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ACETYLENE TERMINATED MATRIX RESINS

I. J. Goldfarb, C. Y-C. Lee, F. E. Arnold, and T. E. Helminiak
Materials Laboratory
Air Force Wright Aeronautical Laboratories

The synthesis of resins with terminal acetylene groups have provided a promising technology to yield high performance structural materials. Because these resins cure through an addition reaction, no volatile by-products are produced during the processing. The cured products have high thermal stability and good properties retention after exposure to humidity. Resins with a wide variety of different chemical structures between the terminal acetylene groups have been synthesized in the Materials Laboratory, and their mechanical properties have been studied. The ability of the acetylene cured polymers to give good mechanical properties has been demonstrated by the resins with quinoxaline structures. Processibility of these resins can be manipulated by varying the chain length between the acetylene groups or by blending in different amounts of reactive deluents. Processing conditions similar to the state-of-the-art epoxy can be attained by using backbone structures like ether-sulfone or bis-phenol-A. The wide range of mechanical properties and processing conditions attainable by this class of resins should allow them to be used in a wide variety of applications.

INTRODUCTION

A variety of aromatic and aromatic heterocyclic oligomers with terminal acetylene units have been reported (Ref 1-3) in recent years for use as addition curable moisture resistant thermoset resins. Long term use temperatures for these materials are in the range of 250-550°F with short term usage at 600-650°F depending on the specific molecular structure between acetylene cure sites. A substantial effort in our laboratory has been directed toward the synthesis and characterization of acetylene terminated oligomers. These materials can be classified into rigid (high T_g) and flexible (low T_g) systems. For higher use temperatures, the rigid aromatic heterocyclic oligomeric backbones are employed which exhibit higher T_g's after cure. Materials which process analogous to the state-of-the-art epoxides require the more flexible (e.g. phenylene R systems) where R refers to the functional group which imparts the flexibility to the oligomeric backbone. This paper is an attempt to scope the chemistry and the range of processing and mechanical properties presently attainable by this class of resins. It is not a complete survey of previous work in this technology area but selective resins are chosen to demonstrate their versatility and properties. The data reported are in general not optimized because of the limited quantities of these resins.

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CURE CHEMISTRY

Studies of various acetylene terminated monomers have demonstrated that the polymerization is a free radical propogationof the acetylene moiety to a linear conjugated polyene (Ref 4). The kinetic chain length of this reaction is unusually short (6-8 acetylene units) and termination is first order. This early stage of reaction of a difunctional acetylene is depicted in Figure 1. A proposed model to account for these observations is as follows: A thermally induced free radical probably involving two molecules of monomer initiates the propogation of one acetylene per monomer unit into a conjugated polyene. This results in a cluster-shaped species whose growth is inhibited by the steric hindrance of the pendent groups attached to the acetylene. Although the free radical at the hub of the cluster is still reactive, its growth becomes increasingly more difficult as the reaction proceeds reaching a finite limit. Based on this model one would predict a steady growth of free radicals to a high concentration. Electron paramagnetic resonance of polymerizing acetylene terminated sulfone verifies such a growth of free radicals to unusually high concentrations (Ref 5). Involvement of the pendant acetylenes of a cluster in subsequent polyene formation reactions yields a crosslinked network whose crosslink sites are the polyenes. This model would lead to the prediction that a high degree of cure completion would be required in order to obtain good tensile properties. In addition it would be expected that the monomer size should influence the average polyene length and hence the number of arms per cluster. This in turn would have a direct effect on the network topology which should manifest itself in mechanical behavior. Studies to explore the size effect are currently underway. Studies to date support the proposed model with no evidence of any further reaction of the polyene species, but trimerization to an aromatic species, although stericly improbable, is possible and has been observed in small quantities. It has been demonstrated that polymerization of acetylene terminated monomers can be initiated at lower temperatures using transition metal-organic compounds (Ref 6). Although the effect on network structure has not been determined, preliminary mechanical characterization of initiated polymers indicates an effect may be present. As might be expected for a free radical polymerization, cure studies in air and nitrogen have clearly shown that the rate of cure is markedly reduced in air (Ref 7). The mechanical properties are appparently favorably influenced by an air cure (Ref 8).

