Thermal decomposition of poly(aryl ether ketones)

J. N. Hay* and D. J. Kemmish†
The Department of Chemistry, The University of Birmingham, PO Box 363, Edgbaston, Birmingham B15 2TT, UK

(Received 17 March 1987; revised 28 April 1987; accepted 1 May 1987)

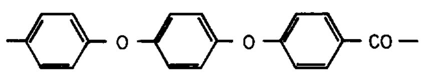
Thermogravimetry has been used to study the isothermal decomposition of poly(aryl ether ether ketone) and poly(aryl ether ketone) and the kinetics of decomposition established from the evolved volatiles. Both products and measured activation energies were consistent with a chain scission process occurring at ether and carbonyl linkages. The volatile decomposition products were analysed by mass spectroscopy and were found to contain various oligomers together with phenol and dibenzofuran. The volatile products were richer in hydrogen than the parent polymers, at the expense of a carbon-like insoluble residue. The degradation products are accounted for in terms of random chain scission and transfer reactions.

(Keywords: poly(aryl ether ether ketone); poly(aryl ether ketone); thermogravimetry; degradation; chain scission oligomers)

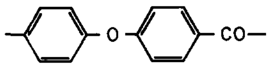
INTRODUCTION

Much of the commercial interest in aryl ketone polymers stems from their high glass temperature and melting point, and also in their increased thermal stability over conventional engineering polymers. The higher melting point gives dimensional stability and reasonable retention of mechanical properties to temperatures in excess of 300°C, but dependent on test procedures.

In this study thermogravimetry has been used to investigate the decomposition mechanism of both poly(aryl ether ether ketone) (PEEK) and poly(aryl ether ketone) (PEK) with the aim of identifying those features which lead to thermal instability, avoidance of which would lead to higher maximum service temperatures. PEEK has the repeat unit:



and PEK is closely similar:



EXPERIMENTAL

Samples of both PEK and PEEK were supplied by ICI Petrochemical and Polymer Ltd as research samples. We are indebted to Dr P. A. Staniland for the gift of these samples and a list of their characteristics.

The thermogravimetric balance comprised a Perkin–Elmer Autobalance AD-2 reading to 1 μg, a Stanton–Redcroft furnace and temperature control unit, and an analogue-to-digital (A/D) converter interfaced to an Apple-IIe microcomputer.

Degradations were carried out on 10–30 mg discs cut from moulded sheets, and contained within open aluminium pans under oxygen-free nitrogen purging at $0.5\,\mathrm{dm^3\,min^{-1}}$. Prior to moulding and degradation studies, the polymer was pre-dried *in vacuo* at 373 K to prevent hydrolytic degradation, and it was moulded at 673 K for 90 s.

Volatile degradation products were condensed in liquid-nitrogen traps and analysed by chromatography and mass spectroscopy, using a Kratos MS80RF and a temperature probe. The temperature of the probe was increased progressively from 293 to 720 K during the analysis. Ionization was by electron bombardment.

Relative molecular-weight averages were determined as polystyrene equivalents using a Waters 150C GPC gel permeation chromatography system. Four columns of crosslinked divinylbenzene/polystyrene gels (two of 10^6, one of 10^5 and one of 10^3 porosity) were used in a mixed solvent of *o*-dichlorobenzene/*p*-chlorophenol at 313 K. Sample and molecular-weight characteristics are listed in *Tables 1* and *2*.

RESULTS

Degradation rate studies

Initial studies were carried out to confirm that little or no degradation of the polymers had taken place during sample preparation. No significant changes in molecular weight were observed up to 573 K on prolonged heating *in vacuo*, or in air at 473 K (see *Table 2*). However, prolonged heating above 673 K led to the development of insolubility and colouring of the polymer. Subsequent cooling from this temperature produced materials with reduced crystallinity, and a decrease in isothermal crystallization rate constants. Observation of the processes of crystallization on a hot-stage microscope showed that both nucleation and growth of the spherulites had been reduced, and there were regions of the melt which would not crystallize. These observations were clearly indicative of crosslink formation.

