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Degradation of poly(*p*-phenylene benzobisthiazole) (PBT) rigid rod, poly(ether ether ketone ether ketone) (PEEKEK) semi-flexible coil, and a grafted "hairy rod" polymer containing PBT and PEEKEK

YAN CHEN, W. T. K. STEVENSON*
Department of Chemistry, and National Institute for Aviation Research, Wichita State University, Wichita, KS 67208, USA

E. J. SOLOSKI
University of Dayton Research Institute, 300 College Park, Dayton, OH 45469, USA

T. VICKSTROM
Department of Chemistry, Oklahoma State University, Stillwater, OK 74078, USA

C. Y-C. LEE
AFOSR, Bolling Air Force Base, Washington, DC 20332, USA

R. EVERS
Polymer Branch, Materials Laboratory, Air Force Wright Aeronautical Laboratories, Wright Patterson Air Force Base, OH 45433, USA

Thermal degradation pathways of the rigid-rod polymer, poly(*p*-phenylene benzobisthiazole, PBT) have been elucidated by thermal volatilization analysis and related techniques. Processes are characterized by the expulsion of hydrogen sulphide, acetylene, and some carbon disulphide. Evidence is presented for the production and subsequent polymerization of aromatic nitriles and for the existence of thermal rearrangements to produce quinoline derivatives. A similar analysis of the semi-flexible coil polymer, poly(ether ether ketone ether ketone, PEEKEK) revealed the importance of directed chain-scission processes to form oligomers, carbon monoxide expulsion with radical recombination to produce biphenyl linkages, and aromatic fusions to produce fluorenone-type derivatives. Examination of a "hairy rod" comb-type graft copolymer of PBT and PEEKEK revealed some instability introduced by the grafting process and determined that the graft site thermally isomerized through oxygen migration to yield xanthone-based heterocyclic intermediates of degradation.

1. Introduction

Thermally stable rigid-rod liquid-crystalline polymers have attracted attention for their potential use as the fibrous component of advanced carbon-based composite materials. A few, most notably Kevlar^R, are in current production. Others, such as poly(*p*-phenylene benzobisthiazole) or PBT, are currently subject to process optimization prior to bulk commercial production [1].

Thermally stable and crystallizable aromatic ether ketone-based polymers, exemplified by ICIs poly (ether ether ketone) or PEEK, have enjoyed commercial success as the resin component of high-performance carbon-based composites. Poly (ether ether ketone ether ketone) or PEEKEK is a material similar to PEEK in composition but containing aromatic ketones separated alternately with di- and tri-phenyl ethers.

The Air Force has recently introduced the term "molecular composite" to characterize their attempts to mimic the mechanisms of fibrous reinforcement on a molecular scale, or at least at the dimensions of a microphase-separated polymer blend [2]. Simply stated, a rigid-rod polymer is blended with a semi-flexible coil-forming polymer under conditions of shear sufficient to orient rod-containing domains within a continuous isotropic coil matrix. Mechanisms of stress transfer and reinforcement within "molecular composites" of this type are under current investigation [3].

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* Author to whom communications should be addressed.

It is common knowledge that the phase boundary in most polymer blends is a thermodynamically unstable region [4], and that efficient dispersion is maintained only due to the high viscosity of the solid blend which discourages macrophase separation. The physical properties of blend systems improve dramatically as domain size is reduced. Interfacial free energy may be lowered and dispersion improved through the addition of a polymeric surfactant in much the same fashion as with liquid emulsion systems. Previous work has suggested that interactions between the components of polymer-blend systems can modify the degradation pathway of individual components of the blend, and that such interactions are amplified if the two polymers are joined into a block copolymer structure [5, 6].

We have prepared a "hairy rod" comb-type graft copolymer for use as a potential surfactant in the PBT–PEEKEK molecular composite system. As a preliminary to detailed morphological and structural investigations of this high-temperature material, we give here a mechanistic interpretation of processes which are operative in the thermal deterioration of the three individual components of this proposed "molecular composite", namely PBT, PEEKEK, and PBT–g–PEEKEK, with a view to determining the degradation pathways of the two homopolymers, to identify modifications introduced by intimate contact in the graft copolymer, and to characterize any new chemistry introduced with the graft site.

2. Experimental procedure

2.1. Thermogravimetry (TG) and differential scanning calorimetry (DSC)

Polymers were heated in a dynamic helium atmosphere, at a heating rate of 20 °C min^{-1}, to end temperatures of 500 °C (DSC) or 900 °C (TG) in the Du Pont TGA 951 thermal analysis system.

2.2. Thermal volatilization analysis (TVA)

Thermal volatilization analysis (TVA) of polymer samples was performed under high-vacuum conditions on samples in the 10–250 mg mass range. The sample was placed in a quartz crucible which was inserted into a Vicor^{R} tube, which was, in turn, inserted into a programmable muffle furnace, and attached to the vacuum line through an adaptor with an internal cold finger. True sample temperatures were obtained using an established procedure [7]. Residual cross-linked and carbonized material was removed from the crucible at the end of the experiment, and oligomers from the internal cold finger.

A series TVA configuration was implemented using four Edwards PRE 10 K gauge heads, connected through an Omega Dataplex 10 signal-switching clock to a strip chart recorder. Oven thermocouple readings were linearized using an Omega TAC-81K thermocouple to millivolt convertor and recorded simultaneously with the Pirani gauge outputs.

2.4. Sub-ambient thermal volatilization analysis (SATVA)

Condensable products of degradation were trapped in the vacuum line at − 196 °C and transferred to the SATVA trap, also held at − 196 °C and surrounded by paraffin wax to ensure a slow and reproducible warm up to room temperature over an approximately 100 min time interval. Material evolving from the trap was detected and recorded by a Pirani gauge simultaneously with trap temperature [8]. Gas fractions were directed to arms of a vacuum fractionating grid for isolation and subsequent analysis by ancillary methods.

2.4. Gas chromatography–mass spectroscopy (GC–MS)

Oligomeric and high boiling point condensable volatile products of degradation were analysed by GC–MS using a Hewlet Packard 5890 gas chromatograph coupled to a VG TS-250 mass spectrometer. Separations were performed on a 1 μm × 30 m × 0.32 mm i.d. Alltech Econo-Cap SE-30 capillary column using a 5 °C min^{-1} ramp from 50 °C to 300 °C. The column was held at 50 °C for 5 min after injection to remove solvent and at 300 °C for 10 min at the end of the run. An attempt was made to identify isolates through electronic comparison with the NBS 70 eV Mass Spectra library.

2.5. Infrared spectroscopy

Infrared spectra were recorded using a Nicolet 5 MX Fourier Transform IR spectrometer. Oligomeric products of degradation were examined either as thin films deposited from solvent on to salt plates, or as KBr discs. Condensable volatiles were trapped on the vacuum line at − 196 °C and transferred to a sealed gas-phase IR cell for analysis. A quantitative estimate of acetylene and carbon disulphide production was made using an IR gas cell previously calibrated using aliquots of those materials manipulated into the cell on a high-vacuum manifold. (Quantities/pressures of CS_2 were sufficiently low that the material was manipulated as a gas.) Noncondensable gases were immobilized on the vacuum line at − 196 °C in a 0.5 nm molecular sieve trap, warmed to room temperature, and transferred to an IR gas cell-containing molecular sieve at − 196 °C for subsequent analysis by gas phase IR spectroscopy.

2.6. Nuclear magnetic resonance (NMR) spectroscopy

High boiling point liquids and oligomers and reference compounds were examined by proton and ^{13}C NMR spectroscopy in deuterated solvents with TMS as a internal reference using a Varian XL-300 Fourier Transform NMR spectrometer. Decoupled ^{13}C NMR spectra were obtained using a standard S2 pulse sequence with Waltz-16 decoupling.

3. Results and discussion

3.1. Polymer synthesis and characterization

The synthesis of these polymers will be described in detail in forthcoming communications. To avoid duplication in the literature, processes are described here in conceptual fashion without reference to excessive experimental detail.

3.1.1. Poly(p-phenylene benzobisthiazole) (PBT)

PBT was synthesized by condensation of terephthalic acid with the dichloride salt of 2,5 dimercapto *p*-phenylene diamine in polyphosphoric acid using benzoic acid as an end capper. The intrinsic viscosity of the polymer in methanesulphonic acid was 21.4 dl g^{-1}. The repeat unit of PBT is shown in Fig. 1.

