

DEGRADATION OF AN ACETYLENE TERMINATED SULFONE (ATS) RESIN

I. In an oxygen free environment

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A study of the rates and mechanisms of degradation of an acetylene terminated sulfone resin, more precisely, bis[4-(3-ethynyl phenoxy) phenyl] sulfone and its higher oligomers, under high vacuum conditions, and under a flowing atmosphere of nitrogen, was made using techniques such as programmed thermogravimetry (TG), Thermal Volatilization Analysis (TVA), and Sub Ambient Thermal Volatilization Analysis (SATVA). Gravimetric product analyses made in conjunction with quantitative Infrared and Nuclear Magnetic Resonance Spectroscopy were used to develop a quantitative product distribution for the process. By so doing, we established the sulfone residue as the thermal weak link in the system, and identified two overlapping processes of backbone polyphenylether thermal decomposition; a low temperature process involving scissions promoted by the sulfone moiety, and a higher temperature process involving more random scissions of residual sulfone free polyphenylethers.

The preeminence of epoxy resins in thermoset technology has rested in part on the family of volatile free condensates which may be prepared using this type of resin in conjunction with a variety of curatives [1]. In contrast, most other condensation or step growth reactions produce small molecule side products. These by products present few problems during the synthesis of thermoplastic step growth polymers, indeed their removal via distillation or by the application of vacuum to the reactor, provides a simple means of driving up the molecular weight of the product [2].

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In contrast, a condensation reaction which produces volatile side products, if employed in the synthesis of a thermoset resin, will enhance the stress concentrating porosity or void content of that resin.

Recently, however, epoxy resins have been found wanting with regards the performance and stability criterion demanded of modern tactical aircraft. Alternatives such as the polyimides are currently available. However, these materials express volatiles during cure to produce voids even under pressure in an autoclave. For this reason, polyimides require for their successful preparation a good deal of skill and familiarity with the material on the part of the operator if the void content is to be kept within specifications.

With this in mind, the U.S. Air Force instigated an exploratory program to produce an alternative family of high performance matrix resins, the outcome of which resulted in the development of the "AT" or acetylene terminated resin concept.

In brief, the AT concept involves the preparation of thermally stable resin precursors, end capped with terminal acetylenes able to thermally polymerize, in the absence of added catalyst, through a free radical mechanism, to a heavily crosslinked product. The absence of hardener removes the formulatory step from the resin preparation, increasing both batch to batch homogeneity and shelf life. The absence of catalyst residues increases high temperature stability. Finally, the absence of volatile side products associated with the cross linking reaction reduces the porosity of the final product.

To date, a number of acetylene terminated resins have been synthesized by the Air Force under the AT program. One such resin, designated acetylene terminated sulfone, or ATS, more properly defined as bis[4-(3-ethynyl phenoxy)phenyl] sulfone, was synthesized for the Air Force in pilot plant quantity by Gulf Chemicals Inc. [3] because preliminary studies had indicated that the incorporation of sulfone linkages into the AT resin backbone increased the room temperature processability of the material. This structure, designated "ATS-G" and reproduced in Fig. 1, was then subjected to a battery of tests to determine processability, cure characteristics, mechanical properties, and thermal and oxidative stabilities. In this publication, we report on the thermal stability of ATS resin, measurements made both as an aid to its direct evaluation as a high temperature resin, and to establish the presence or absence of thermal or oxidative "weak links" in the resin backbone to be eliminated in future syntheses aimed towards a more stable product. Future communications in this series will describe the degradation of ATS-G resin in air and under partially anaerobic conditions.

Materials and methods

The resin

The Acetylene Terminated Sulfone (ATS) resin mixture examined here was prepared by the Gulftm Chemical Company using a three step synthesis [3]. First of all, sulfonyl diphenol was end capped with m-dibromobenzene using the Ullman ether condensation reaction. Terminal bromines were then replaced using 2-methyl-3-butyn-2-ol in the presence of a palladium catalyst, and the adduct hydrolysed to the terminal acetylene by a basic work up. Multiple condensations are allowed in this type of synthesis, for example between one phenyl bromide end capped sulfonyl diphenol and another molecule of sulfonyl diphenol, to form "oligomeric" species. The extent of oligomerization will depend on the ratio of sulfonyl diphenol to m-dibromobenzene in the reactor during the first step of synthesis. In our case the ratio was adjusted to achieve a nominal monomer content of about 70 wt%.

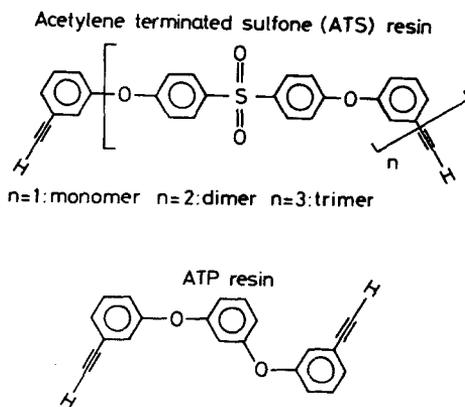


Fig. 1 Resin structures

ATP monomer, kindly supplied by Dr. B. Reinhardt of the Polymer Division, was used as received. This material, with structure similar to the ATS resin, save for the omission of the bridging sulfones, is depicted also in Figure 1 for the purpose of structural comparison with the ATS resin.

Preparation of carbonyl sulfide

Carbonyl sulfide, a low yield product of thermal degradation of ATS resin, was synthesized as a reference material to aid in the construction of Infrared calibration curves for the quantitative application of gas phase Infrared spectroscopy to a product analysis. The material was synthesized using a simplified version of an established procedure [4].

