The thermal degradation of poly(aryl-ether-ether-ketone) (PEEK) as monitored by pyrolysis-CG/MS and TG/MS

Day, M.; Cooney, J. D.; Wiles, D. M.

Publisher's version / Version de l'éditeur:
https://doi.org/10.1016/0165-2370(90)80005-9
Journal of Analytical and Applied Pyrolysis, 18, 2, pp. 163-173, 1990-11

31856

Journal of Analytical and Applied Pyrolysis, 18 (1990) 163–173
Elsevier Science Publishers B.V., Amsterdam

THE THERMAL DEGRADATION OF POLY(ARYL–ETHER–ETHER–KETONE) (PEEK) AS MONITORED BY PYROLYSIS–GC/MS AND TG/MS *

M. DAY *, J.D. COONEY and D.M. WILES

Division of Chemistry, National Research Council of Canada, Ottawa, Ontario K1A 0R6 (Canada)

(Received March 14, 1990; accepted June 20, 1990)

ABSTRACT

The thermal degradation of poly(aryl–ether–ether–ketone) has been studied over a range of pyrolysis conditions using both a flash pyrolysis–gas chromatography/mass spectrometry technique (Py–GC/MS) and a thermogravimetry/mass spectrometry technique. The major volatile thermal decomposition product was found to be phenol, which dominated all other volatile species especially under the least severe pyrolysis conditions. Under more severe pyrolysis conditions, such as those encountered in the Py–GC/MS experiments, a much wider range of volatile products was obtained. The results have been interpreted to imply that the primary random chain scission reactions occur at the ether linkages and it is only under more severe pyrolysis conditions that random chain scission also involves the ketone linkage.

Gas chromatography; mass spectrometry; poly(aryl–ether–ether–ketone); pyrolysis; thermogravimetry.

INTRODUCTION

Advanced composites play an important role in the design and fabrication of key components in aerospace and automotive applications owing to their ease of processing and low densities when compared with conventional materials. A wide range of materials is currently being evaluated; these include fibre-reinforced thermoplastics, which have the added advantages of improved damage tolerance, repairability and easier fabrication. Poly(aryl–ether–ether–ketone) (PEEK) and its composites with carbon fibres is one such material which has received considerable attention. However, because the resin is thermoplastic, there is some concern regarding the retention of these advantageous properties. In previous studies we have used both

* Issued as NRCC #31856.

0165-2370/90/$03.50

differential scanning calorimetry [1–3] and thermogravimetry (TG) [4–7] to study the influence of thermal processing on the thermal stability of PEEK. In the TG studies we determined kinetic parameters which were used to assess potential lifetimes. However, in none of these studies were the actual chemical degradation mechanisms evaluated; only the chemical kinetics of the overall weight-loss processes were determined.

In this study, pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) and thermogravimetry/mass spectrometry (TG/MS) have been used to identify the products of the thermal decomposition of PEEK. Knowledge of the degradation products should make it possible to postulate the chemical decomposition reactions leading to the formation of these products. Using this information, it may be possible to suggest the key features which limit the thermal stability of PEEK and to identify potential areas which could lead to the development of newer polymers of greater thermal stability.

Previous studies of the gaseous products of the thermal decomposition of PEEK and its fibreglass composites [8–10] in helium using TG/MS showed phenol to be the major degradation product. These workers also detected minor amounts of diphenyl ether, diphenyl sulphide, diphenyl sulphone, SO_2, CO_2 and benzene. A similar study [11] in air and nitrogen revealed the same products plus benzoquinone, the concentration of which was highest in an oxidative environment. A third study [12] identified hydroxyl- and hydro-terminated oligomers in addition to phenol and benzofuran derivatives in the gaseous products obtained from PEEK heated at 500 °C in nitrogen.

EXPERIMENTAL

The PEEK polymer used in this work was the same as that used in our previous studies [4–7], i.e. a 0.217 mm diameter monofilament prepared from ICI resin by Albany International.

