Variation in unit cell parameters of aromatic polymers with crystallization temperature[*]

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Several excellent crystallographic analyses of poly(ether ether ketone) (PEEK) have been reported but variations in the measured unit cell dimensions have been noted which are considered to be outside experimental error. Because of the importance of the unit cell dimensions in determining the crystalline density and in particular in measuring the degree of crystallinity we have repeated these studies with corrections for sample transparency (absorption coefficient) and geometry and with allowance for random errors. A statistical analysis has been carried out on the effect of each of these and this confirms that the unit cell dimensions are dependent on crystallization temperature. Similar studies on poly(ether ketone) (PEK) do not follow this trend, although this polymer has a similar crystallographic unit cell. Defects within the crystal structure of PEEK, such as mismatch of adjacent chains, might be expected to occur at low crystallization temperature, but this is not considered to be the reason for the observed dependence. Instead, differences in packing and variations in the angle between the plane of adjacent phenyl groups is considered to be responsible.

(Keywords: poly(ether ether ketone); poly(ether ketone); unit cell dimensions; crystallinity; X-ray transparency; absorption coefficient)

INTRODUCTION

A number of structure determinations have been carried out on poly(ether ether ketone) (PEEK). Dawson and Blundell[1] and Hay *et al.*[2] measured the unit cell dimensions of unoriented polymer, while Ruedo *et al.*[3] used drawn material. All three quote different values for the unit cell dimensions (*Table 1a*). These differences are not systematic, and exceed the expected errors of such determinations. Furthermore, similar studies on poly(ether ketone) (PEK)[1,4] do not show these differences (*Table 1b*). A recent paper by Wakelyn[5] highlights these anomalies with PEEK in that he observed that the unit cell dimensions appear to vary with crystallization temperature (*Table 1c*). However, he offered no explanation for the observation and indeed did not consider experimental accuracy. Accordingly, it is still uncertain if these variations are due to differences in experimental procedures used by the various authors, or to differences in the sample geometry, such as warping on cooling.

In this work, the unit cell dimensions of PEEK have been determined as a function of crystallization temperature and also degree of crystallinity in order to determine the size of the variations. Several sources of error have been considered to determine if they could account for the observed differences, and a comparison has been made with PEK to test the generality of the effect with another polymer which could be crystallized over a wide temperature range. Finally, various structural models were considered to test if they could account for unit cell variations.

EXPERIMENTAL

Moulded sheets, 1 mm thick, were prepared from PEEK moulding powder as described elsewhere, and quenched from the moulding temperature in ice/water[6]. The sheets were shown to be amorphous by differential scanning calorimetry and wide angle X-ray scattering. Samples were annealed at various temperatures for 1 h.

Accurate peak positions were determined by using a Picker automated powder diffractometer with a step-scan interval of 0.10° (2θ). The diffractometer was calibrated

Table 1 Unit cell parameters

(a) PEEK

a (nm)	*b* (nm)	*c* (nm)	Ref.
0.775	0.59	1.0056	1
0.7781±0.0009	0.5922±0.0010	1.0056±0.0014	2
0.775±0.001	0.589±0.001	0.9883±0.005	3
0.783±0.002	0.594±0.001	0.986±0.004	11

(b) PEK

a (nm)	*b* (nm)	*c* (nm)	Ref.
0.765±0.001	0.597±0.001	1.009±0.002	4
0.763	0.596	1.00	1

(c) PEEK – crystallization temperature dependence, after Wakelyn[5]

Temp. (°C)	*a* (nm)	*b* (nm)	*c* (nm)
189	0.7843	0.5937	3.0074
216	0.7844	0.5912	3.0138
241	0.7845	0.5906	2.9858
264	0.7787	0.5855	3.0210
282	0.7769	0.5857	3.0376
306	0.7741	0.5848	3.0050
323	0.7733	0.5844	3.0013

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with a quartz standard and used as described elsewhere[2,4].

RESULTS

Scattered intensities were measured as a function of Bragg angle, 2θ, for various polymers prepared by annealing at a range of temperatures from 180 to 320°C. The scattered intensity from an amorphous sample was scaled according to the crystallinity of the sample and subtracted from the crystalline pattern. The program PROFIT[7] was used to determine the positions, widths and intensities of all peaks of the pattern. The difference plot shows that this procedure was successful, as can be seen from *Figure 1*.

