

STRUCTURAL ANALYSIS OF PEKEKK(T/I) USING WAXD, IMAGING PLATES AND SAXS*

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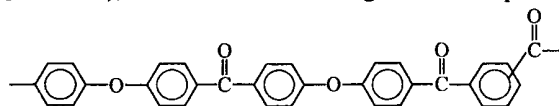
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Abstract Structures and crystal form transition of the novel aryl ether ketone polymer containing *meta*-phenylene linkage: PEKEKK(T/I) were investigated by wide angle X-ray diffraction (WAXD), imaging plates (IPs) and small angle X-ray scattering (SAXS). The energy of activation of the decomposition reaction and degree of crystallinity of PEKEKK(T/I) were determined by WAXD and thermo-gravimetric analysis (TGA), respectively. Results obtained from WAXD and IPs show that crystal forms I and II coexist in the PEKEKK(T/I) samples isothermally cold crystallized in the temperature range from 180°C to 240°C and only form I occurs in PEKEKK(T/I) samples isothermally cold crystallized at 270°C. The radius of gyration (R_g), thickness of microregions with electron-density fluctuations (E) and distribution of particle sizes were investigated by SAXS.

Keywords PEKEKK, WAXD, Imaging plates, SAXS, Structural analysis

INTRODUCTION

Poly(aryl ether ketone)s and their copolymers are the most common members of a new class of high-temperature, high-performance engineering thermoplastics with potential applications. Among them, PEKEKK(T/I) is a novel member of this family with high glass transition temperature ($T_g = 152^\circ\text{C}$), melting point ($T_m = 331^\circ\text{C}$) and decomposition temperature ($T_d = 545^\circ\text{C}$), and it has the following chemical repeating unit:



PEKEKK (T/I)

Polymorphism in PEEK, PEKK and other poly(aryl ether ketone)s obtained by solvent-induced crystallization or cold crystallization has been reported^[1–4]. The form II structure of PEKK differs from the more stable form I structure (normally induced by melt crystallization) which has a two-chain orthorhombic unit cell with chains located at the corner and center of the unit cell^[2]. There is no evidence to indicate that a change in chain conformation is associated with the polymorphism^[3]. WAXD patterns reveal that form II crystal structure is formed at low temperatures (high undercooling), and it is transformed into form I at high temperature.

SAXS reflects the electron-density fluctuations within a sample, which could be used to characterize the parameters of particles over a length range larger than the usual interatomic distances. The scattering capacity depends on the difference of electronic density between the crystalline particles and non-crystalline medium. The

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Porod law, which is one of the most important theories of SAXS, is mainly used to study the two-phase system with interface. However, deviations from the Porod law will be take place because of the interphase structures in polymers.

Recently, imaging plates for X-ray, electron or neutron detectors have been spotlighted and utilized in the field of polymer science for their advantages of short exposure time, two-dimensional observation and high sensitivity^[5, 6]. In this work, we present results from our studies of crystal structure and transition of PEKEKK(T/I) by TGA, WAXD, IPs and SAXS.

EXPERIMENTAL

Materials and Sample Preparation

PEKEKK(T/I) was synthesized by electrophilic Friedel-Crafts acylation condensation of 1,4-diphenoxybenzophenone with terephthaloyl chloride (T) and isophthaloyl chloride (I) with a T/I ratio of 1.

The samples were prepared for cold crystallization experiments according to the following procedure: the PEKEKK(T/I) were first placed on a hot stage preset at 420°C, after melting and pressing into flat disks for 10 min, the samples were quenched in an ice-water bath, producing amorphous PEKEKK(T/I) samples. Then these amorphous samples were divided into several parts and isothermally crystallized at 180, 200, 220, 240, and 270°C for 4 h, respectively.

Methods of Characterization

Thermal measurements were performed on a Perkin-Elmer DSC-7 differential scanning calorimeter. The temperatures and heat flow scales were carefully calibrated using standard indium materials over a wide temperature range. The sample weight was typically 8–10 mg. Samples were sealed in nitrogen-filled aluminum pans and heated at a rate of 10 K/min.

