

Thermolysis of acetylene terminated sulfone resins. II. Oligomeric and residual products of degradation

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Resins from acetylene terminated sulfone (ATS) fractions and related model compounds have been pyrolysed to 1000°C under high vacuum conditions. The residual and oligomeric product fractions of degradation were isolated using the technique of thermal volatilization analysis (TVA). The residues from degradation were weighed and subjected to compositional analysis by infrared (IR) spectroscopy. The oligomeric products of degradation were weighed, isolated into preparative TLC bands, and identified through the joint application of IR and proton nuclear magnetic resonance (NMR) spectroscopies and chemical ionization mass spectroscopy (CIMS). The residues from thermal degradation proved somewhat intractable. On the other hand, analysis of the oligomeric product fractions provided a wealth of identifiable derivatives which confirmed the major role that random scissions play in the degradation process. Residue yields were shown to increase with the polyene concentration in the cured resin. In contrast, the yields of oligomeric products were shown to be inversely related to polyene concentration in the cured resin. ATS and ATB resin were also aged at 250°C and at 300°C in air. Both resins were stable to weight loss at 250°C but ablated slowly at 300°C in air. The ageing process was accompanied by oxidation of the polyene to carbonyl containing derivatives which are stable at 250°C but unstable at 300°C. The AT resins were significantly more stable to weight loss than epoxy resins containing similar structural motifs.

INTRODUCTION

The acetylene terminated or 'AT' concept for the construction of thermally stable resin systems has been championed by the US Air Force as a viable alternative to current resin binders for fiber reinforced composites. The AT system cures through the thermal oligomerization of terminal acetylenes.¹ The precursor possesses a long shelf life at room temperature and can be cured in the absence of additives or catalysts which often lower the thermal stability of the final product. In this communication we continue an investigation

into the thermal degradation of acetylene terminated sulfone (ATS) based resin systems begun in Part I of this series.² The synthesis of the resin precursor, bis[4-(3-ethynyl phenoxy) phenyl] sulfone and its higher oligomers has been covered previously.³

Polymeric materials, when subjected to thermal stress in the form of programmed heating under high vacuum conditions, are degraded by processes, the rates and mechanisms of which are structurally dependent. The products of polymer degradation may be grouped into four 'fractions' depending upon their volatility under high vacuum conditions. For a proper mechanistic description of polymeric degradation pathways it is essential that the complete product distribution of the polymer be elucidated.

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The noncondensable volatile product fraction of degradation is volatile at -196°C at pressures up to a few torr in a high vacuum system. It may contain any of the permanent gases; for example, hydrogen, carbon monoxide, nitrogen, oxygen and methane.

The condensable volatile product fraction of degradation is composed of material which is volatile at room temperature and involatile at -196°C in a high vacuum manifold. It is usually composed of material of molecular weight up to 100–150 a.m.u.

The oligomeric (or 'cold ring') product fraction of degradation is composed of material in the molecular weight range 150–800 a.m.u. It is volatile at elevated temperatures such as would be encountered in a degradation assembly, but involatile at room temperature under high vacuum conditions. As such, it condenses onto the degradation tube immediately above the hot zone—hence the trivial label 'cold ring fraction'.⁴

The residue of degradation is composed of material which is involatile at degradation temperatures and therefore remains in the oven assembly. It is often high in carbon content, heavily crosslinked, and 'charred'—especially if the polymer was exposed to high temperatures during the degradation experiment.

In Part 1 of this series, we identified the four major volatile forming processes of thermal degradation of acetylene terminated sulfone based resins, and provided a detailed examination of the condensable and noncondensable volatile product distributions from those processes.² In this, the second of a three part series on this topic, we first of all gain an appreciation of the oxidative stability (and hence commercial utility) of ATS resins through long term ageing studies made in air, and in comparison with other commercial resin systems. We next quantify and probe spectroscopically the residues of degradation of ATS resins to 1000°C and intermediate temperatures under vacuum. We also provide a detailed examination of the oligomeric or high boiling point product fraction of degradation. We end by identifying individual compounds in the oligomeric product fraction with one or other of the first two volatile forming processes of degradation. In these two offerings, we therefore detail the complete product distribution of degradation of ATS polymers. In Part 3 of this series, we draw on these analyses as a basis for the construction of mechanistic

pathways for the decomposition of the ATS resin network.

EXPERIMENTAL

Isothermal ageing studies

Epoxy resins were based on the diglycidyl ether of bisphenol A (Epon 828tm, Shell Chemicals). The epoxy and amine equivalent weights were balanced and the resin was fully cured in isothermal steps with diaminodiphenyl methane (DDM), diaminodiphenyl sulfone (DDS), or *m*-phenylene diamine (all technical grade, used without purification). Acetylene terminated sulfone (ATS-G) and acetylene terminated Bisphenol A (bis[4-(3-ethynyl phenoxy) bisphenol A] or ATB) resin was cured in air at $10^{\circ}\text{C}/\text{min}$ to an end temperature of 250°C then soaked at 300°C for 10 min. The resin was ground cryogenically in a Tekmartm microanalytical mill, and aged in air at $(250 \text{ or } 300 \pm 3)^{\circ}\text{C}$ in a Thermolyne 1300tm muffle furnace driven by an Omega CN500SSR controller or under N_2 in a Lindbergtm No. 55122 tubular muffle furnace driven by the same controller. Samples of ATS and ATB resin were also cured onto NaCl disks, aged, and examined by IR spectroscopy using a Nicolet MX-S FTIR spectrometer.

The residue of degradation

Gravimetric analysis

At the end of the CATVA experiment² the oven head assembly was dismantled and the crucible with its residue of degradation carefully removed from the quartz degradation tube with spring loaded pincers. The pre-weighed crucible was re-weighed to estimate the mass of residue which was expressed as a percentage of the original sample mass.

Elemental analysis

The carbon, hydrogen, sulfur and oxygen contents of the residues of partial degradation were estimated by elemental analysis, and used in conjunction with total residue weights to

construct element loss curves for the resin as a function of temperature.

IR spectroscopy

The residues of partial degradation were incorporated into KBr disks and examined by IR spectroscopy. In general, a good dispersion of residue throughout the disk was difficult to achieve because of the intractable nature of the material. The spectra obtained by this method were, therefore, often highly attenuated and distorted, and open only to qualitative interpretation. Better spectra were obtained by degrading polymer samples which had been cured onto NaCl salt plates. (The disadvantage of this method is that exact temperatures of degradation are often difficult to achieve, especially under programmed conditions, due to the unique thermal lag across each salt plate.)

The oligomeric or cold ring product fraction of degradation

Gravimetric analysis

A removable pyrex jacket was wedged onto the end of the oven assembly internal cold finger.⁵ The degradation experiment was performed, after which the jacket was removed, weighed, washed clean with solvent, and reweighed to estimate the mass of oligomeric product material. The recovered material was stored for subsequent analysis. This method, for example, allowed us to weigh a 15 mg product mixture with an accuracy of ± 1 mg.

