Nonisothermal Crystallization Behavior of a Novel Poly(aryl ether ketone): PEDEKmK

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ABSTRACT: Nonisothermal melt crystallization kinetics of PEDEKmK linked by *meta*-phenyl and biphenyl was investigated by differential scanning calorimetry (DSC). A convenient and reasonable kinetic approach was used to describe the nonisothermal melt crystallization behavior, and its applicability was verified when the modified Avrami analysis by the Jeziorny and Ozawa equation were applied to the crystallization process. The crystallization activation energy was estimated to be −219 kJ/mol by Kissinger method while crystallizing from the PEDEKmK melt nonisothermally. These observed crystallization characteristics were compared to those of the other members of poly(aryl ether ketone) family. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 67: 815–821, 1998

Key words: PEDEKmK; nonisothermal; crystallization; kinetics; differential scanning calorimetry

INTRODUCTION

Poly(aryl ether ketone)s (PAEKs) as semicrystalline polymers are a new type of high-performance engineering plastics and a promising scientific and industrial material with important structural applications in recent decades. Commonly, the phenyl rings in PAEKs are all *para*-linked, giving rise to a high melting temperature (T_m), which is too high for convenient processing. Recently, some other variants have been exploited, which contain *meta*-phenyl and biphenyl units in the polymer backbone so as to modify the T_m without reducing their glass transtion temperature (T_g).[1–3]

The material studied in this article is one particular variant of PAEKs labeled PEDEKmK, which has the chemical repeating unit shown in Scheme 1. PEDEKmK is interesting because the ratio between its T_g (160°C) and T_m (303°C), both expressed in Kelvin, is unusually high: 0.75 in

contrast to the 0.50 to 0.67 values found for the majority of thermoplastics. This suggests that, while relatively low processing temperatures are required during the manufacture into end products, the application temperature of PEDEKmK (related to T_g) could be relatively high.[4]

The preparation of PEDEKmK and a description of its unusual crystallization and melting behavior had been reported (where labelled PK99).[5,6] In our previous work, the morphology of PEDEKmK had been investigated by polarizing optical microscopy (POM), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS), and electron diffraction (ED).[7] A distinct change in lamellar thickness and orientation, spherulitic morphology had been observed due to the crystal melting and recrystallization. Recently, we have reported the crystal structure and polymorphism induced by uniaxial drawing of PEDEKmK.[8] It had been found that a second crystal modification (form II) can be induced by uniaxial drawing above T_g, which always coexists with form I.

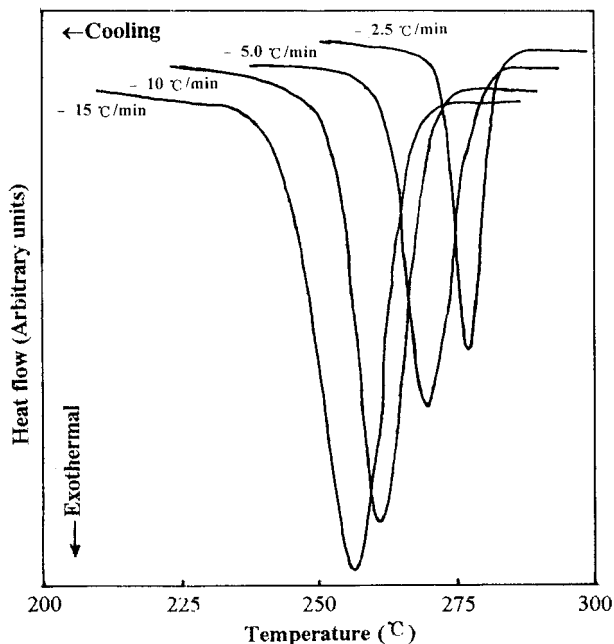The isothermal melt and cold crystallization ki-

Scheme 1
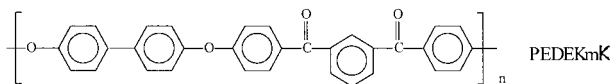
netics had been studied in the preceding work on the same material.[9] As the practical processes such as extrusion, molding, and film production were usually performed under dynamic noniso-thermal conditions, the present article reported the nonisothermal crystallization behavior of PEDEKmK.