The Py–GC/MS experiments were performed using a Pyroprobe 120 pyrolyser from Chemical Data Systems coupled to a Perkin–Elmer Sigma 3B gas chromatograph fitted with a Hewlett–Packard 5970 Series Mass Selective Detector. The samples (0.2–0.4 mg) were pyrolysed in quartz tubes using the coil probe attachment. Five nominally set pyrolysis heating temperatures between 1000 and 1500 °C were selected and used with the ramp setting off and an isothermal hold time of 10 s. Calibration of the probe at these settings indicated that the actual sample temperature profiles were much lower than these nominally set temperatures. The calibrated response of a 30 gauge Chromel–Alumel thermocouple placed in the same position as the sample is shown in Fig. 1 for the five instrumentally set pyrolysis temperatures used in this study. Separation of the pyrolysis products was

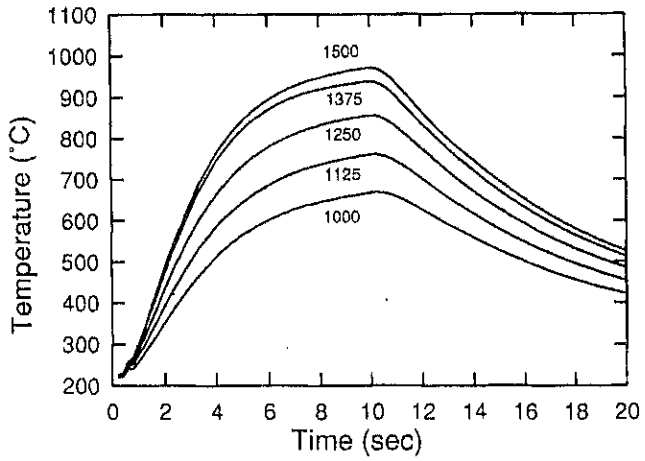


Fig. 1. Temperature profiles recorded at the pyrolysis sample position at the indicated pyrolysis temperature settings.

achieved using a 30 m × 0.25 μm coated DB-5 capillary column, temperature programmed from 120 to 280 °C at 10 °C/min after an initial hold of 4 min at 120 °C. The mass spectrometer was connected to the gas chromatograph by a heated interface maintained at 280 °C.

The TG/MS experiments were performed using a DuPont Model 951 thermobalance controlled by a 2100 thermal analysis station. The pyrolysis products, during weight loss, were sampled by means of a heated capillary line running directly from a position above the sample to the mass spectrometer using a direct interface maintained at 200 °C. Data were collected over a mass range of 45–202 dalton. The samples analysed were of the order of 12 mg and were heated in nitrogen (50 mL/min) at 10 °C/min up to 850 °C. The thermograms obtained were then combined with the mass spectrometer total ion chromatogram (TIC) to allow the simultaneous identification of the evolved gases as a function of weight loss.

RESULTS

The effectiveness of the pyrolysis conditions in producing volatiles during the Py–GC/MS experiments was assessed by measuring the weights of the samples in the quartz tube before and after pyrolysis. These values are summarized in Table 1 and correspond to the mean and standard deviation of at least four experiments at each pyrolysis condition.

A typical pyrogram is shown in Fig. 2, while the major pyrolysis products identified in this figure are presented in the order of increasing retention times in Table 2. Peaks were identified by their mass spectra and in many cases were confirmed by comparison with authentic samples. Although

TABLE 1

Percentage weight loss of PEEK samples subjected to Py–GC/MS

Nominally set pyrolysis temperature (°C)	Peak pyrolysis temperature (°C)	Weight loss (%)
1000	668	14± 8
1125	760	51±18
1250	856	58± 9
1375	938	65±14
1500	971	75± 6

Table 2 does not give an exhaustive list of all of the pyrolysis products produced from PEEK, it can be seen from Fig. 2 that they represent over 95% of the compounds detected by our analysis system. It should be noted, however, that the mass spectrometer was set at a lower m/z limit of 40 so that species with molecular weights less than 40 would not be detected.

The actual evolution of these species as a function of the PEEK pyrolysis temperature are presented in Figs. 3–6. The data presented in these figures have been normalized to moles of volatile product per mole of polymer subjected to pyrolysis (without a correction for the weight pyrolysed). To facilitate the calculations a value of 20060 has been taken for the initial molecular weight of the polymer (based upon solution viscosity measure-