IR and nuclear magnetic resonance (NMR) spectroscopy

Oligomeric product fractions of degradation were analyzed by IR spectroscopy as thin films cast from chloroform onto salt plates, using a Beckman[™] 33 grating IR spectrometer. The same materials were analyzed by proton NMR spectroscopy, in deuteriochloroform at room temperature, using a Varian[™] EM360, 60 MHz continuous wave spectrometer.

Thin layer chromatography (TLC)

Oligomeric product fractions of degradation of all the polymers studied in this work were separated into four sub-fractions by TLC using SiO₂ (F₂₅₄) with methylene chloride as the mobile

phase. On the basis of IR and NMR studies of the four fractions, combined with TLC separations of reference materials made under the same conditions, the gross composition of each sub-fraction was ascertained.

Preparative thin layer chromatography

(i) *Gravimetric analysis.* Preparative TLC separations of oligomeric product fractions of degradation were performed on (20 × 20 × 0.2) cm SiO₂ F₂₅₄ plates using methylene chloride as a developing agent. Separated bands were stripped from the plate using tetrahydrofuran (THF) solvent, evaporated to dryness, and weighed to estimate their weight percent of the original mixture. Recoveries ranged from 95% to 105% of the eluted mixture depending on the efficiency of the solvent removal after the experiment. The absolute yield of each TLC sub-fraction was estimated by a simple calculation relating its weight percentage in the original product mixture to the corresponding weight percentage of the latter in the original polymer.

(ii) *IR and NMR spectroscopy.* Materials isolated by preparative TLC were examined by IR and NMR spectroscopy as outlined previously.

(iii) *Chemical ionization mass spectrometry (CIMS).* TLC sub-fractions were introduced to the solid sample probe of a Finnegan[™] 4021 mass spectrometer at 30°C. The probe was warmed as required under programmed conditions to evaporate the material and identify the most abundant parent ions in each mixture. (It must be noted in passing that some components of these mixtures may escape detection by this technique. For example, more volatile components may be lost on pump down while less volatile material, especially if present in small quantities, may evolve between scans. In addition, the possibility exists that a fraction of material may crosslink on the probe to form an involatile residue.)

(iv) *Joint application of the above techniques.* Microstructural information from IR and NMR spectroscopy was combined with parent ion molecular weights obtained using CIMS and polarity measurements by TLC to identify individual species in sub-fractions which were isolated by the preparative TLC method.

DISCUSSION

Isothermal ageing experiments

Isothermal ageing experiments in air were performed to determine the oxidative stability of acetylene terminated sulfone (ATS-G) resin by gravimetry and to gain some qualitative understanding of the oxidation pathway by IR spectroscopy. We chose to examine also the stability of acetylene terminated bisphenol A (ATB) monomer resin to compare the influence of sulfone and Bisphenol A bridges on the thermal stability of AT resin. We also evaluated the performance of the ATS and ATB resins against a selection of Bisphenol A based epoxy resins.

(i) *Weight loss by gravimetry.* We have determined previously that ATS resin is stable to weight loss at 250°C.¹ We chose, therefore, to perform weight loss experiments at 300°C. The results of these experiments are plotted in Fig. 1. The ATS and ATB resins (open triangles and circles respectively) lose weight monotonically and achieve a residue of about 90% after 200 h at 300°C in air. Replacing sulfones with bisphenol A did not appear to influence the oxidative stability of the resin. The AT resins were significantly

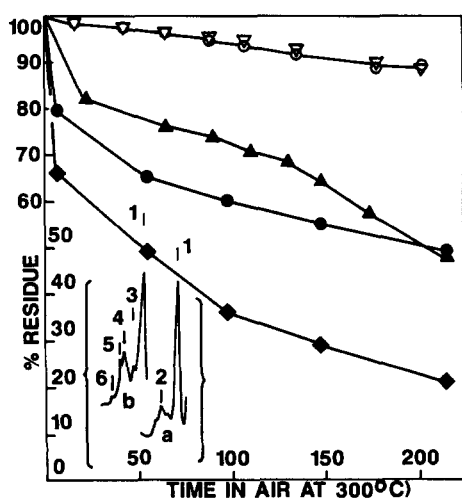


Fig. 1. Weight loss curves in air at 300°C (Δ , ATS resin; \circ , ATB resin). Other entries are stoichiometric epoxy resins based on the diglycidyl ether of bisphenol A or DGEBA (Epon 828[™]), fully cured with diaminodiphenyl sulfone or DDS (\blacktriangle), diaminodiphenyl methane or DDM (\bullet), *m*-phenylene diamine or mPDA (\blacklozenge). Inserts: (a) FTIR spectra of ATS-G resin, cured to 250°C at 10°C/min in air as a thin film: 1, 1579 cm^{-1} ; 2, 1726 cm^{-1} . (b) as in (a) but after 82 h at 250°C in air: 3, 1671 cm^{-1} ; 4, 1742 cm^{-1} ; 5, 1779 cm^{-1} ; 6, 1852 cm^{-1} .

more stable to weight loss than representative Bisphenol A based epoxy resins, which affected stability according to curative type. All three epoxy resins suffered an early precipitous weight loss followed by a slower weight loss regime. A resin cured with diaminodiphenyl sulfone (DDS: filled triangles) was the most stable, followed by resin cured with diaminodiphenyl methane (DDM; filled circles), with the *m*-phenylene diamine cured resin (mPDA: filled diamonds) as the least stable of the three. The AT resins would, therefore, appear to be significantly more stable than epoxy resins containing similar structural features.

(ii) *(IR) spectroscopy.* Aged AT resins were examined by IR spectroscopy to gain some insight into the nature of the oxidative process. The AT resin system cures through the conversion of terminal acetylenes into a polyene oligomer. Resin cured in air develops a complex set of overlapping absorbances around 1725 cm^{-1} (Fig. 1, insert a, peak 2), accompanied by the formation of some hydroxyls (around 3400–3500 cm^{-1}). We have previously speculated that the polyene crosslink is rapidly oxidized (or peroxidized) to a carbonyl and hydroxyl containing derivative.¹

The oxidation of ATS and ATB resins at 250°C and 300°C was followed using the ratio of the integrated carbonyl absorbance (around 1740 cm^{-1}) against that of the corresponding aromatic absorbance band at (c.) 1580 cm^{-1} which is assumed to change little during the experiment. Uncured resin does not absorb in the IR spectrum above 1700 cm^{-1} (corresponding 1740/1580 ratios for ATS = 0.03, ATB = 0.01). Changes in the saturated C—H stretching region with time for ATB in air at 250°C were also followed by this technique. The initial sample thicknesses were adjusted to achieve an absorbance of 1 a.u. \pm 5% at the very intense 1242 cm^{-1} absorbance band, common to both ATS and ATB resin, thus ensuring sample thicknesses of only a few μm and absorbances which follow Beers law.