Volatiles were produced from both PEK and PEEK at measurable rates between 700 and 800 K and were

---

* To whom all correspondence should be addressed
† Present address: ICI plc, Wilton Works, Middlesbrough, Cleveland TS6 8JA, UK

0032-3861/87/122047-05$03.00

Table 1 Sample characteristics

Polymer	Sample ref.	Melt viscosity[a] (kN s m^{-2})	Form
PEEK	A	0.21	Powder
PEEK	C	0.45	Moulding pellets
PEK	G	0.23	Powder

[a] At 670 K and at a shear rate of 1000 s^{-1} in a capillary rheometer

Table 2 Molecular-weight distribution

		Molecular-weight averages		
Sample ref.	Treatment	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w$ ($\times 10^{-3}$)	$D = \bar{M}_w/\bar{M}_n$
A	As received	12	30	2.5
C	As received	46	114	2.5
C	Heated in air: 1.5 min, 673 K	46	115	2.5
C	Heated in N_2: 16 h, 573 K	51	114	2.2
C	Heated in air: 16 h, 573 K	gel		
C	Heated in air: 16 h, 473 K	46	114	2.5

accompanied by the production of an insoluble black residue, corresponding to approximately 60% of the original mass. Isothermal rate measurements were carried out following the weight and differential weight losses with time (see *Figure 1*). Attempts were made to fit a generalized rate expression, i.e.

$$-\mathrm{d}w/\mathrm{d}t = k(1-\alpha)^n \qquad (1)$$

relating changes in the weight w to time t, with k the overall rate constant, α the extent of reaction and n the internal order with respect to polymer. For most polymer systems α is generally taken to be 1.0. However, as can be seen from the t.g.a. trace, equation (1) cannot adequately describe the overall process of volatiles evolution, since an induction period was present followed by an initial period of accelerating reaction. The general shape of the weight loss vs. time curves was either that of an inhibited radical reaction, in which the inhibitor is used up in the degradation reaction, or that of scission reactions in which volatiles are only produced in the later stages of decomposition.

Because of the complexities of the decomposition, further attempts to analyse the reaction kinetics from curve fitting the t.g.a. curves were abandoned, and relative rate constants were measured instead from rates of evolution at constant extents of reaction. An activation energy of 310±50 kJ mol^{-1} was determined for PEEK and 320±50 kJ mol^{-1} for PEK over the temperature range 700–800 K for both PEK and PEEK. There were no significant differences between the degradation characteristics of the two polymers.

Analysis of the degradation products

The non-volatile residue. This was a black solid which was insoluble in a refluxing 1:1 mixture of *o*-dichlorobenzene/*p*-chlorophenol. Elemental analysis showed that it was richer in carbon and more deficient in oxygen compared with the parent polymer (see *Table 3*). I.r. spectra were featureless, with very broad diffuse lines and considerable scatter. The general features were consistent with a poly(ether ketone) backbone.

The volatile products. At 779 K, 30% of the original weight volatilzed and these products were collected in a liquid-nitrogen trap. With PEK a crystalline solid was condensed prior to the trap. All were analysed by g.p.c., thin-layer chromatography, i.r. spectroscopy and mass spectroscopy.

G.p.c. analysis was carried out in *o*-dichlorobenzene solutions using a 50 Å column. *Figure 2* shows the chromatograms obtained. The volatile products are clearly mixtures with at least 7–10 components. By calibrating the elution volume–molecular weight dependence with a series of model compounds, it became apparent that separation was occurring by molecular structure rather than by hydrodynamic volume (see