EXPERIMENTAL

Materials and Preparation

PEDEKmK was prepared by polycondensation of 1,3-bis(4-fluorobenzoyl)benzene and 4,4′-biphe-nol as described by Liggat and Staniland.[3] The inherent viscosity of the polymer used is 0.83 dL/g (measured at 25°C on a 0.1% solution of the polymer in 98% sulphuric acid). The number-average molecular weight $\overline{M}_n$ of sample is 10,000.

Figure 1 Heat flow versus temperature during non-isothermal melt crystallization of PEDEKmK at the indicated cooling rates.

Table I   Peak Temperature (T_p), Time (t_{max}), Crystallization Enthalpy (ΔH_c), and Relative Crystallinity (X_t) at Maximum Rate of Heat Flow During Nonisothermal Melt Crystallization of PEDEKmK

Φ (°C/min)	T_p (°C)	t_{max} (min)	ΔH_c (J/g)	X_t (%)
−2.5	276.8	4.29	45.43	49
−5.0	269.7	2.91	44.51	50
−10	260.9	1.83	41.62	50
−15	256.3	1.37	38.22	46

Differential Scanning Calorimetry

Nonisothermal melt crystallization kinetics were carried out *in situ* using a Perkin−Elmer DSC-7 calibrated with indium and zinc stan-dards. The sample was heated up to 350°C and held there for 10 min in order to eliminate small residual nuclei that might act as seed crystals. Then, the melt was cooled to crystallize at se-lected constant rates Φ (in the range from 2.5 to 15°C/min). The exothermal curves of heat flow as a function of temperature were recorded and analyzed. All operations were performed under a nitrogen purge. Sample weight varied between 4−6 mg.

RESULTS AND DISCUSSION

Nonisothermal Crystallization Kinetic Analysis by Modified Avrami Equation

The crystallization exotherms of PEDEKmK at dif-ferent cooling rates were presented in Figure 1. It could be seen that for nonisothermal melt crystalli-zation, as the cooling rate Φ increased, the peak temperature T_p shifted to lower temperature region. The values of T_p, their corresponding peak times t_{max}, the crystallization enthalpies ΔH_c, and the rel-ative crystallinity X_t were collected in Table I. The relative crystallinity X_t as a function of crystalliza-tion temperature is defined as

$$X_t = \frac{\int_{T_o}^{T} \left(\frac{dH_c}{dT}\right) dT}{\int_{T_o}^{T_\infty} \left(\frac{dH_c}{dT}\right) dT} \tag{1}$$

where T_o and T_∞ represent the onset and end tem-
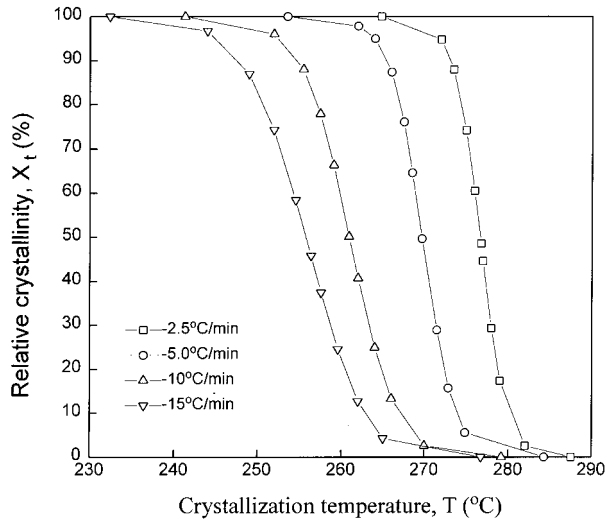
Figure 2 Development of relative crystallinity with temperature for nonisothermal melt crystallization of PEDEKmK.

peratures of crystallization, respectively. The development of X_t with crystallization temperature at various cooling rates is illustrated in Figure 2. Generally, all these curves had the same sigmoidal. This implied that only the lag effect of cooling rate on crystallization were observed for these curves.

