and conventional PE were melt mixed at a certain prescription (12 : 88) in a roller mill at 150–155°C for 15 min. The resulting sheet was compression molded at 160°C for 30 min into a plate with a thickness of 4 mm.

Nonisothermal DSC crystallization

A Mettler Toledo DSC-821E apparatus was used to measure nonisothermal crystallization kinetics of HDPE and PE/PE-g-MAH/Org-MMT (88 : 9 : 3). The temperature and heat flow were calibrated with indium at a corresponding cooling rate. All measurements were carried out in nitrogen atmosphere. The raw samples were held at 180°C for 5 min to eliminate

any previous thermal history and then were cooled at constant rates of 5, 10, 20, or 40°C/min. The exothermic crystallization curves were then recorded as a function of temperature.

RESULTS AND DISCUSSION

Crystallization behavior of HDPE and PE/PE-g-MAH/Org-MMT nanocomposite

The crystallization exotherms of HDPE and PE/PE-g-MAH/Org-MMT nanocomposite at various cooling rates are presented in Figure 1. Some useful parameters, such as the crystallization peak temperature (T_p) and relative degree of crystallinity (X_t) as a function of crystallization temperature, can be obtained from these curves to describe the nonisothermal crystallization behavior of HDPE and PE/PE-g-MAH/Org-MMT. At a given cooling rate, T_p of PE/PE-g-MAH/Org-MMT nanocomposite is higher than that of HDPE as shown in Table I. This phenomenon can be explained by the heterogeneous nucleation effect of the Org-MMT particle and PE-g-MAH on PE macromolecule segments. Melted PE macromolecule segments can be easily attached to the surface of the Org-MMT particle, which leads to crystallization of PE molecules at a higher crystallization temperature.

TABLE I
Nonisothermal Crystallization Kinetic Parameters for HDPE and PE/PE-g-MAH/Org-MMT Nanocomposite

Sample	ϕ (K/min)	n	Z_c	$t_{1/2}$ (s)	T_p (K)	ΔE (kJ/mol)
HDPE	5	1.51	0.94	45.0	390.3	304.6
	10	1.51	1.04	33.6	387.9	
	20	1.57	1.05	22.2	384.7	
	40	1.60	1.06	18.0	381.8	
PE/PE-g-MAH/Org-MMT	5	1.76	0.96	35.4	392.8	223.7
	10	1.73	1.05	26.4	389.2	
	20	1.74	1.06	19.8	386.4	
	40	1.80	1.09	15.0	382.5	

Figure 2 Patterns of X_t versus T during the nonisothermal crystallization process of PE/PE-*g*-MAH/Org-MMT (88 : 9 : 3).
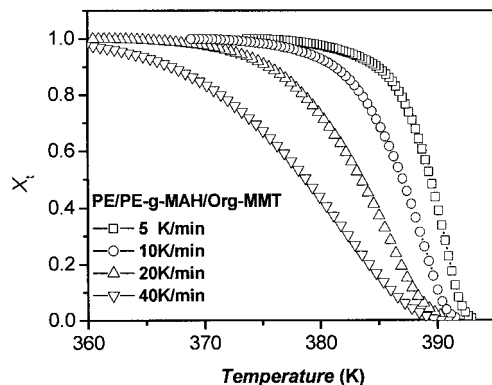

Figure 4 Plots of $\ln[-\ln(1 - X_t)]$ versus $\ln t$ during the nonisothermal crystallization process for PE/PE-*g*-MAH/ Org-MMT (88 : 9 : 3).

Nonisothermal crystallization kinetics of PE and PE-*g*-MAH/Org-MMT nanocomposite

The relative degree of crystallinity, X_t, as a function of crystallization temperature, T, is defined as

$$X_t = \int_{T_0}^{T} (dH_c/dT)dT \bigg/ \int_{T_0}^{T_\infty} (dH_c/dT)dT \qquad (1)$$

