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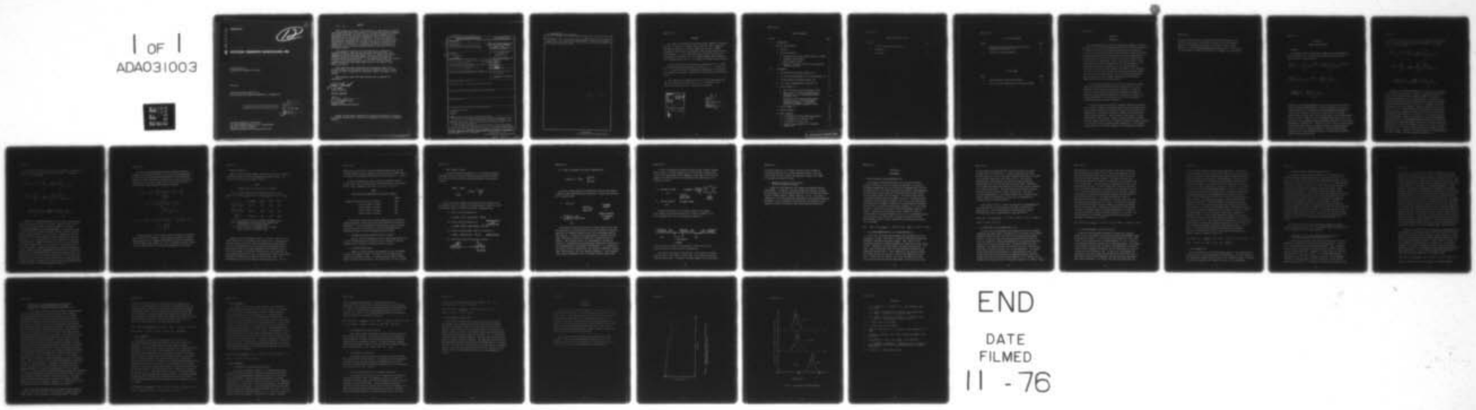

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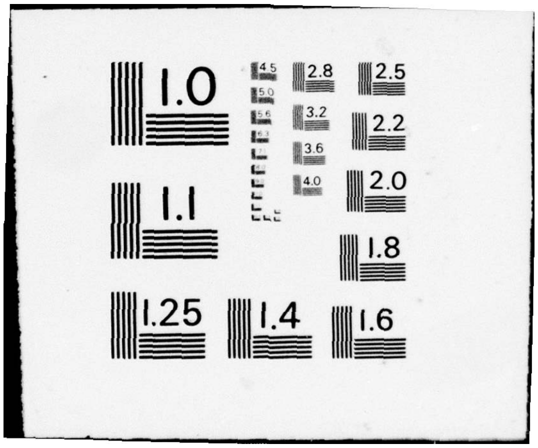
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ACETYLENE TERMINATED QUINOXALINES ATQ

POLYMER BRANCH
NONMETALLIC MATERIALS DIVISION

JUNE 1976

TECHNICAL REPORT AFML-TR-76-71
FINAL REPORT FOR PERIOD NOVEMBER 1974 - OCTOBER 1975

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO 45433

NOTICE

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, Work Unit No. 73400469, "Polymers for Matrix Resins and Adhesives with Improved Processibilities and Performance". It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the Project Scientist.

This report has been reviewed by the Information Office (IO) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nations.

This technical report has been reviewed and is approved for publication.

Fred E Arnold

F. E. ARNOLD
Project Scientist

FOR THE COMMANDER

R.L.Van Deus

R. L. VAN DEUSEN, Chief
Polymer Branch
Nonmetallic Materials Division

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A series of acetylene terminated phenylquinoxaline oligomers have been prepared which cure by addition, without the evolution of volatiles. The synthesis utilized the novel terminal acetylene end-capping reagent, 3-(3,4-diaminophenoxy)phenyl acetylene.

The end-capped oligomers were soluble (20-30%) in low boiling organic solvents and exhibited a high degree of flow at their softening temperatures. Thermal analytical data obtained on the oligomers indicated initial softening in the vicinity of 160°C and a strong polymerization exotherm (continued)

012 320

maximizing at 274°C. Cured samples (8 hrs at 280°C) exhibited Tg's of approximately 320°C. Mass spectrometry-thermogravimetric analysis of the polymers demonstrated that no volatiles were emitted during cure, and that decomposition of the resins initiated at 465°C.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734004, Work Unit No. 73400469, "Polymers for Matrix Resins and Adhesives with Improved Processibilities and Performance." It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFML Project Scientist.

The work described in this report was conducted by Dr. R. L. Kovar of the Univeristy of Dayton Research Institute, Dr. G. F. L. Ehlers and Dr. F. E. Arnold of the Air Force Materials Laboratory. The manuscript was released by the authors in March 1976 for publication as a technical report.

The authors wish to thank Mr. Kurt R. Fisch for obtaining the DSC, TMA and isothermal aging data, and Dr. Ivan J. Goldfarb for mass spectrometry-thermogravimetric analyses of the polymers.

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SECTION I

INTRODUCTION

The polycondensation of aromatic tetraamines and aromatic bis-benzils has been found to give rise to phenylated quinoxaline polymers (Reference 1) of potential utility as high temperature matrix resins and adhesives. In addition to possessing excellent thermal stability, these high molecular weight polymers also exhibit moderate glass transition temperatures and desirable solubility-fusibility characteristics that would facilitate their processing. Nevertheless, further consideration reveals certain drawbacks which hinder the development of the class of polymers. The elimination of volatile by-products during the polymerization via condensation reactions creates problems with respect to void formation in the cured resin, while the inherent structure of the molecular backbone seriously limits the number of possible cure reactions which might be used to raise the Tg of the polymer without causing corresponding deleterious effects on the thermal stability.

To overcome such difficulties, we set out to synthesize a readily processable polyphenylquinoxaline system that would cure to a high performance resin without the evolution of volatiles. A reactive oligomer approach was taken with special attention being given to obtaining a useful compromise between the synthesis of oligomer, the processing parameters, the conditions of cure, and the ultimately attained thermal and mechanical properties.