3.1.2. Poly(ether ether ketone ether ketone) (PEEKEK)

PEEKEK was synthesized by a Friedel Craft condensation of 1,4 dihydroxy benzene, diphenyl ether, with 4,4′ dicarboxy diphenyl ether in methanesulphonic acid. The intrinsic viscosity of the PEEKEK polymer, also in methanesulphonic acid, was measured as 1.1 dl g^{-1}. The structure of PEEKEK is shown in Fig. 1.

3.1.3. PBT-g-PEEKEK

PBT containing an average of one graft site per 10 repeat units was synthesized by a proprietary method. PEEKEK was grafted to the PBT in methane sulphonic acid solvent after which ungrafted PEEKEK was removed by extensive extraction with that solvent. The PEEKEK content in the graft polymer was determined by elemental analysis as 56 wt %. An intrinsic viscosity of 5.5 dl g^{-1} was measured in methane sulphonic acid. The branch structure is drawn in Fig. 1, with points of attachment to the rigid rod and coil indicated by Roman numerals.

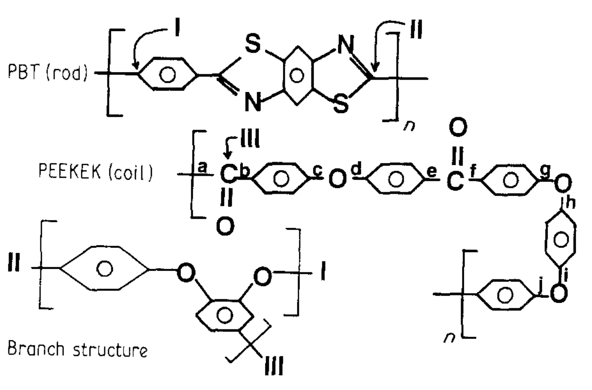

Figure 1 The repeat units of PBT (poly[*p*-phenylene benzobisthiazole]), PEEKEK (poly[ether ether ketone ether ketone]), and the branch structure used to connect the two into the comb polymer PBT-g-PEEKEK are shown. I, II, and III represent points of attachment.

3.2. Degradation of PBT

3.2.1. Thermogravimetry

PBT is a thermally stable polymer, as indicated by the TG curve reproduced in Fig. 2 (curve a). Weight loss under inert gas commences at about 675 °C. Approximately 28 wt % of the sample is ablated at 900 °C. Comparison of the weight-loss curve with its first derivative (Fig. 3a) indicates a single overall process which attains a rate maximum (at a heating rate of 20 °C min^{-1}) around 767 °C. Programmed thermogravimetry performed at a single heating rate is, of course, unable to determine if a measured weight-loss process of this type is the result of a single chemical event or of a cascade of reactions with similar kinetic parameters (activation energy, etc.) [9].

3.2.2. Thermal volatilization analysis (TVA)

A comparison of a derivative weight-loss curve with a volatile emission curve often yields valuable insight into the degradation profile and the nature of the product distribution. For example, the d*w*/d*T* curve is a measure of total mass loss while the volatile emission profile is a non-linear measure of the rate of production of low molecular weight products only. Reproduced in Fig. 4 (bottom, full line) is the total volatile

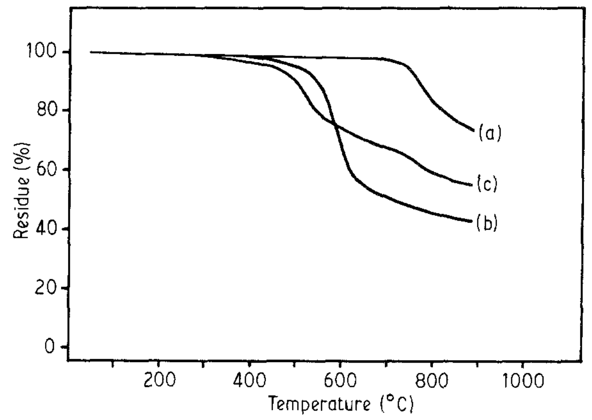

Figure 2 Programmed thermogravimetry (TG) at 20 °C min^{-1} under helium of (a) PBT, onset temperature 675 °C; (b) PEEKEK, onset temperature 424 °C; and (c) PBT-g-PEEKEK, onset temperature 301 °C; sample sizes under 10 mg.

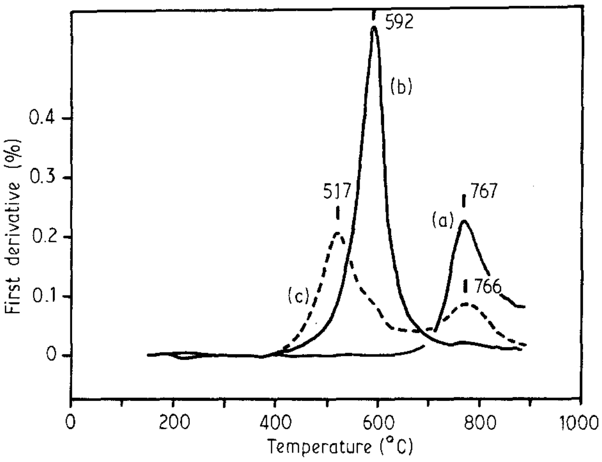

Figure 3 First derivative of weight loss from (a) PBT, (b) PEEKEK, and (c) PBT-g-PEEKEK heated at 20 °C min^{-1} under helium in the TG experiment.

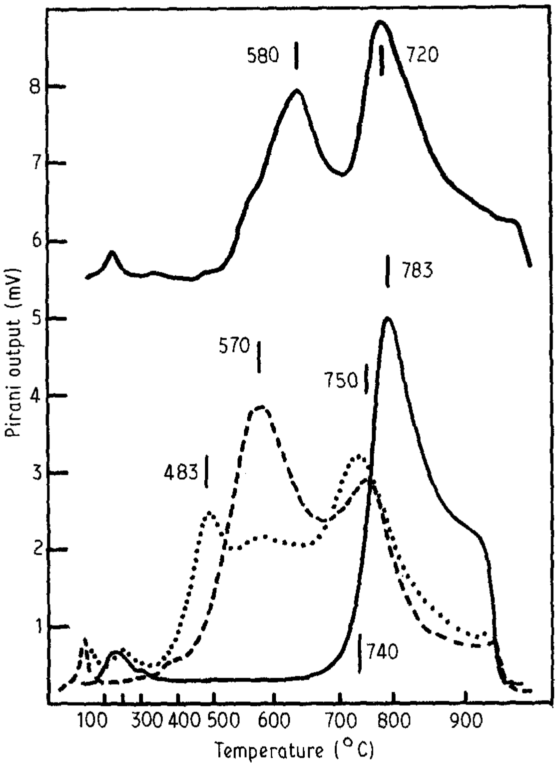

Figure 4 Volatile emission curves at a nominal heating rate of 20 °C min^{-1} for 25 mg of (——) PBT, (– – –) PEEKEK and (···) PBT-g-PEEKEK. Upper curve: volatiles from PBT (11.3 mg) and PEEKEK (12.9 mg) degraded separately but simultaneously in a divided crucible.

