Characterization of Acetylene Terminated Sulfone (ATS) Resin. II. Thermal Analysis of the Resin

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SYNOPSIS

The kinetics and thermodynamics of the cure and post-cure reactions of an acetylene terminated sulfone (ATS) resin mixture and pure fractions from that mixture were studied using differential scanning calorimetry. Thermal stabilities were measured by programmed thermogravimetry under helium, and oxidative stabilities using isothermal thermogravimetry in air. Microstructural changes accompanying the cure reaction were identified using infrared spectroscopy. Early products of thermal degradation were trapped for identification and quantitative analysis using the technique of sub-ambient thermal volatilization analysis. We found that glass transition temperatures increase with crosslink density in the resin, that oxygen is able to copolymerize or couple with the polyenes to produce peroxides or hydroperoxides (respectively) which subsequently decompose to form terminal alcohols on the polyene, that weight loss in air at 600°F is an oxidative process that is insensitive to resin crosslink density, and that sulfone functionality constitutes the thermal weak link in the ATS resin system.

INTRODUCTION

In recent years interest and investment in carbon-based composite materials has outstripped all unbiased projections made in the last decade. Mainly, this has been a marketing phenomenon in which new niches for the product have been identified and successfully filled by a tailoring of existing systems or by the development of a new material. One such "niche," is the use of composite materials in extreme environments, namely under large static or fluctuating stresses at either very high or very low temperatures. In such situations, the venerable (but still only partially understood) epoxy resin-based composites are often found wanting, being unable to meet specifications for strength, stiffness, or durability.

In recent years, much attention has focused on the development of alternative high-performance resin systems. The acetylene terminated or "AT" concept, vigorously promoted by some at the Air Force, offers a viable alternative to the polyimides and other high-performance systems which cure via condensation processes, through a resin cure-based on a thermal (catalyst free) polymerization of terminal acetylene functionality attached to a stiff, thermally stable resin backbone. This process has been directly shown to proceed through a free radical intermediate, and to involve the formation of an oligomeric polyene whose reactivity decreases with length, presumably due to a progressive delocalization of the propagating free radical.[1] An addition reaction of this type does not produce volatiles, so void formation in the product is not a problem. The reaction can proceed in the absence of added catalyst which often contributes to long-term instability in the cured resin and increases batch to batch variations in formulations with that resin.

The chemical characterization of an acetylene terminated sulfone (ATS) resin (more properly, bis[4-(3-ethynyl phenoxy)phenyl]sulfone), prepared for the Air Force in pilot plant quantity by Gulf Chemicals Inc.[2] and designated ATS-G, was

the subject of an earlier communication.[3] In essence, we sought, through a careful analysis of the uncured material, some new insight into the process of resin synthesis, and, in addition, to lay the groundwork for detailed studies into the behavior of the resin in the relatively low-temperature region of cure and post-cure (reported here), and into the rates and mechanisms of higher temperature processes of degradation (to be reported).

To give this current discussion meaning, we must, at this point, review some background material from a previous paper in this series.[3] ATS resin, as synthesized by the Gulf Chemical "route",[2] was prepared by reacting the condensation product of sulfonyl diphenol and m-dibromobenzene with 2-methyl-3-butyn-2-ol in the presence of a palladium catalyst. The "acetone adduct" so formed was then hydrolysed to the corresponding terminal acetylene. Depending on the ratio of sulfonyl diphenol to m-dibromobenzene used in the first reaction, the ATS monomer will be contaminated by "dimer" and "trimer" fractions in proportions dictated by the feedstock composition, in much the same manner as the diglycidyl ether of bisphenol A is usually synthesized with some dimer and trimer. The ATS-G mixture was found to contain about 68 wt % monomer, 15 wt % dimer, and 4 wt % trimer. In addition, four anomalous fractions were recovered by column chromatography. "Fraction 4" (2 wt %) was shown to consist of uncharacterized, abnormally end capped monomer, "Fraction 5" (0.6 wt %) to consist of the partially hydrolysed acetone adduct intermediate. "Fractions 6 and 7" (0.4 wt % and 5 wt %, respectively) appeared to be dimeric and trimeric *coupling products* of two and three ATS species respectively, at the palladium catalyst. Both materials were shown to be chelators of palladium by virtue of internal diol functionality introduced during the coupling reaction, and to be the major palladium "carriers" in the resin.[3]

Small amounts of resorcinol (3 wt %) were also detected in the resin. This material, (a feedstock impurity?), probably contributed to the extra "anomalous" phenoxy content detected in the pure ATS fractions by nuclear magnetic resonance (NMR) spectroscopy, through incorporation into the ATS backbone in much the same manner as sulfonyl diphenol. In addition to toluene solvent (1.2 wt %), small amounts of diethynyl benzene ± (0.3 wt %)—formed by the acetylation of uncondensed m-dibromobenzene, and of diethynyl diphenylether DEDPE (0.1 wt %)—probably formed by acetylation of the condensation product of resorcinol and

m-dibromobenzene, were also detected. It must be noted that this compositional breakdown is not normalized to 100 wt % material due to cumulative errors in the analysis.

MATERIALS AND METHODS

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) of the ATS-G mixture and components of that mixture was performed using either a DuPont 990 DSC or a Perkin-Elmer DSC-2 coupled to a Bascom Turner data acquisition system. The former was used for qualitative measurements, and the latter for the more quantitative measurements used for the determination of cure kinetics and apparent activation energies, and for the construction of the isothermal "reaction window" plots discussed in the text.

Infrared Spectroscopy

Infrared spectra of fully and partially cured resin were obtained as follows: A thin film of the resin was deposited onto a freshly polished salt plate, then heated at a rate of 5°C/min under high vacuum conditions in the TVA oven assembly (described later in this text) to an appropriate end temperature of 300°C or less. The salt plate with its resin coating was cooled to room temperature under high vacuum conditions and its infrared (IR) spectrum recorded using a Beckman IR-33 grating spectrophotometer. (It must be noted that the thermal lag across each salt plate is unique with the result that end or upper temperature limits of the warm up cycle could be estimated, at best, with an accuracy of ± 10°C.)

