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HIGH PERFORMANCE POLYMERS: MATRIX RESINS HIGH STRENGTH  
POLYQUINOXALINES A (U) COLORADO STATE UNIV FORT  
COLLINS DEPT OF CHEMISTRY J K STILLE FEB 87

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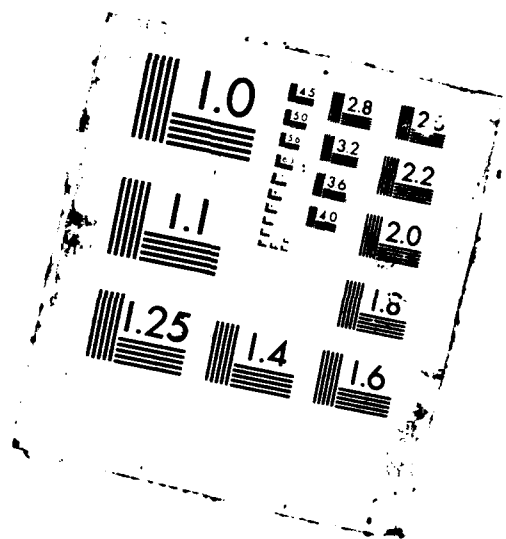
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| 19. KEY WORDS (Continue on reverse side if necessary and identify by block number)<br><b>Polyquinolines      Rigid-rod Polymers<br/>Polyimides      Poly(p-phenylene)<br/>Matrix Resins      Conducting Polymers<br/>Composites</b> <b>Quinolines</b>                                                                                                                                                                                                                                                                                |                                     |                                                                                                 |
| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br><b>The synthesis of low molecular weight polyquinolines and polyimides containing biphenylene end-caps, with and without acetylenic units in the main chain, were synthesized and evaluated as matrix resins for fiber reinforced composites. The best composite properties were obtained with an exact equivalent biphenylene groups and acetylenic groups, since these groups generate crosslinks by the formation of phenanthrene units.</b> |                                     |                                                                                                 |

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Rigid rod polyquinolines containing two pendent triphenylene oxide side chains per recurring unit are not appreciably solubilized by these groups, even though these polymers have reduced crystallinity.

Rigid-rod polyquinolines containing E-stilbene units in the main chain undergo photoisomerization to Z-stilbene units. This has the effect of converting the rigid rod to a non rod-like polymer containing the Z-unit, thereby reducing the viscosity of polymer solutions and allowing a polymer film to contract on irradiation.

Poly-*p*-phenylenes have been prepared by the pyrolysis of soluble, processable precursor poly(5,6-dihydroxy-2-cyclohexen-1,4-ylene) derivatives. The precursor can be spin-coated and then thermally converted to the thermally stable, conducting polyphenylene.

The conductivities of a series of doped polyquinolines have been determined.

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# HIGH PERFORMANCE POLYMERS: MATRIX RESINS, HIGH STRENGTH POLYQUINOXALINES AND CONDUCTING POLYAROMATICS

