Crystallization of poly(aryl ether ketones): 3. The crystal structure of poly(ether ether ketone ketone) (PEEKK)*

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The unit cell of poly(ether ether ketone ketone) was determined to be orthorhombic, as in other poly(aryl ether ketones). Comparing different poly(aryl ether ketones) it was found that the crystallographic parameters depend on the ether to ketone ratio. With increasing ketone content, the dimensions of the *a*-axis decrease, whereas the dimensions of the *b*- and *c*-axes increase. The volume of the unit cell also increases. It could be shown that the crystallographic parameters also depend on the annealing conditions. This implies a variation of the crystallographic density, which, surprisingly, depends only on the annealing temperature and not on the ether to ketone ratio. These phenomena can be explained by changes in the packing of the molecules in the crystalline regions, which obviously depend on the thermal history. This has an influence on the X-ray diffraction pattern but not on the enthalpy of fusion. Therefore, determination of the degree of crystallinity should be carried out preferably using differential scanning calorimetry.

(Keywords: poly(aryl ether ketone); crystallization; structure)

INTRODUCTION

Poly(aryl ether ketones) have been called high performance polymers as they exceed other thermoplastic polymers in their mechanical and physical properties as well as in their chemical resistance. Poly(ether ether ketone ketone) (PEEKK) is synthesized in a polycondensation process and has a chemical structure with a regular sequence of ether and ketone units, two at a time. Poly(aryl ether ketones) combine an extremely high thermal resistance up to 260°C with very good mechanical properties, i.e. an elevated Young's modulus and a high impact strength. A marked β-relaxation maximum at low temperatures enables the material to dissipate mechanical energy. A possible application is, for example, the spring suspension of valves in car engines.

PEEKK is a thermoplastic material with a melting point of 370°C and can thus be processed by conventional injection moulding machines, calenders or dies to moulded parts, films or fibres. Usually, the polymer is partially crystalline and depending on the processing conditions, the degree of crystallinity ranges between 0% and 40%. It is important to know the degree of crystallinity, as many properties, especially the mechanical ones strongly depend on it[1–4]. Consequently, we investigated the crystalline structure of PEEKK.

The family of aromatic polyarylates comprises, among others, poly(phenylene ether) (PPE), poly(ether ketone) (PEK), poly(ether ether ketone) (PEEK), or other combinations of ether and ketone units. In this paper, the crystalline structure of PEEKK will be investigated and compared to the structure of other polyarylates. Also, we will study phenomena which occur upon annealing.

EXPERIMENTAL

The various poly(ether ketones) are distributed by the following companies. PEK is a product of Raychem Inc. and has the tradename 'Stilan I'®. PEEK by the name of 'Victrex 380 G'® is synthesized by ICI. PEEKK is a product of Hoechst AG and available under the name of 'Hostatec'®. Finally, PEKEKK is a product of BASF and sold under the tradename 'Ultrapek'®. All the materials have similar molecular weight[5] of ~30 000.

Structural analysis was carried out mainly by wide-angle X-ray scattering (WAXS), using either a flat film camera or a Stoe transmittive goniometer. Highly oriented fibres were used to determine the unit cell and non-oriented quenched samples were taken for the thermal treatment of the different materials.

Thermal investigations were carried out using a Perkin–Elmer differential calorimeter (DSC 7).

RESULTS OF STRUCTURAL ANALYSIS

Determination of the unit cell

Polyarylates, such as PPE, PEK and PEEK have similar crystal structures[6–9]. They all crystallize in an orthorhombic lattice. The chains are aligned parallel to the *c*-axis of the unit cell, which is formed by two chains, one of them running through the centre of the cell and one at each of the four edges, shared by three additional neighbours each. The projection orthogonal to the *c*-axis is displayed in *Figure 1*.

Taking these results into account, it can be expected that PEEKK crystallizes in a similar way. To investigate this, highly oriented fibres were melt spun. *Figures 2* and *3* show an X-ray diffractogram perpendicular to the chain axis and its schematic representation, respectively.

In comparison to PEEK, the number of reflections of the partially crystalline PEEKK is extraordinarily high.

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* Dedicated to Prof. Dr. H. Cherdron on the occasion of his 60th birthday

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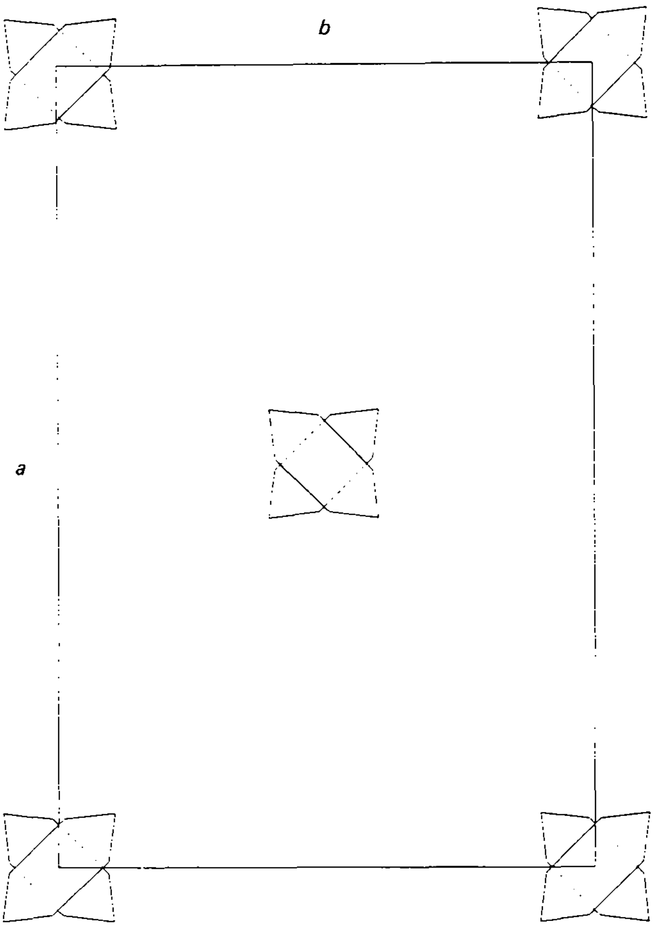