where T_0 and T_∞ represent the onset and end of crystallization temperatures, respectively, and H_c is the enthalpy of crystallization. The development of the relative degree of crystallinity as a function of temperature for nanocomposite (PE/PE-*g*-MAH/Org-MMT = 88 : 9 : 3) at various cooling rates is shown in Figure 2. The plots of X_t versus T for HDPE (not presented here) are similar. All these curves have the same sigmoidal shape, implying that only the lag effect of cooling rate on crystallization is observed. The horizontal temperature axis in Figure 2 can be transferred into a time scale (Fig. 3) by the equation $t = (T_0 - T)/\phi$ (where T is the temperature at crystallization time t, and ϕ is the cooling rate). The results show that the faster the cooling rate, the shorter the time for com-
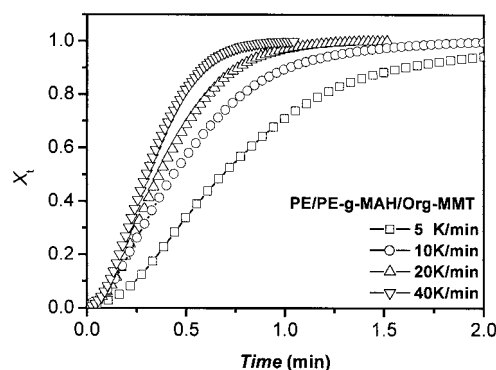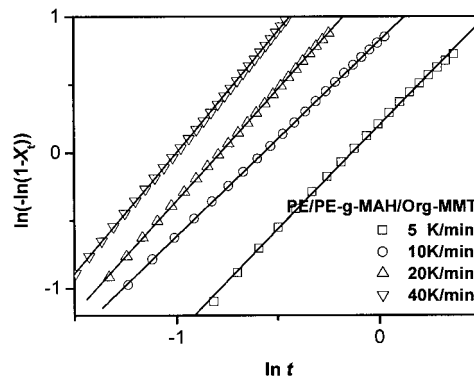
pleting crystallization. The half-times of nonisothermal crystallization ($t_{1/2}$) obtained from Figure 3 for HDPE and PE/PE-*g*-MAH/Org-MMT are listed in Table I. As expected, the value of $t_{1/2}$ decreases with increasing cooling rate for HDPE and PE/PE-*g*-MAH/ Org-MMT. Moreover, at a given cooling rate, the value of $t_{1/2}$ for PE/PE-*g*-MAH/Org-MMT composite is lower than that for HDPE, showing that the addition of Org-MMT and PE-*g*-MAH can accelerate the overall crystallization process.

The Avrami equation is used to describe the nonisothermal kinetics of HDPE and nanocomposite, which is based on the assumption that the crystallization temperature is constant[21]

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

where the exponent n is a mechanism constant that depends on the type of nucleation and growth process parameters, and Z_t is a composite rate constant involving both nucleation and growth rate parameters. By using eq. (2) in the double-logarithmic form,

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

and plotting $\ln[-\ln(1 - X_t)]$ against $\ln t$ for each cooling rate, a straight line is obtained with the data at a low degree of crystallization (shown in Fig. 4). Thus, two adjustable parameters, Z_t and n, can be estimated. It should be taken into account that in nonisothermal crystallization, Z_t and n do not have the same physical significance as in isothermal crystallization because the temperature changes under nonisothermal condition, which affects the rates of both nucleation and spherulite growth. In this case, Z_t and n are two adjustable parameters only to be fit to data. Although the physical meanings of Z_t and n cannot be related in a simple way under nonisothermal condition, eq. (3) can still provide further insight into the kinetics of nonisothermal crystalliza-
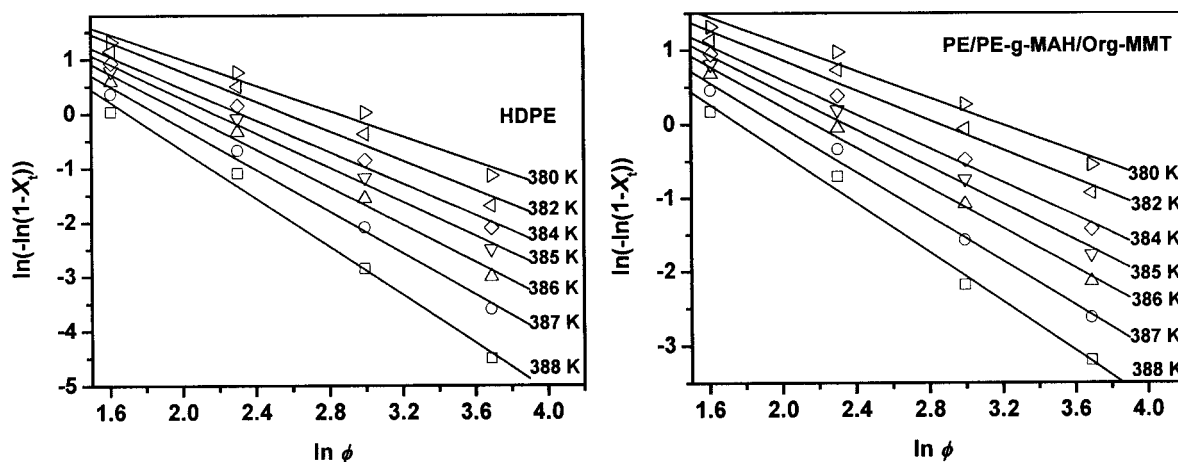