A Perkin-Elmer instrument for thermogravimetric analysis was used to investigate the thermal stability of PEKEKK(T/I) in a temperature range from 300°C to 1000°C with a scanning rate of 10 K/min.

WAXD experiments were performed at room temperature using a Rigaku D/max 2500V X-ray diffractometer in combination with an 18 kW rotating-anode generator, imaging plates and curved graphite crystal filtered Cu K α_1 radiation ($\lambda = 0.15406$ nm). WAXD data were collected from $2\theta = 10$ – 60° with a step interval of 0.02° .

SAXS experiments were carried out at room temperature using a Rigaku D/max 2500V X-ray diffractometer operated at 50 kV and 200 mA with a 4-slit collimation system. Data were collected from $2\theta = 0.07$ – 2° .

Imaging plates, with a size of 127×127 mm, were supplied by Fuji Photo Films Co. Ltd. IPs measurements were performed with the diffractometer operating at 50 kV and 200 mA. The distance between the IPs and samples was 50 mm. In the X-ray diffraction system, intensity data were read out as digital values so that they were readily processed with a personal computer (PC). Substantially, the patterns of PEKEKK(T/I) were displayed on the CRT of the PC and analyzed by Rigaku R-AXIS Display Software.

RESULTS AND DISCUSSION

Thermal Analysis

The thermal analysis of PEKEKK(T/I) was performed on amorphous films heated from 180°C to 350°C at 10 K/min, and held there for 10 min to remove all residual crystallinity, and then cooled to 100°C again at -10 K/min (Fig. 1). After the amorphous sample was heated through the glass transition, it exhibited a well-defined cold crystallization exotherm ($T_{cc} = 210.5^\circ\text{C}$) in the 193–223°C region, which was then followed by a final melting endotherm ($T_m = 331.3^\circ\text{C}$, the peak value). During the cooling from the melt, a melt crystallization exotherm ($T_{mc} = 271.4^\circ\text{C}$) appeared in the range of 250–290°C.

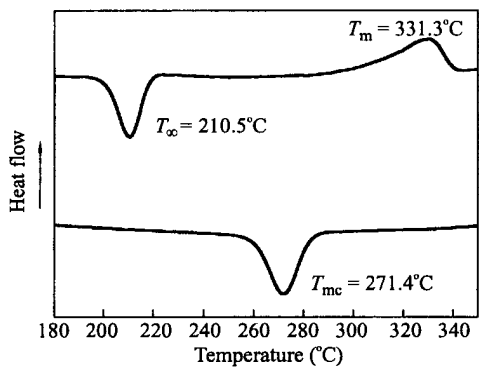


Fig. 1 DSC curve of amorphous PEKEKK(T/I), measured at a heating and cooling rate of 10 K/min

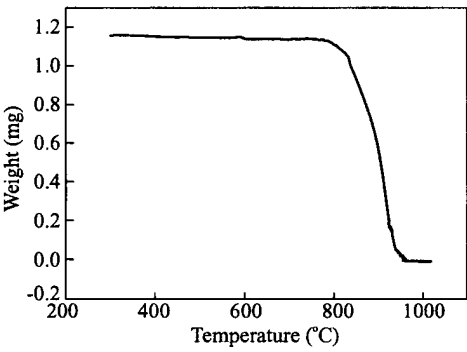


Fig. 2 Thermogram for decomposition reaction of PEKEKK(T/I)

Figure 2 is a continuous trace of change in sample weight as a function of temperature where PEKEKK(T/I) was heated from 300°C to 1000°C and a high decomposition temperature (loss 5 wt% in $T_d = 545^\circ\text{C}$) was observed. The Freeman-Carroll Equation^[7] is used to evaluate the reaction kinetics

$$\frac{\Delta \lg(\frac{d\alpha}{dT})}{\Delta \lg(1-\alpha)} = -\frac{E}{2.303R} \cdot \frac{\Delta(\frac{1}{T})}{\Delta \lg(1-\alpha)} + n \tag{1}$$

where α = rate of weight loss, E = energy of activation, R = gas constant, n = order of decomposition reaction, and T = absolute temperature. The parameters of the Freeman-Carroll equation are listed in Table 1. Figure 3 illustrates the plot of