Figure 1 Crystal structure of polyarylates in a projection on the *a*-*b* plane

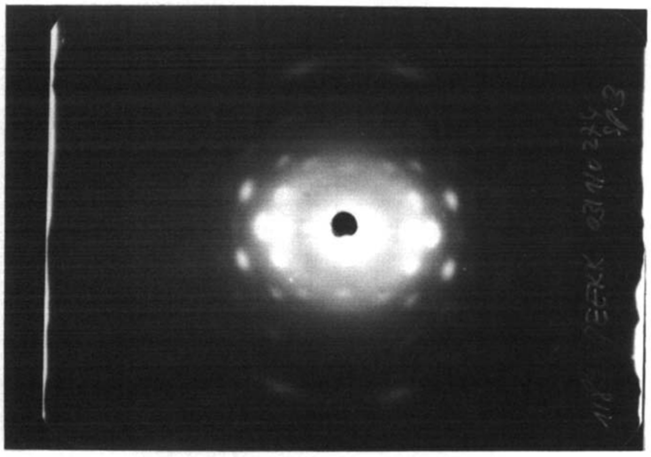

Figure 2 Flat-camera diffraction pattern of highly oriented fibres of PEEKK

The reflections are very sharp, indicating that the crystalline regions are very well aligned along the *c*-direction and also that a high perfection of the crystals is present. Furthermore, the number of detectable orders of the reflections is unusually high, in some cases up to four orders. Layer lines show up clearly on the meridian. This indicates a large extension of the crystals and a high perfection. This is confirmed by the low half value width of the reflections as measured by the goniometer traces.

The positions of the reflections on the flat film suggest an orthorhombic lattice. The corresponding higher orders of a reflection display a collinearity on a line perpendicular to the equator. Since orthogonality in reciprocal space means an orthogonal lattice, we can assume an orthorhombic lattice for PEEKK.

Table 1 displays all the reflections and their Miller indices as well as their intensities. It can be seen from *Table 1* that most of the reflections can be indexed. The dimensions of the unit cell have the following values: $a = 7.747$ Å, $b = 6.003$ Å, $c = 10.100$ Å. These values have been used to calculate the position of the reflections, where the (1 1 0), (2 0 0) and (1 1 1) reflections have been used as basic values. Their exact positions were determined in a goniometer trace of the equatorial reflections (cf. *Figure 4*). The observed and calculated positions of the reflections show very good agreement.

One reflection does not fit with this indexing. It is an equatorial reflection at a scattering angle of $s = 5.51$ Å. It can be concluded from the calculation of the various

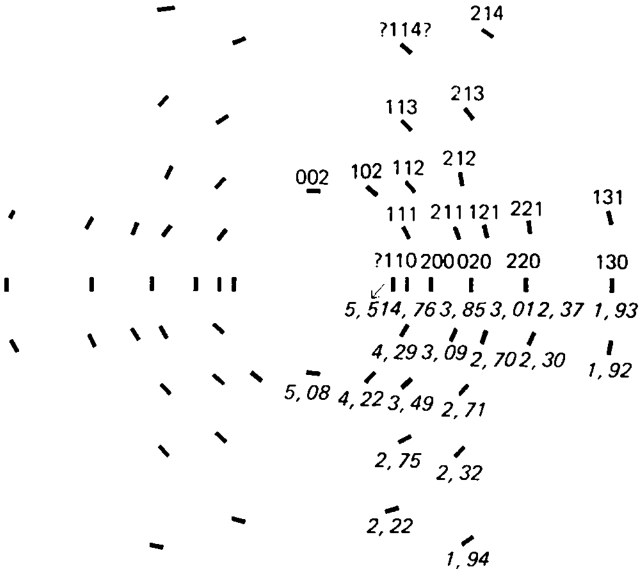

Figure 3 Schematic representation of *Figure 2*

Table 1 X-ray reflections of PEEKK

Reflection (*hkl*)	Calculated (Å)	Observed (Å)	Intensity[a]
110	4.75	4.76	vs
200	3.87	3.85	vs
020	3.00	3.01	w
220	2.37	2.37	vw
130	1.94	1.93	vw
111	4.29	4.29	s
211	3.10	3.09	ms
121	2.70	2.70	vw
221	2.31	2.30	vw
131	1.90	1.92	vw
002	5.05	5.08	ms
102	4.23	4.22	w
112	3.46	3.49	mw
212	2.74	2.71	vw
113	2.75	2.75	w
213	2.34	2.32	vvw
214	2.00	1.94	vw
x_1(114)	2.23[b]	2.22	ms
x_2(011)	5.16	5.51	w

[a] Very strong, vs; medium strong, ms; strong, s; medium weak, mw; weak, w; very weak, vw; very very weak, vvw

