

## POLYQUINOLINES: VERSATILE AROMATICS WITH DIVERSE PROPERTIES

J.K. Stille

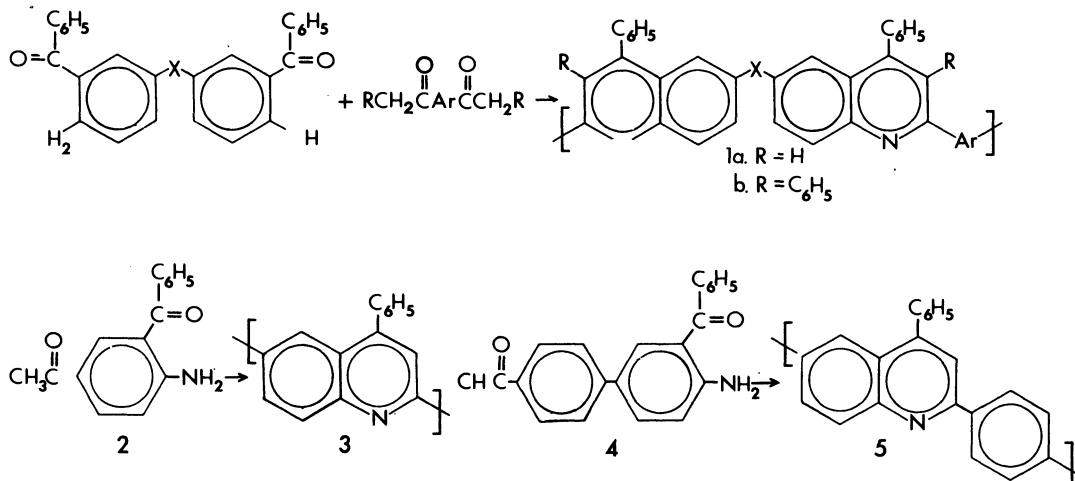
Colorado State University, Fort Collins, Colorado 80523, USA

**Abstract** - Polyquinolines can be synthesized by a polymerization reaction which allows a variety of structural modifications, resulting in a range of chain stiffness that can be altered from a relatively flexible polymer with a low glass transition temperature to a rod-like molecule with a high glass transition temperature. The polymerization reaction is acid catalyzed, but is carried out most effectively by a new polymerization agent, dicresyl phosphate. Most of the polymers are soluble in common organic solvents, such that fiber can be dry-spun and transparent films can be cast from solution. Excellent thermal stability is observed for these materials. Other rigid polyquinolines that have high transition temperatures and are highly crystalline are not as readily fabricated.

In order to utilize the processability exhibited by the flexible, amorphous polyquinolines, yet increase the use temperature to much above their glass transition temperatures (250-350°), polyquinolines containing biphenylene units in the main chain have been synthesized. These polymers crosslink thermally by a ring-opening reaction of the biphenylene unit. Incorporation of biphenylene into a variety of other high performance polyaromatics also allows these materials to undergo facile curing.

### INTRODUCTION

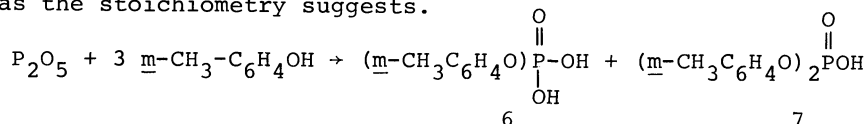
Thermally stable polymers containing quinoline units in the chain can be synthesized by a polymerization reaction that allows a variety of structural modifications, resulting in a range of chain stiffness that can be altered from a relatively flexible polymer with a low glass transition temperature to a rod-like molecule with a high glass transition temperature (Ref. 1&2). Most of the materials have high crystalline transition temperatures, but a low degree of crystallinity (Ref. 3&4). For example, polyquinolines 1 (X=O) containing some flexibility, exhibit lower transition temperatures (T<sub>g</sub>=265-350°, T<sub>m</sub>=450-480°) and lower crystallinity (<20%) than the rigid polyquinoline 3 (T<sub>g</sub>=415°, T<sub>m</sub>=552°, >50% crystallinity) or 5. (T<sub>g</sub>=375, T<sub>m</sub>=580°, >70% crystallinity).