Normalized absorbances for resin oxidized at 250°C are plotted in Fig. 2. The ATB resin is the more susceptible to oxidation, developing a normalized carbonyl absorbance of about 0.8 units during cure. The carbonyl content increases thereafter to an ultimate value of about 1.2 units. The ATS resin develops a lower carbonyl content

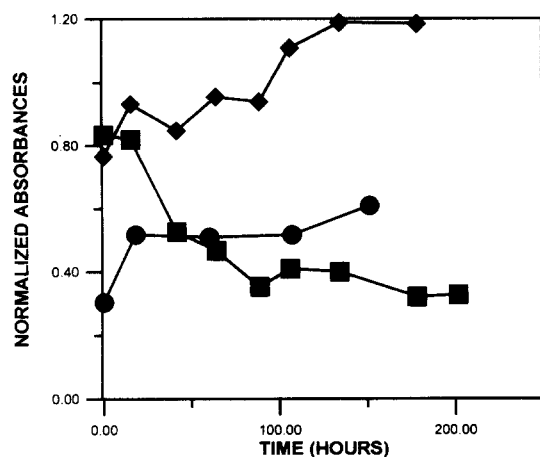


Fig. 2. Development of IR absorbances normalized to the 1580 cm^{-1} band in ATS and ATB resins accompanying air oxidation at 250°C . ●, the carbonyl region from the spectrum of ATS resin; ◆, the carbonyl region from the spectrum of ATB resin; ■, the saturated C—H stretching region from the spectrum of ATB resin.

of about 0.3 units during cure, rising to a value of about 0.5 upon further oxidation. The normalized saturated carbon C—H stretching mode drops from an initial value of about 0.8 units to about 0.3 units over a 100-h period and remains constant thereafter. It would seem that some bridging isopropyl units in ATB resin are subject to removal from the resin at 250°C , presumably by oxidation, and may contribute to the buildup of carbonyl absorbance in that resin. (The saturated C—H absorbance bands from ATB around 3000 cm^{-1} effectively disappear after 41.5 h oxidation at 300°C).

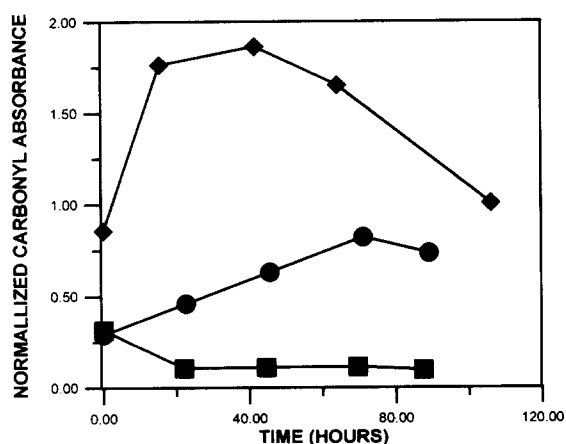


Fig. 3. Development of IR absorbances normalized to the 1580 cm^{-1} band in ATS and ATB resins accompanying degradation at 300°C (●, the carbonyl region from the spectrum of ATS resin degraded in air; ◆, the carbonyl region from the spectrum of ATB resin degraded in air; ■, the carbonyl region from the spectrum of ATS resin degraded under nitrogen).

Normalized carbonyl absorbances from ATS and ATB resin are plotted in Fig. 3 as a function of ageing time at 300°C . ATS resin aged in air at this temperature (filled circles) develops additional carbonyl absorbance which increases monotonically for about 70 h after which a small drop is observed. The ATB resin (filled diamonds) accumulates carbonyls for about 40 h at 300°C after which a significant drop is observed which we believe to arise from the ablation of completely oxidized precursors. (Spectra at longer times are weak and difficult to interpret due to sample ablation.) Carbonyls introduced to ATS resin during cure (filled squares) are removed by heat treatment under nitrogen at 300°C .

Additional experiments were next performed to elucidate further the effect of temperature and atmosphere on the ageing process. As expected, both ATS and ATB resin, preoxidized at 250°C , experienced a substantial growth in carbonyl content upon further oxidation at 300°C . In contrast, the normalized carbonyl content in ATS resin, preoxidized for 24.5 h at 250°C in air, is reduced from 0.46 to 0.40 (a 13% drop) after 116 h further oxidation at 300°C . The normalized carbonyl content in ATB resin, preoxidized for 178 h at 250°C in air, drops from 1.19 to a value of 0.70 (a much larger 41% drop) after only 46 h at 300°C under nitrogen.

In summary, the long term ageing of ATS and ATB resin is accompanied by the incorporation of oxygen as carbonyls. Oxidation is significantly faster at 300°C than at 250°C , at which the resin is stable to weight loss. The oxygen content in resin aged at 250°C rises monotonically. In contrast, resin aged at 300°C achieves a maximum relative oxygen content after which carbonyl material is removed (presumably) through competitive ablation of the resin. Carbonyls in oxidized ATS appear more thermally stable than carbonyls in oxidized ATB resin. We presume, therefore, that carbonyls from the oxidation of the isopropyls in ATB resin are less thermally stable than carbonyl derivatives of the polyene crosslink, common to both resins.

The residues of thermal degradation of ATS polymers

The residues of thermal degradation at 1020°C of ATS and related polymers were estimated

Table 1. Residues of thermal degradation to 1020°C of resins from ATS fractions and related polymers

Polymer	Residue of cured polymer ^a (wt%)
ATP monomer (for comparison)	60.1
ATS monomer	54.5
ATS-G	53.2
ATS dimer	49.6
Radel (for comparison)	35.2

^a At a heating rate of 5°C/min and with a sample size of 100 mg.

gravimetrically. It can be seen from Table 1 that a very high proportion of ATP monomer bis[4-(3-ethynyl phenoxy) resorcinol] is converted to involatile 'char' on thermolysis. This is not surprising in light of the fact that this material contains a high proportion of polyene crosslinks which (we show here) promote char formation in the closely related ATS polymers. In addition, it does not contain any sulfone groups which have been shown previously to promote (relatively) low temperature bond scissions in AT polymers. Radel, in contrast, contains the same basic polyphenylether sulfone moieties as the ATS resins but does not contain the polyene crosslinks common to all AT polymers.¹ As expected, it is less efficiently converted to char than the ATS resins. As an aside, it should be noted that the yield of noncondensables from Radel is also less than from the ATS resins, presumably because less of the thermoplastic remains in the hot zone at the temperatures at which hetero-atoms are expelled from the growing polyaromatic condensates which constitute the final char.