Quantitative IR spectra of condensable volatile products of the early stages of the thermal degradation of ATS resins were obtained by first condensing such products in a trap in the TVA vacuum fractionating manifold, then transferring them quantitatively to the cold finger of an IR gas cell, previously calibrated with pure aliquots of the gas in question. The IR spectrum of the gas was then recorded for comparison with the calibration curve previously constructed for that gas. Using sulfur dioxide as an example, quantitative measurements were performed at 2490 cm^{-1}.

Thermogravimetric Analysis

The weight loss profile of ATS resin heated at a rate of 5°C/min to 1000°C under helium was recorded

using the TGA module of the DuPont 990 thermal analyzer. Briefly, uncured resin was loaded into the TGA pan and cured and degraded in the same experiment. Isothermal weight loss profiles in air were recorded using an apparatus especially constructed for that purpose.[4] In this experiment 10 samples of resin (cured or uncured) are loaded onto a microprocessor-controlled carousel and placed in a stable air oven. At times predetermined by the operator, the samples are automatically lifted from the heat sink block, individually weighed, and returned to the block to continue the experiment. In both these experiments the weight loss was indicated by plotting the residue as a percentage of the initial sample weight. In the programmed experiments this was plotted as a function of temperature, and in the isothermal experiments, as a function of time.

Thermal Volatilization Analysis (TVA) and Sub-Ambient Thermal Volatilization Analysis (SATVA)

The thermal volatilization analysis (TVA) experiment developed by I. C. McNeill at the University of Glasgow[5] consists of an oven assembly in which material (usually polymer) is degraded under high vacuum conditions, and a vacuum fractionating manifold is utilized for the entrapment for subsequent analysis of the condensable and noncondensable product fractions of thermal degradation of that material. The rates of volatile production are recorded by electronic (Pirani) pressure gauges during the course of the experiment. A plot of dynamic system pressure versus oven temperature is then used to construct the TVA curve for the material.

The residue of degradation is recovered from the furnace at the end of the experiment and the oligomeric products from an internal cold finger onto which they condense during the course of the degradation experiment. Condensable volatile products of degradation are condensed into a trap in the vacuum line surrounded by frozen wax and held at $-196°C$. On removal of the cooling media the trap slowly warms to room temperature and both the trap temperature and the pressure in the vacuum line are recorded as material evolves into the vacuum manifold according to volatility, in what has come to be known as the sub-ambient thermal volatilization (SATVA) experiment. In this work condensable volatiles from the resin were condensed into, and evolved from, the SATVA trap to a second trap, and hence to the calibrated gas phase infrared cell for quantitative analysis.

DISCUSSION

Differential Scanning Calorimetry

The DSC technique was used to study the kinetics (rates) and thermodynamics (heats of reaction and apparent activation energies) of the acetylene-based cure reactions of ATS-G and its component fractions.

When used qualitatively, a carefully weighed portion of resin was sealed into a DSC pan and ramped from sub-ambient temperatures to some predetermined upper temperature at a rate of $10°C/min$. We were interested in transitions of the uncured resin at or around room temperature which could be associated with resin processability, and in the rate profile of the polymerization exotherm. The glass transition temperature of the fully cured resin was then measured by rescanning the sample at the same heating rate. In some instances the effects of exposure to elevated temperatures on the resin T_g was measured by multiple scans of the sample in the DSC apparatus to some predetermined upper temperature, yielding results presented later in this paper.

Glass transition temperatures of the cured and uncured material were interpreted as onset temperatures of baseline changes as recorded in the DSC trace, the latter often being accompanied by a broad hysteresis endotherm. Melting points of the uncured resin (where applicable) were identified as sharp low-temperature endotherms which did not change the baseline of the scan.

The ATS monomer fraction was recovered as a tacky, viscous liquid after isolation by column chromatography, from which solvent could not be efficiently removed by pumping under vacuum. The material was, therefore, freeze-dried and recovered as a fine powder. On storage at room temperature over a period of months, however, the material coalesced to a tacky mass. All other fractions were recovered as fine powders which did not flow on storage. ATS monomer is, therefore, the only homologue of the series with room temperature "tack and drape" as required for prepregging applications. This behavior is reflected in low-temperature DSC scans of the monomer fraction depicted in Figure 1. When first heated from $-40°C$ to above ambient temperature, the material exhibits a glass transition at about 17°C, and what appears to be a melting transition achieving a rate maximum at about 57°C. On subsequent rescans the "melting transition" vanishes and the glass transition becomes lowered
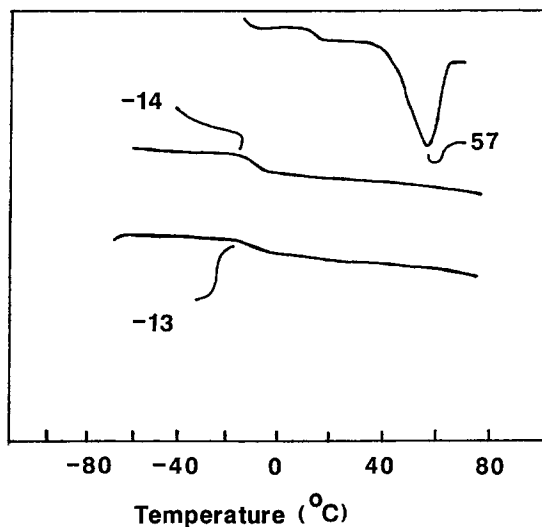
Figure 1 Low temperature differential scanning calorimetry of ATS monomer: Upper trace—first scan, middle trace—second scan, bottom trace—third scan.

to a reproducible $-(13$ to $14)\,°C$. This behavior is reminiscent of some epoxy resins which develop a pseudo "crystallinity" on standing at low temperatures for several months but which will not rapidly (e.g., in a few days) recrystallize after heating. Important features of these low temperature DSC scans, as summarized in Table I, agree with our assertion that monomer is the only fraction capable of viscous flow at room temperature. For example, ATS dimer possesses a T_g sufficiently above room temperature $(53°C)$ to make gravity-induced flow unlikely. Perhaps fortuitously, the ATS-G resin mixture also possesses room temperature "tack and drape," presumably as a result of its high-monomer content and the destructuring effect of added impurities.

