Molecular analysis of the melting behaviour of poly(aryl-ether-ether-ketone)

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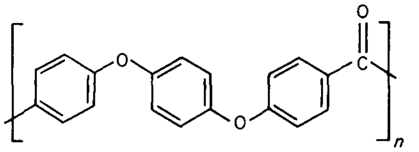
The melting behaviour of poly(aryl-ether-ether-ketone) (PEEK) was investigated using Fourier transform infra-red (*FT*i.r.) spectroscopy and differential scanning calorimetry (d.s.c.) as part of a study of a carbon fibre reinforced PEEK composite. Digital spectral subtraction was utilized to derive the characteristic spectra of the amorphous and crystalline phases of the polymer. Local order in the amorphous phase of PEEK was observed when the polymer was melted below its equilibrium melting temperature ($T_m^* = 395$°C). The local order is associated with the diphenyl ether moiety. Molecular segments in the ordered regions may assume different orientations on the surface of potassium bromide salt crystals, depending upon whether PEEK is processed at 380°C or 400°C. Molecular analysis by *FT*i.r. correlates well with data obtained by d.s.c.

(Keywords: PEEK; *FT*-i.r.; thermal analysis; melting; crystallization)

INTRODUCTION

Poly(aryl-ether-ether-ketone) (PEEK) is a semi-crystalline thermoplastic which possesses great potential as a matrix polymer for high performance composites. A number of synthetic routes to crystallizable PEEK (I) have been reported[1-3].


(I)

Condensation polymerization of the potassium salt of hydroquinone and 4,4′-difluorobenzophenone in dimethyl sulphoxide at about 150°C was studied by Johnson *et al.*[1]. Attwood *et al.*[2] prepared high molecular weight PEEK from 4,4′-difluorobenzophenone and the potassium derivative of hydroquinone, using diphenyl sulphone as solvent, at a temperature close to the melting point of the polymer (280°C–340°C). The glass transition temperature and the melting point of this polymer were determined by differential scanning calorimetry to be 144°C and 335°C, respectively. Recently, Kricheldorf and Bier[3] showed that PEEK can also be made via the bulk condensation of 4,4′-difluorobenzophenone and silylated hydroquinone at elevated temperatures (220°C–320°C).

Studies of the mechanical properties of PEEK[2,4-6,10] as well as its carbon fibre composites[4,7-9] have been reported. Compared with the state-of-the-art carbon fibre/epoxy composites, PEEK composites were shown to have higher fracture toughness, tensile strength and flexural strength; better retention of flexural and tensile properties at elevated temperatures; excellent dimensional stability, and outstanding resistances to creep, delamination and attack by moisure and organic solvents. The results also indicated that PEEK composites have lower flammability and are less succeptible to fatigue and thermal ageing. The outstanding properties of PEEK were attributed to its crystallinity. However, exposure to radiation reduces the degree of crystallinity and depresses the melting temperature of PEEK[10].

In carbon fibre/PEEK composites, morphological features were seen on the fibre surface which suggested that the fibre surfaces act as nucleation sites for the polymer when it cools from the melt[4]. Depending on the type of carbon fibre, transcrystallinity has also been seen to occur along the whole fibre surface[7]. The observed interaction between the fibre surface and PEEK concurs with the excellent interfacial adhesion of the composites.

To study the interfacial region in carbon fibre-reinforced PEEK composites, it is essential that the crystallization behaviour of PEEK be well understood. Studies of crystal morphology have been done on fibres[11], moulded plaques[11,12,14], die-drawn oriented rods[13] and annealed melt-quenched powders[15]. Crystallographic parameters from wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) analyses revealed that PEEK has a similar crystal structure to that of poly(*p*-phenylene oxide)[11-15]. Thermal analysis using differential scanning calorimetry (d.s.c.) indicated that the pattern of thermal transitions of PEEK closely resembles that of poly(ethylene terephthalate), with the main transitions occurring at about 75°C higher[12]. Blundell *et al.*[11,12] also suggested that the morphology of PEEK is consistent with the concept of lamellar stacks which consist of alternating layers of crystalline and amorphous regions, and that the ketone and ether linkages are interchangeable with only minor distortion on chain packing in crystalline regions. The use of multiple internal reflection dispersive infra-red spectroscopy has been discussed in a note by Chalmers *et al.*[16]. They showed that the relative intensities of a number of bands correlate to the change in the degree of crystallinity of PEEK as measured by WAXD.