During the nonisothermal melt crystallization process, the relation between crystallization time t and the corresponding temperature T is given by

$$t = \frac{T_o - T}{\Phi} \qquad (2)$$

According to eq. (2), the horizontal temperature axis of Figure 2 can be transformed into the time scale (Fig. 3). It indicates that the higher the cooling rate, the shorter the time of crystallization completion.

Most methods for describing the crystallization kinetics are based on the Avrami equation,[10,11] which assumed that the relative degree of crystallinity developed with crystallization time t,

$$1 - X_t = \exp(-Z_t t^n) \qquad (3)$$

where the exponent n is a mechanism constant, which depends on the type of nucleation and growth process; and Z_t is a composite rate constant involving both nucleation and growth rate parameters. While eq. (3) is reasonable to certain

extent for many systems, a number of researchers tried to use it to fit experimental results obtained from crystallizing polymers and proposed some modified forms.[12,13] Considering the nonisothermal character of the process investigated, Jeziorny[14] pointed out that the value of rate parameter Z_t should be adequately corrected. The factor which should be considered was the cooling rate Φ. Assuming constant or approximately constant Φ, the final form of the parameter characterizing the kinetics of nonisothermal crystallization was given as follows:

$$\log Z_c = \frac{\log Z_t}{\Phi} \qquad (4)$$

By using eq. (1), the well-known double logarithmic plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ are shown in Figure 4. Each curve showed an initial linear portion, subsequently tending to level off slightly. Usually, this deviation was considered to be due to the secondary crystallization, which was caused by the spherulite impingement in the later stage. The linear portions were almost parallel to each other, shifting to longer time with decreasing Φ. This indicated that the nucleation mechanism and crystal growth geometries were similar for the primary crystallization at all cooling rates. The values of n and Z_c (corrected by Z_t), determined from the slope and intercept of the initial linear portion in Figure 4, respectively, are listed in Table
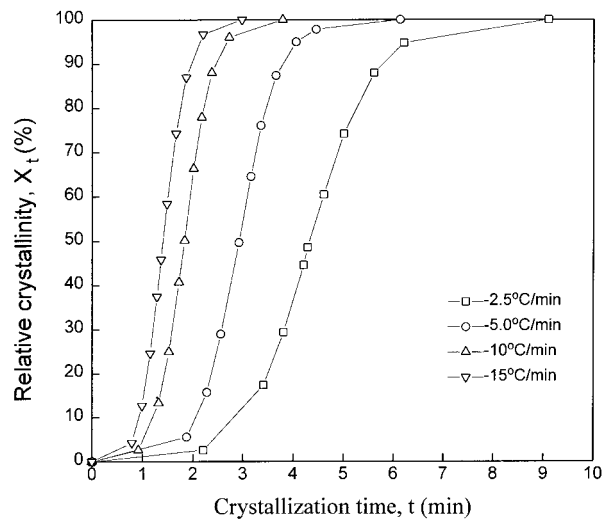
Figure 3 Relative crystallinity versus time during nonisothermal melt crystallization process of PEDEKmK.
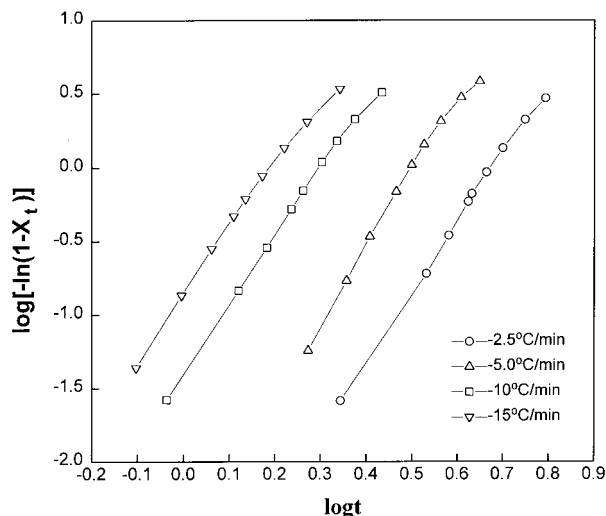
Figure 4 Plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ for nonisothermal melt crystallization of PEDEKmK.

