Isothermal and Nonisothermal Melt Crystallization Kinetics of a Novel Poly(aryl ether ketone ether ketone ketone) Containing a *meta*-Phenyl Linkage

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ABSTRACT: The isothermal and nonisothermal melt crystallization kinetics of a novel poly(aryl ether ketone ether ketone ketone) containing a *meta*-phenyl linkage (PEKEKmK) were studied by differential scanning calorimetry. The Avrami equation was used to analyze the isothermal crystallization kinetics of PEKEKmK. The crystallization mechanism did not change within the crystallization temperature range, but the crystallization rate decreased with an increase in the crystallization temperature. The equilibrium melting point, T_m^0, was determined to be 327°C according to the Hoffman–Weeks equation. Moreover, the nonisothermal crystallization kinetics of PEKEKmK was also investigated by the Avrami equation as modified by Jeziorny. It was found that the nonisothermal crystallization behavior of PEKEKmK could be described well by this method at various cooling rates, although the parameters n and Z_c did not have the same clear physical meaning as for isothermal crystallization kinetics. The thermal properties and crystallization characteristics of PEKEKmK were compared with those of all-*para* PEKEKK(T) and PEKEKK(T/I) with a T/I ratio of 1. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 4775–4779, 2006

Key words: poly(aryl ether ketone); crystallization; differential scanning calorimetry (DSC)

INTRODUCTION

Semicrystalline aryl ether ketone polymers (PAEKs) such as poly(aryl ether ether ketone) (PEEK) belong to a class of materials known as engineering thermoplastics. PEEK has a relatively high degree of crystallinity and a melting point (T_m) of 334°C. However, PEEK suffers from poor creep behavior above its relatively low glass-transition temperature (T_g) of 143°C. Therefore, the synthesis of new variants has been the focus of many studies. It is recognized that polymers with aromatic units linked in an all-*para* fashion in many instances can have crystalline melting points too high for convenient processing. However, the incorporation of some *meta* linkages into the polymer backbone can reduce the melting point without adversely affecting the T_g.[1,2]

A unique member of the poly(aryl ether ketone) family is poly(aryl ether ketone ether ketone ketone) (PEKEKK). PEKEKK can be prepared from 1,4-diphenoxybenzophenone (DPBP), terephthaloyl chloride (T), and isophthaloyl chloride (I) with different ratios of T to I along the electrophilic polycondensation route.

The chemical structures of the PEKEKKs investigated in the present study are in Scheme 1.

Gardner et al. reported that all-*para* PEKEKK(T) and PEKEKK(T/I) with a T/I ratio of 1 showed polymorphism for crystallization that was in the form of an amorphous glassy state (cold crystallization) or that was solvent induced.[3] We previously studied the crystallization behavior of PEKEKK(T) and PEKEKK(T/I)[4–6] and also determined the crystal structure of PEKEKmK by wide-angle X-ray diffraction. We proposed an orthorhombic unit cell containing two chains, with $a = 0.772$ nm, $b = 0.604$ nm, and $c = 2.572$ nm. We also investigated variation in unit cell parameters with the crystallization temperature of PEKEKmK.[7] It is well known that the properties of semicrystalline polymers depend very much on the processing conditions. Therefore, in the present study we investigated the isothermal and nonisothermal melt crystallization kinetics of PEKEKmK by differential scanning calorimetry (DSC) in order to gain a better understanding of the relationship between structure and properties. We also compared the observed crystallization characteristics of PEKEKmK with those of PEKEKK(T) and PEKEKK(T/I).

EXPERIMENTAL

PEKEKmK was synthesized with 1,4-diphenoxybenzophenone and isophthaloyl chloride along the elec-

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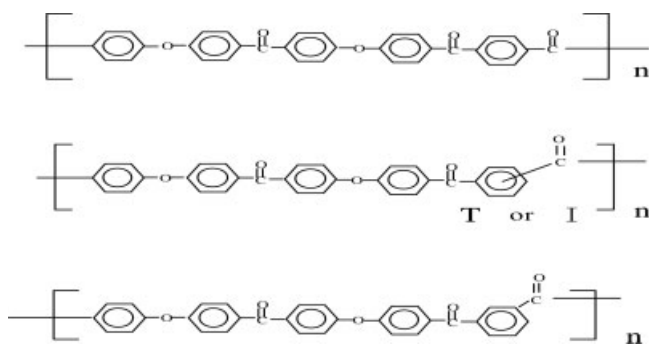
Scheme 1

trophilic polycondensation route.[8] The glass-transition temperature, 147°C, and the melting point, 309°C, were measured by differential scanning calorimetry. The inherent viscosity of the polymer used in this study was 0.96 dL/g (measured at 25°C on a 0.1% solution of the polymer in 98% sulfuric acid).