Sublimed sulfur was placed in a quartz tube on the vacuum line and warmed under vacuum to remove water. Carbon monoxide was condensed onto activated molecular sieve on the vacuum line at -196°C to remove carbon dioxide and water. The trap was then opened to the pumps to flush off less tightly bound oxygen. The carbon monoxide (1.68 g) was then expanded through a cold trap to the oven assembly and reacted over the sulfur (1.6 g) for 20 min at 650° , and the product purified by trap to trap distillation on the vacuum line. A small portion was routed to the SATVA trap for separation by the SATVA experiment and found to be essentially free of impurities. No carbon dioxide or sulfur dioxide could be detected in the product mixture using gas phase infrared spectroscopy, affirming that we successfully removed carbon dioxide and oxygen from the carbon monoxide feed gas.

Thermogravimetry

Programmed thermogravimetry (TG) at a heating rate of 5 deg/min to end temperatures up to 1000 deg/min was performed using the TG module of a DuPont 990 Thermal analyser. Heating was performed under nitrogen to monitor thermal decompositions. Derivative weight loss profiles were also recorded in this experiment to aid in the determination of temperatures which corresponded to the beginnings and rate maxima of weight loss processes.

Thermal Volatilization Analysis

The pressure developed in a continuously pumped vacuum line, as a result of the production of volatile products of polymer degradation at elevated temperatures, is proportional to both the nature of those products and their rates of formation. This effect has been successfully exploited by I.C. McNeill and co workers at the University of Glasgow in the development of the Thermal Volatilization Analysis or TVA technique for the analysis of polymer thermal degradation [5].

The data described in this report was generated by heating polymer in quartz crucibles within a quartz vacuum tube and supported inside a Marshaltm 2000 F programmable muffle furnace. Samples were heated to end or upper temperatures of up to 1020° at a heating rate of 5 deg/min. Oven calibrations were performed according to an established procedure [6].

Pressures within the vacuum line were measured using four Edwardstm PR10-C Pirani pressure gauges in series and separated by traps held at successively lower temperatures. The system used here is illustrated in Fig. 2. The first gauge measured the total volatile flux. The second gauge was positioned after a -75° cold trap, the third after a -196° cold trap, and the fourth after a trap held at -196° and containing 5 A molecular sieve. Differences in pressure between gauges 1 and 2 indicated the proportion of involatile liquid (for example, water) in the product mixture. Differences in readings between gauges 2 and 3 indicated the proportion of condensable gas (for example, carbon dioxide) in the product mixture. Gauge 3 measured the amount of noncondensable gas (carbon monoxide, hydrogen etc.) in the product mixture. Gauge 4 in this system was used to measure the amount of hydrogen in the gas flux using an effect we have designated as Adsorption TVA [7]. We have labelled the combined TVA and adsorption TVA experiments as "CATVA" for convenience. Analog signals from the gauges were routed through an Omegatm Dataplex 10 signal switcher to a flat bed recorder concurrently with oven temperatures via a Chromel/Alumel thermocouple, to generate the TVA trace for the material.

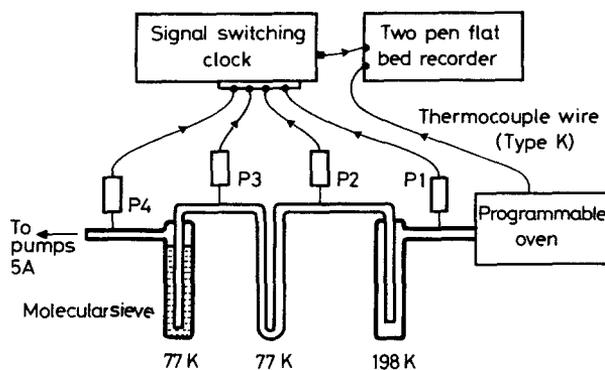


Fig. 2 A schematic of the 'in series' Thermal Volatilization Analysis (TVA) experiment. Pirani gauge #1 (P1) measures the total volatile flux, P2 measures material volatile at -75°C, P3 - 'noncondensable material'. P4 - hydrogen

Residual and oligomeric products of degradation

Upon completion of the TVA experiment, the degradation tube was opened and the mass of polymer residue from, usually, a 100 mg sample of resin, estimated to an accuracy of ± 1 mg by direct weighing. The quantity of oligomeric material was also estimated by gravimetry to an accuracy of ± 0.1 mg through the weighing of condensate on a removable jacket positioned around a water cooled finger held just above the oven assembly [7]. Samples approximately 250 mg in size were usually degraded in this experiment to produce about 15 mg of condensate. Oligomeric material was then subjected to analysis by Infrared Spectroscopy.

Volatile products of degradation

(1) Sub-ambient thermal volatilization analysis

The technique of Sub-Ambient Thermal Volatilization Analysis (SATVA), also developed by McNeill [8], separates for analysis the condensable volatile products of polymer thermal degradation. The experimental design used here is illustrated in Figure 3. On completion of the TVA experiment, condensable volatiles are routed to the SATVA trap by through pumping. The trap, initially held at -196° , is warmed to room temperature and condensed material is separated according to volatility. The jacketing wax slows down the warm up rate to achieve a controlled heating rate in the trap. Evolved material is measured by an adjacent Pirani gauge and routed to a fractionating grid on the vacuum line for subsequent analysis. Results are recorded by co-plotting both trap temperature (thermocouple output) and Pirani gauge output, both as functions of time.

