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SYNTHESIS AND PROPERTIES OF REACTIVE DILUENTS FOR
ACETYLENE TERMINATED PHENYLQUINOXALINE OLIGOMERS

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio with Dr. F. E. Arnold as the AFML Project Scientist. Co-authors were Mr. B. A. Reinhardt and Dr. F. E. Arnold, Air Force Materials Laboratory, (AFWAL/MLBP).

This report covers research conducted from April 1979 to December 1979.

The authors wish to thank Mr. E. J. Soloski for the determination of glass transition temperatures of the diluent/oligomer mixtures.

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SECTION I
INTRODUCTION

To meet a variety of advanced aircraft and aerospace requirements, there is a need for high temperature thermoset resins for matrix and adhesive applications. Such resins, because of their complexity of structure, have critical processing difficulties when required to conform to the state-of-the-art processing criteria. OSHA requirements negate processing such materials from solvent base systems, thereby necessitating fabrication via melt techniques.

Recent advances (References 1 through 4) in high temperature thermoset systems have provided a family of new moisture insensitive matrix materials based on the phenylquinoxaline backbone and primary acetylene end groups. The acetylene variety can be thermally homopolymerized via addition reactions, between 200°C and 250°C to form a moisture insensitive high temperature resin system. Although the materials show excellent resistance to heat and environmental surroundings, they lack the necessary flow required for melt processing because of their high glass transition temperature (T_g) (140-170°C).

An approach to provide melt processability to these high T_g systems is the use of a diluent. The diluent must act as a plasticizer thereby lowering the T_g of the oligomer and at the same time reduce the bulk viscosity of the system. The ideal diluent would be one which plasticizes the oligomer during the initial prepregging operation and then co-react with the oligomer to become part of the thermoset network. The success or failure of this type of an approach is primarily dependent on the diluent compatibility with the oligomer.

The objective of this work is to synthesize various reactive diluents of specific molecular structure which would be compatible with acetylene terminated quinoxaline oligomers. The purpose of the work is to demonstrate the melt processability of these high T_g systems.

SECTION II

DISCUSSION AND RESULTS

The most attractive acetylene-terminated phenylquinoxaline oligomer, from the standpoint of properties and potential low cost economics, is BATQ-H (Reference 3). The oligomer (Figure 1) is prepared from the reaction of 3,3',4,4'-tetraaminobiphenyl and 1,4-(4-benziloxy) benzene in a two-to-one molar ratio of reactants. The derived orthodiamine end-capped quinoxaline oligomer is then reacted with excess 4-(3-ethynylphenoxy) benzil in tetrahydrofuran. The material exhibits a glass Tg of 165°C by differential scanning calorimetry (DSC) ($\Delta=20^\circ\text{C}/\text{min}$) and a strong polymerization exotherm initiating at 200°C and maximizing at approximately 275°C. Rheological studies (Reference 5) with BATQ-H have shown the material to have insufficient flow properties for melt processing. The high temperatures required (190-200°C) approach the polymerization exotherm thereby limiting the processing window of the material.

Previous work in our laboratory (Reference 4) has shown the bis-ethynyl compound 6-(3-ethynylphenoxy)-3-(4,3-ethynylphenoxy)-2-phenylquinoxaline (Ia) to be completely compatible with BATQ-H. The material exhibits a Tg of 30°C and at a concentration of 20 percent depresses the Tg of BATQ-H by 49°C. One can consider the material to be compatible since it is analogous to the end groups of BATQ-H (Figure 1, Section A). The drawback of Ia is its high cost in being prepared from equal molar amounts of 4-(3-ethynylphenoxy) benzil and 3,4-diaminophenoxy phenylacetylene.

It was felt that other structures common to the BATQ-H backbone would be potential candidates for reactive diluents. In particular, the mono and diacetylenic structures based on the diphenoxy linkage (Figure 1, Section B) would not only offer a favorable contingency for compatibility, but could exhibit very low Tg's. The most effective reactive diluent for the BATQ-H system would be one of minimum molecular weight between reaction sites, thereby providing the lowest possible Tg, yet have a molecular structure which would be compatible with the oligomer.