A cure exotherm produced by a sample of ATS dimer is reproduced in Figure 2. On the chart we show such important features as the temperatures corresponding to the onset and the rate maximum of polymerization, the latter being a better defined and less subjective measurement than the former. Also shown is the small post-polymerization exotherm which was observed in scans involving all well-defined ATS fractions and of the ATS-G mixture itself. In the same trace we show also the corresponding re-scan for the measurement of fully cured resin T_g. Such information as it relates to the ATS-G mixture and its constituents is summarized in Tables II and III.

Concentrating on the ATS monomer, dimer, and trimer fractions, we can see that temperatures corresponding to the onset of polymerization are in-

versely proportional to the "size" of the polymerizing species. This effect is also observed in the ATS-G mixture which begins to polymerize at a temperature about 40°C lower than the pure monomer. The temperatures corresponding to the rate maxima of polymerization appear less sensitive to resin structure and vary a maximum of 10°C between fractions. Impurity fractions 4, 5, and 7, all begin to polymerize at low temperatures, but achieve rate maxima at temperatures close to the normal ATS fractions. With the exception of fraction 5, all others underwent an observable post-cure process between 300°C and 400°C. That experienced by fraction 4 is complicated by a low-temperature weight loss process which superimposes an endotherm in this temperature region, with the result that two exotherms appear to be produced. The endotherm observed in the corresponding DSC curve for fraction 7 has a similar explanation. Both ATS trimer and fraction 4 produce a similar low-temperature shoulder on the major cure exotherm. We, therefore, contend, that the abnormal reactivity of the ATS trimer fraction is a result of its contamination by a residual amount of fraction 4, from which it was separated by column chromatography.

If we turn to the measurements of glass transition temperature, we find that the T_g of cured resin from the monomer is higher than that from the dimer, which in turn is higher than that from the trimer fraction. Glass transition temperatures in ATS resins are, therefore, strongly dependent on crosslink density. Values for the ATS-G resin mixture could not be measured by DSC, as is often the case for very heavily crosslinked systems. The T_g of fully cured ATS-G has been extrapolated to be about 371°C by manipulation of data from torsion impregnated cloth analysis (TICA) experiments on partially cured resin.[6,7] In reality, we must assume that at least a proportion of the abnormal fractions

Table I Low Temperature DSC of Uncured ATS-G and its Component Fractions

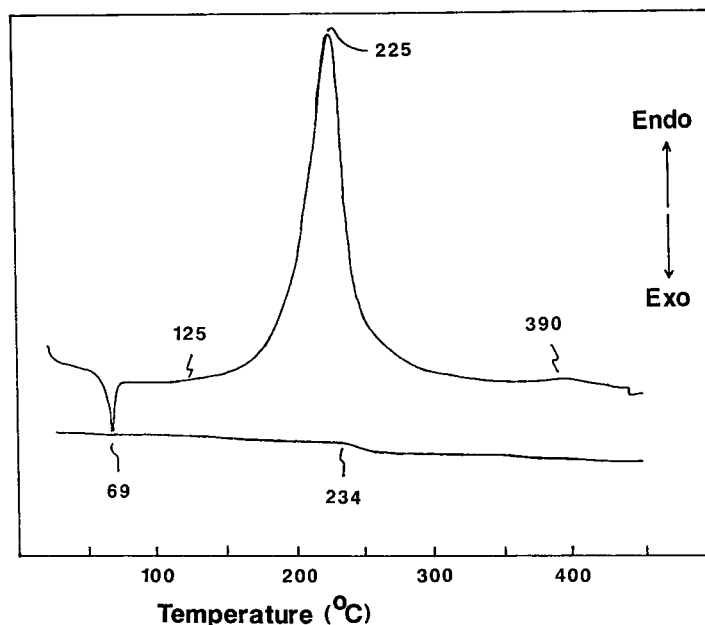| Material	T_g (°C)	T_m (°C)
ATS-G	×	×
ATS monomer	−14	57
ATS dimer	53	69
ATS trimer	80	×
Fraction 4	43	×
Fraction 5	57	×
Fraction 7	55	×

×: Not observed.

Figure 2   Upper—differential scanning calorimetry of the cure exotherm of ATS dimer. Lower—differential scanning calorimetry of the fully cured resin.

in the ATS-G resin mixture are beginning to thermally degrade in this temperature interval, so an ultimate T_g for this resin mixture may be somewhat problematic.

More quantitative measurements of the cure reactions were performed by ramping the uncured resin through the cure exotherm at six different heating rates to produce raw data which was analyzed by the Friedman method[8] using a computer program developed at AFWAL/MLBP.[9] Isothermal "reaction window" plots were then constructed using the kinetic and thermodynamic parameters so measured.

In Table IV kinetic parameters are obtained by the Friedman method. In the first column heats of reaction for selected fractions on a calorie per gram

basis are listed. As expected, these decrease as the resin backbone increases in length. The second column lists reaction-adjusted heats to reflect the solvent content of the fractions in question, and in the third column are listed apparent activation energies so measured. In the fourth column we have estimated heats of reaction on a molar basis where feasable. As can be seen, the activation energies for the polymerization of ATS-G, monomer, and dimer, do not vary much. On the other hand, that measured for the trimer is significantly lower, lending some credence to the presence of impurities able to alter the mechanism of polymerization. Heats of reaction on a molar basis increase from ATS monomer, to the dimer, and finally to the ATS-G resin mixture. That for ATS trimer is significantly higher than for

Table II   DSC of Uncured ATS-G and Isolates from that Mixture at a Heating Rate of 10°C/min

Material	Onset of Polymerization (°C)	T_{max} of Polymerization (°C)	T_{max} of the Post-Cure Reaction (°C)
ATS-G	100	215	360 (exo)
ATS monomer	140	223	395 (exo)
ATS dimer	125	225	390 (exo)
ATS trimer	110	214	340 (exo)
Fraction 4	100	202	305, 340 (exo)
Fraction 5	90	225	X
Fraction 7	100	215	350 (endo)

X: Could not be measured.