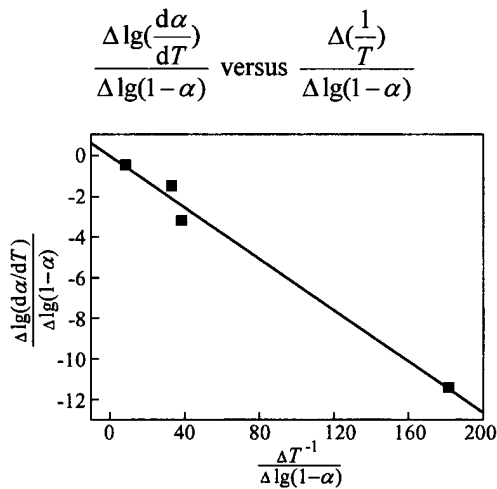


Fig. 3 Kinetics of decomposition reaction of PEKEKK(T/I)

Table 1. Parameters of Freeman-Carroll equation

Temperature range (K)	$\Delta \frac{1}{T} \times 10^5 \text{ (K}^{-1}\text{)}$	$\Delta \lg(1-\alpha)$	$\Delta \lg(\frac{d\alpha}{dT})$	$\frac{\Delta(\frac{1}{T})}{\Delta \lg(1-\alpha)}$	$\frac{\Delta \lg(\frac{d\alpha}{dT})}{\Delta \lg(1-\alpha)}$
800–830	–4.518	–0.0249	0.285	181.446	–11.446
830–860	–4.203	–0.109	0.346	38.560	–3.174
860–890	–3.920	–0.119	0.176	32.941	–1.479
890–920	–3.664	–0.440	0.212	8.327	–0.482

The values of order and activation energy of the decomposition reaction are calculated to be 0.6 and 120.63 kJ/mol, respectively. The low value of the decomposition reaction order reveals that the thermal stability of PEKEKK(T/I) is high, and the high value of the energy of activation indicates that PEKEKK(T/I) is a high-temperature performance engineering thermoplastic.

Analysis by WAXD and IPs

Figure 4 illustrates a series of WAXD patterns of PEKEKK(T/I) cold crystallized between T_m and T_g from the glassy state. It can be seen that there was a progressive change in the height and width of peaks for the cold crystallized samples with increasing temperature. This could be regarded as a change toward higher crystallinity or a gradual increase in crystalline order. All the diffraction patterns indicate that in this temperature range, PEKEKK(T/I) mainly crystallizes in the form I structure from the glassy state. Meanwhile, a minor form II structure is formed, and therefore, mixed form I and form II reflections appear from 180 °C to 240 °C. As the cold crystallization at 270 °C is conducted, the 002 diffraction peak of form II disappears and form I structure is significantly enhanced, which means that PEKEKK(T/I) isothermally cold crystallizes into form I at 270 °C, while PEKEKK(T/I) isothermally cold crystallized in the temperature range from 180 °C to 240 °C exhibits the coexistence of forms I and II. The diffraction patterns of PEKEKK(T/I) are also recorded by imaging plates as shown in Fig. 5(a–f).

