

# Characterization of Acetylene Terminated Sulfone (ATS) Resin. I. Chemical Characterization of the Resin

W. T. K. STEVENSON\* and I. J. GOLDFARB†

AFWAL/MLBP, Wright Patterson Air Force Base, Dayton, Ohio 45433

## SYNOPSIS

An acetylene terminated sulfone resin mixture, prepared under contract for the Air Force, was subjected to a fairly extensive compositional analysis. Monomer, dimer, higher oligomers, solvents, and anomalous side products of synthesis were isolated, identified, and quantified using separatory procedures such as column chromatography and thin film flash distillation, in conjunction with techniques of chemical analysis such as infrared and nuclear magnetic resonance spectroscopy, size exclusion chromatography, and elemental analysis. By these means we were able to precisely characterize the resin mixture and, by so doing, identify some side products of synthesis; most notably, a class of abnormal coupling product able to chelate palladium (a catalyst used in acetylation of the resin) and, therefore, accelerate subsequent acetylene polymerizations in the resin mixture.

## INTRODUCTION

Acetylene terminated resins have generated much interest as candidate high performance matrix resins for aerospace applications. This interest has hinged upon several attractive features of the material including a chain addition mechanism of cure which promises void-free laminates,<sup>1</sup> a thermally initiated cure without added catalyst or hardener which holds open the possibility of long shelf lives and batch-to-batch homogeneity approaching that of the thermoplastics,<sup>2</sup> and high glass transition temperatures<sup>3</sup> and thermal stabilities made possible by the incorporation of wholly aromatic precursors into a heavily crosslinked polyene network. As part of an extensive thrust in this area, the Air Force commissioned Gulf Chemicals, Inc. to produce a pilot plant quantity of acetylene terminated sulfone resin (more properly, bis[4-(3-ethynyl phenoxy)phenyl]sulfone and its higher oligomers.<sup>4</sup> In this paper we report a thorough chemical analysis, first of all as a necessary prelim-

inary to a systematic study of this material, designated ATS-G, by techniques of thermal analysis, and secondly, to report the methodology used, to encourage others that a detailed analysis of a complex resin mixture (as is rarely performed in practice) is indeed possible, and can lead to some interesting insights into the material itself.

To make the following discussion more meaningful a short description of the synthetic pathway to ATS-G must be made here. In brief, sulfonyl diphenol was first end-capped with dibromo benzene (95% m/5% p) through an Ullman ether condensation. The bromine end groups were then replaced by 2-methyl-3-butyn-2-ol in the presence of a palladium catalyst<sup>4</sup> and the "acetone adduct" so formed base hydrolysed to the corresponding acetylene-terminated resin.

In common with most resins of interest to the aerospace community, this material is prepared as a mixture of the monomer and higher homologues, solvents and byproducts of synthesis. Although at first glance an undesirable feature of this class of material, it must be stated that such "solutions" are often more processible than their pure counterparts due to suppressed crystallization of the major components, with subsequent lowering of viscosity and improved processability of the mixture. Oligomers are formed during the first reaction of this sequence.

\* To whom correspondence should be addressed at Department of Chemistry, Wichita State University, Wichita, KS 67208.

† Present address: Department of Chemistry, Wright State University, Dayton, OH, 45455.

Journal of Applied Polymer Science, Vol. 42, 665-677 (1991)

Not subject to copyright in the United States.

Published by John Wiley & Sons, Inc. CCC 0021-8995/91/030655-13\$04.00

For example, the oligomer designated as ATS dimer is formed by condensation of the phenyl bromide end capped by sulfonyl diphenol with another sulfonyl diphenol, followed by phenyl bromination (condensation with *m*-dibromo benzene) of the phenolic end group to form an adduct containing two sulfones, which is subsequently acetylated to form ATS dimer. The molecular weight distribution of the resin is therefore controlled by the ratio of sulfonyl diphenol to *m*-dibromobenzene in the first step of synthesis. The ratio used to prepare this batch of resin was adjusted to produce a nominal monomer content of 70–80%. Representative structures are detailed in Figure 1. In light of the analyses to follow, it may seem that the ATS-G mixture is unduly complex. In reality, it is less so than most commercial systems with added hardener.

## MATERIALS AND METHODS

### Column Chromatography

Higher molecular weight components of the ATS-G mixture were isolated by preparative column chromatography using separatory systems developed on an *ad hoc* basis. Conditions of separation are discussed below and represented schematically in Figure 2.

(1) *Monomer isolation*: Chromatographic grade silica gel was made more absorptive (regenerated) by heating to 700+ °C. The ATS-G mixture was deposited over a 1 m × 5 cm d. column of regenerated silica gel and monomer (F1) was extracted with methylene chloride as the only mobile component of the mixture. Other components of the mixture were recovered by stripping the column with THF solvent.

(2) *Isolation of F7, an abnormal coupling product of synthesis*: The mixture recovered after isolation

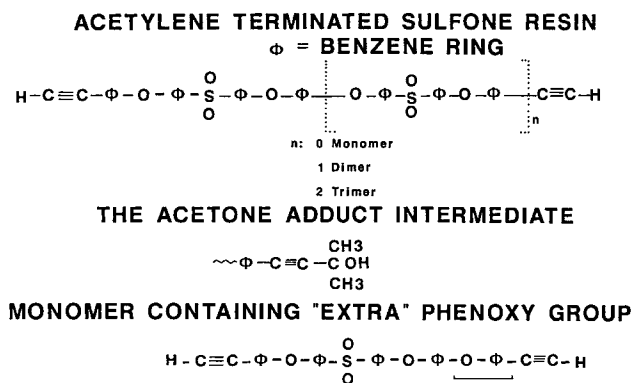


Figure 1 Resin structures.

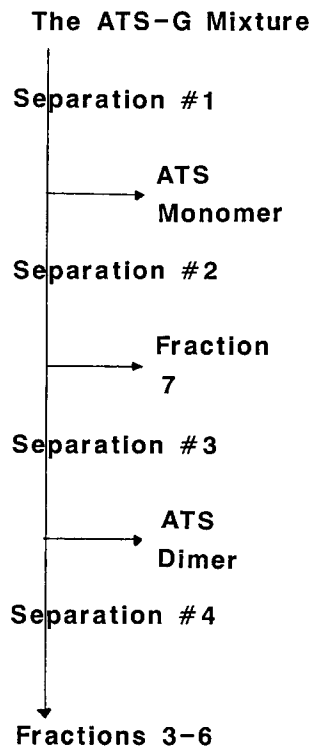


Figure 2 Schematic representation of fraction separations.

of monomer was layered over a 1 m × 5 cm d. column of regenerated silica gel. The column was conditioned with pet. ether and extractions were then performed using mixtures of pet. ether and THF (30 vol % max.). F7 was isolated as the only *immobile* component of the mixture and was recovered by stripping the column with THF.