Isothermal and nonisothermal melt crystallization kinetic were studied using a Perkin Elmer differential scanning calorimeter (DSC-7, Norwalk, CT). Indium and zinc standards were used for temperature calibration. For isothermal melt crystallization studies, the samples were first melted at 350°C for 5 min to eliminate any residual crystal nuclei that might act as seed crystals and then cooled to a predetermined temperature, T_c, in the range of 252°C–260°C at 80°C/min. The relative degree of crystallinity, X_t, was calculated by

$$X_t = \frac{X_c(t)}{X_{c,\infty}} \quad (1)$$

where $X_{c,\infty}$ is the ultimate crystallinity and $X_c(t)$ is the crystallinity at time t, which are the total area and the area at time t of the exothermic area in the DSC trace,

respectively. For nonisothermal melt crystallization studies, samples were first melted at 350°C for 5 min and then cooled at various constant cooling rates (−2.5°C/min, −5.0°C/min, −10°C/min, −15°C/min, or −20°C/min). The relative degree of crystallinity was calculated in the same way as in the isothermal melt crystallization study.

RESULTS AND DISCUSSION

Isothermal crystallization kinetics from Avrami analysis

DSC is probably the most convenient and widely used method of studying the crystallization kinetics of polymers. In the present study, the isothermal and nonisothermal crystallization kinetics of PEKEKmK were also studied with DSC. As described in the Experimental section, isothermal melt crystallization of PEKEKmK was studied by cooling the melt rapidly to the crystallization temperature (252°C–260°C). The isothermal crystallization process of PEKEKmK was analyzed with the well-known Avrami equation,[9,10] which assumes that the relative degree of crystallinity, X_t, developing with time t is

$$X_t = 1 - \exp(-kt^n) \quad (2)$$

where k is the crystallization rate constant depending on the nucleation and growth rates and n is the Avrami exponent depending on the nature of the nucleation and growth geometry of the crystals. Figure 1 shows the Avrami plots of PEKEKmK crystallized at three crystallization temperatures. The Avrami parameters n and k could be obtained from the slope and the interception, respectively, of the plot of $\log[-\ln(1 - X_t)]$ versus $\log t$, as shown in Figure 1 (the curves for 254°C
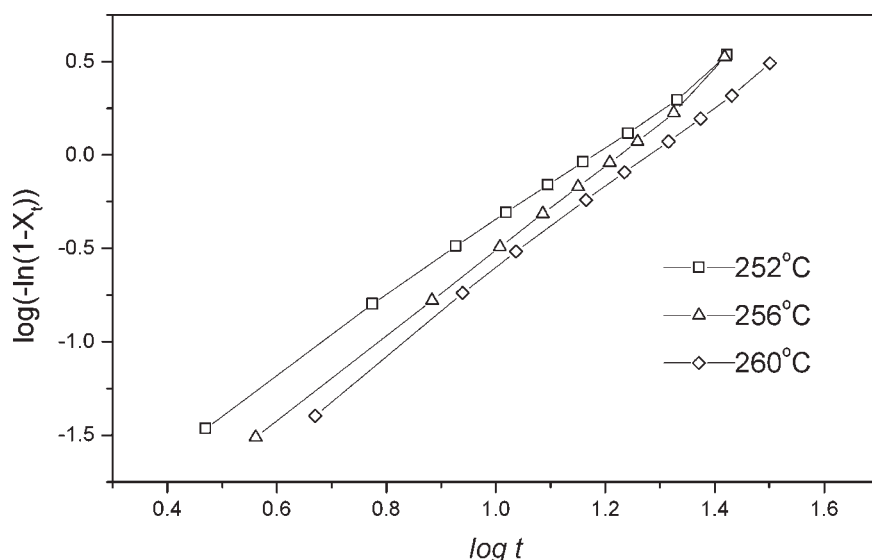

Figure 1 Plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ for isothermal melt crystallization.