(2) Infrared spectroscopy

Condensable volatile products of thermal degradation were transferred to the cold finger of a Infrared gas cell on the vacuum line, and Infrared spectra were obtained using a Beckmantm IR-33 grating spectrophotometer. Gas quantities were obtained by reference to previously determined calibration curves constructed for either of carbon dioxide, sulfur dioxide, or carbonyl sulfide, obtained through measurement of the Infrared spectrum of precisely metered quantities of the gas. Preliminary experiments showed that errors, such as would be introduced, if, for example, the presence of water in the I.R. cell would limit the volatility of carbon dioxide and sulfur dioxide through the formation of the corresponding acids, were negligible

and did not complicate the analysis of gas mixtures. We could, by this experiment measure with accuracy quantities of gas as low as $2 \cdot 10^{-5}$ mole.

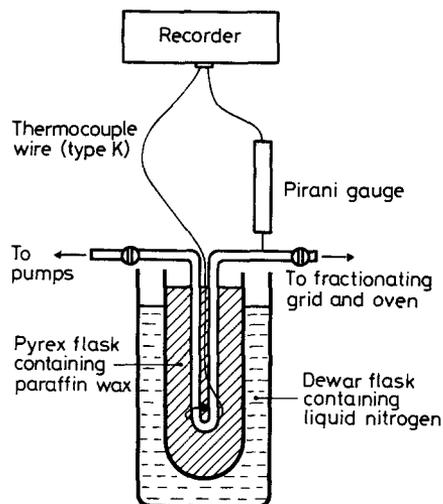


Fig. 3 A Sub-Ambient Thermal Volatilization Analysis (SATVA) assembly. The "U"bend design allows for a rapid charging of material, and for a discharging, either toward the pumping system, or to a product collection grid on the vacuum line

Calibration curves for sulfur dioxide were constructed using its corresponding absorbance at 2490 cm^{-1} , for carbon dioxide using absorbances at 3720 cm^{-1} , 3610 cm^{-1} , and 2300 cm^{-1} , and for carbonyl sulfide using absorbances at 2040 cm^{-1} and 2900 cm^{-1} . Corresponding curves for carbon monoxide and methane were constructed based on absorbances at 2150 cm^{-1} and 3020 cm^{-1} respectively.

At the end of the TVA experiment noncondensable volatile gas (carbon monoxide and methane) was transferred to a molecular sieve containing cold finger, attached to a gas phase Infrared cell adjacent to the trap, by warming the trap and cooling the finger to -196° . The Infrared spectrum of the gas mixture was then obtained by warming the gas mixture in the cell to room temperature and recording its I.R. spectrum using the Beckman spectrometer. Gas transfer by this method may be complicated by the concentrating nature of the molecular sieve and cannot be assumed to proceed with 100% efficiency. With this in mind, the system was calibrated by first transferring precise quantities of the pure gas to the cold trap then to the Infrared cell. By so doing, we were able to simulate the gas transfer step per-

formed after the TVA experiment to obtain calibration curves for both carbon monoxide and methane, allowing for an accurate measurement of as little as $2 \cdot 10^{-5}$ mole of the two gases in a noncondensable gas product mixture.

(3) Proton nuclear magnetic resonance spectroscopy

Involatile components of the condensable volatile product fraction of degradation were distilled to a small cold finger on the vacuum line. A measured amount of deuterated acetone, stored on the vacuum line over activated molecular sieve, was then condensed over the product mixture, which was removed from the manifold, warmed, and transferred to an N.M.R. tube for subsequent analysis.

Discussion

Thermal volatilization analysis and programmed thermogravimetry

The non linear pressure response of a Pirani gauge is such that low system pressures produce a relatively high output from the Wheatstone bridge circuit which constitutes the heart of the gauge [9]. In contrast, gauge output is compressed towards higher pressure readings, with the result that processes which produce trace amounts of volatiles are identifiable alongside others which produce large quantities of volatile material. Nonetheless, the TVA experiment is sensitive only towards those processes which produce volatile material. In contrast, the TG experiment measures the cumulative weight loss from a material, and a comparison between the two can often throw light upon the rate profile of production of oligomeric products of polymer degradation.

Although potentially useful it has been shown in the past that such comparisons are often fraught with uncertainty due to the fact that a blanketing atmosphere is often able to suppress the evolution of high molecular weight products of polymer thermal degradation, especially at low temperatures, with the result that a TG experiment performed under an inert atmosphere can produce a considerably different weight loss profile from that generated under vacuum. In order to properly compare the TVA and TG experiments, the weight loss profile for the resin in a vacuum and under an inert atmosphere must be proven to be similar. To do this, we weighed the residue of interrupted TVA experiments for comparison with the continuous weight loss profile generated by the TG experiment to yield the results plotted in Fig. 4,

illustrating well the good agreement between the results of the two experiments applied to this class of thermally stable resin.