(3) *Isolation of ATS dimer (F2)*: The residual mixture after isolation of F7 was layered onto a 1 m × 5 cm d. column of fresh silica gel with UV indicator in a quartz column, and dimer was isolated as the first band eluted from the column as indicated by a hand held UV lamp. The column was then stripped of less mobile material using pure THF.

(4) *Isolation of other components of the mixture, namely F3-F6*: The residual mixture recovered after isolation of ATS dimer was chromatographed on a 1 m × 5 cm d. column of silica gel with UV indicator in quartz using 15% diethyl ether in chloroform. Fractions 3–6 were recovered respectively as the first four (and only detectable) eluent bands.

### Elemental Analysis

A carbon, hydrogen, and sulfur analysis of ATS-G and component fractions was performed using stan-

**Table I Chromatographic Separations of ATS Monomer from the ATS-G Resin Mixture**

No. of Separations	Material Separated (g)	% Recovered	Wt % Monomer	Wt % Other Material
5	112.67	97.5 ± 2.9	71.0 ± 0.8	29.0 ± 0.8

dard techniques of microanalysis. A trace element analysis for copper, palladium, and silicon was performed using atomic absorption spectroscopy.

### Size Exclusion Chromatography

The hydrodynamic volumes of ATS-G and its component fractions were obtained using size exclusion chromatography. Analyses were performed in THF using microstyragel columns in a Waters Associates liquid chromatograph.

### Infrared and NMR Spectroscopy

ATS fractions were analyzed by infrared spectroscopy as thin films deposited from chloroform onto salt plates using a Beckman IR 33 grating spectrometer. Proton NMR spectra were obtained at room temperature in deuteriochloroform using a Varian EM 360, 60 MHz CW spectrometer. Proton decoupled carbon 13 NMR spectra were obtained using a Varian XL-100, FT-NMR spectrometer.

### Thermal Volatilization Analysis and Sub-Ambient Thermal Volatilization Analysis

A full discussion of this family of separatory techniques developed by I. C. McNeill and coworkers at the University of Glasgow is available elsewhere.<sup>5</sup> For our purposes they may be thought of as high vacuum microdistillation techniques for an analysis of the rates of production of, and for the quantitative separation of, the major product fractions of polymer degradation, prior to their subsequent analysis by ancillary techniques such as gas chromatography or infrared spectroscopy. Condensable volatile impu-

rities in the ATS-G mixture were flashed from thin films of the resin by ramped heating under high vacuum conditions, trapped on the vacuum line at -196°C, and separated by sub-ambient thermal volatilization analysis for subsequent spectroscopic identification. Higher molecular weight material was evaporated from the resin mixture on programmed heating under high vacuum conditions and condensed onto a cap placed over an internal cold finger held above the oven assembly in the vacuum line<sup>6</sup> from which it could be removed by rinsing with solvent for spectroscopic and other analysis.

### Thin Layer Chromatography

High molecular weight material evolved from ATS-G on programmed heating under high vacuum conditions was separated using preparative thin layer chromatography (TLC) on UV active silica gel. On completion of the separations, plates were rotated and resolved material collected by stripping with THF. Fraction weights were estimated by gravimetry and structures by a joint application of spectroscopy, size exclusion chromatography (SEC), and chemical ionization mass spectroscopy (CIMS).

## RESULTS AND DISCUSSION

### Separations by Column Chromatography

The results of chromatographic separations performed on the ATS-G resin mixture are reproduced in Tables I-IV. An almost complete recovery was obtained in each instance. Values above 100% indicate an incomplete removal of solvent. The feed

**Table II Chromatographic Separations of F7 from the Mixture Designated as "Other Material" With Regards the Isolation of ATS Monomer**

No. of Separations	Material Separated (g)	% Recovered	Wt % F7	Wt % Other Material
3	25.0	101.0 ± 0.8	18.4 ± 1.6	81.6 ± 1.6

**Table III Chromatographic Separations of ATS Dimer from the Mixture Designated as "Other Material" With Regards the Isolation of F7**

No. of Separations	Material Separated (g)	% Recovered	Wt % ATS Dimer	Wt % Other Material
2	9.41	104.5 ± 0.5	67 ± 2	33 ± 2

mixture for the separation reported in Table II is the residual mixture of the separation reported in Table I, and so on. It must be noted here that these separations are useful only for the isolation of involatile high molecular weight components of the ATS-G mixture and so a compositional distribution based only on the contents of Tables I-IV will be in error. For a full and accurate analysis of the resin, we require also the content of lower molecular weight species (to be discussed in a subsequent section of this report). For convenience, we have labeled the first isolated fraction (F1) as ATS monomer and the third (F2) as ATS dimer to aid in the interpretation of the first four tables. We will subsequently prove these labels true by chemical analysis of the isolates.

#### Elemental Analysis of Fractions From ATS-G

ATS-G and important fractions from that mixture were subjected to analysis for carbon, hydrogen, sulfur, palladium, copper, and silicon. Levels of the first three are reported in Table V and of the second three in Table VI. From Table V we can see that the major element levels in ATS-G, F1, F2, and F7 are all similar. Even so, some differences are worth comment. For example, the high hydrogen content of F7 indicates that it contains some saturated or olefinic material, while its low sulfur content indicates a resin backbone somewhat different from the normal ATS structure.

The low levels of palladium in fractions 1-4 indicate that the metal is not in any way bound to

those structures. Conversely, the high levels of the metal detected in F5-F7 indicate the presence of structures able to efficiently chelate the metal, especially considering the work-up those samples had experienced prior to analysis (passage through fresh and regenerated silica gel, etc.).

#### Size Exclusion Chromatography

ATS-G and isolates from column chromatography were next examined by size exclusion chromatography. Due to the relatively narrow molecular weight range of components of the resin mixture the technique was not particularly useful in the characterization of the neat resin itself, as evidenced by the chromatogram reported in Figure 3, but yielded better results when applied to isolated components of the mixture.

