

Influence of Annealing on Structure of Poly(aryl ether ether ketone ketone) Revealed by SAXS

TIANXI LIU, ZHISHEN MO, HONGFANG ZHANG, GUANG LI

Polymer Physics Laboratory, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

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ABSTRACT: Structural studies of poly(aryl ether ether ketone ketone) (PEEKK) using small-angle X-ray scattering and one-dimensional electron density correlation function methods revealed that its aggregated state structure was significantly influenced by the annealing temperature. The long period L , the average thickness of the lamellae d , the electron density difference between the crystalline and amorphous regions $\eta_c - \eta_a$, and the invariant Q increased with increasing annealing temperature, but it was opposite to the case of the specific inner surfaces O_s . A transition zone existed between the traditional "two phases" with a dimension about 0.5 nm for semicrystalline PEEKK.
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Key words: PEEKK; SAXS; annealing; structure

INTRODUCTION

In the past decades, much research interest has been devoted to a kind of semicrystalline high-performance engineering thermoplastic, poly(aryl ether ketone)s, due to their excellent physical and mechanical properties. Recently, a number of novel variants have been exploited to meet more extensive requirements in scientific research and practical applications.^{1–3} Among them, poly(aryl ether ether ketone ketone) (PEEKK), developed by Hoechst Co., possesses a higher thermal resistance by introducing a more rigid ketone moiety; moreover, its mechanical, physical, and other properties which are compatible with those of PEEK are still maintained.⁴

It is well known that a semicrystalline polymer will crystallize when cooled from the melt or

heated from the amorphous state to the temperature region between the glass transition temperature (T_g) and the melting temperature (T_m), and its degree of crystallinity generally falls within the range of 0–50% depending on the processing conditions. So, the properties of crystalline polymer are strongly dependent on the crystalline structure and morphology developed during processing or under different crystallization conditions. Up to now, the isothermal and nonisothermal crystallization kinetics from the molten and amorphous states,^{5–7} double-peak melting behavior,⁸ crystal structure, morphology, degree of crystallinity, and drawing-induced polymorphism of PEEKK have been investigated using DSC, WAXD, TEM, electron diffraction (ED), and uniaxial drawing experiments.^{4,9–12}

In practical production and research, the annealing treatment is a very useful crystallization technique, which is usually applied to accelerate the secondary crystallization process under the temperature of the maximum crystallization rate. The objective of the present study was to relate the annealing temperature of PEEKK to its micro-

Correspondence to: Z. Mo.

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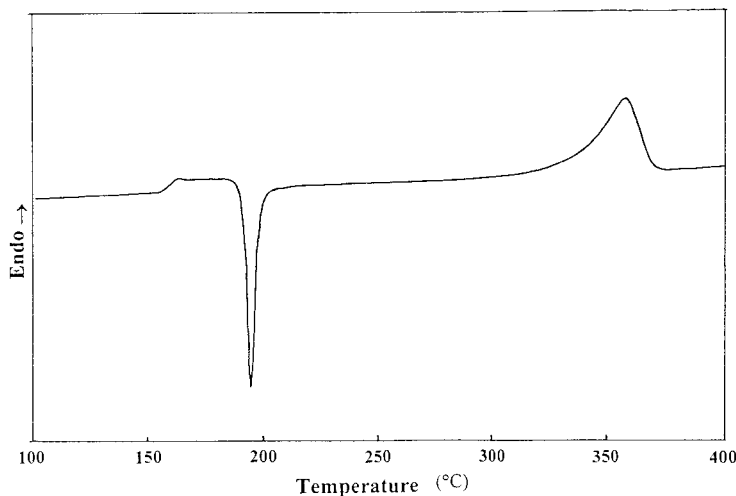


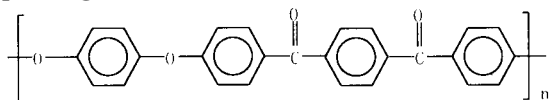
Figure 1 DSC trace of the amorphous PEEKK sample. Heating rate is 10°C/min.

structure using small-angle X-ray scattering (SAXS).

