The crystal structure of poly(ether ketone) copolymers

D. J. Blundell* and V. Bayon
ICI Wilton Research Centre, PO Box 90, Wilton, Middlesbrough, Cleveland TS6 8JE, UK
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The morphology of isothermally crystallized samples of two copolymers of poly(ether ketone) (PEK) has been examined using X-ray diffraction and differential scanning calorimetry (d.s.c.) techniques and compared with that of the PEK homopolymer. One copolymer contains 15 mol% of aryl ether sulfone (ES) units, whose homopolymer, 'PES', does not normally crystallize. The second copolymer contains 33 mol% of ether biphenyl ether ketone (EDEK) units, whose homopolymer, 'PEDEK', does crystallize. The crystal structure of PEDEK has a close resemblance to that of poly(ether ether ketone) (PEEK) and has a unit cell with $a = 7.72$ Å, $b = 5.94$ Å and $c = 37.5$ Å. Both the ES and EDEK copolymers have a depressed T_m and reduced crystallinity. D.s.c. scans of both copolymers and PEK show a small low-temperature endotherm about 20°C above the crystallization temperature, together with an almost invariant final endotherm. At lower crystallization temperatures, the EDEK copolymer can show an additional middle endotherm at 315°C, which is associated with the melting of an EDEK lattice, which is then replaced by a higher-melting EK lattice. The formation of the EDEK structures is difficult to reproduce and indicates a competition in the kinetics of nucleation of the crystals. The ES copolymer crystallizes over the middle of the crystallization range with an EK cell consistent with exclusion of ES units. However, in the lower- and higher-temperature regions there is a change in the diffraction, indicating an association of the ES units with the crystals. At lower temperatures the ES copolymer can also show a middle d.s.c. peak.

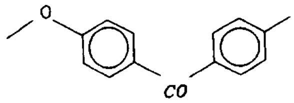
(Keywords: poly(ether ketone); differential scanning calorimetry; wide-angle X-ray scattering; copolymers; non-crystallizable comonomer; crystallizable comonomer; crystal structure)

INTRODUCTION

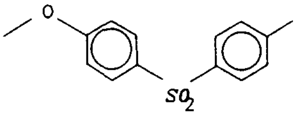
Aryl ether ketone polymers such as poly(ether ketone) (PEK) and poly(ether ether ketone) (PEEK) are of interest as tough high-temperature thermoplastics. The properties of these polymers can be modified by varying the ratio of ether/ketone groups[1]. The conformations of the crystalline chains around the ether and the ketone links are very similar, so that this form of modification has very little effect on the crystal structure[2] and morphology[3]. The main effect is on the glass transition temperature and melting point, which increase systematically with increasing ketone content[4].

An alternative approach to property modification of thermoplastics is to copolymerize comonomer units whose shape and conformation are incompatible with the crystalline conformation of the parent homopolymer and are thus excluded from the crystal lattice. This can reduce the crystallinity and crystal lamellar thickness and depress the melting point. The rejection of the comonomer units into the amorphous regions can also modify the glass transition.

This paper is concerned with copolymers based on the polymer PEK, where the notation E and K refers to the ether and ketone links between phenyl rings:

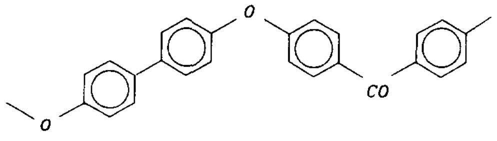


Two contrasting copolymers are considered. The first uses a sulfone-containing comonomer, which will be denoted as ES and has the structure:



The ES unit has a preferred conformation that is not compatible with the normal crystal lattice of PEK; the bond angle at the sulfone is significantly smaller and the bordering phenyls are torsionally rotated perpendicular to the plane of the sulfone bond[5]. The homopolymer PES formed from 100% ES units is totally amorphous.

The second copolymer contains the comonomer denoted as EDEK, where D represents a biphenyl unit:



Although this unit can easily adopt conformations around the E and K links that are the same as those of PEK, the extra length of the unit precludes it fitting into the PEK lattice. Nevertheless, when crystallized as the regular homopolymer PEDEK, the polymer can crystallize readily into its own unique lattice. In this copolymer there is therefore the potential for sequences of EDEK units to come together to form a competing crystal to that of PEK.

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* To whom correspondence should be addressed

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Only one copolymer of each type is described here. The compositions that have been chosen are those which give a similar melting-point depression relative to PEK. The paper is particularly concerned with the crystal morphology of the copolymers. The study involves characterization by d.s.c., WAXS and SAXS of samples that have been isothermally crystallized. Parallel observations are made on control samples of homopolymer PEK. In order to clarify some of the observations, the paper also presents crystal structure data on the homopolymer PEDEK.