TABLE I
Parameters n, k, t_{max}, $t_{1/2}$, and $\tau_{1/2}$ from Avrami Analysis of Isothermal Melt Crystallization for PEKEKmK

T_c (°C)	n	k (min^{-n})	$t_{1/2}$ (min)	$\tau_{1/2}$ (min^{-1})	t_{max} (min)
252	2.1	3.892×10^{-3}	12.527	7.98×10^{-2}	10.323
254	2.3	1.850×10^{-3}	13.152	7.60×10^{-2}	12.035
256	2.3	1.473×10^{-3}	14.191	7.05×10^{-2}	13.290
258	2.3	1.456×10^{-3}	14.264	7.01×10^{-2}	13.358
260	2.2	1.386×10^{-3}	16.229	6.16×10^{-2}	15.118

and 258°C not shown). The values of n and k are listed in Table I, which shows that n remained almost the same with an increase in the crystallization temperature, indicating the crystallization mechanism did not change with the crystallization temperature. The melting point of PEKEKmK can be as high as 309°C, so it is not so easy to study its crystallization and morphology with a hot-stage optical microscope. Morphological proof is necessary to correctly describe the nucleation and growth pattern of PEKEKmK; this cannot be accomplished on the basis of DSC results alone. It can also be seen from Table I that k decreased with increasing T_c, indicating that with isothermal melt crystallization, the crystals grew slowly at a lower degree of supercooling (higher crystallization temperature) because the dominant factor was nucleation. The half-life, $t_{1/2}$, defined as the time at $X_t = 0.5$, is an important parameter for analyzing crystallization kinetics; it can also be calculated using the relation

$$t_{1/2} = \left(\frac{\ln 2}{k}\right)^{1/n} \tag{3}$$

Usually, the rate of crystallization, G, is described as the reciprocal of $t_{1/2}$, that is, $G = T_{1/2} = (t_{1/2})^{-1}$.

Because t_{max} is the solution of $dQ/dt = 0$ [where $Q(t)$ is the heat flow rate], it can be written in terms of n and k, obtaining

$$t_{max} = \left(\frac{(n-1)}{nk}\right)^{1/n} \tag{4}$$

Using the values of n and k listed in Table I, eqs. (3) and (4), respectively, were used to calculate the values of $t_{1/2}$, $\tau_{1/2}$, and t_{max}, also shown in Table I. It can be seen from Table I that $t_{1/2}$ and t_{max} increased with crystallization temperature, whereas the $\tau_{1/2}$ decreased with an increase in the crystallization temperatures. All the results showed that the isothermal crystallization from the melt was retarded with an increasing crystallization temperature. This was consistent with the trend for k noted above.

Estimation of equilibrium melting point

The equilibrium melting point temperature (T_m^O) is very important for studying isothermal crystallization. According to theoretical considerations by Hoffman and Weeks,[11] T_m^O can be obtained by the intersection of the resulting straight line with line $T_m = T_c$, and the dependence of T_m on T_c is given by

$$T_m = T_m^o\left(1 - \frac{1}{2\beta}\right) + \frac{1}{2\beta}T_c \tag{5}$$

where T_m^O is the equilibrium melting point and β is the growth of lamella thickness during crystallization. The Hoffman–Weeks plot is shown in Figure 2. The T_m^O obtained from the plot was 327°C, which was considerably lower than those of PEKEKK(T)
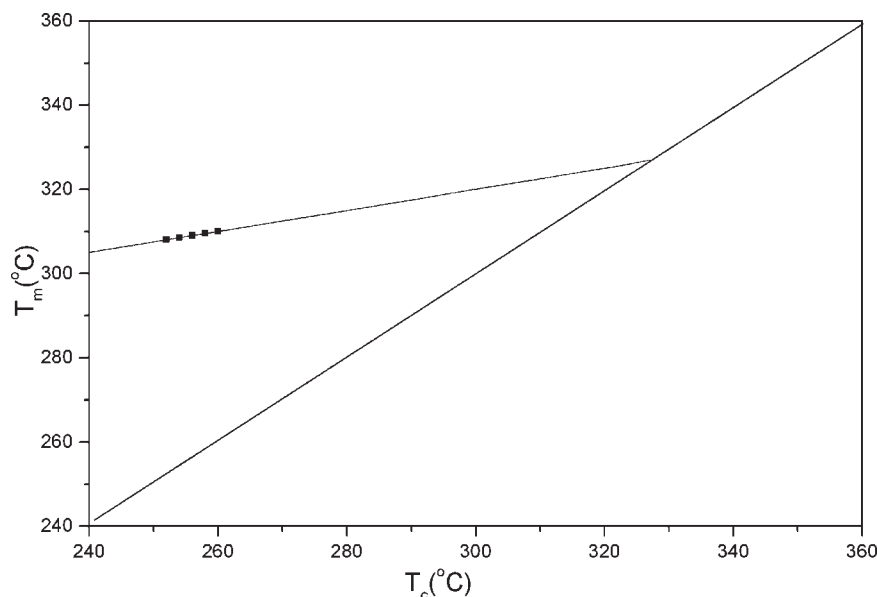