[b] Not collinear to 11*l*

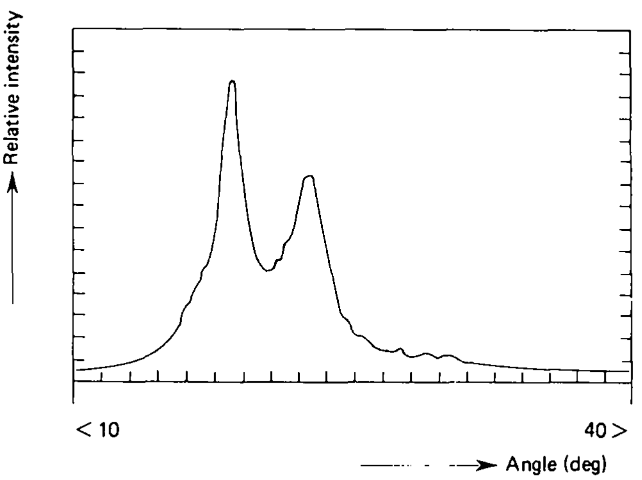

Figure 4 Goniometer trace of the equatorial reflections of PEEKK

reflections that there is no reflection with a similar s value. The only possible reflection in the vicinity of this value is the (0 1 1) reflection with $s = 5.16$ Å. This can be excluded as it is not within the maximum tolerable standard error. It should be mentioned in this context that such a reflection does not show up for PEK, PEEK or other poly(aryl ether ketones). We have to assume that it is an artifact due to sample impurity.

The analysis of the diffractogram displays a collinearity of the (1 1 0), (1 1 1), (1 1 2) and (1 1 3) reflections and orthogonality to the equator, following the rules of the scattering diagram of an orthogonal lattice in reciprocal space. This is confirmed by the fact that the (2 1 1), (2 1 2), (2 1 3) and (2 1 4) reflections can be found on a straight line. Slight deviations towards a hyperbolic shape on the right-hand side of the diffractogram are due to a small tilt of the angle between the fibre axis and the primary beam.

The (1 1 4) reflection, however, shows up slightly beneath the $11l$ line, which can also be found for the $(\bar{1}\ \bar{1}\ \bar{4})$ reflection. This can be explained as follows. The intensity of the reflection is only medium strong. With increasing layer line number, the curvature of the reflection is approaching the meridional direction and for that reason, a systematic error may arise in the determination of the centre of the higher order reflections. Slight deviations are therefore tolerable for the (1 1 4) reflection.

Another explanation is connected with the observation that the (1 1 4) reflection and the unknown reflection x_2 at an angle $s = 5.58$ Å are positioned on the same line. This leads to the assumption that the '(1 1 4)' reflection is of higher order than the first equatorial reflection. It is however very improbable that other orders of the reflection are missing but the fourth is present. Therefore we conclude that the assignment of the (1 1 4) reflection is correct.

Chemical structure and physical properties of poly(aryl ether ketones)

The crystalline structures of different poly(aryl ether ketones) display several similarities. Here we will evaluate some of the crystallographic properties that the materials investigated have in common; one of the properties is the orthorhombic lattice.

A projection of the molecules perpendicular to the chain axis, i.e. to the c-axis, is displayed in *Figure 1*. It can be assumed that the packing of the molecules is similar for PEEKK and for other poly(aryl ether ketones), such as PEK and PEEK, as described in the literature[6,9]. There are, however, some slight differences between each of these, as the monomer units differ in length and in the splay angle of the connecting oxygen (ether) or carbon atom (ketone), respectively. Thus the C–O bond of the ether has a length of 1.36 Å and the C–C bond has a length of 1.47 Å[6]. The bond angles are 124° for the ether unit and 126° for the ketone unit[10]. For that reason it is obvious that the molecular structure of the crystals is different from polymer to polymer and, as we will show later, depends on the ether to ketone ratio. In this sense the group of PEKs comprises PPE, having a ketone content of 0%, PEEK with a ketone content of 33%, PEK and PEEKK having 50% ketone each, and finally PEKEKK with a ketone content of 60%. In this way it is possible to connect the crystallographic parameters with the chemical composition of the material. This is shown in *Figure 5*, which was completed with values reported in the literature[7–9].

A definite trend can be seen. With increasing ketone content the length of the c-axis increases due to the ketone unit being longer than the ether unit. Furthermore, a variation in the basis of the unit cell can be seen. The length of the a-axis decreases, whereas the length of the b-axis increases. The result is an increase in the volume of the unit cell with increasing ketone content (*Figure 6*).

Using stoichiometrics, the crystallographic density was calculated and an astonishing result was found. Although the ketone content increased, the density remained constant within experimental error, as shown in *Figure 7*. It should be mentioned in this context, that in the literature somewhat differing values are reported for the crystallographic parameters[6–9]. We believe that this discrepancy may be due to different preparation techniques. Our investigations revealed that the crystallographic parameters depend strongly on the thermal history of the sample and on the annealing conditions.

A further property of the PEKs which depends on the ketone content is the melting point, which increases almost linearly (*Figure 8*). It is known that the ketone unit displays a more rigid behaviour than the ether unit. A consequence of this is an increase in the melting point. Similar behaviour could be observed in rigid rod-like molecules such as statistical copolymers containing p-hydroxybenzoic acid[11].

Comparison of the X-ray diffractograms

A goniometric trace of a non-oriented sample does not display the high resolution of a flat film diagram, but it allows accurate determination of the position and the intensities of characteristic reflections. The spectra of the different poly(aryl ether ketones), which are displayed in *Figure 9*, are very similar to each other and can be regarded as characteristic for PEKs. As a matter of course, the position of the reflections differ from one material to the other. *Table 2* gives an overview of the different materials and their structural parameters. The influence of the crystallization conditions cannot be excluded in this instance.