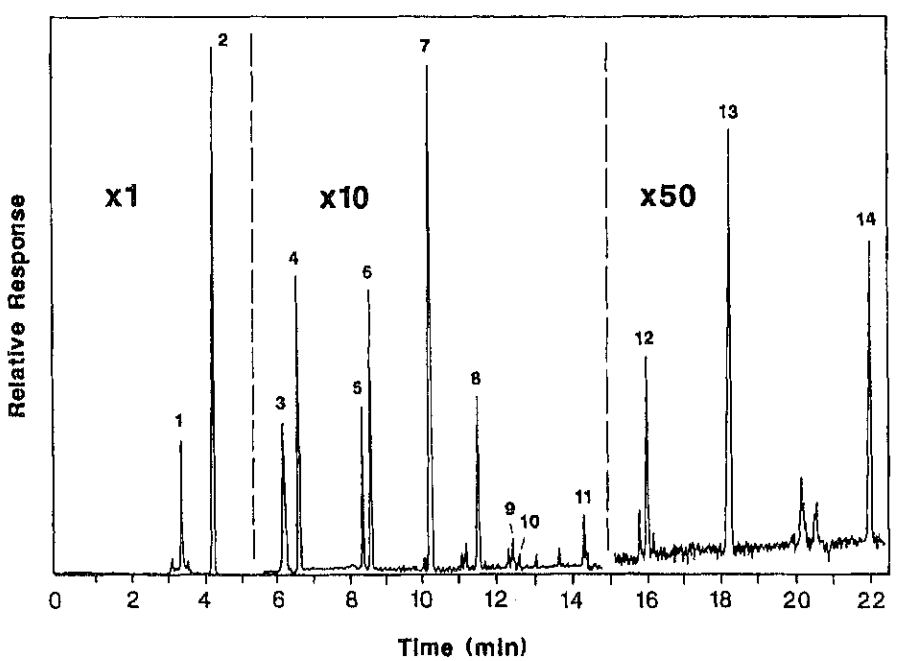


Fig. 2. Typical pyrogram of PEEK pyrolysed at a peak pyrolysis temperature of 971° C.

TABLE 2

Pyrolysis products identified in the pyrolysis of PEEK

Peak No.	Retention time (min)	Compound	Molecular weight	Major mass fragments	Checked by authentic compound
1	3.4	Benzene	78	78, 50, 77, 51, 52, 44	✓
2	4.2	Phenol	94	94, 66, 65, 55, 63, 51	✓
3	6.2	Naphthalene	128	128, 127, 51, 129, 102, 126	✓
4	6.6	Hydroquinone	110	110, 53, 81, 54, 55, 82	✓
5	8.3	Biphenyl	154	154, 153, 152, 76, 155, 51	✓
6	8.6	Diphenyl ether	170	170, 141, 51, 142, 77, 169	✓
7	10.2	Dibenzofuran	168	168, 139, 169, 63, 84, 140	✓
8	11.5	Benzophenone	182	105, 77, 182, 51, 181, 183	✓
9	12.4	4-Phenylphenol	170	170, 141, 115, 169, 171, 139	✓
10	12.6	4-Phenoxyphenol	186	186, 51, 109, 78	✓
11	14.3	2-Dibenzofuranol	184	184, 185, 127, 128, 77, 155	
12	15.9	Hydroxy-benzophenone	198	121, 198, 77, 93, 65, 51	✓
13	18.2	Diphenoxy-benzene	262	262, 77, 51, 263, 246, 185	✓
14	21.8	Bis(phenoxy)-benzophenone	355	197, 274, 77, 105, 115, 181	

ments [13]) which corresponds to 70 repeat units of the aryl ether, ether, ketone chain.

The evolution of phenol and benzene as a function of peak pyrolysis temperature is shown in Fig. 3. The yield of these two products always dominated the volatile gas composition analysed, irrespective of the pyroly-

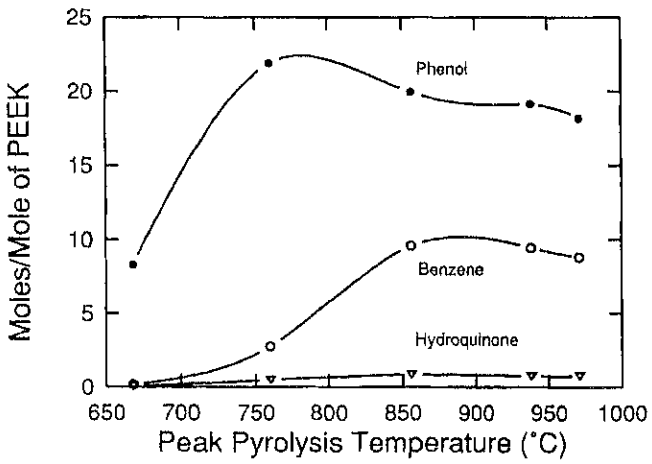


Fig. 3. Evolution of phenol, benzene and hydroquinone as a function of the peak pyrolysis temperature.