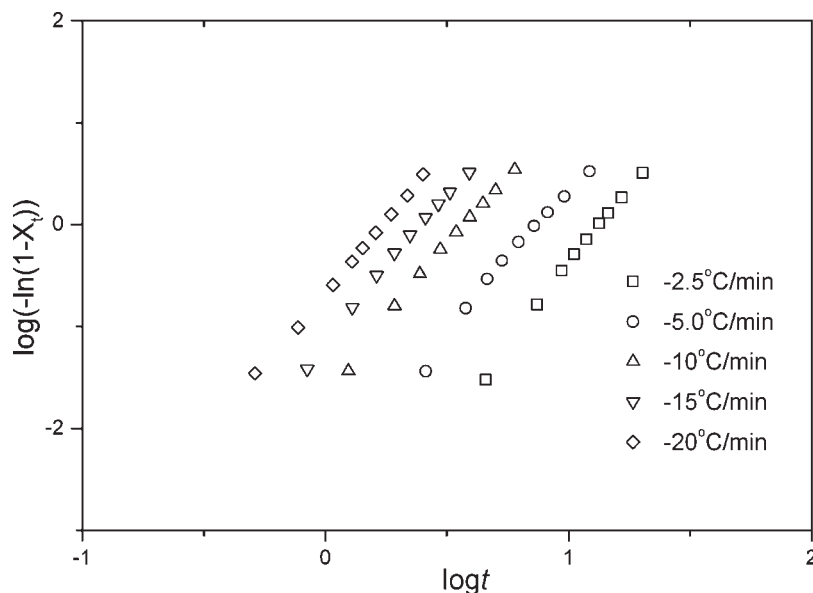**Figure 2** Hoffman–Weeks plot of PEKEKmK.

Figure 3 Plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ for nonisothermal melt crystallization.

$(406^\circ C)^5$ and PEKEKK(T/I) $(353^\circ C).^6$ The differences in equilibrium melting point can be explained by differences in the flexibility of the polymer chains as a result of incorporation of *meta*-phenyl linkages.

Nonisothermal crystallization kinetics

It is important and practical to study the kinetics of nonisothermal crystallization because most polymer processing operations are carried out under nonisothermal conditions. Therefore, nonisothermal melt crystallization kinetics of PEKEKmK was also investigated in the present study. Although it is reasona-

ble to use the well-known Avrami equation to analyze isothermal crystallization kinetics of many systems to a certain extent, some modified forms have been proposed to fit experimental results obtained from nonisothermal crystallization processes. In previous works[4,6] we showed that the Ozawa method[12] is not suitable for analyzing the nonisothermal crystallization behavior of PAEKs. Given the nonisothermal character of the investigated process, Jeziorny[13] suggested that the rate parameter, Z_t, should be corrected by a factor, that is, the cooling rate (Φ). Z_t was also the crystallization rate constant, depending on nucleation and growth rate, and had the same
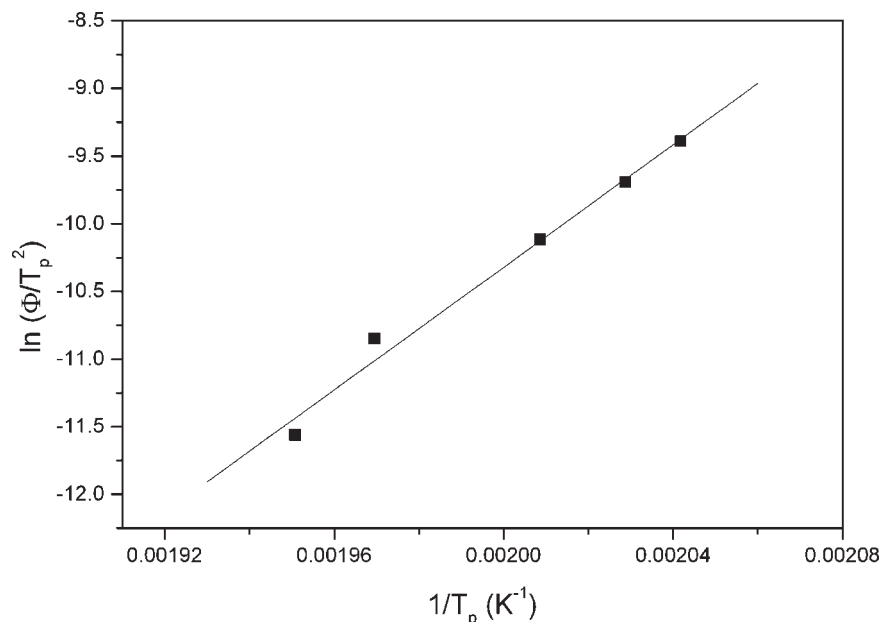