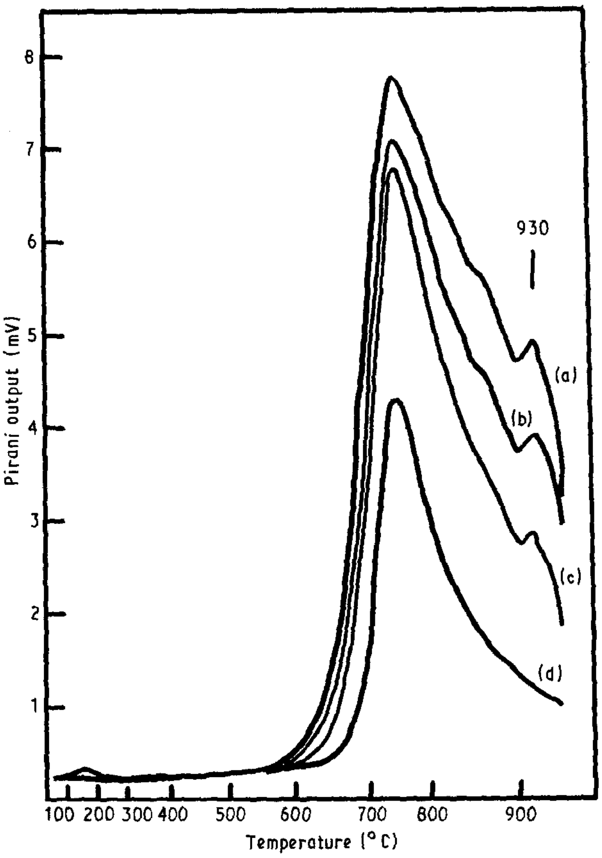

Figure 5 TVA of 150 mg PBT at a nominal heating rate of 20 °C min^{-1}. (a) Total volatiles, (b) material volatile at −75 °C in the vacuum line, (c) noncondensables, (d) hydrogen.

emission curve from a 25 mg sample of PBT subjected to a heating rate of 20 °C min^{-1}. The curve shape suggests a single overall process with a rate maximum at 783 °C and a shoulder at higher temperatures. Differences in the absolute positions of the rate maxima in this instance (767 °C for the TG experiment, 783 °C for the volatile emission experiment) are more likely due to the presence/absence of a blanketing atmosphere than to some difference in the rate profiles for formation of low and high boiling point products.

The development of thermal volatilization analysis (TVA) is documented in a body of publications summarized in McNeill's review article [10]. A series TVA experiment is employed here, comprising Pirani gauges situated before and after sub-ambient vacuum traps held at −75 and −196 °C, in order to examine the volatility spectrum of the condensable and noncondensable products of degradation as a function of the oven temperature, which, in our experiments, was ramped from room temperature to 1000 °C. The fractionating train was modified through the addition of a 0.5 mm molecular sieve trap at −196 °C, to trap noncondensable gases, with the exception of hydrogen which is volatile under those conditions [11, 12].

A TVA experiment, performed on a 150 mg of PBT (Fig. 5), gives some indication of the composition of the volatile products of degradation as a function of temperature. The topmost curve, corresponding to a total volatile flux, is analogous to the emission curve in Fig. 4, modified only by the larger sample size (coupled to the non-linear Pirani response). The single-rate maxima below 800 °C is reproduced and accompanied by a second-rate maxima at 930 °C. Comparison of all four traces in descending order reveals that the rate profiles for the formation of material volatile at room temperature, at −75, −196 and −196 °C over 0.5 nm molecular sieve (hydrogen) are all similar, and indicate an overall reaction which produces a mixture of condensables, and noncondensables including hydrogen. The higher temperature process produces noncondensable gas, most probably methane but not hydrogen (due to the absence in the bottom curve of a rate maximum superimposed over the high-temperature "tail" of the dominant process).

3.2.3. Qualitative infrared (IR) spectroscopy

With the exception of the residue of degradation which proved intractable, all product fractions were examined by infrared (IR) spectroscopy. By this method, methane was identified as a second noncondensable product of degradation. (The other, hydrogen, was identified through application of the TVA experiment.)

Infrared spectra of condensable volatile products of degradation of a 25 mg sample of PBT are reproduced in Fig. 6a. The doublet at ~ 3300 cm^{-1}, the sharp singlet at 715 cm^{-1}, and the very intense multiplet at around 1530–1540 cm^{-1} identified acetylene and carbon disulphide as products of degradation. Examination of a larger sample (insert) identified ammonia as a trace product of degradation.

Oligomeric products of degradation were produced in small quantities only, and proved insoluble in

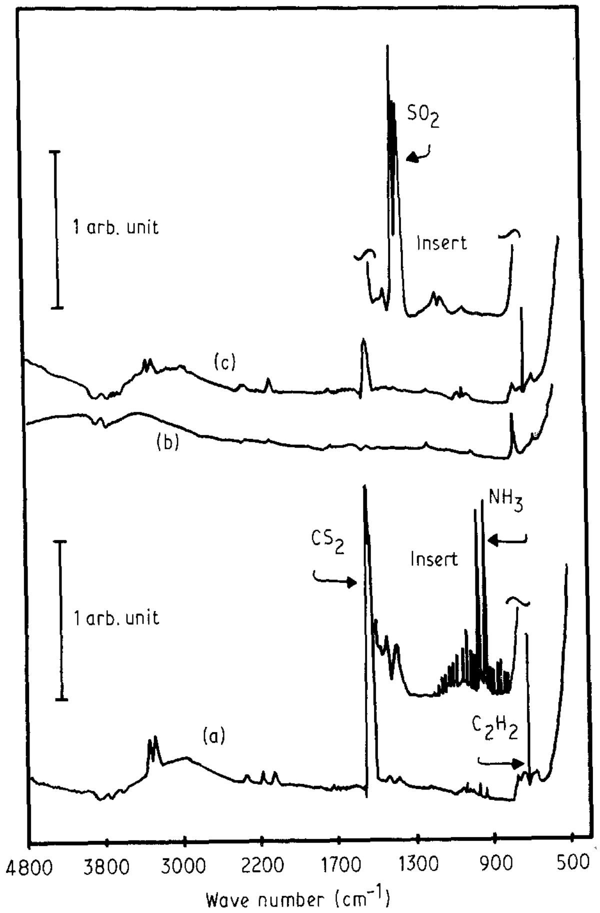

Figure 6 Gas-phase infrared spectra of condensable gases from (a) PBT, (b) PEEKEK, (c) PBT-g-PEEKEK, heated to 1000 °C at 20 °C min^{-1}: complete spectra from 25 mg samples, inserts from 150 mg samples.

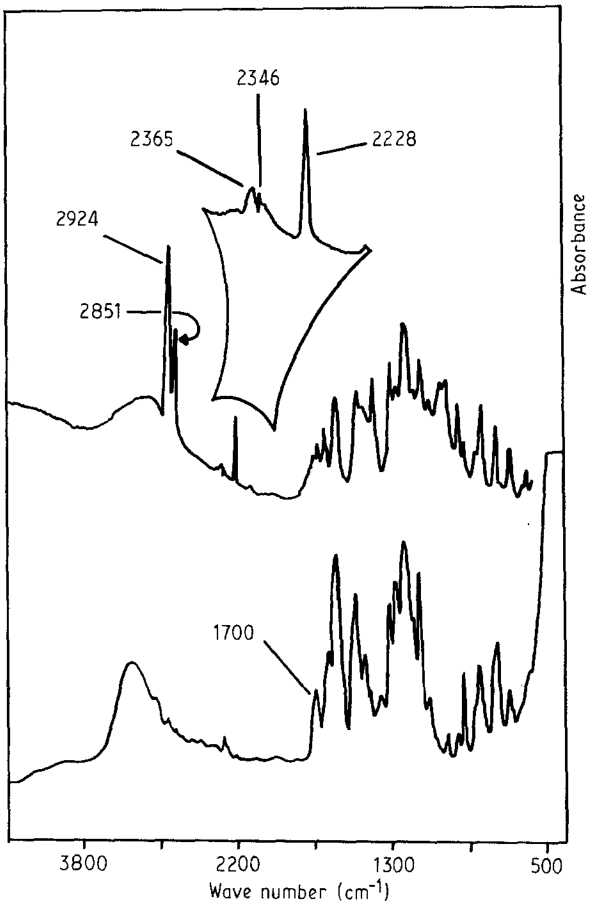

Figure 7 Infrared spectra of oligomeric products from PEEKEK (lower spectrum), thin film from chloroform; and PBT (upper spectrum with insert), KBr disc.

common laboratory solvents. Material from several experiments was combined and examined as a KBr disc. Major features in the spectrum, as reproduced in Fig. 7 (top), included absorbances at 2924 and 2851 cm^{-1} due to saturated hydrocarbon functionality, and at 2228 and $\sim 2350\ \mathrm{cm}^{-1}$, absorbances characteristic of free and polymerized nitriles [13]. The cold-ring product fraction of degradation is subjected to high temperatures after collection due to radiative heat transfer from the oven. It is possible that the insolubility of this fraction may be linked to these nitrile polymerizations.

3.2.4. Sub-ambient thermal volatilization analysis (SATVA)

The condensable volatile product fraction of thermal degradation of a 150 mg sample of PBT, heated to 1000 °C at a rate of 20 °C min^{-1}, is reproduced in Fig. 8. (Products from a 25 mg sample were separated as depicted in Fig. 13a for comparison with those from other polymers.) Fraction 2 was shown by IR spectroscopy to be a composite of acetylene and carbon disulphide, and fraction 3 to contain ammonia. It must be mentioned that pure acetylene evaporated from the SATVA trap at a shorter time and lower trap temperature than observed in these experiments. We do not, at this time, have a reasoned argument for this discrepancy.