EXPERIMENTAL

The ES copolymer contained 15 mol% of ES units relative to EK. An analysis by ^{13}C n.m.r. indicates that ES units occur randomly in the chain.

The EDEK copolymer contained 33 mol% of EDEK units relative to EK. However, in this case, ^{13}C n.m.r. does indicate a small degree of clustering of EK units into EKEK diads.

The two copolymers and a control PEK homopolymer were compression moulded into sheets about 250 μm thick and quenched into a cold water bath to form amorphous samples. Smaller pieces were cut from the sheet and were clamped lightly in a preheated press at various temperatures for 1 h to allow the sample to crystallize isothermally. *Table 1* lists the samples prepared. The time of crystallization was chosen on the basis of preliminary isothermal d.s.c. experiments to be suitable to complete the primary crystallization process at the temperatures. For the ES copolymer sample crystallized at 320°C, it was judged necessary to increase the crystallization time to 24 h. For the PEK homopolymer, the crystallization rate was much faster and resulted in some of the samples crystallizing during heating to the isothermal temperature. Therefore for the PEK sample crystallized at 320 and 350°C, the sheets were melted in a press that could be rapidly air cooled to the isothermal temperature.

D.s.c. scans of the samples were obtained with a calibrated Perkin-Elmer DSC7 on 10 mg samples heated at 20°C min^{-1}.

Wide-angle X-ray scattering (WAXS) scans were obtained in the symmetrical transmission mode from a Philips Vertical Diffractometer.

Small-angle X-ray scattering (SAXS) was measured with a Kratky camera equipped with a position-sensitive detector. A constant background intensity was subtracted before desmearing and then multiplying by a Lorentz factor $4\pi s^2$.

CRYSTAL STRUCTURE OF HOMOPOLYMER PEDEK

We were fortunate to have available for our studies a small quantity of the homopolymer PEDEK, which had been synthesized in our laboratories by P. A. Staniland. This material could be moulded and quenched into amorphous films and could be readily crystallized to a crystallinity in excess of 30%. The molecular weight was sufficiently high to enable the sample to be oriented. D.s.c. examination of quenched and crystallized material showed a T_g at 164°C and a peak melting point of 425°C.

A small sample of a quenched amorphous film of PEDEK was drawn and crystallized to make a uniaxially oriented specimen. The X-ray photograph gave a well developed fibre pattern, which is shown in *Figure 1*. The pattern bears a strong resemblance to that found for PEEK and PEK, the main difference being a greater number of layer lines. The original negative shows that even the strongest equatorial spot is in fact composed of separate reflections closely located on different layer lines. Several meridional reflections can be detected by tilting the specimen or by making meridional diffractometer scans. They can be indexed as even orders of a chain repeat 37.5 Å long. The equatorial and off-axis reflections

Table 1 Summary of results

Preparation temperature (°C)	D.s.c. lower T_m (°C)	D.s.c. upper T_m (°C)	WAXS crystallinity (%)	SAXS long period (Å)	Apparent lamellar thickness (Å)
PEK homopolymer					
quench		372	0		
200	218	374	24	94	21
230	248	373	26	101	24
260	279	373	27	105	26
290	307	374	32	109	33
320	340	373	33	140	43
350	375	380	30	170	48
ES copolymer					
quench		337	0		
200	218	335	23	104	22
230	249	336	24	102	22
260	275	338	26	115	28
290	305	345	24	132	29
310	324	346	15	142	18
320		347	13	180	20
EDEK copolymer					
quench		335			
200	223	335	20		
230	250	335	20	115	21
260	277	335	23	133	28
290	308	335	21	149	28
310	328	347	20	133	24

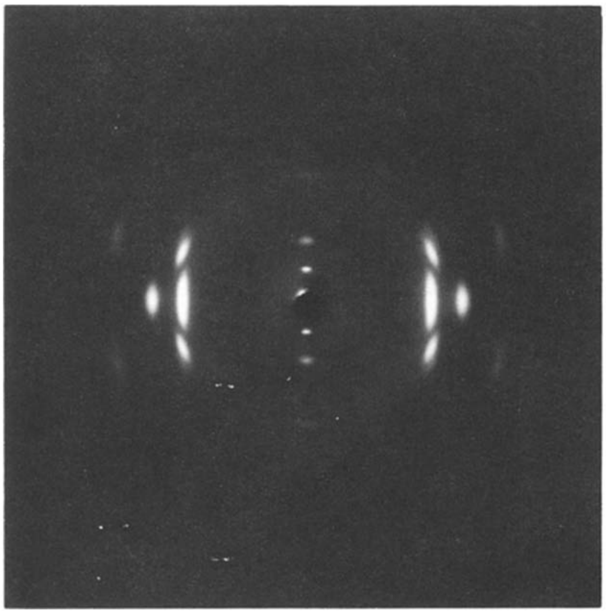
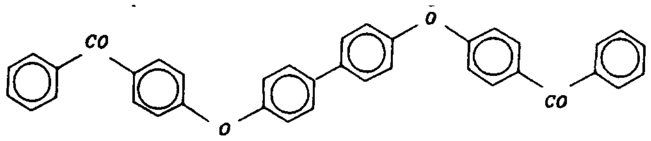