Resin from monomeric acetylene terminated sulfone, by virtue of its higher initial acetylene concentration, will exhibit a higher concentration of polyenes after polymerization than will resin from ATS dimer. By the same argument it can be shown that resin from ATS-G will exhibit a polyene concentration, after polymerization, intermediate between ATS monomer and dimer. It can be seen from Table 1 that the yields of residual material follow this trend with the highest yield corresponding to the material with the highest polyene concentration. The presence of polyene crosslinks in ATS, would, therefore, appear to constitute a stabilizing, or high char promoting influence on the material. The yields of noncondensable volatile product from ATS polymers follow a similar trend, with the highest

yields from the most heavily crosslinked polymer of the series, in this instance ATS monomer.

Elemental analysis of residues of degradation

The carbon, hydrogen, oxygen and sulfur contents of residues of the partial degradation of resin from ATS-G were examined by elemental analysis, from which element loss curves were constructed for each element as illustrated in Fig. 4. Carbon, as expected, constitutes the bulk of ATS-G. As such, its loss curve more or less parallels that of the corresponding TG weight loss curve for the polymer. Sulfur, which is initially contained in sulfone bridges was shown earlier to be removed from the resin as SO₂ and H₂S, and to promote early weight loss in ATS polymers under isothermal conditions.^{1,2}

The early precipitous loss of sulfur from ATS-G heated under programmed conditions indicates that the sulfone linkage plays a similar role under programmed heating conditions. A change of slope in the sulfur loss curve at approximately 500°C suggests a possible change in its mode of volatilization from the polymer—an observation confirmed later in this report by quantitative gas phase IR spectroscopy. A small amount of sulfur is retained by the residue of degradation to 1020°C presumably within fused ring heterocycles.

The loss of elemental oxygen from ATS-G closely parallels that of sulfur up to about 530°C. In common with sulfur, the oxygen loss profile changes curve shape, but at the higher tempera-

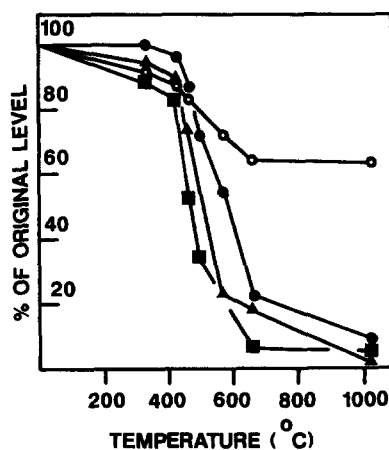


Fig. 4. Element loss curves for residues of ATS-G resin formed during programmed degradation to 1020°C at 5°C/min under vacuum (○, carbon; ●, hydrogen; ▲, oxygen; ■, sulfur; sample sizes: 100 mg; sample surface areas: c. 10 cm²).

ture of 550°C, above which oxygen is removed from the polymer as carbon monoxide and carbon dioxide as was discussed earlier.² The residue of degradation to 1020°C contains a little stable oxygen, presumably within fused ring heterocycles.

Hydrogen is removed from ATS-G in a manner similar to that of oxygen except with a profile which is skewed to higher temperatures. Above 600°C it is removed from the polymer as methane and hydrogen gas.²

In general terms the changes in the slope of the sulfur, oxygen and hydrogen emission curves may be linked to the 'watershed' transition between processes 1 and 2 of degradation and the later processes (Nos 3 and 4).²

IR spectroscopy of residues of degradation

The residues of partial degradation of ATS-G under high vacuum conditions were examined by IR spectroscopy yielding spectra as depicted in Fig. 5. The intractable nature of the cured resin limited its dispersion in the KBr matrix, with the result that spectroscopic analyses could be made only on a qualitative basis. Even so, it was observed from this work that sulfone and phenyl ether linkages are progressively removed from the resin on heating and are completely absent from the residue of programmed degradation to 576°C. Infrared active aromatic material is still detectable in large quantities at 576°C, in small quantities at 661°C, but not at all in the residue of degradation to 1020°C, due to progressive ring

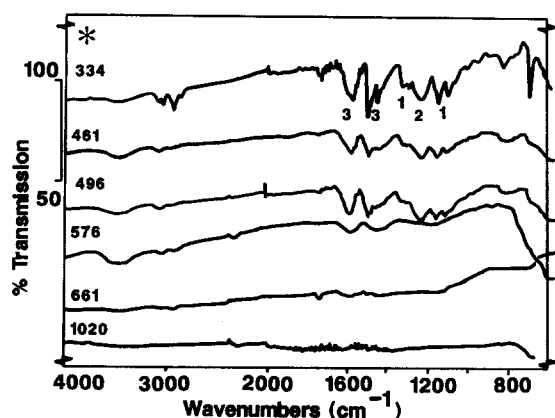


Fig. 5. Infrared spectra of residues of partial degradation of ATS-G resin under high vacuum conditions at a heating rate of 5°C/min to the end temperatures indicated on the figure under the asterisk. Samples were prepared as KBr disks. Annotated absorbances: (1) sulfone linkage; (2) phenylether linkage; (3) aromatic material.

fusions which eventually transform the residue to disordered carbon which is difficult to observe by IR spectroscopy.⁶

The high boiling point product fraction of degradation

Gravimetric analysis

Yields of high boiling point products from cured ATS monomer and dimer and ATS-G are depicted in Table 2(a). In contrast to the residue yields discussed previously, it can be seen that the yields of oligomer are inversely related to the polyene concentration in the polymer, with the highest yield of oligomer from the resin containing the lowest polyene concentration (cured ATS dimer) and the longest polyphenyl ether segments.

IR spectroscopy

(i) *Material produced from room temperature to 1020°C.* The IR spectra of the high boiling point products, evaporated from ATS-G, ATS monomer, ATS dimer and ATS trimer on heating to 1020°C were similar. Absorbances were also similar to those contained within the IR spectrum of the cured resin.⁷ The identification of sulfones and polyphenyl ethers suggests a product mixture similar in overall composition to

Table 2. (a) Gravimetric analysis of high boiling point product fractions of thermal degradation to 1020°C of ATS polymers

Product fraction	Cured resin (wt%)		
	ATS monomer	ATS-G	ATS dimer
The high boiling point product fraction of degradation	4.4	5.4	11.3

(b) Gravimetric analysis of sub-fractions, isolated by preparative TLC from the high boiling point product fraction of thermal degradation to 1020°C of ATS polymers

TLC fraction no.	R_f	Cured resin (wt%)		
		ATS monomer	ATS-G	ATS dimer
1	0.7	1.4	1.6	2.6
2	0.3	0.6	0.7	1.9
3	0.2	1.1	1.6	3.6
4	0.0	1.3	1.5	3.2

the base resin backbone, presumably produced by evaporation of those products of chain scissions falling into the correct molecular weight range to condense above the oven. In addition, the presence of hydroxyls indicates that a proportion of the polyphenylether linkages in the resin succumb to thermal scissions.