The crystallinity, X, of the samples was determined by two methods. (1) From WAXS using the relative areas under the crystalline peaks, A_c, and amorphous background, A_m, using,

$$X_x = (1 + A_m/A_c)^{-1} \tag{1}$$

(2) From the measured densities of the samples, ρ_{obs}, since

$$X_d = (\rho_{obs} - \rho_a)/(\rho_c - \rho_a) \tag{2}$$

where ρ_c and ρ_a are the crystalline and amorphous densities.

The cell dimensions were determined by using Cohen's least squares method[8] to minimize $\Delta\sin^2\theta$ and hence $\Delta\theta = \theta_{obs} - \theta_{calc}$. The least-square parameters for samples crystallized at different temperatures and for different degrees of crystallinity are listed in *Table 2*. Nine reflections were used in these calculations, namely 110, 111, 200, 211, 020, and the partly resolved doublets, 212 and 121, and 302 and 023. The progressive decrease in all three dimensions, a, b and c, can be seen from *Figure 2*. The only exception was for the sample crystallized at 250°C – all the values obtained at this temperature were anomalous. The sample annealed at this temperature was obtained by heating rapidly from below the glass transition temperature and some crystallization may have occurred on heating through this temperature range, especially since it contained the region of maximum crystallization rate. A second sample was prepared by quenching from above the melting point to 248°C directly. The data for this sample have the same temperature dependence as for the other samples. Furthermore, cell dimensions determined by Hay *et al.*[2] for a sample annealed at about 200°C correspond to a temperature of 205°C in *Figure 2*.

The following corrections were made.

Sample transparency

Careful measurements were made of sample thickness, to determine if there was any sample distortion on cooling. Small differences were observed between samples but these were taken into account in subsequent analyses. The linear absorption coefficient, μ, for CuKα radiation was the same for all samples, to within experimental error, i.e. $0.651 \pm 0.006\,\text{mm}^{-1}$. Peak shifts due to the transparency of the sample to X-rays will be appreciable. A correction for transparency was made by taking into account the effective volume of the specimen at each diffraction angle[9].

Other systematic errors

There is clearly a reduction in volume of the unit cell as the annealing temperature increases, but transparency does not entirely remove systematic errors, as can be seen from the sum of the residuals $\delta\ (= 1/d_{cal}^2 - 1/d_{obs}^2)$ in *Table 3*. A possible cause of the residual error is a shift

Table 2 Unit cell dimensions as a function of crystallization temperature (this work)

Sample	Temp. (°C)	a (nm)	b (nm)	c (nm)	V_c (nm^3)
1	184	0.7852(23)	0.5921(29)	0.998(10)	0.464(4)
2	217	0.7828(15)	0.5900(19)	0.995(7)	0.470(3)
3	248	0.7775(12)	0.5882(15)	0.990(4)	0.453(2)
4	250	0.7857(17)	0.5924(22)	0.998(7)	0.464(3)
5	303	0.7724(6)	0.5869(7)	0.989(3)	0.448(1)
6	323	0.7707(5)	0.5875(7)	0.990(2)	0.448(1)

Temperature dependence of cell dimensions:

$$a = (-1.12 \pm 0.23) \times 10^{-4}\,T + 0.808 \pm 0.006\ \text{nm}$$
$$b = (-0.35 \pm 0.08) \times 10^{-4}\,T + 0.599 \pm 0.002\ \text{nm}$$
$$c = (-0.66 \pm 0.10) \times 10^{-4}\,T + 1.011 \pm 0.003\ \text{nm}$$
$$V = (-0.12 \pm 0.02) \times 10^{-3}\,T + 0.488 \pm 0.006\ \text{nm}^3$$
$$a/b = -0.11 \pm 0.03 \times 10^{-3}\,T + 1.35 \pm 0.02$$
$$c/b = 1.686 \pm 0.001$$