Figure 1 X-ray photo of an annealed, oriented sample of homopolymer PEDEK

can be indexed on an orthorhombic cell whose lateral dimensions are close to that of PEEK where $a = 7.72$ Å, $b = 5.94$ Å and $c = 37.5$ Å.

Identification of the crystal structure in this cell has been considerably aided by associated studies on the related oligomer molecule:



Crystals of this material could be grown and have been examined to give a full crystal structure. Details are reported elsewhere[6]. In this crystal the oligomer molecules stack together with a conformation exactly analogous to PEEK but with the two rings of the biphenyl unit essentially coplanar. On the basis of this oligomer structure and the above observed lattice parameters, the CERIUS diffraction modelling software has been used to build the crystal cell of PEDEK shown in *Figure 2*. There are two chemical repeats in the chain direction of the unit cell. The predicted fibre pattern shown in *Figure 3* brings out all the main features of the experimental pattern.

A simulated powder diffractogram based on this structure is shown in *Figure 4* and agrees well with the experimentally derived pattern shown in *Figure 5*. This derived pattern for the crystalline component was obtained from the pattern of a crystalline isotropic film by subtracting a fitted curve obtained from amorphous polymer. It should be noted that, because of the closeness of the crystal cell lateral dimensions to those of PEK, the first and third peaks at 19° and 23° respectively are at positions close to the {1 1 0} and {2 0 0} reflections of the pattern of PEK. However, the second peak at 20° is shifted to lower angles compared with the {1 1 1} of PEK.

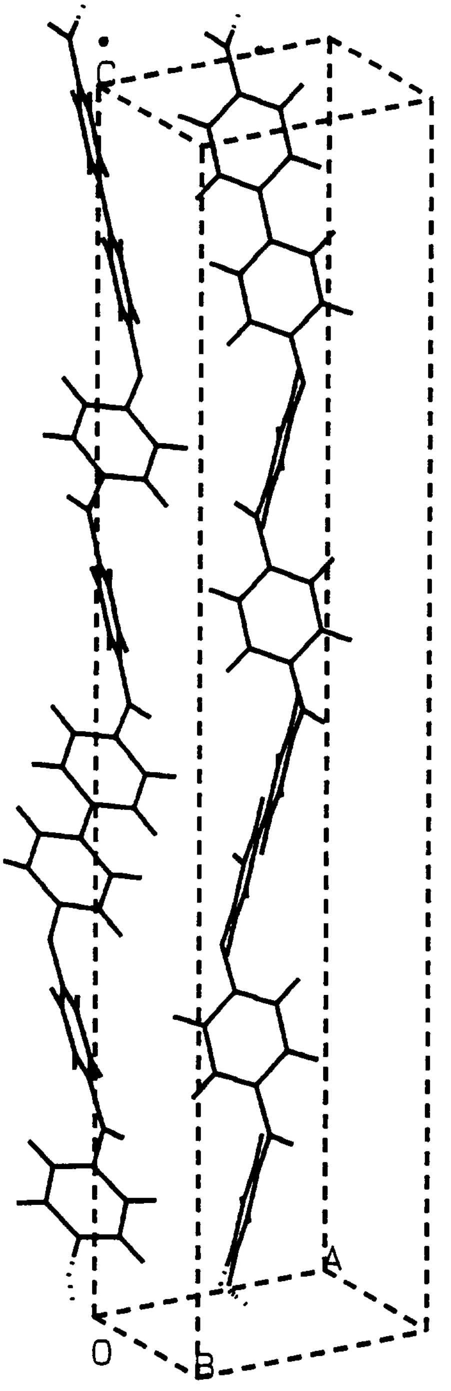


Figure 2 View of proposed crystal structure of PEDEK

OBSERVATIONS ON PEK CONTROL

D.s.c. scans from the amorphous and the isothermally crystallized PEK samples are shown in *Figure 6*. The profiles show all the features that have often been reported for this type of polymer[7]. The amorphous sample shows a T_g step at 152°C followed by a sharp crystallization exotherm and finally a melting endotherm at around 370°C. The isothermally crystallized samples have a very indistinct T_g process but show a two-peak melting pattern consisting of a small peak at about 20° above the previous crystallization temperature and a larger melting process whose position at around 373°C is almost invariant with crystallization temperature. The occurrence of two peaks for isothermally crystallized samples is well established in this class of polymer[7,8,10]. There is some degree of controversy over the interpretation of the first peak. One view is that it indicates the onset of an ordering and recrystallization