Saturated carbons were also observed to be present in this product fraction of the degradation. The relative concentrations of saturated material appear to increase with the polyene concentration in the original polymer. The apparent low concentration of saturated material in the high boiling point product fraction of the degradation of ATP monomer presumably reflects the absence of sulfones in the original resin, which encourage lower temperature chain fragmentations, producing pendant polyphenylethers able to carry off fragments of polyene degradation/rearrangement.

(ii) *Material produced from room temperature to 532°C.* An end or upper temperature of 532°C is intermediate between processes 1 and 2 of the thermal degradation of ATS polymers.² The oligomeric products of the degradation of ATS polymers are produced by these two processes. Thus, it was felt that an examination of the products essentially released by the first, or lower temperature process could prove potentially informative.

The IR spectrum of high boiling point material evolved from ATS monomer on heating to this

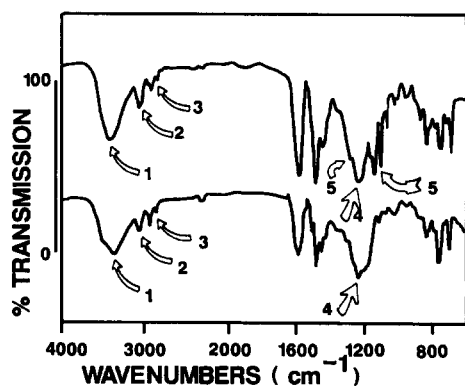


Fig. 6. Infrared spectra of high boiling point product fractions of thermal degradation of pre-cured resin from ATS monomer; top: to an end temperature of 532°C; bottom: oligomers from resin which had been pre-degraded to 532°C then reheated to 1020°C under high vacuum conditions. Samples were prepared as thin films on NaCl disks. (1) Hydroxyl groups; (2) aromatic material; (3) saturated material; (4) phenylether linkages; (5) sulfone linkages.

upper temperature limit is shown in Fig. 6. By comparing it with the IR spectrum of material evolved from the corresponding polymer on heating to 1020°C, it can be seen to possess most or all of the structures contained in the latter.

(iii) *Material produced from 532°C to 1020°C.* Having established the major structures contained in the oligomeric products of the first process of degradation, the study was completed by an examination of those products associated with the second process of degradation. Samples of ATS monomer and dimer were pre-heated to 532°C. The degradation tube was cooled to room temperature under vacuum. The oligomers produced in process 1 of the degradation were then removed from the cold finger above the oven. The sample was then re-heated to 1020°C. Preliminary experiments had indicated that processes 3 and 4 of the degradation of this class of material do not produce oligomeric products. Those collected could therefore be identified unambiguously with the second process of degradation.

The IR spectra of the high boiling point products of the thermal degradation of ATS monomer and dimer in the temperature interval 532–1020°C were similar in appearance. The IR spectrum of material evolved from cured ATS monomer is shown in Fig. 6. The major features of this spectrum are similar to those produced by the oligomeric product fraction of degradation to 1020°C of resin from ATS monomer (and other ATS polymers), except for the absence of absorbance bands associated with sulfones in the product fraction.

(iv) *Summary.* Infrared spectra of the high boiling point product fractions of the degradation of ATS polymers are similar to those of the polymers from which they were evolved. This indicates that the former are produced predominantly by bond scissions rather than by functional group rearrangements. The pronounced concentrations of hydroxylic end groups in these oligomer fractions indicate that a proportion of these bond scissions involve the polyphenylether linkage.

Oligomers produced above 532°C do not contain sulfone linkages. This was expected in view of the fact that 532°C is close to temperatures which correspond to the end of process 1 of the degradation of ATS polymers—a

process which has been shown by elemental analysis to quantitatively remove sulfur from the polymer in the form of sulfur dioxide.

Thin layer chromatography (TLC) of material evolved from ATS and related polymers

We discussed earlier the use of TLC to identify the four eluent fractions which together comprise the oligomeric product fraction of the degradation of ATS polymers. Having established its utility, we endeavored to use the technique to establish the presence or absence of these eluent bands in the oligomeric product fractions of the degradation of ATS and structurally related polymers collected between well defined temperature intervals. The results of a number of simple spot tests on these product fractions and on some reference compounds are related in Table 3.

In qualitative terms, the high boiling point product fractions of degradation to 1020°C of all ATS polymers contained the same eluent bands. This implies, of course, that similar pathways of degradation are operative in all these polymers. The high boiling product fraction of degradation from Radel™ thermoplastic also contained similar structural types, reinforcing our belief that the bulk of this product fraction originates in the backbone of the ATS resin which is structurally similar to the thermoplastic Radel™ polymer. Material which separates to a retention index of 0.3 has been shown to contain one sulfone group per residue. As expected, therefore, the high boiling point product fraction evolved from ATP monomer did not express this fraction.

The high boiling point product fractions evolved from precured ATS monomer and ATS dimer in the temperature intervals RT–532°C and 532–1020°C were also examined by TLC in an attempt to clarify further the high boiling point products of processes 1 and 2 of the degradation (of ATS polymers). Qualitatively, TLC indicated that processes 1 and 2 produced similar high boiling point products by, presumably, bond scissions within the polyphenylether backbone of the resin. As expected (in view of the IR measurements discussed earlier), the product distribution from the earlier process contained sulfones, unlike the products from the second process which were sulfone free. The element loss curves of Fig. 4 indicate that ATS polymers retain some elemental sulfur at 532°C. Its absence, in the form of sulfones, is strong circumstantial evidence for the transformation of sulfone to another structural type such as sulfoxide or sulfide, as will be discussed in Part 3 of this report.

We next set out to measure by gravimetry the yields of each individual fraction as isolated by preparative TLC from the original product mixture, using procedures outlined in Part 1 of this series. Our results, expressed as a percentage of the initial sample weight, may be examined in Table 2(b).

As expected, in view of the results summarized in Table 2(a), the relative yield of each sub-fraction increased from ATS monomer through ATS-G to ATS dimer. Concentrating on products from the ATS monomer and ATS dimer we can see that sub-fractions 3 and 4 are present

Table 3. Thin layer chromatography of the oligomeric product fractions of the thermal degradation of ATS and related polymers

Polymer	Temperature interval (°C)	Sub.F ⁿ .1 ^a R _f = 0.7	Sub.F ⁿ .2 ^b R _f = 0.3	Sub.F ⁿ .3 ^c R _f = 0.2	Sub.F ⁿ .4 ^d R _f = 0
ATS-G	RT–1020°C	P	P	P	P
ATS monomer	RT–1020°C	P	P	P	P
ATS dimer	RT–1020°C	P	P	P	P
ATS trimer	RT–1020°C	P	P	P	P
Radel	RT–1020°C	P	P	P	P
ATP monomer	RT–1020°C	P	A	P	P
ATS monomer	RT–532°C	P	P	P	P
ATS dimer	RT–532°C	P	P	P	P
ATS monomer	532–1020°C	P	A	P	P
ATS dimer	532–1020°C	P	A	P	P

Sample reference compounds: R_f = 0.7^a, diphenyl, phenylether; R_f = 0.3^b, ATS monomer fraction; R_f = 0.2^c, ATS dimer fraction, phenol, *p*-phenoxy phenol, *m,m*-phenoxy phenol; R_f = 0^d, resorcinol, catechol, hydroquinone.