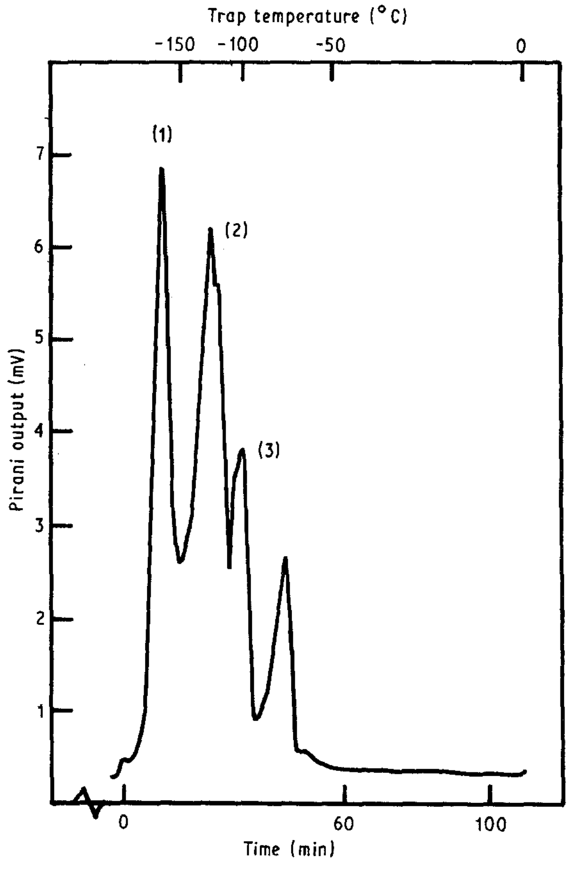

Figure 8 SATVA of condensable volatiles from 150 mg PBT heated at 20 °C min^{-1} to 1000 °C. (1) Hydrogen sulphide, (2) acetylene and carbon disulphide, (3) ammonia.

Fraction 1 did not reveal any measurable IR absorbances, even in repeat experiments using much larger samples. Material collected after degrading a 500 mg sample was bubbled through a 2 wt % solution of lead nitrate and produced a large precipitate of lead sulphide. From these experiments we concluded that fraction 1 contained hydrogen sulphide only.

To determine the condensable volatile product distribution as a function of temperature, a further sample of PBT was degraded to 1000 °C and "packets" of condensable volatile products collected for separation by SATVA. As indicated in Fig. 9, PBT does not release volatiles until at least 570 °C. The two fractions observed at lower temperatures correspond to traces of carbon dioxide and water in the vacuum line. On a comparitive basis, it can be seen that most hydrogen sulphide is produced below 765 °C and most acetylene and carbon disulphide, above 765 °C, which would indicate that hydrogen sulphide is not produced simultaneously with either of the latter. The production of ammonia is limited to the lower temperature interval.

3.2.5. Quantitative gas-phase infrared (IR) spectroscopy

An estimate of the cumulative productions of acetylene and carbon disulphide was made by quantitative gas-phase IR spectroscopy using the 715 cm^{-1} absorbance as a marker for acetylene and the absorbance at 1532 cm^{-1} as a measure of carbon disulphide. As indicated in Fig. 10, similar quantities of both materials are produced on a mass basis. However, on a molar basis, the production of acetylene far exceeds that of carbon disulphide. We may estimate the onset temperatures for the production of both acetylene and carbon disulphide at around 700 °C. However, insufficient data points were collected for a numerical differentiation to allow for determination of rate maxima of production. By normalizing product yields to a unit value at 950 °C (Fig. 10, insert) we were able to show that carbon disulphide and acetylene are not formed by a concerted process.

3.2.6. Gas chromatography–mass spectroscopy (GC–MS)

The oligomeric product fraction of PBT degradation was insoluble and could not be examined by GC–MS. However, products associated with the degradation of PBT could be isolated from the oligomeric product fraction of degradation of the graft copolymer. Products reported in Table I were identified by library matching and produced a mass spectrum verified by visual examination as completely free of impurity and

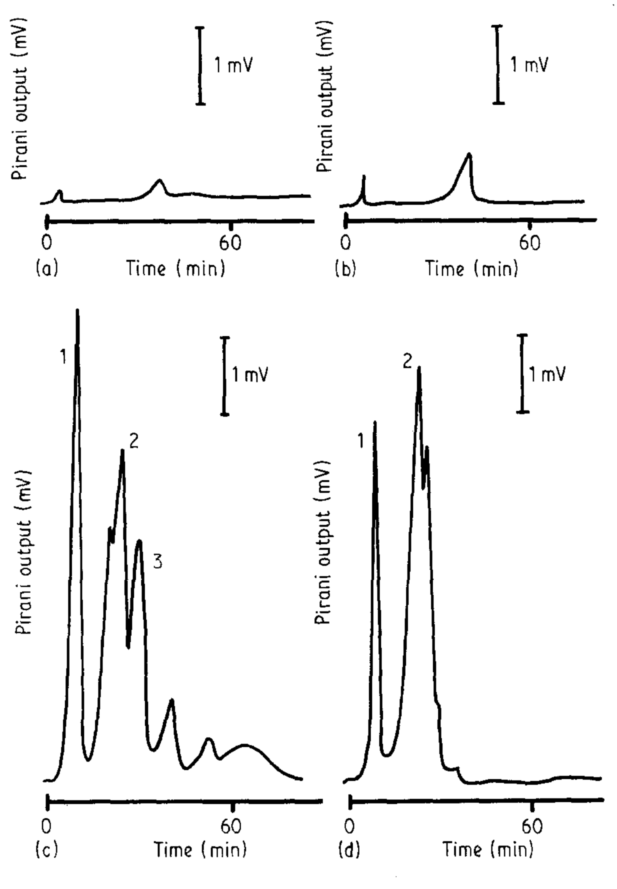

Figure 9 SATVA of condensable volatile "packets" from 150 mg PBT heated to 1000 °C at a nominal rate of 20 °C min^{-1}: experiment commences (time = 0) with the SATVA trap at − 196 °C. (a) 25–520 °C, (b) 520–570 °C, (c) 570–765 °C, (d) 765–1000 °C. (1) Hydrogen sulphide, (2) acetylene and carbon disulphide, (3) ammonia.

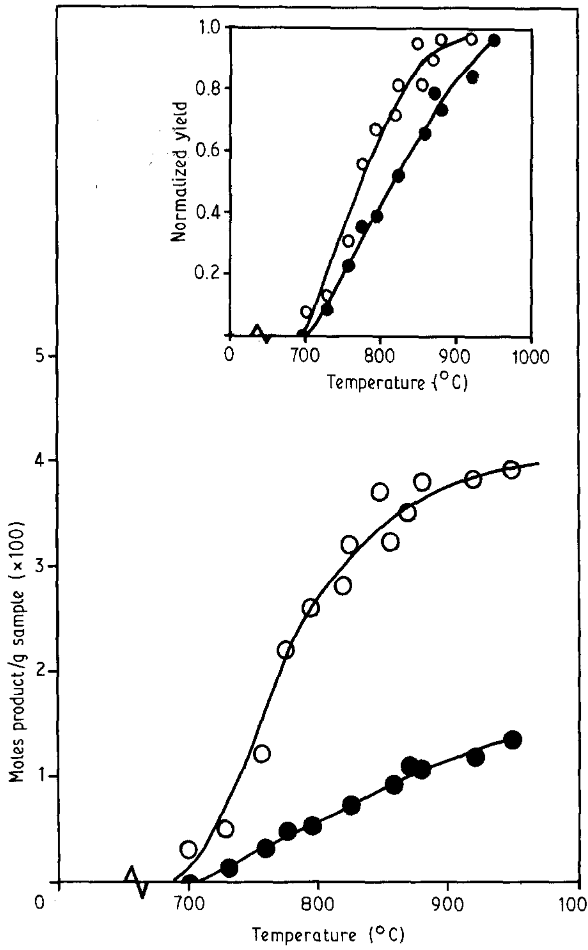

Figure 10 Cumulative production of (○) acetylene and (●) carbon disulphide in PBT heated under vacuum to 1000 °C. Upper insert: both sets of measurements normalized to yield at 950 °C set at 1.0.