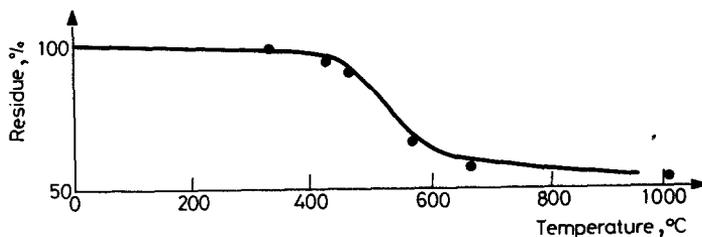


Fig. 4 A comparison between the residues of partial degradation of the ATS-G resin mixture performed at a heating rate of 5 deg/min in the TVA experiment (dots), with the continuous weight loss profile generated by a TG experiment performed under helium at the same heating rate (line)

A combined TVA/TG trace for ATS-G resin is shown in Fig. 5. Typically in this experiment, a 100 mg sample of resin was placed in the quartz crucible. The resin melt flowed then cured in situ during the early part of the TVA experiment and was subsequently degraded at higher temperatures. On the same trace we have also plotted results of a corresponding TGA trace for the resin. It must be emphasized here that due to the large surface area afforded by the crucibles (about 10 cm²), the film thickness achieved in the TVA experiment, even with the larger sample size, is less than that formed in the platinum sample pan used in the TG experiment, with the result that degradations in the TVA experiment are less subject to diffusional control than those performed in the TG experiment.

From examination of the TVA trace, we can see that volatile production achieved a double rate maximum at 637° and 744°, through reactions which predominantly resulted in the production of a mixture of noncondensables including hydrogen (a later publication in preparation will link these processes to the aromatic ring condensations which constitute the latter stages of char formation in the resin). The large Pirani responses in this higher temperature region are out of all proportion to the weight lost there, and are linked to the inordinately high Pirani gauge response to noncondensable gas [9]. A low temperature shoulder on the first rate maximum identified lower temperature reactions, which, in the main, produced condensable and oligomeric material. A comparison with the TG experiment indicated that most weight was lost by the resin in this temperature interval. (It will be shown later in this report that two overlapping processes of thermal

degradation are operative in this temperature interval.) From the TG experiment we could infer that the bulk weight loss process, corresponding to the low temperature "shoulder" on the TVA curve, is operative between 435° and 600°.

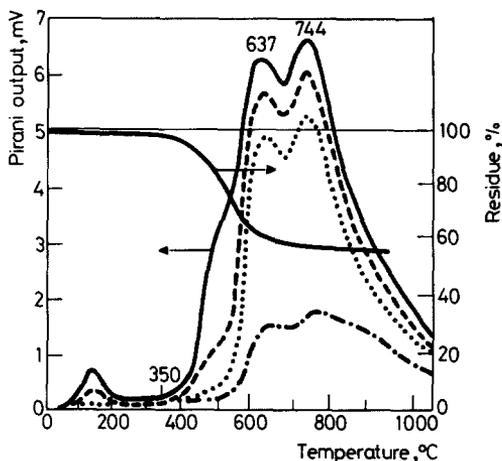


Fig. 5 A composite plot of the CATVA trace for a 100.0 mg sample of the ATS-G resin mixture obtained at a heating rate of 5 deg/min, and the corresponding TG trace for the material obtained under helium at the same heating rate. Continuous line: material volatile at 0°C, Broken line: material volatile at -75°C, Dots: material volatile at -196°C, Mixed broken line: hydrogen

The enhanced sensitivity of the TVA experiment over the TG experiment, with regards weight loss processes producing volatiles, may be observed by comparing temperatures which correspond to the onset of the degradation process as measured by the two techniques: 350° for the TVA technique and 400° for the TG technique.

Infrared spectroscopy of noncondensable volatile products of degradation

On completion of the TVA experiment, trapped noncondensables were analysed by Infrared spectroscopy to yield spectra such as are depicted in Fig. 6 (A), showing clearly the presence of both methane and carbon monoxide in this product fraction. A quantitative estimation of both products was made as an average over three experiments. This information is recorded in Table 1.

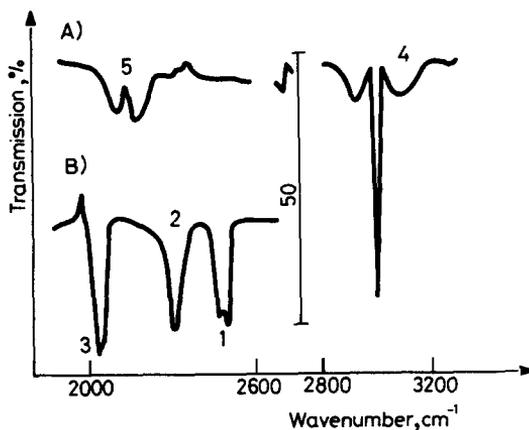


Fig. 6 Gas phase Infrared spectra of (A) Noncondensable and (B) Condensable volatile products of degradation to 1020°C of the ATS-G resin mixture in the TVA experiment. (1) - Sulfur dioxide, (2) - Carbon dioxide, (3) - Carbonyl sulfide, (4) - Methane, (5) - Carbon monoxide

Table 1 Products of degradation of ATS-G resin to 1020°C under vacuum at a heating rate of 5 deg/min

Product	Yield (wt.% of the cured resin)
Residue	53.2
Phenol	11.9
Sulfur dioxide	10.7
Oligometric material	6.5
Carbon monoxide	6.2
Water	5.0
Methane	3.0
Benzene	2.2
Carbon dioxide	1.2
Hydrogen sulfide	0.6*
Carbonyl sulfide	0.3
Hydrogen	Negligible
TOTAL	100.8

*By difference (see text)

As previously stated, higher temperature reactions of ATS polymers will be the subject of a future report and will not be discussed here in any detail. Suffice is to say that both carbon monoxide and methane are the product of

high temperature aromatic polycondensations of the polyphenol resin nucleated around the cyclized polyene backbone. In fact, the double rate maxima in the TVA curve may be thought of as defining the rate profile of the two processes which convert the ATS-G resin residue to glassy carbon.

