

# Thermal Degradation of Poly(aryl-Ether-Ether-Ketone): Experimental Evaluation of Crosslinking Reactions\*

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## Synopsis

Poly(aryl-ether-ether-ketone) (PEEK) has been heated at 400°C in both nitrogen and air. The extent of thermal degradation has been monitored by a variety of techniques including: solution viscometry, UV-visible spectroscopy, <sup>13</sup>C high-resolution cross-polarization/magic angle spinning nuclear magnetic resonance and Fourier transform infrared spectroscopy. The results indicate, that in a nonoxidative environment such as nitrogen, PEEK is relatively stable at 400°C for periods up to 6 h. Under oxidative conditions chain scission reactions occur and crosslinks are formed causing a reduction in the crystallizability of the material and discoloration of the polymer. The spectroscopic evidence suggests that the chain cleavage occurs adjacent to the carbonyl functional groups. Subsequent hydrogen abstraction from the aromatic ring then leads to crosslinking between adjacent aryl rings.

## INTRODUCTION

In the past few years, a whole range of resins and fiber-reinforced composites have been developed based on new, tough high-temperature thermoplastics.<sup>1-3</sup> Poly(aryl-ether-ether-ketone) (PEEK) is one such polymer which is generating a great deal of interest, especially as a structural material in the aerospace industry.<sup>4,5</sup> One of the major advantages claimed for these thermoplastics is their ease of melt processing which also implies that the material can be reworked and repaired several times by heat treatment. However, recent studies have shown that the physical and mechanical properties of the resin and the composites can be greatly influenced by thermal processing cycles.<sup>6-10</sup> The selection and control of the processing conditions is therefore essential in optimising the physical and mechanical properties of the final material. In a previous paper<sup>11</sup> we reported a systematic study of the effects of processing time, temperature, and environment (such as nitrogen or air) on the crystallinity and crystallisation kinetics of PEEK. In this study,<sup>11</sup> it was suggested that the reduction in the rate of crystallisation and crystallizability of PEEK, when heated in air above its melting point, was due to crosslinking of the polymer. Although the occurrence of crosslinking in thermally-treated PEEK in air has been reported previously,<sup>12,13</sup> no detailed study has been conducted with the exception of an investigation in which elemental sulphur was incorporated into PEEK to deliberately induce the crosslinking reactions.<sup>14,15</sup> In the present study,

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various measurements have been made on PEEK subjected to a variety of heat treatments. Solutions of PEEK samples were characterised by viscosity measurements and UV-visible spectroscopy; and estimations of the weights of insoluble fractions were made to determine the extent of crosslinking. Furthermore, the results of both  $^{13}\text{C}$  high-resolution cross-polarization/magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR) are also reported in order to provide a better understanding of the chemical processes occurring during the thermal treatment of PEEK.

## EXPERIMENTAL

### Materials

Commercial grade PEEK powder 450P (supplied by ICI) was used in this study.

Methane sulphonic acid (99% pure), 1,2-dichlorobenzene (98.5% pure), 4-chlorophenol (99+% pure), and 1-chloronaphthalene (90% pure) were all obtained from Aldrich Chemical Co. and used as received without further purification.

### Heat Treatment

The samples to be used in the viscosity, gel, UV-visible spectroscopy, and NMR determinations were placed in glass ampules and then heated in an oven maintained at 400°C for the prescribed period of time. In the case of experiments conducted under nitrogen, the samples were initially degassed under vacuum before nitrogen was introduced into the tubes. The tubes were then sealed off. After the heat treatment, the samples were removed from the oven and allowed to cool to room temperature. The solidified samples were then ground (10 min) into a powder using a Spex freezer mill cooled with liquid nitrogen.

### Dissolution in Methane Sulphonic Acid and Gel Determination

The methane sulphonic acid solutions were obtained by dissolving 0.3 g of sample in 30 mL of acid. To facilitate the solubilizing process these mixtures were initially placed in an ultrasonic cleaner bath for 1 h and then left to stand for 18 h at room temperature. The solution was then given a 10 min ultrasonic bath treatment before being filtered through a medium grade sintered glass crucible. The filtrate was used for viscometry and UV-visible spectra determinations while the residue was washed three times with 5 mL aliquots of methane sulphonic acid, followed by similar amounts of water and ethyl alcohol. The residual solid was dried in a vacuum oven at 100°C to determine the gel fraction. Although not essential for the solubilization process, the use of the sonic bath was found to reduce the processing time. Comparison of viscosity data obtained from materials dissolved by this technique with those dissolved by a more gradual shaking process indicated no significant differences.