It is remarkable that the intensity of the (2 0 0) reflection increases with increasing ketone content. The ratio of the intensity of the (2 0 0) reflection to that of the (1 1 0) reflection increases linearly. This indicates a

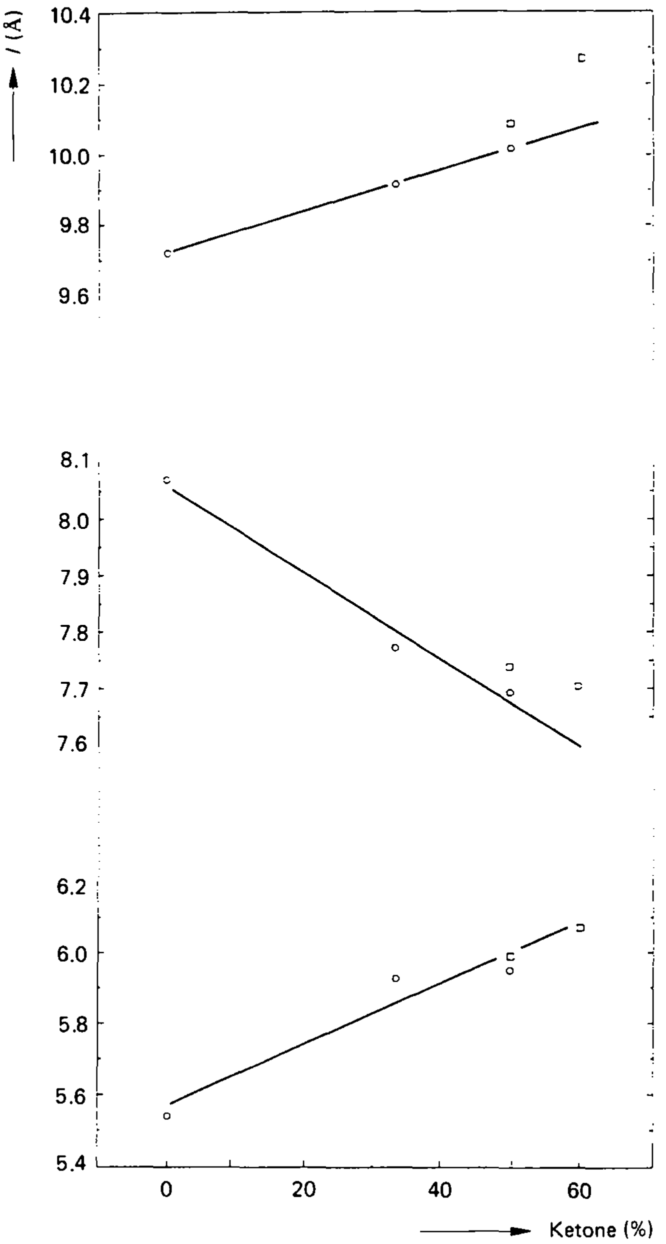

Figure 5 Crystallographic parameters of various polyarylates as a function of ketone content

variation in the shape of the crystallites. Obviously, there is a preferential growth in the '*a*' direction with increasing ketone content. Similar effects can be studied in ethylene–propylene copolymers.

Spherulitic morphology

In order to obtain some more information on the structure of PEEKK, we performed small angle X-ray scattering of highly oriented fibres using a Kiessig camera. The distance between the sample and the photographic film was 400 mm. The diffractogram is shown in *Figure 10*.

It can be seen that the small angle reflections are split up into a four point diagram which is rather diffuse. We concluded that the sample has a fibrillar structure with alternating crystalline and amorphous regions, which form lamellae. The long period was determined to be 85 Å. The fact that a clover leaf diagram is generated can be interpreted as a tilt of the lamellae from the direction perpendicular to the fibrillar axis, i.e. the *c*-axis, as in a herring-bone pattern.

The diffusivity of the reflections leads to the assumption that the arrangement of the crystalline and the amorphous regions is rather irregular, depending either on the distance of the lamellae from each other or the planarity of the lamellae. These phenomena are well known from other fibres, such as polyethylene and polypropylene[12,13].

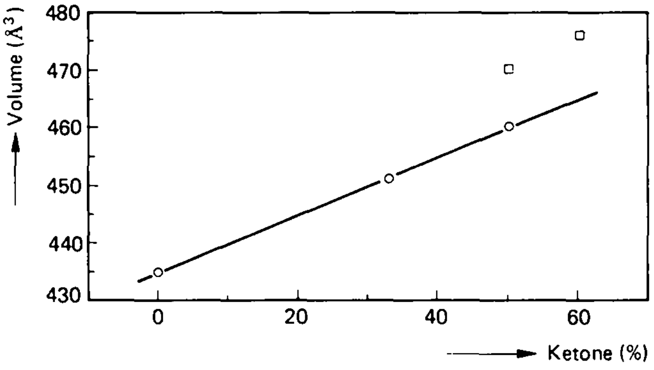

Figure 6 Volume of the unit cell of various polyarylates as a function of ketone content

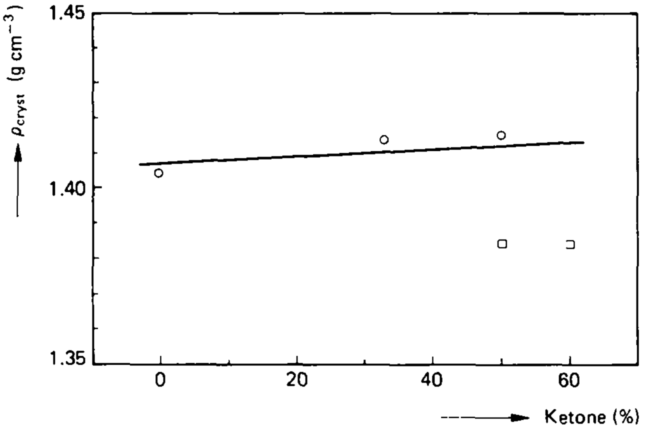

Figure 7 Crystallographic density of various polyarylates as a function of ketone content