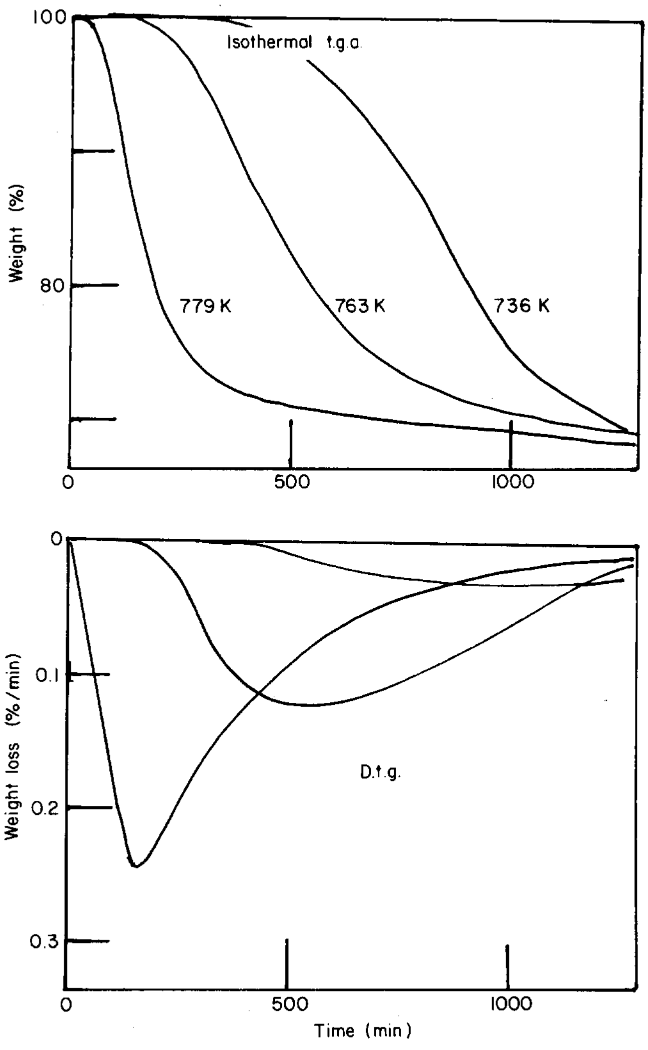


Figure 1 Isothermal thermogravimetric and differential thermogravimetric analysis of PEEK

Table 3 Elemental analysis

	Observed		Calc.	
	C (%)	H (%)	C (%)	H (%)
PEEK	79.4	3.3	79.2	4.1
PEEK non-volatile product	85.1	3.1		
PEK	79.5	3.6	79.6	4.1
PEK non-volatile product	88.8	4.2		

Tables 4 and *5*), and each component had different refractive index response. Measurement of the molecular-weight averages of the volatile degradation products was clearly a meaningless exercise. A major component, with a negative response, was phenol, present in all the polymer degradation products.

Three distinct mixtures were resolved by thin-layer chromatography, using chloroform/ethanol as a mixed solvent. All of them absorbed u.v. radiation, $\lambda = 254$ nm, and one corresponded to phenol with a standard retention factor of 0.48. Each component was removed from the plate, extracted with chloroform, and evaporated onto the probe of the mass spectrometer. The material with retention factor of 0.48 was identified conclusively as phenol. The others were mixtures of oligomers and are analysed below by a second procedure.