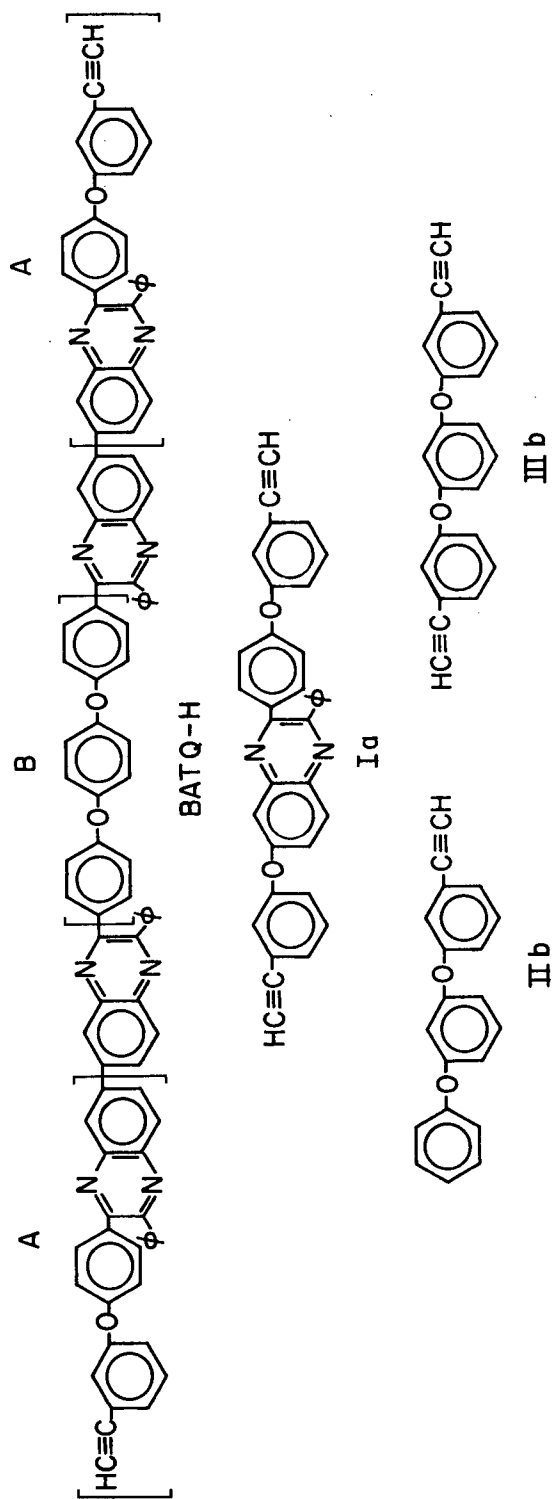
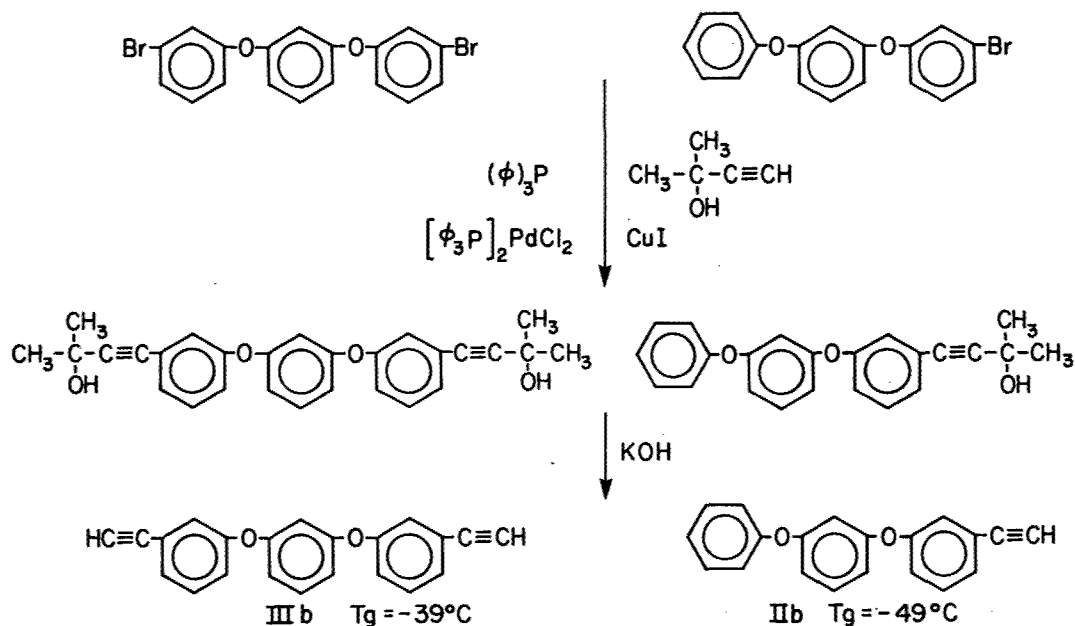
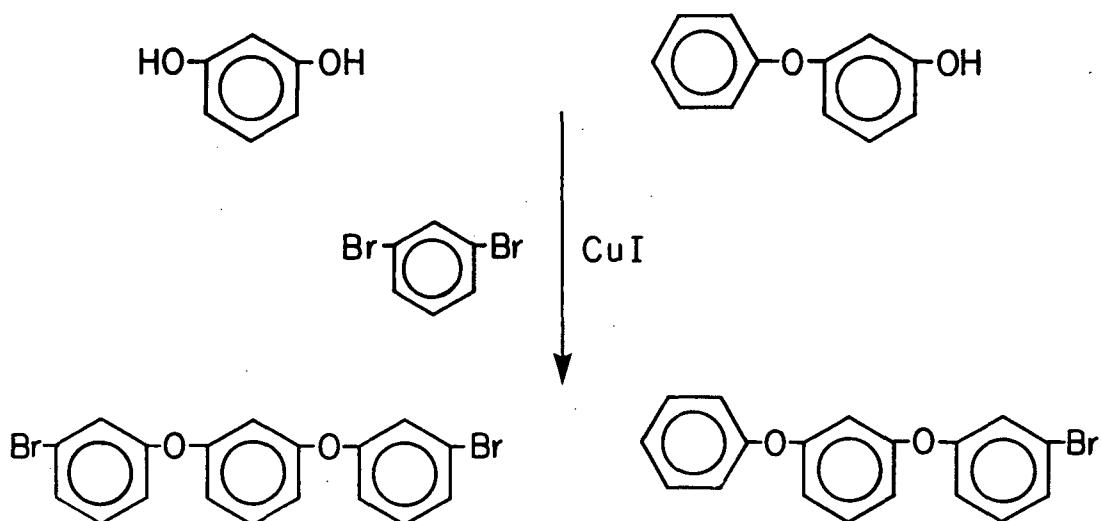