TABLE I High boiling point products of PBT degradation, normalized to the most abundant product in the spectrum set to 100

(a) From the graft copolymer heated to 1000 °C	
Benzothiazole, 2-phenyl	19
Dicyanobenzene	10
(b) From the graft copolymer heated to 570 °C	
None	
(c) From the graft copolymer heated to 570–1000 °C	
Quinoline, 2-Phenylthio	100
Benzothiazole, 2-Phenyl	59
Dicyanobenzene[a]	6

[a] Isomer(s) cannot be determined unambiguously by GC–MS.

eluted with retention times which concur with expected volatility. It must be noted that a GC–MS separation will emphasize lower boiling point fragments, and that identified materials should not be thought of as unique products of degradation but as *representatives* of product families.

3.2.7. Mechanisms of PBT degradation

Mechanistic pathways for the degradation of PBT may be proposed which are consistent with the product distribution. For example, the production of methane gas coupled to an appearance of saturated hydrocarbon functionality is suggestive of aromatic ring fragmentations. These products, by collecting hydrogen, may facilitate aromatic ring fusions.

The production of hydrogen is usually associated with aromatic ring fusions (which must take place in an ablative polymer such as PBT). The production of carbon disulphide and hydrogen sulphide suggest that thiazole linkages may decompose through competing mechanisms. Acetylene production may accompany aromatic ring fragmentations or may accompany a concerted rearrangement of the repeat residue.

The overall process must also be consistent with the results of elemental analysis, which, coupled to weight loss measurements, indicates that 22% original carbon, 79.9% original hydrogen, 66% original nitrogen, and 87.1% original sulphur is removed from the polymer on heating to 950 °C at a rate of 20 °C min^{-1}; in other words, that heteroatoms are quantitatively removed by processes of degradation.

We have formulated two pathways of degradation which appear to be supported by experimental evidence, and which are illustrated using representative products. The first, in Fig. 11, postulates a rearrangement of the thiazole linkage to generate an aromatic nitrile (such as is observed in the cold-ring product fraction of degradation). A representative product of this type, 1,4 dicyano benzene, is shown, partly polymerized into an insoluble network. Nitrile formation is accompanied by chain scission to produce mercapto functionality which may decompose to yield hydrogen sulphide. Scissions further along the chain may then account for the production of benzothiazole and benzothiazole (2-phenyl)-type derivatives.

The measured large quantity of acetylene in the product distribution (on a molar basis) runs contrary to the measured thermal stability of the polymer, if acetylene is associated with random aromatic fragmentations. Instead, the detection of quinoline (2-phenylthio) in the product distribution allows us to postulate a concerted rearrangement of the PBT unit, such as is sketched in Fig. 12; to remove acetylene from the polymer and yield 2-thio quinolines, a portion of which may fragment to yield volatile product as is shown in the figure.

It must be emphasized that these mechanistic pathways do not represent exclusive mechanisms of degradation. For example, we have declined to comment on the production of carbon disulphide (reaction of hydrogen sulphide as it percolates through the polymer with a thiazole linkage, concerted rearrangement involving neighbouring repeat units?) or on the precise mechanism by which methane and saturated hydrocarbon functionality is generated in the oligomeric product fraction of degradation.

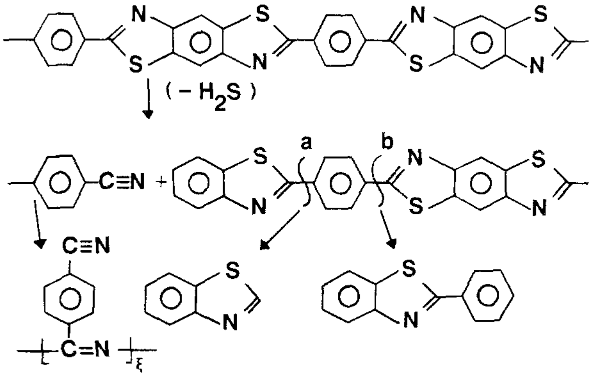

Figure 11 Degradation of PBT to produce hydrogen sulphide, aromatic nitriles, benzothiazole, and 2-benzothiazole (2-phenyl)-type derivatives.

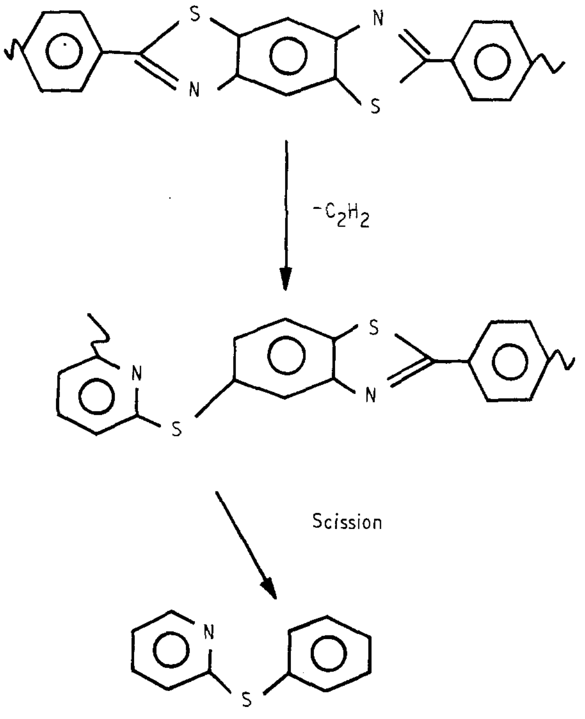

Figure 12 Degradation of PBT to produce acetylene and quinoline, 2-phenylthio-type derivatives.

3.3. Degradation of PEEKEK

3.3.1. Thermogravimetry (TG)

PEEKEK was subjected to thermogravimetric analysis to yield the weight-loss profile indicated in Fig. 2b with associated derivative, as illustrated in Fig. 3b. PEEKEK is less stable thermally than PBT and exhibits both a lower threshold for the degradation process (424 °C) and an earlier rate maximum (592 °C) and a smaller residue (43%) at 900 °C. As with PBT, weight loss appears to proceed through a single overall process which terminates at about 600 °C to leave a residue which thereafter ablates in a monotonic fashion.

3.3.2. Thermal volatilization analysis

A volatile emission curve generated by a 25 mg sample of PEEKEK is reproduced in Fig. 4 (broken line). Volatiles begin to be produced above 400 °C and achieve rate maxima at 570 and 740 °C, the lower corresponding to the bulk weight-loss process, and the upper to material evolved at higher temperatures. The Pirani gauge is very sensitive to noncondensable volatiles which may be detected in quantities which do not register in the TG experiment, from which it may be safely assumed that these higher temperature products of degradation are mainly noncondensable in nature. Scarcity of material precluded use of the series TVA experiment to determine product volatility as a function of temperature.

3.3.3. Qualitative infrared (IR) spectroscopy

The IR spectrum of the condensable volatile product fraction of degradation of a 25 mg sample of PEEKEK (Fig. 6b), indicated an absence of low boiling point products of degradation. Insufficient material prevented a similar analysis of the noncondensable volatile products of PEEKEK degradation. The detection of significant quantities of carbon monoxide in the product distribution of PEEKEK–g–PBT (56 wt % PEEKEK) may, however, be viewed as strong circumstantial evidence for the production of CO in the degradation of PEEKEK homopolymer.

The infrared spectrum of oligomeric products of degradation as a thin film on an NaCl salt plate (Fig. 7, bottom) revealed not only the presence of aryl ketones (1700 cm^{-1}) and ethers (1238 cm^{-1}) as expected, but also a considerable hydroxyl content which may be viewed as positive proof for the operation of aryl ether scission processes.

3.3.4. Sub-ambient thermal volatilization analysis (SATVA)

Condensable volatiles from a 25 mg sample of PEEKEK heated under programmed conditions to 1000 °C, were separated by SATVA to yield the trace depicted in Fig. 13b. The Pirani response is non-linear, with the result that large quantities of material give smaller "peaks" than expected. For this reason, it may be seen that thermally degraded PEEKEK produces only a small quantity of condensable volatiles; a finding observed with other polymers which degrade through processes of chain scission (unpublished work with epoxy-based systems). Fraction 3 was identified as water by gas-phase IR spectroscopy and fraction 4 as diphenyl ether by GC–MS. We could not positively identify the low boiling point product due to lack of material which prevented us from working with a larger sample.