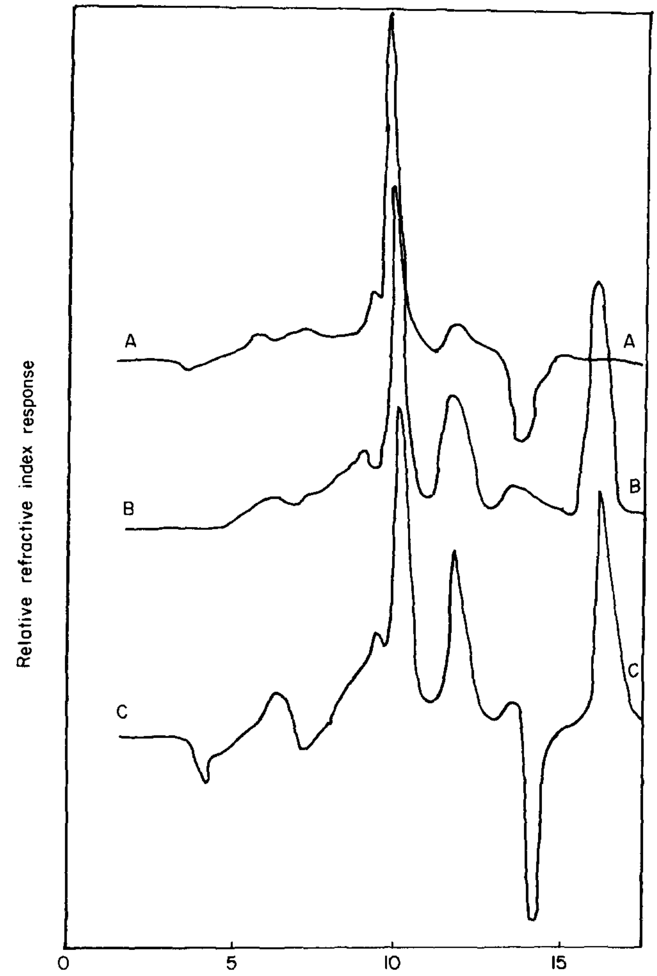


Figure 2 G.p.c. chromatograms of degradation products: A, from PEEK; B, solid from PEK; and C, liquid from PEK

Table 4 Chromatographic characteristics: g.p.c. elution volumes

Compound	Elution volume (cm^3)	Detector response
Benzene	10.7	–
Phenol	14.0	–
Hydroquinone	10.9	+
Benzaldehyde	10.7	+
Benzophenone	9.7	+
p-Hydroxybenzophenone	13.2	+
p-Phenoxyphenol	12.6	+

Table 5 Chromatographic characteristics: t.l.c. analysis

Sample	Retention factor	Intensity of u.v. light response ($\lambda = 245$ nm)
PEEK	0.26	weak
	0.48	very strong
	0.95	strong
PEK	0.48	strong

Table 6 I.r. absorption bands of volatile product

Wavenumber (cm^{-1})	Assignment	Intensity
3700–3500	Phenolic, H–O str.	v. broad
1640	Di(aryl ketone), C=O str.	strong
1520–40	Aryl, C–C str.	strong
1210	Di(aryl ether), C–O str.	medium
850	*p*-Benzene sub., C–H def.	weak
790, 730	Ring sub., C–H def.	medium

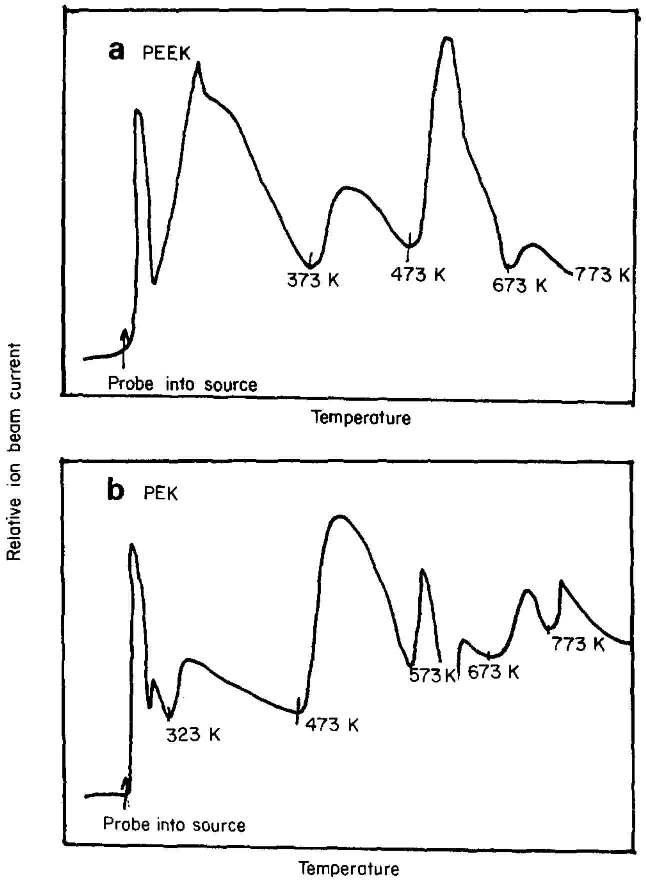


Figure 3 Temperature probe separation of degradation products: (a) PEEK; and (b) PEK products