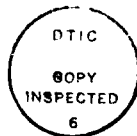
Final Report

J. K. Stille

6 February 1984 - 5 February 1987

U.S. Army Research Office

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Department of Chemistry

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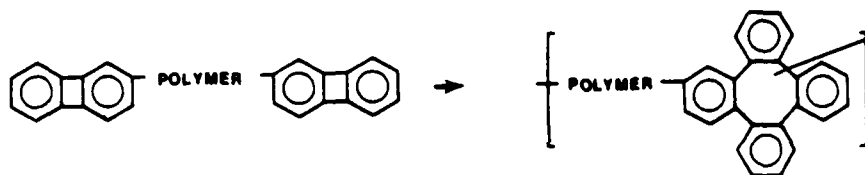
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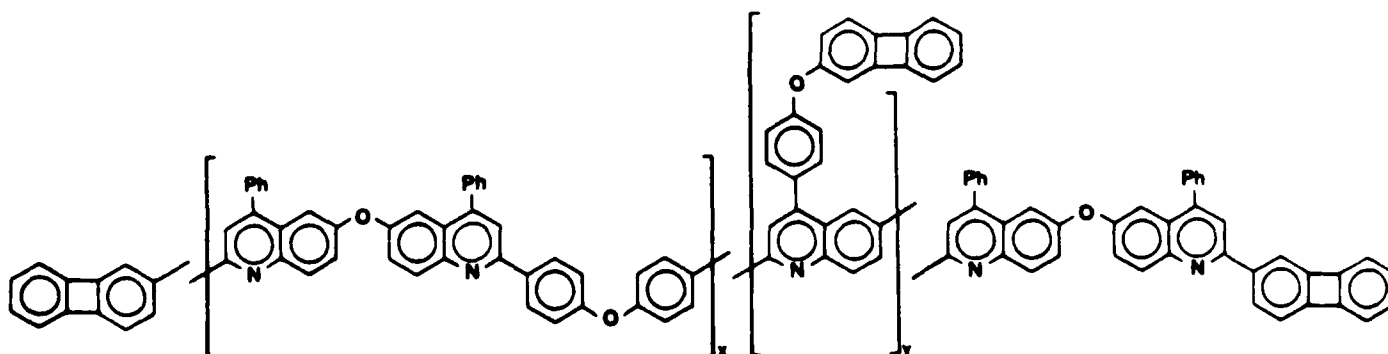
## MATRIX RESINS AND CROSS-LINKING REACTIONS FOR COMPOSITES.

Biphenylene end-capped polyquinoline prepolymers (DP = 3, 11, 22) had been shown to undergo rapid curing at  $\sim 325\text{--}350^\circ\text{C}$ , and graphite reinforced composites could be prepared that displayed excellent initial properties and low weight loss after oxidative aging at  $316^\circ\text{C}$ . However, the mechanical properties were severely diminished after aging for 50-100 h at  $316^\circ\text{C}$  in air. This relatively poor oxidative stability was attributed to the fact that the main reaction of the biphenylene end-caps

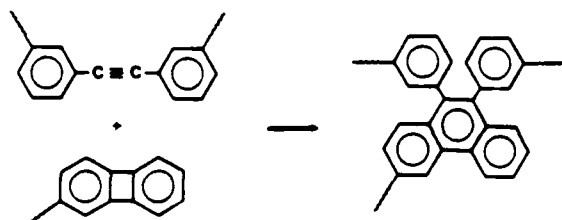


was the dimerization to tetraphenylene, leading to a chain extension, and that the tetraphenylene unit (as well as unreacted biphenylene) were points of facile oxidative degradation. Accordingly the following research was initiated in an effort to overcome these problems.

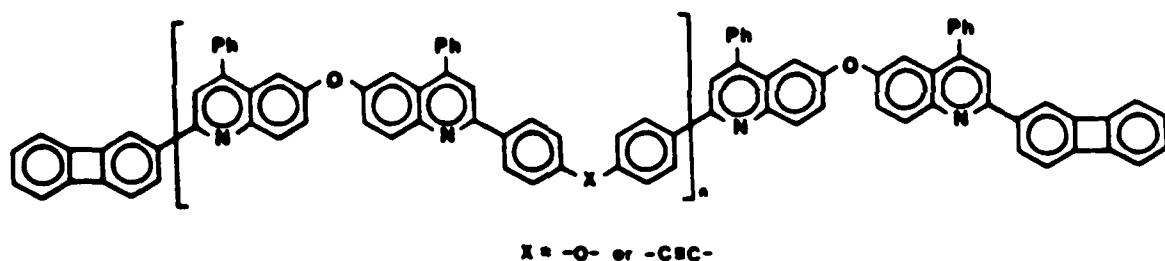
Oligomeric polyquinolines (shown) containing both biphenylene end-caps and pendant biphenylenes solved the crosslinking problem, but did not address the problem of thermooxidative stability of the resins.