MECHANICAL PROPERTIES

To demonstrate that AT cured systems can attain good mechanical properties, the results for a quinoxaline resin (ATQ) are shown as an example. This quinoxaline resin, whose structure is as shown in Figure 2, is prepared by endcapping quinoxaline oligomers with 3-(3,4-diaminophenoxy)phenylacetylene (Ref 1). The neat resin mechanical properties of this system are listed in Table I (Ref 9). The test specimens were post-cured at 700°F under nitrogen for 1 hour. The fully cured T_g of this resin is 321°C. The data listed in Table I indicate good tensile strength at room temperature. The resins have also been tested at 450°F. The mechanical properties at both temperatures are not affected by aging at 200°F, 94% humidity environment. This resin has also been evaluated as a matrix in an unidirectional graphite composite. Prepreg tapes were prepared by drum winding at room temperature using Hercules HT-S fiber and solutions of the ATQ resin in

methylene chloride (Ref 10). The laminates were fabricated in a press at 550°F for 2 hours under 200 psi pressure and post-cured in an oven at 600°F for 16 hours. The composite data are listed in Table II (Ref 1). Again the properties are good and seemingly unaffected after 30 days of aging at 160°F/95% relative humidity environments. The ability of the cured AT systems to maintain high temperature properties, even with relatively flexible backbones, can be demonstrated by the mechanical properties of the bis-phenol-A (ATB) resin. The synthesis and characterization of this resin are being reported elsewhere (Ref 11). The structure is shown in Figure 3. The neat resin tensile data are listed in Table III. This resin has good retention of properties at 350°F. Again, aging in severe wet environment (immersed in 160°F water till saturation) does not seriously affect its mechanical properties. Preliminary short beam shear data of the ATB/graphite composite (Ref 12) show values of 12 ksi at room temperature and 7.5 ksi at 350°F.

PROCESSABILITY

The AT resins can be used in a wide range of processing temperature and conditions. Resins with high molecular weight and rigid backbones usually have very short time in the melt state, and require rather extreme processing conditions like compression molding at high temperature. At the other extremes, resins with flexible backbones can exhibit the "tack and drape" characteristics of the state-of-the-art epoxy resins. At moderately high temperature, this type of resin remains in the liquid state for an extended period of time. Because they are single component systems, these resins do not have the problems associated with mixing-in high temperature melting components. An example of an AT system that shows the high temperature processing characteristic is another quinoxaline resin that is end-capped with 4-(3-ethynylphenoxy)benzil (Ref 1). The structure of this resin (BATQ) is shown in Figure 4. This resin has a high uncured T_g of 185°C. The isothermal viscosity curves as a function of cure time are shown in Figure 5. In order to mold this resin into tensile dog-bone specimens for testing, the resins were processed at 180°C under 18 ksi pressure for 1 hour, then cured for 1 hour at 220°C in the mold under the same pressure. The tensile data of these specimens after post curing at 250°C for 4½ hours are quite good; with a tensile strength of 13.4 ksi and 13.1 ksi before and after moisture aging respectively. The viscosity profile of the ATB however, is quite different. At 25°C, the viscosity of this resin is 10^3 poise (as measured by dynamic measurement at 10 rad/sec) (see Fig. 6). At 80°C, the viscosity level is less than 1 poise and can be poured through narrow channels of processing molds. Because of the low uncured viscosity, this resin can be tailored to suit different viscosity requirements for specific processing needs by B-staging the resin to appropriate degrees.

Molecular Weight Effect

By changing the molecular weight between the acetylene groups the thermo-rheological profiles of a system can be drastically modified. Figure 5 shows the isothermal viscosity curves of a series of quinoxaline resins. The lowest molecular weight structure, shown in Figure 4, is referred to as SBQ (Ref 1). It is obvious that with decreasing oligomer chain lengths, the processing window (time in melt state) is increased to allow easier processing. The fracture toughness (K_0) measurement of this series also indicate that the toughness decreases with decreasing chain length (Fig. 7).

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Reactive Diluents

Another approach that can improve the processability of a resin is to blend it with reactive diluents (Ref 13). The BATQ described in the previous section is very difficult to process because of its high uncured T_g. When a reactive diluent is blended in with a resin, the glass transition temperature of the mixture is lowered than the unblended resin. The mixture can then be processed at a temperature unreachable by the unblended resin. Also because of the lower processing temperature, the kinetic rate of the cure is slower as well, thus affording further improvement of the processing window. Because of the reactivity of the diluents, they will be incorporated into the final network during cure. Both difunctional and monofunctional acetylene terminated phenylene oxide have been used as reactive diluents with BATQ resin. The isothermal cure viscosity curves of the blends are shown in Figure 8. Substantial improvement in processing can be realized by the small amount of diluents added. At low concentration, the diluents do not appear to adversely affect the mechanical properties of the resin. However, at higher concentration, the properties of the resin can be seriously compromised.