I.r. spectra of the component exhibited characteristic absorption bands as listed in *Table 6*. No absorption at 2800 cm^{-1}, characteristic of aldehyde C–H stretching, was observed, and the carbonyl absorption at 1640 cm^{-1} was considered to be due to di(aryl ketones) only. Di(aryl ether) C–O–C bonds were also present. In general the spectra were similar to those of PEEK and PEK and consistent with the presence of low-molecular-weight oligomers and phenol.

The products were also analysed by probe separation mass spectroscopy. In this, the temperature of the probe was slowly increased and mass spectra recorded at maxima in the ion beam current (see *Figure 3*). At least eight components are present in the volatile degradation products. Each mass spectrum indicated that they were closely related and members of homologous series.

In order to ensure no further degradation or re-equilibration of the products during heating, the ambient-temperature mass spectra were also measured (see *Figure 4*).

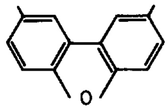
Apart from the identification of phenol, and its fragments, assignment was assisted by the occurrence of fragments of mass 105 and 121, attributable to:

$$\text{Ph–CO}^{+\cdot} \quad \text{and} \quad \text{HO–Ph–CO}^{+\cdot}$$

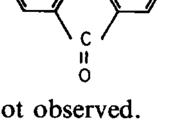
A number of molecular ions and fragmentation sequences could be identified, and these are summarized in *Tables 7* and *8*. Not all the species are attributable to simple oligomers, produced by chain scission, since losses of ether (A), phenylene (B) and carbonyl (C) have to be invoked to account for the mass peak sequences observed, i.e.

$$652 \xrightarrow{-\text{B}} 567 \xrightarrow{-\text{A}} 560 \xrightarrow{-\text{B}} 484 \xrightarrow{-\text{C}} 456 \xrightarrow{-\text{AB}} 364$$

The molecular mass at 168 corresponds to benzofuran:



This could be formed in the decomposition from diphenyl ether. It has been identified in the decomposition products of poly(1,4-phenylene oxide)[1] by g.c./mass spectroscopy, as a dimer, mass 334. There was proportionally less benzofuran derivatives in PEK than in PEEK. The corresponding carbonyl derivative, i.e.



with mass 180 was not observed.