P, sub-fraction is present; A, sub-fraction is absent.

in higher proportions in the product fraction from the latter. These sub-fractions, on average, contain higher molecular weight material than the other two, and so become relatively more prominent in the product fraction from the resin possessing the higher Mc (or lower crosslink density).

Composition of sub-fractions isolated by preparative thin layer chromatography

Having estimated the gravimetric yields of sub-fractions isolated by preparative TLC, we next performed a structural analysis to ascertain the most probable composition of each sub-fraction using IR spectroscopy, NMR spectroscopy, and CIMS in tandem. To avoid repetition, we detail our investigation of one eluent band (sub-fraction 1, $R_f = 0.7$) and summarize the results of our other experiments.

TLC eluent fraction ($R_f = 0.7$)

(i) *IR spectroscopy of the first eluent band (F1).* The IR spectra of high boiling products of the degradation of ATS monomer, ATS-G, and ATS dimer show those fractions to be similar in composition. The IR spectrum of products from cured ATS-G is shown in Fig. 7. All product fractions contained aromatic residues,

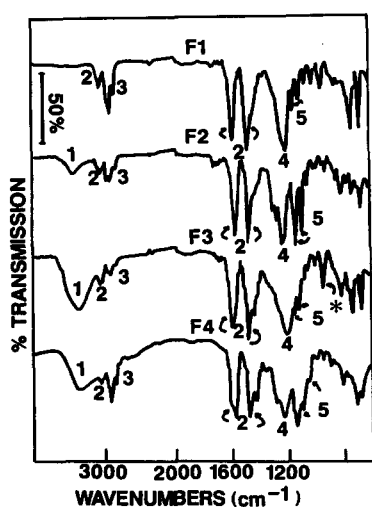


Fig. 7. Infrared spectra of fractions 1-4 (F1, ..., F4) isolated by preparative TLC from the oligomeric product fraction of thermal degradation to 1020°C of resin from ATS-G. Samples were prepared as thin films on NaCl disks. (1) Hydroxyl groups; (2) aromatic material; (3) saturated material; (4) phenylether linkages; (5) sulfone linkages. The absorbance denoted by the asterisk in the spectrum of F3 may be produced by a sulfoxide group.

phenylether linkages, and some saturated material. As expected, in view of previous discussions, the proportion of saturated material in these product fractions was shown to increase with the polyene concentration in the resin from which it was volatilized (conc. in ATS monomer > conc. in ATS-G > conc. in ATS dimer) with the presumption that it originated within the polyene moiety or its thermal derivative.

(ii) *NMR spectroscopy of the first eluent band (F1).* The technique of proton NMR spectroscopy shows that product fractions from cured ATS monomer, dimer, and ATS-G are similar in composition. The NMR spectrum of material from cured ATS-G is shown in Fig. 8. The bulk of the saturated functionality was clearly shown to be methyl groups by virtue of the sharp singlet observed in all three spectra. By comparing the relative proportions of protonated aromatics to aliphatics we again show that the concentration of saturated material increases with the crosslink density in the initial polymer. The aromatic signals produced by the eluent sub-fraction from ATS monomer are rather featureless. On the other hand, some sharp signals characteristic of *m*-polyphenylethers are observable in the NMR

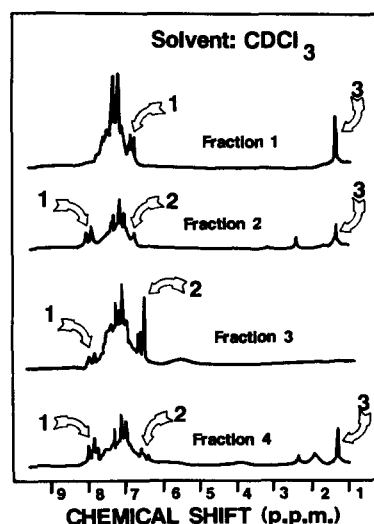


Fig. 8. Proton NMR spectra, in CDCl_3 with TMS as a marker, of fractions 1-4 (F1, ..., F4) isolated by preparative TLC from the oligomeric product fraction of thermal degradation to 1020°C of resin from ATS-G. F1: signals designated as No. 1 below 7 ppm are produced by polyphenylethers; F2, F3 and F4: signals designated as No. 1 around 8 ppm are due to aromatic protons adjacent to a sulfone group; F2, F3 and F4: signals designated as No. 2 below 7 ppm are produced by polyphenylethers. Signals designated as No. 3 around 1.3 ppm in the spectra of F1, F2, and F4 are produced by saturated material.

spectra of fractions from ATS-G and ATS dimer. Their concentration in the appropriate sub-fraction increases from that produced by ATS-G to that produced by ATS dimer, presumably reflecting the longer polyphenylether segments initially present in the latter polymer.

(iii) *CIMS of the first eluent band (F1)*. Chemical ionization mass spectra of material which originated in ATS monomer, ATS-G and ATS dimer were obtained by procedures outlined in the Experimental section of this report. The parent ion masses so obtained by this method are listed in Table 4.

(iv) *Structural assignments*. Information contained in the IR and NMR spectra was combined with results from TLC and CIMS to propose structures for the components of sub-fraction 1. These most probable structures are depicted in Table 5. Our structural assignments are consistent with an eluent fraction made up of polyphenyl ethers with some biphenyl content, and partially end capped with a methyl group.

TLC eluent fraction 2 ($R_f = 0.3$)

The proton NMR spectra of the second eluent fraction as isolated from degrading ATS monomer, ATS-G and ATS dimer are similar. We therefore reproduce, in Fig. 8, the NMR spectrum of material from ATS-G only. The corresponding IR spectra of products from the three polymers were also similar. Thus only one is reproduced in Fig. 7.