### **Dissolution in 4-Chlorophenol/1,2-Dichlorobenzene (3/2)**

PEEK was found to be soluble in a 3 : 2 w/w solution of 4-chlorophenol : 1,2-dichlorobenzene. In this study we prepared 0.1% solutions by adding the sample to the solvent and refluxing for 15 min at 195°C. The solution was then cooled and filtered to give solutions that were used in UV-visible measurements.

### **UV-Visible Spectroscopy**

The UV-visible absorption spectra of 0.0005% w/v solutions in methane sulphonic acid were recorded using 1 cm cells with a HP 8540A Spectrophotometer. The spectra of the 4-chloro-phenol/1,2-dichlorobenzene (3/2) solutions were made using 0.005% w/v solutions in 1 mm cells.

### **Solution Viscosities**

The solution viscosities were measured in an Ubbelohde viscometer at 30°C. The solutions for the viscosity measurements were made up from the above methane sulphonic acid filtrate used in the gel determinations. To the filtrate (approximately 30 mL) was added 50 mL of water to precipitate the PEEK. The resultant precipitate was then filtered, washed with water and ethyl alcohol before being dried in a vacuum oven at 100°C. The dried samples were then once more weighed accurately and dissolved in fresh methane sulfonic acid and the intrinsic viscosity  $[\eta]$  was taken as the arithmetical mean of the reduced  $[\eta]_R$  and the inherent  $[\eta]_I$  viscosities extrapolated to zero concentration.

### **Infrared Spectroscopy**

The FTIR spectra, of thin polymer films cast from hot 1-chloropnathalene solution on sodium chloride discs, were obtained on a Perkin-Elmer 1500 Fourier Transform Infrared Spectrophotometer. These films were initially air dried before being further dried in a vacuum oven at 100°C. In this study, the original PEEK was cast on the discs and the disc and film were subjected to heat treatments.

### **Nuclear Magnetic Resonance Measurements**

The  $^{13}\text{C}$  NMR measurements of solid PEEK samples were carried out at 75.4 MHz using a Bruker MSL-300 spectrometer. Single shot cross-polarization sequences of 1–5 msec were used with rf field amplitudes of 70 KHz, and delay times of 2 sec. Magic angle spinning rates of 7–8 KHz were achieved with a Doty Scientific probe.

## **RESULTS AND DISCUSSION**

### **Solution Viscosities and Gel Formation**

The influence of treatment at 400°C on the intrinsic viscosity of soluble polymer and on insoluble gel formation as a function of heating time in air is presented in Figure 1. The measured viscosities of each of the solutions did not change with time. This observation is consistent with the fact methane sulfonic

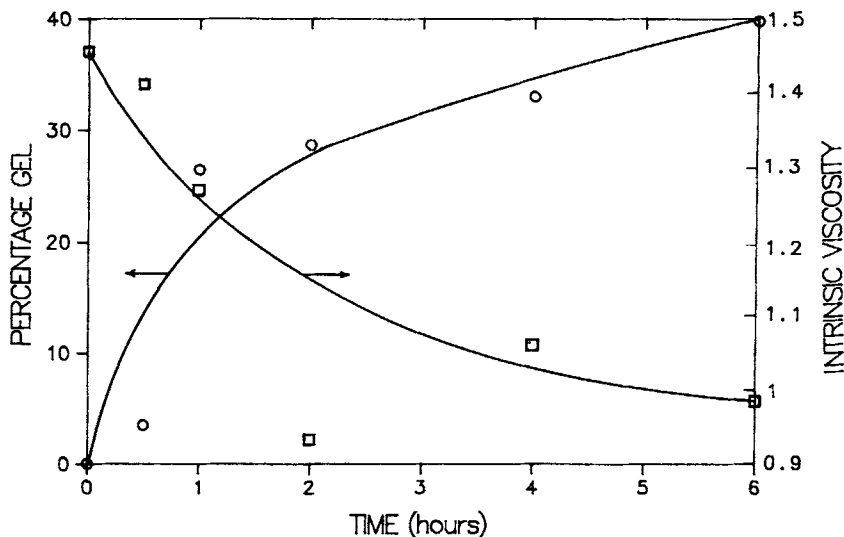


Fig. 1. Percentage insoluble gel and intrinsic viscosities measured in methane sulphonic acid solution after heating in air for different lengths of time.