Figure 3 Patterns of X_t versus t during the nonisothermal crystallization process of PE/PE-*g*-MAH/Org-MMT (88 : 9 : 3).

Figure 5 Plots of $\ln[-\ln(1 - X_t)]$ versus $\ln \phi$ during the nonisothermal crystallization process for HDPE and PE/PE-*g*-MAH/Org-MMT (88 : 9 : 3).

tion. The final form of the parameter characterizing the kinetics of nonisothermal crystallization was given by Jeziorny[7]

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

The results obtained from the Avrami plots and the Jeziorny method are listed in Table I. The exponent n varies from 1.51 to 1.61 for HDPE and from 1.73 to 1.80 for PE/PE-*g*-MAH/Org-MMT, respectively. Although the exponent n in nonisothermal crystallization displayed a wide range of values and was more scattered than those obtained from isothermal crystallization,[22] it is interesting that the exponent n for PE/PE-*g*-MAH/Org-MMT was larger than that for HDPE at the corresponding cooling rate. This result shows that Org-MMT and PE-*g*-MAH act as a nucleating agent in the PE matrix just as in PP matrix.[16]

Assuming that the nonisothermal crystallization process may be composed of infinitesimally small isothermal crystallization steps, Ozawa[8] extended the Avrami equation to the nonisothermal case as

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

where $K(T)$ is the function of cooling rate which is related to the overall crystallization rate and indicates how fast crystallization proceeds, ϕ is the cooling rate, and m is the Ozawa exponent, which depends on the dimension of the crystal growth. The double-logarithmic form of eq. (5) is

$$\ln[-\ln(1 - X_t)] = \ln K(T) - m \ln \phi \qquad (6)$$

A plot of $\ln[-\ln(1 - X_t)]$ against $\ln \phi$ at a given temperature should result in a straight line if the Ozawa method is valid. Thus, $K(T)$ and m can be estimated from the intercept and the slope, respec-

tively. The results based on Ozawa method are shown in Figure 5 and Table II. The curves in the plots of $\ln[-\ln(1 - X_t)]$ against $\ln \phi$ for HDPE and PE/PE-*g*-MAH/Org-MMT exhibit a good linear relationship. These results show that HDPE and PE/PE-*g*-MAH/Org-MMT can be analyzed by the Ozawa method. The exponent m varies from 0.91 to 1.63 for HDPE and from 1.17 to 2.22 for nanocomposite. Although the exponent m in nonisothermal crystallization covers a wide range of values, it is interesting that the exponent m for nanocomposite is larger than that for HDPE at every crystallization temperature. The difference in the exponent m between HDPE and the nanocomposite indicates the dimension of crystal growth of the nanocomposite is different from that of HDPE. The cooling rate function $K(T)$ for both HDPE and the nanocomposite increases systematically with decreasing the crystal-

TABLE II
Nonisothermal Crystallization Kinetic Parameters for HDPE and PE/PE-*g*-MAH/Org-MMT Nanocomposite at Different Crystallization Temperatures

Sample	T(K)	m	$K(T)$
HDPE	388	1.67	17.98
	387	1.51	18.36
	386	1.37	18.45
	385	1.26	19.05
	384	1.15	19.18
	382	1.01	19.93
	380	0.91	19.81
PE/PE-g-MAH/Org-MMT	388	2.22	28.16
	387	1.92	29.76
	386	1.73	31.44
	385	1.58	33.22
	384	1.46	33.55
	382	1.36	36.42
	380	1.17	43.77

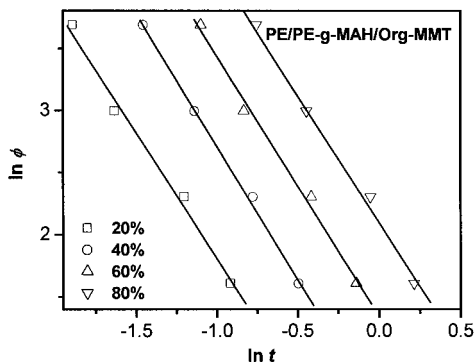**Figure 6** Plots of ln ϕ versus ln t during the nonisothermal crystallization process for PE/PE-g-MAH/Org-MMT (88 : 9 : 3).