Both the IR and NMR spectra indicate that the material in this sub-fraction contains sulfone linkages in a polyphenylether backbone. The broadening of the aromatic resonances towards 8 ppm in the NMR spectra suggest (albeit tentatively) that some diphenyl type linkages are

Table 4. Parent ion masses by CIMS of sub-fraction 1, isolated by preparative TLC from the high boiling point product fraction of degradation to 1020°C of ATS polymers

ATS monomer	Parent ions (a.m.u.) from:	
	ATS-G	ATS dimer
184		
246	246	246
		260
262	262	262
338		338
352		352

Table 5. Structural assignments for the components of sub-fraction 1 as isolated by preparative TLC from oligomeric product fractions of degradation of ATS polymers

ATS monomer	Products from: ATS-G	ATS dimer
$\Phi \circ \Phi \text{CH}_3$ $\Phi \Phi \circ \Phi$	$\Phi \Phi \circ \Phi$	$\Phi \Phi \circ \Phi$ $\Phi \Phi \circ \Phi \text{CH}_3$
$\Phi \circ \Phi \circ \Phi$ $\Phi \Phi \circ \Phi \circ \Phi$ $\Phi \circ \Phi \Phi \circ \Phi$ $\Phi \circ \Phi \Phi \circ \Phi \text{CH}_3$	$\Phi \circ \Phi \circ \Phi$	$\Phi \circ \Phi \circ \Phi$ $\Phi \Phi \circ \Phi \circ \Phi$ $\Phi \circ \Phi \Phi \circ \Phi$ $\Phi \circ \Phi \Phi \circ \Phi \text{CH}_3$

Φ , phenyl group; $\Phi \circ \Phi$, phenyl ether group; $\Phi \Phi$, biphenyl group; CH_3 , methyl group.

present in the material from all three polymers. The second sub-fraction from ATS monomer contained practically no saturated material and the corresponding sub-fraction from ATS dimer contained only a little saturated material in quantities too small for accurate analysis. On the other hand, the corresponding sub-fraction from ATS-G was shown to contain a complex mixture of saturates, presumably from some of its anomalous constituents such as F4, etc.⁷ A low concentration of hydroxylic material was detected by IR spectroscopy but not by NMR spectroscopy, presumably because of the greater sensitivity of the former towards this functionality.

Chemical ionization mass spectra of the second eluent fraction as isolated from the products of degradation from cured ATS monomer, ATS-G and ATS dimer were next obtained as outlined in the previous section. Based on a synthesis of these three techniques, the structures collected in Table 6 were identified. Note the inclusion of bridging sulfones, the (quantitative) absence of

Table 6. Structural assignments for the components of sub-fraction 2 as isolated by preparative TLC from oligomeric product fractions of degradation of ATS polymers

ATS monomer	Products from: ATS-G	ATS dimer
$\Phi \circ \Phi \circ \text{H}^a$ $\Phi \circ \Phi \Phi \circ \text{H}^a$ $\Phi \circ \Phi \text{SO}_2 \Phi$	$\Phi \circ \Phi \circ \text{H}^a$ $\Phi \circ \Phi \Phi \circ \text{H}^a$ $\Phi \circ \Phi \text{SO}_2 \Phi$	$\Phi \circ \Phi \circ \text{H}^a$ $\Phi \circ \Phi \Phi \circ \text{H}^a$ $\Phi \circ \Phi \text{SO}_2 \Phi$ $\Phi \circ \Phi \circ \Phi \Phi \circ \text{H}$ $\Phi \circ \Phi \text{SO}_2 \Phi \circ \Phi$ $\Phi \circ \Phi \text{SO}_2 \Phi \circ \Phi \text{CH}_3$

^a Designates a minor component.

Φ , phenyl group; $\Phi \circ \Phi$, phenyl ether group; $\Phi \Phi$, biphenyl group; $-\text{SO}_2-$, sulfone unit; $-\text{OH}$, hydroxyl functionality; CH_3 , methyl group.

hydroxyl ends, and the incorporation of some biphenyl groupings into the product distribution.

TLC eluent fraction 3 ($R_f = 0.2$)

By a joint examination of the IR and NMR spectra of material released from cured ATS resin (Figs 6 and 8 respectively) it can be seen to contain some diphenyl linkages (broadening of the NMR spectra toward 8 ppm), massive amounts of hydroxylic material (at 3400 cm^{-1} in the IR spectrum), probably as a result of polyphenyl ether scissions in the polymer; and small quantities of sulfone, most probably as a result of incomplete separation of this fraction from sub-fraction 2. (Indeed, an incomplete separation of this type would also explain the presence of hydroxyls in eluent fraction 2.)

Eluent fractions from ATS monomer, dimer and ATS-G were shown to also contain polyphenylethers as revealed by the NMR signal pattern below 6.5 ppm, in quantities which increased from ATS monomer (barely detectable) through ATS-G to ATS dimer. This trend is probably a simple reflection of the relative average resin backbone lengths in the three polymers. Parent ion masses were obtained by CIMS and the information synthesized to identify the products listed in Table 7. Identified fragments contained phenyl ethers, biphenyl groupings, and were monohydroxylated.

TLC eluent fraction 4 ($R_f = 0$)

The IR and proton NMR spectra of material from ATS monomer, ATS-G and ATS dimer were similar in appearance. The IR and NMR spectra of material from ATS-G are shown in Figs 7 and 8 respectively. An examination of these spectra indicated the presence of sulfone linkages in some quantity, a relatively large

Table 7. Structural assignments for the components of sub-fraction 3 as isolated by preparative TLC from oligomeric product fractions of degradation of ATS polymers

ATS monomer	Resin from: ATS-G	ATS dimer
$\Phi\Phi\cdot\text{H}$	$\Phi\Phi\cdot\text{H}$	$\Phi\Phi\cdot\text{H}$
$\Phi\cdot\Phi\Phi\cdot\text{H}$	$\Phi\cdot\Phi\cdot\text{H}$	$\Phi\cdot\Phi\cdot\text{H}$
		$\Phi\cdot\Phi\text{SO}_2\Phi^a$
		$\Phi\cdot\Phi\text{SO}_2\Phi\cdot\Phi^a$
		$\text{H}\cdot\Phi\Phi\cdot\Phi\cdot\text{H}^a$

^a Designates a minor component.

Φ , phenyl group; $\Phi\cdot\Phi$, phenyl ether group; $\Phi\Phi$, biphenyl group; $-\text{SO}_2-$, sulfone unit; $-\text{OH}$, hydroxyl functionality.

hydroxyl and polyphenyl ether content, some saturated material, and some biphenyls. The large amount of resorcinol in the product fraction from cured ATS-G is not reflected in the composition of the products from the other (purer) resins from ATS monomer and dimer. Most probably, resorcinol (a raw material for resin synthesis)³ was trapped in ATS-G on vitrification of the resin and was simply released upon decomposition of the resin network. Parent ion masses were obtained by CIMS and the information was synthesized to identify the compounds listed in Table 8. Sulfones, phenyl ethers and biphenyls are all represented in these products which may be classified as containing a sulfone plus a hydroxyl, two hydroxyls (a diol), or as a diol containing a sulfone bridge.

Assignment of high boiling products to either process 1 or 2 of degradation

We end this discussion by assigning high boiling products to either of processes 1 or 2 of the degradation, as defined in Part 1 of this series. It must be restated that these products (Tables 9 and 10) must be considered only as representative of the entire high boiling point product distribution of the degradation.