acid is a nonsulfonating solvent for PEEK, unlike sulphuric acid.<sup>16-18</sup> The data shown in Figure 1 clearly indicate that heating in air causes a marked increase in the insoluble fraction as the exposure time increases, with the greatest increase occurring in the first 60 min of heating. Prolonged heating in air resulted only in a slight further increase in the insoluble fraction. While the amount of insoluble material increased, the intrinsic viscosities obtained for the soluble fractions showed a gradual decrease which began to level off after about 2-3 h. Contrary to the data noted above for samples heated in air, samples heated in a nitrogen atmosphere for up to 6 h at 400°C showed very little change in measured intrinsic viscosity or insoluble gel. This evidence therefore suggests that PEEK heated in air at 400°C undergoes oxidative chain scission reactions leading to a reduction in intrinsic viscosity as a result of the production of lower-molecular-weight species. However, associated with these processes are chain branching reactions leading to crosslinking, causing the formation of a network system which cannot be dissolved in methane sulfonic acid.

These crosslinking reactions have been reported by others.<sup>12,14,19</sup> In addition some preliminary data in our laboratory have shown that changes occur in melt viscosity measurements of PEEK, held at 400°C in air for various time periods.<sup>20</sup>

### UV-Visible Spectra

Heating PEEK at 400°C resulted in a progressive darkening of the samples from an original off-white color through grey to a distinct brown color for the sample heated in air for 6 h. While some color changes were noted in the samples heated in nitrogen, they were far less intense than in air with the 6 h nitrogen sample showing only a slight change from the original color and certainly less of a color change than the sample that had been heated for 30 min in air.

Initially, UV-visible spectra were recorded in methane sulfonic acid and Figure 2 shows three typical spectra. These spectra are similar to those reported previously for PEEK in concentrated sulfuric acid,<sup>17,18</sup> where the yellowish red nature of the solution has been attributed to the absorption at 414 nm assigned to the protonation of the carbonyl group. Heat treatment of the PEEK samples showed a reduction in the intensity of the absorbance spectra as is evident in Figure 2. The degree of reduction of the absorption at 414 nm is plotted in Figure 3 as a function of heating time. Because these data are based upon the total original weight before removal (by filtration) of the gel fraction, part of the observed reduction can be attributed to a concentration effect. However, correction for the insoluble fraction still leaves a marked reduction in the concentration of protonated carbonyl species due to heat treatment at 400°C. Interestingly, heating in nitrogen at 400°C also appears to be responsible for a reduction in the number of carbonyl species capable of protonation.

In order to get a better insight into the nature of the discoloration process, UV-visible spectra were also recorded in 4-chlorophenol/1,2-dichlorobenzene solutions (3/2) with some of the spectra shown in Figure 4. The advantages of using this solvent lie in the absence of a peak around 414 nm associated with protonation by the solvent which means that the color changes in the visible region are much clearer. Spectra could not be recorded below 295 nm because