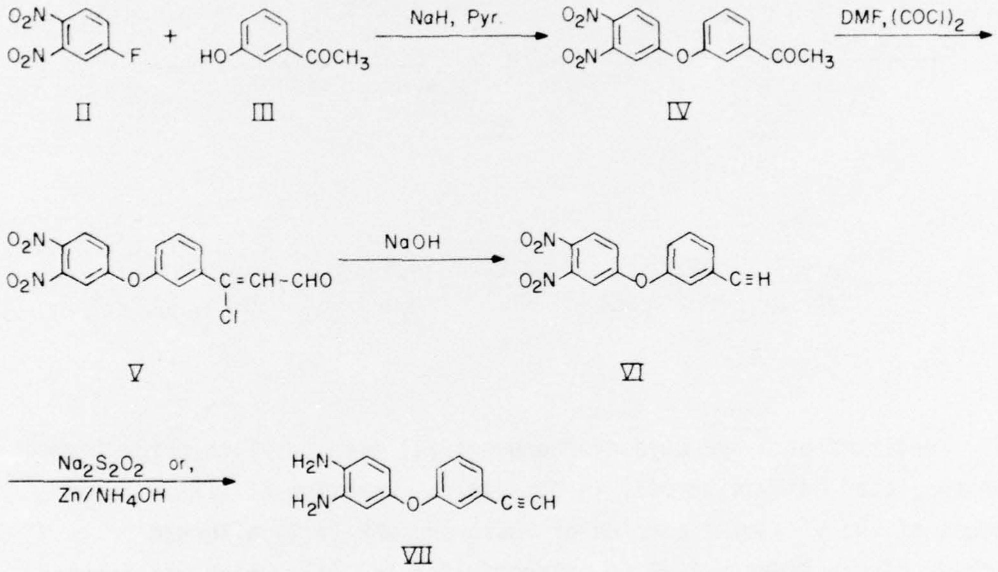
The polymer system selected was an acetylene terminated quinoxaline (ATQ) oligomer expected to have good solubility and flow properties and to be capable of undergoing an addition curing reaction under moderate temperature-time conditions to provide a thermally stable product with useful strength properties. The ATQ polymer systems appear to offer advantage over other reactive oligomer systems utilizing unsaturated end-caps, namely stability over 1,3-dipolar cycloaddition systems (Reference 2), and solubility over polyimide systems (Reference 3). With respect to the latter, the use of ATQ oligomers of varying molecular weights is not restricted by solubility limitations of the parent polymer system. A potential problem associated with the synthesis of the end-capping agent for ATQ oligomers was resolved in this work by the successful synthesis of 3-[3,4-diaminophenyoxy]phenyl acetylene (VII). This provides for the synthesis of a family of reactive ATQ oligomers for investigation.

SECTION II

RESULTS AND DISCUSSION

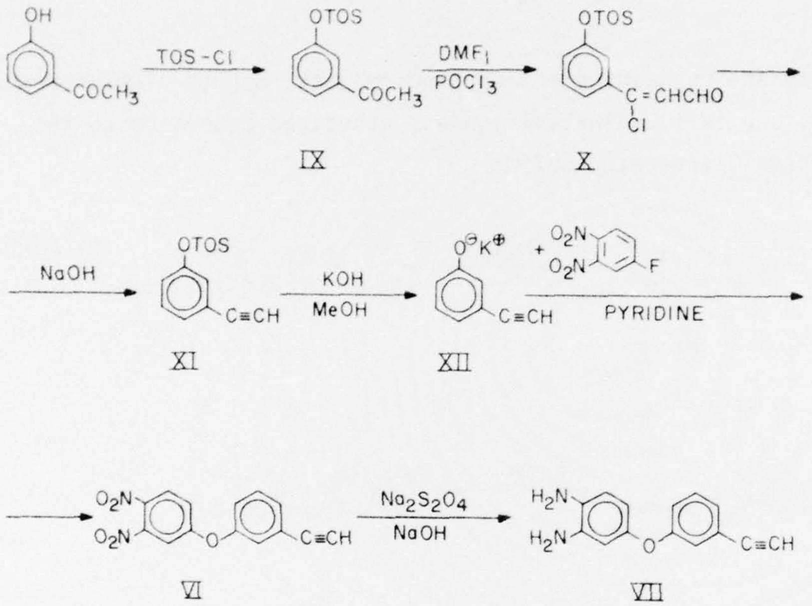
1. SYNTHESIS

The acetylene containing end-capping reagent, 3-[3,4-diaminophenoxy] phenyl acetylene (VII), initially was synthesized according to the reaction scheme illustrated below:



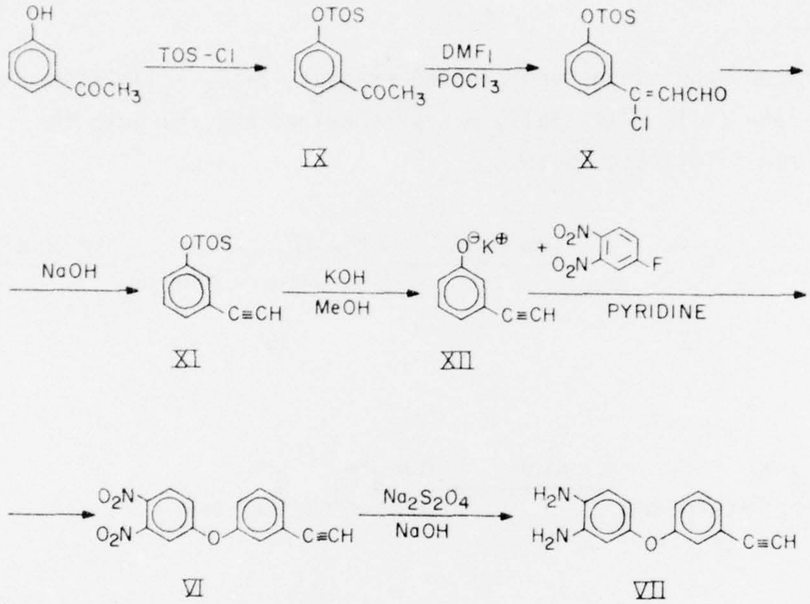
Treatment of 3-hydroxyacetophenone (III) with sodium hydride in pyridine solution formed the phenolate anion, which upon reaction with 1-fluoro-3,4-dinitrobenzene (II) afforded 3-[3,4-dinitrophenoxy]acetophenone (IV) in 60% yield. Reaction of (IV) with an excess of the 1:1 Vilsmeyer complex of $POCl_3$ and DMF gave 3-[3,4-dinitrophenoxy]-α-chlorocinnamaldehyde (V) in 73% yield. Addition of hot 0.5N aqueous sodium hydroxide to a hot solution of (V) in dioxane produced the acetylene derivative, 3-[3,4-dinitrophenoxy]phenyl acetylene (VI). Reduction of (VI) to the end-capping reagent (VII) was achieved by the use of sodium dithionite in aqueous methanol solution or by zinc in ammonium hydroxide. The diaminophenoxyphenyl acetylene (VII) slowly decomposed even under nitrogen and was therefore prepared immediately before use.

An improved synthetic route to (VII) was subsequently devised which offered significantly higher yields of final product. The reaction scheme is illustrated below:



Treatment of 3-hydroxyacetophenone (III) with tosyl chloride formed the tosylated derivative (IX) in 83% yield. Reaction of (IX) with an excess of the Vilsmeyer complex of $POCl_3$ and DMF (1:1) afforded α-chlorocinnamaldehyde-3-yl-(p-toluenesulfonate) (X), which was reacted in crude form with 0.5N sodium hydroxide solution, producing 3-ethynylphenyl(p-toluenesulfonate) (XI) in 76% yield. Treatment of (XI) with two equivalents of KOH in methanolic solution yielded a mixture of the potassium salt of p-toluenesulfonic acid and compound (XII), potassium 3-ethynylphenolate. Removal of solvent by co-distillation with benzene and subsequent lyophilization left a mixture of the potassium salts as a dry, white powder. Addition of pyridine and 3,4-dinitrofluorobenzene (1 mole) formed 3-[3,4-dinitrophenoxy]phenyl acetylene (VI) in 84% yield. Reduction to the diaminophenoxyphenyl acetylene end-capping reagent (VII) achieved 85% by reaction of a methanol solution of (VI) with a ten molar equivalent of a 1:1 mixture of sodium dithionite and a sodium hydroxide in aqueous solution. Compound (VII), being unstable for prolonged periods even under nitrogen, was prepared immediately before use.