CONCLUSIONS

The acetylene terminated resins are a promising thermoset technology because of its addition cure reaction, good thermal properties and excellent properties retention after exposure to humid environments. By incorporating appropriate chemical structures between the terminal acetylene groups, one can obtain matrices with good mechanical properties after cure. The wide range of viscosity profiles before cure attainable by these resins makes them a versatile technology for designing thermoset systems for specific application requirements.

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TABLE I
Mechanical Properties of Neat Resin ATQ

Test Temperature	Tensile Strength MPa (ksi)	
	Dry	Wet
RT	98(14)	98(14)
450°F	27(3.8)	32(4.5)

TABLE II
ATQ/HT-S Composite Properties

Property	RT	500°F	300°F Aged*	450°F Aged*
Flexural Strength - ksi	221	194	221	198
Flexural Modulus - Msi	19.5	18.1	19.5	19.1
Short Beam Shear - ksi	15	-	-	-

*30 days at 71°C 95% RH.

TABLE III
ATB Neat Resin Mechanical Properties

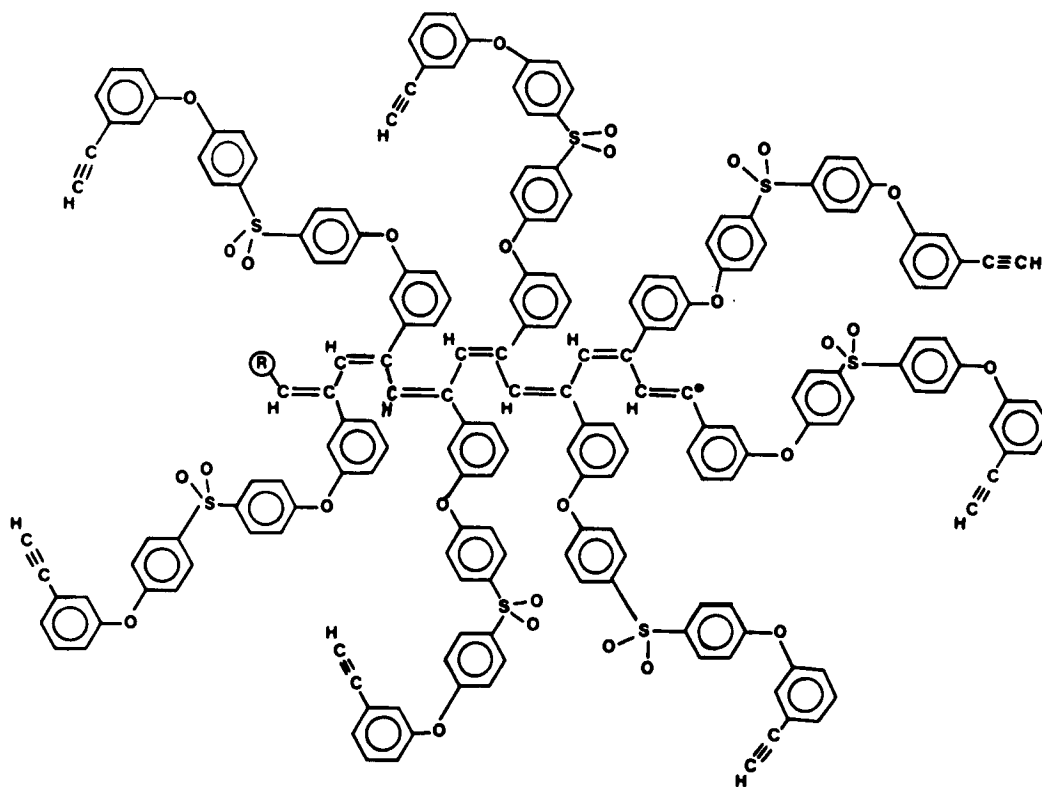|	RT		200°F		350°F	
	Dry	Aged*	Dry	Aged*	Dry	Aged*
Elongation at Break - %	3.5	3.1	4.4	3.4	6	7
Tensile Strength - ksi	9.8	8.5	8.3	7.2	5.8	5.5

*Immersed in 160°F water till saturation.
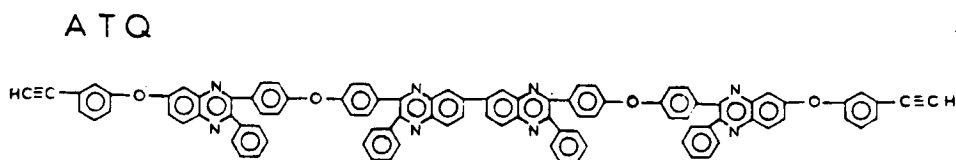
FIGURE 1.   Early Stage of Cure.

