Variations in the crystal lattice of PEEK and related *para*-substituted aromatic polymers:
1. Thermal expansion

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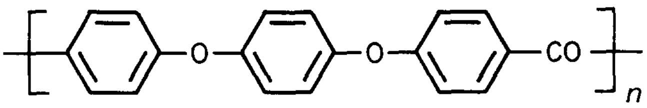
Uniaxially oriented films of PEEK have been examined by X-ray diffractometry over the temperature range 20 to 290°C in order to determine the expansion of the crystal lattice. The *a* and *b* lattice parameters were measured from equatorial scans using the 110, 200 and 020 reflections and the *c* parameter from meridional scans using the 002 reflection. The expansion rate in the *a* direction is about three times that of the *b* direction, while the change in *c* is almost negligible. Close to the T_g at around 145°C, there is an increase in the expansion coefficient of *a* and a reduction in the *b* coefficient. The overall expansion of the cell volume is essentially linear with a volume expansion coefficient of 1.65×10^{-4}°C^{-1}.

(Keywords: PEEK; crystal lattice expansion; expansion coefficients)

INTRODUCTION

The semicrystalline aromatic polymer PEEK, with the formula:



is gaining in recognition as a high performance thermoplastic. Quite apart from its industrial interest, its crystalline structure has aroused comment on account of variations in the lattice. There is a very close similarity in the crystal cells of PEEK and the related polymer PEK, indicating that the ether and ketone links can be interchanged with very little disturbance to the lattice[1,2]. This raises the possibility of random stacking of ketone and ether links of neighbouring chains in the crystal[1,3]. There have also been observations that the lattice dimensions depend on thermal crystallization history[4,5].

This present series of two papers provides further observations concerned with variations in the crystal lattice. Part 1 describes the use of an X-ray diffraction hot stage to study the reversible thermal expansion behaviour of the cell when the polymer is heated up to its melting point. Part 2[6] examines how the lattice and, in fact, the crystal structure changes when the sequence and proportion of the ether and ketone links are varied. Both parts use a common approach in monitoring the lattice dimensions. Both utilize samples of polymer film that has been uniaxially drawn so that the key (*hkl*) reflections can be readily observed with equatorial and meridional X-ray diffraction scans.

In order to study the reversible thermal expansion of the unit cell, it is important to avoid the effects due to crystallization history already alluded to above[4,5]. The oriented polymer sample was therefore annealed at 325°C which is close to the melting point of about 335°C. This enabled the crystals to stabilize before examination in the X-ray hot stage.

In discussing the PEEK cell, we will refer to the effective orthorhombic sub-cell which is now generally accepted by most workers[1,3,7,8]. This cell involves a pseudo chain repeat of about 10 Å which corresponds to two phenyl groups rather than the six phenyl rings that would be needed to encompass a full spatial chemical repeat. The sub-cell repeat thus refers to an average spatial repeat for two phenyls averaged over all the ether and ketone links.

EXPERIMENTAL

Materials

ICI's 'Victrex' PEEK was extruded onto a cooled metal roller to give an amorphous unoriented film. The film was then uniaxially drawn at 149°C to a draw ratio of 3:1 and then annealed under constraint at 325°C for 18 h. The final film thickness was 80 μm.

X-ray hot stage

The film sample was examined in the transmission mode using copper K_α with a Philips vertical goniometer to which was attached a thermostatically controlled hot stage. The hot stage consisted of an insulated brass block with cut channels for the insertion of the sample and the passage of X-rays. For equatorial scans the sample was inserted with the draw direction along the goniometer axis and with the plane of the film perpendicular to the incident beam. For the meridional scans the sample was inserted with the draw axis perpendicular to the goniometer axis and with the plane of the film tilted 9° away from the position perpendicular to the beam. This

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optimizes the collection of intensity from the 002 reflection which occurs at $2\theta \simeq 18°$.

The samples were dusted with silicon powder to provide an internal calibration for the 2θ scale from the 111 silicon reflection. Corrections for the 111 spacings were made according to reference data[9]. Previous tests were carried out with fine thermocouples inserted between polymer films in order to derive a correction for the temperature lag between the sample and the hot stage block.