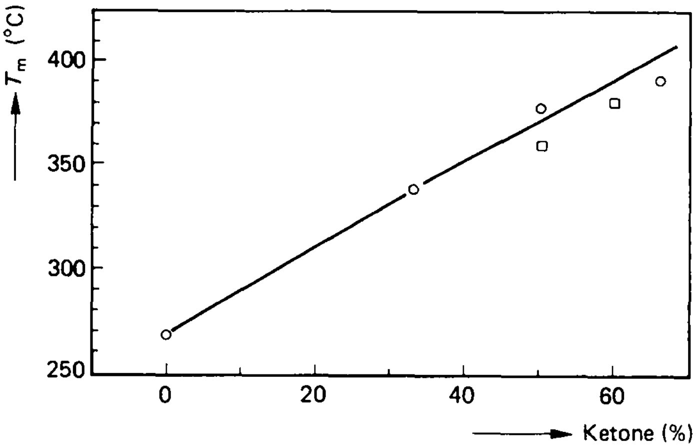

Figure 8 Melting temperature of various polyarylates as a function of ketone content

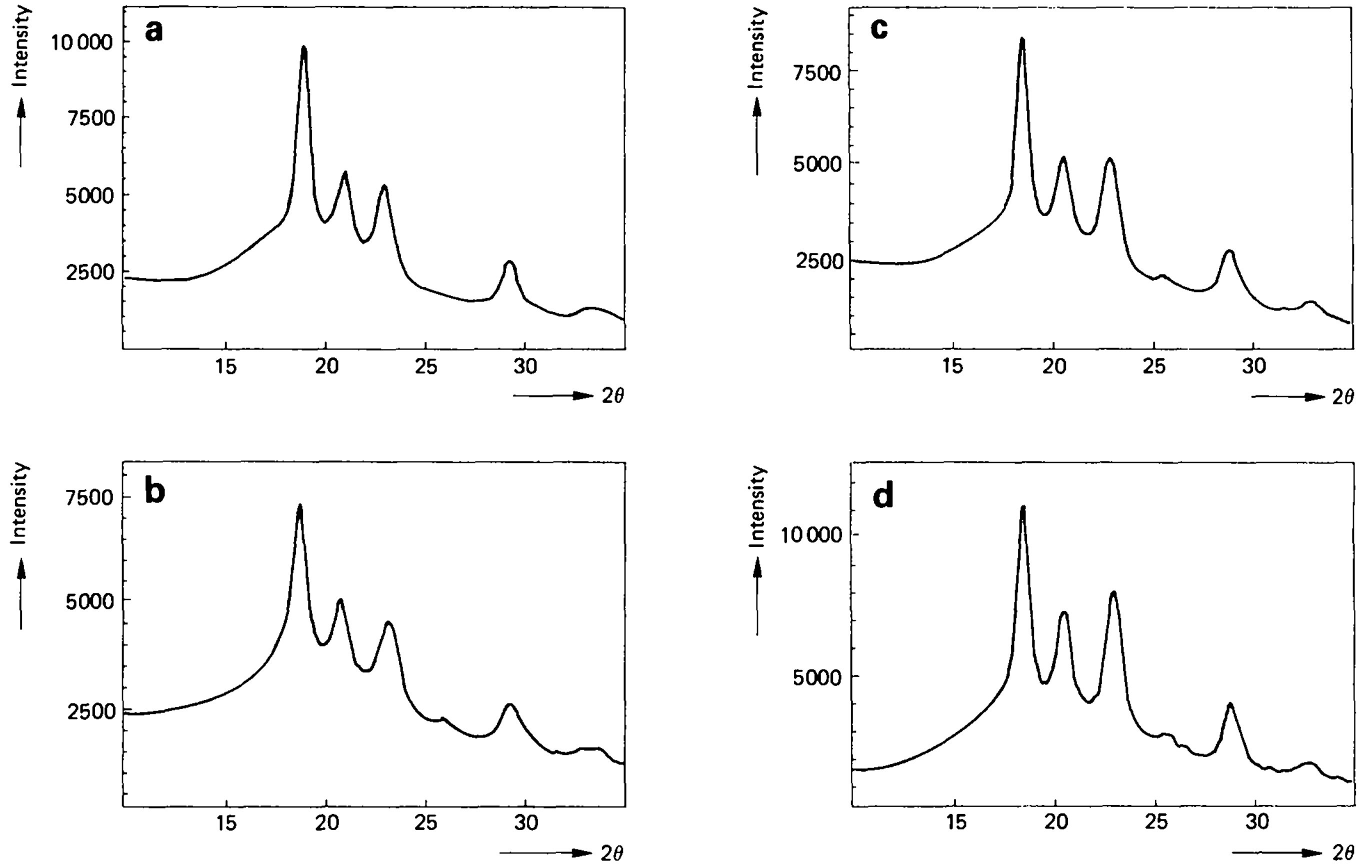

Figure 9 Wide angle X-ray scattering goniometer traces of PEEK, PEK, PEEKK and PEKEKK