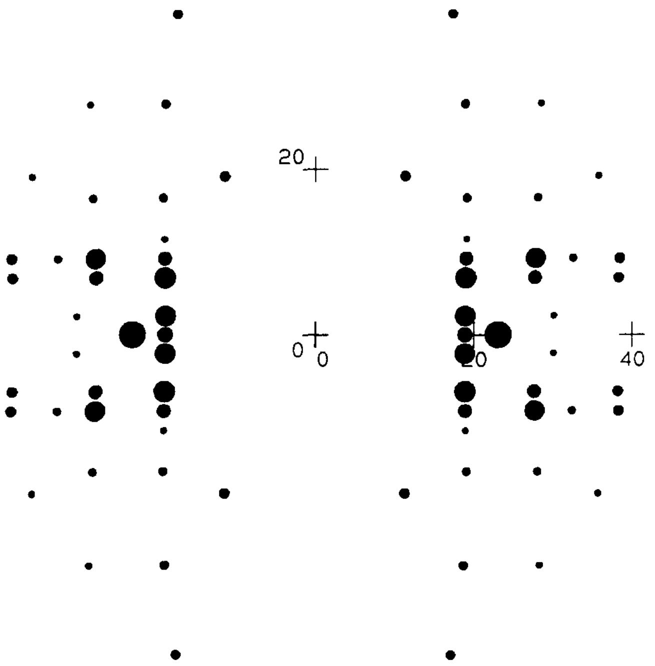


Figure 3 Simulated fibre pattern of PEDEK derived from cell in *Figure 2*

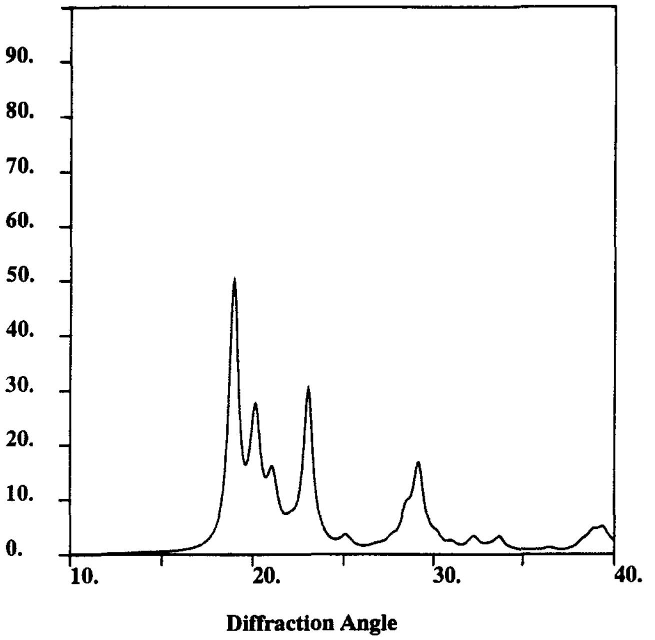


Figure 4 Simulated powder pattern of PEDEK derived from cell in *Figure 2*

process involving substantially the whole population of the crystals created during the isothermal crystallization process, and that the recrystallization terminates with the final melting process[8,9]. An alternative view is that the first peak is associated only with the melting of a secondary crystal population of constrained crystallites and that the melting of the main population occurs in the region of the larger upper peak[10,11].

Selected WAXS diffractograms are shown in *Figure 7*. With increasing crystallization temperature, the crystalline reflections increase in intensity and sharpness, indicating increased crystallinity and larger, less distorted, crystallites. As noted by previous workers the positions of the peaks also shift, indicating a small change in lattice parameters[12,13]. The shift is largest for the {2 0 0} reflection and involves a shift to higher angles with higher crystallization temperatures. *Table 1* lists the X-ray crystallinity estimates derived from these curves by scaling and fitting the curve from amorphous polymer.

Table 1 also lists the SAXS long periods and the apparent lamellar thickness, which is obtained by

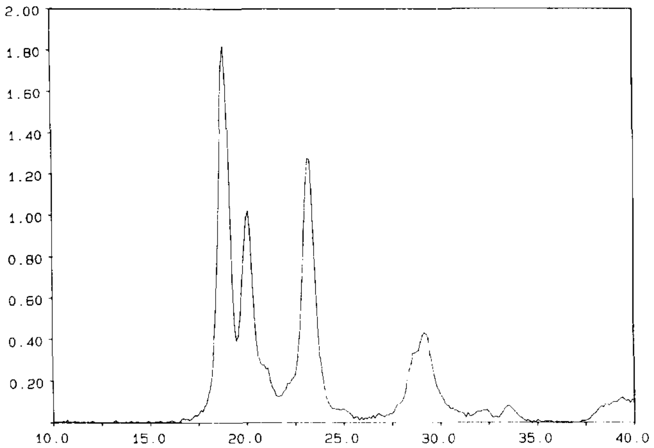


Figure 5 Experimentally derived powder pattern for the crystalline component of an isotropic PEDEK sample