SATVA of the condensable volatile product fraction of degradation

On completion of the TVA experiment, condensable volatiles were routed to the SATVA trap for separation and analysis. A typical SATVA trace, produced by a separation of volatiles generated by a programmed warm up to 1020°, is reproduced in Fig. 7. In this trace, as in all others, volatility band structural assignments were made based on the results of gas phase Infrared spectroscopy of the pure fraction isolated on the fractionation grid (if volatile), or, (if less volatile), on the results of a liquid phase Infrared and proton N.M.R. spectroscopic analysis of the pure fraction. By these means we showed the major condensable volatile products of thermal degradation of the resin to be sulfur dioxide, water, phenol, and benzene, accompanied by smaller quantities of carbon dioxide, carbonyl sulfide, and hydrogen sulfide.

If we separate for analysis, packets of volatiles generated in successively higher temperature intervals, for example, between 283° and 424°, as depicted in Fig. 8; between 461° and 496°, and also between 567° 625°, both as depicted in Fig. 9, we can identify changes in product distributions which must reflect changes in the processes operative over those temperature intervals. For example, the major products generated over the lowest temperature interval are sulfur dioxide, phenol, and water. Water is easily recognized as a low temperature product of decomposition of abnormal species in the ATS-G resin mixture [10]. The presence of small amounts of phenol and sulfur dioxide, however, indicate the beginnings of chain scission of the backbone resin. On examination of Fig. 9, we can see that the yields of phenol and sulfur dioxide increase with temperature, at least to an end temperature of 496°. From the same figure we can see that phenol continues to be produced at still higher temperatures, accompanied by large quantities of benzene and water, but without the sulfur dioxide. Ancillary experiments performed at intermediate temperatures indicated that the two processes overlap and that the lower of the two (producing sulfur dioxide and phenol) is operative over a wider temperature interval than the higher temperature process.

Quantitative analysis of condensable volatile products of thermal degradation

The condensable volatile product fraction of degradation of the ATS-G resin was subjected to quantitative analysis using the techniques of gas phase Infrared spectroscopy and proton N.M.R. spectroscopy. Essentially, the condensable volatiles from a 250 mg sample were divided into two "packets" by the SATVA experiment. The more volatile packet, containing sulfur dioxide and lighter material, was routed to a gas phase I.R. cell, and the less volatile packet, containing benzene and less volatile material, to a cold finger for subsequent dilution by deuterated solvent and examination by N.M.R. spectroscopy.

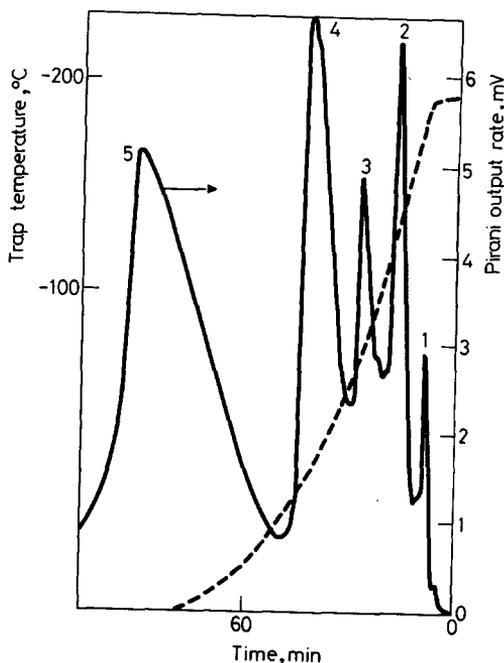


Fig. 7 An SATVA trace of the condensable volatile product fraction of degradation to 1020°C of ATS-G. Sample size 101.6 mg. Solid line: Pirani pressure trace, Broken line: Thermocouple reading (Trap temperature). (1) CO₂, COS, H₂S, (2) SO₂, (3) Benzene, (4) H₂O, (5) Phenol

Details of the infrared measurements have been discussed previously and need not be reproduced here. A sample spectrum is reproduced in Fig. 6B. Results of the Infrared analyses are reported in Table 1. The preferred

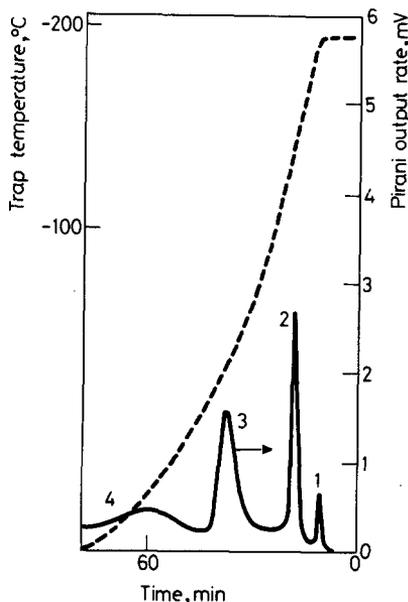


Fig. 8 An SATVA trace of the condensable volatile product fraction of programmed degradation of ATS-G under vacuum at a rate of 5 deg/min in the temperature interval (283-424) $^{\circ}$ C. Sample size 101 mg. Solid line: Pirani pressure trace, Broken line: Thermocouple reading (Trap temperature). (1) CO₂, COS, H₂S, (2) SO₂, (3) H₂O, (4) Phenol