From the results of Table VII, it can be seen that the effective hydrodynamic volumes of F1, F2, and F3 (which will later be shown to be ATS monomer, dimer, and trimer respectively by NMR spectroscopy) lie in an approximate ratio of 1 : 2 : 3, as would be expected of those molecules. The effective "size" of fractions 4 and 5, which will be shown to be anomalously end-capped monomeric fractions, are somewhat higher than that of ATS monomer itself. The effective "size" of fraction 6 is about double that of ATS monomer, slightly smaller than expected upon subsequent characterization as a dimeric coupling product of ATS monomer itself at the palladium catalyst. The effective hydrodynamic volume of ATS dimer, which is less than double the

**Table IV Chromatographic Separation of F3-F6 From the Mixture Designated as "Other Material" With Regards the Isolation of ATS Dimer**

Column Load (g)	% Recovery	Wt % F3	Wt % F4	Wt % F5	Wt % F6
2.97	99	60	27	8	5

**Table V Major Element Analysis of ATS-G and its Component Fractions as Isolated by Column Chromatography**

Material	% Carbon	% Hydrogen	% Sulfur
ATS-G	75.50	3.775	6.92
F1	76.63	3.925	6.47
F2	73.40	3.82	7.75
F3	71.31	3.62	7.55
F7	74.51	5.30	6.07

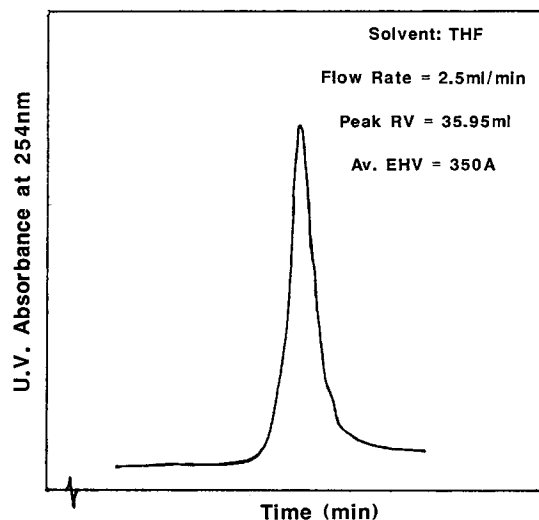
**Table VI Trace Element Analysis of ATS-G and its Component Fractions**

Material	Pd (ppm)	Cu (ppm)	Si (ppm)
ATS-G	30.4	15	16
F1	< 1.5	< 0.5	16
F2	< 1.5	1	22
F3	1.8	1	16
F4	3	×	×
F5	44	×	×
F6	166	×	×
F7	806	17	90

molecular weight of ATS monomer, is about double that of ATS monomer, leading one to expect that a molecule such as F6 with about double the molecular weight of ATS monomer should exhibit more than double the EHV of ATS monomer. The effective size of fraction 7 is consistent with its subsequent identification as ATS monomer which had been trimerized by the palladium catalyst. The major impurity in F7 (though still present in small amounts) was subsequently characterized as resorcinol and the minor as some type of three-ring polyphenolic compound.

#### Infrared Spectroscopy of ATS-G and its Component Fractions

ATS-G, the acetone adduct of ATS-G (supplied by F. Arnold), and F1–F7, were next subjected to a functional group analysis by infrared spectroscopy, a typical spectrum being reproduced in Figure 4. All fractions were shown to contain aromatic material ( $3080\text{ cm}^{-1}$ , w), terminal acetylene functionality ( $3300\text{ cm}^{-1}$ , m), sulfone linkages ( $1290\text{--}1330\text{ cm}^{-1}$ , doublet, s), and ( $1090\text{--}1150\text{ cm}^{-1}$ , doublet, s), and benzyl ether linkages ( $1240\text{ cm}^{-1}$ , broad s). Although producing "fingerprint" spectra at low wavenumbers similar to that of ATS monomer, fractions 2 and 3 do produce extra absorbances at  $930\text{ cm}^{-1}$  and  $955\text{ cm}^{-1}$  which may be assigned to  $\text{SO}_2\text{O}\text{O}\text{O}\text{SO}_2$  linkages in the material. In addition, fractions 4–7 were shown to contain hydrogen bonded hydroxyls ( $3400\text{ cm}^{-1}$ , broad, m). Fractions 6 and 7, in addition, were also shown to contain free hydroxyls ( $3660\text{ cm}^{-1}$ , sharp, m). Fractions 5–7 were all characterized by a triplet of absorbances between  $2800\text{ cm}^{-1}$  and  $3000\text{ cm}^{-1}$  which are similar in position to those produced by the gem dimethyl groups of the acetone adduct of ATS monomer (supplied as a reference compound by Dr. F. Arnold).

**Figure 3** Size exclusion chromatogram of the ATS-G resin mixture in THF solvent.

#### Proton NMR Spectroscopy of ATS-G and its Component Fractions

Proton NMR spectroscopy proved the major tool in our structural elucidation of fractions separated from the ATS-G mixture by column chromatography. A representative spectrum is shown in Figure 5. Based on prior experience with these materials we could identify spectral regions for subsequent signal integration. In the following discussion the region designated in Figure 5 as "A," between 8.1 ppm and 7.8 ppm, can be identified with aromatic

**Table VII Size Exclusion Chromatography of ATS-G and its Component Fractions as Isolated by Column Chromatography**

Material	Effective Hydrodynamic Volume ( $\text{Å}^3$ )	Comments
ATS-G	350	Composite peak
F1	310	Single peak
F2	600	—
F3	950	—
F4	480	—
F5	480	—
F6	600	—
F7	1300 (major) 210 (minor) 65 (minor)	Composite peak

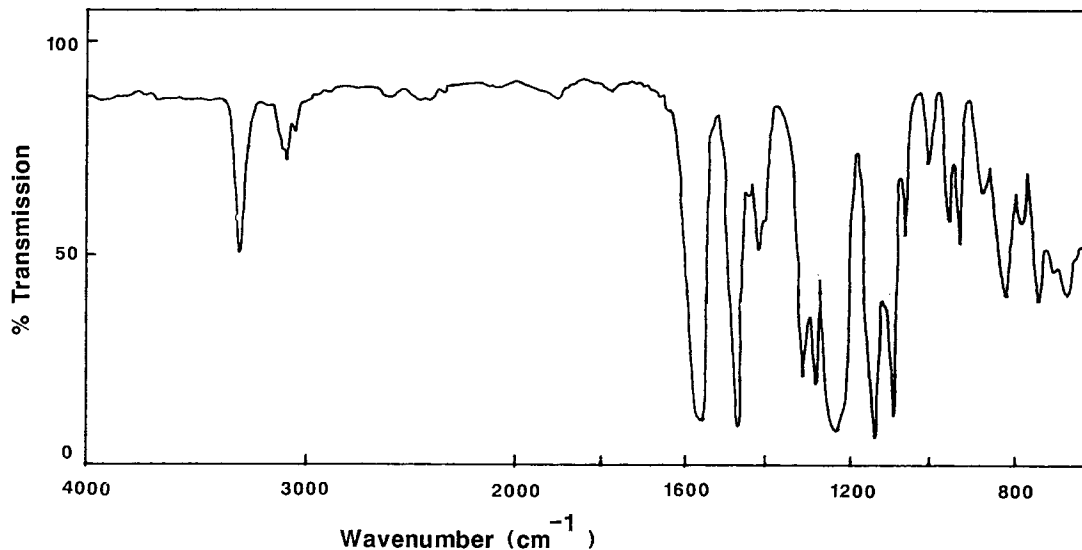


Figure 4 Infrared spectrum of ATS dimer as a thin film on a sodium chloride salt plate.