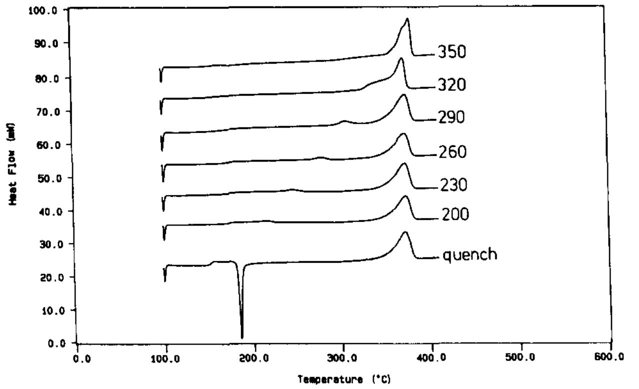


Figure 6 D.s.c. scans from PEK homopolymer samples crystallized at indicated temperatures

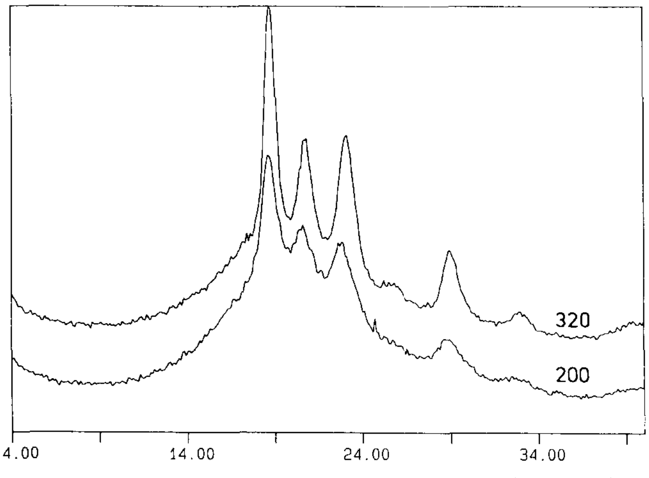


Figure 7 WAXS scans from PEK homopolymer samples crystallized at indicated temperatures

multiplying the long period by the X-ray crystallinity. This value for lamellar thickness only has any significance if one can assume a uniform population of stacked lamellae. (Strictly this calculation should also use the volume fraction crystallinity rather than the weight fraction; however, the correction is small.)

ES COPOLYMER

Figure 8 shows the d.s.c. heating scans of the ES copolymer samples. Many of the features are qualitatively similar to the scans from the PEK control. The main difference is a 35° depression in the final melting process and a reduction in the resolution and area of the peaks. The onset T_g for the quenched sample occurs at 164°C. In the isothermally crystallized samples there is again a smaller lower endotherm about 20°C above the crystallization temperature. There are, however, two additional features to note.

First, for the sample crystallized at 320°C, there is a distinct crystallization exotherm at around 190°C. This indicates that, during the preparation of the sample, there was still material present with the potential to crystallize at the end of the allotted crystallization time. This diagnosis is confirmed by the X-ray crystallinity (see *Table 1*), which shows a substantial reduction compared with the sample crystallized at 290°C. There is a similar reduction of crystallinity for the 310°C sample although there is very little d.s.c. evidence for further crystallization on heating. One reason for a reduced crystallinity could be that insufficient time was allowed to complete the isothermal crystallization process. However, since separate d.s.c. isothermal measurements show that the time allowed was at least three times longer than the time to reach the peak in the crystallization process, a more likely explanation is that the thickness of the lamellar crystals growing at 320°C is higher than the length of many of the uninterrupted sequences of EK between the ES comonomer units. Thus it is envisaged that, while crystallizing at 320°C, only the longer EK sequences can be incorporated into crystals. After quenching, the frozen amorphous material will still contain shorter EK sequences that have the potential to crystallize below 320°C where the crystals will be thinner. On subsequent heating in the d.s.c. beyond T_g, these shorter sequences will take part in the crystallization process at 190°C.

The second feature to note is the extra melting endotherm at around 300°C in the sample isothermally crystallized at 200°C. A similar effect to this is also observed in the EDEK copolymer samples, and it is discussed further below.