The largely amorphous polyquinolines, of which 1 is representative, are characterized by high moduli below the glass transition temperature ( $E' = 6 \times 10^{10}$  dyn/cm<sup>2</sup>, 1a, X=O, Ar=4,4'-C<sub>6</sub>H<sub>4</sub>OC<sub>6</sub>H<sub>4</sub>), and good solubility in common organic solvents. In addition, all polyquinolines show excellent thermal stability as determined by thermal gravimetric analysis.

#### POLYMERIZATION

The polymerization reaction of an aromatic bis-*o*-aminoketone with an aromatic bisketomethylene monomer has been shown (Ref. 1&2) to give high molecular weight polyquinoline by acid catalysis. The reaction is first order in aminoketone concentration and first order in ketomethylene concentration. Optimum polymerization rates and molecular weights were obtained in mixtures of *m*-cresol and the reaction product of *m*-cresol and phosphorus pentoxide (Ref. 1&2). The reaction product has now been shown by <sup>31</sup>P nmr to consist of an equimolar mixture of mono-(6) and di-*m*-cresol (7) esters of phosphoric acid, as the stoichiometry suggests.



Both esters, 6 and 7 have been independently synthesized (Ref.5), and although mixtures of ester 6 and *m*-cresol were marginally effective as a polymerization medium, ester 7 with *m*-cresol effected the polymerization at about the same rate as the *m*-cresol phosphorous pentoxide reaction mixture. One added advantage of the independently synthesized (and purified) diester 7 is that much higher molecular weights could be obtained. The upper degree of polymerization attainable in the phosphorus pentoxide *m*-cresol reaction mixture appears to be about 320, possibly as a result of some side reaction with one or more of the monomer functional groups. Acid catalyzed cyclotrimerization has been suggested (Ref.2) as a reaction which would not only consume ketomethylene groups, but also would lead to branching. Polymerization in a mixture of *m*-cresol and 7, however, gives a DP>550 in 24 h.

#### PROPERTIES

In most cases, the processability of thermally stable polymers is limited by insolubility or high phase transition temperatures. A soluble polyaromatic is often amorphous and has a relatively low glass transition temperature. If the T<sub>g</sub> or T<sub>m</sub> of thermally stable amorphous or crystalline polyaromatics are low such that they can be processed by melt techniques, then their use temperature is low, limited by T<sub>g</sub> or T<sub>m</sub>.

Polyquinolines of the general structure 1 are largely amorphous and have glass transition temperatures of 350° or lower. Thus, although they are soluble in common organic solvents, and can be readily fabricated from solution, their use temperature is limited to 350° or lower. The use temperature cannot be raised to the crystalline transition temperatures since annealing does not develop sufficient crystallinity.

Polyquinolines 3 and 5 are sufficiently crystalline and have high enough crystalline transition temperatures, 480° and 580°, respectively, but are soluble only in strong acids such as sulfuric acid. The storage moduli of each one is also sufficiently high, ( $E' = 4 \times 10^{10}$  dyn/cm<sup>2</sup> even above their glass transition temperatures ( $E' = 2.5 \times 10^{10}$  dyn/cm<sup>2</sup> such that good mechanical properties are retained up to T<sub>m</sub>. Although a copolymer obtained from the polymerization of equimolar amounts of 2 and 4 retained the good thermal (T<sub>m</sub> = 518°, T<sub>g</sub> = 330°) and mechanical ( $E'_{(250)} = 3.5 \times 10^{10}$  dyn/cm<sup>2</sup>;  $E'_{(>350)} = 2.6 \times 10^{10}$  dyn/cm<sup>2</sup>) properties characteristic of the homopolymers, the copolymer retained a surprisingly high degree of crystallinity and was also insoluble in common organic solvents.