protons *immediately* adjacent to a sulfone linkage (4 per sulfone). The region designated as "B" between the chemical shift limits of 7.5 ppm and 7.2 ppm is identified with aromatic protons immediately adjacent to those protons designated as "A" protons on the same rings. The region designated "C" corresponds to all other aromatic protons (if separable from B). Acetylenic protons at 3.1 ppm are designated as "D," and with respect to F7, signals at 2.3 ppm and 1.4 ppm are designated as "E" and "F"

respectively. Proton peak ratios are listed in Table VIII. It must be stated here that while peak integrals obtained using a low-powered continuous wave instrument of this type may lack in absolute precision, they reasonably accurately and reproducibly represent relative peak areas, especially when averaged over a number of scans.

If each sulfone group is surrounded by 4 protons designated "A" in a molecule containing two acetylenes, then a graph can be drawn to relate the A/

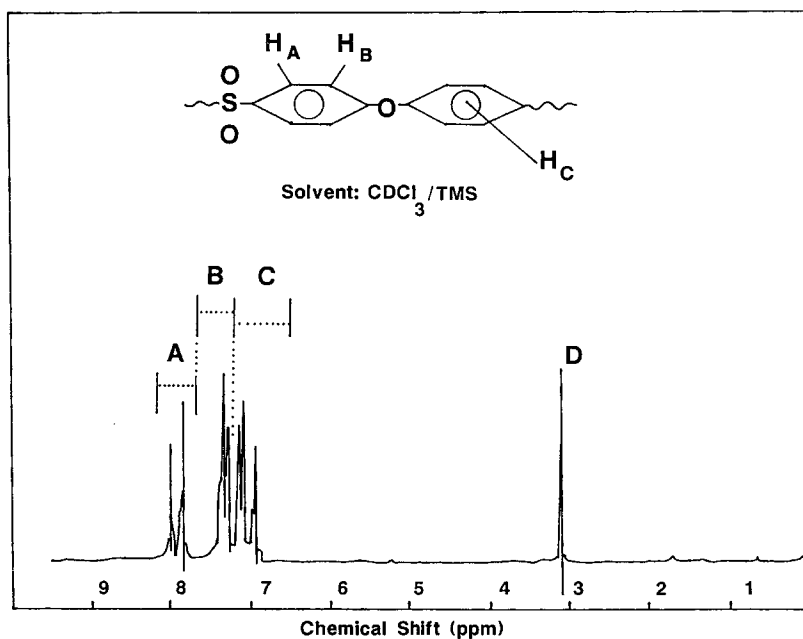


Figure 5 Proton NMR spectrum of ATS monomer in deuteriochloroform.

**Table VIII Proton NMR Peak Integrals of Relevance to This Discussion**

Material	Signals Used	Ratios
ATS-G	A/(B + C)/D	1.0/3.5/0.4
The acetone adduct of ATS monomer	A/B/C	1.0/1.0/2.0
F1	A/B/C/D	1.0/1.0/2.1/0.5
F2	A/B/C/D	1.0/1.0/1.9/0.25
F3	A/(B + C)/D	1.0/2.7/0.17
F4	A/(B + C)/D	1.0/3.0/0.3
F5	A/(B + C)/D	1.0/3.0/0.2
F7	A/(B + C)/D/E/F	1.0/3.3/0.2/0.3/1.75

D ratio in the NMR spectrum to the sulfone content of the molecule. This rationale was applied to those fractions known to be 100% acetylene terminated to yield the results shown in Table IX, from which it can be seen that F1, F2, and F3 are indeed ATS monomer, dimer, and trimer as earlier stated, and that fraction 7 contains 3 sulfones per molecule. By a simple manipulation of the proton ratios of Table 8, it can also be shown that the ATS fractions contain "extra" phenoxy groupings (as defined in Fig. 1) over and above those expected, were ATS and its component fractions to be formed only by the reactions discussed in the introduction to this text. To do so we simply constructed graphs relating the (B + C)/A proton ratios (as defined in Fig. 5) to extra phenoxy content. For example, the corresponding ratio for ATS monomer should be 3.0. If the molecule contained one extra phenoxy linkage the ratio would rise to 4.0 and so on. By these means we could show that ATS monomer contained an extra phenoxy content "x" (or  $[\text{O}]_x$ ) of 0.15, ATS dimer of 0.8, and ATS trimer of 1.0 rings per molecule. Lacking definitive knowledge, we have assumed that this extra functionality is a result of incorporation into the ATS molecule of resorcinol which we assume to have originated as an impurity in the sulfonyldiphenol feedstock. Applying this analysis to fraction 7 we arrive at an extra phenoxy

(or equivalent) content of 3.0 rings per molecule in comparison with ATS trimer (both containing three sulfones per molecule), supporting our contention that the material is no homolog of the regular ATS backbone.