method of analysis of the less volatile fractions - gas chromatography, being unavailable to us, we employed a combination of gravimetry and N.M.R. spectroscopy to effect our analysis. In brief, the product fraction was condensed into a small container which was weighed with precision. The fraction was then condensed into a small cold finger for analysis by N.M.R. spectroscopy, and the container reweighed to determine the mass of product, which we found to be highly reproducible, provided that sufficient care had been taken in the distillation and weighing steps. A typical N.M.R. spectrum of this product mixture is reproduced in Fig. 10. The proportions of phenol : water : benzene were estimated by simple integration and comparison of signals associated with the three molecules by the cut and weigh method. For example, signal in region "A" of the figure is produced by the benzene component of the mixture, signal in region "B" is produced by phenol, and the hydroxyl signal "C" is produced both by water and phenol in the product mixture. The mole ratio of benzene : water : phenol would,

therefore, be represented as $C/6: (A-B/5)/2 : B/5$ in terms of signal integration. By combining the product ratios with fraction mass, we arrived at the absolute quantities of benzene, water, and phenol reported in Table 1 as a weight fraction of the original polymer mass.

Analysis of hydrogen sulfide

Hydrogen sulfide was identified by smell as a component of the condensable volatile products of degradation, but could not be estimated quantitatively as the compound lacks associated definitive Infrared absorbances. We, therefore, set out to infer the presence of hydrogen sulfide by difference.

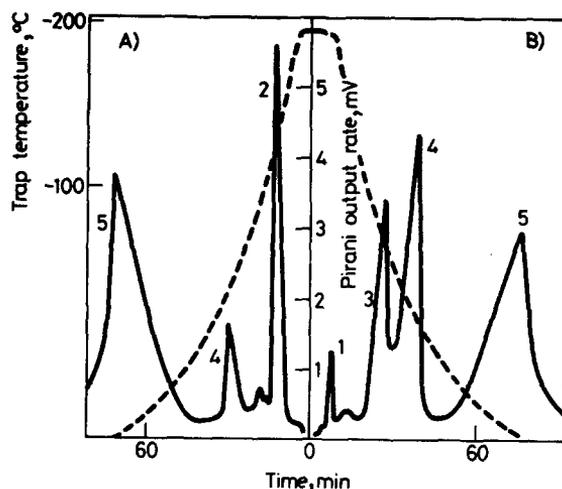


Fig. 9 A comparison between "Packets" of condensable volatile products of degradation of ATS-G in (A). The temperature interval (461-496) $^{\circ}$ C and (B) in the temperature interval (567-625) $^{\circ}$ C. Solid line: Pirani output, Broken line: (---) Thermocouple output (Trap temperature). (1) CO₂, COS, H₂S, (2) SO₂, (3) Benzene, (4) H₂O, (5) Phenol

Ancillary SATVA experiments established that hydrogen sulfide is in a volatility range with carbonyl sulfide and carbon dioxide, and so should accompany the more volatile products of degradation usually isolated for quantitative analysis by Infrared spectroscopy. We, therefore, weighed this fraction by the procedure developed for the N.M.R. analysis, estimated other constituents by Infrared spectroscopy, and arrived at a residual mass approximating 0.6 wt.% of the cured polymer as reported in Table 2. We were encouraged by the good agreement between this figure and that obtained through a breakdown of the fate of sulfur as a constituent of the

product fractions of degradation, measured by Infrared spectroscopy of the condensable volatile product fraction, and by elemental analysis of the oligomeric and residual product fractions of degradation as reported in Table 3.

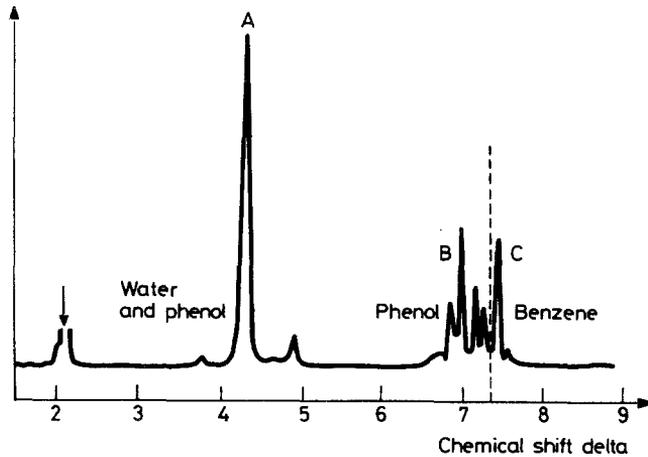


Fig. 10 A proton N.M.R. spectrum in d_6 -acetone of higher molecular weight condensable volatile products of degradation to 1020°C of ATS-G. "A, B and C" refer to separate regions of the spectrum which were integrated for a quantitative analysis of the mixture (see text)

Table 2 Gravimetry of the condensable volatile products, of thermal degradation to 1020°C of the ATS-G resin mixture, contained in fractions 1 and 2 as separated by SATVA

Product	wt.% of the cured resin
Sulfur dioxide	10.7
Carbon dioxide	1.2
Carbonyl sulfide	0.3
Total	12.2
SATVA fractions 1 and 2	12.8
Material unaccounted	0.6 wt.% of the cured polymer*

*cf Table 3

Table 3 Distribution of sulfur in the products of thermal degradation to 1020°C of ATS-G, contained in SATVA fractions 1 and 2

Product	wt.% of the cured polymer
Sulfur in the residue of degradation	6.1
Sulfur in the oligomeric product fraction of degradation	0.1
Sulfur dioxide	81.1
Carbonyl sulfide	2.5
Total	89.8
Unaccounted for	10.2 (about 0.7 wt% of the cured polymer)*