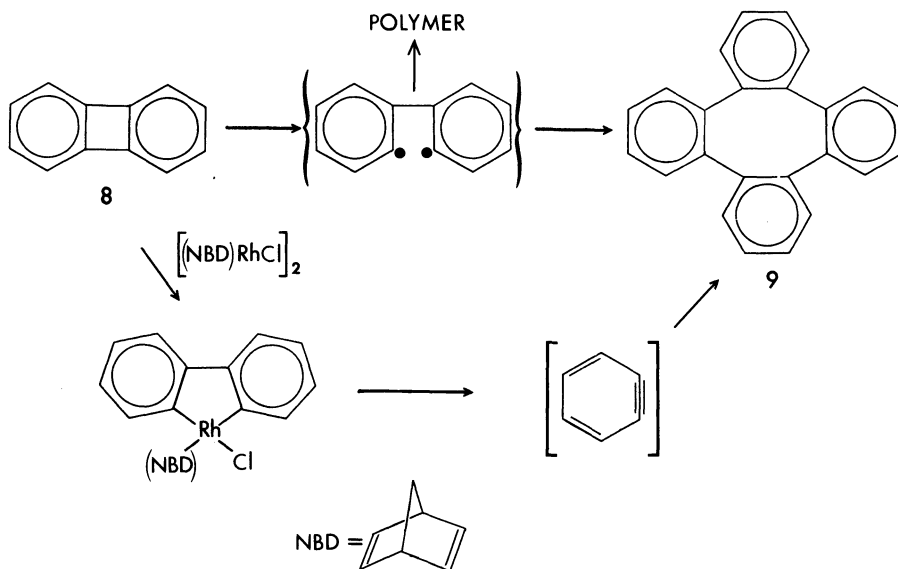
#### CROSSLINKING REACTIONS

One approach to the problem of obtaining a readily processable polymer with a high use temperature is to crosslink the polymer after its fabrication. Unfortunately there are few good crosslinking reactions for polyaromatics, in part because of their chemically inert structure and the reduced chain mobility. Such a reaction must take place at a convenient temperature

without the evolution of volatiles to produce a thermally stable product structure. The temperature of the reaction should be above  $T_g$ , but below the polymer decomposition temperature.

We have developed such a reaction that is applicable to crosslinking a variety of polyaromatic structures, and have applied it to a number of polyaromatics including polyquinolines (Ref. 7&8).

Biphenylene (8) undergoes thermolysis at  $\sim 400^\circ$  and, depending on the reaction conditions, yields tetrabenzocyclooctatetraene (9), polymer, or biphenyl--resulting from radical abstraction of hydrogen from solvent (Ref. 9&10) Although the structure of the polymer was not determined, it likely contains poly-(o-phenylene) segments. These reports suggest a diradical as the reactive intermediate in pyrolysis. Thus, any structure formed as a result of the thermolysis of a biphenylene unit in a thermally stable polymer would be expected to maintain the high temperature structural integrity of the polymer.



Rhodium catalysts are known to open strained cyclic hydrocarbons by an oxidative addition mechanism (Ref. 11). Thermolysis of biphenylene containing a catalytic amount of the rhodium catalyst at  $200^\circ C$  produced dibenzocyclooctatetraene in a 44% yield (recrystallized) and polymer. Thus, the products of the catalyzed reaction are the same as those obtained from the uncatalyzed thermolysis. By analogy to the cubane reaction (Ref. 11), however, it might be expected the benzyne is the reactive intermediate. This temperature is approximately  $200^\circ C$  lower than that required for the uncatalyzed reaction.

The incorporation of varying portions of biphenylene in place of diphenylether into a polyquinoline was accomplished by balancing the appropriate amounts of 2,6-diacetylbiphenylene in place of 4,4'-diacetyldiphenylether under standard polymerization conditions.

The glass transition temperature of the parent polyquinoline containing all biphenylene units was lowered by increasing the content of diphenylether units; copolymer 10c had a lower  $T_g$  than the homopolymer 10d. A reaction exotherm attributed to the opening of the biphenylene ring was observed above  $300^\circ$ . The time required for curing depended on the curing temperature ( $340-380^\circ$ ) as well as the biphenylene content of the polymer. The onset of the exotherm for crosslinking increased with an increasing biphenylene amount and paralleled the increase in  $T_g$  (Fig. 1).