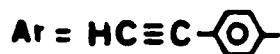
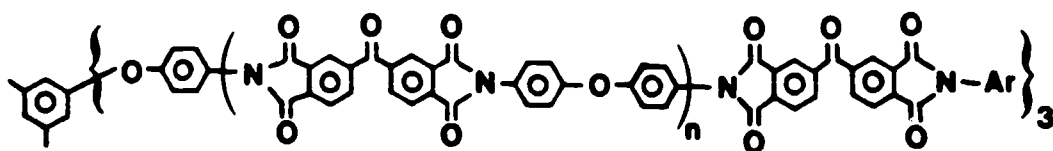
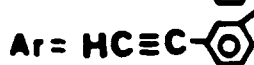
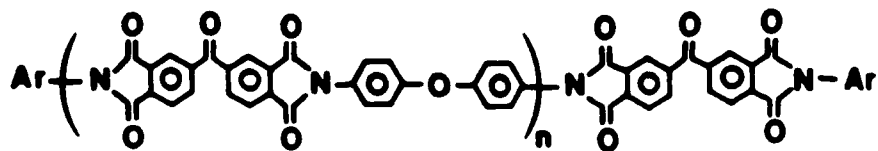
However, when oligomeric polyquinolines were synthesized such that they contained biphenylene end-caps along with acetylenic units in the polymer main chain, a superior matrix resin was obtained as a result of a reaction of the biphenylene ends with the acetylene to yield a phenanthrene crosslink. Composites containing



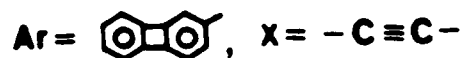
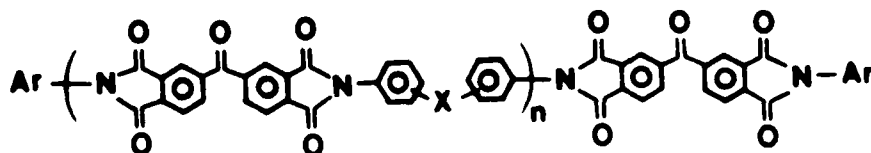
exactly an equivalent number of biphenylene and acetylene groups in the matrix resin had excellent mechanical properties, which were maintained after aging at 316°C for 400 h.

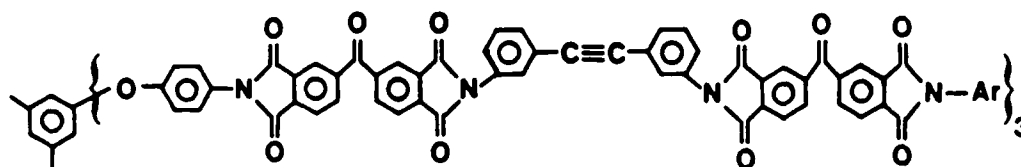


More recently, a series of polyimides containing not only reactive acetylenic and biphenylene groups but also variations in a number of structural features have been synthesized. First, biphenylene or acetylene end-capped prepolymers containing a linear chain or a three-armed star configuration were prepared. Melt processing of a blend of acetylene and biphenylene containing polymers, especially those with the star geometry, give high quality films.

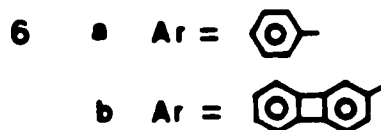
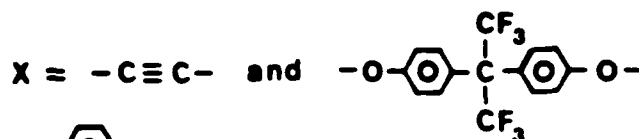
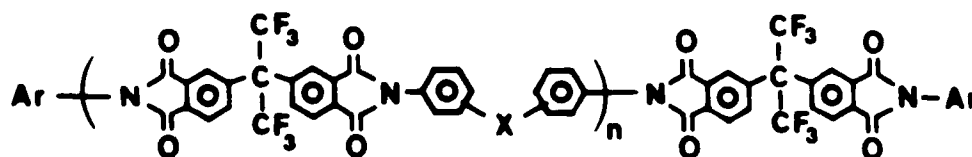
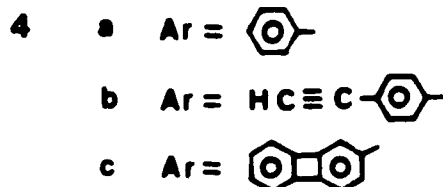
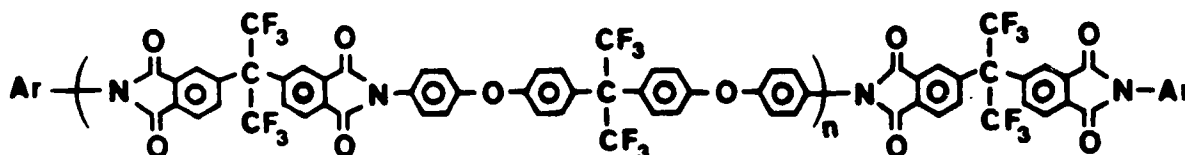