ATQ

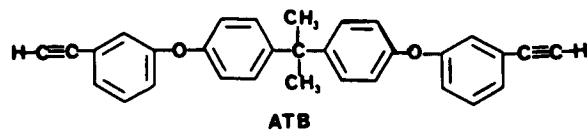FIGURE 2.   Molecular Structure of ATQ.

FIGURE 3.   Molecular Structure of ATB.

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BATQ
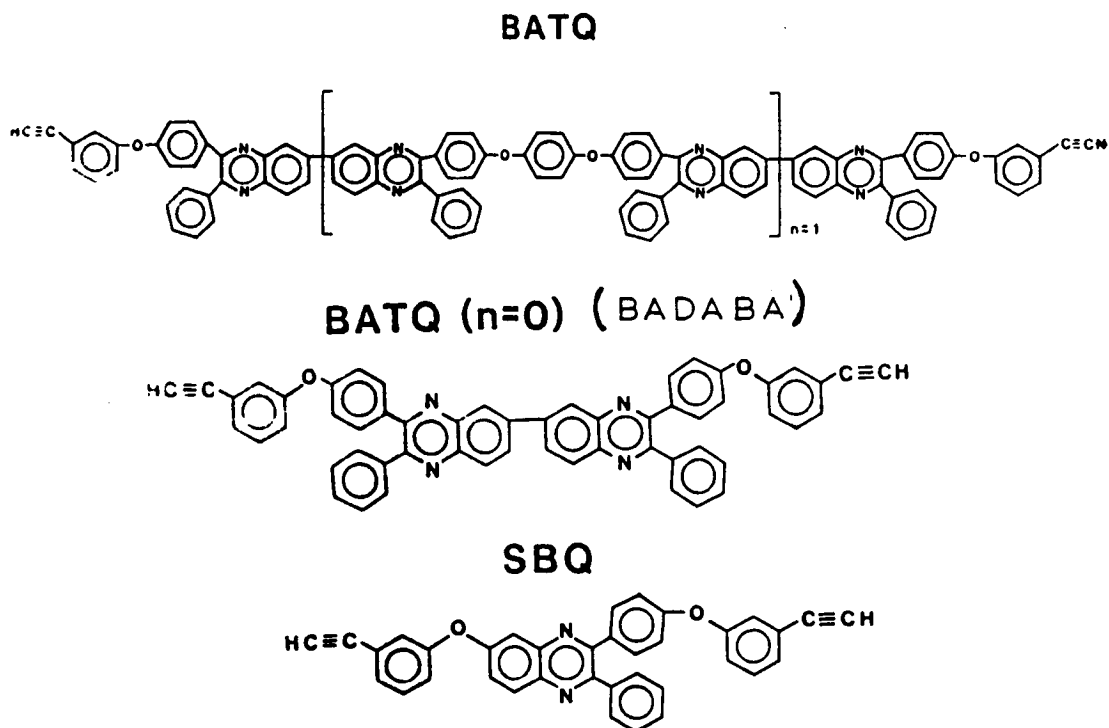

BATQ (n=0) (BADABA)

SBQ

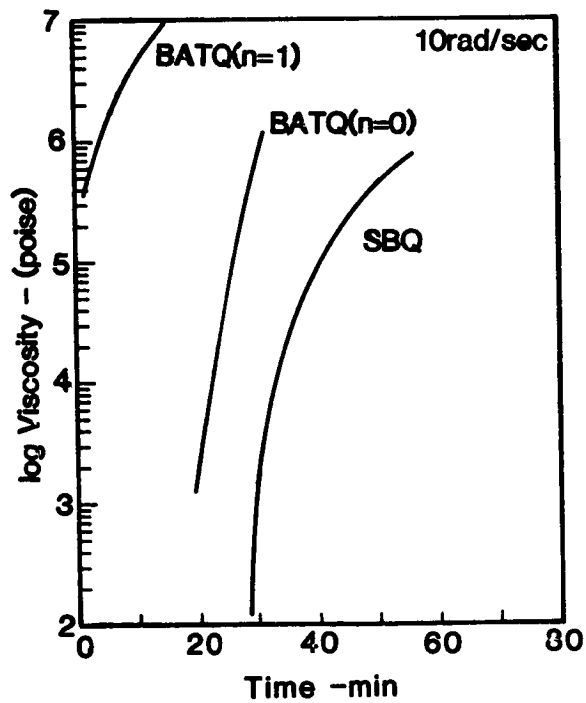FIGURE 4. Molecular Structure of BATQ, BADABA, and SBQ.