Table III Glass Transition Temperatures of Fully Cured ATS-G and its Component Fractions

Material	T_g (°C)
ATS-G	×
ATS monomer	328
ATS dimer	234
ATS trimer	225
Fraction 4	225
Fraction 5	205
Fraction 7	247

×: Could not be measured.

the other fractions. It would appear that impurities in the ATS-G mixture appear to measurably increase heats of reaction and decrease activation energies of reaction with regard to the use of ATS monomer as a reference material, but that the net effect on the ATS-G resin mixture is minimal.

Reaction window plots, so constructed from the programmed heating experiments essentially define a *time* to achieve a specified conversion at a specified temperature under isothermal conditions. By inspection of the reaction window plot for 5% conversion to cured resin shown in Figure 3, we can see quite clearly the anomalous behavior of ATS trimer which is much more reactive than the other fractions in the initial stages of reaction, as well as the apparent similarity of reactivity of those other fractions. If we compare this behavior with that observed at 50% and 95% conversion, we can see that reactivity converges at higher conversions, especially at the higher temperatures which would probably be used in a "real" cure cycle for the resin. Everything considered, it would appear that the *net* effect of impurities in the ATS-G resin mixture does not significantly change its cure chemistry from that of the pure monomer.
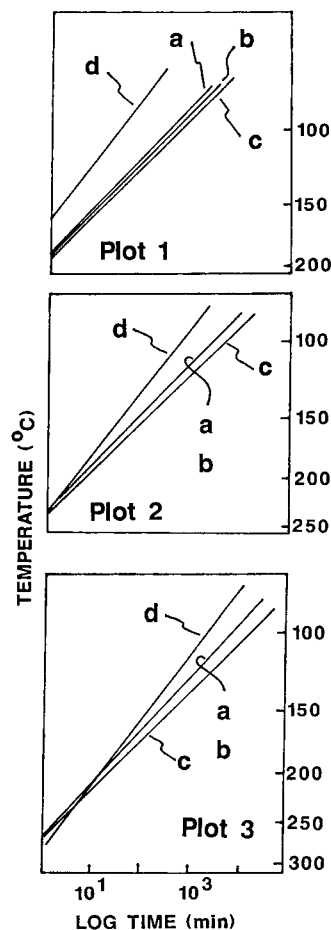

Figure 3 Reaction window plots for the conversion of (a) ATS-G, (b) ATS monomer, (c) ATS dimer, an (d) ATS trimer, to cured resin. *Plot 1*—5% conversio , *Plot 2*—50% conversion, *Plot 3*—95% conversion.

Infrared Spectroscopy of Partially and Fully Cured ATS-G

Direct evidence that ATS resin cures by a free radical polymerization of terminal acetylenes is available through an examination of the build-up of sig-

Table IV Kinetic and Thermodynamic Parameters for the Cure Reaction of ATS-G and its Component Fractions

Material	Heat of Reaction (cal/g)	Corrected for Solvent (cal/g)	Apparent Activation Energy (kcal)	Heat of Reaction (kcal/mol)
ATS-G	115.95	117.72	21.304	70.40[a]
ATS monomer	132.01	141.95	21.306	65.86
ATS dimer	79.29	80.50	22.681	68.26
ATS trimer	62.04	63.31	17.315	75.34

[a] An *estimate* based on an "average" molecular weight of the ATS-G mixture as estimated from the compositional analysis.
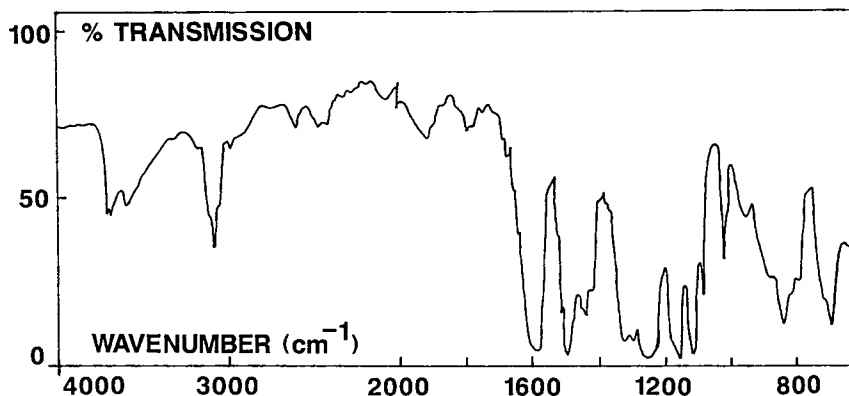
Figure 4   Infrared spectrum of ATS monomer, heated to approximately 300°C under vacuum at a rate of 5°C/min.

nals associated with free radicals in polymerizing resin using electron spin resonance (ESR) spectroscopy.[1] Examination of the molecular weight distributions of polyphenyl acetylenes[10] indicates also that the process of termination is unimolecular and involves a rearrangement of the growing chain end. We are of the opinion here that the growing polyene clusters which constitute the effective crosslink in AT systems, reach a limiting size dependent not on an operation of the classical free radical termination processes, but on an enhanced delocalization and reduced mobility of the growing chain end. This is supported by the ESR measurements which show an unusually high radical concentration in curing ATS resin were the termination reaction to involve the destruction of radicals as in Conventional Free Radical Polymerization.

To check for an involvement of oxygen in the polymerization process, we performed, by infrared (IR) spectroscopy, a microstructural analysis of ATS resin at various stages of a vacuum cure. An IR spectrum of fully cured ATS monomer is shown in Figure 4. This spectrum is reproducible and representative of that produced by fully cured ATS-G, ATS dimer, and ATS trimer. As expected, the terminal acetylenes are completely consumed as indicated by the absence of the associated C—H stretch at 3300 cm^{-1}, to form structures which absorb in the region 3200–2800 cm^{-1}. The appearance of a small but measurable population of free hydroxylic material was not expected on the basis of a straightforward free radical polymerization reaction, but may be explained if oxygen is assumed to have participated in that polymerization reaction. In fact, similar features have been observed (without comment) in the IR spectra of thermally cured diethynyl phenylether.[11]