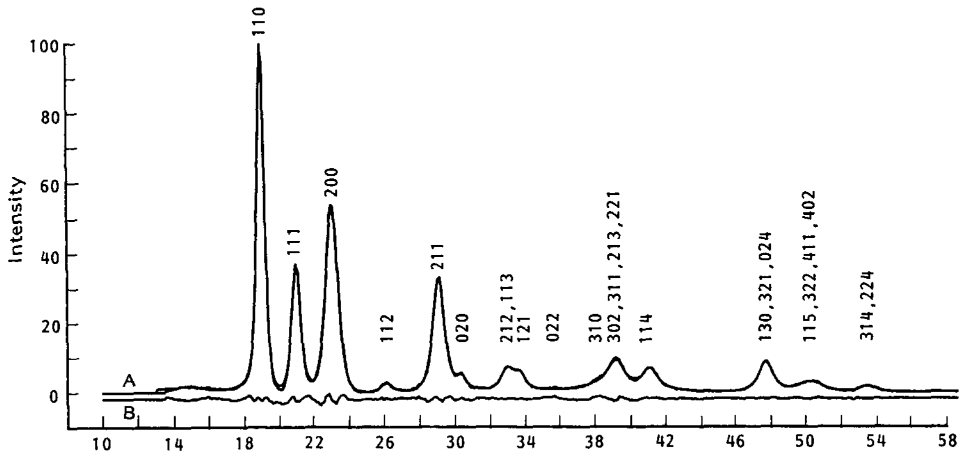

Figure 1 A, X-ray diffractogram of PEEK after subtraction of the amorphous background, for sample 5 crystallized at 308°C. B, Difference between calculated and observed diffractogram