An improved synthetic route to (VII) was subsequently devised which offered significantly higher yields of final product. The reaction scheme is illustrated below:



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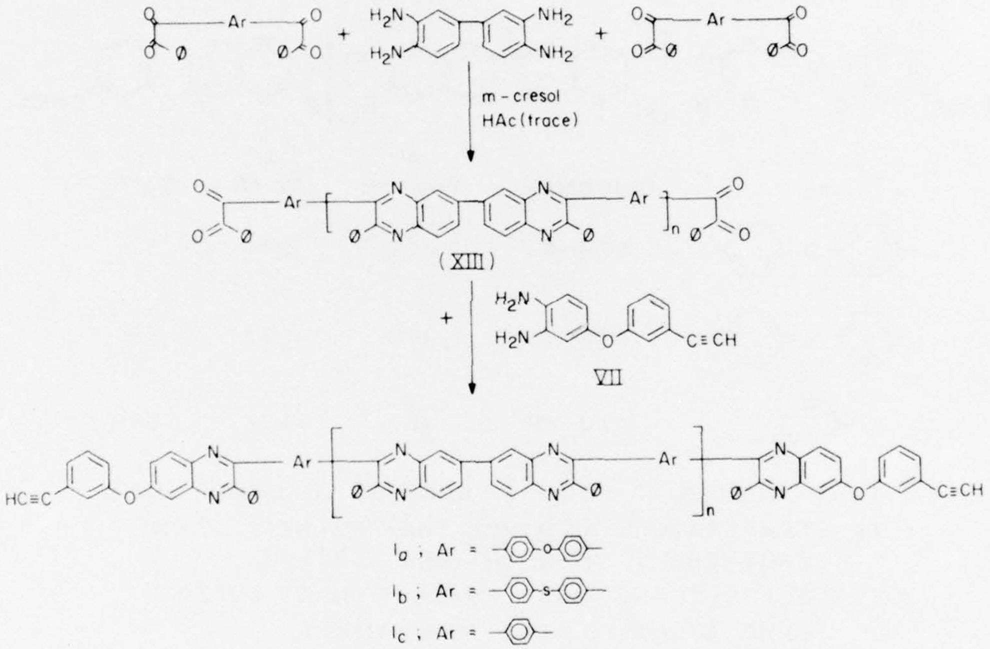
The benzil end-capped phenylquinoxaline oligomers (XIII) were prepared by the dropwise addition of a solution of diaminobenzidene in m-cresol to a solution containing twofold excess of the appropriate aromatic bis-benzil dissolved in m-cresol with a trace of acetic acid. The addition of end-capping reagent (VII) to the solution of (XIII) yielded the acetylene terminated quinoxaline oligomers.



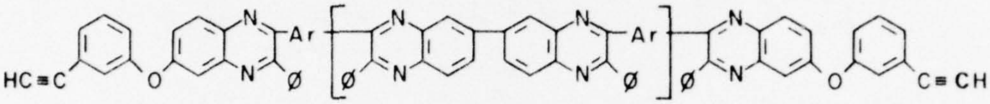
Dropwise addition of the reaction mixture, from above into methanol precipitated the ATQ oligomers. Purification was achieved by repeated reprecipitation of the oligomers from methylene chloride into methanol. The ATQ oligomers were soluble (20 - 30%) in low boiling organic solvents such as methylene chloride, chloroform tetrahydrofuran, and dioxane.

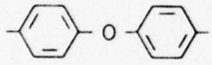
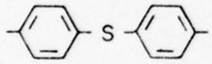
2. PHYSICAL PROPERTIES

Samples of the three ATQ oligomers were tested by means of differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). The results of the study are tabulated in Table 1:

TABLE 1

THERMAL ANALYTICAL DATA OF ATQ SYSTEMS



Ar	OLIGOMER	Tsoft °C[a]	Tp °C[b]	Tg °C[c]
	ATQ-O	159	274	321
	ATQ-S	144	277	331
	ATQ-PP	161	277	340

a. Tsoft = SOFTENING POINT OF UNCURED OLIGOMER (DSC).

b. Tp = TEMPERATURE AT WHICH THE POLYMERIZATION EXOTHERM IS AT A MAXIMUM (DSC).

c. Tg = GLASS TRANSITION TEMPERATURE OF CURED (8 HR. AT 280°C) POLYMER (TMA).

Analysis of the ATQ oligomers by DSC (Δ = 20°C/min.) shows an initial strong baseline shift attributed to the softening point of the oligomers, a strong exotherm initiating at 200°C and maximizing at approximately 275°C for the polymerization of the terminal acetylene groups, while a weak baseline shift at the higher temperatures, associated with the Tg of the cured polymer, could only be detected on DSC scans with the cure being accomplished during the scan. An exception was the ATQ-S pre-polymer, which gave a reproducible Tg signal on DSC, but none on TMA. The extrapolated onset of the DSC baseline shift was taken as Tg. For the determination of the glass transition temperature after cure, the TMA expansion (change of rate of expansion) and for penetration modes (point of highest rate of penetration) were used, also at a rate of T = 20°C/min.

To arrive at optimum the curing conditions indicated in Table 1 (eight hours at 280°C) cured pellets of ATQ-O were studied in more detail by TMA. Table 2 summarizes the results (averages of two runs).

TABLE 2

GLASS TRANSITION TEMPERATURES OF CURED ATQ-O SAMPLES

	Tg(°C)
Pellets Cured 2 hrs at 270°C, nitrogen	300
30 min at 380°C, nitrogen	312
2 hrs at 280°C, nitrogen	318
8 hrs at 280°C, nitrogen	321
8 hrs at 371°C, nitrogen	344

A curing time of eight hours at 280°C appeared to be a reasonable compromise between a maximum Tg and the lowest possible curing time and temperature. It could be assumed that these optional curing conditions would also apply to ATQ-S and ATQ-PP, since the same polymerization temperatures (Table 1) and curing mechanisms were involved.

a. Thermogravimetric-Mass Spectral Analysis (TGA-MS)

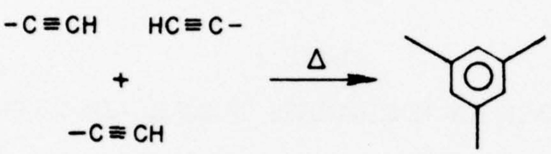
Analysis of the ATQ samples by means of TGA-MS demonstrated that no volatiles were emitted in the region of cure (200-300°C), and that decomposition of the resins initiated at 465°C (in vacuo).

b. Isothermal Aging Studies

Samples of the ATQ polymers were exposed to an air environment at 600°F for a number of hours. The results of the isothermal aging study are illustrated in Figure 1. Respective weight losses for ATQ-O. ATQ-PP, and ATQ-S after 150 hours in air at 600°F are, 12%, 22%, and 30%.

c. Model Compound Studies

Previous publications (References 2, 3) describing acetylene terminated polymers assumed that the cure reaction involved a simple trimerization of three terminal acetylene end-groups into an aromatic crosslink.