*cf Table 2

The oligomeric and residual product fractions of degradation

A gravimetric analysis of the oligomeric and residual product fractions of degradation was performed as outlined in the experimental section of this report. In addition, we obtained the Infrared spectrum of the oligomeric product fraction of degradation of ATS-G to 1020°. Sample was prepared for this experiment by simply depositing the material onto a salt disk from chloroform solvent after rinsing from the cold finger. The spectrum, reproduced in Fig. 11, indicated that this product fraction contained functionality identical to that displayed by the original resin (spectrum reproduced in reference 10), with the addition of some saturated material, which we will show in a future publication to arise from fragmentations of the polyene or its thermal derivative. This indicated that oligomers were formed by simple scissions of the resin backbone, to eventually produce a fraction of sufficient volatility to evaporate from the hot zone. A gravimetric analysis of both product fractions is reported in Table 1. ATS is, therefore, shown as a high char yield resin with a residue of thermolysis to 1020° at 5 deg/min exceeding 50%, and to produce about 6 wt.% of oligomeric material as a product of those same reactions which "chop" the resin backbone and evaporate also more volatile products such as sulfur dioxide, phenol, water, and benzene from the residue of degradation.

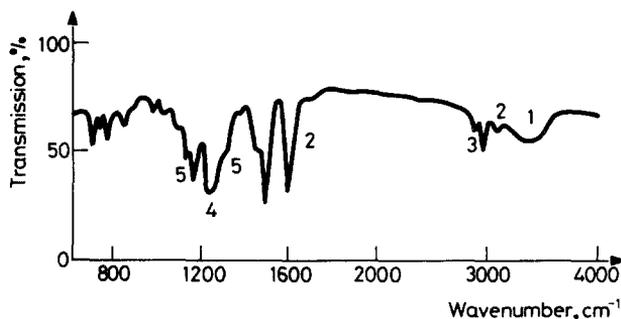


Fig. 11 Infrared spectrum of the oligomeric product fraction produced on thermal degradation to 1020°C of a precured ATS-G resin mixture. (1) Hydroxylic material, (2) Aromatic material, (3) Saturated material, (4) Phenylether linkages, (5) Sulfone linkages

Degradation of ATP monomer

Our findings so far appeared to suggest that the backbone sulfones of the ATS-G resin constituted the thermal weak link in this class of material. To prove (or disprove) this finding, we determined to degrade ATP monomer under the same conditions, using the TVA and TG experiments, to gain information of the behaviour of this sulfone free system for comparison with the ATS resin.

A combined TG/TVA trace for ATP monomer is shown in Fig. 12, and that for the ATS-G resin in Fig. 5. Similarities exist between the behaviour of the two systems. For example, they both share a double rate maximum of noncondensable volatile production, related to polyene nucleated polyaromatizations of the char at high temperatures. However, the pronounced low temperature shoulder on the first noncondensable rate maximum is much reduced in the TVA trace produced by the ATP monomer. Examination of the corresponding TG trace for this material showed that a smaller amount of material is evaporated overall from the ATP resin, which is, in turn, more efficiently converted to char than the ATS-G resin as evidenced by its higher residue yield under the same conditions (a 60.1% weight retention to 1020° as opposed to a 53.2% weight retention achieved by the ATS-G resin under the same conditions). As the only major structural difference between the two materials corresponds to an absence or presence of bridging sulfones, it would appear that this linkage promotes low temperature backbone scissions in the ATS-G resin.

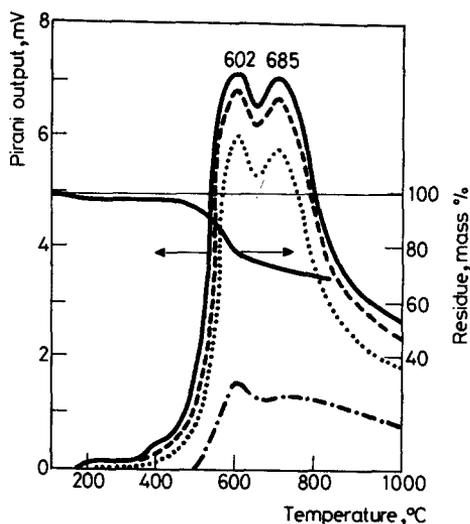


Fig. 12 A composite plot of the SATVA trace for a 105.3 mg sample of ATP resin obtained at a heating rate of $5^{\circ}\text{C}/\text{min}$, and the corresponding TG trace for the material under helium obtained at the same heating rate. Continuous line: material volatile at 0°C , Broken line: material volatile at -75°C , Dots: material volatile at -196°C , mixed broken line: hydrogen

This observation is corroborated by a qualitative comparison of SATVA traces corresponding to separations of condensable volatile products of degradation of the two systems to an end temperature of 1020° . As expected, sulfur dioxide is absent from the product distribution from ATP monomer (Fig. 13). More importantly, both benzene and phenol are produced in smaller quantities in the absence of the sulfone linkage. We can rationalize this if the lower temperature process of degradation of ATS resin mentioned earlier is promoted by sulfones. In their absence the process would be suppressed with a concurrent reduction in the amounts of phenol (which is formed as a co-product of this process). Phenol would continue to be produced by more random higher temperature polyphenyl ether scissions but the overall yield of the material would be reduced.

Mechanisms of degradation

To a first approximation, we may divide the process of thermal degradation of ATS resin into two phases. At lower temperatures, the predominant reactions are those of chain scission to produce a range of condensable and

oligomeric products. At higher temperatures the chain scission processes are supplanted by polyaromatic ring fusions, which we will show in a future communication to be nucleated on the polyene crosslink, or more properly, its thermal derivative in that temperature region.