This behavior was further observed by partially curing ATS-G under programmed heating conditions and observing the appearance of hydroxylic material. The results, recorded in Figure 5, indicate
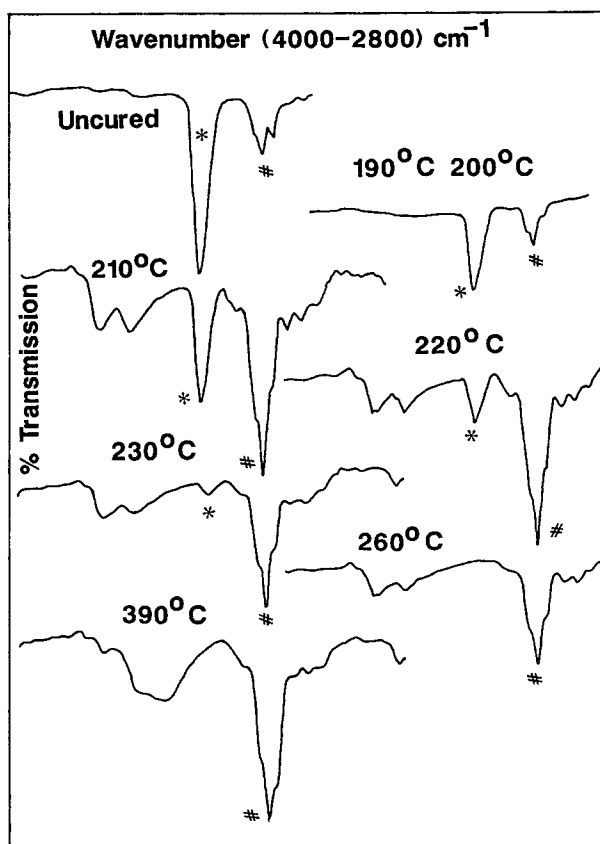

Figure 5   Infrared spectrum of ATS-G, partially and completely cured by heating at a rate of 5°C/min. ∗— Acetylene C—H stretch at 3300 cm^{-1}. #—Aromatic C—H stretch at 3030 cm^{-1}.

that such functionality begins to be formed at about 200°C in the polymerizing mixture. As normal peroxide groups are known to decompose in this temperature interval, it seems quite feasible that oxygen could be copolymerized to some extent with the growing polyene chain to form unstable links which thereafter break down to reduce the polyene chain length and produce hydroxylic functionality. This explanation is, of course, somewhat difficult to support in the case of resin cured under high vacuum conditions. We could alternatively presume a post-polymerization coupling of the delocalized *but not terminated* polyenes with oxygen after the cure cycle. The first appearance of hydroxylic functionality at 200°C would then coincide with the first appearance of polyene functionality in the curing resin. Further work is needed to clarify this point.

Isothermal Low Temperature Thermogravimetry in Air

Destined for use at high temperatures, it is important to know the practical upper use temperatures of this class of resin. As extrapolations of such parameters from short-term programmed experiments are generally unreliable, we performed isothermal aging experiments in air using weight loss as a simple marker of instability.

Samples of ATS-G, monomer, and dimer, pre-cured by programmed heating to 234°C at a programmed heating rate of 5°C/min, were placed in the isothermal aging apparatus and aged in air at 260°C (500°F) for 200 h to yield the weight loss curve shown in Figure 6. The same samples were then heated to 316°C (600°F) for another 200 h to yield a second weight loss curve shown in Figure 7. As can be seen from these curves, the ATS polymers are stable with respect to weight loss at 260°C but unstable at 316°C in air. No noticeable effect of
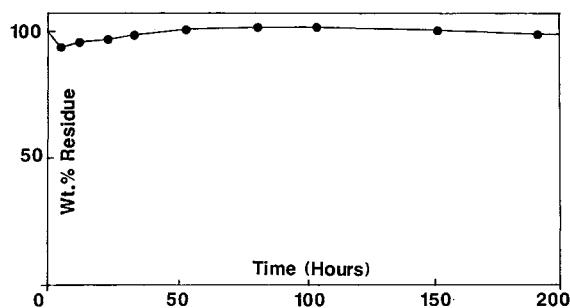

Figure 6 Isothermal weight loss curves in air at 260°C for ATS-G, ATS monomer, and ATS dimer. *Curves superimpose* (dot size indicates spread of data).
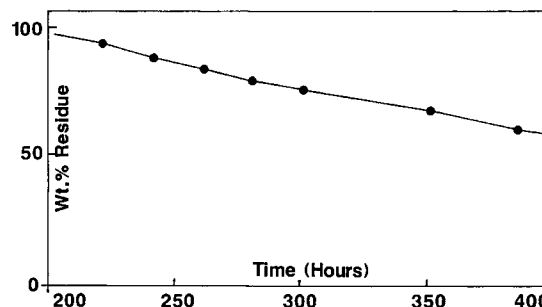

Figure 7 Isothermal weight loss curves in air at 316°C for ATS-G, ATS monomer, and ATS dimer. *Curves superimpose* (dot size indicates spread of data).

crosslink density on resin stability was observed at these temperatures.

It is of more than academic interest to determine whether or not this instability at 316°C is due to a thermal or an oxidative process. To this end, a sample of ATS monomer was cured to a final temperature of 270°C under vacuum at a heating rate of 5°C/min. The polymer sample was removed from the oven assembly, weighed (481.5 mg), returned to the oven assembly, pumped to high vacuum, and carefully heated to 328 ± 5°C to avoid temperature overshoot. This temperature was maintained for 10.5 h with constant monitoring of vacuum quality via recorded Pirani gauge output. Condensable volatile products of degradation of the polymer during this time period were collected in a trap on the vacuum line held at −196°C for subsequent separation by sub-ambient thermal volatilization analysis (SATVA). The polymer was then cooled to room temperature under vacuum and reweighed (479.8 mg). The weight lost by the polymer during this time period, was, therefore, 1.7 mg or 0.4 wt % of the initial sample. At such low extents of conversion, we can assume the weight loss process to proceed at a constant rate (if auto-acceleration or retardation does not set in). If so, by extrapolation, we can assume that about 4% of the sample weight should be volatilized after 100 h at 328°C in the absence of oxygen. In contrast, approximately 25 wt % of this polymer is lost in air at the lower temperature of 316°C over this time period. The weight loss process operative in air at 316°C is, therefore, most probably of an oxidative nature.