EXPERIMENTAL

Materials and Samples

PEKKK was synthesized from 1,4-bis(4-fluorobenzoyl)benzene and hydroquinone by a nucleophilic route,¹³ which has the following chemical repeating unit:



PEKKK

The resulting powder sample, whose number-average molecular weight was around 10,000, was put into a hot press at 400°C and held there for 10 min, then quenched into ice/water to obtain the brown transparent amorphous film with a thickness of about 0.5 mm (measured density $\rho_a = 1.2705 \text{ g/cm}^3$ by the liquid-density balance in the mixed solution of *n*-heptane/carbon tetrachloride). The DSC trace of the amorphous sample is presented in Figure 1, from which three thermal transition temperatures, $T_g = 155^\circ\text{C}$, the cold crystallization temperature $T_{c,h} = 186^\circ\text{C}$, and $T_m = 360^\circ\text{C}$ were obtained (heating rate 10°C/min). The crystallized specimens were obtained by cutting from the amorphous film and crystallizing them isothermally at different annealing temperatures, T_a , in the range 180–350°C.

Small-Angle X-ray Scattering Measurements

SAXS experiments were performed at ambient temperature with a Philips PW-1700 X-ray diffractometer equipped with a Kratky small-angle X-ray camera, a step-scanning device, and a scintillation counter for recording the scattering intensity. The distance between the sample and detector was 20 cm. All measurements were made with a $\text{CuK}\alpha$ radiation source ($\lambda = 0.1542 \text{ nm}$) operating at 45 kV and 40 mA. Monochromatization was achieved using a graphite crystal. The exposure time was 2 h for all the samples investigated. This counting time was long enough to avoid the influence of noise on the scattering intensity, so that during the process of data collection the count error was less than 1% for the largest angle. The scattering intensities were corrected for absorption, background scattering, and incident X-ray intensity fluctuations of the samples. Desmeared scattering intensities were obtained by adopting a procedure developed by Schmidt.¹⁴ The resulting curves were converted to the absolute scattering intensity using a calibrated Lupolen (polyethylene, BASF, Ludwigshafen) standard sample.¹⁵

RESULTS AND DISCUSSION

As a semicrystalline polymer, PEEKK can crystallize from the rubbery state at temperatures between 160 and 360°C. With such a wide range of crystallization temperature, the crystalline mor-

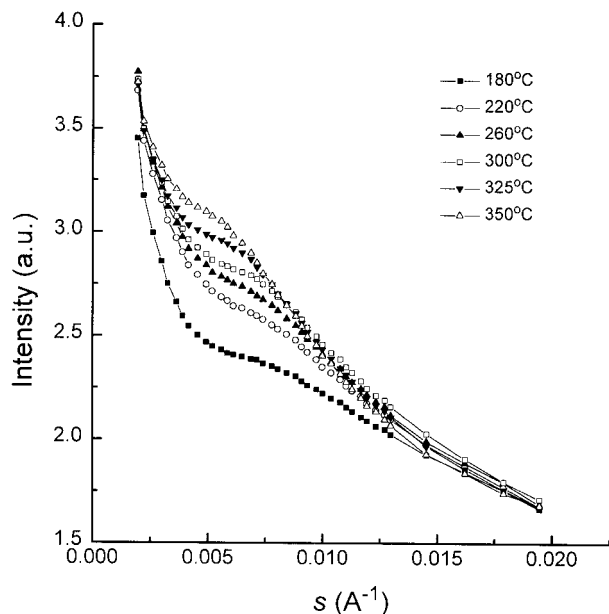


Figure 2 SAXS curves of scattering intensity (in arb units) versus scattering vector s for the isotropic PEEKK samples annealed at indicated temperatures for 1 h.

phology of PEEKK may be strongly dependent on the thermal treatment, and the resulting changes of the morphology from the thermal history may also influence the mechanical properties of PEEKK.¹⁶

SAXS reflects electron-density fluctuations within a sample over a length range larger than the usual interatomic distances. Semicrystalline PEEKK, which consists of a simplified two-phase system of alternating crystalline domains and an amorphous matrix, could be assumed to be a system with fluctuating electron density, and it should scatter X-rays. The SAXS curves of PEEKK annealed at various temperatures are shown in Figure 2. It could be seen that the scattering intensities increased gradually with increasing T_a , that is, the annealing temperature had a significant effect on the microstructure of PEEKK. The previous report revealed that the degree of crystallinity ($W_{c,x}$) of PEEKK is influenced by the annealing temperature and that the sample densities (ρ_s) and crystal densities (ρ_c) increase while increasing T_a (Table I).¹⁰ Taking into account the variability of the crystal density with the annealing temperature, the density difference between the crystalline and amorphous regions $\Delta\rho = \rho_c - \rho_a$ was not constant. Increasing T_a increases the moving ability of the molecular

chains of PEEKK, and some of the disordered molecular chains in the amorphous region were transformed and crystallized into the crystalline region. The result was that the density difference of the two phases increased with the annealing temperature.