Since biphenylene underwent a rhodium catalyzed ring-opening at much lower temperatures to afford the same products as obtained from the uncatalyzed reaction, curing was carried out on polymer samples containing catalytic amounts of norbornadiene-chlororhodium(I) dimer. Generally, lower temperatures and shorter reaction times were used to effect the same crosslinking

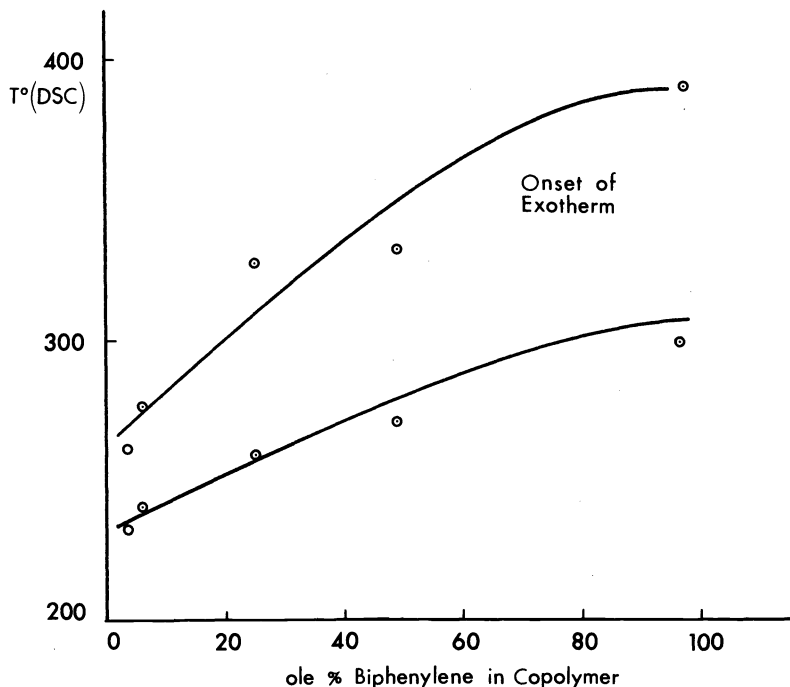
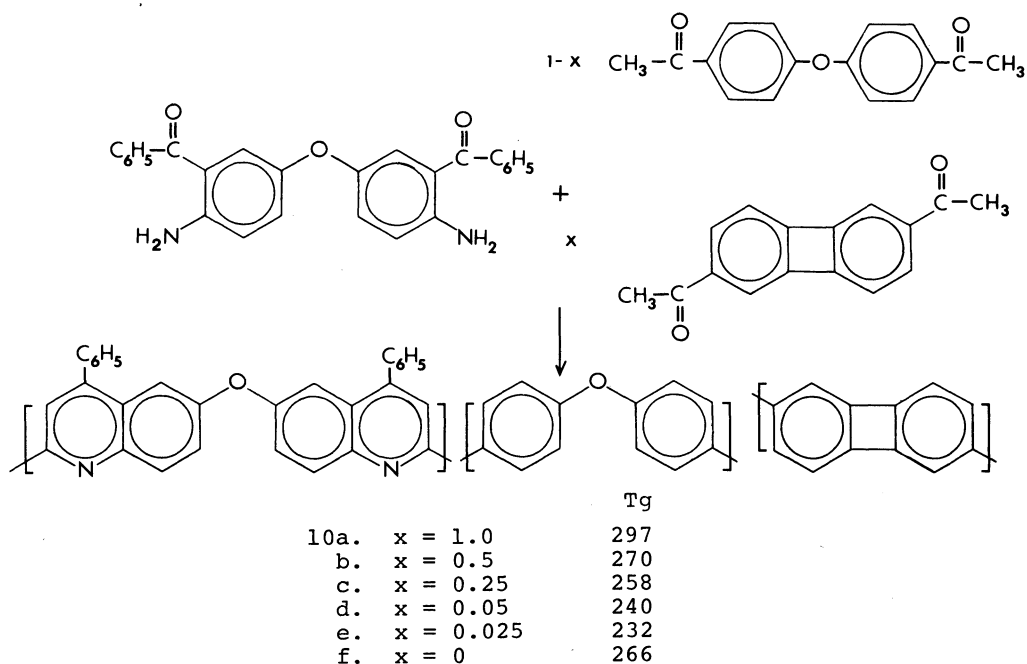