II. The average value of the Avrami exponent was $n = 4.6$, which suggested that the primary crystallization stage for nonisothermal melt crystallization might correspond to a three-dimensional spherical growth with thermal nucleation.[13] For nonisothermal melt crystallization, the rate parameter Z_c decreased; but the half-time $t_{1/2}$ of crystallization increased with increasing the cooling rate Φ. The change of Z_c values indicated the effect of dominance of both nucleation and growth processes.

In common, the secondary stage was considered to be due to the effect of the slower crystallization or further perfection of crystal, which were caused by the spherulite impingement in the later stage of crystallization or due to the reorganization of initially poorly crystallized macromolecules or small and metastable crystals. It was well known that, if the secondary crystallization was not completed at a longer period, the product would continue crystallizing in the course of appli-
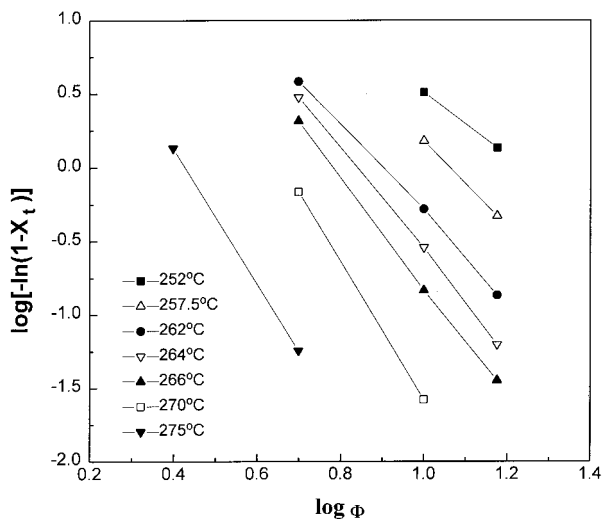
cation. This would lead to a continuous change in the properties of the product. Therefore, in order to obtain the materials with more stable and better properties, the annealing technique was usually used in the practical production, where the thermal treatment was always performed to accelerate the secondary crystallization process under the temperature of the maximum crystallization rate.

Nonisothermal Crystallization Kinetic Analysis by Ozawa Equation

As the nonisothermal crystallization was a rate-dependent process, assuming that the polymer melt was cooled at a constant rate and the mathematical derivation of Evans[15] was valid, and accounting for the effect of cooling rate on crystallization, Ozawa[16] modified the Avrami equation by replacing t in eq. (3) with T/Φ, as follows:

$$1 - X_t = \exp\left[-\frac{K(T)}{\Phi^m}\right] \tag{5}$$

where $K(T)$ was cooling function, and m was Ozawa exponent that depended on the crystal growth and nucleation mechanism. According to the double logarithmic form of eq. (5), the results of Ozawa analysis were presented in Figure 5 by plotting as $\log[-\ln(1 - X_t)]$ versus $\log \Phi$ for temperatures in the range from 252 to 275°C. A series of lines were obtained, and it indicated Ozawa analysis could relatively satisfactorily deal

Table II Effect of Cooling Rates on the Crystallization Kinetics of PEDEKmK

Φ (°C/min)	n	Z_t	Z_c	$t_{1/2}$ (min)[a]
−2.5	4.9	5.3×10^{-4}	20.43	0.50
−5.0	4.3	1.4×10^{-3}	3.72	0.68
−10	5.0	4.5×10^{-4}	2.16	0.80
−15	4.0	1.5×10^{-3}	1.54	0.82

[a] $t_{1/2} = (\ln 2/Z_c)^{1/n}$.