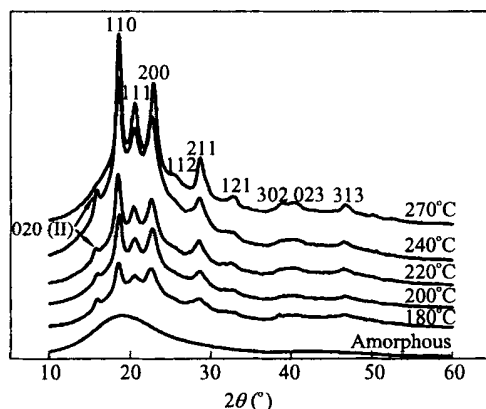


Fig. 4 WAXD patterns of PEKEKK(T/I) cold crystallized at different temperatures

Figure 5(a) shows a diffuse scattering pattern of PEKEKK(T/I) quenched in ice water and it is obviously amorphous. Fig. 5(b–f) illustrate the diffraction patterns of PEKEKK(T/I) isothermally crystallized at 180, 200, 220, 240 and 270 °C, respectively. Five strong diffraction circles of 020(II), 110, 111, 200 and 211 planes corresponding to 2θ of 15.88°, 18.58°, 20.56°, 22.86° and 28.68° are observable (Fig. 5e). The 020(II) diffraction peak of form II is taken as the character of coexistence of form II to form I, and it disappears at 270 °C (Fig. 5f). Moreover, the 110 diffraction peak becomes stronger, when form II is not detected. It could be seen that there was a progressive change in the intensities and width of peaks with increasing temperature. This had to be characterized as a change toward higher crystallinity or a gradual increase in crystalline order. Therefore, the WAXD pattern of PEKEKK(T/I) cold crystallized at 270 °C was selected to determine the crystal form I structure and the diffraction data are listed in Table 2. The similarity of the diffraction patterns between PEEK and PEKEKK(T/I) suggests that the latter also has a closely related crystal structure. Taking that into account, it could be expected that PEKEKK(T/I) might crystallize in a similar way as PEEK. By using a trial and error method, the 9 reflections could be satisfactorily indexed according to an orthorhombic unit cell with dimensions $a = 0.777$ nm, $b = 0.605$ nm, $c = 1.013$ nm for form I of PEKEKK(T/I). The observed and calculated interplanar spacing, d_o and d_c , are in agreement with each other. Form II of PEKEKK(T/I) with a two-chain orthorhombic unit cell having $a = 0.417$ nm, $b = 1.134$ nm and $c = 1.013$ nm, obtained by solvent-induced crystallization in

CH_2Cl_2 solvent^[8], differs from the more stable form I in the relative placement of the chains.