3.3.5. Gas chromatography–mass spectroscopy (GC–MS)

The product distribution of thermally degraded

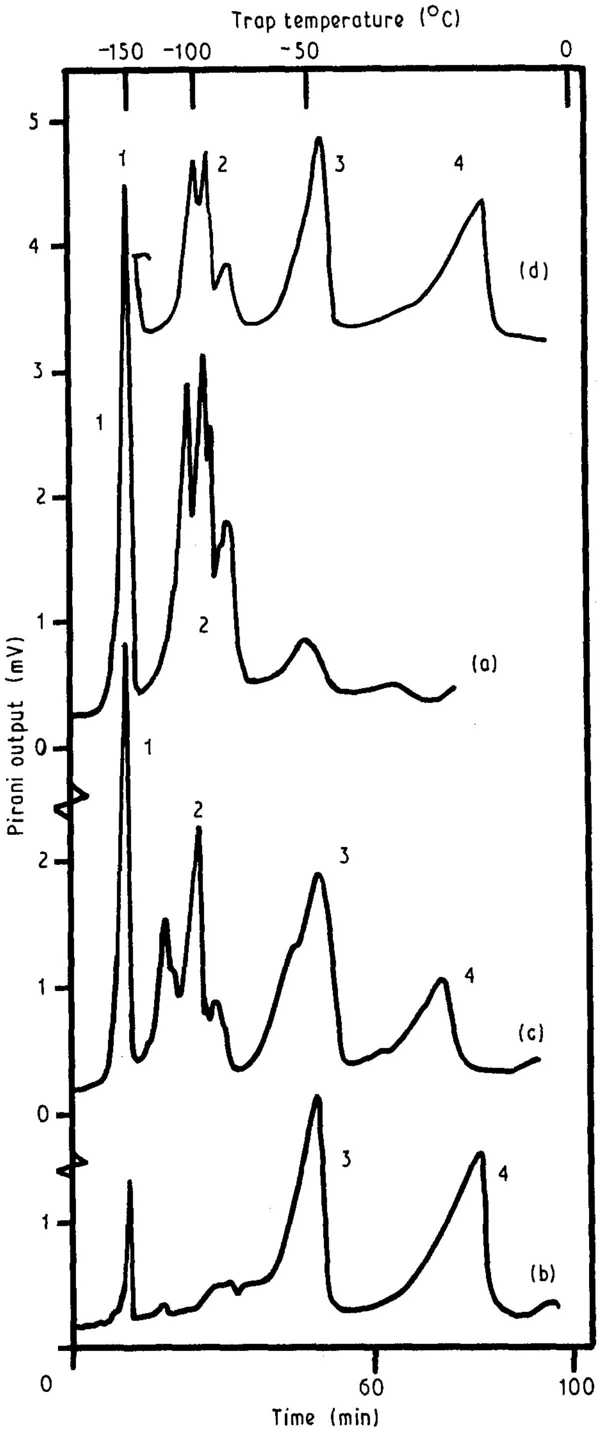

Figure 13 SATVA of condensable volatiles from 25 mg of (a) PBT, (b) PEEKEK, (c) PBT–g–PEEKEK, (d) 11.3 mg PBT + 12.9 mg PEEKEK in divided crucible, all heated to 1000 °C at a nominal rate of 20 °C min^{-1}. (1) Hydrogen sulphide; (2) acetylene, carbon disulphide, ammonia; (3) water; (4) diphenyl ether with (c) *p*-hydroxysulphonic acid.

PEEKEK contains a complex mixture of high boiling point materials (though not as complex as from the graft copolymer). To illustrate this complexity we have reproduced in Fig. 14 a GC–MS chromatograph of oligomeric products of degradation to 1000 °C and have identified four representative fractions for a comparison of peak size and relative position. Identifiable products of PEEKEK degradation to 1000 °C are collected in Table IIa. Products collected over three temperature intervals and attributable to the PEEKEK component of the graft copolymer are mentioned in Table IIb–d.

Oligomeric products of PEEKEK degradation appear to fall into two categories, those which result from a primary scission process (for example, phenoxy phenol) and those which have been structurally modified in the hot zone before evaporation to the cold finger (for example, 9H-fluoren-9-one and biphenyl-containing compounds).

3.3.6. Mechanisms of PEEKEK degradation

PEEKEK is a thermally stable polymer, though not as stable as PBT. PEEKEK appears to volatilize in bulk between about 400 and 700 °C to produce a small amount of condensable volatiles and a greater quantity of oligomer. Above 700 °C the material continues to evaporate in monotonic fashion. The TVA experiment being more sensitive than TG towards low boiling point products of degradation, is able to detect a high-temperature rate maximum for the production of volatiles.

The relatively high yield of oligomers, the detection of hydroxyl functionality in that fraction, and the identification of high boiling products which appear to be removed from the polymer without alteration, all testify to the importance of random or directed chain scissions.

A rationalization of these scission processes may be made through reference to Fig. 1. For example, water may be formed through removal of hydroxyl functionality generated by scissions of the phenoxy linkage. Phenoxy phenol may be generated by scissions at bond "b" and "e", "f" and "i", or "a" and "h". Scissions at the aryl ketone (at "a" "b" "e" or "f") are confirmed as feasible by the presence of (presumably *p*-) hydroxy benzaldehyde in the product distribution.

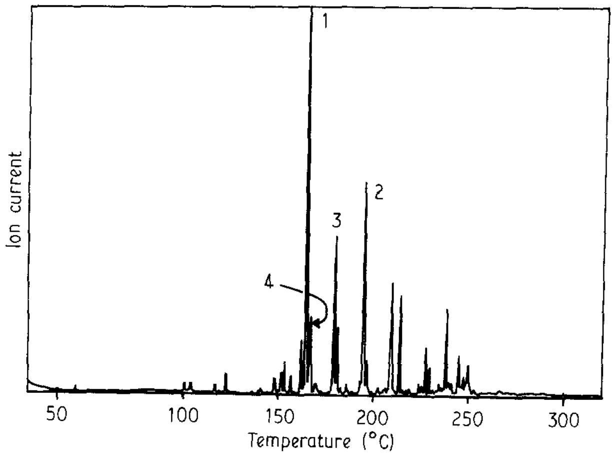

Figure 14 GC–MS separation of oligomeric products of PEEKEK degradation on a 1 μm × 30 m × 0.32 mm i.d. SE-30 Alltech Econo-Cap capillary column at a heating rate of 5 °C min^{-1}. (1) Phenol, phenoxy, (2) methanone, (4-hydroxy phenyl)phenyl; (3) dibenzo B, E 1,4 dioxin (4) 9H-fluoren-9-one.

The high yield of methanone (4-hydroxyphenyl), phenyl and the low yield of benzophenone testify to the influence of the aryl ketone and the importance of resonance stabilization in these phenoxy bond scissions. Assuming that unpaired electrons on a phenoxy oxygen are better able to engage in resonance stabilization than others on the benzene ring, and that resonance of phenoxy radicals is enhanced through access to the aryl ketone, we may postulate that scissions to produce benzophenone around carbonyls "ab" or "ef" produce only one aryl ketone-stabilized phenoxy radical. In contrast, scissions to produce methanone (4-hydroxyphenyl) phenyl at "i" and "c" or at "d" and "h" produce two aryl ketone resonance-stabilized phenoxy radicals.

Illustrated in Fig. 15 are processes which result in the formation of biphenylated products and fluorenone derivatives. The production of large quantities of carbon monoxide as a product of PEEKEK degradation (inferred from degradation of the graft copolymer) may only be reconciled with a high char yield if the chain scission is accompanied by a rapid radical recombination to form the biphenyl linkage, and this is illustrated as a concerted process in Fig. 15. The biphenyl group, through its capacity for resonance stabilization, may direct adjacent phenoxy scission and be removed from the polymer as an alcohol or diol.