Figure 1. Reactive Diluents for Benzil End-capped Acetylene Terminated Quinoxaline Oligomer BATQ-H

The diphenoxy acetylene containing reactive diluents, 1-phenoxy-3-(3-ethynylphenoxy) benzene IIb and 1,3-bis-(3-ethynylphenoxy) benzene IIIb were prepared from the mono and dibromophenyl ethers. Direct displacement of the bromo groups with 2-methyl-3-butyn-2-ol was carried out utilizing the catalyst system made up of triphenylphosphine, cuprous iodide and bistrisphenylphosphine palladium chloride. Conversion of the secondary acetylenes to primary acetylenes was carried out by hydrolytic displacement of acetone with potassium hydroxide in toluene.



The mono and bisbromophenylether precursors were prepared by the Ullmann ether synthesis from mono and dihydroxy aromatics and m-dibromobenzene. The Ullmann ether synthesis (Reference 6) was found to be the key reaction in the low cost synthesis of 4,4'-bis(3-ethynylphenoxy) diphenylsulfone (ATS), a new acetylene terminated sulfone matrix and adhesive resin recently prepared in our laboratory (Reference 7). Utilization of this procedure provides a potential low cost preparative method for the acetylene containing reactive diluents.



Samples of the reactive diluents were mixed in various percentages with the acetylene terminated oligomer BATQ-H. To assure homogeneity in mixing, the diluents and BATQ-H were dissolved in methylene chloride after which the solvent was removed under reduced pressure.

The reactive diluents I Ib and IIIb exhibited Tg's of -49°C and -39°C , respectively. The lower the Tg of the diluent, the more effectively it can act as a plasticizer for the oligomer. The depression of the Tg of BATQ-H as a function of diluent concentration is shown in Table 1. The diluents showed very good compatibility with BATQ-H as evidenced by a single Tg of the mixture, determined by DSC. An incompatible mixture would display their inherent Tg's while a partially compatible mixture would show a Tg of the mixture along with strong signals from the original Tg's. It should be stated, however, that the extent of compatibility can only be ascertained on the basis of the sensitivity of the method, in this case DSC.

The various mixtures of diluent and oligomer were co-cured at 280°C for six hours under a nitrogen atmosphere. The Tg's of the co-cured mixtures were determined by thermal mechanical analysis (TMA) at a heating rate of $20^{\circ}\text{C}/\text{min}$. It is interesting to note (Table 1) that the mono-acetylenic diluent I Ib when co-cured with BATQ-H exhibited a Tg lower than the cure temperature or the thermal history of the mixture.

TABLE 1
GLASS TRANSITION TEMPERATURES OF
OLIGOMER/DILUENT MIXTURES

<u>% Diluent</u>	<u>% Oligomer</u>	<u>Tg^oC (a) Uncured</u>	<u>Tg^oC (b) Co-Cured (d)</u>	<u>Reduction (c) Tg^oC</u>
100 I Ib	0	-49		
100 IIIb	0	-39		
0	100	165		
20 I Ib	80	91	223	74
30 I Ib	70	70	184	95
10 IIIb	90	106	311	59
20 IIIb	80	72	306	93
30 IIIb	70	58	314	107

(a) Determined by DSC at a heating rate of 20^oC/min.

(b) Determined by TMA at a heating rate of 20^oC/min.

(c) Reduction in Tg of oligomer resulting from reactive diluent.

(d) Mixture co-cured at 280^oC for six hours under nitrogen.

