

New Acetylene-Terminated Phenylquinoxaline Oligomers

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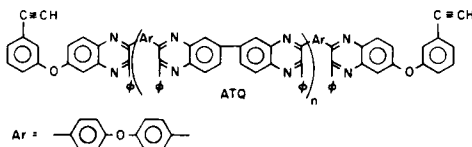
Synopsis

A series of new acetylene-terminated phenylquinoxaline oligomers and diacetylene compounds have been prepared utilizing 4-(3-ethynylphenoxy)benzil. The amorphous materials with molecular weights from 500 to 1460 exhibited softening in the 25–160°C range with a strong polymerization exotherm reaching a maximum at 270–290°C. The addition nonvolatile cure provides materials which show excellent thermoxidative stability and processability for high-temperature matrix and adhesive resins.

INTRODUCTION

A substantial effort in our laboratory has been directed toward improving the processability of the high temperature resistant aromatic heterocyclic polymer systems. As a class of materials, the heterocyclics are the most attractive for high temperature applications, however, the most difficult to process. A very promising approach has been the use of acetylene-terminated heterocyclic oligomers¹ which cure via nonvolatile addition reactions. The terminal acetylene groups thermally homopolymerize to generate a fused aromatic system with excellent thermoxidative stability, comparable to the heterocyclic backbone.

We recently reported² the acetylene-terminated phenylquinoxaline (ATQ) oligomers which displayed a variety of properties desirable for processing and show excellent potential as a moisture insensitive adhesive³ and matrix⁴ material. A major drawback in the ATQ system is the difficulty in working with 3-(3,4-diaminophenoxy)phenylacetylene utilized as the oligomer end-capping agent. This compound is difficult to prepare and has a very limited shelf life. Very recently, a system analogous to the ATQ's has been reported⁵ wherein a benzil end-capping agent, 4-(4-ethynylphenoxy)benzil, was utilized. Softening temperature reported for the prepolymer systems synthesized via this end-capper were considerably higher, however, than those for the corresponding ATQ system. The higher softening behavior is most likely due to the ethynyl group being para to the phenoxy aromatic.



This paper is concerned with the synthesis of a stable, acetylene-containing benzil end-capping agent, 4-(3-ethynylphenoxy)benzil, which was reacted with

diamine terminated oligomers to afford a series of benzil end-capped acetylene terminated phenylquinoxalines (BATQ's). The modification of structure retained the meta-ethynyl orientation thereby generating amorphous low softening oligomers.

EXPERIMENTAL

3-Ethynylphenyl-p-toluenesulfonate was prepared according to a known procedure.²

1,4-Bis(4-benziloxy)benzene was prepared by the nitro-displacement procedure of Relles et al.⁶

Other Bis-benzils were prepared by the published procedures of Hergenrother.⁷

3-Ethynylphenol—A solution of sodium hydroxide (20.0 g, 0.500 mole) in water (50 ml) was added to a solution of 3-ethynylphenyl *p*-toluene-sulfonate (21.3 g, 0.0783 mole) in methanol (150 ml), and the mixture was distilled under nitrogen over a 90 min period during which time 100 ml of distillate was removed. The reaction mixture was then cooled to 23°C, diluted with deaerated water (150 ml), and extracted (3 × 50 ml) with hexane. The water layer was poured into a mixture of sulfuric acid (50 ml) and ice (500 g) and extracted (3 × 50 ml) with ether. The combined ether layers were washed with water (3 × 50 ml) and the ether was distilled under nitrogen to leave 8.80 g (96%) of 3-ethynylphenol as a yellow liquid which showed a single spot upon TLC analysis and was used without further purification for the subsequent reaction. An analytical sample was obtained by chromatography on silica gel with chloroform as eluent.

ANAL. Calc. for C₂₂H₁₄O₃: C, 81.34; H, 5.12; molecular weight, 118. Found: C, 81.14; H, 5.09; molecular weight, 118 (by mass spectrometry).

4-(3-Ethynylphenoxy)benzil (I)—To a solution of 3-ethynylphenol (4.75 g, 0.0403 mole) in dimethylsulfoxide (50 ml) under nitrogen was added sodium methoxide (2.17 g, 0.0402 mole). The mixture was stirred for 30 min at 23°C, transferred to an addition funnel under nitrogen, and added over a 20 min period to a solution of 4-nitrobenzil (9.30 g, 0.0365 mole) in dimethylsulfoxide (100 ml) stirred at 90°C under nitrogen. When addition was complete, the reaction mixture was stirred overnight at 23°C and poured into a solution of sodium hydroxide (50 g) in ice water (1 liter). Extraction with toluene (3 × 50 ml) followed by chromatography on silica gel with benzene as eluent afforded 5.80 g (49%) of 4-(3-ethynylphenoxy)benzil as a yellow oil which solidified upon standing at 23°C overnight to a pale yellow solid, melting point 79–81°C.