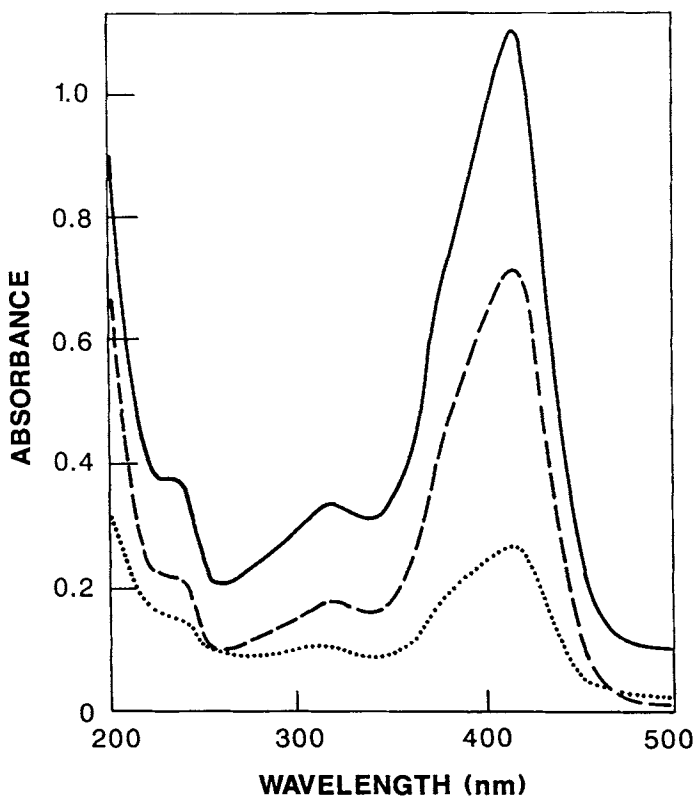


Fig. 2. UV visible spectra of PEEK samples in methane sulfonic acid after being heated at 400°C for 6 h in nitrogen (---) and 6 h in air (···). Original samples (—).

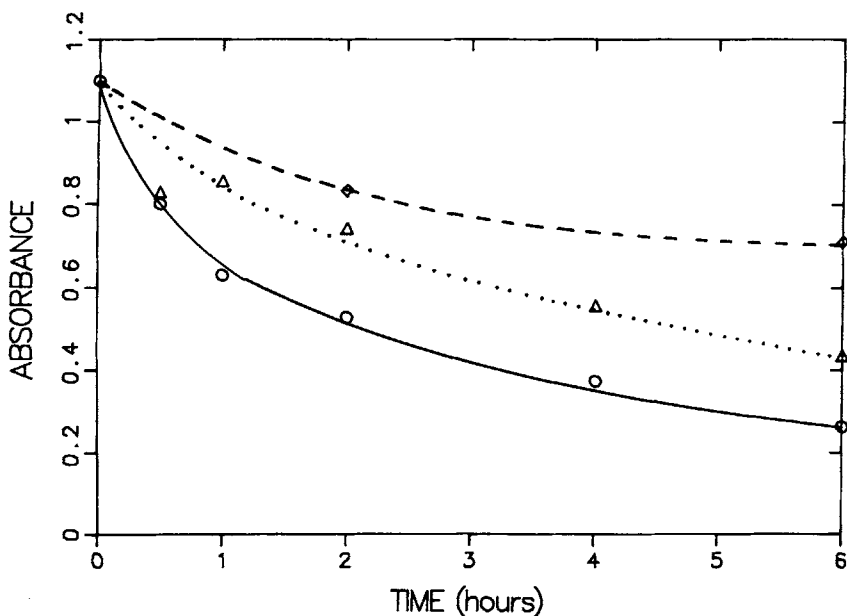


Fig. 3. Absorbance intensity measured at 414 nm in methane sulphonic acid for PEEK samples heated in air (—) and nitrogen (---) for different periods of time. Absorbance values of air heated samples corrected for insoluble gel fractions (· · ·).

of the intense absorbance of the solvent. However, the absorbances at 300, 350, and 400 nm have been measured as a function of heating time and the data are presented in Table I. From this table, it can be seen that in the case of heat treatment in air there is a decrease in absorbance at 300 nm as a function of heat treatment. However, as was noted in the case of methane sulfonic acid, a gel fraction was formed and was filtered off before measuring the UV-spectrum. This must once again be responsible for part of the reduction in the absorbance values measured. However, as far as discoloration is concerned, this is related to the absorbance in the visible region. In the case of samples heated in air, the longer the heating time, the greater the absorbance value in the visible region as noted by the values reported at 400 nm. Clearly, the discoloration of PEEK is not solely limited to the insoluble cross-linked network formation, but also due to increased conjugation in the linear molecules remaining. Heating in nitrogen, meanwhile, caused a slight increase in the absorbance at 300 nm but little change in the visible portion of the spectra associated with discoloration.