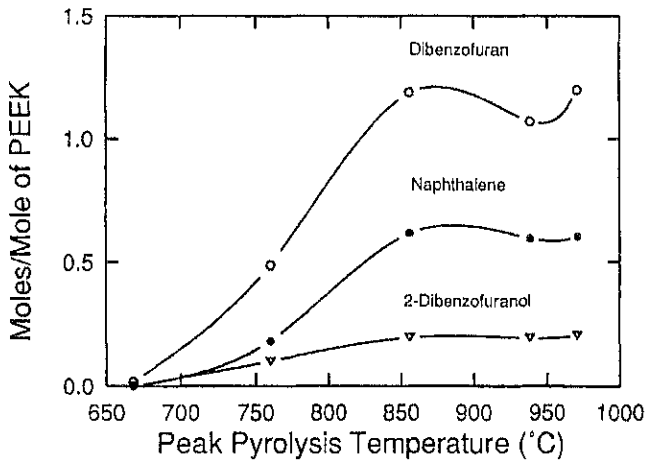


Fig. 4. Evolution of dibenzofuran, naphthalene and 2-dibenzofuranol as a function of the peak pyrolysis temperature.

sis temperature, yielding 20–50 times the concentration of the next major volatile pyrolysis product. Interestingly, both species rapidly approach a maximum concentration around the peak pyrolysis temperatures of 760–850 °C. A condition noted with all the species monitored (see also Figs. 4–6) was the levelling off of the yield above the peak pyrolysis temperature of about 850 °C.

Also listed in Fig. 3 is the evolution curve for hydroquinone, the other volatile monoaromatic species detected. Benzaldehyde, another expected monoaromatic species, was not detected unambiguously. Tests with an authentic sample of benzaldehyde indicated that its retention time was

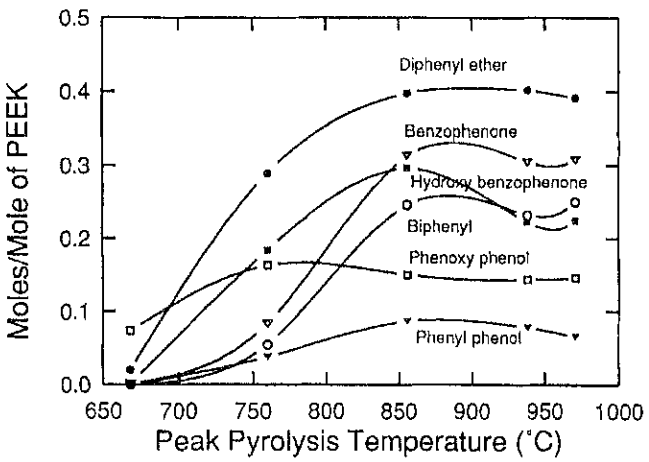


Fig. 5. Evolution of diphenyl ether, benzophenone, hydroxybenzophenone, biphenyl, phenoxyphenol and phenylphenol as a function of the peak pyrolysis temperature.

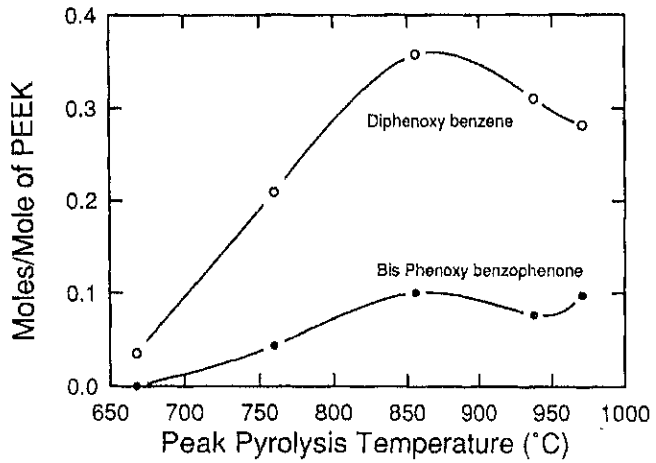


Fig. 6. Evolution of diphenoxybenzene and bis(phenoxy)benzophenone as a function of the peak pyrolysis temperature.

almost identical to that of phenol. An attempt to quantify benzaldehyde in the presence of such a large amount of phenol made using single ion analysis was not successful.