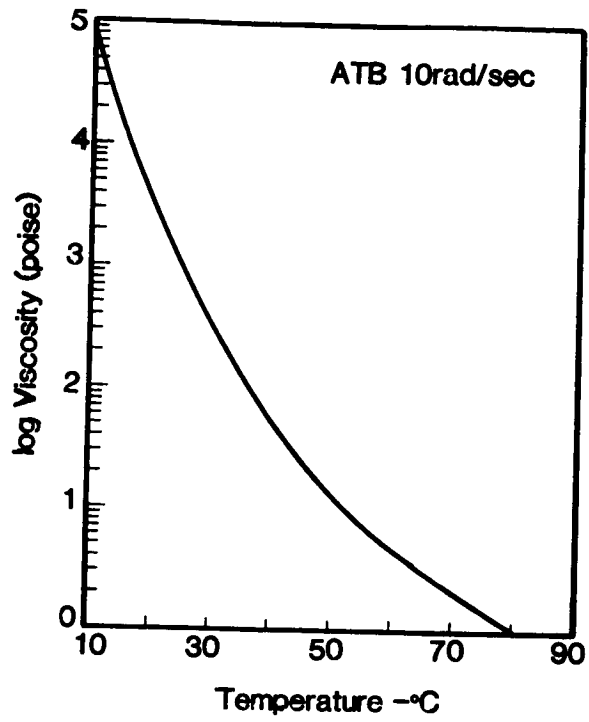FIGURE 5. Isothermal Cure Viscosity of the Quinoxaline Resins.

FIGURE 6. Viscosity of ATB.

FRACTURE TOUGHNESS VS NORMALIZED CHAINLENGTH
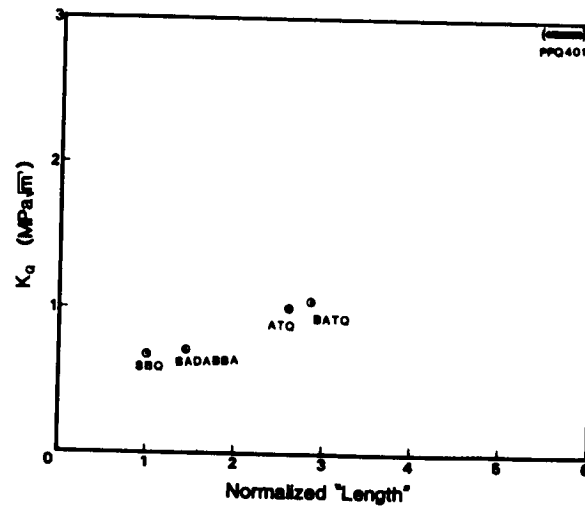FOR ACETYLENE TERMINATED QUINOXALINES
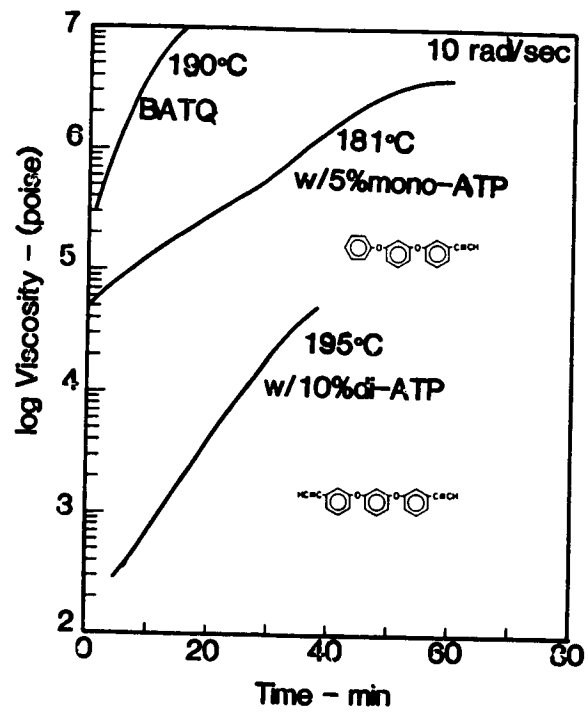
FIGURE 7. Fracture Toughness of the Quinoxaline Resins.

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FIGURE 8.   Isothermal Cure Viscosity of BATQ with Reactive Diluents.