We know that the removal of sulfur dioxide from ATS resin is the definitive marker of process 1 of the degradation. We also know that the sulfone linkage is completely removed from the residues of the degradation to higher temperatures. We therefore consider sulfone containing oligomers unequivocally as products of process 1 of the degradation. The biphenyl linkage is formed through radical recombination

Table 8. Structural assignments for the components of sub-fraction 4 as isolated by preparative TLC from oligomeric product fractions of degradation of ATS polymers

ATS monomer	Resin from: ATS-G	ATS dimer
$\text{H}\cdot\Phi\Phi\cdot\text{H}$	$\text{H}\cdot\Phi\cdot\text{H}$	
$\text{H}\cdot\Phi\text{SO}_2\Phi\cdot\text{H}$	$\text{H}\cdot\Phi\Phi\cdot\text{H}$	$\text{H}\cdot\Phi\Phi\cdot\text{H}$
$\text{H}\cdot\Phi\Phi\cdot\Phi^a$		
	$\text{H}\cdot\Phi\Phi\cdot\Phi\cdot\text{H}$	
$\Phi\cdot\Phi\text{SO}_2\Phi\cdot\text{H}$	$\Phi\cdot\Phi\text{SO}_2\Phi\cdot\text{H}$	$\text{H}\cdot\Phi\Phi\cdot\Phi\cdot\text{H}$
	$\Phi\cdot\Phi\cdot\Phi\text{SO}_2\Phi\cdot\text{H}$	$\Phi\cdot\Phi\text{SO}_2\Phi\cdot\text{H}$
	H	$\Phi\cdot\Phi\cdot\Phi\text{SO}_2\Phi\cdot\text{H}$
		$\text{H}\cdot\Phi\Phi\cdot\Phi\cdot\Phi\text{SO}_2\Phi\cdot\text{H}$

^a Designates a minor component.

Φ , phenyl group; $\Phi\cdot\Phi$, phenyl ether group; $\Phi\Phi$, biphenyl group; $-\text{SO}_2-$, sulfone unit; $-\text{OH}$, hydroxyl functionality.

Table 9. Some high boiling point products of process 1 of degradation of ATS polymers

ATS monomer	Resin from: ATS-G	ATS dimer
$\Phi \circ \Phi \text{SO}_2 \Phi$	$\Phi \circ \Phi \text{SO}_2 \Phi$	$\Phi \circ \Phi \text{SO}_2 \Phi$
$\Phi \circ \Phi \text{SO}_2 \Phi \circ \Phi$		
$\Phi \circ \Phi \text{SO}_2 \Phi \circ \Phi \text{CH}_3$		$\Phi \circ \Phi \text{SO}_2 \Phi \circ \Phi \text{CH}_3$
$\text{H} \circ \Phi \text{SO}_2 \Phi \circ \text{H}$	$\Phi \circ \Phi \text{SO}_2 \Phi \circ \text{H}$	$\Phi \circ \Phi \text{SO}_2 \Phi \circ \text{H}$
$\Phi \circ \Phi \text{SO}_2 \Phi \circ \text{H}$	$\Phi \circ \Phi \circ \Phi \text{SO}_2 \Phi \circ \text{H}$	$\Phi \circ \Phi \circ \Phi \text{SO}_2 \Phi \circ \text{H}$
		$\text{H} \circ \Phi \Phi \circ \Phi \circ \Phi \text{SO}_2 \Phi \circ \text{H}$

Φ , phenyl group; $\Phi \circ \Phi$, phenyl ether group; $\Phi \Phi$, biphenyl group; $-\text{SO}_2-$, sulfone unit; $-\text{H}$, hydroxyl functionality; CH_3 , methyl group.

Table 10. Some high boiling point products of process 2 of degradation of ATS polymers

ATS monomer	Resin from: ATS-G	ATS dimer
$\Phi \circ \Phi \text{CH}_3$		$\Phi \Phi \circ \Phi$
$\Phi \Phi \circ \Phi$	$\Phi \Phi \circ \Phi$	$\Phi \circ \Phi \circ \Phi$
$\Phi \circ \Phi \circ \Phi^a$	$\Phi \circ \Phi \circ \Phi$	$\Phi \circ \Phi \Phi \circ \Phi$
$\Phi \circ \Phi \Phi \circ \Phi$		$\Phi \Phi \circ \Phi \circ \Phi$
$\Phi \Phi \circ \Phi \circ \Phi$		$\Phi \Phi \circ \Phi \text{CH}_3$
$\Phi \circ \Phi \Phi \circ \Phi \text{CH}_3$		$\Phi \circ \Phi \Phi \circ \Phi \text{CH}_3$
$\Phi \Phi \circ \text{H}$	$\Phi \Phi \circ \text{H}$	$\Phi \Phi \circ \text{H}$
$\Phi \circ \Phi \circ \text{H}^a$	$\Phi \circ \Phi \circ \text{H}$	$\Phi \circ \Phi \circ \text{H}$
$\Phi \circ \Phi \Phi \circ \text{H}$	$\Phi \circ \Phi \Phi \circ \text{H}$	$\Phi \circ \Phi \Phi \circ \text{H}$
		$\Phi \circ \Phi \Phi \circ \Phi \circ \text{H}$
		$\Phi \circ \Phi \circ \Phi \circ \text{H}^a$
$\text{H} \circ \Phi \Phi \circ \text{H}$	$\text{H} \circ \Phi \Phi \circ \text{H}$	$\text{H} \circ \Phi \Phi \circ \text{H}$
$\text{H} \circ \Phi \Phi \circ \Phi \circ \text{H}^a$	$\text{H} \circ \Phi \Phi \circ \Phi \circ \text{H}$	$\text{H} \circ \Phi \Phi \circ \Phi \circ \text{H}$

^a Designates a minor component.

Φ , phenyl group; $\Phi \circ \Phi$, phenyl ether group; $\Phi \Phi$, biphenyl group; $\circ \text{H}$, hydroxyl functionality; CH_3 , methyl group.

after expulsion of SO_2 . Products which contain the biphenyl linkage are, therefore, assigned to process 2 of the degradation. That a product containing both a sulfone and a biphenyl was detected (Table 9, line 7) is proof that the two processes overlap at a heating ramp of $5^\circ\text{C}/\text{min}$. Sulfone free phenyl ethers have been assigned (with somewhat less certainty) to the second, less directed process of degradation. Fragments, end capped with methyls, are produced through the decomposition of the polyene crosslink (or its thermal derivative). The distribution of methyl ends throughout the entire spectrum of products

is proof that the polyenes break down (or rearrange) over a wide temperature interval.

CONCLUSIONS

We have determined that AT resins are oxidatively stable in comparison with epoxy resins containing similar structural features. We have also determined that oxidation proceeds through the formation of thermally stable carbonyl containing intermediates which are ablated through further oxidations or thermal decomposition.

We have also characterized the microstructural changes which accompany the carbonization of ATS resin and have identified a large number of high boiling point products of the thermal degradation which were assigned to either of the first two processes of thermal degradation of the ATS resin system.

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