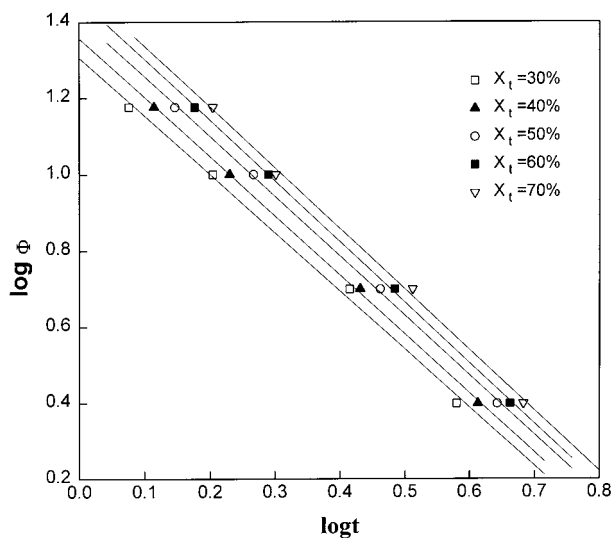**Figure 5** Ozawa plots of nonisothermal melt crystallization of PEDEKmK.

Table III   Cooling Function $K(T)$ and Ozawa Exponent m of Nonisothermal Melt Crystallization for PEDEKmK at Different Temperatures

Temperature (°C)	252	257.5	262	264	266	270	275
$K(T)$	4.4×10^2	1.2×10^3	5.1×10^2	8.6×10^2	7.9×10^2	1.3×10^3	8.9×10^1
m	2.1	2.9	3.0	3.5	3.7	4.7	4.6

with the nonisothermal melt crystallization process of PEDEKmK. This case was different from those observed in PEEK[17] and PEEKK,[18] where only some obvious zigzag plots were obtained. From these lines, the cooling function $K(T)$ and Ozawa exponent m could be determined from the intercept and slope, respectively (Table III). On the whole, the exponent m increased as the crystallization temperature increased. The average value of m was 3.5; that is, $m \approx n - 1$. From Ozawa's theory,[16] it could be derived that some so-called predetermined nuclei exist before cooling the melt; that is to say, there still existed a small quantity of unmolten residual crystal or some impurities in the polymer. It might indicate a heterogeneous nucleation form.

Nonisothermal Crystallization Kinetic Analysis by Combining the Avrami Equation with the Ozawa Equation

While the Ozawa equation could describe the nonisothermal crystallization behavior of PEDEKmK

**Figure 6**   Plots of $\log \Phi$ versus $\log t$ for nonisothermal melt crystallization of PEDEKmK.

to some extent, it was proven to fail to adequately describe the nonisothermal crystallization kinetics for many polymer systems, such as PE,[19] PEEK,[17] and PEEKK,[18] in which a large portion of crystallization was attributed to the secondary process. In addition, as the crystallinity was related to the cooling rate Φ and crystallization time t (or temperature T), the relation between Φ and t could be built up at a given crystallinity. Here, a convenient kinetic method was adopted to deal with nonisothermal data by combining the Avrami equation [eq. (1)] with the Ozawa equation [eq. (5)], as follows[18]:

$$\log \Phi = \log F(T) - a \log t \qquad (6)$$

where the parameter $F(T) = [K(T)/Z_t]^{1/m}$ refers to the value of cooling rate, which has to be chosen at unit crystallization time when the measured system amounts to a certain degree of crystallinity; a is the ratio of the Avrami exponent n to the Ozawa exponent m (i.e., $a = n/m$). According to eq. (6), the plot of $\log \Phi$ versus $\log t$ gave a series of straight lines at a given relative degree of crystallinity (Fig. 6). The kinetic parameter $F(T)$ and the exponent a could be estimated by the intercept and slope of these lines, respectively (Table IV). It showed that $F(T)$ systematically increased as increasing the relative crystallinity, but the values of a were almost constant about 1.6. From the above results of the modified Avrami analysis and the Ozawa analysis, the value of a ($=n/m$) could be calculated to be 1.3, which was relatively con-