Condensable volatiles trapped during the 10.5 h duration of the experiment were analyzed by SATVA to yield the results shown in Figure 8. It will be shown later that sulfur dioxide and phenol constitute also the initial condensable volatile prod-
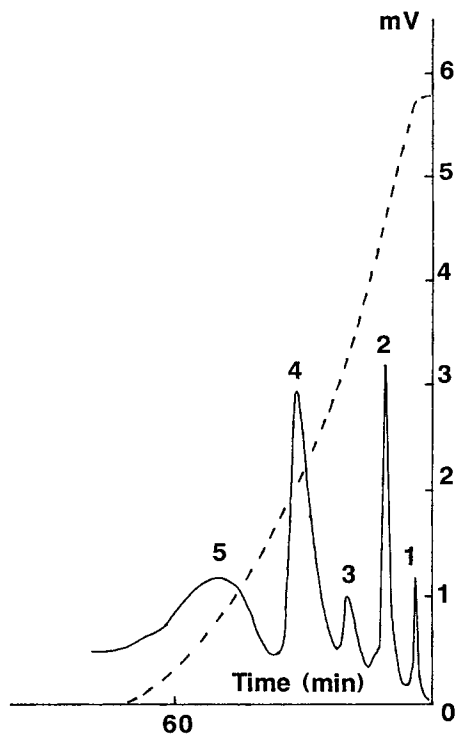
Figure 8 SATVA of the condensable volatile product fractions of isothermal degradation of pre-cured ATS monomer at 328°C for 10.5 h under high-vacuum conditions. Full line: Pirani gauge output, dotted line: (−) thermocouple output (SATVA trap temperature). Sample size: 481.5 mg. (1) CO_2, (2) SO_2, (3) benzene, (4) water, (5) phenol.

ucts of thermal degradation of ATS polymers at a programmed heating rate of 5°C/min. Here, it is interesting to note their production at even lower temperatures under isothermal conditions. It is also interesting to note the presence of benzene and water in the product distribution of degradation. Benzene is, of course, the solvent from which the ATS monomer was recovered after isolation by column chromatography. Water is probably formed by decomposition of terminal hydroxylic functionality on the polyene, the formation of which is discussed in the previous section.

The T_g of the aged sample was shown to be 336°C by differential scanning calorimetry (DSC). It must be concluded that the high temperature post-cure process referred to in a subsequent section also operates at the relatively low temperature of 328°C if given sufficient time. The high T_g of this sample indicates that the process has been driven almost to completion at a temperature where thermal degradation has been shown to be minimal. This would

tend to indicate that a prolonged period of post-cure at a relatively low temperature may be the most efficient way to complete the ATS network without degradation. It remains to be seen whether or not such an approach could gain commercial acceptance.

The aged sample was shown in the same DSC experiment to produce a relatively large and well-defined exotherm beginning at approximately 360°C. This exotherm is not associated with the polymerization of terminal acetylenes because none are present in the sample at this stage of the cure process. It is also probably not associated with the post-cure process because such a process must be close to completion. It may be a result of thermal isomerizations of the polyene crosslink to a more stable configuration. It may also be a result of a partial cyclization of the polyene network. It is unlikely that such an exotherm could result from the relatively slow processes of thermal degradation operative in this temperature range.

DSC of ATS Dimer

The T_g of the ATS monomer which had been pre-cured to 450°C at a heating rate of 10°C/min has been shown by DSC to occur at approximately 320°C. On the other hand, the T_g of ATS-G attained by a ramped warm-up of uncured resin at a heating rate of 2°C/min to 400°C in the TICA experiment was shown (by extrapolation) to be 366°C.[7] Work reported here suggests that the T_g of the ATS-G resin mixture should be lower than that of pure ATS resin, due to its lower crosslink density. One possible simple solution to this discrepancy would be to postulate that the ATS network undergoes some thermal degradation in the temperature interval 400–450°C. Although not destined for use at these temperatures, this observation does warrant some follow-up work on the basis that a post-cure in this temperature interval is thought to be required to fully develop the physical properties of ATS resin. A knowledge of possible degradation of the network in this temperature interval would alert the operator to a more precise control of the post-cure process.

More detailed DSC measurements were performed to test these assumptions using ATS dimer which had been isolated from the ATS mixture. ATS dimer was chosen for these measurements because of its easily detectable and well-defined T_g. To test the effect of thermal history on T_g, ATS dimer was subjected to repeated ramped heating experiments in the DSC cell to yield the thermograms illustrated in Figure 9.
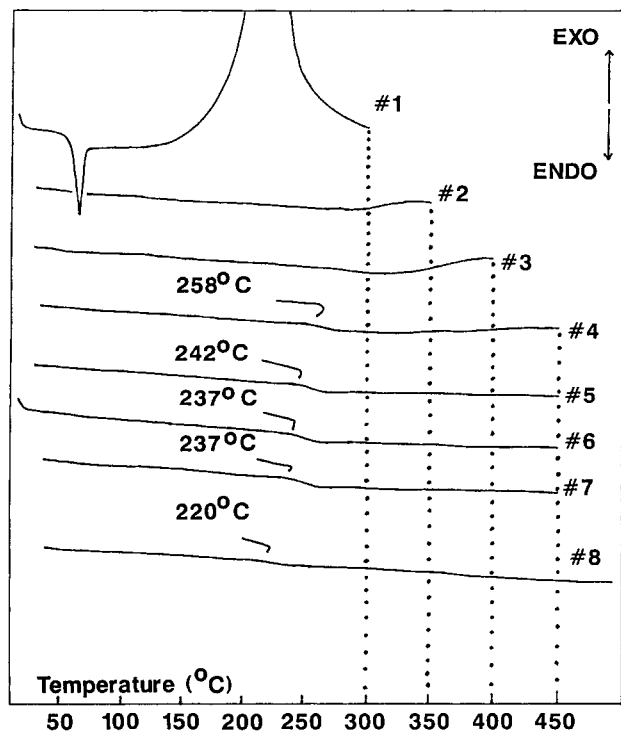
Figure 9 Differential scanning calorimetry (DSC) of ATS dimer under nitrogen at a heating rate of 10°C/min.