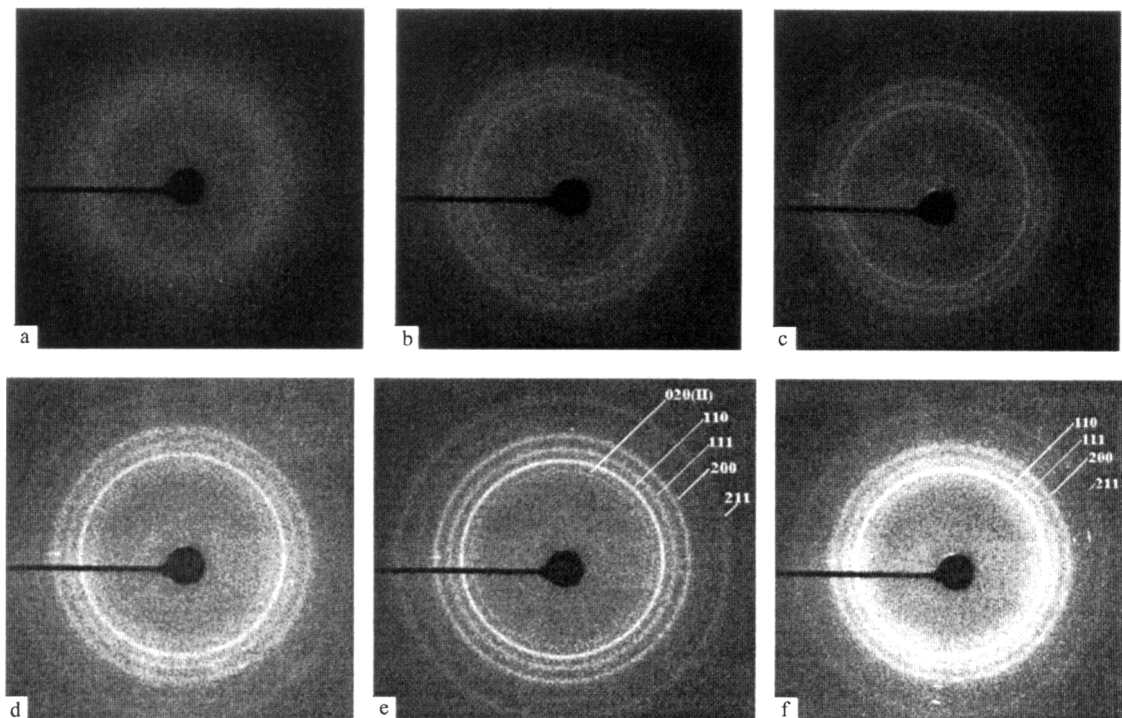


Fig. 5 Imaging plates of PEKEKK(T/I)

a) Amorphous sample; b) Cold crystallized at 180°C; c) Cold crystallized at 200°C; d) Cold crystallized at 220°C; e) Cold crystallized at 240°C; f) Cold crystallized at 270°C

By means of the graphic multippeak resolution method^[9], the degree of crystallinity of PEKEKK(T/I) determined by WAXD is calculated as follows^[10, 11]:

$$W_{c,x} = \frac{\sum_i C_{i,hkl}(\theta) I_{i,hkl}(\theta)}{\sum_i C_{i,hkl}(\theta) I_{i,hkl}(\theta) + k_i C_a(\theta) I_a(\theta)} x \quad (2)$$

where $I_{i,hkl}(\theta)$ = relative intensities of the (hkl) crystalline peaks, $I_a(\theta)$ = relative intensity of the non-crystalline peak, $C_{i,hkl}(\theta)$ = correction factors of (hkl) crystalline peaks, $C_a(\theta)$ = correction factor of non-crystalline peak, the total correction factor $K = C_a(\theta) \cdot k_i$, and k_i is the relative scattering coefficient, which is a ratio of calculated diffraction intensity ($\sum I_{i,cal}$) to total scattering intensity ($\sum I_{i,total}$) for unit weight of crystalline polymer $k_i = \sum I_{i,cal} / \sum I_{i,total}$ ($k_i \leq 1$). Here, $C_{i,hkl}(\theta)$ or $C_a(\theta)$ can be calculated by the following equation:

$$\begin{aligned} C_{i,hkl}^{-1} \text{ or } C_a^{-1}(\theta) &= f^2 \cdot \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \cdot e^{-2B(\sin \theta / \lambda)^2} \\ &= \sum N_i f_i^2 \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} e^{-2B(\sin \theta / \lambda)^2} \end{aligned} \quad (3)$$

where f = atomic scattering factor of a repeating unit, f_i = scattering factor of the i^{th} atom, N_i = number of the i^{th} atom in a repeating unit, 2θ = Bragg angle, $(1 + \cos^2 2\theta) / \sin^2 \theta \cos \theta$ = angle factor (LP), $e^{-2B(\sin \theta / \lambda)^2}$ = temperature factor (T), and $2B = 10$.

The atomic scattering factor f_i can be approximately expressed by:

$$f_i(\sin \theta / \lambda) = \sum_{i=1}^4 a_i e^{-b_i (\sin \theta / \lambda)^2} + c \tag{4}$$

where values of *a*, *b* and *c* are given in Ref. [12].

WAXD patterns of PEKEKK(T/I) annealed at different temperatures reveal one non-crystalline peak at 19.02° and 10 crystalline peaks (see Fig. 4). The relative intensities (relative area) of all the crystal peaks were calculated and the results are shown in Table 2.

Table 2. X-ray diffraction data of PEKEKK(T/I).