Fig. 1. Dependence of Exotherm Onset on Biphenylene Content

reaction. The thermal mechanical analysis of polymers **10c** and **10d** showed that curing at 380°C for 1 h was sufficient to erase the glass transition temperature. In polymer **10e**, a very high glass transition temperature is observed after curing at 380°C for 1 h. At 380°C, the effect of curing time on the glass transition temperature of this polymer (**10e**) containing only 2.5% biphenylene units, is to increase T<sub>g</sub>. Rhodium catalysis does this more effectively (Fig. 2). At a curing time of 3 min, the difference in the rhodium cures and the catalyzed curing is most pronounced with polymer **10c** containing 25% biphenylene. Generally, curing was accompanied by insolubility in all solvents, an increase in T<sub>g</sub> and finally disappearance of T<sub>g</sub>.

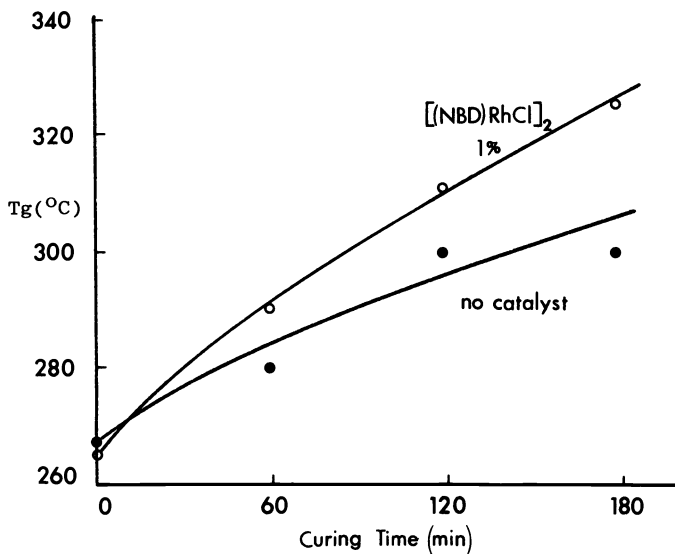
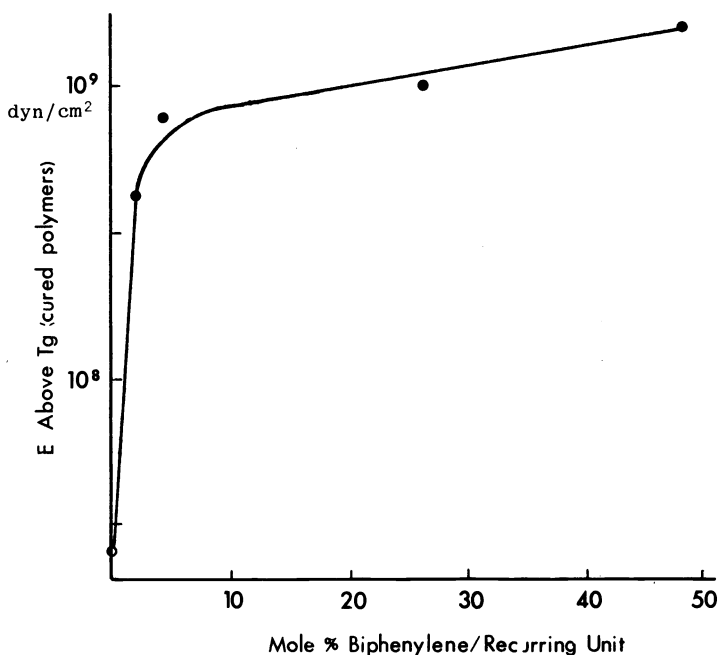


Fig. 2. Copolymer 10e Curing

The dynamic mechanical properties of uncured and cured films of polyquinolines 10a-f were obtained from room temperature up to 380°C. Under the mild tensile stresses required, the mechanical performances of films are relatively constant up to the glass transition temperature.