The difference of electron density ($\eta_c - \eta_a$) can be calculated by¹⁷

$$\eta_c - \eta_a = \frac{Ze}{M} (\rho_c - \rho_a) \quad (\text{mol e cm}^{-3}) \quad (1)$$

where M is the molecular weight of the repeat unit, and Ze , the number of electrons outside of core per mole. The difference of the electron density also increases with T_a as in the case of $\Delta\rho$, due to the changes in density arising from the transformation of the amorphous phase into the crystalline one as T_a increases.

To demonstrate the alterations of the scattering intensities more clearly, the Lorentz-corrected curves of $I s^2$ versus the scattering vector s is illustrated in Figure 3. A strong increase of the overall intensity was observed with increasing annealing temperature. Additionally, the angle position of the maximum scattering peak was shifted to smaller values with increase of T_a , indicating an increase in the long period L , which could be calculated from the maximum peak using the Bragg equation (Table I). A similar effect of the annealing temperature on L was observed to that in the case of the density difference. Increasing annealing temperature was accompanied by an increase in the overall long period, on the one hand, presumably because it resulted in a melting out of some small and unstable crystallites and forced the crystal defects and chain ends to incorporate into the amorphous regions. On the other hand, it might be caused by the thermal expansion of the crystals and the amorphous regions. In referring to the value of the volume expansion coefficient ($1.65 \times 10^{-4} \text{C}^{-1}$) reported by Blundell and D'Mello for PEEK,¹⁸ the thermal expansion effect was estimated to be approximately 3–6% within the selected temperature region.

If the system is assumed to be a random heterogeneous system with particles of the same shape but different size and if there are no interparticle interferences or multiple scattering effects, on the basis of the Debye–Bueche theory,¹⁹ the scattering intensity $I(s)$ can be described as

$$I(s) = K\bar{\eta}^2 \int_0^\infty \gamma(r)r^2 \sin(sr)/(sr)dr \quad (2)$$

Table I Structural Parameters of the Aggregated State for PEEKK Annealed at Different Temperatures

T_a (°C)	180	220	260	300	325	350
ρ_s (g cm ⁻³) ^a	1.3046	1.3085	1.3143	1.3188	1.3200	1.3268
ρ_c (g cm ⁻³) ^b	1.3837	1.3906	1.3975	1.4006	1.4040	1.4070
$\rho_c - \rho_a$ (g cm ⁻³)	0.1132	0.1201	0.1270	0.1301	0.1335	0.1365
$\eta_c - \eta_a$ (mol e cm ⁻³)	0.0416	0.0441	0.0466	0.0478	0.0490	0.0501
$W_{c,x}$ (%) ^c	29.7	34.3	37.6	39.3	40.5	43.9
L (nm)	8.4	8.6	10.8	11.0	11.3	13.5
d (nm)	1.62	2.04	2.18	2.27	2.36	2.54
d_{tr} (nm)	0.46	0.45	0.41	0.36	0.49	0.50
$Q/10^3$ (mol e cm ⁻³) ²	2.9	4.8	5.1	5.8	6.1	6.3
O_s (nm ⁻¹)	0.238	0.232	0.185	0.182	0.177	0.148
$A/10^4$ (mol e cm ⁻³) ²	-1.53	-2.29	-3.07	-3.53	-3.94	-4.84

^a Measured by suspension method in an *n*-heptane/carbon tetrachloride mixed solution using a PZ-B-5 liquid-density balance.

^b Calculated from the unit cell parameters at various annealing temperatures.

^c Wide-angle X-ray diffraction (WAXD) results.

where K is a constant related to the incident X-ray intensity, the properties of the scattering system, and the Kratky camera; $s = 2 \sin \theta / \lambda$; η^2 is the mean-square fluctuation of the electron density at the characteristic length of the particles $r = 0$; and $\gamma(r)$ is the three-dimensional correlation function. If we assume that the variation of the electron density obeys a "linear model," that is, the density variations occur mainly along the di-

rection perpendicular to the lamellae, then we can use the one-dimensional electron-density correlation function (1D EDCF) for treating $K(Z)$, which can be written as

$$K(Z) = \langle [\eta(Z') - \langle \eta \rangle][\eta(Z + Z') - \langle \eta \rangle] \rangle \quad (3)$$

where Z is the direction normal to lamellar stacks and the angular brackets indicate averaging over all coordinate points Z' within a representative stack which will pass through an amorphous layer and a crystalline layer. $\langle \eta \rangle$ denotes the mean electron density. $K(Z)$ can be obtained by Fourier transformation of $I(s)$:

$$K(Z) = \int_{S_1=0}^{S_2 \rightarrow \infty} 4\pi s^2 I(s) \cos(2\pi s Z) ds \quad (4)$$

As an example, the derived typical 1D EDCF $K(Z)$ of the lamellar structure for PEEKK annealed at 350°C is demonstrated in Figure 4.