It is the purpose of this paper to study fundamental molecular behaviour of the melting and its subsequent influence on the crystallization of PEEK. Emphasis is

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placed on the disordered phase, which is not amenable to X-ray studies. Using Fourier transform infra-red (*FT*i.r.) spectroscopy and differential scanning calorimetry (d.s.c.), the structure and morphology of PEEK were studied. Subtle differences, revealed by digital subtraction of absorbance spectra, between samples of different degree of crystallinity due to different processing conditions, were detected by *FT*i.r. They provide important clues to structural and morphological changes which take place during the melt processing of PEEK.

EXPERIMENTAL

PEEK powder with a number-average molecular weight of about 12 000 g/mol was obtained from ICI. Thin films were melt-cast on KBr salt plates. They were then heated to above the melting point at either 380°C or 400°C for approximately 10 min. Oxidative degradation of the polymer samples due to this short period of exposure was not observed. Some of the coated salt plates were quenched into liquid nitrogen or ice water. Some were allowed to cool slowly to room temperature. Annealing of the samples was done in an air furnace at various temperatures for various time intervals. The samples were then allowed to cool slowly to room temperature.

Digitized spectra were recorded on a Digilab FTS-20E Fourier transform infra-red spectrometer using liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. The spectrometer was constantly purged with dry nitrogen to reduce atmospheric moisture. All spectra were obtained at room temperature with 2 cm^{-1} resolution and 500 scans, using double precision software.

Powder PEEK was placed in capped aluminium pans for thermal analysis. Samples for d.s.c. measurement were prepared to have approximately the same weight (5.5 ± 1.0 mg) on a Perkin–Elmer AD-2 Autobalance. A capped aluminium pan with the same weight of aluminium was used as the reference. The polymer samples in the capped pans were prepared thermally in five different ways; as-received (no further heat treatment of the polymer-filled pans), quenched from 380°C or from 400°C (the polymer-filled pans were heated to 380°C or 400°C in a furnace, then quenched into liquid nitrogen), and cooled from 380°C or 400°C (the polymer-filled pans were heated to 380°C or 400°C in a furnace then allowed to cool gradually to room temperature).

Thermal analysis was done on a Perkin–Elmer DSC-2 differential scanning calorimeter. The thermograms were recorded from 303 K (30°C) to 678 K (405°C) at a heating rate of 20 K/min. Throughout the d.s.c. experiments, a dry nitrogen purge of 200 cm^3/min was used.

RESULTS AND DISCUSSION

Characteristic spectra of PEEK

Typical spectra in the fingerprint region of a quenched and a highly annealed PEEK melt-cast film are shown in *Figure 1* (spectra 1A and 1B, respectively). Distinctive spectral features of a quenched sample included the carbonyl stretching vibration at 1655 cm^{-1}, a shoulder at 1252 cm^{-1} and two overlapping broad bands at 863 and 841 cm^{-1}. In the spectrum of an annealed sample, the carbonyl stretching frequency is shifted to 1648 cm^{-1} and the shoulder at 1252 cm^{-1} is weakened. The shift in the carbonyl stretching frequency from 1655 to 1648 cm^{-1} is probably due to the movement of the two phenyl rings of the benzophenone moiety to approach coplanarity upon crystallization, which result in an increase in conjugation.