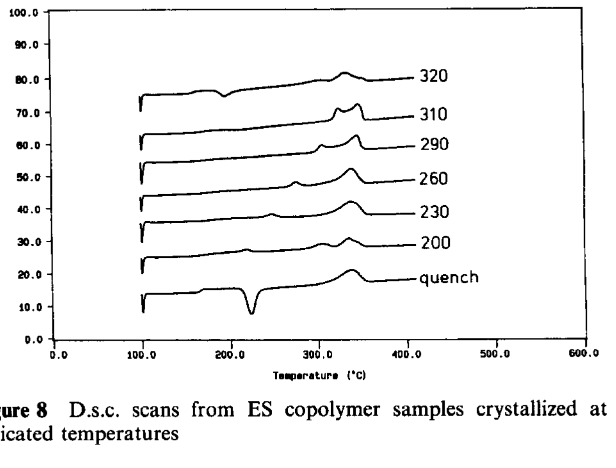


Figure 8 D.s.c. scans from ES copolymer samples crystallized at indicated temperatures

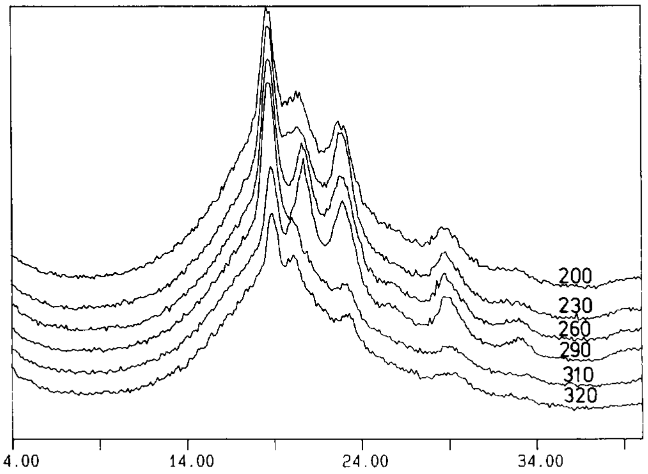


Figure 9 WAXS scans from ES copolymer samples crystallized at indicated temperatures

The WAXS scans for the ES copolymers are shown in *Figure 9*. The crystallinities judged from the area associated with the crystalline reflections gradually increase with crystallization temperature up to 290°C. Beyond 290°C there is the reduction in crystallinity already alluded to above. There are, however, also some curious changes in the peak positions. In the middle of the temperature range at 260 and 290°C, the peak profiles are consistent with those of the PEK homopolymer. At lower temperatures, the {1 1 1} peak loses resolution and appears to shift to a lower angle, indicating a possible imperfection in the EK lattice. At higher temperatures, the peaks are well resolved but the {1 1 1} is now clearly at a lower angle, suggesting a distinct difference from the normal PEK crystal.

One implication of the shift in peak position is that the thicker crystals that grow at the higher temperatures are causing the otherwise non-crystallizable ES units to become associated with the crystal lamellae as a result of the shortage of long uninterrupted sequences of EK. Information on the conformation at the sulfone link of the ES unit is limited. *Ab initio* calculations by Kendrick[5] of diphenylsulfone show that the two phenyls on each side of the sulfone are torsionally rotated by 90° compared with about 35° at ether and ketone links. This is consistent with crystal structure data of the model compound dichlorodiphenylsulfone[14]. It also agrees with the conclusions of Jones[15] from experimental radial distribution functions from amorphous PES polymer. The calculations[5] indicate that the ability of the phenyls to swivel cooperatively from the 90° conformation would be very limited and unlikely to be more than 10°. This 90° conformation is incompatible with the PEK lattice. An isolated ES unit with the 90° conformation could not easily exist as a simple point defect in a PEK lattice, since it would also dislocate the lattice alignment of a neighbouring EK sequence.

Nevertheless, from the diffraction evidence the ES units do appear to be modifying the lattice regularity. One way this could happen is if a specific sequence (e.g. KEKESEKEK) could pack together laterally in a precise way that allowed the ES units from adjacent chains to pack with their preferred conformation. However, if the ES units occur randomly in a chain, there would be insufficient numbers of any one particular sequence to account for the observed crystallinity. Alternatively, enough ES units might become concentrated at the lamellar interface with a particular conformation relative to the stems in the lamellae and thus give rise to an effective regularity that was capable of modifying the normal {1 1 1} diffraction maximum.

EDEK COPOLYMER

The d.s.c. scans for the EDEK copolymer samples are shown in *Figure 10*. Some of the characteristics of the PEK homopolymer and the ES copolymer also occur here, namely a smaller, lower endotherm about 20°C above the isothermal crystallization temperature and an almost invariant final melting peak (which in this case is depressed by about 35°C compared with PEK). The T_g onset for the quenched sample occurs at 158°C.