Table IV   Kinetic Parameters of Nonisothermal Crystallization for PEDEKmK at Different Degrees of Crystallinity by the Combination of the Avrami–Ozawa Equation

X_t (%)	30	40	50	60	70
$F(T)$	20.2	22.8	25.8	28.9	31.3
a	1.5	1.6	1.6	1.6	1.6
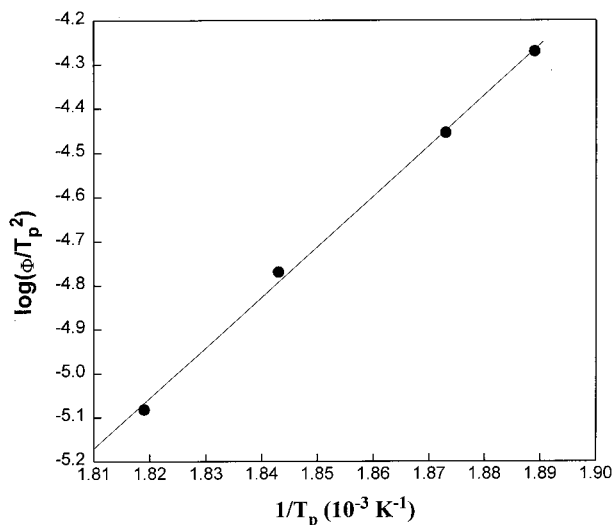
Figure 7 Kissinger plots for estimating the energy of nonisothermal melt crystallization of PEDEKmK.

sistent with this result. It also indicated that this kinetic approach was reasonable and applicable for nonisothermal crystallization process.

Activation Energy of Nonisothermal Crystallization by Kissinger Method

Considering the variation of the peak temperature T_p with the cooling rate Φ in differential thermal analysis, the activation energy ΔE was determined by the Kissinger equation as the following form[20]:

$$\frac{d\left(\ln \dfrac{\Phi}{T_p^2}\right)}{d\left(\dfrac{1}{T_p}\right)} = -\frac{\Delta E}{R} \tag{7}$$

where R is the universal gas constant; the rest of the parameters have meanings as above-mentioned. Accordingly, in the light of the results in Table I, the slopes of $\log(\Phi/T_p^2)$ versus $1/T_p$ will give $\Delta E/R$ (Fig. 7). Then, the activation energy was found to be -219 kJ/mol for the nonisothermal melt crystallization of PEDEKmK. Since it has to release energy while transforming the molten fluid into the crystalline state, the value of ΔE for the melt crystallization is negative in the light of the concept of heat quantity in physical chemistry. Moreover, it was very useful to compare this results to those of PEEKK (-189 kJ/

mol)[18] and PEDEKK (-176 kJ/mol)[21] previously reported. It could be found that the activation energy for the nonisothermal melt crystallization of PEDEKmK was higher in magnitude than those of the latter two polymers. This result can be explained as follows. ΔE is the activation energy required to transport molecular segments to the crystallization surface, and the stiffer molecular chain of PEEKK and PEDEKK linked in the *para* form are more apt to "freeze" from the fluid state when crystallizing into the crystalline state. The energy barrier overcome by the supercooled phase for melt crystallization of PEEKK and PEDEKK are smaller than that of PEDEKmK; the consequence is that the activation energies of the two former are smaller than that of the latter.