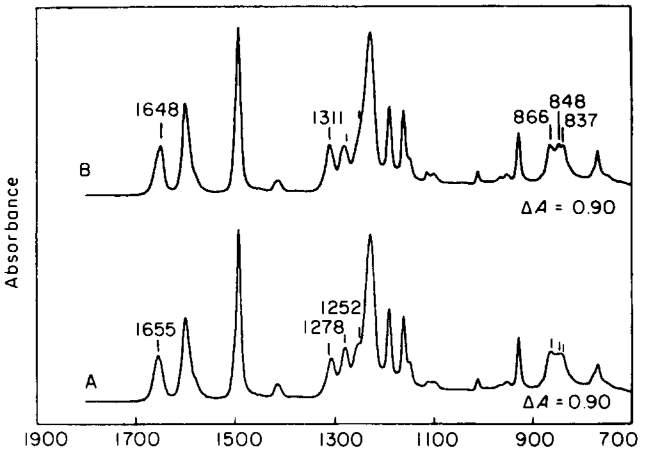

Figure 1 Transmission *FT*i.r. spectra of melt-cast PEEK films. (A) quenched sample; (B) annealed sample

Digital spectral subtraction was used to derive the characteristic spectra of the amorphous and crystalline phases of PEEK. The procedure for obtaining such difference spectra of a semi-crystalline polymer has been well documented[17,18]. The spectrum of the disordered phase was isolated by subtracting a fraction of the spectrum of the annealed sample from that of the quenched sample. Likewise, the spectrum of the ordered phase was obtained by subtracting the spectrum of the quenched sample from that of the annealed one. The appropriate scaling factors (fractions to be subtracted) were determined on a trial and error basis such that no negative absorbance band can be seen in the difference spectra. The technique has been successfully applied to *trans*-1,4-polychloroprene[19], poly(vinyl chloride)[20], poly(ethylene terephthalate)[21], polypropylene[22], isotactic polystyrene[23] and poly[*N*,*N*′-bis(phenoxyphenyl) pyromellitimide][24].

Figure 2 shows the difference spectra which are characteristic of the ordered and disordered phases of PEEK. They were derived from the spectra of a sample quenched from 400°C into liquid nitrogen and subsequently heated at 360°C for 1 h, then slowly cooled to room temperature. As expected, the bands in the spectrum of the ordered phase (spectrum B in *Figure 2*) are sharper than those of the disordered phase (spectrum A in *Figure 2*). One distinctive feature of the crystalline difference spectrum is the strong doublet at 1244 and 1227 cm^{-1}. In the same region in the amorphous spectrum, only one band at 1227 cm^{-1} is seen. Whether the band at 1227 cm^{-1} newly arises in the crystalline phase or is simply the result of frequency shift and intensification of the band at 1255 cm^{-1} requires further study.

It may not be completely accurate to call spectrum B in *Figure 2* the crystalline spectrum. More precisely, it is the characteristic spectrum of the segments of the polymer chains in the preferred conformation (i.e. ordered chain segments).

Difference spectra were also derived from film samples quenched into ice-water from 380°C and subsequently annealed at 325°C for 16 h or 335°C for 1 h, or heated at 360°C for 2 h, before cooling to room temperature. They

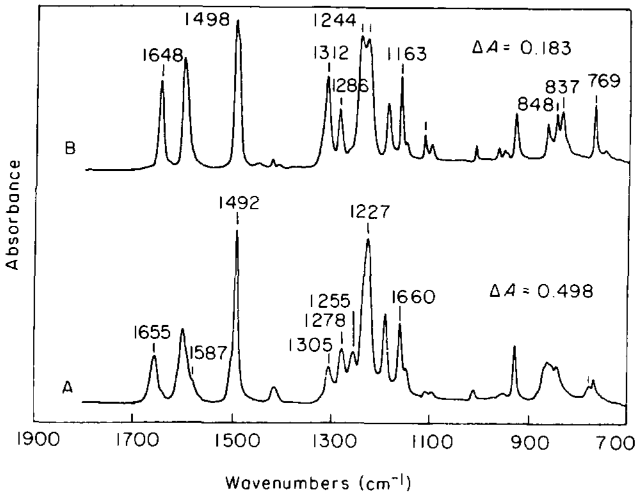

Figure 2 Spectra of the crystalline and amorphous phases of PEEK. (A) difference spectrum characteristic of the amorphous phase; (B) difference spectrum characteristic of the crystalline phase

Table 1 Observed frequencies of PEEK (cm^{-1})[a]