ANAL. Calc. for C₂₂H₁₄O₃: C, 80.97; H, 4.32; molecular weight, 326. Found: C, 80.40; H, 3.86; molecular weight, 325 (by mass spectrometry).

General Oligomer Preparation—A solution of bis-benzil (1 mole) in *m*-cresol was added dropwise to a solution of tetraamine (2 moles) in *m*-cresol at 90–100°C under nitrogen. After addition, the reaction mixture was stirred for 2 hr at 90–100°C and then precipitated into a solution of 10% sodium hydroxide (sufficient quantity to neutralize the *m*-cresol) in methanol. Purification was accomplished by two reprecipitations from tetrahydrofuran into methanol.

3,3'-Bis(4-[3-ethynylphenoxy]phenyl)-2,2'-diphenyl-6,6'-biquinoxaline (BA-DAB-BA)—To 200 ml of tetrahydrofuran stirred at 23°C under nitrogen

was added 11.00 g (0.0337 mole) of (I) followed by 3.44 g (0.0161 mole) of 3,3'-diaminobenzidine. After 1 min of stirring to permit complete solution, 4 ml of glacial acetic acid was added. The reaction mixture was then stirred overnight (20 hr total) at 23°C and poured, with stirring, into 1200 ml of water. The resultant orange suspension was extracted 2 × 100 ml with dichloromethane, and the combined organic layers were extracted once with 400 ml of 5% Na₂CO₃ and 2 × 400 ml with water. The dichloromethane layer was concentrated to 100 ml diluted with 100 ml of ethyl acetate and poured, with stirring, into 1 liter of methanol. The precipitate which formed was collected (11.3 g, 88%), redissolved in 100 ml of dichloromethane, diluted with 100 ml of ethyl acetate, and reprecipitated with 1 liter of methanol to afford 10.3 g (81%) after drying overnight at 23°C under reduced pressure.

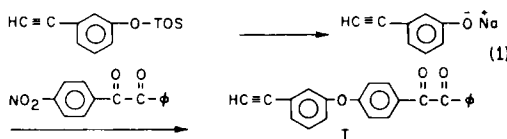
ANAL. Calc. for C₅₆H₃₄N₄O₂: C, 84.63; H, 4.28; N, 7.04. Found: C, 84.42, 84.57; H, 4.19, 4.24; N, 6.96, 6.99.

6 - (3 - Ethynylphenoxy)-3-(4-[3-ethynylphenoxy]phenyl)-2-phenylquinoxaline (AA-BA)—A mixture of 15.0 (0.0528 mole) of 3-(3,4-dinitrophenoxy)-phenylacetylene and 600 ml of methanol was heated at reflux until solution was complete (solution A). A mixture of 368 g (2.11 mole) of sodium dithionite and 1200 ml of water was heated at 60°C until solution was complete at which point a solution of 41.6 g (2.11 mole) of sodium hydroxide in 400 ml of water was added immediately followed by solution A. A deep purple color formed during the addition and quickly faded to afford a milky yellow solution. An additional 200 ml of methanol was added causing a lightening of the color, and the reaction mixture was stirred for 30 min and then extracted 3 × 250 ml with chloroform. The combined chloroform extracts were washed 3 × 250 ml with water and then added to a solution of 7.91 g (0.0243 mole) of 4-(3-ethynylphenoxy)benzil in 150 ml of *m*-cresol stirred under nitrogen. The reaction mixture was stirred overnight (16 hr), the chloroform was removed by distillation and the remaining solution was poured into a mixture of 500 ml of 20% NaOH solution and 500 g of ice and then extracted 3 × 250 ml with chloroform. The combined chloroform extracts were extracted 3 × 250 ml with water and distilled to dryness on a rotary evaporator. The oily residue was dissolved in 500 ml of carbon tetrachloride and chromatographed on a column of silica gel (2 in. × 2 ft). The column was first eluted with 1 liter of carbon tetrachloride to remove high *R_f* impurities and then with benzene to remove the yellow band containing the AA-BA. The benzene eluate was reduced in volume and freeze dried to give 9.73 g (79%) of AA-BA which softened at 25°C. Upon standing overnight, the fluffy product collapsed to a very viscous semisolid.