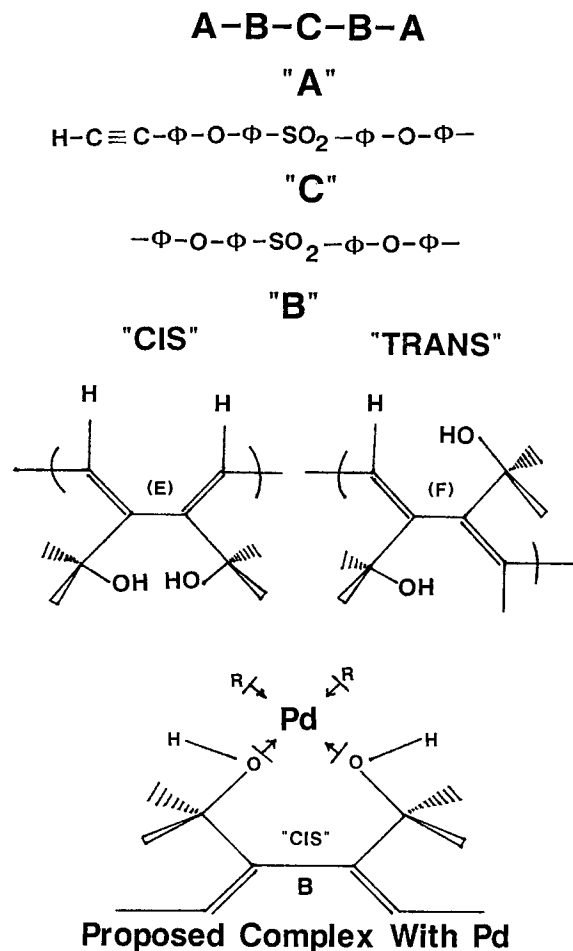
With regard to other information from the proton NMR spectra, we could, by comparison, show that fraction 5 was the incompletely hydrolysed "acetone adduct" of ATS monomer as defined in Figure 1. From the A/D proton ratio (as defined in Fig. 5) we estimated that approximately 32% hydrolysis of the adduct to the corresponding acetylene had occurred in this fraction. Fraction 4, on the other hand, was shown to consist of abnormal "acetone adduct" end groups which resisted definitive identification. The NMR spectrum of fraction 6 was to all intents and purposes identical to that of fraction 7 except for small differences in the proton ratios which could not, in any case, be recorded accurately due to the small amount of material available for analysis.

### Characterization of Fraction 7

Fraction 7, as the major palladium carrier in ATS-G and a hitherto unidentified component of the mixture, was subjected to detailed analyses which are recounted here to support our proposed structure for the material.

**Table IX Relationship of A/D Proton Ratios to Sulfone Content of ATS Fractions as Separated by Column Chromatography**

Material	A/D Proton Ratio	Sulfones/ Molecule	Comments
F1	1.9	1	ATS monomer
F2	4.0	2	ATS dimer
F3	6.0	3	ATS trimer
F7	6.0	3	Similar in this respect to ATS trimer



**Figure 6** Structure of fraction 7 as separated by column chromatography from the ATS-G mixture including proposed complex with palladium.

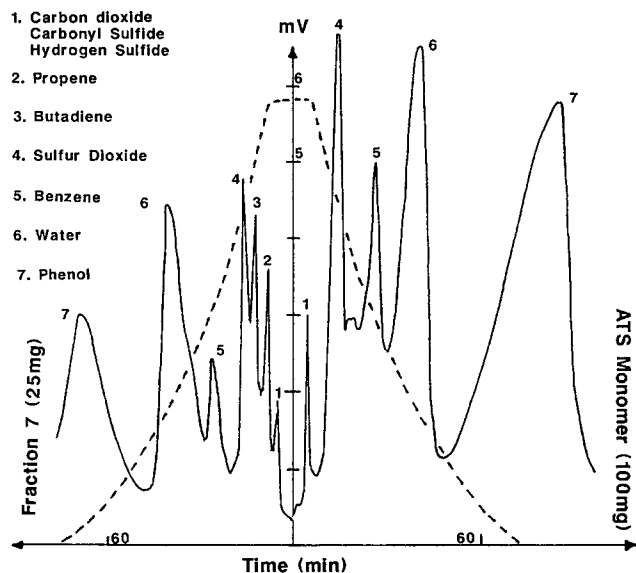
The material is highly colored and, therefore, conjugated; soluble in methylene chloride, chloroform, ethylene diamine, and ether solvents, but insoluble in carbon tetrachloride, benzene, toluene, and water. The material was shown by TLC to be polar or highly polarizable, and by SEC to consist of one component of  $EHV = 1300$  cubic Å, along with traces of impurities. Atomic absorption spectroscopy showed it to be able to efficiently chelate palladium and to be the major carrier of that metal in ATS-G. The metal could be removed from fraction 7 by extraction of the fraction with water after deposition onto silica gel, and is, therefore, probably complexed rather than bound to the molecule through covalent bonds. The material was also shown to be stable to rather severe base hydrolysis, and, therefore, not to contain the normal acetone adduct linkage. From joint application of IR and proton NMR spectroscopy, fraction 7 was shown to

be 100% acetylene terminated, to contain three sulfones per molecule, and three more phenoxy (or their equivalent) than ATS dimer, along with two deshielded gem dimethyl sites. The material was also shown to contain both free- and hydrogen-bonded hydroxyls. The carbon 13 NMR spectrum of fraction 7 in the region of 100–200 ppm was similar to that of the other fractions with the addition of a strong, protonated carbon signal at 125.3 ppm which could not be assigned to a normal carbon site of the ATS molecule. In addition, fraction 7 produced signals generated by saturated protonated carbons at 30.1 ppm designated as "E," at 30.3 ppm designated as "F," and deshielded unprotonated carbons at 67.8 ppm.

On the basis of these results, we have proposed a most probable structure for fraction 7 which is illustrated in Figure 6, in which the moieties A, B, and C are linked as A-B-C-B-A. Essentially, we propose that fraction 7 is the abnormal coupling product of three ATS monomers on the palladium catalyst. This structure satisfies all the requirements of the previous discussion. For example, the *cis* and *trans* linkages of the bridging group would contribute to the hydrogen-bonded and free hydroxyls, while the requirements of three sulfones per molecule and the requirements of three phenoxy content would be met by the contribution of the vinylic protons and the extra phenoxy to the proton ratios. From the proton NMR spectra of the material and the ratio of peaks E/F we could estimate a *cis/trans* ratio of 14/85 for the bridging functionality. The calculated  $A/(B + C)/D/(E + F)$  ratios for this proposed structure are 1.0/3.33/0.16/2.00 which agree well with the ratios measured. We assume that palladium is complexed to the *cis* form of the compound.

Supporting evidence for this structure may be had from an analysis of the products of thermal degradation of fraction 7. To this end we heated a sample of fraction 7 to 1020°C in the thermal volatilization analysis (TVA) assembly, and collected the condensable volatile products of degradation for separation by sub-ambient thermal volatilization analysis (SATVA). In Figure 7 we compare the SATVA traces of products from fraction 7 and from ATS monomer which had been degraded under identical conditions, from which can be seen the close similarity of condensable volatile product distributions with the exception of butadiene and propene, present in the product distribution from fraction 7 and absent from the corresponding products from ATS monomer. (We degraded a larger sample of ATS monomer, to emphasize small peaks in the SATVA trace. Even so, we could not detect any propene or

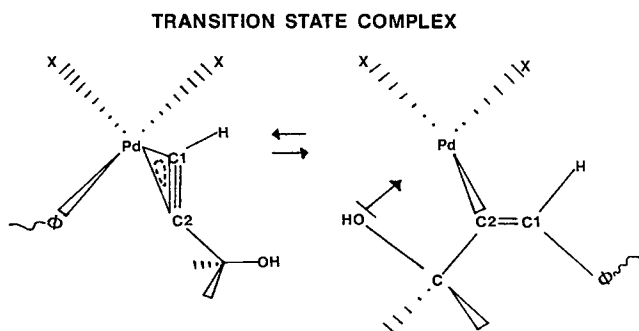




**Figure 7** A comparison between the condensable volatile products of programmed degradation to 1020°C of ATS monomer and fraction 7, as separated by column chromatography from the ATS-G resin mixture. Full line: Pirani output (mV); broken line: (-) thermocouple output (trap temperature).

butadiene.) We propose that these extra species are formed by the decomposition of the vinyl acetone linkage of the latter.