No.	2θ(°)	d _o (nm)	d _c (nm)	I/I ₀	h k l	T	L _p	f ²	C(θ)
1	18.58	0.4772	0.4774	100	110	0.897	74.661	794.476	1
2	20.56	0.4316	0.4318	63	111	0.876	60.430	711.276	1.41
3	22.86	0.3887	0.3885	74	200	0.850	48.710	626.786	2.05
4	25.56	0.3482	0.3474	25	112	0.815	38.025	533.410	3.22
5	28.68	0.3110	0.3111	34	211	0.774	29.708	447.495	5.17
6	38.98	0.2309	0.2306	11	302	0.632	15.433	269.875	-
7	40.44	0.2229	0.2253	11	023	0.606	13.925	249.198	-
8	46.64	0.1946	0.1946	10	313	0.515	9.934	193.778	-
9*	19.02	-	-	-	-	0.889	68.528	760.865	1.15

*Amorphous peak, *k_t* = 0.42

Using Eqs. (2), (3), and (4), the correction factors in the formula of degree of crystallinity for the crystalline and non-crystalline peaks were calculated and listed in Table 2. The correction factors of crystalline peaks *C*₁₁₀(θ) = 1, *C*₁₁₁(θ) = 1.41, *C*₂₀₀(θ) = 2.05, *C*₁₁₂(θ) = 3.22 and *C*₂₁₁(θ) = 5.17, and the correction factor of non-crystalline peak *C_a*(θ) = 1.15. The total correction factor *K* = *k_i* • *C_a*(θ) = 0.48. Using the data above, Eq. (2) can be further obtained.

$$W_{c,x} = \frac{I_{110} + 1.41I_{111} + 2.05I_{200} + 3.22I_{112} + 5.17I_{211}}{I_{110} + 1.41I_{111} + 2.05I_{200} + 3.22I_{112} + 5.17I_{211} + 0.48I_a} \tag{5}$$

The *W_{c,x}* of PEKEKK(T/I) was calculated according to Eq. (5). As shown in Fig. 6, at the same crystallization time (4 h), the degree of crystallinity systematically increases with increasing cold crystallization temperature. The reason is that the cold crystallization process improves the regularity of the chains and enhances the growth of secondary crystallization.

SAXS Analysis

The plots of SAXS intensities *I*(*q*) versus scattering vector *q* for the PEKEKK(T/I) are shown in Fig. 7. Scattering intensities increase with increasing degree of crystallinity. According to Guinier's theory^[13], the angular dependence of scattering intensity *I* can be given by the following approximate formula which is valid at small scattering angles.

$$I(q) = I_e N n^2 e^{-\frac{q^2 R_g^2}{3}} \tag{6}$$

where *I_e* is the scattering intensity of an electron, *N* is the number of the particles, *n* is the electron number in each particle, *R_g* is the radius of gyration, *q* is the scattering vector and *q* = 4πsinθ/λ, λ is the wavelength of X-ray and 2θ is the scattering angle.

The logarithm of Eq. (6) is

$$\ln I(q) = -\frac{R_g^2}{3} q^2 + \ln(I_e N n^2) = K q^2 + B \tag{7}$$

where *K* = −*R_g²*/3 and *B* = ln(*I_e* *Nn*²). *K* is the slope, *B* is the intercept in the plot of ln*I*(*q*) versus *q*², and *I_e* *Nn*² is

the intensity coefficient. R_g and $I_e N n^2$ are given by

$$R_g = \sqrt{-3K} \quad (8)$$

$$I_e N n^2 = e^B \quad (9)$$

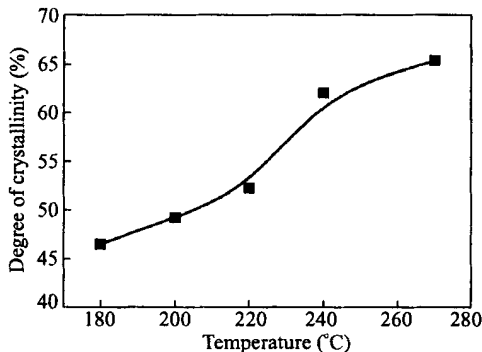


Fig. 6 Degree of crystallinities of PEKEKK(T/I) cold crystallized at different temperatures