As we employed a simplified two-phase model to analyze the SAXS data, the long period L should be obtained as $L = l_c + l_a$; here, l_c and l_a are the thicknesses of crystal lamellae and the amorphous regions, respectively. But, according to the Babinet's principle, SAXS cannot determine which of the two phases (phase 1 with l_1 , phase 2 with l_2 , and $l_1 \leq l_2$) refers to the crystals and which to the amorphous phase. Recently, Cebe's research group reported that two different approaches had been followed in the assignment of the crystal thickness for PEEK.²⁰ Jonas et al.

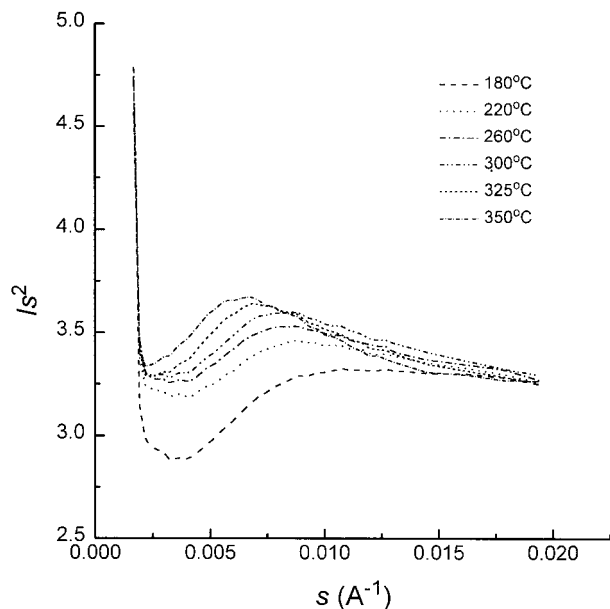


Figure 3 Lorentz-corrected curves of Is^2 versus scattering vector s for the isotropic PEEKK samples annealed at various temperatures.

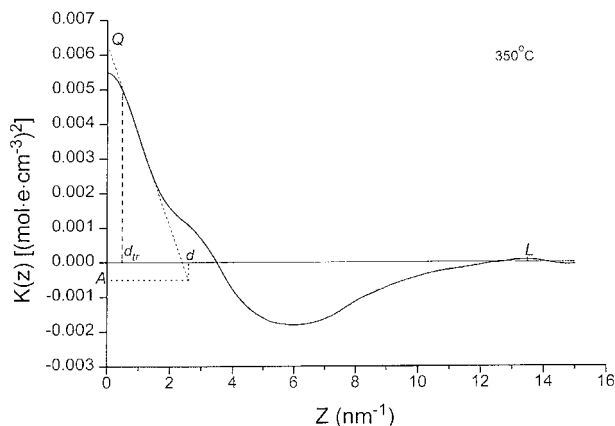


Figure 4 Representative analysis of the one-dimensional electron-density correlation function. The long period L , the average lamellar thickness d , and the thickness of transition zone d_{tr} are indicated on the abscissa. The invariant Q and the baseline coordinate A [calculated by using eq. (5)] are shown on the $K(Z)$ axis.

chose the shorter length for l_c in their SAXS studies, and they pointed out that for PEEK $l_c < l_a$ since the density of the amorphous phase within the semicrystalline sample, ρ_{ac} , is greater than that in the purely amorphous sample ρ_{a0} .²¹ The opposite choice, of a longer length for l_c , results in a lower amorphous phase density, $\rho_{ac} < \rho_{a0}$, which is not observed experimentally.²¹ Fougnyes et al. also chose l_c to be the shorter length, based on the temperature dependence of the longer and shorter lengths. Only the shorter length increases with annealing temperature.^{22,23} The opposite choice was made by Hsiao et al.^{24,25} In Cebe's work on PPS, they agreed with the former choice and assigned the minority fraction (shorter length, l_1) to the crystal lamellae.²⁰

Here, in the PEEKK system which was very similar to PEEK, since the crystallinity fraction $W_{c,x}$ was less than 0.5, the shorter length, l_1 , was chosen as the thickness of crystal lamellae, l_c . As Strobl et al. pointed out, if one wishes to investigate samples with $W_{c,x} > 0.5$, all the related equations mentioned above could be applied after making the following replacements²⁶:

$$W_{c,x} \leftrightarrow W_a = (1 - W_{c,x})$$

$$\eta_a \leftrightarrow \eta_c$$

In this case, the thickness of lamellae d (indicated in Fig. 4) denotes the number average over the

thickness of the amorphous layers. This evidently follows from the Babinet's reciprocity theorem.²⁶