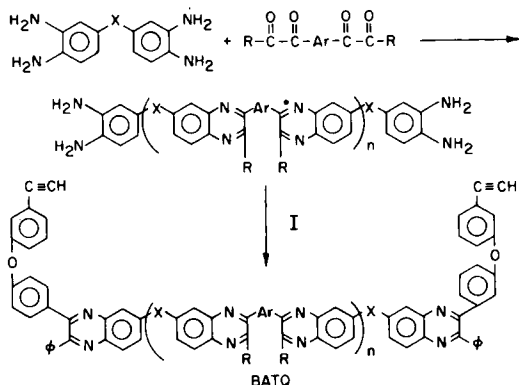
ANAL. Calc. for C₃₆H₂₂N₂O₂: C, 84.03; H, 4.31; N, 5.45. Found: C, 84.14, 84.27; H, 4.43; 4.40; N, 5.31, 5.19.

RESULTS AND DISCUSSION

The synthesis of the new-endcapping agent 4-(3-ethynylphenoxy)benzil (I) is shown in reaction scheme I. Hydrolysis of 3-ethynylphenyl-*p*-toluenesulfonate followed by nucleophilic displacement of the nitro group on 4-nitrobenzil provided a 47% overall yield of I. The material exhibits excellent shelf life in contrast to the diaminophenoxyphenyl acetylene² which slowly decomposed even under a nitrogen atmosphere.



The benzil end-capped oligomers were prepared by the reaction of various aromatic tetraamines with aromatic benzils in 2 to 1 molar ratio of reactants. The ortho diamine end-capped quinoxaline oligomers were then reacted with excess I in *m*-cresol. All the oligomers prepared were soluble [(20–30)%] in low-boiling organic solvents such as methylene chloride, chloroform, dioxane and tetrahydrofuran. Purification of the BATQs was carried out by reprecipitation from tetrahydrofuran into methanol. The various structures prepared are shown in Figure 1.

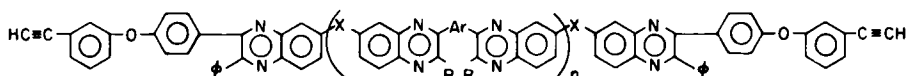


The thermal behavior of the BATQ oligomers was studied by both differential scanning calorimetry (DSC) and thermomechanical analysis (TMA). Samples of each oligomer were then cured at 280°C for 6 hr under nitrogen and the T_g 's after cure were determined. The results of the thermoanalytical measurements are summarized in Table I.

As can be seen, the softening behavior is similar for all of the oligomers except for BATQ-S which is higher and BATQ-O,P which is substantially lower. The flexibility inherent in the BATQ-O,P structure is probably responsible for the lower softening point, a desirable feature, but the same flexibility also apparently prevents the T_g after cure from reaching the cure temperature, placing undesirable restrictions on the use temperature. A similar anomalously low T_g after cure can be seen for BATQ-P. The remaining BATQ's exhibit cure temperatures and T_g after cure temperatures analogous to the ATQ system. The differential between the temperature ranges for softening and cure should afford a sufficient "window" to prevent premature cure before softening is complete.

Analysis of the BATQ 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 450°C (in vacuo). Isothermal aging studies showed weight losses of less than 30% after 200 hr at 600°F in air.

Analysis of the BATQ oligomers by TLC (Baker-flex silica gel 1B-F with chloroform as developer) separated the mixture into components apparently corresponding to $n = 0, 1, 2, 3,$ and >3 . TLC analysis of the ATQ systems revealed an analogous distribution of components. A chromatographic separation of BATQ-M into its components was carried out on a dry column of silica gel. Chloroform eluted 8% of the $n = 0$ component 3,3'-bis(4-[3-ethynylphenoxy]phenyl)-2,2'-diphenyl-6,6'-biquinoxaline (BA-DAB-BA) which displayed an identical R_F value upon TLC, and elemental analysis as a sample independently synthesized from 3,3'-diaminobenzidine and I. No separation into the 6,6'; 6,7';



| OLIGOMER | X | R | Ar |
|----------|---|---|----|
| BATQ-O | - | | |
| BATQ-M | - | | |
| BATQ-S | - | | |
| BATQ-P | - | | |
| BATQ-H | 0 | | |
| BATQ-O,O | 0 | | |
| BATQ-O,P | 0 | | |
| BATQ-O,M | 0 | | |

Fig. 1. Structures of BATQ oligomers prepared.

and 7,7' biquinoxaline isomers was observed. Chloroform-ether (2:1) eluted 88% of a material containing predominantly the $n = 1, 2,$ and 3 components (by TLC analysis); and tetrahydrofuran eluted the remaining 4% which was comprised mainly of the $n > 3$ oligomeric components.