It was our opinion, however, that terminal acetylene groups could simultaneously react via a number of alternate routes in addition to the trimerization reaction, several of which are illustrated below:

(1) Glaser coupling (Reference 4):

$$2\ -\text{C}\equiv\text{CH} \xrightarrow{\Delta} -\text{C}\equiv\text{C}-\text{C}\equiv\text{C}- \xrightarrow{\Delta}$$

(2) Strauss coupling (Reference 5):

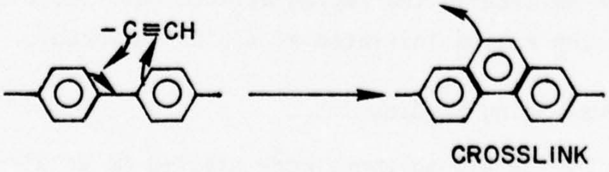
$$2\ -\text{C}\equiv\text{CH} \xrightarrow{\Delta} -\text{C}\equiv\text{C}-\text{CH}=\text{CH}- \xrightarrow{\Delta}$$

REARRANGEMENT
AND
AROMATIZATION

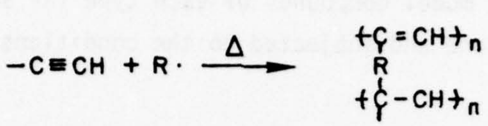
(3) Strauss or Glaser product reaction (Reference 6):

$$-\text{C}\equiv\text{CH} + -\text{C}\equiv\text{C}-\text{CH}=\text{CH}- \xrightarrow{\Delta} \text{AROMATIZATION}$$

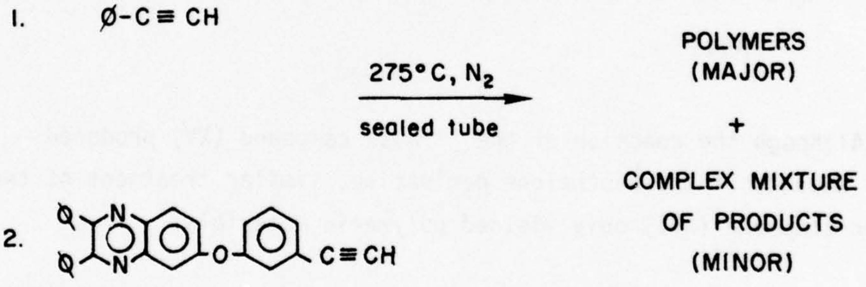
(4) Diels Alder reaction with polymer backbone:



(5) Linear or branched free radical polymerization:



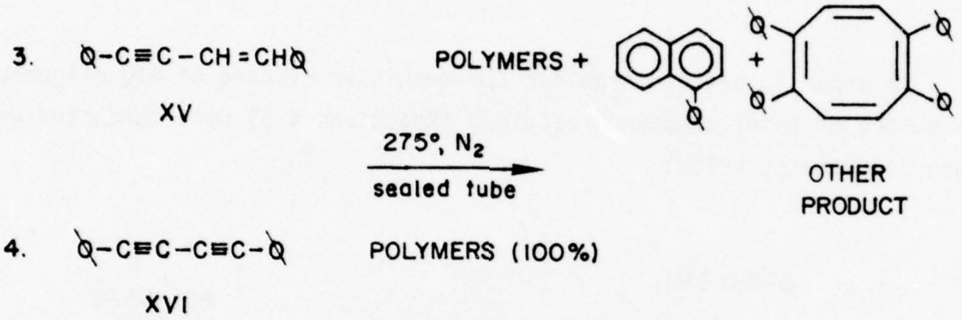
In order to better establish the mechanism of cure of ATQ oligomers, a number of model compound reactions (Reactions 1-5) were conducted which are illustrated below:



XIV

The reactions of phenyl acetylene and of model compound (XIV) under the conditions of cure did not give rise to the formation of significant quantities of trimerized products as the initially proposed mechanism had predicted. In addition to the major amounts of polymeric material (90%), there were isolated small quantities of complex mixtures of products. Mass spectral analysis of these materials indicated the presence of triphenylbenzenes and phenylated naphthalenes from Reaction 1, and correspondingly similar products from Reaction 2. As a comparison the reaction of phenyl acetylene as a 40% solution in benzene or methanol under high pressure at 220°C was reported (Reference 7) to give polymers (75%), phenyl naphthalenes (5%), and triphenyl benzene isomers (20%).

In order to determine the possibility that Strauss or Glaser linkages might initially be formed (mechanisms a or b) which then undergo further reaction and rearrangement, model compounds of each type (XV and XVI) were prepared from phenyl acetylene and subjected to the conditions of cure (Reactions 3 and 4).



Although the reaction of the Strauss compound (XV) produced small amounts of the napthalene derivative, similar treatment of the Glaser compound (XVI) only yielded polymeric materials.

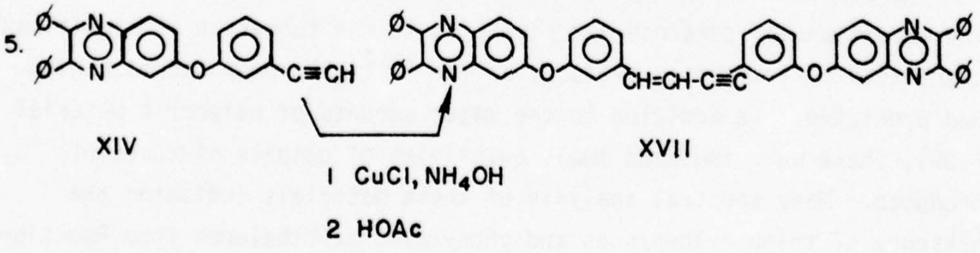


Figure 2 shows the results of DSC analysis of (XIV), (XVII), and an equimolar mixture of (XIV) and (XVII) (Reference 8).

The results from Figure 2 indicate that in the presence of terminal acetylene (XIV), model compound (XVII) reacts via a different mechanism than when heated alone. In general, the model compound studies described previously (Reactions 1-5) indicate that the strongly exothermic crosslinking reaction of the terminal acetylene group is much more complex than initially assumed, and apparently proceeds via a number of simultaneous mechanistic routes.

d. Mechanical Testing of Thin Film and Reinforced Composite Specimens

A number of hot-pressed thin film samples were prepared from the ATQ-0 polymer. In addition, specimens of graphite reinforced laminates were fabricated and tested along with the thin films for tensile strength, flexural strength, modulus, thermal stability, Tg, etc. The results (References 9, 10) were encouraging with respect to the polymers mechanical performance at high temperatures (450-500°F) and the retention of high temperature mechanical properties under adverse moisture conditions.