TABLE II High boiling point products of PEEKEK degradation, normalized to the most abundant product in the spectrum set to 100

(a) From PEEKEK homopolymer heated to 1000 °C	
Phenol, phenoxy	100
Methanone, (4-hydroxyphenyl) phenyl	54
Dibenzo B, E 1,4 dioxin	47
9H-Fluoren-9-one	18
1,1′ Biphenyl, hydroxy[a]	36
Benzophenone	8
1,1′ Biphenyl-diol[a]	5
Benzaldehyde, hydroxy[a]	1
(b) From the graft copolymer heated to 1000 °C	
Methanone, (4-hydroxyphenyl) phenyl	100
Phenol, phenoxy	86
9H-Fluoren-9-one	14
1,1′ Biphenyl, hydroxy[a]	12
1,1′ Biphenyl, diol[a]	11
(c) From the graft copolymer heated to 570 °C	
Phenol, phenoxy	100
1,1′ Biphenyl, hydroxy[a]	26
Methanone, (4-hydroxyphenyl) phenyl	22
1,1′ Biphenyl, diol[a]	15
Benzaldehyde, hydroxy[a]	14
Benzophenone	13
(d) From the graft copolymer heated to 570–1000 °C	
1,1′ Biphenyl, hydroxy[a]	100
Methanone, (4-hydroxyphenyl) phenyl	52
1,1′ Biphenyl, hydroxy[a]	48
Benzaldehyde, hydroxy[a]	4

[a] Isomer(s) cannot be determined unambiguously by GC–MS.

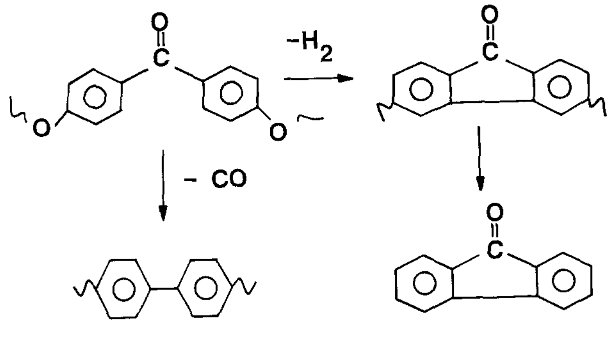

Figure 15 Degradation of PEEKEK to form fluorenone and biphenyl derivatives.

The dehydrogenation of benzophenone to 9H–fluorenone–9–one type structures is of interest in that such may be an initial step in the conversion of these aromatic ether ketone-type polymers to carbonaceous char. The formation of dibenzo dioxin-type structures is more difficult to comment on and appears to suggest that oxygen, probably as terminal hydroxyles, or as a phenoxy radical, may be inserted between aromatic carbons "alpha" to a phenoxy linkage to produce dioxin-type ladder structures. Oxygen migrations appear also to contribute to the degradation of branch structures in the graft copolymer.

3.4. Degradation of PBT–*g*–PEEKEK

3.4.1. Thermogravimetry (TG)

Examination of the TG weight-loss curve and its first derivative at a heating rate of 20 °C min^{-1} (Figs 2c and 3c) reveal a thermal stability intermediate between PEEKEK and PBT. Degradation commences at about 301 °C (below the onset temperature for PEEKEK degradation) and proceeds through two separated processes with rate maxima at 517 and 766 °C to volatilize approximately 45% of the sample at 900 °C. As with the onset temperature of degradation, the rate maxima of the lower temperature process of degradation occurs at a temperature below that observed for PEEKEK homopolymer, we surmise due to the destabilizing influence of the graft sites or by products of the grafting process. In contrast, the higher temperature component of the degradation process, which we attribute to decomposition of PBT residues, appears unaffected by the proximity of the PEEKEK polymer, save for a reduction in the rate maximum which may be attributed to a lowered PBT content in the graft copolymer. A more thorough examination of the degradation process shows this not to be the case.

3.4.2. Thermal volatilization analysis (TVA) and SATVA

A total volatile emission curve for a 25 mg sample of the PBT–g–PEEKEK polymer is reproduced in Fig. 4 (– – –) for comparison with the two homopolymers. A straightforward comparison in this type of experiment is not possible, due to the non-linear nature of the Pirani response. Instead, the cumulative emission curve is contrasted with that generated by a 25 mg sample of PEEKEK and PBT homopolymer degraded in a divided crucible in proportions corresponding to the composition of the graft copolymer. This arrangement, which corresponds to McNeills "trouser tube" experiment [14] produces an emission curve (Fig. 4, upper curve), which indicates that, in the absence of interaction, two rate maxima should be observed, the first at 630 °C and the second at 765 °C. In contrast (Fig. 4, ...), we observe two rate maxima, the first at 483 °C, and a second at 750 °C. Clearly, formation of the graft copolymer introduces alternate pathways for the degradation process.

A series TVA experiment performed on a 150 mg sample of PBT–g–PEEKEK (Fig. 16) indicates that the first process produces a mixture of condensables and noncondensables excluding hydrogen, and that the second includes hydrogen as a product of degradation.

A SATVA analysis of the condensable volatile product fraction of degradation to 1000 °C is not especially revealing. Comparison of the SATVA trace of material from the graft copolymer (Fig. 13c) with those from the homopolymers (a) and (b) and with that from a mixture of the homopolymers degraded separately in a divided crucible (d), indicated a reduced yield of hydrogen sulphide (fraction 1) and reduced production of acetylene/carbon disulphide/ammonia (fraction 2) with respect to PBT but with a different distribution than produced by material degraded in the divided crucible. The yield of water from the graft copolymer is similar to that expected on an additivity basis (compare fraction 3, c and d); however, diphenyl ether in fraction 4, a product of PEEKEK degradation, is accompanied by *p*-hydroxy sulphonic acid as a product of degradation.

Condensable volatiles produced in five temperature intervals between room temperature and 1000 °C are

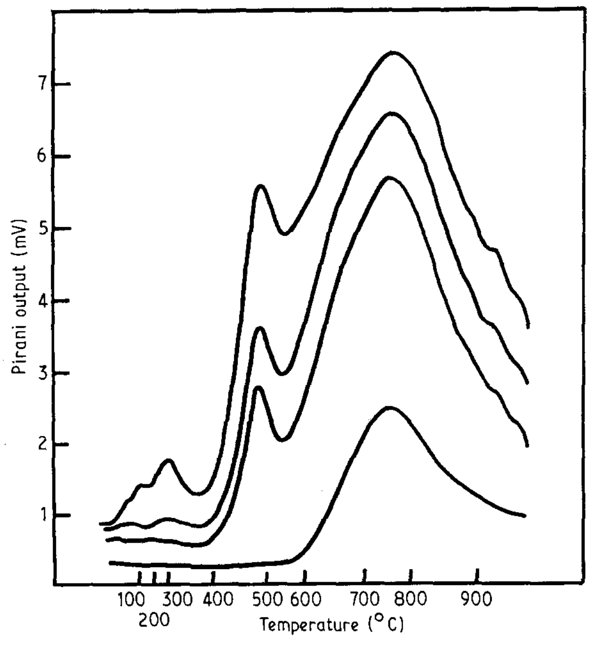

Figure 16 TVA of 150 mg PBT–g–PEEKEK at a nominal heating rate of 20 °C min^{-1}. (a) Total volatiles, (b) material volatile at – 75 °C in the vacuum line, (c) noncondensables, (d) hydrogen.

separated by SATVA in Fig. 17. Material produced above 765 °C may be attributed to the PBT component of the graft copolymer. Material produced between 570 and 765 °C contains products from PBT and PEEKEK segments. Material evolved between 395 and 570 °C originates predominantly from PEEKEK with the addition of sulphur dioxide which cannot be rationalized on the basis of the PEEKEK repeat unit. A small but complex mixture of products, including sulphur dioxide, is formed below 395 °C.

3.4.3. Qualitative infrared (IR) spectroscopy

Examination of the IR spectrum of the condensable volatile product fraction of degradation to 1000 °C of the PBT–g–PEEKEK polymer (Fig. 6c) indicated some changes which could not be accounted for by simple additivity. The reduced acetylene yield may be explained by the reduced content of PBT in the sample, however, the quantitative reduction in CS_2 production may not. Analysis of a larger sample indicates also a suppression of ammonia production and the appearance of sulphur dioxide as a product of degradation. An IR analysis of the noncondensable volatile product fraction of degradation indicated the production of appreciable quantities of carbon monoxide and methane.