Scan 1 (Room Temperature–300°C)

The uncured resin on heating through its T_g underwent a sharp hysteresis endotherm at $\simeq 69°C$ then a polymerization exotherm which achieved a rate maximum at 229°C.

Scan 2 (Room Temperature–350°C)

A glass transition in the sample was not observed during this experiment. A small exothermic process which could be associated with residual cure or with a post-cure process was shown to commence at approximately 300°C. The first explanation would appear likely and would explain its onset at the upper limits of the first scan and the absence of the glass transition which would be obscured by exothermic heat flow. On the other hand, the T_g of ATS dimer is less than 300°C, suggesting that said exotherm may correspond to a post-cure process. A more definitive statement cannot be made on the basis of this evidence alone.

Scan 3 (Room Temperature–400°C)

A broad, poorly defined change of baseline slope was observed during the temperature interval 200–300°C

in place of a well-defined T_g transition. This indicated that the network, at that point, was composed of a mixture of dissimilar structures. An exothermic process was shown to commence at approximately 325°C. With respect to the cure history of the sample, it can be stated with some certainty that terminal acetylenes are not involved in this process.

Scan 4 (Room Temperature–450°C)

A sharp, well-defined T_g transition was observed at 258°C, indicating that the process of network unification or "homogenization" was completed toward the end of Scan 3.

Later scans were as follows: Scan 5 (room temperature–450°C), $T_g = 242°C$; Scan 6 (room temperature–450°C), $T_g = 237°C$; Scan 7 (room temperature–450°C), $T_g = 237°C$; Scan 8 (room temperature–490°C), $T_g = 220°C$.

Aside from the small but measurable exotherm witnessed toward the end of the initial DSC experiments, it can be clearly seen that repeated scans to 450°C degrade the resin network with consequent
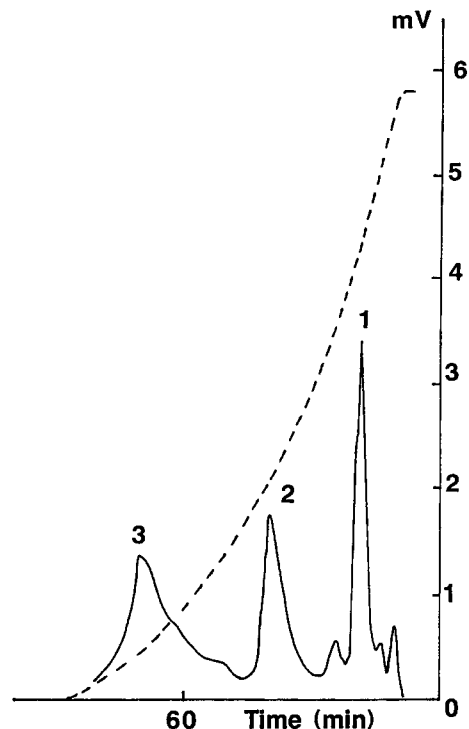

Figure 10 SATVA of the condensable volatile product fraction of programmed thermal degradation to 450°C of ATS dimer. Full line: Pirani gauge output, dotted line: (−)thermocouple output (SATVA trap temperature). Sample size: 109.1 mg. (1) SO_2, (2) water, (3) phenol.

lowering of T_g. To provide corroborating evidence, a sample of ATS dimer was heated to 450°C under high vacuum conditions, and the condensable volatile product fraction examined by SATVA to yield the trace shown in Figure 10. An analysis by quantitative gas phase IR spectroscopy indicated the production of sulfur dioxide or SO_2 at a 1.2 wt % yield of the original sample weight, or 8.3 mol % of the ultimate SO_2 yield from the polymer at a heating rate of 5°C/min (unpublished results).

The observation of SO_2 as a product of degradation is strong evidence for the deterioration of the ATS network, as such would result in the production of some pendent phenyl ethers in the resin with a concomitant lowering of T_g. To complete the link it was, therefore, necessary only to demonstrate that repeat scans in the TVA apparatus produced SO_2 as a product of degradation to further lower T_g in agreement with the DSC measurements. The same sample of ATS dimer, was, therefore, reheated to 450°C in the TVA apparatus and the condensable volatile products of degradation separated by
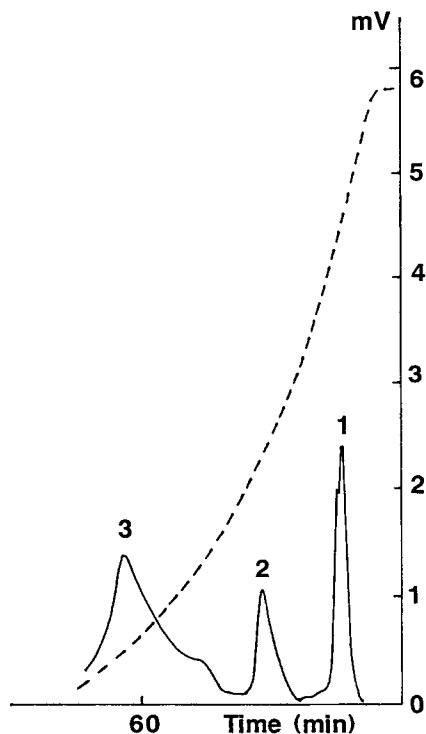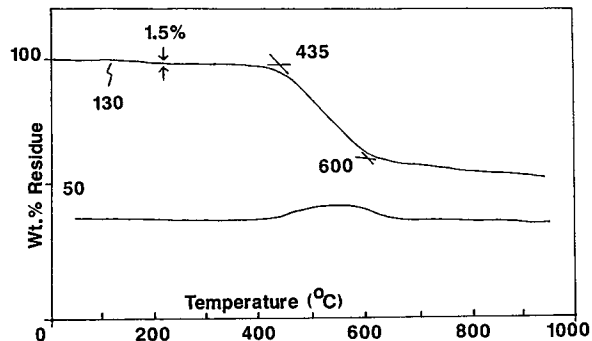

Figure 12 Programmed TGA of ATS-G under helium at a heating rate of 5°C/min.