Quenched	Annealed (325°C, 16 h)	Difference spectra	
		Amorphous	Crystalline
1655 m	1648 m	1655 m	1648 m
1599 s	1601 s	1599 s	1601 s
1585 sh	1585 sh	1587 sh	1591 sh
		1500 sh	1498 vs
1492 vs	1492 vs	1492 vs	1492 vs
1415 w	1412 w	1415 w	1412 vw
1307 m	1311 m	1305 m	1312 m
1278 m	1286 m	1278 m	1286 m
1252 sh		1255 m	
	1244 sh		1244 vs
1227 vs	1227 vs	1227 vs	1227 vs
1190 s	1190 s	1190 s	1190 s
1160 s	1163 s	1160 s	1163 s
1149 vw	1150 sh	1149 vw	1152 vw
1112 w	1115 w	1109 w	1115 w
1099 w	1100 w	1096 w	1100 w
1011 w	1012 w	1011 w	1012 w
	965 vw		965 vw
952 vw	953 vw	952 vw	953 vw
	948 sh		948 sh
928 m	931 m	928 m	931 m
862 m	866 m	862 m	866 m
841 sh	848 m	844 m	848 m
	837 m		837 m
775 sh		775 w	
768 w	769 m	766 w	769 m
	747 sh		747 vw

[a] Abbreviations: vw = very weak; w = weak; m = medium; s = strong; vs = very strong; sh = shoulder

all have spectral features identical to those shown in *Figure 2*. The observed frequencies of the quenched, annealed, amorphous and crystalline spectra are shown in *Table 1* for comparison purposes.

Effect of melting temperature

Figure 3 shows the spectra of PEEK thin films quenched from 380°C (spectrum A in *Figure 3*) and 400°C (spectrum B in *Figure 3*), respectively. The thin films were melt-cast on KBr crystals. Only subtle differences are seen. In samples quenched from 400°C, for example, the band at 1492 cm^{-1} is sharper and narrower, whereas the relative intensities of the 1655 and 1599 cm^{-1} bands with respect to the 1492 cm^{-1} band are reduced.

These differences can best be amplified by spectral subtraction. The difference spectrum is shown in *Figure 4* (spectrum B), where subtraction between spectra obtained at the two different conditions was made. Spectra of the amorphous and crystalline phases of PEEK (spectra A and C in *Figure 4*) are also shown for comparison purposes. Bands which are associated with the carbonyl linkages either show no change (1307 and 1278 cm^{-1} bands) or are slightly positive (1655 and 1415 cm^{-1} bands). Bands which are associated with the out-of-plane bending modes of the aromatic hydrogens, in the region from 1000 cm^{-1} to 750 cm^{-1}, behave similarly.

The striking features of this difference spectrum are the very strong, negative absorbances which correspond to some of the frequencies of the amorphous phase. They are associated with either the asymmetric stretching of the diphenyl ether groups (1277 and 1190 cm^{-1}), the skeletal in-plane vibration of the phenyl rings (1599 and 1492 cm^{-1}) or the in-plane vibrations of the aromatic hydrogens (1160 cm^{-1}). The relative absorbances (ΔA) of this spectrum are almost as large as those of the amorphous spectrum. This suggests that there is a significant difference in the structure of the diphenyl ether segments in the disordered phase at these two melt temperatures. It is likely that quenching from 380°C and 400°C, respectively, results in different orientations of the chain segments on the surface of KBr crystals.

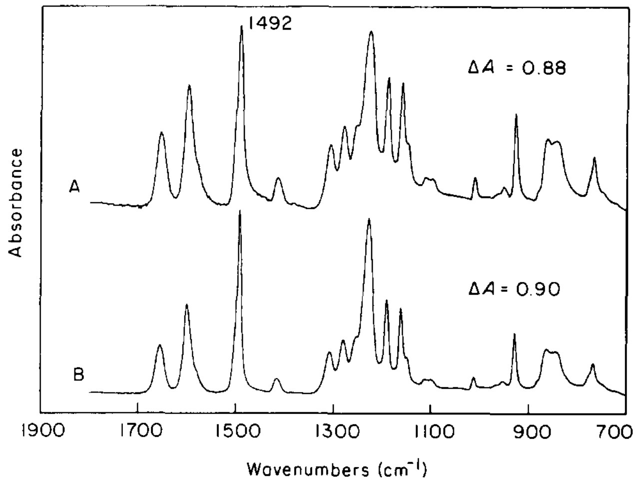

Figure 3 Transmission spectra of PEEK samples quenched from the melt. (A) melt temperature is 380°C; (B) melt temperature is 400°C