Table 2 Unit cells of PPE, PEEK, PEK, PEEKK and PEKEKK

Parameter	PPE[8]	PEEK[6]	PEK[9]	PEEKK[a]	PEKEKK[a]
a-axis (Å)	8.07	7.75	7.70	7.75	7.71
b-axis (Å)	5.54	5.89	5.96	6.00	6.07
c-axis (Å)	9.72	9.88	10.03	10.10	10.27
Volume ($Å^3$)	435	451	460	470	476
Molar weight	368	384	392	392	397
Density ($g\,cm^{-3}$)	1.405	1.414	1.415	1.385	1.384

[a] Our measurements

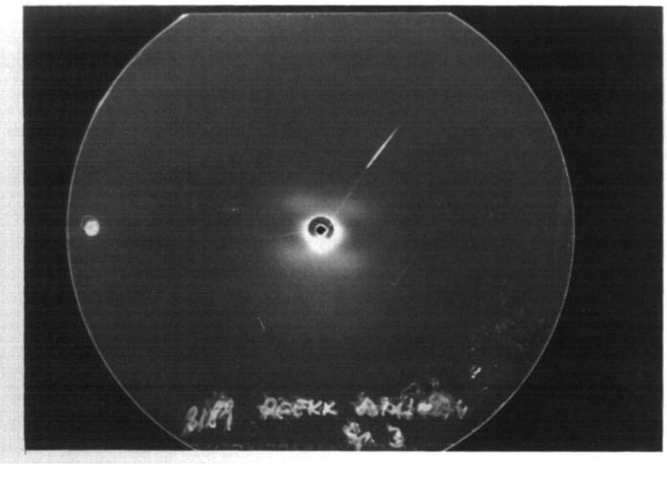

Figure 10 Small angle X-ray scattering diagram of PEEKK

STRUCTURAL CHANGES ON ANNEALING

Crystallographic parameters

In order to study the effects of annealing on the structure, samples were stored for 1 h at various temperatures above the glass transition temperature (T_g) and below the melting temperature (T_m). It is well known that the degree of crystallinity of partially crystalline polymers increases during this process. An increase in the relative intensity and a sharpening of the X-ray reflections confirms that postcrystallization processes have taken place.

Besides the change in the relative intensity, the X-ray reflections display a dislocation of their angular position towards larger angles with increasing annealing temperature. Wakelyn[14] has found a similar behaviour for PEEK. The shift in the X-ray reflections is not due to an extremely small crystallite size. Former investigations by

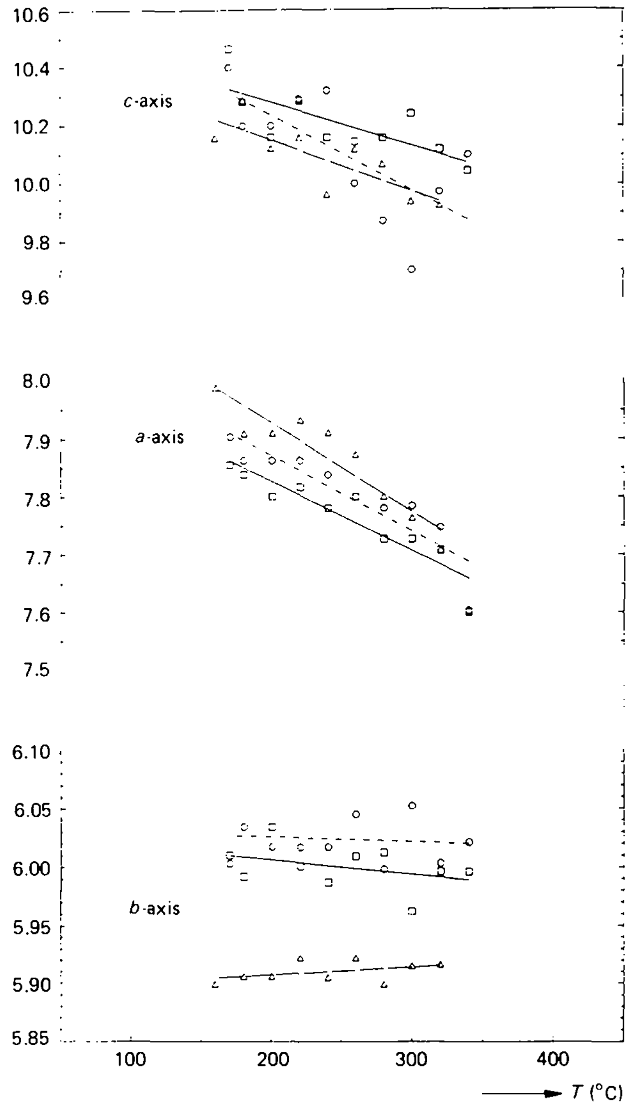

Figure 11 Lattice parameters as a function of annealing temperature for an annealing time of 1 h: (□) PEK; (△) PEEK; (○) PEEKK

Salem[15] on polyamide 6 revealed that a significant shift in the X-ray reflections arises only if the size of the crystallite comprises about five repeat units or less. The reflections of the PEKs studied here have a very small half value width which leads to the conclusion that the crystallite has at least 10 repeat units.

The reflections of every sample have been assigned and with the help of the Bragg equation, the crystallographic parameters a, b and c have been determined (*Figure 11*):

$$\frac{1}{d_{hkl}^2} = \frac{a^2}{h^2} + \frac{b^2}{k^2} + \frac{c^2}{l^2} \qquad (1)$$

An astonishing result was found. The dimensions of the unit cell vary with the annealing temperature. The lengths of the a- and c-axis decrease with increasing annealing temperature, whilst the changes for the c-axis are more pronounced than those observed for the a-axis. The b-axis length remains constant, however, with annealing. Our studies have shown that within standard error, these observations are similar in all the PEKs studied here, i.e. PEK, PEEK and PEEKK. A possible explanation for these phenomena is a change in the molecular arrangement of the crystal due to the elevated mobility of the molecules on annealing and a transition towards a more favourable packing. In the planar projection (cf. *Figure 1*) of the molecule perpendicular to the long axis it can be seen that the most hindered parts of the molecule are the ketone groups, as the double-bonded oxygen is directed orthogonal to the long axis of the molecule. A rotation of the molecule around the c-axis enables a configuration in which the ketone groups hinder each other the least. The consequence of this is that the bond angle of the carbon atom decreases and thus the length of the unit cell in the c-direction decreases. Simultaneously, the less hindered aggregation of the lateral oriented ketone groups evokes a shortening of the a-axis. It is very surprising that no variation in the length of the b-axis could be seen.