Films melt pressed from polyimides containing both the biphenylene end-caps and internal acetylene units had  $T_g$ 's above  $400^\circ\text{C}$  and exhibited excellent mechanical and thermooxidative stability up to  $T_g$ . Unfortunately, all these polyimides were insoluble in common organic solvents, so that in the formation of composites, carbon fibers would have to be brush-coated with the amide-acid instead of the imide.





Both linear and star polyimides with the biphenylene end-cap and internal acetylene units were prepared utilizing dianhydride and diamine monomers containing perfluoroisopropylidene connecting groups. These polyimides are soluble in common organic solvents and show excellent melt flow properties.



The use of certain of these matrix resins in unidirectional graphite fiber reinforced composites are currently under evaluation by us at AVRADCOM Research and Technology Laboratories (NASA Lewis Research Center).

The foregoing work is described in the following publications:

John P. Droske and John K. Stille, *Macromolecules*, **17**, 1 (1984); "Biphenylene End-Capped Polyquinoline Prepolymers: Synthesis, Processing and Curing Reactions."

John P. Droske, Urszula M. Gaik and John K. Stille, *Macromolecules*, **17**, 10 (1984); "Biphenylene End-Capped Aromatic Prepolymers: Polyimides, Poly(ether-keto-sulfones), and Polyquinoxalines."

John P. Droske, John K. Stille and William B. Alston, *Macromolecules*, **17**, 14 (1984); "Biphenylene End-Capped Polyquinolines and Polyimide Prepolymers as Matrix Resins for High-Use-Temperature Composites."

J. K. Stille and J.P. Droske, *J. Macromol. Sci., Chem.*, **A21** (8 & 9), 913 (1984); "Biphenylene End-Capped Polyaromatics."

D. M. Sutherlin and J. K. Stille, *Macromolecules*, **19**, 251 (1986); "Biphenylene- and Phenyl-End-Capped Oligomeric Polyquinolines Containing Pendent Biphenylenes."

D. M. Sutherlin, J. K. Stille and W. B. Alston, *Macromolecules*, **19**, 257 (1986); "Biphenylene- and Phenyl-End-Capped Oligomeric Polyquinolines Containing Acetylene Linkages: Preparation, Processing and Composite Application."

T. Takeichi and J. K. Stille, *Macromolecules*, **19**, 2093 (1986); "Star and Linear Imide Oligomers Containing Reactive End-Caps: Preparation and Thermal Properties."

T. Takeichi and J. K. Stille, *Macromolecules*, **19**, 2103 (1986); "Biphenylene End-Capped Imide Oligomers Having Internal Acetylene Groups in the Backbone: Preparation and Thermal Properties."

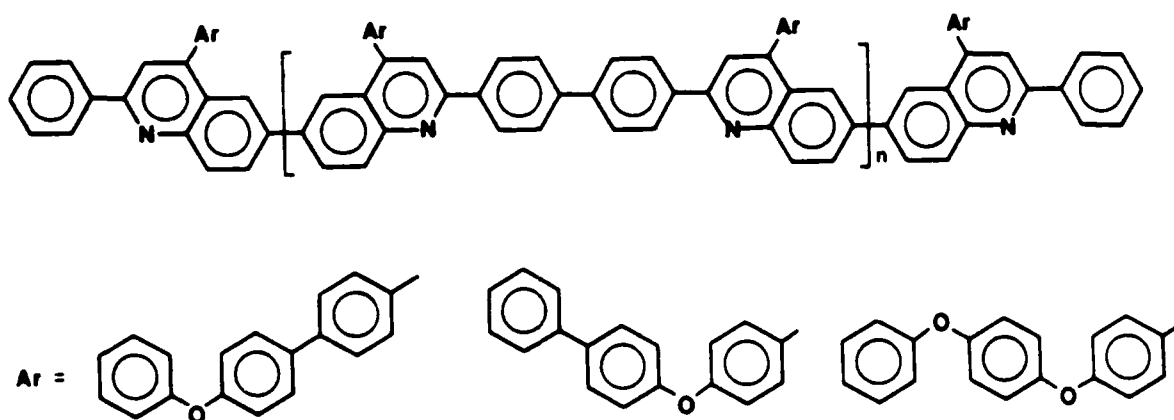
T. Takeichi and J. K. Stille, *Macromolecules*, **19**, 2108 (1986); "Readily Processable Imide Oligomers Containing Perfluoroisopropylidene Connecting Units and Reactive Acetylenic and Biphenylene Groups. Synthesis, Curing and Thermal Properties."