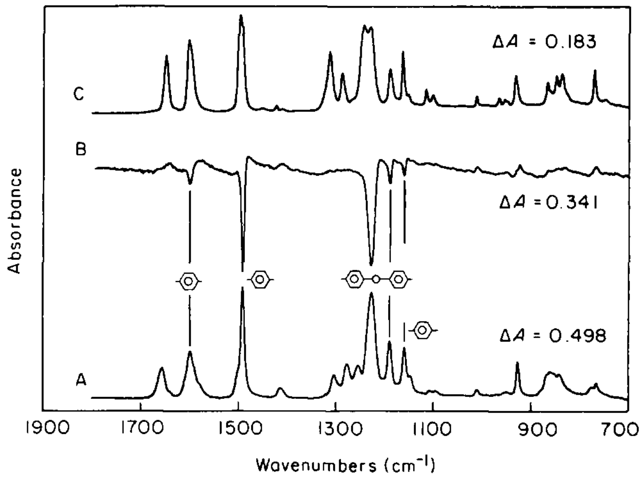

Figure 4 Effect of melting temperature on the structural units of PEEK: (A) amorphous spectrum; (B) difference spectrum of samples melt-quenched from 380°C and 400°C; (C) crystalline spectrum

Samples of PEEK films which were processed differently were also analysed. One set of films (Set 1) was quenched from 380°C and 400°C, then subsequently heated up to a common temperature of 360°C for two hours and cooled slowly to room temperature. Another set (Set 2) was cooled slowly from the melt at 380°C and 400°C to room temperature. Similar subtractions were also done on the spectra within these sets of samples. The difference spectra are compared in *Figure 5*. Spectrum A in *Figure 5* is the result of the subtraction between the spectra of Set 2 (cooled from 380°C minus cooled from 400°C). Spectrum B in *Figure 5* is the result of the subtraction between those of Set 1. Spectrum 5C shows the difference spectrum of the melt-quenched samples (same as spectrum 4B) for comparison purposes.

In the 1800–1050 cm^{-1} region, the difference spectra are almost identical. Negative absorbances at 1599, 1492, 1227, 1190 and 1160 cm^{-1} are seen on all of them. They confirm the significant differences in the molecular structures associated with the diphenyl ether groups of PEEK at these two different temperatures of the melt. The diphenyl ether segments of the PEEK chains may retain a certain degree of local order in the melt even at 380°C, 45°C above the reported T_m. Some remnants of local order may not disappear completely unless PEEK is processed at 400°C (above its equilbrium melting point). The equilibrium melting point T_m^* of an infinite, perfect PEEK crystal has been estimated to be 395°C[12].

The difference spectra of *Figure 5* also confirm the difference in the molecular orientation in the ordered phase. The orientation of the ordered chain segments on the surface of a KBr crystal seems to be influenced by the processing temperature, depending upon whether the polymer was melted at 380°C or 400°C, respectively. The orientation effect is also reflected in the aromatic C–H out-of-plane bending region (1000–750 cm^{-1}). Differences in this region can best be seen in *Figure 6*. The same region of the crystalline and amorphous spectra (spectra A and E in *Figure 6*, respectively) are also shown for comparison purposes. No crystalline feature can be seen in spectrum D (difference spectrum of the melt-quenched samples) and some can be seen in spectrum C (difference spectrum of the samples of Set 1). But spectrum B (difference spectrum of the samples of Set 2) resembles the spectrum of spectroscopically purified crystalline PEEK (spectrum A) the most.