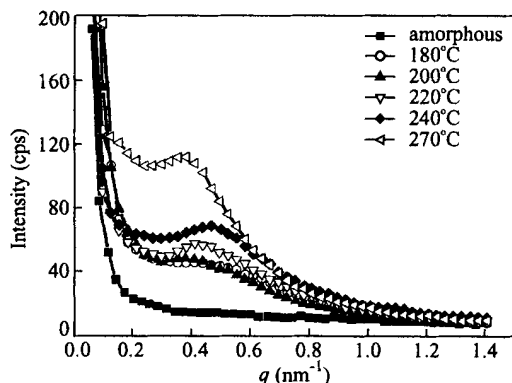


Fig. 7 SAXS curves of PEKEKK(T/I)

For each set of particles of given size, there is a scattering plot corresponding to Eq. (6). The total scattering intensity is the sum of all particle scattering intensities; and it is no longer an exponential relationship. Practically, due to hetero-dispersed character of particles, the experimental plot of $\ln I(q)$ versus q^2 is not a straight line but curved upwards with convexity. The limiting slope of the curve in the small angle range of scattering approaches zero, corresponding to a value of the radius of gyration close to that of the largest particles present in the collection. To sum up, small-angle X-ray scattering allows us to decide whether a system is composed of different sized particles, and roughly to outline the distribution of the particle sizes. The radii of gyration R_g of PEKEKK(T/I) are listed in Table 3.

The radius of gyration (R_g) obtained from Eq. (7) is an average value for all the particles. Obviously, the scattering system consists of particles with different sizes. A distribution function ($P(r)$) was used to describe the distribution of particle sizes according to the theory of logarithmic normal distribution^[14, 15].

$$P(r) = \frac{1}{\sqrt{2\pi} \cdot r \cdot \ln \sigma} \cdot \exp \left[- \left(\frac{\ln r - \ln \mu}{\sqrt{2} \ln \sigma} \right)^2 \right] \quad (10)$$

where r is the radius of particles, μ is the geometrical mean of size distribution, σ is the square root of distribution deviation. μ and σ can be determined by

$$R_g = \exp(\ln \mu + 6 \ln^2 \sigma) \quad (11)$$

$$R_p = \exp(\ln \mu + 2.5 \ln^2 \sigma) \quad (12)$$

hence, $\ln \mu$ and $\ln \sigma$ can be written as

$$\ln \mu = \ln R_g - 1.714 \ln(R_g/R_p) \quad (13)$$

and

$$\ln^2 \sigma = 0.286 \ln(R_g/R_p) \quad (14)$$

where R_g is the radius of gyration, R_p is the Porod radius which is determined by

$$R_p = \frac{3Q}{8\pi K_p'} \quad (15)$$

where K_p' is the Porod constant. According to the Porod law, scattering curves of $q^3 I(q)$ versus q^2 shown in Fig. 8 should tend towards the Porod constant. However, deviations from the Porod law are observed in PEKEKK(T/I). Similar deviation have been reported in other materials^[16–18] and the deviation is due to the non-sharp boundaries between two phases. Additional scattering will be brought on in the system with electron-density fluctuation within microregions (interphase region)^[19], which will result in a positive deviation for the total scattering especially at large angles. The positive deviation from the Porod law could be corrected by fitting the experimental scattering curves. Furthermore, the Porod constant and the thickness of interphase region could be obtained by

$$\ln[q^3 I(q)] = \ln K_p' + \delta^2 q^2 \quad (16)$$

$$E = (2\pi)^{1/2} \delta \quad (17)$$

where δ is correlative to the thickness of microregions and E is the thickness of microregions (interphase region).