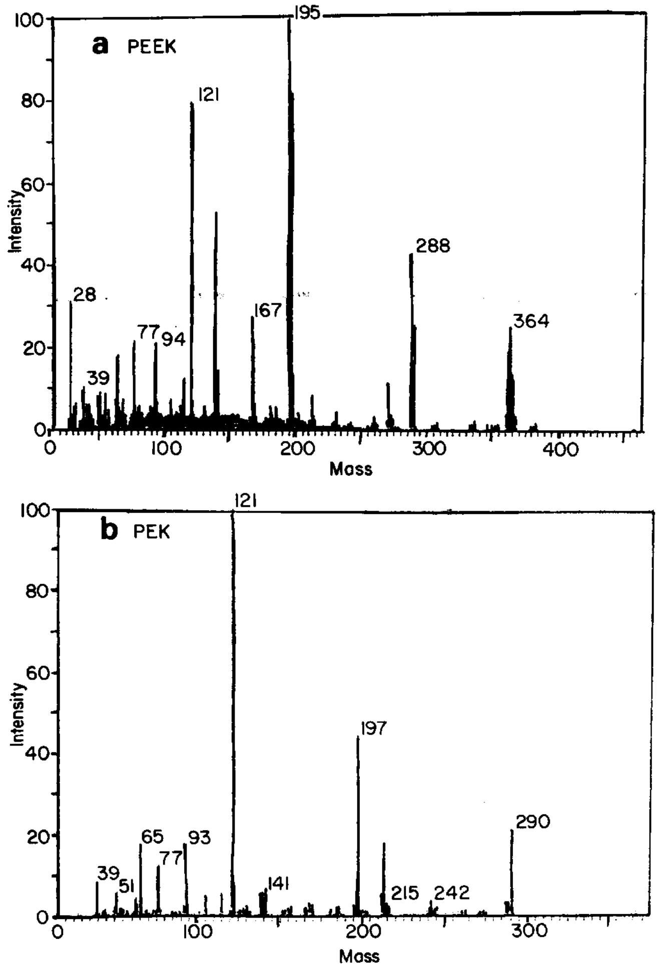


Figure 4 Ambient-temperature mass spectra: (a) volatile PEEK degradation products; (b) volatile PEK degradation products

Table 7 Molecular ions and fragmentation sequences identified in the mass spectra of PEEK decomposition products

Molecular ion	Mass
(HDABCBABABCBH)$^{+\cdot}$	652 top mass
(HDCBABABCBAH)$^{+\cdot}$	576
(HDCBABABCBH)$^{+\cdot}$	560
(HBABABCBABABH)$^{+\cdot}$	550
(HDABCBABABH)$^{+\cdot}$	548
(HDABCBABBH)$^{+\cdot}$	532
(HDCBABABCH)$^{+\cdot}$	484
(HABABCBABABH)$^{+\cdot}$	474
(HDABCBABH)$^{+\cdot}$	456
(HBABCBABAH)$^{+\cdot}$	382
(HDCBABAH)$^{+\cdot}$	380
(HDCBABH)$^{+\cdot}$	364
(HDCDH)$^{+\cdot}$	362
(HDADH)$^{+\cdot}$	350
(HDDH)$^{+\cdot}$	334
(HABABCBAH)$^{+\cdot}$	306
(HDCBAH)$^{+\cdot}$	288
(HDH)$^{+\cdot}$	168

Fragmentation sequences

$(\text{HDCB})^+ \rightarrow (\text{CDH})^+ \rightarrow (\text{HD})^+$
$(\text{HBCBABC})^+ \rightarrow (\text{HBCBABA})^+ \rightarrow (\text{HBCBA})^- \rightarrow (\text{HBCB})^+$
$\rightarrow (\text{HBC})^+ \rightarrow (\text{HB})^+$
$(\text{HABCBABA})^+ \rightarrow (\text{HABCBA})^+ \rightarrow (\text{HABC})^+ \rightarrow (\text{HAB})^+$

in which A = ether link, i.e. –O–
B = phenylene link, i.e. –C_6H_4–
C = carbonyl link, i.e. –C=O–
D = benzofuran unit
H = hydrogen

Table 8 Molecular ions and fragmentation sequences identified in the mass spectra of PEK decomposition products

Molecular ions	Mass
(HBABCBABCBABCBH)$^{+\cdot}$	666 top mass
(HBCBABCBABCBH)$^{+\cdot}$	574
(HBABCBABCBABH)$^{+\cdot}$	562
(HBCBABCBABH)$^{+\cdot}$	470
(HBABCBABCH)$^{+\cdot}$	394
(HBABCBABH)$^{+\cdot}$	366
(HBABCBAH)$^{+\cdot}$	290
(HBABCBH)$^{+\cdot}$	274
(HABCBAH)$^{+\cdot}$	214
(HBABH)$^{+\cdot}$	170
(HDH)$^{+\cdot}$	168

Fragmentation sequences

$(\text{HABCBABCB})^+ \rightarrow (\text{HABCBAB})^+ \rightarrow (\text{HABCB})^+ \rightarrow (\text{HABC})^+$
$(\text{HBCBABCBA})^+ \rightarrow (\text{HBCBABC})^+ \rightarrow (\text{HBCBA})^+ \rightarrow (\text{HBCB})^+$
$\rightarrow (\text{HBC})^+$

in which A = ether link, i.e. –O–,
B = phenylene link, i.e. –C_6H_4–
C = carbonyl link, i.e. –C=O–
D = benzofuran unit

DISCUSSION

The decompostion mechanism

Any mechanism for the decompostion of PEEK and PEK must explain the following observations:

(i) The activation energy for the reaction is similar to the dissociation energy of bonds such as Ph–OCH_3 (418 kJ mol^{-1}) and Ph–$COCH_3$ (397 kJ mol^{-1})[2].