#### **RIGID ROD POLYQUINOLINES CONTAINING PENDENT ARMS.**

Although rigid-rod polyaromatics generally display high strength and possess the thermal and mechanical properties necessary for high temperature applications, they have very limited solubility, or are insoluble in common organic solvents, making

their fabrication difficult. With a number of polyaromatics, solubility has been improved by attachment of phenyl groups to the polymer main chain, as is the case with polyquinoxalines, polyphenylenes, and polyimides. The solubility of a number of polyheterocycle/polyphenylene copolymers is enhanced by the attachment of phenoxyphenyl and phenylthiophenyl pendant groups.

Attachment of the pendent aryl ether groups to a rigid-rod polyquinoline in the 4,4'-positions of the quinoline rings did not appreciably enhance the solubility, however. The polymers maintained relatively high crystalline transition temperatures ( $T_m = 417\text{-}505^\circ\text{C}$ ), although they were not as crystalline as the parent phenylated polyquinoline ( $\text{Ar} = \text{C}_6\text{H}_5$ ).



This work is described in the following publication:

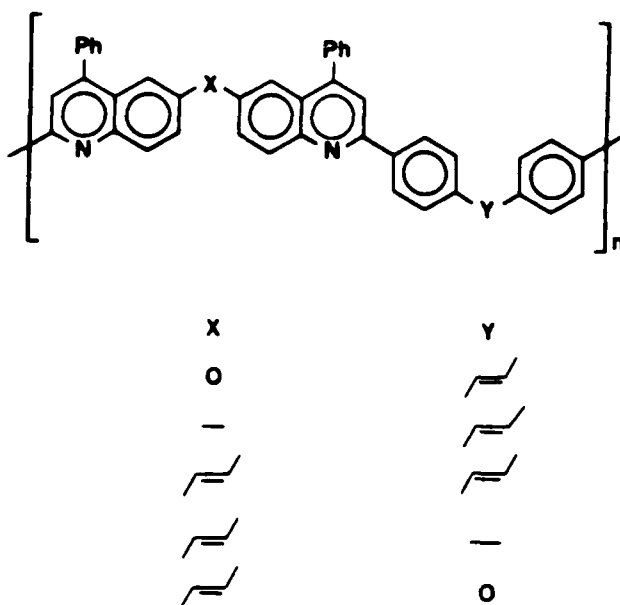
D. M. Sutherlin and J. K. Stille, *Macromolecules*, **18**, 2669 (1985);  
 "Rigid-Rod Polyquinolines with Extended Aryl Ether Pendent Groups: An Approach to Solubility Enhancement."

## POLYMER ISOMERIZATION.

A second approach to solubilizing rigid-rod polymers is to obtain a polymer that is not a rigid-rod, and thus has improved solubility, but can be converted subsequently to a rod-like polymer to attain the high strength, high modulus properties.

Conceivably, this could be effected by the photolysis of a polymer containing photoisomerizable E-Z units in the main chain. Thus, conversion of E units to Z by photolysis would afford improved solubility. Once solution spinning had been accomplished, thermal annealing would produce the E-isomer and regenerate the rigid main chain.

Polyquinolines containing stilbene units were synthesized; photolysis of their solutions decreased the viscosity as much as 23%. When films were irradiated above  $T_g$  the polymer did work, contracting about 5%.