A crucial point of this direct analysis lies in the required knowledge of the base line coordinate A of the self-correlation part, which can be calculated by¹⁷

$$A = -W_{c,x}^2 (\eta_c - \eta_a)^2 \quad (5)$$

Knowing this, from the well-known "self-correlation triangle" which reflects the electron-density correlation within a lamella, one can directly estimate various structural parameters of the aggregated state for PEEKK by making use of some general properties of the correlation function (Fig. 4).¹⁷ The long period L could be determined from the position of the first maximum in the correlation function. The average lamellar thickness d could be determined by the cross point of the baseline with the sloping line of the "self-correlation triangle." The invariant Q is the value of $K(Z)$ at $Z = 0$. The thickness of the transition layer d_{tr} was given by the lower limit of the straight section in the self-correlation range. The lamellar thickness showed an evident dependence on thermal history of the PEEKK samples. The annealing treatment probably enhanced the growth of secondary crystals which had a lower melting point than that of the major lamellae with a higher one (i.e., the so-called double-melting peak).⁶ With increase of the annealing temperature, the degree of crystallinity of PEEKK systematically increased and more perfect crystals were formed because of the rearrangement of the molecular chains and the improvement of the regularity of the chains between the major lamellae. It was the above-mentioned effect that made the annealing technique be widely used in the practical applications to accelerate the secondary crystallization during which the small and metastable crystals within the large lamellae undergo a reorganization and perfection process and cause the common lamellar thickening effect.

From the traditional "ideal two-phase model," the self-correlation section of the SAXS curve was expected to be a straight line. But, in fact, the deviation was usually observed in practical results (Fig. 4), indicating that the boundary between the crystalline and amorphous regions were not clear and sharp and there exists a transition zone with finite width instead of a sharp jump in density. By the curvature of the straight-line

segment in the central section of $K(Z)$, the thickness of the transition layer d_{tr} could be estimated (Fig. 4). At first, the thickness of the transition region gradually decreased with increasing T_a , then increased at T_a above 300°C (Table I). From the DSC curve of Figure 1, the melting range of PEEKK was approximately between 305 and 375°C. Indeed, although the thermal treatment at 325 and 350°C were well below the nominal melting point of PEEKK (360°C), a part of the small crystals already got into a premelting region as the annealing temperature approached the melting point, and some of unstable crystals within the lamellae might begin melting and enter the amorphous phase. This raised the degree of the disorder of the interphase between the crystalline and amorphous regions and might result in the broadening of the transition zone. Although the evaluation of crystallinity from the density data and the interpretation of the physical properties of the semicrystalline polymers were based on the two-phase structure model, the existence of the transition zone was powerfully proved by more and more experimental and theoretical results obtained from many polymer systems.^{27,28}

All these results are collected in Table I. From it, one can find that the thermal history had a strong influence on the structural parameters of the aggregated state of PEEKK. The invariant Q was evaluated by extrapolating the straight-line section of the self-correlation region to the $K(Z)$ axis (Fig. 4). Its physical meaning represented the mean-square electron-density fluctuation, which could satisfactorily explain the changing tendency of the values of Q considering the variation of the electron-density difference with the annealing temperature. The values of the specific inner surface are approximately given by $O_s = 2/L$.¹⁷ They decreased with increasing T_a , which might be tentatively interpreted as follows: Because of the increase of the crystallite size with increasing T_a , the degree of crystallinity increased and the number of particles in the unit volume decreased.

CONCLUSIONS

The structural changes of the aggregated state for PEEKK were studied using small-angle X-ray scattering and one-dimensional electron-density correlation function methods. The results indicate that the annealing temperature has a significant

effect on the structure of PEEKK. With increasing annealing temperature, the degree of crystallinity of PEEKK systematically increases and more perfect crystals are formed because of the rearrangement of the molecular chains and the improvement of the regularity of the chains between the major lamellae. As a consequence, the long period L , the average thickness of lamellae d , the electron-density difference between the crystalline and amorphous regions $\eta_c - \eta_a$, and the invariant Q increase with increase of the annealing temperature. But it is opposite to the case of the specific inner surfaces O_s , because the degree of crystallinity increases and the number of particles in the unit volume decreases due to increase of the crystallite size as T_a increases. There exists a transition zone between the traditional "two phases" with a dimension of about 0.5 nm for semicrystalline PEEKK.

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