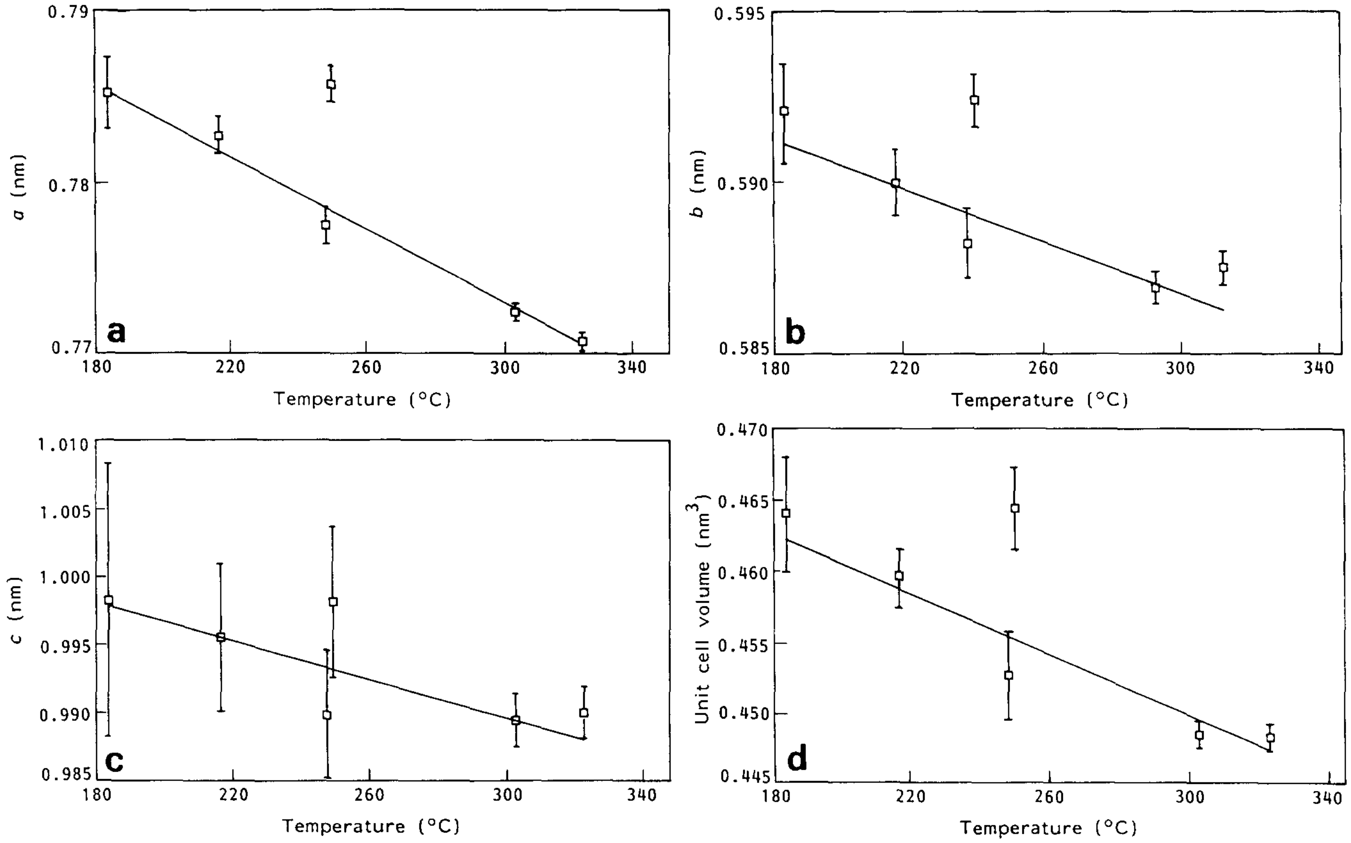

Figure 2 Variations in unit cell dimensions of PEEK with crystallization temperature: (a) *a*; (b) *b*; (c) *c*; (d) unit cell volume

Table 3 Effect of corrections to cell volume, *V*

	Method 1		Method 2		Method 3	
Ref.	*V* (nm^3)	$\sum\delta\times10^6$	*V* (nm^3)	$\sum\delta\times10^6$	*V* (nm^3)	$\sum\delta\times10^6$
1	0.4630	1.54	0.4683	1.43	0.4659	0.04
2	0.4743	0.10	0.4610	0.02	0.4610	−0.01
3	0.4668	0.41	0.4499	0.57	0.4509	−0.02
5	0.4537	1.25	0.4487	1.40	0.4505	0.10

Method 1, uncorrected output from PROFIT
Method 2, after correcting for transparency
Method 3, with $\cos\theta\cot\theta$ extrapolation term in the refinement

displacement of the sample surface from the diffractometer axis. This introduces an error in peak position which varies as $\cos\theta$. Inclusion of an extrapolation function varying as $\cos\theta\cot\theta$ (reference 10) which makes allowance for this effect in the refinement gave consistent results and the residual systematic error is reduced considerably; see *Table 3*. The resulting cell volumes then vary linearly with temperature and are similar to those quoted by Wakelyn[5]. It should be noted that the use of the extrapolation procedures in determining accurate cell dimensions is normally applicable to reflections at high angles which are not available with polymers. In this instance residual systematic errors are therefore reduced, but not removed completely.

Size effects

All the diffraction lines were an order of magnitude broader than the line profiles due solely to the instrument. This is due to the imperfect structure of crystalline PEEK. PROFIT gave reliable peak widths for strong 110, 111 and 211 reflections for all the samples. The width did not vary continuously with angle and depended on *hkl*, but for a given reflection is decreased with increasing annealing temperature. The shape of the line profile was also considered. These were characterized by the parameter $\phi = \mathrm{FWHM}/\beta$, where FWHM is the full width at half the maximum intensity and β, the integral breadth, is the width of a rectangle with the same area and height as the peak. For all the samples and temperatures ϕ was essentially constant, and equal to 0.843 ± 0.008. This value is intermediate between the Lorentzian and Gaussian limits[11]. For the above reflections the form of the line profiles was independent of *hkl* and temperature. This behaviour suggested that crystallite size or an analogous effect is the dominant cause of line broadening and that the shape of the crystallites is similar at different annealing temperatures. An apparent size, *E*, the volume average in a direction perpendicular to the diffracting planes was calculated from β, by means of the Scherrer equation

$$E = \lambda/(\beta\cos\theta)$$

Values of *E*, given in *Table 4*, are of the order of 10 nm and increase with crystallization temperature. Also, the size in the 110 direction is greater than in 111 or 211.

DISCUSSION

There is a progressive change in the unit cell dimensions with crystallization temperature, since none of the corrections eliminates this trend. This is summarized in *Table 2*. However, there is no change in the linear X-ray

Table 4 Apparent crystallite size and crystallinity

	Apparent size E (nm)			Crystallinity (%)		
	hkl					
Sample	110	111	211	X_x	X_d[a]	[b]
1	8.7	6.6	7.1	15	13	14
2	9.0	7.0	7.2			
3	10.4	7.5	7.3	25	24	20
4				24	18	15
5	11.8	10.0	8.8	28	39	26
6				29	44	28

[a] From corrected ρ_c
[b] From ρ_c reference 2

Table 5 Unit cell parameters for PEK

Crystallization temperature (°C)	Unit cell parameters a (nm)	b (nm)	c (nm)
160	0.776±0.003	0.590±0.004	0.995±0.006
260	0.778±0.003	0.602±0.004	0.999±0.007

absorption coefficient of the samples, either as a function of crystallinity or with increasing annealing temperature. From the measured change in unit cell dimensions there is an increase in density over the temperature range of about 4%. This suggests that the mass absorption coefficient must decrease by the same amount, and for this to occur the contents of the unit cell must change, as well as its size. Some re-arrangement of atoms within the cell must occur.