SECTION III

EXPERIMENTAL

1. 3-ACETYL-PHENYL (p-TOLUENESULFONATE) (IX)

To an aqueous solution containing 54.0 g (1.48 mole) of sodium hydroxide dissolved in 2500 ml of water was added 200 g (1.48 mole) of 3'-hydroxy-acetophenone, 280 g (1.48 mole) of p-toluenesulfonyl chloride, and 1500 ml of THF. The resulting mixture was stirred at room temperature for three hours, at which time the THF was distilled from the solution leaving a molten bottom layer of product. The flask was then cooled in ice causing solidification of the product to occur. The white solid was filtered by suction, washed with water, and air-dried. The crude product was crushed to a fine powder, dissolved in a minimum amount of methylene chloride, and the solution filtered rapidly through a 2" x 6" dry column of alumina, eluting with methylene chloride (approximately 2500 ml of eluate). Evaporation of the eluate in vacuo yielded 354 g (83%) of 3-acetyl-phenyl (p-toluenesulfonate) (IX), m.p. 52-3°C. Immediately before use, the material was dried at 100°C in vacuo for two hours, and the molten product cooled to a white crystalline solid which was pulverized to a fine powder.

Anal. Calcd. for $C_{15}H_{14}O_4S$: C, 62.05;H, 4.86. Found: C, 62.12; H, 4.80.

2. 3-(α-CHLOROCINNAMALDEHYDE)-yl-(p-TOLUENESULFONATE) (X)

A five-liter four-necked round-bottomed flask equipped with stirrer, thermometer, nitrogen inlet adapter, and equilibrated addition funnel was thoroughly flamed and purged with nitrogen. Then, 1000 ml of dry, Spectranalyzed Grade N, N-dimethylformamide was added and the flask cooled to 20°C. Phosphorus oxychloride ($POCl_3$) was added dropwise (310 g - 2.0 moles) under nitrogen with rapid stirring (exothermic) maintaining the temperature between 20-25°C. After completion of the addition, cooling was discontinued and the solution stirred at room temperature for one hour. At this point the solution in the flask was dark red in color. To the reaction flask was rapidly added 300 g (1.03 mole) of dry, solid

3-acetyl-phenyl (p-toluenesulfonate), and the solution stirred under nitrogen at 60°C for three hours. The dark yellow reaction mixture was then poured into a four-liter beaker containing two liters of ice-cold distilled water producing a clear, dark solution. Solid sodium bicarbonate was slowly added to the rapidly stirred solution until foaming ceased and a solid yellow precipitate had formed. Additional ice was added to complete precipitation of the product, and the suspension was stirred for two hours. The crude product was filtered by suction, washed with several portions of water, and air-dried. The crude α-chlorocinnamaldehyde-3-yl-(p-toluenesulfonate) thus isolated was used without further purification for the next step, the preparation of 3-ethynyl-phenyl (p-toluenesulfonate).

A pure sample of (X), m.p. 68-90°C was obtained by chromatography of the crude material on a dry column of silica gel, eluting with 2:1 hexane:CH_2 Cl_2. The infrared spectrum (film) between salt plates exhibited characteristic absorptions at, 2480 and 1655 cm^{-1}.

Anal. Calcd. for $C_{16}H_{13}ClO_4S$: C, 57.06; H, 3.89; Cl, 10.53. Found: C, 56.95; H, 3.86; Cl, 10.11.

3. 3-ETHYNYL-PHENYL (p-TOLUENESULFONATE) (XI)

To a five-liter round-bottomed flask equipped with stirrer, condenser, thermometer and powder funnel, was added 20.5 g (0.74 mole) of solid sodium hydroxide, 1500 ml of water, and 1000 ml of p-dioxane (freshly opened bottle). The rapidly stirred mixture was heated to 80°C at which time 125 g (0.37 mole) of α-chlorocinnamaldehyde-3-yl-(p-toluenesulfonate) was added at once through the powder funnel, the funnel being rinsed with p-dioxane. The resulting mixture was stirred at 80°C for 15 minutes, at which time the flask was cooled in ice to room temperature. The contents of the flask were then transferred to a large separatory funnel, and extracted with three 300 ml portions of methylene chloride, saving the aqueous layer also for recovery of small amounts of (V). Analysis of the extract by TLC (SiO_2 strip with UV indicator; eluted with 2:1 hexane: CH_2Cl_2)

showed product (IV) as a dark spot of higher R_f than starting material when viewed under short wave UV light. The combined methylene chloride extracts were washed with two 100 ml portions of 1N sulfuric acid, and then with two 100 ml portions of water. The organic layer was then separated and evaporated to dryness in vacuo below 90°C, yielding a dark oil of crude product. This material was triturated with ice water until solidification occurred. The solid product was filtered and air-dried. The dry solid was pulverized to a fine powder which was placed on top of a 2" x 12" quartz column of dry silica gel (with UV indicator), forming a broad band. This band was packed down by tapping, and was topped off by an extra inch of silica. The column was now eluted using 2:1 hexane:methylene chloride, a broad band of (XI) being visible as a dark zone against a green background in UV light. The column was eluted until all of the desired material had been removed (as evidenced by complete removal of the dark zone). Evaporation of the eluate in vacuo yielded 75 g (76%) of 3-ethynyl-phenyl (p-toluenesulfonate (XI) as a colorless oil which solidified on cooling into white crystals, m.p., 69-70°C. The infrared spectrum (film between salt plates) exhibited the terminal acetylene C-H absorption at, 3250 cm^{-1}.

Anal. Calcd. for $C_{15}H_{12}O_3S$: C, 66.16; H, 4.44. Found: C, 66.06; H, 4.39.

4. 3-(3,4-DINITROPHENOXY) PHENYL ACETYLENE (VI)

A two-liter round-bottomed one-necked flask containing a magnetic footbar stirrer and nitrogen inlet and outlet adapter was thoroughly flamed and purged with nitrogen. To the cooled flask was added 150 g (0.55 mole) of dry, solid 3-ethynyl-phenyl (p-toluenesulfonate), 61.7 g (1.1 mole) of solid potassium hydroxide, and one liter of absolute methanol. The contents of the flask were stirred under nitrogen at room temperature for one hour, at which time a condenser was attached, and the flask heated at reflux on a steam bath for an additional hour. At that point, the condenser was replaced by a distillation head, and methanol distilled from the flask to near dryness (caution-violent bumping!), maintaining the pot temperature below 100°C (steam bath). Dry benzene (one liter) was then added, and the distillation continued to near dryness (steam bath). The remaining benzene was removed from the reaction mixture by freeze-drying under high vacuum, leaving a dry, white residue consisting of a mixture of potassium 3-ethynyl phenolate and potassium p-toluenesulfonate. The reaction flask was again equipped with a nitrogen inlet-outlet adapter and was cooled to 0°C in an ice bath. Dry pyridine (one liter) was added, the solution stirred at 0°C under nitrogen for 15 minutes, and then 102.8 g (0.55 mole) of solid, dry 3,4-dinitrofluorobenzene added all at once. The resulting mixture was stirred at 0°C for one-half hour, at which time the flask was allowed to warm slowly to room temperature over a period of one hour. Finally, the flask was heated at 60°C for 15 minutes to ensure completion of the reaction. Solvent was then removed in vacuo, maintaining the temperature below 80°C. The dark residue was extracted into methylene chloride, and the filtered extracts washed with two successive portions each of water, 0.1N sulfuric acid and again, water. The methylene chloride extracts were separated, evaporated to a small volume in vacuo, and then filtered through a 2" x 12" dry column of silica gel, eluting with methylene chloride. The eluate was evaporated to dryness in vacuo and the residue triturated with a small quantity of methanol at 0°C, causing solidification to occur. The crude solid thus obtained was filtered, dried, and recrystallized from methanol three times yielding 131 g (84% yield) of 3-(3,4-dinitrophenoxy)phenyl acetylene as pale yellow crystals, m.p. = 68-9°C. The infrared spectrum (KBr pellet) exhibited the terminal acetylene C-H absorption at 3225 cm^{-1}, and nitro-group absorptions at, 1560(sh), 1440(sh), 1525(sh), and 1335 cm^{-1}.