(ii) The induction period for volatiles evolution is up to 3 h at 763 K.

(iii) PEK decomposes at a similar rate to PEEK.

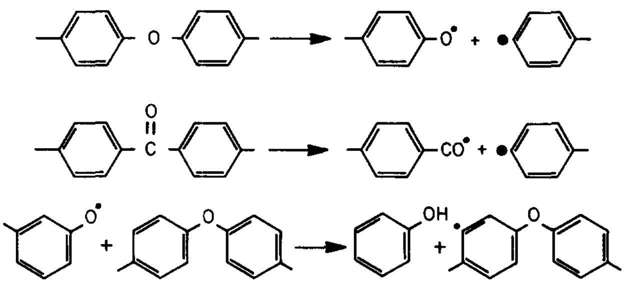
(iv) Hydroxyl- and hydro-terminated oligomers, phenol and benzofuran derivatives are present in the volatile products.

(v) The involatile residue is richer in carbon and deficient of oxygen.

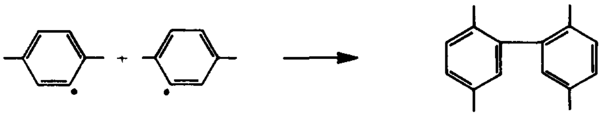
(vi) Crosslinking occurs at an early stage in the decomposition.

The products of the decompositions are chain fragments with minor structural alterations, and their abundance is consistent with their volatility at the decomposition temperature. The products imply a random scission of the chain, at either the ether or carbonyl links. There is conflicting evidence about which bond is the more stable. Most of the products contain terminal hydroxy groups and there are none with aldehyde units. This suggests that the ether links are less thermally stable. However, the presence of benzofuran terminal units in the volatile products, and the absence of indene derivatives, also implies that the carbonyl-to-phenylene bonds are more readily broken, particularly with PEK, than the ether-to-phenylene ones.

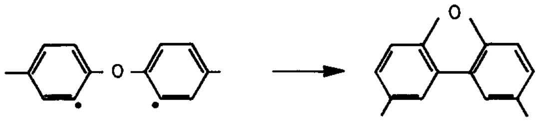
The radicals produced are relatively stable, and do not depolymerize. They terminate by transfer abstracting hydrogen:



or by combination with an adjacent radical to produce crosslinks:



or by internal combination, to produce benzofuran derivatives:



The initial production of volatiles is low since only chain scissions produced near a chain end, or on a branch, or near a previous scission, will have sufficient mobility to diffuse out of the melt. However, as the decomposition proceeds the number of chain ends progressively increases. Two random scissions at the required chain separation to produce a volatile oligomer will become more probable, and the rate of volatilization will increase, limited finally by the progressive production of a crosslinked residue. This could account for the observed induction period and the accelerating production of volatiles with conversion. Finally, the activation energy for volatiles production will be determined primarily by the strength of the bonds broken in the production of radicals.

CONCLUSIONS

Degradation is initiated by random homolytic scission of either the ether or the carbonyl bonds in the polymer chains. The radicals produced abstract hydrogen from adjacent phenylene units, or terminate by combination to produce crosslinks. The products of the scission, if sufficiently mobile, will volatilize. Cyclization to benzofuran derivatives can also occur.

The stability of the chain appears to be inherent in the basic chemical structure of the covalent chain, and in particular is not chain-end-activated.

ACKNOWLEDGEMENTS

D.J.K. wishes to thank the SERC and International Paints Ltd for the award of a CASE during the tenure of this work.

REFERENCES

1 Jachowica, J., Kryszewski, M. and Sobol, A. *Polymer* 1979, **20**, 995
2 Cox and Pilchers 'Thermochemistry of Organic and Organometallic Compounds', Academic Press, London and New York, 1970