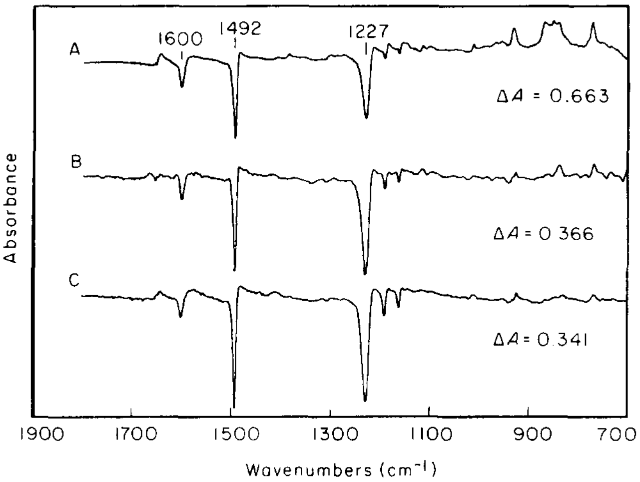

Figure 5 Difference spectra of PEEK: (A) slow-cooled from 380°C minus slow-cooled from 400°C; (B) melt-quenched from 380°C, then annealed at 360°C minus melt-quenched from 400°C, then annealed at 360°C; (C) melt-quenched from 380°C minus melt-quenched from 400°C

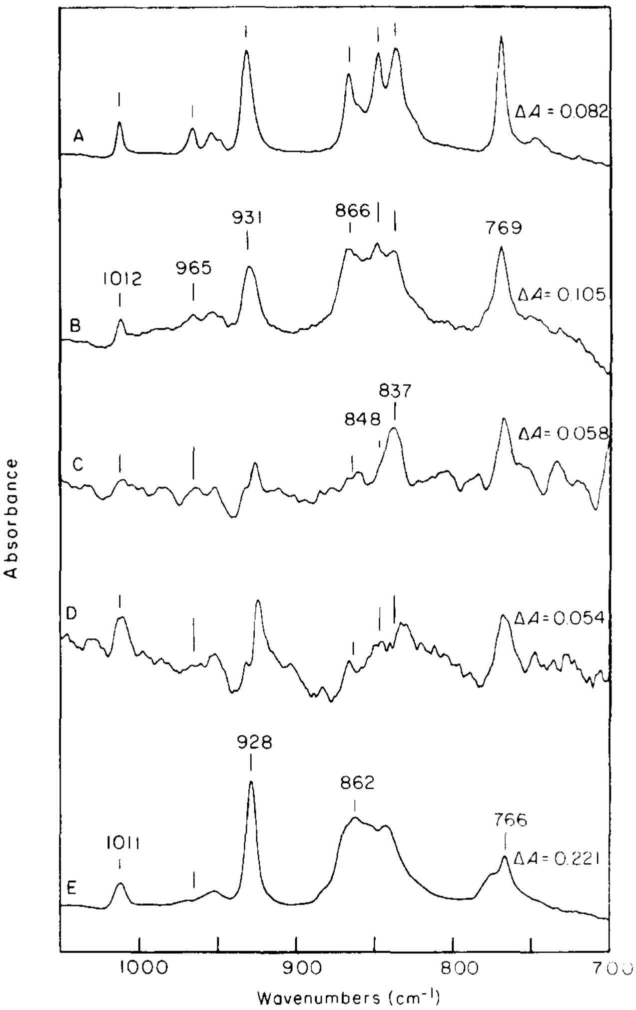

Figure 6 Difference spectra in the aromatic C–H out-of-plane bending region: (A) crystalline spectrum; (B) slow-cooled from 380°C minus slow-cooled from 400°C; (C) melt-quenched from 380°C, then annealed at 360°C minus melt-quenched from 400°C, then annealed at 360°C; (D) melt-quenched from 380°C minus melt-quenched from 400°C; (E) amorphous spectrum

The spectral features associated with the benzophenone moiety show little change or slightly positive whereas those of the diphenyl ether groups are intensified in the samples melted at 400°C. Thus the molecular axis is more parallel to the KBr crystal plane at 400°C. The plane of the phenyl groups also becomes more parallel at this temperature. However, the molecule can never lay flat on the KBr surface because of the inherent steric strain. Annealing of the quenched samples or slow-cooling them from their respective melt temperatures (i.e. increasing the crystalline contents of the samples) intensifies the difference in the orientation of the molecular chains, as indicated by *Figure 6*. If different orientations can be induced on the surface of KBr crystals by melt-processing PEEK at different temperatures, it is possible that the same effect can be induced on other surfaces such as those of glass, carbon and organic fibres.