Anal. Calcd. for, $C_{14}H_8N_2O_5$: M.W. = 284, C, 59.16, H, 2.84, N, 9.86, O, 28.15.

Found: C, 59.01, H, 2.82, N, 9.85, M.W. = 284(M.S.).

5. ATQ-O OLIGOMER (Ia)

Due to the sensitivity of the end-capping reagent, 3-(3,4-diaminophenoxy) phenyl acetylene (slowly decomposing at room temperature even under nitrogen), the compound was prepared only after the initial synthesis of benzil end-capped quinoxaline oligomer had been completed, and was utilized immediately.

a. Benzil End-Capped Quinoxaline Oligomer (XIII)

To a rapidly stirred solution containing 84.7 g (195 mole) of 4,4'-bis(phenylglyoxaloyl)diphenylether and 5 ml of glacial acetic acid in 400 ml of m-cresol (freshly distilled) was added dropwise, under a nitrogen atmosphere, a solution containing 20.8 g (97 moles) of 3,3'-diaminobenzidine (high purity) dissolved in 400 ml of m-cresol (the tetraamine was kept in solution during the addition by warming the addition funnel). After completion of the addition, the reaction mixture was stirred at room temperature for two hours at which time a distilling apparatus was attached to the reaction flask, and m-cresol was distilled from the flask until one-half the original volume remained. A 5 ml aliquot was removed and precipitated into methanol, producing a yellow polymer. The small quantity of end-capped oligomer thus obtained was reprecipitated three times from methylene chloride into methanol, air-dried, and then redissolved in a small amount of methylene chloride. This solution was coated onto a sodium chloride plate as a film, the film dried at 100°C for five minutes, and the infrared spectrum determined. The IR spectrum exhibited a strong absorption at 1660 cm^{-1} for the diketone carbonyl end-groups of the polymer.

The m-cresol solution of benzil end-capped oligomer was saved for the end-capping reaction with 3-(3,4-diaminophenoxy)phenyl acetylene (VII), which is described in the following procedures.

b. Reduction of 3-(3,4-Dinitrophenoxy)Phenyl Acetylene to 3-(3,4-Diaminophenoxy)Phenyl Acetylene (VII)

To a five-liter Erlenmeyer flask equipped with magnetic stirrer was added 460 g (2.64 mole) of sodium dithionite ($Na_2S_2O_4$) and 1.5 liters of water. Dissolution was affected by heating to 60°C. Then, a solution containing 104 g (2.64 moles) of sodium hydroxide dissolved in 500 ml of water was added to the flask. Meanwhile, in another two-liter flask was dissolved 75.0 g (2.64×10^{-1} mole) of 3-(3,4-dinitrophenoxy)phenyl acetylene (VI) in 1.5 liters of methanol by heating. The hot methanol solution of (VIII) was added as rapidly as possible (caution-possible foaming) to the rapidly stirred solution of dithionite, rinsing the flask with methanol. A dark purple color formed immediately, which slowly changed to yellow, and then to milky white. If the reaction mixture remained yellow, then hot methanol was added in portions until the white suspension was obtained, evidence that the reduction was complete. Most of the methanol was then removed from the reaction solution in vacuo on a rotary evaporator, maintaining the temperature below 60°C. After removal of the methanol, the aqueous white suspension of end-capping reagent was cooled to room temperature and transferred to a five-liter separatory funnel, rinsing the flask with water and methylene chloride. An additional one-liter of ice water was added, and the solution was extracted with four 200 ml portions of methylene chloride. The combined methylene chloride extracts were transferred to a two-liter Erlenmeyer flask, and reduced in volume by one-half, by boiling on the steam bath with nitrogen being bubbled through the solution to prevent bumping and decomposition. The resulting concentrated solution was then washed with two 500 ml portions of deaerated water, back extracting each time with methylene chloride. The methylene chloride solution of product was once again concentrated to a small volume approximately 200 ml) by boiling on the steam bath with a nitrogen bubbler. The concentrated solution of 3-(3,4-diaminophenoxy)phenyl acetylene was then used immediately in the end-capping reaction of benzil-end-capped oligomer (described below).

An analytical sample of (VII) was obtained by chromatography of the crude material on a dry quartz column of silica gel (with UV indicator). Elution with methylene chloride removed traces of impurities. Further elution of the column using ethyl acetate produced a second band under UV light which contained the product. Careful removal of solvent in vacuo, below 50°C afforded (VII) as a colorless oil. The infrared spectrum (film between salt plates) exhibited a sharp acetylene C-H absorption at 3265 cm^{-1} superimposed upon the broad diamine absorptions which appeared as a series of shoulders between 3400 and 3200 cm^{-1}. There was no residual absorption in the carbonyl region.

Anal. Calcd. for $C_{14}H_{12}N_2O$: M.W. = 224.26, C, 74.98;H, 5.39;N, 12.49.

Found: C, 74.43; H, 5.31; N, 11.98; M.W. = 224 (mass spectrum).

c. Reaction of 3-(3,4-Diaminophenoxy) Phenyl Acetylene with the Benzil End-Capped Quinoxaline Oligomer; Preparation of Acetylene Terminated Quinoxaline (ATQ-O)

To the m-cresol solution of benzil end-capped oligomer prepared in Part a of the procedure was rapidly added the freshly prepared concentrated methylene chloride solution containing 3-(3,4-diaminophenoxy)phenyl acetylene, rinsing the flask with methylene chloride. A distillation apparatus was then attached, and the flask heated on a steam bath with stirring, to distill off the methylene chloride which had been added, and begin the end-capping reaction. The temperature was then raised sufficiently so that m-cresol distilled rapidly from the flask, and distillation continued (1/2 hr) until the volume had been reduced to approximately 300 ml. At this point, the solution was tested for completeness of the end-capping reaction by the removal of a 5 ml aliquot and precipitation into methanol. The small amount of yellow polymer that precipitated was filtered, washed with methanol, and then reprecipitated twice from methylene chloride into methanol, the methylene chloride being boiled away each time. The purified polymer sample was filtered, dried, and redissolved in a small amount of methylene chloride. The concentrated solution was coated onto a sodium chloride plate, and the plate dried in an oven at 100°C for five minutes. The infrared spectrum was then determined, showing absorptions at 3290 cm^{-1} (acetylene C≡C-H), 3060 cm^{-1} (aromatic C-H), and the complete absence of absorption at 1660 cm^{-1} (carbonyl region). The absence of carbonyl absorption as well as the high intensity of the acetylene C-H absorption were the determining factors in assessing the completeness of the end-capping reaction. If residual carbonyl absorption had been detected, then additional 3-(3,4-diaminophenoxy)phenyl acetylene would have been prepared and added to the reaction mixture according to the above procedure. The amount required would be estimated from the intensity of carbonyl absorption observed in the IR of the polymer. However, in all reactions run to date no additional amounts of acetylene end-capper were required.