After phenol and benzene the next major volatile fraction was dibenzofuran. The evolution of this species is presented in Fig. 4 along with those of naphthalene and 2-dibenzofuranol, the other polynuclear aromatic species formed in the pyrolysis of PEEK. It should be noted that the production profiles of all these species are very similar, and resemble those of benzene and hydroquinone, i.e. there is a rise in evolution with peak pyrolysis temperature up to about 850 °C, above which the concentration appears to remain constant.

Several species containing two aryl groups connected together through either ether or carbonyl linkages were detected along with biphenyl itself. The formation of these species as a function of peak pyrolysis temperature is shown in Fig. 5. Once again the evolution curves reflect those characteristics already noted for the other species.

In Fig. 6 the evolution of diphenoxybenzene and bis(phenoxy)benzophenone are plotted. This bis(phenoxy)benzophenone (MW = 355) had the largest mass fragment ($m^+ = 274$) detected by the separation and analysis system employed in this study. However, the results reported by Hay and Kemmish [12] lead us to expect other higher molecular weight oligomers.

The results of the TG/MS experiments are given in Fig. 7, and show that the major weight loss for PEEK in nitrogen under these heating conditions occurs between 540 and 640 °C, above which the rate is much slower. Comparison of the derivative of the weight loss curve with the TIC monitored by the mass spectrometer clearly reveals the similarities between the two responses.

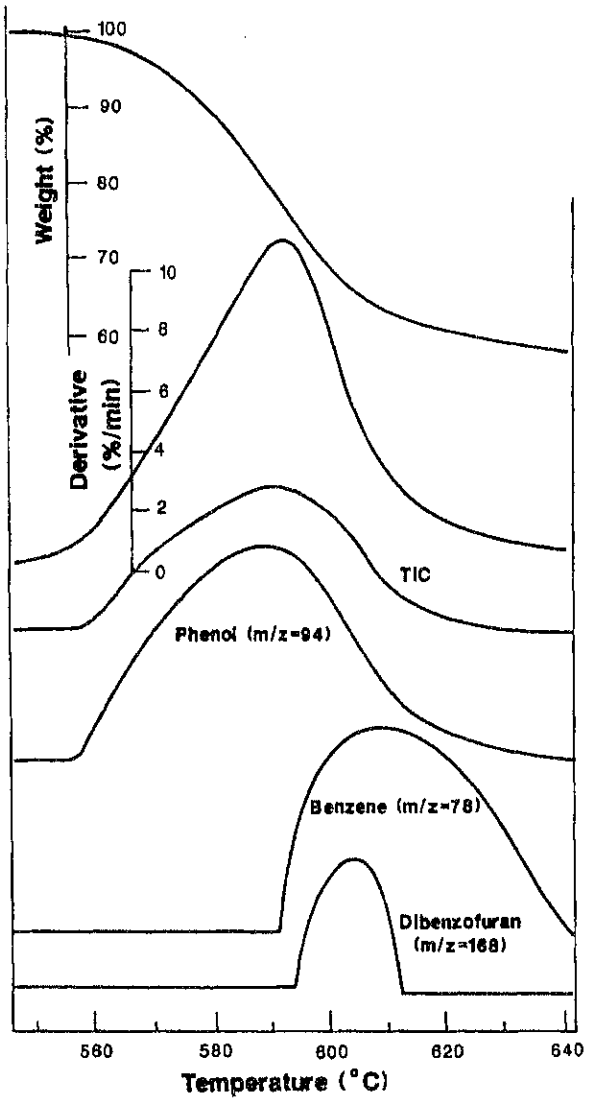


Fig. 7. Thermogravimetric weight loss and first derivative, along with TIC plot and single ion plots for phenol ($m/z = 94$), benzene ($m/z = 78$) and dibenzofuran ($m/z = 168$) recorded during a TG experiment at a heating rate of 10 °C/min.