Our proposed origin of fraction 7 is illustrated in Figure 8. In the illustration we propose that the X's represent bromines and that  $\phi$ - represent the terminal benzene of a diphenoxylated sulfonyl diphenol molecule (minus the bromine which may occupy one of the "X" positions on the complex). We assume that the rate determining step in the formation of the acetone adduct probably involves the removal of the electron-deficient H<sub>1</sub> atom by a halogen ligand to form HBr, increasing the electron density on C<sub>1</sub> and promoting the reformation of a carbon-carbon

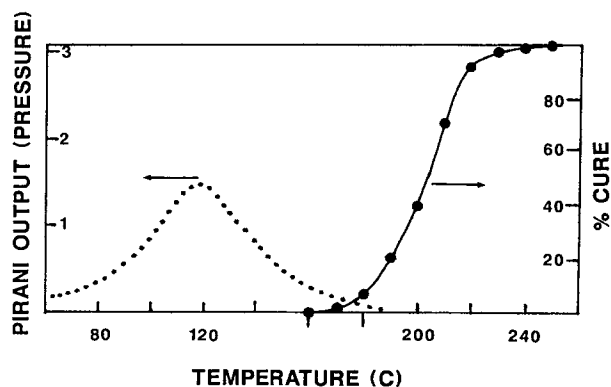


**Figure 8** Proposed transition state complex in the synthesis of the acetone adduct intermediate of ATS resin.

bond with subsequent expulsion of the adduct from the complex. If halogen is unavailable, then a C<sub>2</sub>-C<sub>2</sub> bond forming reaction would produce instead the vinyl acetone adduct linkage. Molecules which contain one such linkage would be expected to be more plentiful than those containing two such linkages. As the situation is reversed here, with fraction 7 being more plentiful than fraction 6, we can only assume that the dimer is quantitatively removed from the mixture during synthesis at the diethylamine extraction step of the product work up.

### Solvent and Other Condensable Volatile Components of the ATS-G Mixture

It is common knowledge that the extent of vaporization of a substrate (all other parameters being equal) is a function of ambient pressure. For this reason it came as no surprise that solvents *and* some higher molecular weight materials are evolved on heating a thin film of ATS pre-polymer prior to its vitrification. As stated previously, we intended to characterize this evaporated fraction in an attempt to gain some fresh insight into the composition of the ATS-G mixture and reasonably pure fractions of ATS monomer, dimer, and trimer previously isolated from that mixture by column chromatography. As a preliminary, we first ascertained the proportions of material evaporated from well-defined thin films of uncured resin by programmed heating under high vacuum conditions. Torsion impregnated cloth analysis (TICA) measurements<sup>7</sup> had shown that ATS-G resin vitrifies at about 19% conversion to cured resin. We assume here that solvent is efficiently removed from the resin in thin film form up to the gel point. In Figure 9 we plot both the rate



**Figure 9** A comparison between the solvent emission curve from ATS-G resin heated at 5°C/min in thin film form under high vacuum, and the conversion curve to cured resin as measured by DSC under the same conditions.

**Table X Gravimetric Product Distributions for the Programmed Cure Cycles of ATS-G, ATS Monomer, and ATS Dimer Under High Vacuum Conditions**

Material	Film Thickness ( $\mu\text{m}$ )	Weight % Volatilization	Weight % High Molecular Weight Material	Weight % Solvent
ATS-G	95	7.2	5.7	1.5
ATS monomer	95	17.4	12.3	5.1
ATS dimer	95	$\cong 1$	Negligible	Negligible
ATS trimer	95	Negligible	Negligible	Negligible

curve for solvent removal and the resin conversion curve as measured by DSC at the same heating rate, from which it can be seen that the two do not significantly overlap. As such, solvent may be assumed to be efficiently removed from thin films of the resin at a heating rate of  $5^\circ\text{C}/\text{min}$  prior to its vitrification.

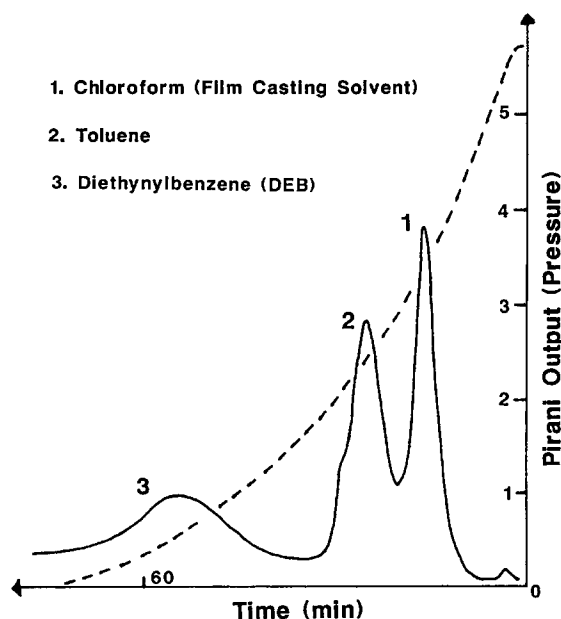
Gravimetric product distributions for the programmed cure cycles of ATS-G, ATS monomer, and ATS dimer are shown in Table X. Solvent levels were estimated as the difference between the mass lost by the resin and the mass of oligomeric material condensed onto the internal cold finger in the vacuum line. As expected, ATS monomer with its lower molecular weight, is more efficiently evaporated in thin film form than higher molecular weight dimer, trimer, or ATS-G itself, which contains a proportion of dimer and trimer. Perhaps as a result of its room temperature "tack and drape," ATS monomer was also shown to contain more solvent than the other fractions. ATS dimer and trimer, both recovered after fractionation and lyophilization as stable fine powders, did not contain any appreciable quantity of solvent, nor did they themselves evaporate to any extent on heating.