When it had been determined that the end-capping reaction had been complete, the m-cresol solution of ATQ-O polymer was added dropwise to three liters of stirred methanol, causing precipitation. The crude product was filtered, washed with several portions of methanol, and air-dried. The dried polymer was redissolved in methylene chloride, the solution reduced in volume to one liter, and this solution precipitated into methanol (three liters), the methylene chloride being boiled away on the steam bath. The yellow polymer thus obtained was collected and reprecipitated from methylene chloride into methanol twice again, utilizing the same procedure, and the purified ATQ-O polymer dried at 115°C in vacuo for 12 hours before use. The yield was 127 g (95%).

Anal. Calcd. for $C_{96}H_{58}N_8O_4$ (n=1); M. W. = 1387; C, 83.10; H, 4.21; N, 8.08. Found: C, 82.32; H, 4.05; N, 7.82; M.W. = 1460 (VPO).

6. ATQ-S OLIGOMER Ib

To a rapidly stirred solution containing 2.1 g (4.7 mmoles) of 4,4'-(phenylglyoxaloyl)diphenylsulfide and 1 ml of glacial acetic acid dissolved in 25 ml of m-cresol was slowly added, under a nitrogen atmosphere, a solution containing 0.5 g (2.33 moles) of 3,3'-diaminobenzidine dissolved in 25 ml of m-cresol. After completion of the addition, the reaction mixture was heated at reflux for one hour, at which time one-half of the m-cresol was distilled out of the reaction mixture. To the cooled reaction mixture was added 1 ml of glacial acetic acid, followed by a solution containing 1.05 g (4.7 mmoles) of 4-(3-ethynylphenoxy)-orthophenylenediamine dissolved in 10 ml of m-cresol. The mixture was stirred at room temperature for one-half hour and then heated to reflux for 15 minutes during which time m-cresol was distilled from the flask to decrease the volume of the solution to 10 ml. The cooled reaction mixture was then added dropwise to 100 ml of stirred methanol, causing precipitation. The yellow end-capped oligomer was twice reprecipitated from methylene chloride into methanol with the methylene chloride being boiled away each time yielding 3.3 g (99%) of oligomer.

Calculated for $C_{96}H_{58}N_8O_2S_2$ (n=1); C, 81.23; H, 412; N, 7.89; O, 2.25; S, 4.51. Found: C, 81.01; H, 4.13; N, 7.82; S, 4.22.

7. ATQ-pp OLIGOMER Ic

To a rapidly stirred solution containing 0.64 g (1.87 mmoles) of 1,4-(phenylglyoxaloyl)benzene and 1 ml of glacial acetic acid dissolved in 25 ml of m-cresol was slowly added, under a nitrogen atmosphere, a solution containing 0.2 g (0.93 mmole) of 3,3'-diaminobenzidine dissolved in 25 ml of m-cresol. After completion of the addition, the reaction mixture was heated at reflux for one hour, at which time one-half of the m-cresol was distilled out of the reaction mixture. To the cooled reaction mixture was added 1 ml of glacial acetic acid, followed by a solution containing 0.47 g (1.87 mmoles) of 4-(3-ethynylphenoxy)-ortho-phenylenediamine dissolved in 10 ml of m-cresol. The mixture was stirred at room temperature for one-half hour and then heated to reflux for ten minutes during which time m-cresol was distilled from the flask to decrease the volume of the solution to 10 ml. The cooled reaction mixture was then added to 100 ml of stirred methanol, causing precipitation. The yellow end-capped oligomer was twice reprecipitated from methylene chloride into methanol with the methylene chloride being boiled away each time, yielding 1.05 g (96%) of the oligomer.

Calculated for $C_{84}H_{50}N_8O_2$ (n=1): C, 83.79; H, 4.20; N, 9.34; O, 2.67.

Found: C, 83.66; H, 4.18; N, 9.25.

8. MODEL COMPOUNDS

a. 2,3-Diphenyl-6-(3-Ethynylphenyl)Quinoxaline

A solution containing 17.6 mmole of 3-4-diaminophenoxy)phenyl acetylene dissolved in methylene chloride was prepared by the reduction of 3-(3,4-dinitrophenoxy)phenyl acetylene according to the previously described procedure. The solution was rapidly added to a solution containing 3.7 g (17.6 mmole) of benzil dissolved in 50 ml of isopropanol containing 5 ml of acetic acid. The mixture was heated on the steam bath and distilled to near dryness. Ice water was then added, and the crude product collected by filtration, washed with water, and dried. Thus, the material obtained was chromatographed on a 1" x 12" dry quartz column of silica gel (with UV indicator). Elution with 3:1 hexane: methylene chloride removed unreacted benzil. Continued elution with 1:1 hexane:methylene chloride produced a second fluorescent band containing the product. Recrystallization from methanol/methylene chloride afforded 5.7 g (82%) of 2,3-diphenyl-6-(3-ethynylphenoxy)quinoxaline as white crystals, m.p. 163-4°C. The infrared spectrum (KBr pellet) exhibited a terminal acetylene C-H absorption at 3235 cm^{-1}.

Anal. Calcd. for, $C_{28}H_{18}N_2O$: M. W. = 398.5; C, 84.40; H, 4.55; N, 7.03; O, 4.02. Found: C, 84.38; H, 4.50; N, 6.98; M.W. = 398 (M.S.).

b. 1,4-Diphenyl-Buta-1-ene-3-yne (XV)

Dry cuprous phenyl acetylide was refluxed in glacial acetic acid under nitrogen for one hour. The reaction mixture was then poured into a large volume of ice water, and the solution extracted into methylene chloride which was evaporated in vacuo. The dark residue was chromatographed on a dry quartz column of silica gel (with UV indicator) yielding (XV) as white crystals, m.p. = 98-9°C (lit.[5] m.p. = 99)

c. 1,4-Diphenyl-1,3-Diyne (XVI)

Dry cuprous phenyl acetylide was refluxed in pyridine solution kept saturated with air for one hour. The reaction mixture was evaporated to dryness in vacuo, and the residue chromatographed on a dry quartz column of silica gel (with UV indicator), yielding (XVI) as white crystals, m.p. = 86-7°C (lit.[4] m.p. = 87-8°C).

d. Strauss Coupling Product XVII from Model Compound XIV

The cuprous salt of (XIV) was first prepared by the addition of an acetone solution of (XIV) to an ammoniacal solution of copper (I) chloride. The yellow product was filtered, washed with water, and dried at 80°C/0.01 mm Hg for nine hours. The dried copper salt was then refluxed in a small amount of glacial acetic acid under nitrogen for one hour, at which time the mixture was poured into ice water. The dark residue was chromatographed on a dry quartz column of silica gel (with

UV indicator), yielding (XVII) as white crystals, m.p. = 120°C (softens at 100°C); m.p. = 137°C (DSC).

Anal. Calcd. for, $C_{56}H_{36}N_4O_2$: C, 84.40; H, 4.55; N, 7.03.