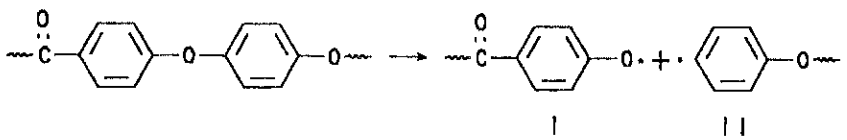
The TIC envelope from the sample has also been searched for the major ions identified in Table 2. The ions associated with the three major volatile products, phenol (m/z 94), benzene (m/z 78) and dibenzofuran (m/z 168) were the only volatile species detected under our experimental conditions. In terms of ion count response there was a marked difference between that of phenol and the other two compounds, benzene and dibenzofuran, which is not indicated in Fig. 7. For example, the peak ion count for phenol was about 950 while the corresponding values for benzene and dibenzofuran

were 40 and 30, respectively. These concentrations, obtained in the TG/MS experiments, indicate a greater dominance of phenol over that noted in the pyroprobe experiments. The onset of the evolution of benzene and dibenzofuran was also noted to occur at higher temperatures than the onset temperature observed for phenol. In fact the formation of benzene and dibenzofuran appear to commence after the phenol evolution has peaked. These findings appear to be consistent with the observed more rapid evolution of phenol in the Py–GC/MS experiments at the lower pyrolysis temperatures.

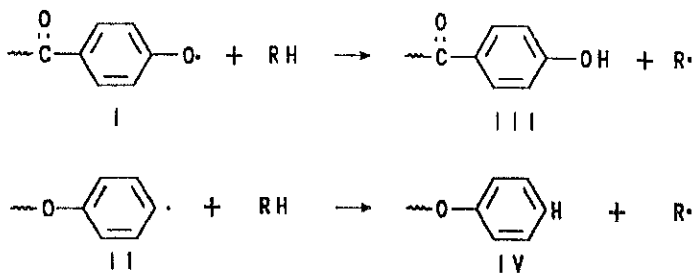
DISCUSSION

The data reported in this study suggest that the major gaseous volatile product of the pyrolysis of PEEK under a variety of pyrolysis conditions is phenol. Other gaseous volatile products such as benzene, dibenzofuran, etc. were detected but in much smaller quantities. Under pyroprobe pyrolysis conditions the detected yield of phenol was always two to three times that of the next major detected component, benzene. However, under the dynamic TG heating conditions, the amount of phenol detected was at least 20 times that of benzene.

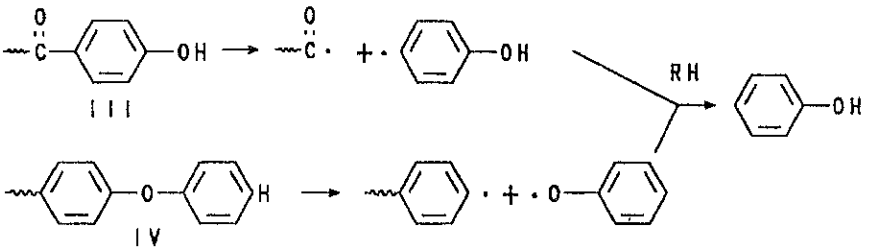
The prime decomposition mechanism must therefore explain the production of phenol in the early chain scission processes. This would imply that the primary chain scission reaction involves the ether linkages rather than the carbonyl linkage, i.e.



Hydrogen abstraction from adjacent polymer chains can then lead to the following stable chain ends.

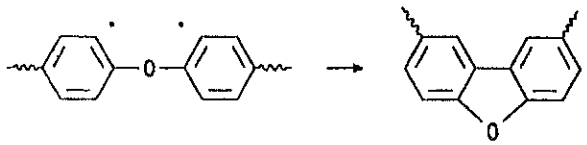


Subsequent cleavage of these chain ends will then give rise to species capable of forming phenol, the major volatile pyrolysis product detected in our study.

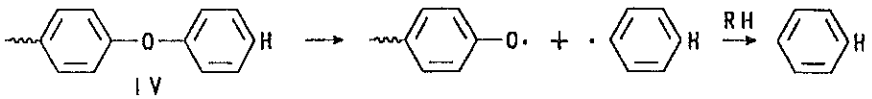


It should be noted that scission of the terminal aryl unit IV could lead to the formation of benzene as well as phenol, but the results of this study indicate that the phenol fraction appears to predominate.