It must be noted that the extent of evaporation from ATS-G or ATS monomer is inversely related to the film thickness used in the experiment. For example, 3.7 wt % and 5.7 wt % of high-boiling point material was evolved from ATS-G upon heating, under otherwise identical conditions, as films approximately  $240\ \mu\text{m}$  and  $95\ \mu\text{m}$  thick respectively.

Solvents and other low molecular weight components evolved from ATS-G were collected on the vacuum line and separated by SATVA fractionation to yield the pressure curve shown in Figure 10. Components of the mixture were identified by gas phase infrared spectroscopy and by proton NMR spectroscopy of the condensed liquids. Toluene, the major component identified by these means, is the incompletely removed solvent of the last stage of synthesis of the resin, while diethynyl benzene is

the reaction product of acetylations of excess *m*-dibromobenzene in the reaction mixture. By NMR spectroscopy we estimated the toluene level in the material as about 1.2% and the diethynyl benzene level as about 0.3% of the mixture.

Solvent evolved from ATS monomer was shown to be benzene by NMR spectroscopy. Although less material was removed from ATS dimer, the SATVA technique proved sensitive enough to confirm the presence of benzene as the major component. These results were expected, as benzene was the solvent from which all fractions were recovered by "freeze drying" after column fractionation. (As expected, noncondensable volatile products were absent from this product distribution).



**Figure 10** SATVA record of solvents removed from ATS-G under high vacuum conditions by programmed heating at  $5^\circ\text{C}/\text{min}$  to  $234^\circ\text{C}$ . Full line: Pirani output (mV); broken line: (-) thermocouple output (trap temperature).

**Table XI Gravimetric Analysis of Subfractions Isolated by Preparative TLC from the High Boiling Point Fraction Evolved From ATS-G and ATS Monomer on Programmed Heating Under High Vacuum Conditions**

Subfraction	$R_f$ (CH <sub>2</sub> Cl <sub>2</sub> /SiO <sub>2</sub> )	Weight % of Uncured Polymer	
		ATS-G	ATS Monomer
1	0.7	0.4	≡ 0.1
2	0.3	2.7	11.9
3	0.0	2.7	< 0.1

### Higher Molecular Weight Volatiles

Oligomeric condensates were separated into three subfractions by preparative TLC. Subfractions were characterized by gravimetry, SEC, by IR, and NMR spectrometry, and by CIMS.

Preweighed subfractions were isolated by preparative TLC, recovered in high yield (> 90 wt %), and examined by gravimetry to yield the results reproduced in Table XI. A number of similar reference compounds, separated under identical conditions, provided a data base for identification of the gross composition of solute fractions. By such comparisons, subfraction 1 was shown to be composed of polyphenylethers, subfraction 2 to consist of polyphenylethers containing one sulfone group, and subfraction 3 to be composed of polyphenylethers, end capped by two hydroxyl groups, which in addition may also contain one or more sulfone linkages.

As indicated in Table XI, high boiling point material volatilized from ATS-G on curing, consists of an approximately 50/50 mixture (by weight) of subfractions 2 and 3 while that volatilized from ATS monomer was shown to be composed predominantly of subfraction 2 (> 99 wt %) with trace quantities of subfractions 1 and 3.

The effective hydrodynamic radii (EHR), in tetrahydrofuran (THF), of components of subfractions 1-3, isolated by preparative TLC from oligomers from ATS-G, were obtained by SEC. The results of this analysis are reproduced in Table XII. As with the TLC experiments discussed above, some information could be gleaned from this experiment on the basis of comparisons with reference compounds, in this instance, of hydrodynamic radii.

On the basis of this type of comparison, subfraction 1 (120 Å) is probably composed of simple aromatics which contain two benzene rings. By a similar analysis, subfraction 2 is almost certainly shown to contain relatively pure ATS monomer (310 Å).

The major component of subfraction 3 contains one benzene ring (55 Å), a smaller component contains two benzene rings (120 Å), and an even smaller component (310 Å) is probably residual ATS monomer, incompletely fractionated by the TLC experiment.

The same subfractions were examined by IR spectroscopy as thin films on sodium chloride salt plates. The IR spectrum of subfraction 1 showed it to contain aromatic material (3080 cm<sup>-1</sup>), terminal acetylenes (3300 cm<sup>-1</sup>), saturated material (2940 cm<sup>-1</sup> and 2860 cm<sup>-1</sup>) and phenyl ethers (1260 cm<sup>-1</sup>). Infrared spectra of subfraction 2 from ATS-G and ATS monomer both indicated the presence of small concentrations of saturated material (2960 cm<sup>-1</sup>, 2930 cm<sup>-1</sup>, and 2860 cm<sup>-1</sup>), terminal acetylenes (3300 cm<sup>-1</sup>), aromatic material (3080 cm<sup>-1</sup>), phenyl ethers (1250 cm<sup>-1</sup>) and sulfone bridges [ $\approx$  1300 cm<sup>-1</sup> (doublet)], [ $\approx$  1125 cm<sup>-1</sup> (doublet)]. The IR spectrum of subfraction 3 indicated that it contained aromatic material (3070 cm<sup>-1</sup>), hydroxyl groups [3400 cm<sup>-1</sup>, (broad)], a small concentration of terminal acetylenes (3300 cm<sup>-1</sup>), and phenoxy linkages (1190 cm<sup>-1</sup>, 1120 cm<sup>-1</sup>).

**Table XII SEC Analysis of Subcomponents Isolated by Preparative TLC From the High Boiling Point Fraction Evolved From ATS-G on Programmed Curing Under High Vacuum Conditions**

Subfraction	$R_f$ (CH <sub>2</sub> Cl <sub>2</sub> /SiO <sub>2</sub> )	Effective Hydrodynamic Radius (EHR)
1	0.7	120
2	0.3	310
3	0.0	55 (major) 120 (minor) 310 (minor)

**Table XIII Chemical Ionization Mass Spectroscopy (CIMS) of Subfractions Isolated by Preparative TLC from the High Boiling Point Fraction Evolved from ATS-G and ATS Monomer on Programmed Curing Under High Vacuum Conditions**

Subfraction	$R_f(\text{CH}_2\text{Cl}_2/\text{SiO}_2)$	Parent Ion Masses (amu)	
		ATS-G	ATS Monomer
1	0.7	218	218
2	0.3	—	386 (minor) 450 (major)
3	0.0	110 (major) 278 (minor)	—

The same subfractions isolated by preparative TLC were examined by proton NMR spectroscopy. Data relating to "subfraction" 1 from both materials is not reported due to a lack of sufficient material for analysis.