### Infrared Spectroscopy

Figure 5 shows the changes occurring in the fingerprint region of the IR spectra of PEEK samples heated for increasing periods of time at 400°C in air. These data indicate that as the polymer is heated there is a gradual loss of the spectral features presumably due to degradation and volatilization of material. The loss of material on heating in air has been noted previously in thermogravimetric studies.<sup>21</sup> It is interesting to note that although there is a gradual loss

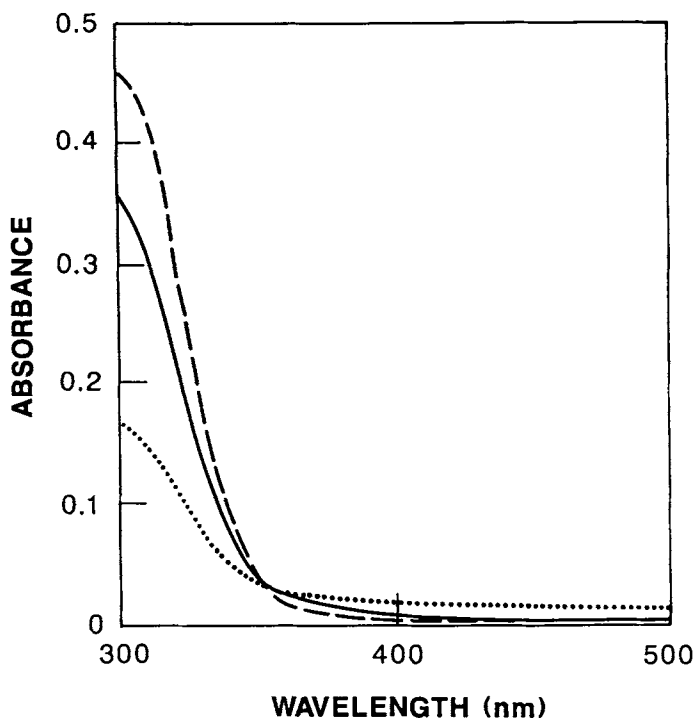


Fig. 4. UV-visible spectra of PEEK samples in 4-chlorophenol/1,2-dichlorobenzene (3/2) solution after being heated at 400°C for 6 h in nitrogen (---) and 6 h in air (· · ·). Original sample shown (—).

of spectral features during heating, the spectra appear to show no new features emerging or specific features disappearing. However, there appear to be some changes in relative intensities of certain peaks. Using the spectral assignments reported by Nguyen and Ishida<sup>22-24</sup> the following changes appear to be occurring as a result of heat treatment. The carbonyl stretching vibration absorbing at  $1650\text{ cm}^{-1}$ , appears to shift slightly to higher wavenumbers and relative to the

TABLE I  
Absorbance of Filtered 0.005% Solutions in 4-Chlorophenol/1,2-Dichlorobenzene (3/2)  
Solutions at 25°C in 1 mm Cells

Heating time (hours)	Atmosphere	Absorbance at		
		300 nm	350 nm	400 nm
0	Air	0.3614	0.0351	0.0065
0.5	Air	0.3248	0.0253	0.0065
1	Air	0.3232	0.0239	0.0070
2	Air	0.2232	0.0229	0.0082
4	Air	0.2302	0.0302	0.0135
6	Air	0.1700	0.0330	0.0225
2	N <sub>2</sub>	0.4045	0.0287	0.0060
6	N <sub>2</sub>	0.4565	0.0375	0.0068