Besides, it is well known that the thermal history in the melt could affect the crystallization behavior of polymer. Thereby, unmolten crystalline seeds or local chain organization still could remain at temperatures above the melting point.[22] Accordingly, the presence of such primary nuclei decreases the crystallization free energy barrier and thus increases the crystallization rate. Such a phenomenon is also defined as self-nucleation. Therefore, for melt crystallization cooling from the molten state, the stiffer and ordered molecular segments of PEDEKK ($T_m = 410°C$) and PEEKK ($T_m = 360°C$), which can be considered as the local order section, may serve as the primary nuclei and can induce the melt crystallization. This would result in a decrease of crystallization free energy barrier; that is to say, their values of ΔE for melt crystallization in magnitude are lower than that of PEDEKmK.

CONCLUSIONS

A systematic study of the nonisothermal melt crystallization kinetics of PEDEKmK has been performed by several mathematical model through DSC experiment. The application of the modified Avrami equation and the Ozawa equation on this polymer system confirmed the reasonability and applicability of a convenient kinetic method previously established by combining the Avrami and Ozawa equations.

The activation energy of nonisothermal melt crystallization was determined by the Kissinger method, which was higher than those of PEEKK and PEDEKK; and the differences between them could be interpreted by the flexibility and rigidity of molecular chain of the polymers, i.e., the compo-

sition of polymer chains (such as the ratio of ether-to-ketone and the *para*- or *meta*-linkage form).

REFERENCES

1. I. Y. Chang, *SAMPE Q.,* **19,** 29 (1988).
2. P. A. Staniland, *Bull. Soc. Chim. Belg.,* **98,** 667 (1989).
3. J. J. Liggat and P. A. Staniland, *Polym. Commun.,* **32,** 450 (1991).
4. L. Abate, S. Calanna, A. Pollicino, and A. Recca, *Polym. Eng. Sci.,* **36,** 1782 (1996).
5. D. J. Blundell, J. J. Liggat, and A. Flory, *Polymer,* **33,** 2475 (1992).
6. D. J. Blundell, *Polymer,* **33,** 3773 (1992).
7. S. E. Wang, J. Z. Wang, H. F. Zhang, Z. W. Wu, and Z. S. Mo, *Macromol. Chem. Phys.,* **197,** 1643 (1996).
8. S. E. Wang, J. Z. Wang, Z. S. Mo, H. F. Zhang, and Z. W. Wu, *Macromol. Chem. Phys.,* **197,** 4079 (1996).
9. T. X. Liu, Z. S. Mo, S. E. Wang, H. F. Zhang, J. Z. Wang, H. Na, and Z. W. Wu, *J. Appl. Polym. Sci.,* **64,** 1451 (1997).
10. M. Avrami, *J. Chem. Phys.,* **7,** 1103 (1939).
11. M. Avrami, *J. Chem. Phys.,* **8,** 212 (1940).
12. L. Mandelkern, *Crystallization of Polymers,* McGraw-Hill, New York, 1964.
13. B. Wunderlich, *Macromolecular Physics,* Vol. 2, Academic Press, New York, 1977.
14. A. Jeziorny, *Polymer,* **19,** 1142 (1978).
15. U. R. Evans, *Trans. Faraday Soc.,* **41,** 365 (1945).
16. T. Ozawa, *Polymer,* **12,** 150 (1971).
17. P. Cebe and S.-D. Hong, *Polymer,* **27,** 1183 (1986).
18. T. X. Liu, Z. S. Mo, S. E. Wang, and H. F. Zhang, *Polym. Eng. Sci.,* **37,** 568 (1997).
19. M. Eder and A. Wlochowicz, *Polymer,* **24,** 1593 (1983).
20. H. E. Kissinger, *J. Res. Natl. Bur. Stds.,* **57,** 217 (1956).
21. T. X. Liu, Z. S. Mo, H. Na, H. F. Zhang, *J. Polym. Eng.,* to appear.
22. Y. Lee and R. S. Porter, *Macromolecules,* **21,** 2770 (1988).