This falls in line with the recent investigation (Reference 8) into the AT cure mechanism. It was shown that the initial cure of a difunctional acetylene involves the formation of a low molecular weight conjugated polyene. Each polyene repeat unit contains a pendant acetylene group which could further react to form the three-dimensional network structure. A monofunctional acetylene would form a polyene without a pendant acetylene for further cure; therefore, a less crosslinked system and lower T_g than a difunctional diluent. The addition of a small amount of monofunctional material to the BATQ-H oligomer should theoretically provide a tougher more durable matrix system.

Specimens were prepared by pressing the uncured powder mixture at 40,000 psi into 12-mm diameter by 2-mm thick pellets. Pellets were also prepared in a similar manner for the oligomer alone. In a series of runs, the pellets were placed between preheated parallel plates in a Rheometrics RMS-7200 Mechanical Spectrometer. The pellets were subjected to low frequency (160 mHz) sinusoidal shear rate viscosity measurements at constant temperatures. The results of the runs are shown in Figure 2 together with the temperatures used.

As seen from Figure 2, the processing window for the mixture (30% diluent) is greatly expanded over that of the oligomer alone. For example, the amount of time allowed for processing the mixture over the oligomer alone is increased 12 minutes at 195°C and 41 minutes at 176°C for the viscosity of 10^4 poise. Furthermore, the presence of the reactive diluent permits processing at the lower temperature of 154°C with times greater than one hour whereas the oligomer alone exhibits no flow below 180°C.