However, in most of the scans there is also a third middle endotherm similar to that seen in one of the ES samples. This third peak occurs at about the same position (315°C) and becomes merged with the lower endotherm when the crystallization temperature reaches 290°C. This fact, that the position of the peak is almost invariant, infers the presence of a distinct crystal species that either completely melts or is converted into another more stable form when the temperature reaches this value.

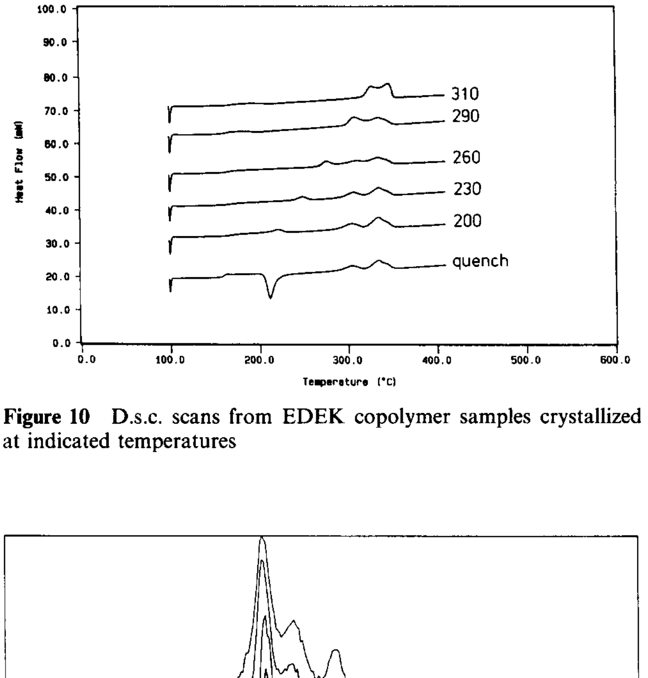


Figure 10 D.s.c. scans from EDEK copolymer samples crystallized at indicated temperatures

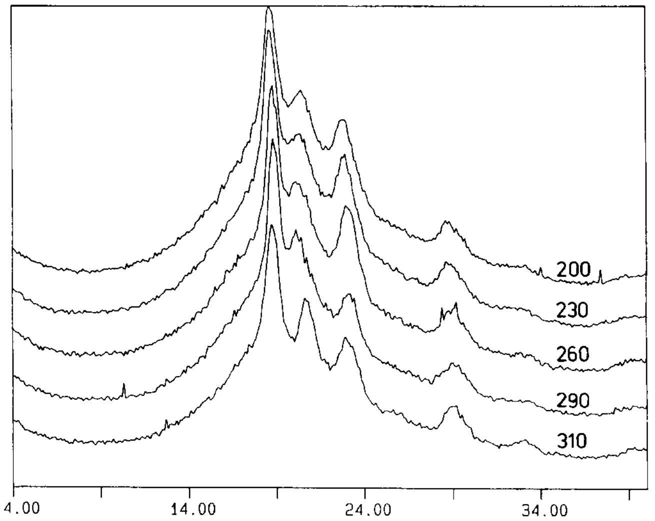


Figure 11 WAXS scans from EDEK copolymer samples crystallized at indicated temperatures

The WAXS diffraction data shown in *Figure 11* provide more insight into this phenomenon. Comparison with the corresponding data for PEK in *Figure 7* shows that it is only for the sample crystallized at 310°C that the middle of the three main diffraction peaks coincides with the {1 1 1} of PEK. For all the samples crystallized at lower temperatures, the middle peak has shifted to a lower diffraction angle. There is also a shift in the {2 0 0}, which is consistent with the lattice expansion and distortion already reported[12,13]. However, the shift in the {1 1 1} is much larger and is more consistent with a complete change of lattice. In fact, in all these other cases the total diffraction pattern closely resembles that of PEDEK homopolymer shown in *Figure 5*. This suggests that, when the copolymer has been crystallized below 315°C, the crystals have been formed from sequences of EDEK rather than EK. The fact that the crystals melt at 315°C rather than the 425°C of PEDEK homopolymer can be attributed to the limited availability of long EDEK sequences, which are able to form the thicker lamellae that are needed to remain stable up to 425°C.

In view of the novelty of this phenomenon, several attempts were made to repeat these observations by isothermally crystallizing new samples. Much to our astonishment, all subsequent attempts failed to reproduce samples whose d.s.c. scan exhibited the middle melting endotherm. Furthermore, the WAXS patterns of those subsequent samples crystallized at lower temperature now showed the {1 1 1} diffraction peak closer to that expected for PEK. The inference of these observations is that, despite all attempts to reproduce the experiment, there was an undetected difference in the procedure, which caused the copolymer to prefer to form lamellae made from EK sequences rather than EDEK as on the first occasion.