Found: C, 84.38; H, 4.50; N, 6.88.

9. MODEL COMPOUND CURE REACTIONS

A typical model compound cure reaction was conducted as follows: The material to be tested was placed into an ampoule and the ampoule flushed with nitrogen and flamed. The ampoule was sealed, and then placed in a Wood's metal btah at 275°C for two hours. The ampoule was removed, cooled, and broken. The fragments were extracted with methylene chloride, and the extracts filtered and analyzed by TLC. In addition to large quantities of polymeric material, there were also detected smaller amounts of complex mixtures of products. The methylene chloride solution was evaporated to dryness, and the residue chromatographed on a dry quartz column of silica gel (with UV indicator), eluting the mixture of oligomeric products. The eluate was evaporated, and the residue submitted for mass spectral analysis to determine the identity of as many components as possible.

SECTION IV

CONCLUSIONS

The goals set forth in the introduction of this report have been realized with the synthesis of the acetylene terminated quinoxaline (ATQ) polymer system. The polymer exhibits excellent processing characteristics (solubility and flow properties), thermal oxidative stability, and mechanical properties. The terminal acetylene groups homopolymerize by both inter- and intramolecular addition reactions leading to highly fused aromatic ring system which are moisture insensitive. The ATQ polymer system is the first thermosetting matrix material found to exhibit high temperature (450-500°F) moisture resistance.

Thus, this work demonstrates the great potential of end-group acetylene chemistry to provide 350-650°F moisture resistant resin systems for future Air Force applications. Follow-on research work is continuing in this vein for both matrix resins and adhesives.

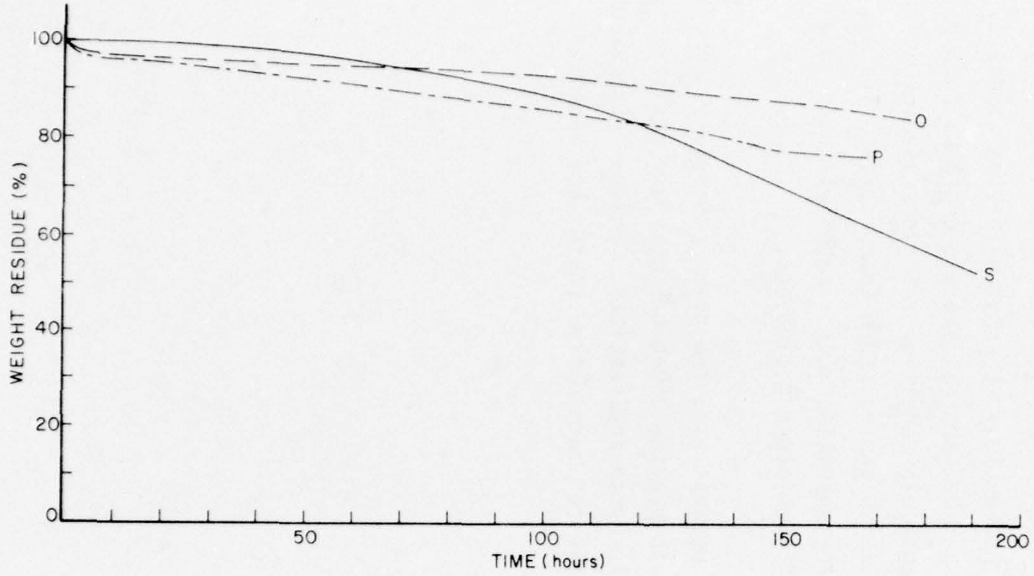


Figure 1. Weight Losses of ATQ-O, ATQ-P, and ATQ-S During Isothermal Aging at 600°F In Air

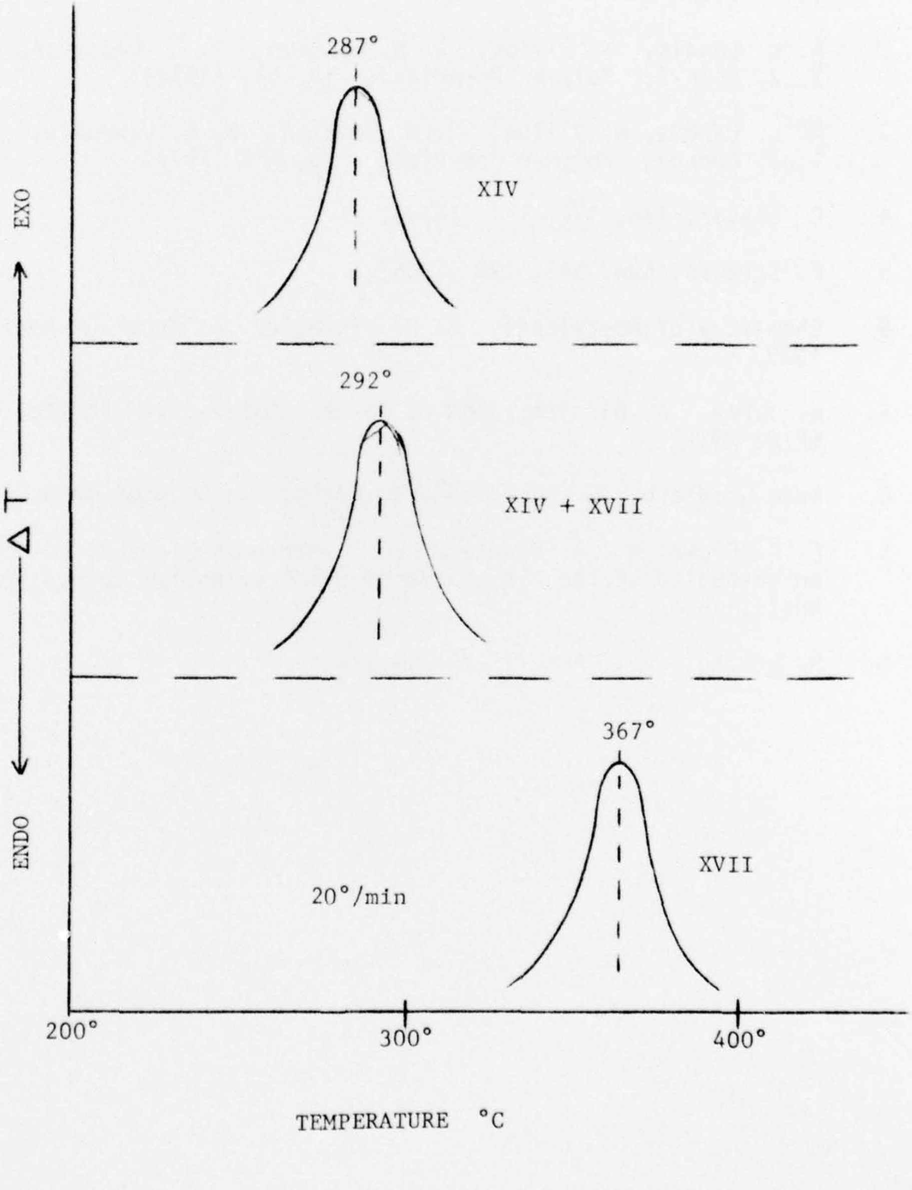


Figure 2. DSC Analysis of Model Compounds

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