Having the values for a, b and c, we can calculate the volume and the density of the unit cell corresponding to every annealing temperature, as displayed in *Figures 12* and *13*. The result is that the volume decreases with increasing annealing temperature and thus the crystalline density increases. This trend is valid for all the PEKs investigated here. PEK and PEEKK have similar values but the values for PEEK are smaller. Disagreements with

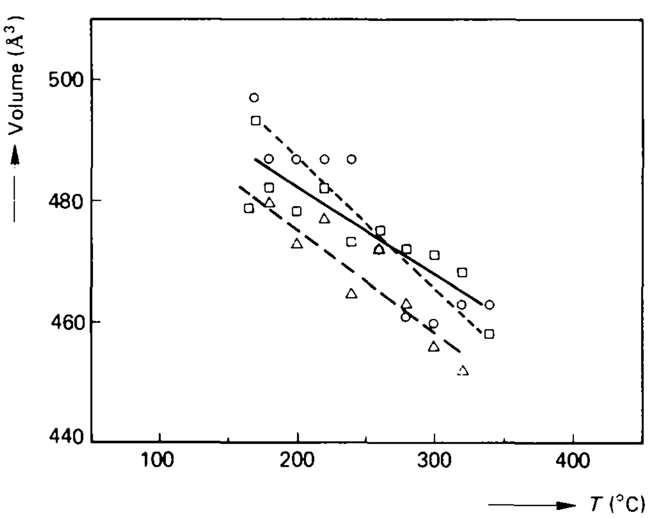

Figure 12 Volume of the unit cell as a function of annealing temperature for an annealing time of 1 h: (□) PEK; (△) PEEK; (○) PEEKK

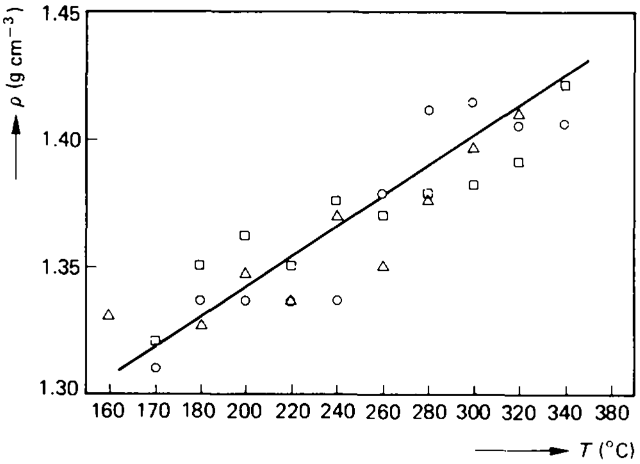

Figure 13 Crystallographic density as a function of annealing temperature for an annealing time of 1 h: (□) PEK; (△) PEEK; (○) PEEKK

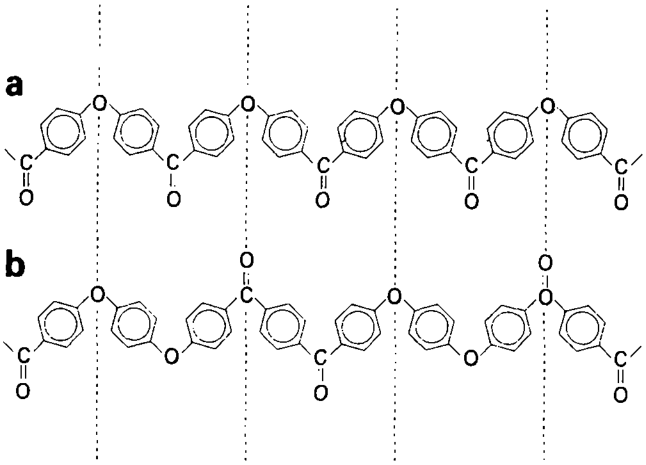

Figure 14 Planar projection (parallel to the molecule) of PEK (a) and PEEKK (b)

the values in *Table 2* can be explained by differences in the thermal pretreatment.

The crystalline densities increase for all the samples investigated and taking experimental errors into account, it can be seen that they are independent of the ketone content of the polymer. The crystalline density is determined only by the thermal history of the sample. This is in agreement with the results described above.

Within experimental error, the unit cell volume of the various annealed samples of PEK and PEEKK are comparable. There are however differences in the dimensions of the axes of the unit cell. In the case of PEEKK, the values for the *a*- and *b*-axes are larger and the values for the *c*-axis are smaller than in the case of PEK. A consequence of this is a difference in the extension of the basis area (cf. *Figure 11*).