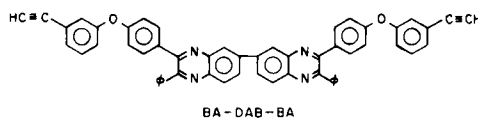


TABLE I
Thermoanalytical Data on BATQ's

| Oligomer | Softening onset ^a (°C) | Maximum rate softening ^a (°C) | Cure onset ^b (°C) | Maximum rate cure ^b (°C) | T _g after cure ^{b,c} (°C) |
|----------|-----------------------------------|--|------------------------------|-------------------------------------|---|
| BATQ-O | 145 | 172 | 215 | 276 | 310 |
| BATQ-M | 145 | 175 | 215 | 274 | 311 |
| BATQ-S | 160 | 180 | 215 | 273 | 309 |
| BATQ-P | 145 | 162 | 210 | 283 | 275 |
| BATQ-H | 150 | 170 | 200 | 280 | 322 |
| BATQ-O,O | 145 | 170 | 210 | 280 | 298 |
| BATQ-O,M | 145 | 167 | 200 | 285 | 290 |
| BATQ-O,P | 125 | 140 | 195 | 293 | 257 |

^a Determined by TMA at 20°C/min under nitrogen.

^b Determined by DSC at 20°C/min under nitrogen.

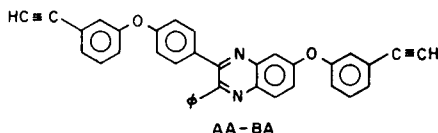
^c Cured at 280°C for 6 hr under nitrogen.

Analysis of (BA-DAB-BA) by TMA revealed a softening range commencing at 75°C and maximizing at 100°C. DSC analysis showed a cure exotherm beginning around 200°C and maximizing at 266°C. After curing a sample for 6 hr at 260°C, a T_g of 300°C was obtained by both DSC and TMA.

Analysis by TMA of the $n = 1-3$ oligomer mixture of BATQ-M from column chromatography revealed an initiation of softening at 150°C, only slightly higher than for unchromatographed BATQ-M. The softening rate of the chromatographed BATQ-M did not maximize until 200°C, however, significantly higher than the 175°C obtained for the unchromatographed material. It is thus apparent that the presence of the BA-DAB-BA and the oligomers of $n > 3$ exerts a great influence upon softening rate even at the 12% concentration level. The DSC trace of the cure exotherm was virtually identical for both the chromatographed and unchromatographed material, commencing around 200°C and maximizing at 274°C with a slight shoulder at 220°C.

In view of its low softening point, its standard BATQ-like curing behavior, and its high T_G after cure, the use of BA-DAB-BA by itself would afford the best combination of processing and cure characteristics of any of the BATQ's. Its disadvantages are the greater amount of 4-(3-ethynyl-phenoxy)benzil required for its preparation and its lower molecular weight between crosslinks after cure. The fact that its presence in a mixture with a BATQ substantially improves the softening behavior suggests the addition of BA-DAB-BA as a reactive diluent to BATQ systems to afford a preselected choice of initial T_g . This would be particularly advantageous if the bulk viscosity of the softened BATQ does not afford a sufficient "window" for cure.

The most effective reactive diluent for the ATQ and BATQ systems would be one of minimum molecular weight between reaction sites, thereby providing the lowest possible T_g , yet have a molecular structure which would be compatible with the oligomers. Reaction of I with 3-(3,4-diaminophenoxy)phenylacetylene provided 6-(3-ethynylphenoxy)-3-(4-[3-ethynylphenoxy])-2-phenylquinoxaline (AA-BA) which exhibited a softening range of 20-25°C by TMA. DSC (20°C/min) revealed an onset of the cure exotherm at 150°C with a maximum at 258°C. After 6 hr of cure at 260°C; the softening temperature was raised to 275°C. It was found that (AA-BA) was completely miscible and compatible with the BATQ-H oligomer as evidenced by a single T_g of mixtures of the two components. For example, a mixture of 20% (AB-BA) and 80% BATQ-H exhibited a T_g of 116°C which after cure at 280°C increased to 305°C.



A preliminary evaluation of (AA-BA) material was carried out to determine its potential as a matrix resin for high-temperature graphite composites, since it exhibited excellent physical characteristics for processing. The material could be melt prepregged at 174°F and exhibited good tack and drape. Graphite laminates were fabricated at 350°F for 30 min under 200 psi and then postcured overnight in a circulating air oven at 500°F. Short beam shear strengths of around 8500 psi were achieved at room temperature with good retention of mechanical properties at 450 (90%) and at 500°F (74%).

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