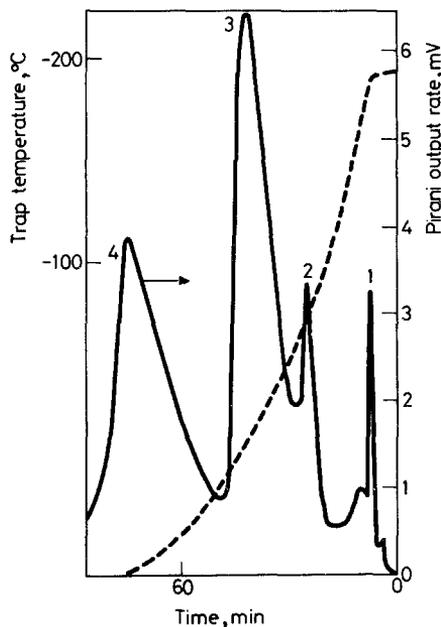


Fig. 13 An SATVA trace of the condensable volatile product fraction of degradation to 1020°C of ATP monomer. Sample size 105.3 mg. Solid line: Pirani pressure trace, Broken line: (—) Thermocouple reading (Trap temperature). (1) CO₂, (2) Benzene, (3) H₂O, (4) Phenol

It will be remembered that two processes of backbone scission have been identified as operative in ATS resin. The first, producing sulfur dioxide and phenol, and the second, phenol, benzene, and water. We can rationalize that phenol may be produced at low temperatures by a directed phenoxy bond scission to produce a radical chain end stabilized by resonance into the sulfone moiety as illustrated in Fig. 14. Subsequent chain scissions at the sulfone linkage would complete the process freeing both phenol and sulfur dioxide to subsequently evaporate from the hot zone. Alternatively, the sulfone link could be independently volatilized from the polymer in the absence of phenol. We have shown that sulfone is quantitatively (>80%) removed from the polymer as sulfur dioxide. It is common knowledge that free radi-

cals are usually deactivated either through processes of termination or of combination [2]. The high char yield from this polymer is a good indicator that a high proportion of those radicals produced by sulfone promoted bond scissions terminate by combination, for, if the converse were true, then the resin backbone would be almost completely evaporated from the hot zone to produce a residue of degradation much less than the 50+ wt.% reported here.

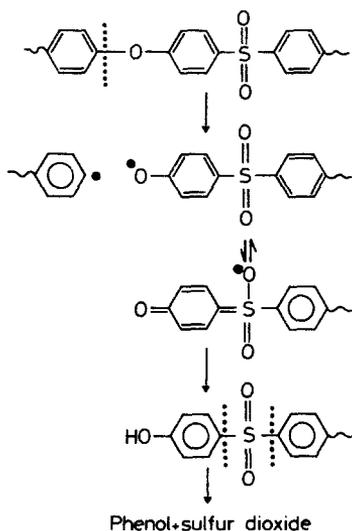


Fig. 14 Directed low temperature phenoxy bond scissions stabilized by resonance into the sulfone group

At higher temperatures we can imagine the scission processes to center around decomposition of, more disordered, residual, sulfone free polyphenyl ethers linked as combination products of the first process, and to produce benzene, phenol, and water through more random chain scissions of that crosslinked resin backbone.

Conclusions

It has been shown that Acetylene Terminated Sulfone (ATS) resin, as synthesized through the condensation of sulfonyl diphenol with *m*-dibromobenzene, followed by acetylation of the chain ends, is a thermally stable or high

char yield resin. We also showed that the bulk weight loss process in the resin corresponded predominantly to scissions of the resin backbone as opposed to reactions involving the polyene crosslink, producing chain segments and fragments able to volatilize from the hot zone. In addition to random scissions at high temperatures, we also observed a more directed scission process at lower temperatures. This process, centered upon the low temperature decomposition of sulfone linkages and the directed scission of adjacent phenyl ethers, produced sulfur dioxide and phenol as products of degradation. This low temperature process quantitatively removed sulfones from the polymer. The detection of absorbances associated with sulfones in the oligomeric or "cold ring" product fraction of degradation indicated that at least some of that product fraction was generated during the low temperature process of degradation. It is ironic, therefore, that the sulfones which so contribute to the low temperature processability of the resin (i.e. its room temperature "tack and drape") should also constitute the thermal weak link in the system.

* * *

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Zusammenfassung — Mittels TG, TVA und SATVA wurde eine Untersuchung der Reaktionsgeschwindigkeit und des Reaktionsmechanismus des Abbaues von Sulfonharz mit endständigem Acetylen (von bis-[4-(3-ethinylphenoxy)phenyl]sulfon und seiner höheren Oligomere) im Hochvakuum bzw. in einer dynamischen Stickstoffatmosphäre durchgeführt.

In Verbindung mit quantitativer IR- und NMR-Spektroskopie wurde eine gravimetrische Analyse der Produkte erstellt, um eine quantitative Produktzusammensetzung des Prozesses zu erhalten. Der Sulfonrest konnte somit als schwaches Kettenglied des Systemes erkannt und zwei überlappende Prozesse der thermischen Zersetzung des hauptkettigen Polyphenylethers identifiziert werden: ein Prozess bei niedrigerer Temperatur beinhaltet durch die Sulfonkomponente geförderte Spaltungen und ein zweiter Prozess verursacht bei höherer Temperatur Random-Spaltungen des verbleibenden sulfonfreien Polyphenylethers.