An explanation for this can be found using a projection of the molecules parallel to the *c*-axis, as shown in *Figure 14*. Although the ketone content of PEK and PEEKK is identical, the molecules differ with respect to their chemical structure. It is clear from the projection that ketone groups alternate 'up' and 'down' in the case of PEEKK as in syndiotactic polymers but not in the case of PEK as in isotactic polymers. It is evident that crystallization occurs readily in the case of the isotactic arrangement, whereas a certain selectivity is needed for the syndiotactic version. From the space filling molecular model it could be seen that PEEKK cannot become 'isotactic' without deviating from the linear aspect of the molecule which is needed for crystallization to occur. Therefore, one can assume that the ketone groups are hindering each other in the crystal, leading to an increased basis area in the case of PEEKK.

It can be generally assumed that an annealing process taking place at a certain temperature is subject to the laws of kinetics. Therefore it can be expected that a variation in the annealing time has an influence on the crystallographic parameters of the sample, too. A similar phenomenon could be detected with liquid crystalline polymers[16]. It is evident that the annealing process is a step towards equilibrium because it is irreversible and takes place spontaneously.

Degree of crystallinity

All of the quenched samples were amorphous as judged by WAXS. By means of differential scanning calorimetry (d.s.c.), however, recrystallization is indeed observed just above T_g but the crystallization enthalpy was $\sim 10\ \mathrm{J\ g^{-1}}$ lower than the heat of subsequent melting. Thus, d.s.c. indicates the existence of some crystallinity within the quenched sample. This result is independent of the heating rate, i.e. there is no influence of recrystallization during heating of the sample.

The increase in annealing temperature of the poly(aryl ether ketones) in *Table 3* results in a continuous increase in crystallinity as obtained by WAXS which flattens off on annealing closer to the melting point. In contrast, the heat of fusion as measured by d.s.c. initially remains almost constant and then increases slightly when the annealing temperature approaches T_m. Additionally performed density measurements essentially confirm the d.s.c. results.

The contradictory degree of crystallinity results of the quenched samples from WAXS and d.s.c. or density measurements may be explained by assuming the formation of very small disturbed crystallites having a very broad distribution with respect to their size or perfection. These crystal nuclei are not detected by WAXS since the absolute degree of crystallinity is $< 10\%$ and the reflections are expected to be very broad. On heating the quenched samples for d.s.c., recrystallization occurs just above T_g where the particular crystallization temperature is determined by the heating rate. The recrystallization enthalpy, however, remains almost independent of the heating rate. The crystals formed by this recrystallization will melt together with the already existing nuclei which recrystallize continuously below the melting point leading to a continuous perfection of crystals. The resulting final T_m depends only on the ether to ketone ratio. The heat of fusion is found to be ~ 35–$40\ \mathrm{J\ g^{-1}}$ for all investigated poly(aryl ether ketones) irrespective of the particular type of the polymer.

During annealing the recrystallization occurs isothermally and the increase in the degree of crystallinity as obtained from WAXS according to the above model may be explained by melting and recrystallization of an increasing portion of the lower end of the crystal distribution with increasing annealing temperature resulting in bigger crystals which are detectable by WAXS. The crystal distribution above the annealing temperature is not affected and thus may not be recorded by WAXS. From the above recrystallization model, however, the d.s.c. results include the crystallinity above the annealing temperature as well. Therefore, d.s.c. sums up the whole region below T_m and thus yields a constant crystallinity. A slight increase in the crystallinity is found only on annealing just below the melting point. Therefore, the correlation between WAXS, and d.s.c., crystallinity will be better the higher the annealing temperature.

By this reasoning, the calculation of the heat of fusion of a completely crystalline poly(aryl ether ketone) from the degree of crystallinity measured by WAXS and the melting enthalpy as observed by d.s.c. yields a meaningful result only after annealing at relatively low undercoolings. At lower annealing temperatures the heat of fusion values are too high for the completely crystalline material because of the inaccurately low crystallinity values measured by WAXS.

The heats of fusion of the completely crystalline polymers estimated according to this scheme are nearly the same for all poly(aryl ether ketones) investigated. The

Table 3 Degree of crystallinity and heat of fusion of isothermally annealed poly(aryl ether ketones)

Annealing temp. (°C)	Degree of cryst. (via WAXS), x_c (%)	Heat of fusion ΔH_m (J g^{-1})	ΔH_m^c (J g^{-1})	Degree of cryst. (via d.s.c.) x_c (%)
PEEK				
Quenched	0	8.5	-	6.5
160	14	39.3	280	29.8
180	21	37.0	176	28.0
200	20	38.3	191	29.0
220	20.5	37.1	181	28.1
240	23.5	37.6	160	28.5
260	27	36.4	135	27.6
280	31.5	42.5	135	32.0
300	32	42.2	132	32.0
320	10	13.2	132	10.0
PEEKK				
Quenched	0	10.7	-	8.6
170	17	38.1	224	30.7
180	18	39.4	219	31.8
200	18.5	36.5	197	29.4
220	24	39.0	162	31.5
240	24.5	38.9	158	31.4
260	29.5	45.3	153	36.5
280	33	42.8	130	34.5
300	36	44.3	123	35.7
320	37.5	46.7	124	37.7

calculated quantity of 130 J g^{-1} corresponds to the value published for PEEK[17].

CONCLUSIONS

The investigation of different poly(aryl ether ketones) has revealed a variation in the crystallographic parameters as a function of the thermal history of the sample. The consequence is a variable crystalline density. Therefore, a measurement of the macroscopic density of the sample does not allow the determination of the degree of crystallinity. Other polymers with flexible chains do not show this behaviour, as the crystallographic density remains constant on annealing, assuming that a change in crystal modification is not involved.

Similar differences can be seen in WAXS curves and from d.s.c. Obviously the different packing of the unit cells mainly influences the intensities of the X-ray reflections. They do not affect the heat of fusion values. Therefore, determination of the degree of crystallinity should be carried out preferably using d.s.c.

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