Previous studies of PEEK and related aromatics have demonstrated that the lamellar crystals are very thin and that under most crystallization conditions the lamellae will be less than 50 Å thick. The SAXS results and the WAXS crystallinities of these present copolymers indicate a similar lamellar morphology with lamellar thicknesses possibly lower than 30 Å. Taking account of this and the large depression in melting point from 425 to 315°C, it is not unreasonable to assume that a sequence of only two EDEK units (36 Å long) is all that is needed to traverse the lamellae. In this copolymer, the EDEK monomer comprises 33% of the molar fraction compared with the EK units and accounts for 48% of the weight. A simple probability calculation based on random occurrence of EK and EDEK shows that the number of sequences of two or more consecutive EDEK units in the chain is able to account for a weight fraction comparable with the observed crystallinity. The degree of clustering of EK units detected by n.m.r. would improve further the chances of longer sequences of EDEK. Furthermore, if one allows the possibility of crystal defects associated with the incorporation of isolated EDEK bordered by EK units, then there is more than enough material available to create the PEDEK-like crystals indicated by the above observations.

In connection with this issue it is worth making the analogy with main-chain liquid-crystal polymers made from the random incorporation of hydroxybenzoic acid (HBA) and hydroxynaphthoic acid (HNA)[16]. Sequences of both HBA and HNA are capable of crystallizing on their own to form their own unique crystals. Detailed analysis, however, indicates that, particularly under fast cooling conditions, ordered regions are formed comprising matching random sequences of both HBA and HNA and creating 'non-periodic layer' (NPL) crystals[16]. It is a possibility that some of the features of NPLs could also be occurring in the present conventional EK/EDEK copolymer.

The possibilities discussed here for the EDEK copolymer may also have implications for the deviation from the PEK diffraction pattern in the ES copolymer. It is possible that the ES is modifying the crystals in a precise way perhaps related to a specific sequence of units being incorporated in the middle or at the boundaries of the lamellae.

The reason why PEDEK crystals were made in the first sample set, whereas in subsequent trials only PEK-like crystals were made, at present remains unexplained. On the basis of weight and molar fractions, one would expect the choice of lamellar type to be balanced in favour of PEK crystals, although the occurrence detected by ^{13}C n.m.r. of clustering of EKEK diads would help to redress this balance. In the nucleation and crystal growth processes there must be a competition in the kinetics between the two possibilities. Such a competition has recently been observed in an aromatic ether ketone and resulted in unusual crystallization and melting phenomena[17,18]. For the moment we presume that, during the first preparation of the copolymer samples, there was a small feature in the temperature history that weighted the nucleation kinetics in favour of the PEDEK-like lamellae.

CONCLUSIONS

In the preliminary experiments, the control homopolymer PEK was found to crystallize isothermally in a manner similar to PEEK, with crystallinity and lamellar thickness increasing with crystallization temperature. Subsequent d.s.c. scans exhibited the well documented phenomenon of two melting endotherms, the first just above the crystallization temperature and the second essentially at a constant temperature.

It was also found that the homopolymer PEDEK crystallized with a crystal structure closely related to that of PEK and PEEK. The conformations at the ether and ketone links are essentially identical. The mode of packing of the chains in the cell is the same except that the biphenyl groups are laterally adjacent and adopt a planar conformation.

In terms of melting-point depression and reduction in crystallinity, both the ES and EDEK copolymers are qualitatively similar and agree with expectations of copolymers in general. However, in terms of crystal structure and melting behaviour, very unusual effects are observed.

In the case of the EDEK copolymer, the concentration of crystallizable EDEK units is high enough for there to be a competition between PEK and PEDEK types of crystals. In the main part of the study the WAXS data showed that PEDEK was favoured at low crystallization temperatures and PEK at temperatures above 300°C. D.s.c. scans of the low-temperature samples show an additional third melting endotherm at 315°C corresponding to the melting of PEDEK and the subsequent recrystallization into PEK crystals. However, it is clear from the inability to reproduce these effects in later experiments that the competition to crystallize between EDEK and EK is very sensitive to the precise conditions of preparation.

The d.s.c. data for the ES copolymer showed more conventional behaviour including evidence at high crystallization temperatures of incomplete crystallization of shorter sequences of EK. There was one scan for the lowest crystallization temperature showing a third endotherm similar in appearance to those associated with PEDEK-like crystals. WAXS scans indicate PEK crystals in the middle crystallization range but show evidence at both higher and lower temperatures of deviations in crystal structure. Since the conformation around the sulfone link in ES is incompatible with the PEK crystal, it is presumed that the ES is modifying the crystals in a precise way, perhaps related to a specific sequence of units being incorporated in the middle or at the boundaries of the lamellae. These could possibly give rise to the change in diffraction and to the one incident in the ES copolymer of a third melting endotherm.

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