Figure 7 shows the d.s.c. traces of PEEK powder samples subjected to various thermal histories. The slight variation in the peak position of the melting endotherm is probably due to the non-corrected baselines. A low temperature transition around 60°C–70°C which has

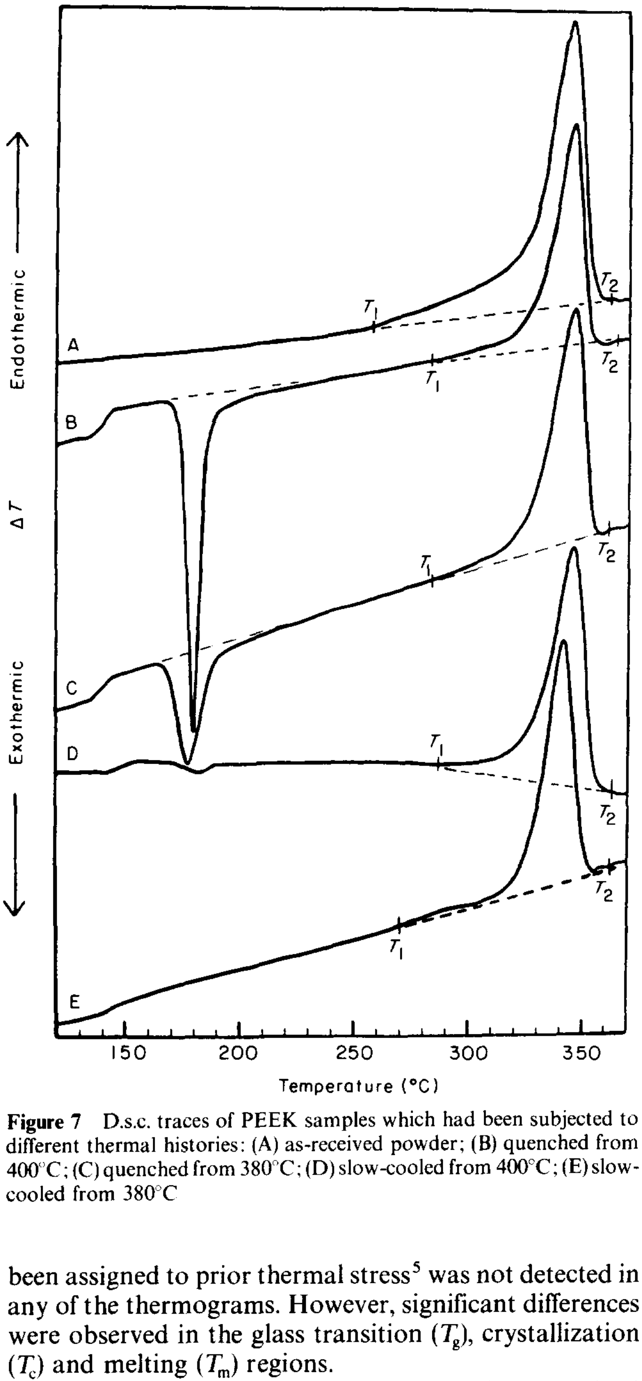

Figure 7 D.s.c. traces of PEEK samples which had been subjected to different thermal histories: (A) as-received powder; (B) quenched from 400°C; (C) quenched from 380°C; (D) slow-cooled from 400°C; (E) slow-cooled from 380°C

been assigned to prior thermal stress[5] was not detected in any of the thermograms. However, significant differences were observed in the glass transition (T_g), crystallization (T_c) and melting (T_m) regions.

Curve A in *Figure 7* is the d.s.c. trace of the as-received powder. The absence of T_g and T_c regions and the presence of a shoulder on the left side of the T_m endotherm reveals that this sample is typical of highly annealed PEEK[12]. Curves B and C in *Figure 7* are traces of samples quenched from 400 and 380°C, respectively. The remarkable difference in the T_c region of the traces also points out the structural differences in the disordered phases of the melt-quenched samples, as *FT*i.r. data have indicated. Curves D and E in *Figure 7* are d.s.c. traces of samples slowly cooled from 400°C and 380°C, respectively. Minor changes in the T_g and T_c regions substantiate the difference in the crystalline contents of the samples as the features of the difference spectrum (curve B in *Figure 6*) have suggested.