As well as crystallite size increasing with crystallization temperature, crystallization rates normally decrease or fewer disordered regions become incorporated within the crystallites. Several types of disorder can be considered.

(1) *Crystal thickness effects.* Molecular segments emerging from the surface of the crystal must have some lateral alignment but would be expected to have a different crystallographic structure from the bulk. They will contribute to the average unit cell dimensions but their contribution will decrease as the crystal size increases. As can be seen above, crystal size increases and unit cell volume decreases as the temperature increases. However, if this is a possible explanation it should be observed with all polymers which crystallize with a lamellar structure and especially with those which can be crystallized over a wide temperature range. Accordingly, PEK was crystallized at two temperatures separated by 100°C, see *Table 5*. There was no trend in crystallographic dimensions with crystallization temperature, and the unit cell volume was essentially constant. The effect is clearly associated with PEEK and not PEK.

(2) *Chain packing.* Disorder can be introduced into the packing of the chains by the misalignment of adjacent molecular chains. The similarity of the Pbcn space group and unit cell dimensions with poly(phenylene oxide), PPO, has been used to suggest a planar zigzag conformation of the phenylene oxide/carbonyl units as a model for the chain conformation of PEEK. The *c*-axis repeat unit in PEEK, PEK and PPO requires that the crystallographic repeat unit, however, involves two aryl rings, while the chemical one in PEEK requires three. Symmetry requires that the crystallographic repeat unit involves six aryl rings and a *c*-axis repeat unit of about 2.95 nm (*Figure 3*). The absence of weak reflections corresponding to this separation suggests a disordered structure in which the ether and ketone units are crystallographically equivalent. This can arise from the irregular stacking of adjacent chains with no register of the carbonyls with one another, and the repeat distance is based on the two aryl units in the planar zigzag (*Figure 3*). However, if this were the explanation for the observed increase in unit cell dimensions the 003 intensity would be expected to develop with increased crystallization temperature. Furthermore, the progressive change in crystallographic dimensions due to the insertion of carbonyl units between ether links, that is from PPO, to PEEK to PEK, leads to a decrease in the *a*-axis dimension, but an increase in the *b*- and *c*-axes (*Figure 4*). Clearly, the trend in two and the opposite trend in one is inconsistent with the decrease observed with all three dimensions, if the improved register of adjacent carbonyl units is to be used as an explanation for the observed temperature dependence. The expansion of the *c*-axis can be attributed to differences between the carbonyl, C–C–C, and the ether, C–O–C, chain angles, and the *b* axis to the interactions between the carbonyl units as shown in *Figure 4*. The arrangement of neighbouring chains from one of random stacking to one in which the chains are stacked more perfectly cannot account for the decrease in the *a*-, *b*- and *c*-axes with crystallization temperature.

There is, however, another source of distortion in the packing of the molecular chains. It has normally been observed that the phenyl groups are at a torsional angle to the plane of the chain, and a single torsional angle alone is sufficient to account for this. The torsional angle corresponds to the tilt of the phenylene group out of the 100 plane[6]. For PEEK, we have recently determined this to be 40.0±0.1° for $a=0.778$, $b=0.592$ and $c=1.006$ nm,