SATVA as before to yield the trace shown in Figure 11. The sulfur dioxide yield in this instance was shown to constitute 0.6 wt % of the original sample, or 4.2 wt % of the maximum sulfur dioxide yield from the polymer.

The relatively small changes in T_g induced by these relatively large yields of SO_2 from ATS dimer, constitute strong circumstantial evidence to indicate that initial sulfone scissions in ATS polymers are often followed by recombination of radical centers to form the bridging diphenyl linkage.

Programmed Thermogravimetry Under Helium

Programmed thermogravimetry (TGA) is a much used technique for the rapid evaluation of the thermal stability of polymeric materials. It is especially useful for comparing and for *ranking* thermal stabilities. If we consider the resin from ATS-G as an example of this class of material, we can see from the TGA trace reproduced in Figure 12 that the material appears stable to a temperature of about 400°C. Approximately 30–40 wt % of the resin is volatilized between about 400–600°C. The thermal derivative of this process appears reasonably stable to further weight loss, at least to 1000°C. Using the TVA technique we will show elsewhere (manuscript in preparation) that the quantitative weight loss process produces sulfur dioxide, carbon dioxide, carbonyl sulfide, benzene, water, phenol, and some higher molecular weight products in a degradation process initiated by decompositions at the sulfone linkages. The polyene centered polyaromatic clusters so formed fuse at temperatures above 600°C to produce carbon monoxide, methane, hydrogen, and a carbonaceous final residue. Points of interest in the TGA curves are summarized in Table V.

We were most interested in ranking the thermal

Figure 11 SATVA of the condensable volatile product fraction of programmed thermal degradation to 450°C of ATS dimer, pre-degraded to 450°C. Full line: Pirani gauge output, dotted line: (−)thermocouple output (SATVA trap temperature). Sample size: 109.1 mg. (1) SO_2, (2) water, (3) phenol.

Table V   Programmed TGA of ATS-G and its Component Fractions at a Heating Rate of 10°C/min

Material	Degradation Commences (°C)	Bulk Degradation Commences (°C)	Approx. Rate Max (°C)	Bulk Degradation Ends (°C)	% Weight Loss to 800°C
ATS-G	375	435	525	600	43.2
ATS monomer	410	460	525	590	40.5
ATS dimer	360	475	545	590	49.4
ATS trimer	310	475	535	590	58.2
Fraction 4	160	435	500	X	50.6
Fraction 5	150	425	485	X	70.9
Fraction 7	290	290/445	350/500	X	70.9

X: Entry could not be measured.

stabilities of cured resin from the pure monomer, dimer, and trimer fractions, and in comparing the behavior of the pure fractions with that of the ATS-G resin mixture. Programmed TGA curves for these materials are reproduced in Figure 13, from which it can be seen that the monomer is more stable than the dimer, which is in turn more stable than the trimer fraction. The thermal stability of this class of material is, therefore, shown to increase with crosslink density (or polyene concentration) in the cured resin.

If we consider the abnormal components of the ATS-G mixture, namely fractions 4, 5, and 7, we observe a more complex degradation pathway as can be seen from an examination of the TGA curve of fraction 7 in Figure 14. Nonetheless, the ATS-G mixture is not adversely affected by the cumulative presence of these impurities, possessing a thermal stability between that of ATS monomer and dimer.
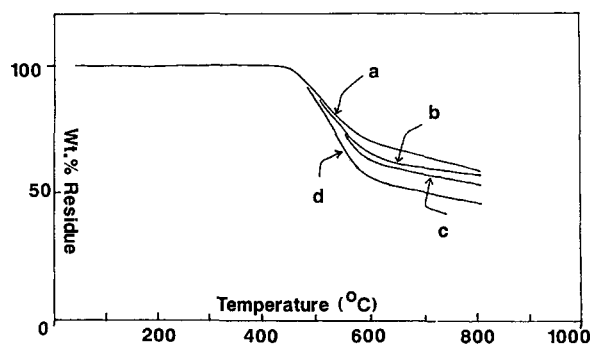
CONCLUSIONS

We have shown that both the glass transition and the thermal stability of cured ATS resin increases with the crosslink density or polyene concentration in the cured material, and that the sulfone bridge rather than the polyene crosslink is the thermal "weak link" in ATS systems. We have also shown that oxygen may participate in the polyene polymerization reaction, and that the impurities in the ATS-G resin mixture act as potential accelerators for that reaction, though their effect on the performance of ATS-G is small, possibly due to the low concentrations involved. We have shown through isothermal aging studies that ATS resin is a good "500°F" resin but a poor "600°F" resin, and that the instability at 600°F (or 316°C) is oxidative in nature and insensitive to crosslink density. We also showed that ATS resin becomes thermally unstable at temperatures above 400°C, and indicated that
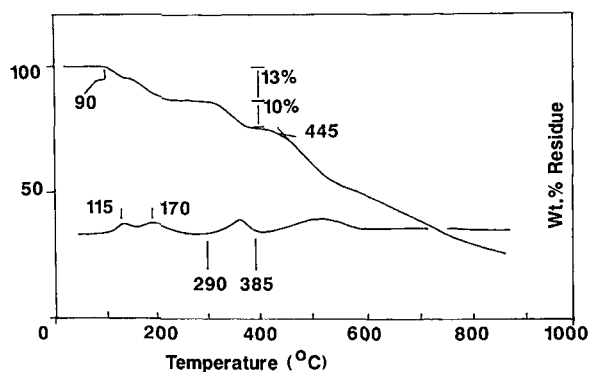

Figure 13   A comparison between solvent loss compensated TGA curves for ATS-G and selected ATS fractions. (a) ATS monomer, (b) ATS-G, (c) ATS dimer, (d) ATS trimer.

Figure 14   Upper—Programmed TGA of fraction 7 under helium at a heating rate of 5°C/min. Lower—Derivative curve.

cure cycles for this class of material should not include a 400+ °C post-cure step. We also gave evidence that the post-cure process is operative in ATS systems at relatively low temperatures over prolonged periods of time, suggesting an alternative to a high-temperature post-cure step.

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