Figure 4 Kissinger plot for estimating the activation energy of nonisothermal crystallization of PEKEKmK.

meaning as k in the Avrami equation for isothermal crystallization part, as described above. Therefore, the final form of the parameter characterizing the kinetics of nonisothermal crystallization is given by $\log Z_c = \log Z_t/\Phi$.

Plots of $\log[-\ln(1 - X_t)]$ versus $\log t$ are shown in Figure 3. The Avrami exponent, n, and the rate parameter, Z_c (corrected by Φ), were obtained from the slope and the intercept, respectively, of these straight lines, shown in Figure 3 and listed in Table II. The value of n was almost unchanged with an increase in the cooling rate. However, Z_c increased with an increased cooling rate. In brief, the Avrami equation as modified by Jeziorny can be used to describe the process of nonisothermal crystallization kinetics of PEKEKmK at various cooling rates, It should be noted that the parameters n and Z_c do not have the same clear physical meaning as they do for isothermal crystallization kinetics, and they are simply two adjustable parameters.

For nonisothermal melt crystallization, the peak temperature, T_p (the temperature at which maximum crystallization occurs), shifted to the low-temperature region with an increasing cooling rate. The activation energy of crystallization was derived from the Kissinger equation[14] in the following form:

$$\left[d(\ln \Phi/T_p{}^2)\right]/\left[d(1/T_p)\right] = -\Delta E/R \qquad (6)$$

where R is the universal gas constant and the rest of the parameters are as defined above. The slope of a plot of $\ln(\Phi/T_p{}^2)$ versus $1/T_p$ gave the activation energy as $\Delta E = -175$ kJ/mol (Fig. 4).

For comparison, the thermal properties and crystallization kinetics parameters of PEKEKKs with different ratios of T/I are summarized in Table III. The T_g, T_m, and equilibrium melting point (T_m^O) decreased with the increasing flexibility of the polymer chains, achieved by incorporating a *meta*-phenyl linkage. However, the average value of the Avrami exponent, n, during isothermal melt crystallization kinetics, which was 2, remained almost unchanged, indicating that PEKEKKs with different ratios of T/I might crystallize in a similar way.

All the aforementioned results indicate that the introduction of a *meta*-phenyl linkage reduced the crystallizability of polymers from the PEKEKK family.

TABLE II
Nonisothermal Melt Crystallization Kinetics Parameters of PEKEKmK

Φ (°C/min)	n	Z_c
−2.5	3.1	3.849×10^{-2}
−5.0	2.9	0.317
−10	2.9	0.686
−15	2.9	0.839
−20	2.8	0.926

TABLE III
Thermal Properties and Crystallization Kinetics Parameters of PEKEKKs

PEKEKK	T_g (°C)	T_m (°C)	T_m^o (°C)	n
PEKEKK(T)	167	384	406	2
PEKEKK(T/I)	152	329	353	2.4
PEKEKK(I)	147	309	327	2.3

n, average value of the Avrami exponent of isothermal melt crystallization.

CONCLUSIONS

The crystallization behavior of a novel poly(aryl ether ketone ether ketone ketone) containing a *meta*-phenyl linkage (PEKEKmK) was studied by DSC. The Avrami equation was used to analyze the isothermal crystallization kinetics of PEKEKmK. The crystallization mechanism did not change within the crystallization temperature range, but the crystallization rate decreased with an increase in crystallization temperature. The equilibrium melting point, T_m^O, also was evaluated using the Hoffman–Weeks equation, which indicated it was 327°C. Moreover, the nonisothermal crystallization kinetics of PEKEKmK was also investigated by the Avrami equation as modified by Jeziorny. It was found that the nonisothermal crystallization behavior of PEKEKmK could be described well by this method at various cooling rates, although the parameters n and Z_c did not have the same clear physical meaning as they did for isothermal crystallization kinetics. The thermal properties and crystallization characteristics of PEKEKmK were compared with those of all-*para* PEKEKK(T) and PEKEKK(T/I) with a T/I ratio of 1. The differences among them could be explained by the variation in the flexibility of the polymer chains.

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