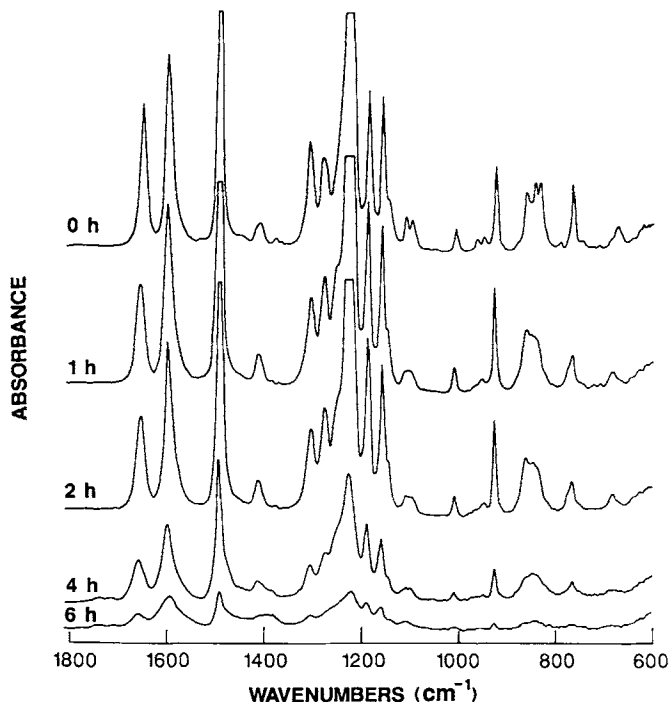


Fig. 5. Transmission IR spectra of PEEK samples heated at 400°C in air for different lengths of time.

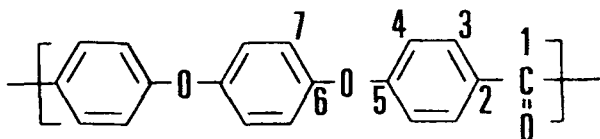
skeletal in plane vibration of the phenyl rings at  $1599\text{ cm}^{-1}$  is getting smaller. This shift in the carbonyl stretching frequency has been associated with an increase in conjugation noted with increased crystallization due to a greater coplanarity of the phenyl rings,<sup>23</sup> and in this study could be due to the greater ordering of the system from network formation as a result of crosslinking reactions. The reduced relative intensity of the carbonyl stretching vibration meanwhile suggests that a reduction in carbonyl groups appears to be taking place.

In a similar manner, the asymmetric stretch of the diphenyl ether groups is shifting from  $1285\text{ cm}^{-1}$  to  $1278\text{ cm}^{-1}$  and increasing in intensity relative to the  $1307\text{ cm}^{-1}$  band associated with the carbonyl linkage. These changes, once again, appear to reconfirm the reduction in carbonyl groups and formation of a more ordered structure. The only other noticeable change is the intensity of the band at  $769\text{ cm}^{-1}$  associated with the out-of-plane bending modes of the aromatic hydrogens. This band which has been associated with the crystalline ordered structure of PEEK shows a reduction in relative intensity when compared to the peak at  $928\text{ cm}^{-1}$ , which has been shown to be independent of crystallinity.<sup>23</sup> This finding initially appears to be in contradiction to the previous changes noted. If, however, crosslinking is occurring through the aromatic hydrogen, then a reduction in this relative band intensity is a possibility as network formation proceeds.



### Nuclear Magnetic Resonance Data

The  $^{13}\text{C}$  conventional CP/MAS spectra of PEEK, which has been heated for various periods of time in air at  $400^\circ\text{C}$  are shown in Figure 6. The assignment of the different carbons to the various peaks are given based upon the data presented by Clark et al.<sup>25,26</sup> using the following numbering system:



Essentially, the spectra after 6 h heat treatment at  $400^\circ\text{C}$  in air are very similar to that of the unheated initial powder. There is very little difference in the broadness of the spectral lines, a distinguishing feature of amorphous and crystalline material.<sup>26</sup> There does, however, appear to be a slight reduction in the ratio of carbon atoms C-5 to C-6, while at the same time there appears to be a change in the ratio of C-4 and C-7 carbon atoms. A possible explanation of these slight changes is that crosslinking is taking place between two adjacent chains to give the following structures:

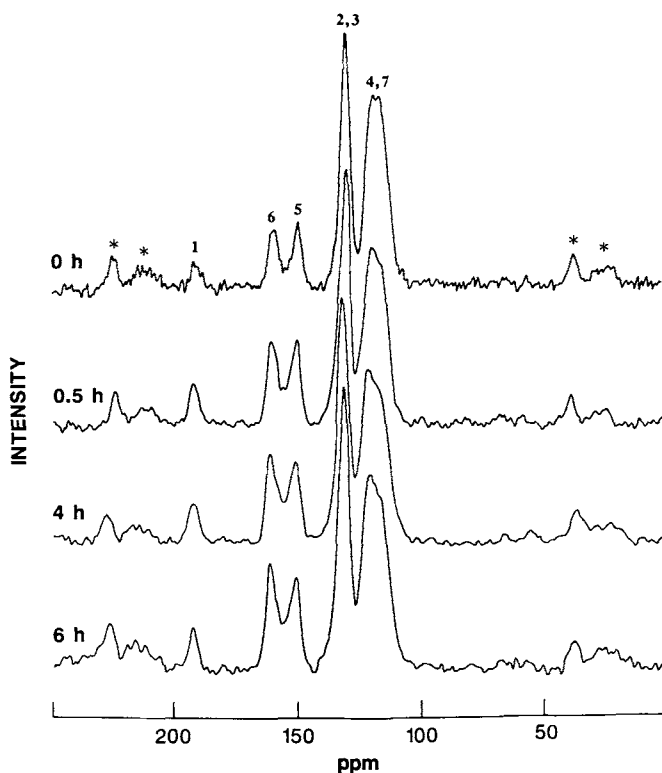
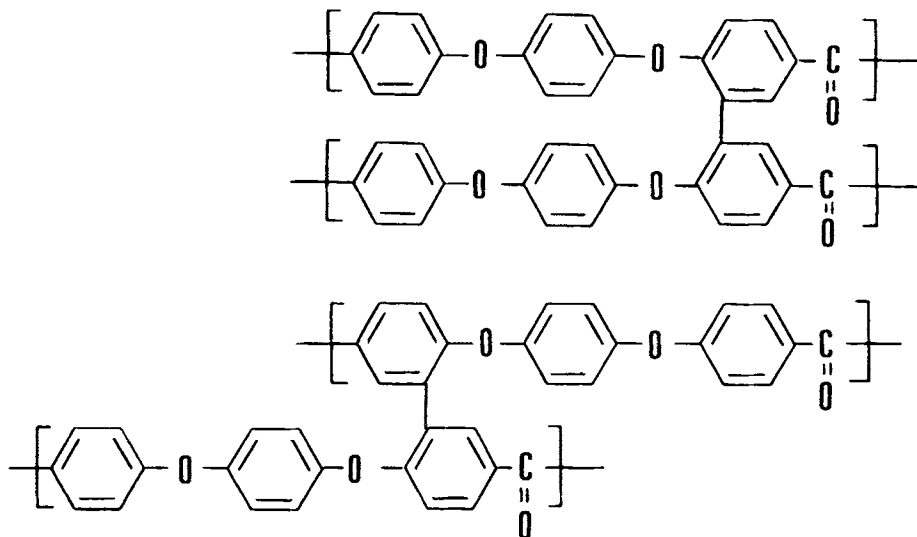


Fig. 6. Solid state  $^{13}\text{C}$  conventional CP/MAS NMR spectra of PEEK samples heated at  $400^\circ\text{C}$  in air for different lengths of time. (Spinning side bands designated \*.)



Both these structures would cause a reduction in both the C5 and C4 signals, as noted.

### CONCLUSIONS

This study has confirmed that PEEK is sensitive to the processing conditions of temperature, time, and environment. In particular processing in an air environment can result in chemical changes as a result of chain scission and crosslinking reactions which can occur at an early stage in the heat treatment process. Although the chemical reactions taking place are not fully understood, it appears that the chain scission process may well occur at the carbonyl linkage and result in the loss of the carbonyl functional groups. Subsequently, hydrogen abstraction takes place from the meta position with respect to the carbonyl to give radicals which are relatively stable. Combination of adjacent radicals then proceeds to produce crosslinks which will restrict the orderly packing between chains resulting in a decrease in the crystallinity of the material.

The information presented in this paper therefore confirms that heating PEEK in air causes reactions such as decomposition, chain branching, and crosslinking to occur. These reactions are capable of influencing the crystallization kinetics and crystallizability of PEEK as measured by DSC.<sup>11</sup>

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