Collection of data

The sample was examined at several fixed temperatures between room temperature and 300°C. Diffraction scans were obtained at each temperature over the range $10 < 2\theta < 35°$ using a 1/6° divergent slit and a 4° receiving slit. Philips APD software was used to define the positions of the major diffraction peaks.

RESULTS AND DISCUSSION

Examples of the equatorial scans are shown in *Figure 1*. The three main *hk0* polymer reflections are 110 at around 19°, 200 near 23° and 020 near 30°. The sharper reflection at $2\theta = 28°$ is the 3.138 Å 111 silicon reflection. The shift in the polymer peaks to lower angles with increasing temperature is clear, particularly for the 200 peak. Corresponding examples of the meridional scan are shown in *Figure 2* with the 002 reflection near 18°. There is little shift with temperature in these cases. All of these shifts of peak positions were reversible on cooling back to room temperature.

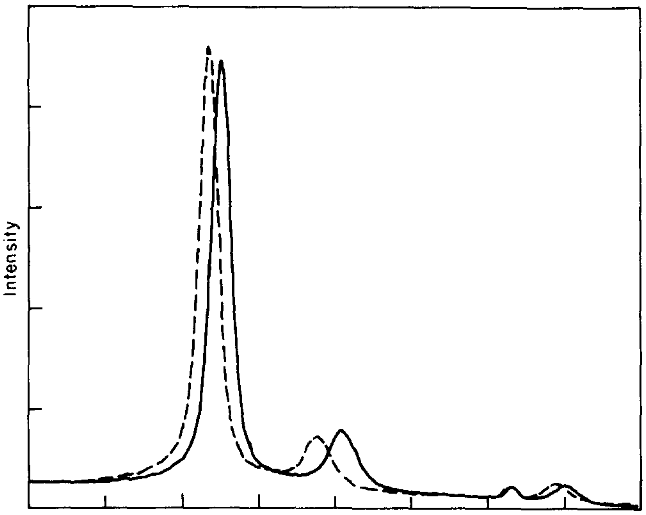

Figure 1 Equatorial scans obtained at ———, 19° and - - -, 291°C

Tables 1 and *2* show the *d* spacing for the relevant (*hkl*) reflection, and the corresponding *a*, *b* and *c* lattice parameters deduced respectively from the (200), (020) and (002) spacing. As an internal consistency check, these *a* and *b* parameters were used to predict the 110 spacing based on the assumption of an orthorhombic cell. The agreement of this prediction with that measured from the observed (110) is well within experimental error.

Plots from the tabulated data are shown in *Figures 3* and *4*. It is clear that the lateral expansion of the unit cell is predominantly in the *a* direction, the percentage change being about three times that in the *b* direction.

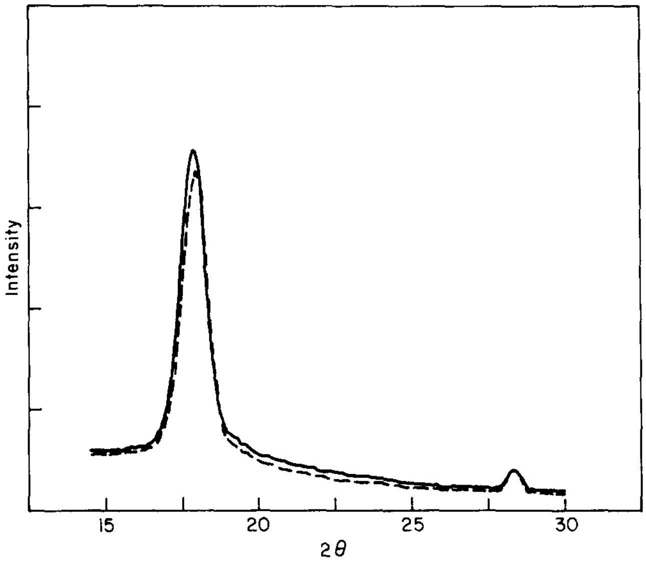

Figure 2 Meridional scans obtained at ———, 19° and - - -, 291°C

Table 2 Data from meridional scans, in Angstrom units

Temperature, °C	Bragg spacing 002	*c* parameter
19	4.939	9.878 ± 0.03
97	4.931	9.861
145	4.939	9.878
193	4.928	9.856
242	4.928	9.856
267	4.928	9.856
291	4.928	9.856