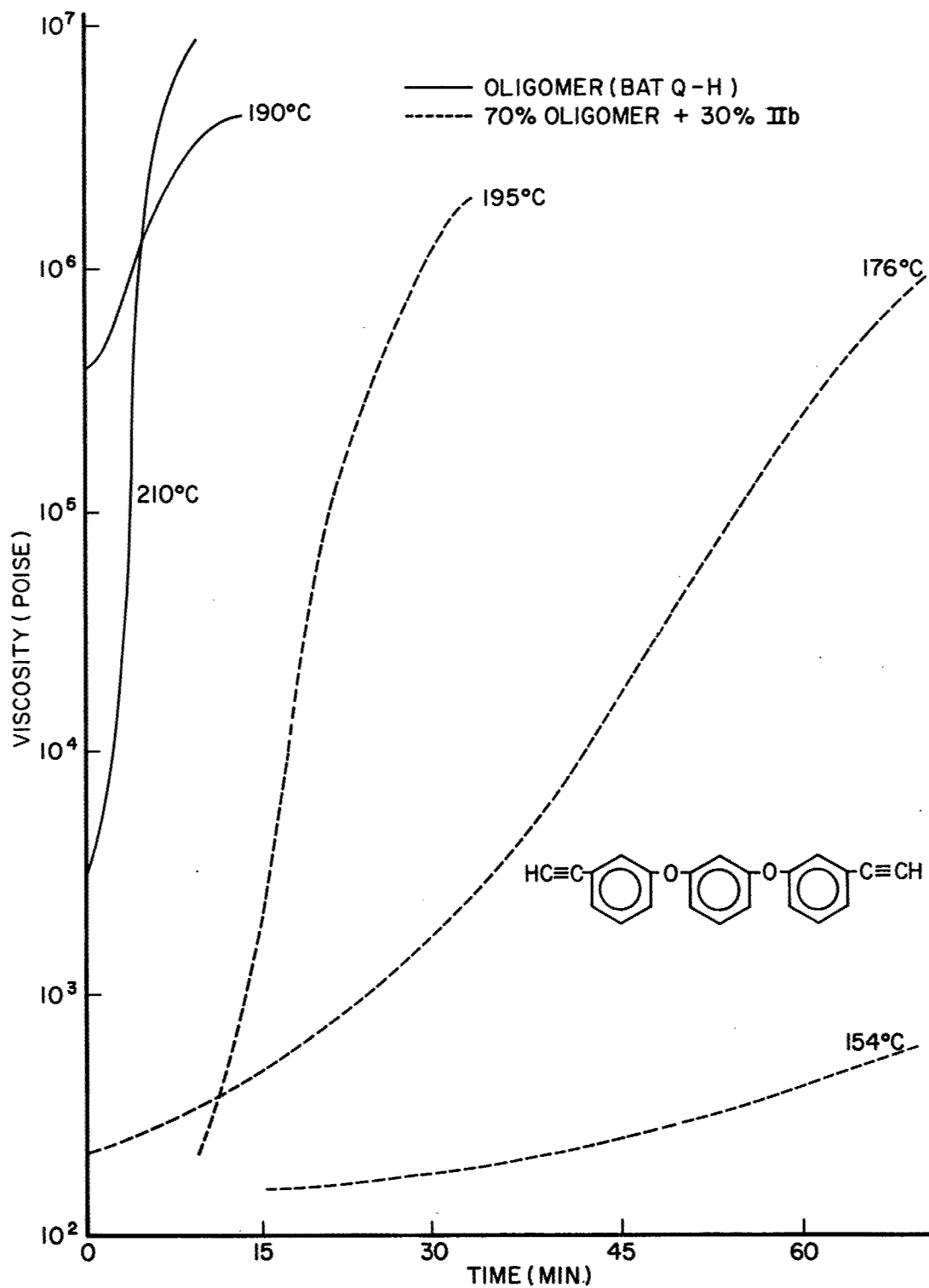


Figure 2. Cure Rheometry for BATQ-H/30%IIb At Constant Temperatures

SECTION III
EXPERIMENTAL

1. 1-PHENOXY-3-(M-BROMOPHENOXY) BENZENE

A mixture of 9.30g (0.050 mol) of m-phenoxyphenol, 35.39g (0.15 mol) m-dibromobenzene, 16.6g (0.12 mol) of anhydrous potassium carbonate and 0.30g (1.14 mmol) of cuprous iodide in 60 ml of pyridine was heated at reflux under nitrogen for 24 hours. The reaction mixture was cooled and poured into 500 ml of 10% HCl. The oil which formed was extracted with methylene chloride and the organic layer washed with 2 - 200 ml portions of H₂O. The methylene chloride layer was dried over MgSO₄ and evaporated under reduced pressure. The resulting oil was chromatographed on silica gel using hexane as the eluent, to yield 8.3g (48%) of a colorless oil (Reference 9).

2. 1-PHENOXY-3-(M-ETHYNYLPHENOXY) BENZENE

A solution of 24.6g (0.726 mol) of 1-phenoxy-3-(m-bromophenoxy) benzene, 6.31g (75.0 mmol) of 2-methyl-3-butyn-2-ol and 0.36g triphenylphosphine in 200 ml triethylamine was degassed with nitrogen for 20 minutes. To the degassed solution was added 0.036g (0.0508 mmol) of bis-triphenylphosphine palladium II dichloride and 0.14g (0.755 mmol) cuprous iodide. The mixture was heated to reflux for 24 hours, cooled to room temperature and the triethylamine removed under reduced pressure. The resulting yellow-green oil was dissolved in methylene chloride, dried over MgSO₄, filtered and chromatographed on silica gel using 1:1 methylene chloride-hexane as the eluent. After solvent was removed under reduced pressure, 24.0g (96%) of an orange oil was recovered.

Analysis Calc'd for C₂₃H₁₉O₃: C,80.21; H,5.56

Found: C,79.85; H,5.39

A solution of 24.0g (0.0697 mol) of the butynol adduct, a mixture of 0.75g of potassium hydroxide dissolved in 20 ml of methanol, and 100 ml of toluene was heated to reflux under nitrogen. During the course of two hours, the methanol and 60 ml of toluene were removed by distillation.

The remaining toluene was removed under reduced pressure. The resulting dark oil was chromatographed on silica gel using 3:1 hexane-methylene chloride as the eluent. The solvent was removed under reduced pressure to give 17.1g (81.7%) of a light yellow, viscous oil. I.R. (Figure 3)

Analysis Calc'd for $C_{20}H_{13}O_2$: C,83.90; H,4.58
Found: C,83.30; H,4.62

3. 1,3-BIS-(M-BROMOPHENOXY) BENZENE

A mixture of 47.0g (0.20 mole) of m-dibromobenzene 10.0g (0.091 mole) of resorcinol, 34.5g (0.25 mole) of anhydrous potassium carbonate, and 0.6g of cuprous iodide in 100 ml of pyridine was heated at reflux under nitrogen for 24 hours. The reaction mixture was cooled and poured into 1000 ml of 10% HCl. Methylene chloride (200 ml) was then added and the organic layer separated. The organic layer was washed with two 100 ml portions of water, dried over anhydrous magnesium sulfate and reduced in volume under reduced pressure to produce a dark viscous oil. The oil was dissolved in n-hexane and chromatographed on a 5cm x 50cm dry silica gel column (quartz) using hexane as the eluent. The second fluorescent band was collected and the solvent removed at 60° under reduced pressure to give 10.4 (27.2%) of a colorless viscous oil. (Reference 10) I.R. (Figure 4)

Analysis Calc'd for $C_{18}H_{12}O_2Br_2$: C,51.46; H,2.88; Br,38.04
Found: C,51.23; H,2.50; Br,37.73

4. 1,3-BIS-(M-ETHYNYLPHENOXY) BENZENE

A mixture of 12.60g (0.03 mole) of 1,3-bis-(m-bromophenoxy)-benzene and 6.03g (0.072 mole) of 2-methyl-3-butyn-2-ol and 100 ml of triethylamine was degassed by passing nitrogen through the solution for 20 minutes. To the reaction mixture was then added 0.03g (0.042 mmol) of bis-triphenylphosphine palladium II dichloride, 0.13g (0.624 mmol) of cuprous iodide and 0.30g (1.14 mmol) of triphenylphosphine. The temperature of the reaction mixture was raised to 80°C and maintained there for 24 hours. The reaction was then cooled to room temperature and the

triethylamine removed under reduced pressure. The resulting yellow-red oil was chromatographed on a 5cm x 60cm dry silica gel column (quartz) using 1:1 hexane-ether as the eluent. The second fluorescent band was collected (appears yellow on the column). The solvent was removed under reduced pressure to yield 10.6g (83%) of a dark viscous oil. I.R. (Figure 5) The product was used in the next step of the reaction sequence without further purification.