The crystalline and amorphous contents of PEEK samples can be calculated from *FT*i.r. and d.s.c. data. A least squares curve-fit of the spectral data was used to calculate the contributions of the components of a heterophase system. In this case, relative contents of the crystalline and amorphous phases of a PEEK sample can be obtained from the best fit of its spectrum by the amorphous and crystalline difference spectra. The techniques to calculate crystalline contents of polymer by d.s.c. have been reviewed elsewhere[25]. In the 'peak area method', the weight per cent crystallinity, $\chi(T_1)$, is given by equation (1)

$$\chi(T_1)=\frac{\Delta A}{\Delta H_f(T_2)}\times(100) \tag{1}$$

where ΔA is the area of the melting endotherm above the baseline between T_1 and T_2; T_1 and T_2 are the temperatures at the onset and completion of melting, $\Delta H_f(T_2)$ is the enthalpy of melting of fully crystalline polymer at T_2. By carefully choosing T_1 and T_2, the areas under the endotherms of *Figure 7* can be obtained. By approximating T_2 to T_m, the value of $\Delta H_f = 130$ J/g given by Blundell and Osborn[12] can be used. Then the crystalline contents of the PEEK samples can be calculated.

The calculated crystalline contents from *FT*i.r. and d.s.c. data for PEEK samples subjected to various thermal histories are compared in *Table 2*. The values by the two methods are reasonably close for the melt-quenched samples but quite different for samples slowly cooled from the melt, even though the trends are in agreement. Since least square curve-fitting was based on the crystalline spectrum, which is the characteristic spectrum of the polymer chain segments in preferred conformation, local order in the amorphous phase of PEEK was included in the calculated crystalline contents. In the melt-quenched samples, the degree of local order in the amorphous phase is low. Its contribution to the degree of crystallinity observable by *FT*i.r. is negligible. Hence, at low degree of crystallinity, calculated values from *FT*i.r. and d.s.c. are in agreement. As the crystalline content of the sample increases, the degree of local order also increases and contributes significantly to the degree of crystallinity observable by *FT*i.r. Thus, the difference between the values of the crystalline content calculated by the two techniques is intensified. Therefore, the percentages shown in the i.r. part of *Table 2* can be more precisely described as the content of the conformers which resemble those of the crystalline phase.

The lack of significant differences in the crystalline contents calculated by the same technique between samples procesed at 380°C and 400°C may be inherent in the analyses. Difference in the orientations of the chain

Table 2 Comparison of crystallinity contents as calculated from *FT*i.r. and d.s.c. data

Sample	% Crystallinity *FT*i.r.	% Crystallinity d.s.c.
Melt quenched from 400°C	23	17
Melt quenched from 380°C	23	21
Cooled from 360°C after quenching from 400°C	51	–
Cooled from 360°C after quenching from 380°C	52	–
Cooled from 400°C	58	22
Cooled from 380°C	62	23
As-received powder	–	33

segments cannot be accounted for in least square curve-fitting of spectral data, thus errors in the calculations were magnified. On the other hand, the choices of T_1 and T_2 in the d.s.c. 'peak area method' directly influence the calculated crystalline contents. The lack of the capability to perform base-line correction on the thermograms made the selection of the temperatures less accurate, and undoubtedly contributed to the experimental errors.

CONCLUSIONS

Using digital spectral subtraction technique, the characteristic spectra of the amorphous and crystalline phases of PEEK have been obtained from samples with different degrees of crystallinity. There is a considerable difference between samples of PEEK which were melted at 380°C and 400°C. Local order associated with the diphenyl ether moiety may remain in the disordered phase unless PEEK is melted at 400°C (above its T_m^*). The orientation of the ordered segments also seems to be influenced by the temperature of the melt, depending upon whether it is at 380°C or 400°C.

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