With regard the proton NMR spectra of subfractions 2 from ATS-G and ATS monomer, the proton doublets ( $\approx 8$  ppm, "A"), multiplets ( $\approx 7.5$  ppm–7.0 ppm, "B"), and singlets ( $\approx 3.1$  ppm, "C"), so observed are characteristic of those produced by uncured ATS molecules. The A/B/C proton ratios for both subfractions are 1.0 :  $\approx 3.2$  : 0.5—a ratio characteristic of ATS monomer as produced by the Gulf Chemicals, Inc. process. The subfraction from ATS-G also contained a small concentration of unidentified saturated material.

In the case of subfraction(s) 3, the broad multiplet at about 7.8 ppm and the sharp multiplet centered on 7.6 ppm (ratio 1 : 3) are characteristic of those produced by resorcinol or *m*-hydroxyphenol. Other components of the mixture were present in

quantities too small for detection by the continuous wave spectrometer used in this work.

CIMS spectra of preparative TLC subfractions were obtained by programmed warming of a small quantity of material inside the spectrometer and recording parent masses as species evaporated into the ion chamber. Parent ion masses so obtained are recorded in Table XIII. (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 quantity, may evolve between scans. In addition, the possibility exists that a fraction of material may crosslink on the probe to form an involatile residue.)

### Structural Assignments

Structural assignments of subfractions isolated by preparative TLC were made by combining the re-

**Table XIV Composition of Subfractions Isolated by Preparative TLC From the High Boiling Point Fractions Evolved From ATS-G and ATS Monomer on Programmed Curing Under High Vacuum Conditions**

Subfraction	$R_f(\text{CH}_2\text{Cl}_2/\text{SiO}_2)$	Most Probable Structure	
		ATS-G	ATS Monomer
1	0.7	*— $\Phi$ O $\Phi$ —* <sup>a</sup>	*— $\Phi$ O $\Phi$ —*
2	0.3	*— $\Phi$ O $\Phi$ SO <sub>2</sub> $\Phi$ O $\Phi$ —*	*— $\Phi$ O $\Phi$ SO <sub>2</sub> $\Phi$ O $\Phi$ —* *— $\Phi$ O $\Phi$ $\Phi$ O $\Phi$ —* (minor) <sup>f</sup>
3	0.0	HO— $\Phi$ —OH HO— $\Phi$ $\Phi$ —OH HO— $\Phi$ $\Phi$ O $\Phi$ —OH *— $\Phi$ O $\Phi$ SO <sub>2</sub> $\Phi$ O $\Phi$ —*	(Major) <sup>b</sup> (Minor) <sup>c</sup> (Minor) <sup>d</sup> (Minor) <sup>e</sup>

Symbols: \*: terminal acetylene;  $\Phi$ : phenyl ring; OH: hydroxyl group; and  $\Phi$ —O— $\Phi$ : phenyl ether linkage.

<sup>a-f</sup> Items for comment in the text (structural assignments not immediately obvious from previous discussion).

**Table XV Composition of the ATS-G Resin Mixture**

Component	Wt % of the Mixture
ATS monomer	68
ATS dimer	15
ATS trimer	4
Fraction 4	2
Fraction 5	0.6
Fraction 6	0.4
Fraction 7	5
DEDPE	0.1
Toluene	1.2
DEB	0.3
Resorcinol	3

sults of the previous analyses. These assignments are illustrated in Table XIV.

Our findings seem to indicate that the major component of subfraction (a) was shown by SEC to possess a backbone containing two benzene rings. The only parent ion detected by CIMS suggested diethynyldiphenylether (DEDPE) as the major component of that mixture. Although saturated material was detected in some quantity by infrared spectroscopy, we must conclude that none is included with a polyphenylether backbone; it would, as such, had possessed a volatility similar to that of DEDPE and would have evaporated from the probe at a similar time to be detected in the same scan. The DEDPE was probably produced by an Ullman ether condensation of two *m*-dibromobenzenes onto water, with subsequent acetylation of the product. The presence of component (b) was confirmed by a joint application of IR and NMR spectroscopy, SEC, and CIMS in conjunction with TLC retention index ( $R_f$ ). The presence of component (c) was confirmed through its hydrodynamic volume as measured in the SEC experiment, and by its TLC retention index. Component (d) was confirmed by its parent ion mass and retention index in the TLC experiment. Component (e) was identified through SEC and IR spectroscopic analysis, and (f), through its parent ion mass as measured by CIMS.

#### Composition of the ATS-G Resin Mixture

By combining the results of the column chromatographic separations with the results of the flash dis-

tillations, we were able to propose a quantitative compositional analysis of the ATS-G resin mixture. A summation of the proportions stated will not equal 100%, due to our decision to round off each number to the nearest percent, except where such would introduce unwarranted relative errors (e.g., by rounding off 0.6% to 1% or 0.4% to 0%). This information is reproduced in Table XV.

## CONCLUSIONS

An acetylene-terminated sulfone resin mixture has been subjected to a reasonably detailed compositional analysis as a preliminary to a subsequent examination of resin cure and stability to be reported in Part II of this paper. By so doing we identified some side reactions of synthesis and isolated the major resin impurities for subsequent studies of their effect on the properties of the cured resin.

Although it may appear from this report that ATS-G is an exceedingly complex mixture, we must restate that in reality, it is less complex than most resin prepregs of interest to the aerospace industry.

The authors would like to acknowledge the technical assistance of Mr. J. Henes, and of Mr. R. Grant who fabricated glassware for this study. W. T. K. Stevenson would like to thank the National Research Council for its funding of his Research Associateship at Wright Patterson Air Force Base for the duration of this work.

## REFERENCES

1. S. Amdur, A. T. Y. Cheng, C. J. Wong, P. Ehrlich, and D. R. Allendoerfer, *J. Polym. Sci. Polym. Chem. Ed.*, **16**, 407 (1978).
2. J. J. Ratto, P. J. Dynes, and C. L. Hamermesh, *J. Polym. Sci. Polym. Chem. Ed.*, **18**, 1035 (1980).
3. P. M. Hergenrother, *J. Macromol. Sci. Rev. Macromol. Chem.*, **C19**, 1 (1980).
4. J. J. Harrison and C. M. Selwitz, AFML-TR-79-4183.
5. I. C. McNeill, in *Developments in Polymer Degradation—1*, N. Grassie, Ed., Applied Science, London, 1977, p. 43.
6. I. C. McNeill and W. T. K. Stevenson, *Polym. Deg. Stability*, **10**, 247 (1985).
7. C. C. Kuo and C. Y-C. Lee, AFWAL-TR-82-4037.

Received March 7, 1990

Accepted April 17, 1990