A mixture of 10.6g of the bis-butynol adduct and 0.75g of KOH in 20 ml of anhydrous methanol were added to 100 ml of toluene and heated to reflux under nitrogen. The methanol and 40 ml of the toluene were then removed by distillation over a period of two hours. The reaction was monitored by TLC on silica gel plates containing fluorescent indicator using 3:1 hexane-methylene chloride as the developing solvent. The product appeared as the first spot to be eluted. The reaction was judged to be complete when no starting material appeared at the origin of the TLC plate after development. After a total reaction time of two hours, the reaction mixture was cooled, and the toluene removed at 35°C under reduced pressure. The red viscous residue was chromatographed on a dry 5cm x 60cm column (quartz) of silica gel using 3:1 hexane-methylene chloride. The first large fluorescent band was collected and the solvent removed at 50°C under high vacuum. The last traces of hexane were removed by pumping on the yellow oil for 18 hours at 0.2 mm pressure. The yield of pure product was 6.1g (79%). I.R. (Figure 6)

Analysis Calc'd for $C_{22}H_{14}O_2$: C,85.07; H,4.54
Found: C,84.72; H,4.23

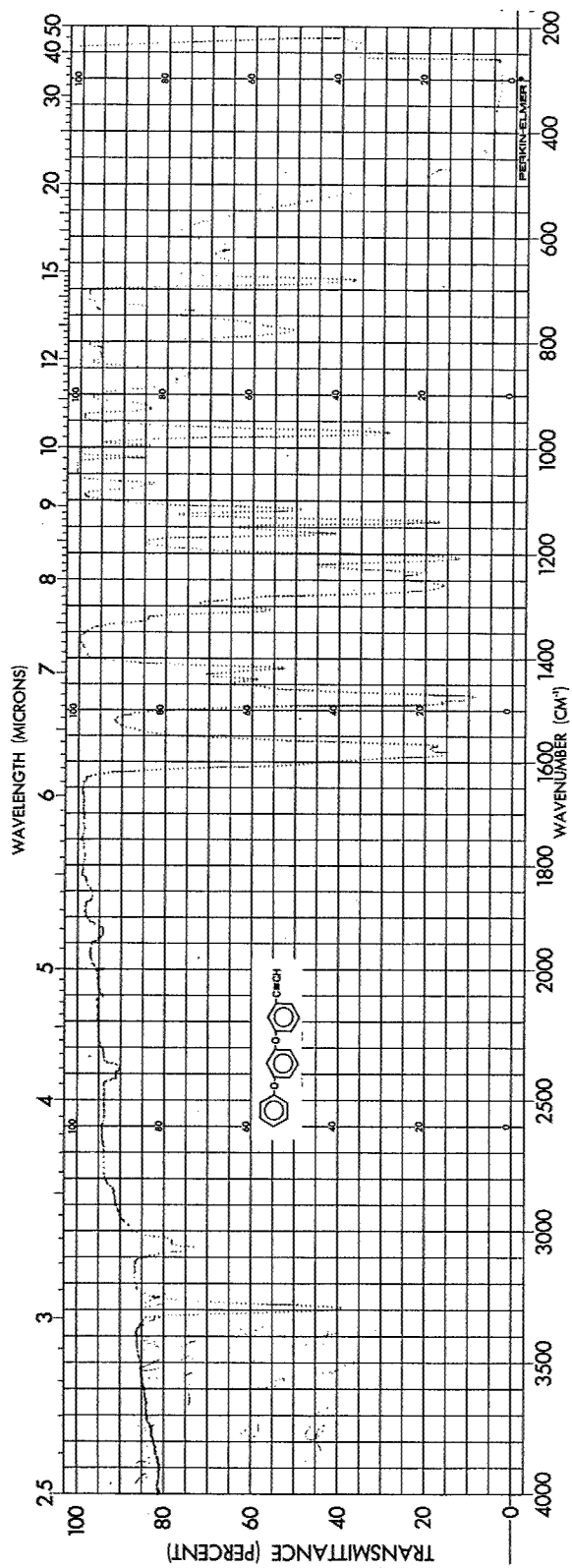


Figure 3. Infrared Spectra of 1-Phenoxy-3-(m-ethynyl)benzene

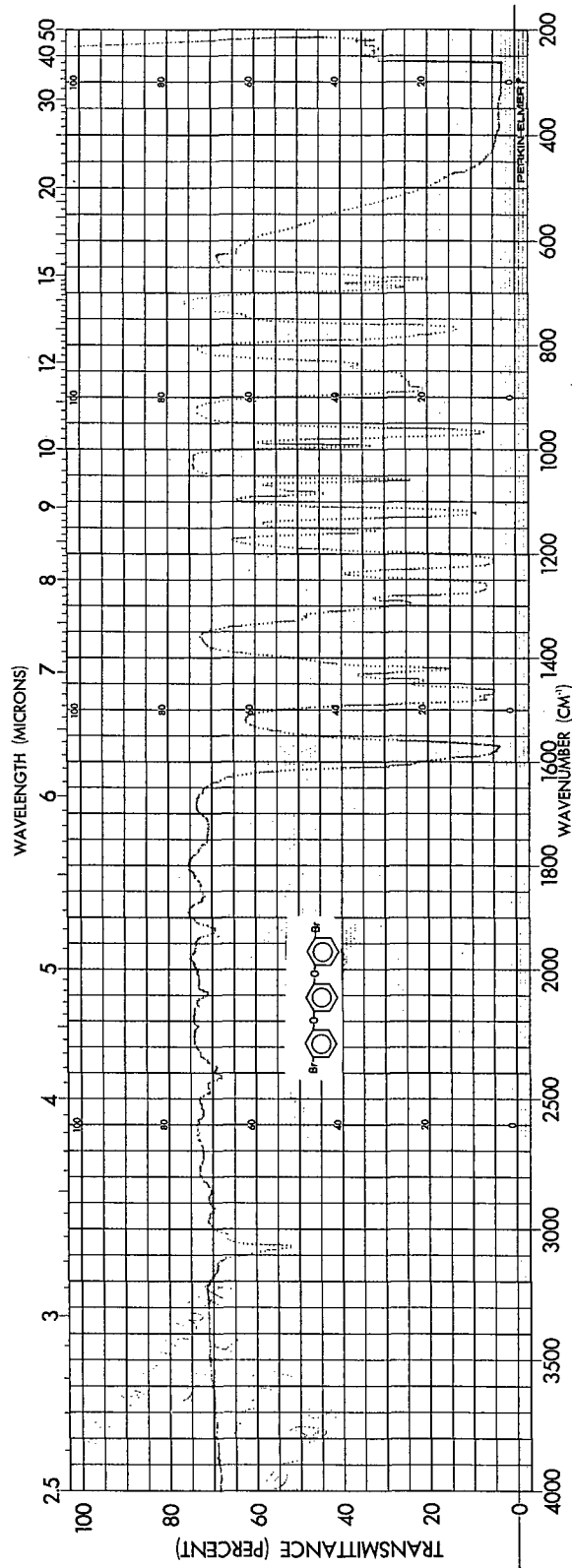


Figure 4. Infrared Spectra of 1,3-Bis-(m-bromophenoxy) benzene

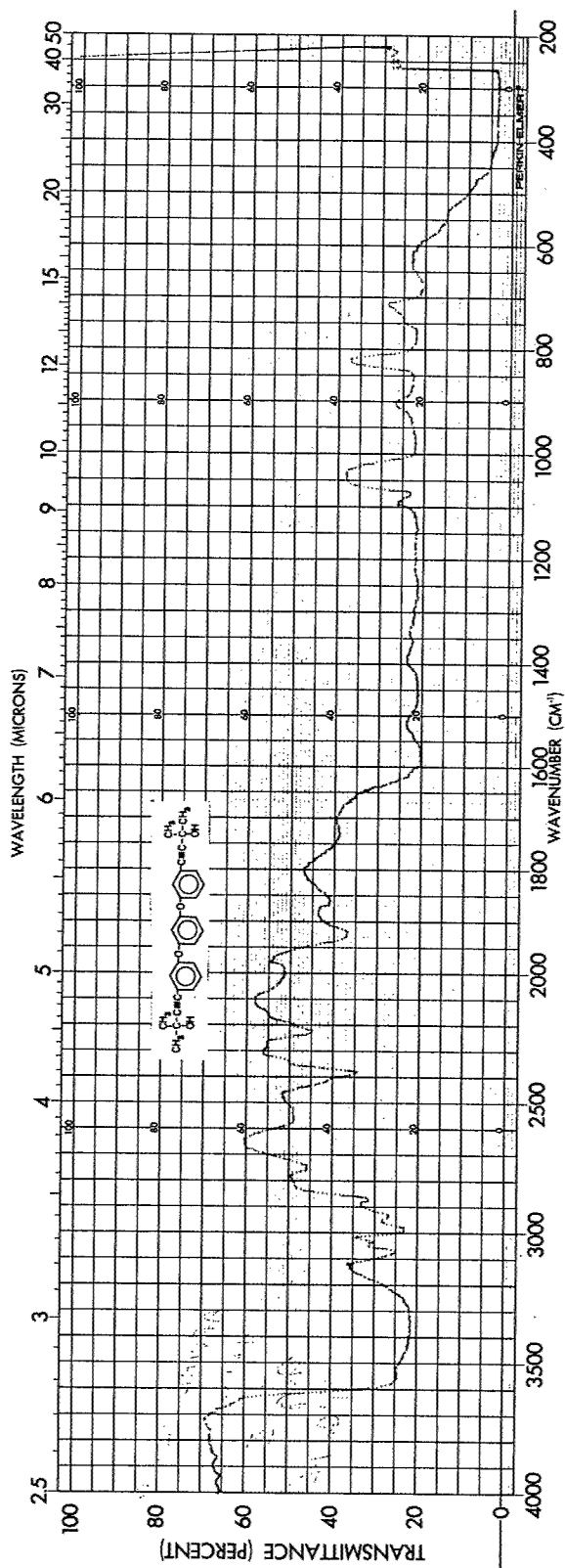


Figure 5. Infrared Spectra of the Bis-butynol Adduct of 1,3-Bis-(m-ethynylphenoxy) benzene

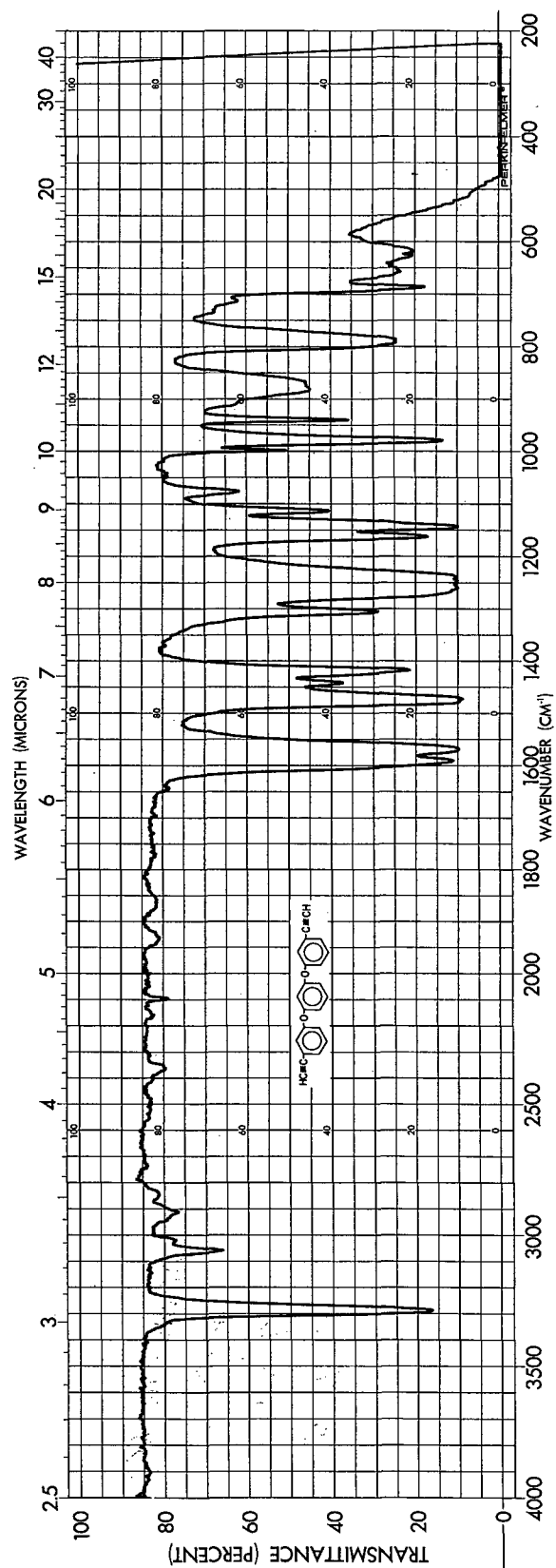


Figure 6. Infrared Spectra of 1,3-Bis-(m-ethynylphenoxy) benzene

SECTION IV

CONCLUSIONS

This work was performed to demonstrate the feasibility of using reactive diluents in the processing of high temperature thermoset oligomers. The reactive diluent lowers the effective softening point of the oligomer, decreases the bulk viscosity during processing, and then becomes dormant by co-reacting with the oligomer.

Two reactive diluents were prepared which exhibited low Tg's and used in conjunction with the acetylene terminated oligomer BATQ-H. It has been shown that tailoring the molecular structure of the diluent to resemble the structure of the oligomer results in a completely compatible system. The results are positive and encouraging, although it is recognized that future work will be required to define more clearly the possible potential of such a process for Air Force use.

Future research in this area should be directed toward the following goals:

1. Determine the minimum amount of reactive diluent required for melt processability.
2. To investigate the influence of the reactive diluent on the thermal, thermaloxidative and mechanical properties.
3. To demonstrate the processing of the system with the actual fabrication of fiber reinforced composites.

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