TABLE III
Nonisothermal Crystallization Kinetic Parameters for HDPE and PE/PE-g-MAH/Org-MMT Nanocomposite at Different Relative Degree of Crystallinity

Sample	X_t (%)	a	$F(T)$
HDPE	20	2.03	0.80
	40	2.14	1.77
	60	2.09	3.83
	80	2.04	8.12
PE/PE-g-MAH/Org-MMT	20	2.54	0.34
	40	2.50	1.13
	60	2.41	3.00
	80	2.42	7.39

lization temperature. At every certain crystallization temperature, the cooling rate function $K(T)$ for nanocomposite is larger than that for HDPE, indicating that nanocomposite crystallizes at a quicker rate than HDPE at every crystallization temperature. This conclusion is consistent with that drawn for analysis of $t_{1/2}$.

A method developed by Liu and coworkers[23] was employed to describe the nonisothermal crystallization to make a comparison. The physical variables relating to the nonisothermal crystallization process are relative degree of crystallinity (X_t), cooling rate (ϕ), and crystallization peak temperature (T_p). At a given crystallinity X_t, both Ozawa and Avrami equations give the relationship

$$\ln \phi = \ln F (T) - a \ln t \tag{7}$$

where $F(T) = [K(T)/Z_t]^{1/m}$ refers to the value of cooling rate which must be chosen within a unit of crystallization time when the measured system amounts to a certain degree of crystallinity, and a is the ratio of the Avrami exponent n to Ozawa exponent m (n/m). According to eq. (7), at a given degree of crystallinity, plotting ln φ versus ln t yields a linear relationship. The kinetic parameter $F(T)$ and a are determined from the intercept and the slope of the lines, respectively. This method has been proven to be applicable in PP/PP-g-MAH/Org-MMT nanocomposites and POM/Org-MMT nanocomposites.[16,17] The results of such an analysis for HDPE and PE/PE-g-MAH/Org-MMT are listed in Figure 6 and Table III. The value of a varies from 2.03 to 2.14 for HDPE, and from 2.41 to 2.54 for PE/PE-g-MAH/Org-MMT. The value of $F(T)$ systematically increases with increasing relative degree of crystallinity. At the same relative degree of crystallinity, the $F(T)$ for PE/PE-g-MAH/Org-MMT is smaller than that for PE, indicating that PE/PE-g-MAH/Org-MMT crystallizes at a quicker rate than HDPE. This

conclusion agrees with the one drawn from Avrami and Ozawa analysis.

Another method often used to evaluate activation energy at various cooling rates, based on eq. (8), was proposed by Kissinger[20]

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

where R is the universal gas constant and ΔE is the activation energy of crystallization. The activation energies of the nonisothermal crystallization of HDPE and the nanocomposite (listed in Table III) are calculated with the data from the plot of $\ln(\phi T_p^2)$ versus $1/T_p$ (Fig. 7). The value of ΔE for PE/PE-g-MAH/Org-MMT is 223.7 J/mol, which is much smaller than that for HDPE (304.6 J/mol). A possible reason is that in nanocomposite the layers of Org-MMT dispersed in PE matrix at nanoscale possess high aspect ratio and are inclined to absorb the segments of macromolecule, which makes the crystallization easier. In addition, the carboxyl groups can also act as a nucleation agent during the crystallization process. These facts result in a decrease in
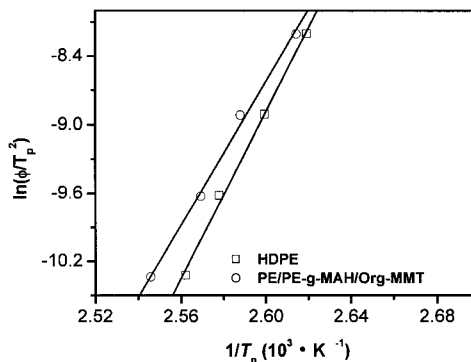

Figure 7 Plots of $\ln(\phi/T_p^2)$ versus $1/T_p$ during the nonisothermal crystallization process for HDPE and PE/PE-g-MAH/Org-MMT (88 : 9 : 3).

the activation energy of the nanocomposite compared with HDPE.