The invariant Q can be determined by^[15]

$$\begin{aligned} Q &= \int_0^\infty q I(q) dq \\ &= \int_0^{q_1} q I(q) dq + \int_{q_1}^{q_2} q I(q) dq + \int_{q_2}^\infty q I(q) dq \end{aligned} \quad (18)$$

where $q = 4\pi \sin \theta / \lambda$, $q_1 - q_2$ is the range of q in which the scattering intensities, $I(q)$, can be obtained immediately from the experiment; $0 - q_1$ is the range of q in which the scattering intensities can be obtained by extrapolation of the values of $I(q)$ in the range from q_1 to q_2 ; $q_2 - \infty$ is the range in which Eq. (19) holds:

$$\int_{q_2}^\infty q I(q) dq = q_2^2 I(q_2) = K_p' / q_2 \quad (19)$$

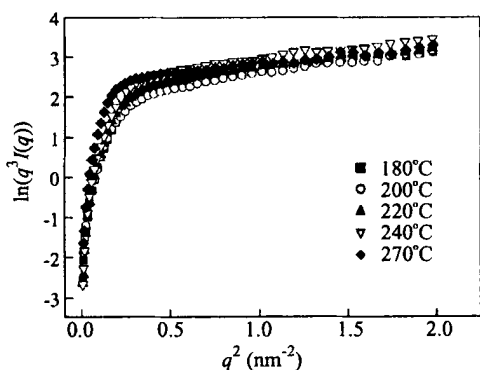


Fig. 8 Scattering curves of $\ln[q^3 I(q)]$ versus q^2

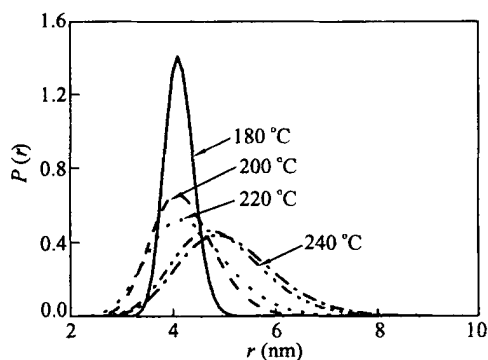


Fig. 9 Distribution of particle sizes $P(r)$ of PEKEKK(T/I)

The results of R_p of PEKEKK(T/I) are listed in Table 3 and the distribution of particle sizes of PEKEKK(T/I) are shown in Fig. 9. The heterogeneous nucleation function dominates, if the crystallization process occurs under high supercooling conditions, e.g. in a quenching process. On the contrary, the homogeneous nucleation function dominates when the crystallization process takes place under low supercooling conditions such as isothermal crystallization at high temperatures. The peak positions of $P(r)$ for PEKEKK(T/I) crystallized at 180°C and 200°C are lower than those of other samples which means the size of the dominated particles are smaller. Though the dominated particles are large, the distribution of particle sizes of PEKEKK(T/I) crystallized at high temperature is wider than that of PEKEKK(T/I) crystallized at low temperatures. This

indicates that crystallization is controlled by nucleation under high supercooling conditions, and there is a nonhomogeneous growth process during the cold crystallization process at high temperatures.

Table 3. Structural parameters of PEKEKK(T/I)

	180°C	200°C	220°C	240°C	270°C
R_g (nm)	4.24	5.35	5.71	5.92	6.16
R_p (nm)	4.13	5.06	5.23	5.39	5.48
E (nm)	2.23	2.19	2.04	1.89	1.72
Q (nm ⁻²)	213.37	300.82	383.62	454.48	485.93
K_p' (nm ⁻³)	6.17	7.10	8.76	10.07	10.59

The results of Porod constants (K_p') and average thickness of microregions (E) are listed in Table 3. Porod constants increase with the increase of crystallization temperature. However, the thickness of the interphase region (E) is about 2 nm and it decreases with the increase of crystallization temperature. The reason is that the mobility of the molecular chains increases and some of the disordered molecular chains in interphase regions may move out and be rearranged into the crystalline region during the crystallization process above T_g .

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