Hay and Kemmish [12] proposed the initial combination of adjacent radicals to explain the formation of dibenzofuran derivatives.



It would appear from our results, however, that dibenzofuran production occurs under our pyrolysis conditions from the subsequent thermal reactions of phenol [14] or even diphenyl ether. This formation of dibenzofuran on heating phenol could explain its formation at the higher pyrolysis temperatures and after the concentration of phenol has peaked (Fig. 7). Although there is a predominance of phenol over benzene at the lower pyrolysis temperatures, under the more energetically favourable higher temperature pyrolysis conditions used in the Py–GC/MS experiments more benzene is detected. This suggests that the alternate chain scission of IV to benzene is more favoured under these conditions.



It should also be noted from Fig. 7 that benzene is a higher temperature degradation product, the concentration of which increases as that of phenol decreases. These observations are in contrast to those observed by Hay and Kemmish [12] who found and identified other compounds (mainly derivatives of benzofuran) in greater abundance than phenol at a pyrolysis temperature of 506 °C.

With respect to the pyrolysis products listed in Table 2 it is clear that in our study all the detected volatile products, with the exception of phenol, benzene and dibenzofuran, are all secondary reaction products produced as the fragments are further degraded into small volatile components detectable by the analysis system. The formation of all these species is attributable to either multiple chain scission reactions of the main polymer chain or recombination reactions of adjacent radicals to produce the desired species.

CONCLUSIONS

It would appear that the degradation of PEEK is initiated by homolytic chain cleavage at the ether bond. The resultant phenolic end groups, produced on subsequent hydrogen abstraction, are cleaved to produce phenol as the initial and major pyrolysis product. Subsequent degradation at higher decomposition temperatures causes other volatile products to be produced as a result of the increased randomness of the chain scission processes. These products include dibenzofuran, biphenyl and naphthalene, which can be formed as a result of radical recombination reactions. The presence of ether-linked molecules or species in the pyrolysis products also suggests that in addition to radical recombination reactions some chain cleavage at the carbonyl groups is occurring in addition to ether bond breakage.

REFERENCES

1 M. Day, T. Suprunchuk, J.D. Cooney and D.M. Wiles, J. Appl. Polym. Sci., 36 (1988) 1097.
2 M. Day, T. Suprunchuk, J.D. Cooney and D.M. Wiles, 20th Int. SAMPE Tech. Conf., 20 (1988) 132.
3 M. Day, T. Suprunchuk, Y. Deslandes and D.M. Wiles, 34th Int. SAMPE Symp., 34 (1989) 1474.
4 M. Day, J.D. Cooney and D.M. Wiles, J. Appl. Polym. Sci., 38 (1989) 323.
5 M. Day, J.D. Cooney and D.M. Wiles, Society of Plastics Engineers 46th Anal. Tech. Conf. (ANTEC 88) April 1988, Atlanta, GA, Vol. 34, p. 933.
6 M. Day, J.D. Cooney and D.M. Wiles, Polym. Eng. Sci., 29 (1989) 19.
7 M. Day, J.D. Cooney and D.M. Wiles, Thermochim. Acta, 147 (1989) 189.
8 R.O. Yelton, T.L. Shell and D.M. Colman, Proc. 33rd American Society for Mass Spectrometry Anal. Conf. on Mass Spectrometry and Applied Topics, San Diego, CA, May 1985.
9 R.O. Yelton, T.L. Shell and R.B. Whitaker, Proc. 14th North American Thermal Analysis Society Conference, September 1985, San Francisco, CA, p. 60.
10 R.O. Yelton, T.L. Shell and R.B. Whitaker, Report 1986, MLM-3331, Order No. DE86006325, Energy Res. Abstr., 11(a) (1986) No. 20488, National Technical Information Service, Springfield, VA, 16pp.
11 R.B. Prime and J.C. Seferis, J. Polym. Sci. Polym. Lett. Ed., 24 (1986) 641.
12 J.N. Hay and D.J. Kemmish, Polymer, 28 (1987) 2047.
13 M. Day, D. Sally and D.M. Wiles, J. Appl. Polym. Sci., 40 (1990) 1615.
14 C. Delaurois, Ann. Mines Belg., 1 (1968) 9.