CONCLUSION

The nonisothermal crystallization kinetics of HDPE and PE/PE-g-MAH/Org-MMT nanocomposite were investigated by DSC at various cooling rates. Avrami analysis modified by Jeziorny, Ozawa analysis, and a method developed by Liu were used to describe the nonisothermal crystallization behavior of the samples. The good linear relationship in every analysis indicated that these methods were successful in describing the nonisothermal crystallization process of these samples. The difference in the exponent n, m, and a between HDPE and nanocomposite indicated that nucleation mechanism and dimension of spherulite growth of the nanocomposite was different from that of HDPE to some extent. The values of half-time ($t_{1/2}$), $K(T)$, and $F(T)$ showed that the crystallization rate increased with the increasing of cooling rates for HDPE and composite, but the crystallization rate of composite was faster than that of HDPE at a given cooling rate. Moreover, the method proposed by Kissinger was used to evaluate the activation energy of the mentioned samples. It was 223.7 kJ/mol for the composite, which was much smaller than that for HDPE (304.6 kJ/mol). Overall, the results indicated that the addition of Org-MMT and PE-g-MAH could accelerate the overall nonisothermal crystallization process of PE.

References

1. Xu, W. B.; He, P. S. J Appl Polym Sci 2001, 80, 304.
2. Supaphol, P.; Spruiell, J. E. Polymer 2000, 41, 1205.
3. Yin, Z. H.; Zhang, Y. L.; Zhang, X. M.; Yin, J. G. J Appl Polym Sci 1997, 63, 1565.
4. Xu, W. B.; Ge, M. L.; He, P. S. J Polym Sci, Part B: Polym Phys 2002, 40, 408.
5. Markus, L. Polym Eng Sci 1998, 38, 610.
6. Nakamura, K.; Watanabe, T.; Katayama, K.; Amano, T. J Appl Polym Sci 1972, 16, 1077.
7. Jeziorny, A. Polymer 1978, 19, 1142.
8. Ozawa, T. Polymer 1971, 12, 150.
9. Di Lorenzo, M. L.; Silvestre, C. Prog Polym Sci 1999, 24, 917.
10. Gupta, A. K.; Rana, S. K.; Deopura, B. L. J Appl Polym Sci 1994, 51, 231.
11. He, T. B.; Porter, R. S. J Appl Polym Sci 1945 1988, 35.
12. Rana, S. K. J Appl Polym Sci 1996, 61, 951.
13. Galante, M. J.; Mandelkern, L.; Alamo, R. G. Polymer 1998, 39, 5105.
14. Wang, Z. G.; Hsiao, B. S.; Sirota, E. B.; Sriivas, S. Polymer 2000, 41, 8825.
15. Xu, W. B.; Liang, G. D.; Wang, W.; Tang, S. P.; He, P. S.; Pan, W. P. J Appl Polym Sci 2003, 88, 3225.
16. Xu, W. B.; Liang, G. D.; Wang, W.; Tang, S. P.; He, P. S.; Pan, W. P. J Appl Polym Sci 2003, 88, 3093.
17. Xu, W. B.; Ge, M. L.; He, P. S.; J Appl Polym Sci 2001, 82, 2281.
18. Wang, K. H.; Choi, M. H.; Koo, C. M.; Choi, Y. S.; Chung, I. J Polymer 2001, 42, 9819.
19. Jeon, H. G.; Jung, H. T.; Lee, S. W.; Hudson, S. D. Polym Bull 1998, 41, 107.
20. Kissinger, H. E. J Res Natl Bur Stand (US) 1956, 57, 217.
21. Avrami, M. J Chem Phys 1941, 9, 177.
22. Srinivas, S.; Babu, J. R.; Rif. E. J. S.; Wilkes, G. L. Polym Eng Sci 1997, 37, 497.
23. Liu, T. X.; Mo, Z. S.; Wang, S. E.; Zhang, H. F. Polym Eng Sci 1997, 37, 568.