Examination of the oligomeric products of degradation to 1000 °C of the PBT–g–PEEKEK polymer produced a spectrum very similar to those from PEEKEK homopolymer (Fig. 7, bottom) with the addition of a small nitrile absorbance and some saturated material almost completely obscured by the hydroxyl absorbance, confirming that, as expected, most of this fraction originated in the PEEKEK component of the polymer.

3.4.4. Gas chromatography–mass spectroscopy (GC–MS)

The oligomeric products from the graft copolymer in three temperature intervals (room temperature to 1000 °C, room temperature to 570 °C, and 570–1000 °C), were analysed by GC–MS. A sample of graft copolymer was heated to 570 °C and the oven quickly removed. The oligomeric products were collected and the sample was then heated to 1000 °C. The products collected after the second experiment were assumed to be formed between 570 and 1000 °C. Examination of the volatile emission curve for this second experiment verifies that degradation of the reheated sample commences before 570 °C so "about" 570 °C would be a better description of the dividing temperature.

Fractions separated and identified were assigned to either the PBT or the PEEKEK component of the graft copolymer or to the bridging structure, on the basis of experiments with the two homopolymers. Products from the PBT component are mentioned in Table Ib and c, from the PEEKEK component in Table IIb–d, and from bridge structures (Table III). Significant oligomeric products of degradation in addition to those assignable to the homopolymers included benzene diol and xanthone derivatives.

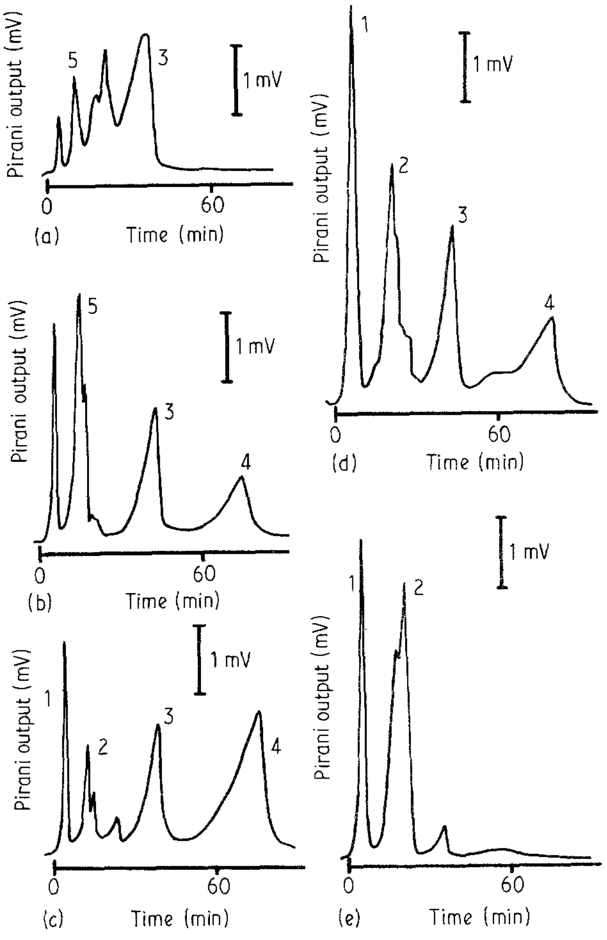

Figure 17 SATVA of condensable volatile "packets" from 150 mg PBT–g–PEEKEK heated to 1000 °C at a nominal rate of 20 °C min^{-1}: experiment commences (time = 0) with the SATVA trap at − 196 °C. (a) 25–395 °C, (b) 395–520 °C, (c) 520–570 °C, (d) 570–765 °C, (e) 765–1000 °C. (1) Hydrogen sulphide; (2) acetylene and carbon disulphide; (3) water; (4) diphenyl ether and *p*-hydroxy sulphonic acid, with traces of benzothiazole, and dicyano benzene; (5) sulphur dioxide.

TABLE III High boiling point products associated with the graft site of PBT–g–PEEKEK, normalized to the most abundant product in the spectrum set to 100

(a) From the graft copolymer heated to 1000 °C	
Xanthone	18
Xanthone, hydroxy[a]	10
Phenol, methyl sulphonyl	3
(b) From the graft copolymer heated to 570 °C	
Benzene diol[a]	39
Phenol, methyl sulphonyl[a]	24
Xanthone	21
Xanthone, hydroxy[a]	9
(c) From the graft copolymer heated to 570–1000 °C	
Xanthone	45
Xanthone, hydroxy[a]	12

[a] Isomer(s) cannot be determined unambiguously by GC–MS.

In addition to assignable products, measurable quantities of methyl sulphonyl phenol were also detected in the oligomeric product fractions of degradation to 1000 °C and to 570 °C (but not above 570 °C) to complement the production of *p*-hydroxy sulphonic acid as detected in the condensable volatile product fraction of degradation.

3.4.5. *Mechanisms of degradation of the graft copolymer*

The thermal stability of both the PEEKEK and the PBT component of the graft copolymer are modified from that of the homopolymers. The PEEKEK component of the graft copolymer is more affected and destabilized by the grafting processes, with a rate maximum of degradation considerably downshifted from that of the parent polymer. A reduced production of carbon disulphide and ammonia testifies also to modifications in the degradation of the PBT component of the polymer.

The detection of sulphur dioxide and aromatic sulphonic acid derivatives in the product spectrum indicates that the sulphonic acid used in the grafting process and in the subsequent high-temperature extraction to remove uncoupled PEEKEK, participates in a side reaction which sulphonates the graft copolymer. Decomposition of these side products may contribute to early instabilities in the polymer.

We rationalize in Fig. 18 a plausible mechanism for the production of xanthone and hydroxy xanthone from the graft site through an oxygen insertion followed by suitable fragmentations to liberate the heterocycle from the polymer. Xanthone and hydroxy xanthone appear to be produced over a wide temperature range and at high temperatures. It would, therefore, be incorrect to associate any instability in the graft copolymer with this process.

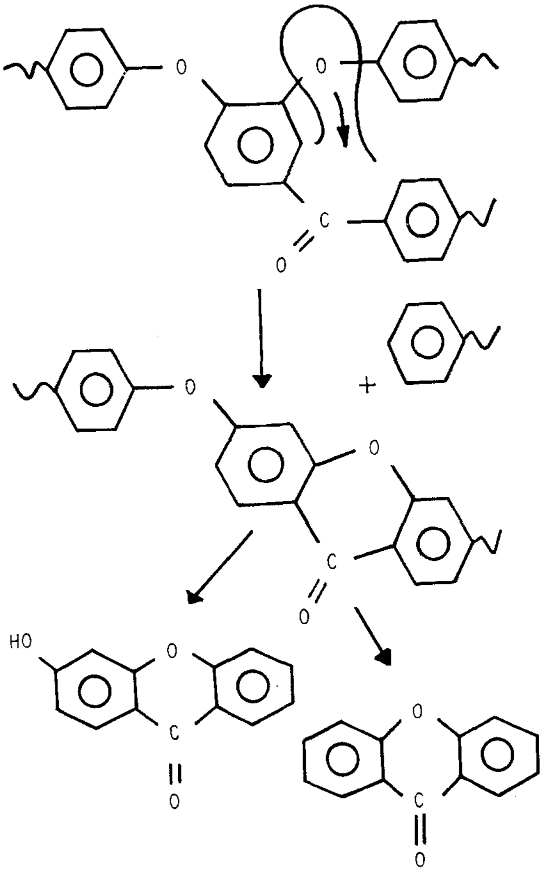

Figure 18 Degradation of graft sites on PBT–g–PEEKEK. Oxygen migration to form xanthone heterocycles followed by possible fragmentations to yield identified products of degradation.

4. Conclusions

PBT and PEEKEK are both thermally stable polymers. The thiazole linkages of PBT undergo rearrangement and some fragmentations in overlapping and competing processes to expel heteroatoms and condense the aromatic rings into a carbonaceous char. At lower temperatures, PEEKEK undergoes processes of directed fragmentations of the phenoxy linkage. At higher temperatures, the polymer is transformed into a carbonaceous char.

Degradation of the graft copolymer proceeds as with the two homopolymers. The graft site appears to rearrange thermally without destabilizing the polymer. However, thermal instability is detected and this may be associated with side products of the grafting process. Long-term isothermal ageing experiments will be required to determine if this instability (lowered onset temperature of thermal degradation, lowered rate maximum for the first process of degradation) affects significantly the performance of the graft copolymer.

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