Table 1 Data from equatorial scans, in Angstrom units

Temperature, °C	Observed Bragg spacings			Predicted (110) spacing	Lattice parameters *a*	*b*
	110	200	020			
19	4.695	3.883	2.955	4.704	7.767 ± 0.015	5.911 ± 0.01
97	4.723	3.917	2.966	4.729	7.834	5.932
145	4.743	3.936	2.977	4.748	7.872	5.953
193	4.755	3.962	2.980	4.763	7.924	5.959
242	4.778	3.994	2.982	4.779	7.987	5.965
267	4.786	4.004	2.986	4.788	8.008	5.973
291	4.798	4.024	2.987	4.797	8.048	5.975

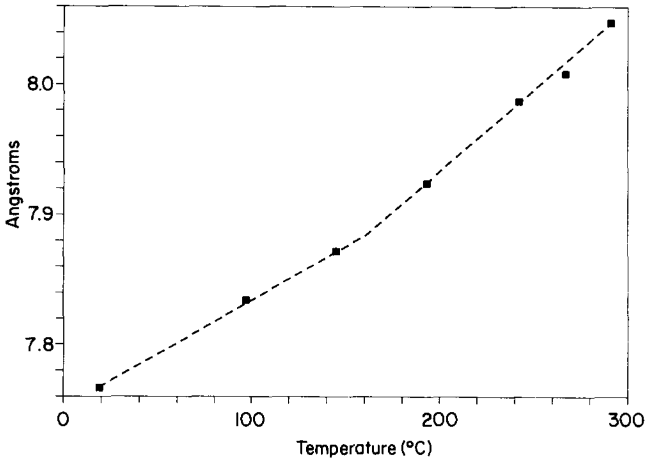

Figure 3 Variation of a lattice parameter with temperature

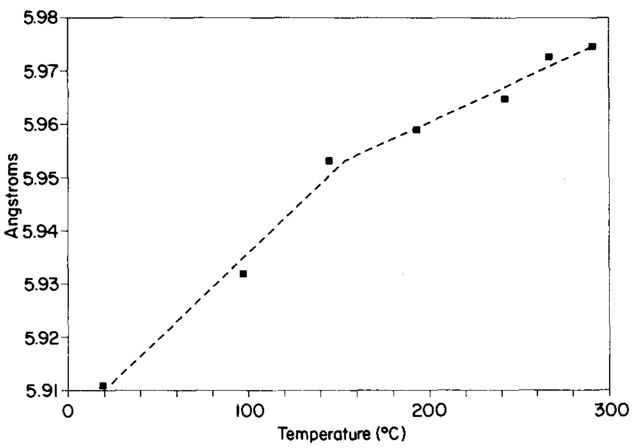

Figure 4 Variation of b lattice parameter with temperature

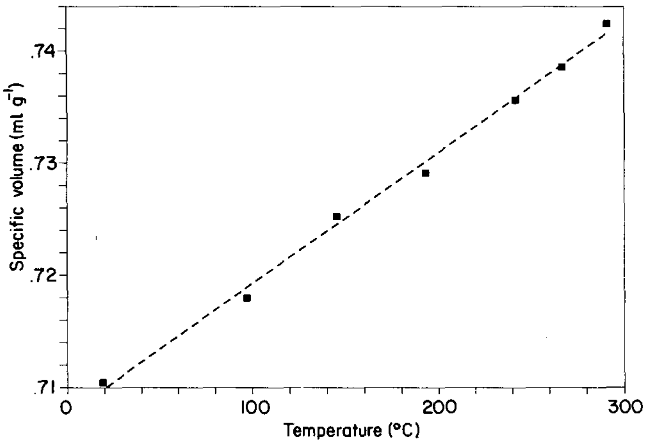

Figure 5 Variation of crystal specific volume with temperature

There is a barely significant shrinkage in the c chain direction, perhaps no more than 0.2% change over a 250°C temperature rise.