The dynamic moduli of the cured polymers at low temperatures (25°-250°) are, as expected, higher than those of the uncured polymers. The glass transition temperatures after curing are 30-60° higher than the uncured samples, as measured by the moduli. More important, the moduli of the cured polymers above  $T_g$  are much higher than those of the homopolymer, 10f, and are a function of the percent biphenylene in the copolymer (Fig. 3). Even a low biphenylene incorporation (2.5%, 10e) is sufficient to raise the value from  $2.4 \times 10^7$  to  $3.8 \times 10^8$  dyn/cm<sup>2</sup> (Fig. 4).

Finally, it is instructive to compare the dynamic storage moduli ( $E'$ ) above  $T_g$  for polymer 10e cured with and without catalyst as a function of curing time (Fig. 5). As expected, the catalytic effect is reflected by the generation of higher moduli for the low curing times.

Fig. 3.  $E'$  of 10e (cured) Above  $T_g$

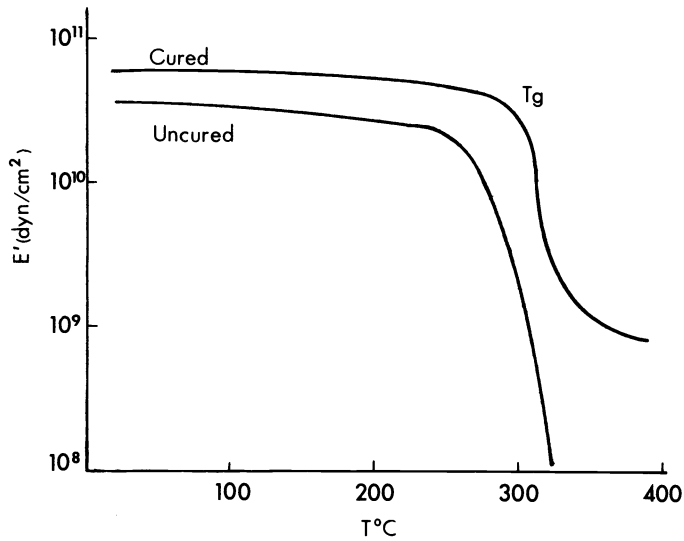


Fig.4. E' of Copolymer 10e vs Temperature

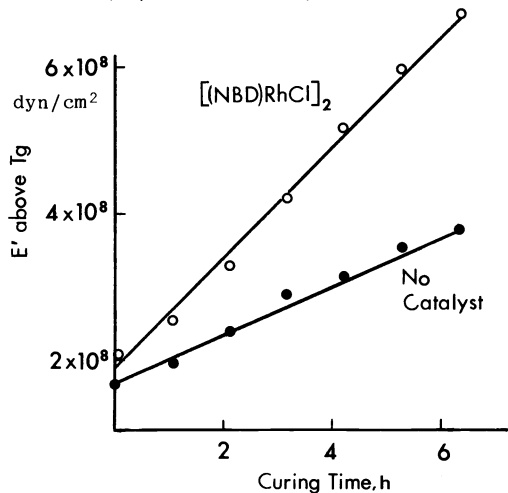
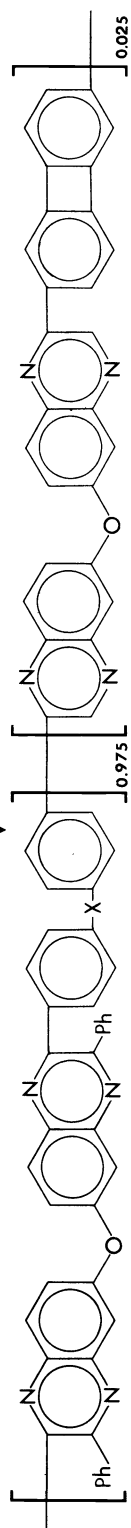
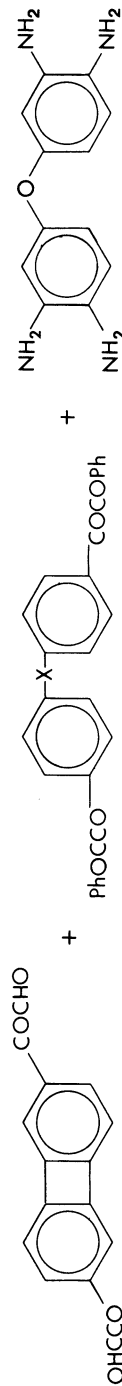
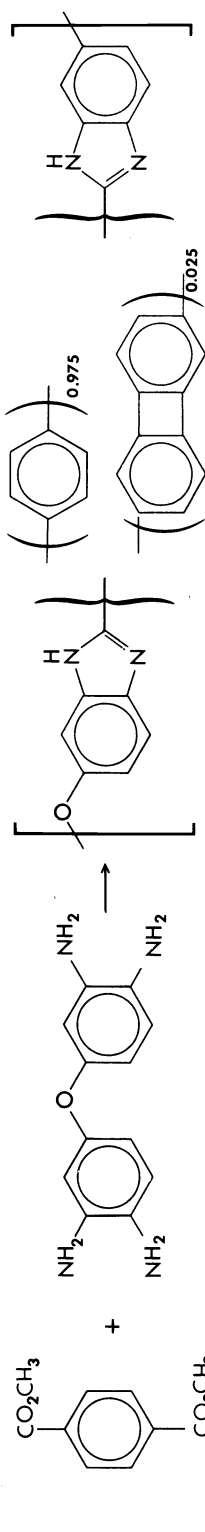
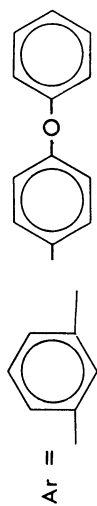
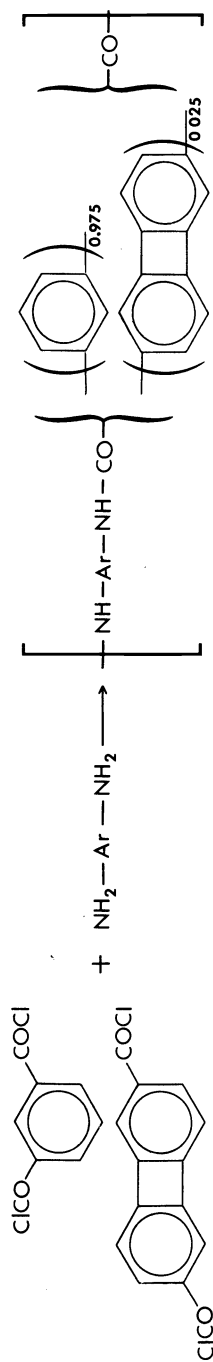


Fig. 5. E' Above Tg vs Curing Time, Copolymer 10e

The thermal gravimetric analysis of cured polymer samples and of the parent polymer (10f) that does not contain the biphenylene units showed breaks at the same temperatures, and under nitrogen, suffered the same weight loss up to 800°. This provides some evidence that in the curing reaction, stable crosslinks are indeed formed.