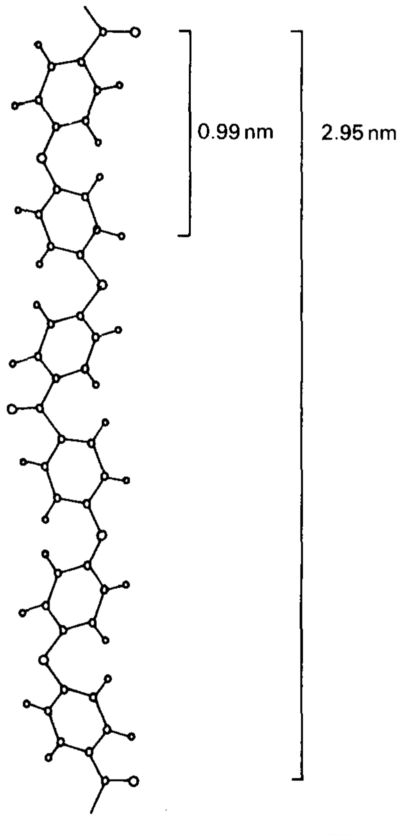

Figure 3 Crystallographic pseudo repeat unit of PEEK

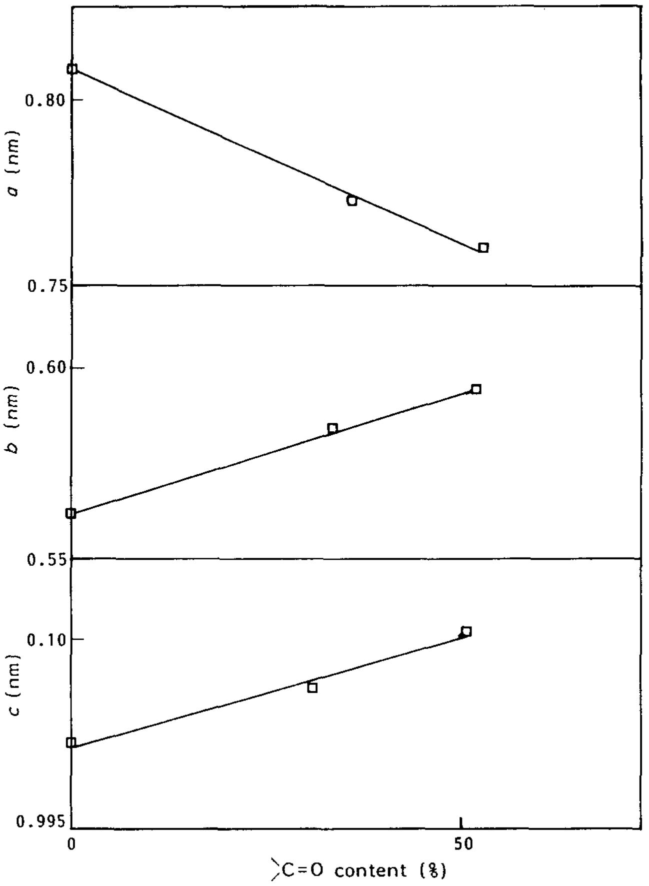

Figure 4 Variation in unit cell dimensions with increasing carbonyl content of the chain for PPO, PEEK and PEK

while Fratini *et al.*[12] have redetermined it as 37° for $a = 0.783$, $b = 0.594$ and $c = 0.986$. The rotational angle for PEK was found to be $34.0 \pm 0.6°$ [7] and for PPO $40 \pm 1°$. The mean ether and carbonyl bond angles for the observed c dimension are 124° for PPO, 126.5° for PEK and 124.6° for PEEK. These are greater than the expected value (120°) and suggest that packing interaction within the crystal reduces the out-of-plane rotation of the phenylene groups, increasing the steric repulsion between the hydrogen atoms in the *ortho* position. This repulsion is relieved by distortion of the ether and carbonyl bonds. Semi-empirical molecular orbital calculations on a monomeric model, i.e. diphenyl ether, benzophenone and phenylenexy-1,4-phenylene carbonylphenylene, have been carried out[13,14]. These indicate that there is a close agreement between c-axis dimension and torsional angle in PEEK, and the small differences observed are due in part to small differences in torsional angle and chain bond distortion. Increasing the crystallization temperature increases the torsional angle and decreases the chain bond distortion with subsequent shortening of the c-axis and closer packing along the a- and b-axes. Separating the effects due to packing disorder between the chains and variations in the torsional angle would be difficult.

CONCLUSIONS

The unit cell dimensions of PEEK have been observed to decrease systematically with increasing crystallization temperature. This is not due to a variation in crystallite size with crystallization temperature since PEK does not exhibit any dependence of unit cell volume on temperature. Instead, these variations are considered to be due to changing disorder in the lateral packing of the molecular chains and in particular to variations in the torsional angle of the phenylene groups about the c-axis. Steric effects of the adjacent *ortho*-hydrogen atoms increase the carbonyl and ether chain angles, and increase the c-axis dimension.

The implication of the effect is, however, quite important, since the crystalline density is dependent on the crystallization temperature, and allowances should be made for this in calculating the degree of crystallinity by means of the density.

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