The changes in a and b are not smoothly linear over the whole temperature range. There are small deviations at about 150°C to a higher rate of expansion in a and a lower rate of expansion in b. We believe it is significant that this occurs near to the glass transition. If one disregards these changes in slopes around 150°C, then linear regression analysis gives the overall expansion behaviour to be:

$$a = 7.7359(1 + 1.33 \times 10^{-4}\, T)$$

$$b = 5.9109(1 + 0.391 \times 10^{-4} T)$$

Figure 5 shows the result of combining the lattice parameter data to calculate the specific volume of the crystal cell assuming the accepted orthorhombic sub-cell structure. The positive and negative changes in the rate of expansion of a and b at around 150°C appear to have cancelled out their effect to give an almost linear change in volume with temperature. This volume data can be fitted by a linear regression analysis to the expression:

$$V_c = 0.7076(1 + 1.65 \times 10^{-4} T)\ \mathrm{ml\ g^{-1}}$$

This volume expression is based on a c parameter that has been derived from the 002 reflection. There is a small inconsistency between the group of stronger $00l$ reflections which is difficult to reconcile[6]. The 006 and 008 both indicate a c parameter which is about 1% higher than that deduced from the 002. If we were to take the 006 and 008 values rather than the 002 value, then the crystal specific volume expression would need to be increased accordingly.

This expression for V_c and in particular the volume expansion coefficient of $1.65 \times 10^{-4}\ \mathrm{deg}^{-1}$ differs significantly from the recent results of Zoller *et al.*[10], who find an expansion coefficient of $2.54 \times 10^{-4}\ \mathrm{deg}^{-1}$. It is difficult to propose an explanation. Zoller *et al.* used an unoriented sample of PEEK rather than an oriented film. We have, however, repeated our experiments with a thin unoriented film and find that the 200 reflection changes in an identical fashion to that of the oriented sample, including the deviation in the behaviour at the glass transition temperature.

As is to be expected, the thermal expansion of the cell is predominantly in the a and b directions perpendicular to the chains which are governed by weaker intermolecular forces. The approximately three times greater expansion rate in the a direction is an indication that the interchain forces are weaker in this direction. The change in the linear expansion rates at the glass transition is presumed to be the result of the onset of mobility of the amorphous regions surrounding the crystals imposing a change in stress on the crystals. It is interesting to note how the change in the expansion rates of the a and b directions are compensated so as to maintain a smooth continuity in the expansion of the overall volume.

CONCLUSIONS

The thermal expansion of the PEEK crystal lattice occurs predominantly perpendicular to the chain, with the expansion rate being about three times greater in the a direction than the b. A change in the rate of expansion occurs around the T_g, with the a direction showing a slight increase in the expansion rate and the b direction showing a compensating decrease. The overall cell volume increases linearly with temperature up to 300°C with a volume expansion coefficient of $1.65 \times 10^{-4}\ \mathrm{deg}^{-1}$ and does not exhibit a change in expansion rate at the T_g.

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REFERENCES

1 Dawson, P. C. and Blundell, D. J. *Polymer* 1980, **21**, 577
2 Rueda, D. R., Ania, F., Richardson, A., Ward, I. M. and Balta Calleja, F. J. *Polym. Commun.* 1983, **24**, 258
3 Fratini, A. V., Cross, E. M., Whitaker, R. B. and Adams, W. W. *Polymer* 1986, **27**, 861
4 Wakelyn, N. T. *J. Polym. Sci., Polym. Lett.* 1987, **25**, 25
5 Hay, J. N., Langford, J. I. and Lloyd, J. R. *Polymer* 1989, **30**, 489
6 Blundell, D. J. and Newton, A. B. *Polymer* 1990, **31**, 308
7 Wakelyn, N. T. *Polym. Commun.* 1984, **25**, 306
8 Hay, J. N., Kemmish, D. J., Langford, J. I. and Rae, A. I. M. *Polym. Commun.* 1984, **25**, 175
9 'International Tables for X-ray Crystallography', Kynoch Press, Birmingham, Vol. III, 1962, p. 126
10 Zoller, P., Kehl, T. A., Starkweather, H. W. and Jones, G. A. *J. Polym. Sci. Polym. Phys.* 1989, **27**, 993