This method of crosslinking polyquinolines is applicable to crosslinking a wide variety of thermally stable polymers, including polyamides, polybenzimidazoles, and polyquinoxalines. Aromatic polyamides have been synthesized by substituting biphenylene-2,6-dicarboxylic acid chloride (2.5 mole percent) for isophthaloyl chloride in polymerization with two different amines, *m*-phenylenediamine and 4,4'-diaminodiphenylether in *N*'-methylpyrrolidone with polyene oxide as an acid acceptor (Ref. 12 & 13). A polyaromatic benzimidazole was synthesized by substituting dimethyl biphenylene-2,6-dicarboxylate (2.5%) for dimethyl terephthalate in polymerization with 3,3'-4,4'-tetraaminodiphenylether tetrahydrochloride in polyphosphoric acid at 200°. Polyquinoxalines were synthesized by substituting 2,6-diglyoxalylbiphenylene (2.5%) for two dibenzils in polymerization with 3,3'-4,4'-tetraaminodiphenylether in a 1:1 mixture of *m*-cresol-xylene at ambient temperature. The cured polymers showed an increase or disappearance of the Tg, complete insolubility in all solvents, and higher moduli, particularly at temperatures above the original Tg.



X = O, nil

Acknowledgement - This work was supported by grants from the Army Research Office, and the National Science Foundation.

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