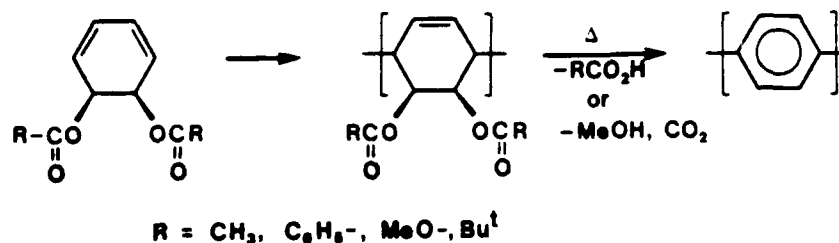
The above work is described in the following publication:

E. K. Zimmermann and J. K. Stille, *Macromolecules*, **18**, 321 (1985);  
 "Photoresponsive Polyquinolines."

### CHAIN RIGIDIFICATION.

The thermal generation of a 1,4-phenylene unit in a polymer from a cyclohexene ring can be used to convert a polymer containing cyclohexene units to poly(p-phenylene). While our own work in this area was proceeding, ICI reported the

synthesis of polyphenylene from a soluble polymer containing cyclohexene diacetate units. [D. G. H. Ballard, A. Courtis, I. M. Shirley and S. C. Taylor, *J. Chem. Soc., Chem. Commun.*, 954 (1983). D. G. H. Ballard, A. Courtis and I. M. Shirley, European Patent 76605, 1983]. Whereas the ICI monomer, 1,3-cyclohexadiene-5,6-diol, was synthesized *via* an enzyme from a bacterium, *Pseudomonas putida*, which glycolates one benzene double bond, we prepared carboxylates of both the cis and trans-diol by conventional chemistry. Polymerization of the cyclohexadiene takes place by free radical initiation, preferentially in the absence of solvent and at low temperatures to produce the highest molecular weight polymer ( $M_n = 12,000 - 20,000$ ), which is soluble in common organic solvents. Thermolysis ( $300^\circ\text{C}$ ) of the cis isomer (shown) proceeds much more cleanly than the trans isomer to give polyphenylene in a reaction that yields the calculated amount of polyphenylene. Thus, the cyclohexene intermediate polymer can be spin coated on a silica wafer to form a clear, transparent



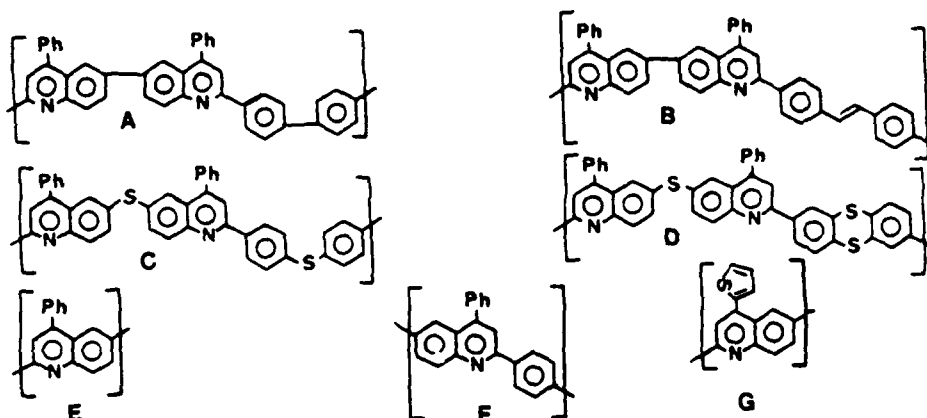
coherent film. Thermolysis yields an insoluble, thermally stable insulating film which, however, can be made conducting with the usual dopants ( $\sigma \approx 10\Omega^{-1}\text{cm}^{-1}$ ).

The results of this work have been submitted for publication.

D. R. McKean and J. K. Stille, *Macromolecules*, in press; "The Electrical Properties of Poly(5,6-dihydroxy-2-cyclohexen-1,4-ylenes) Derivatives."

# CONDUCTING POLYQUINOLINES.

The following polyquinolines were prepared and doped with  $I_2$ ,  $AsF_5$ , sodium naphthalide (Na/naph) or sodium anthracide (Na/anth) with the results shown in the Table. Oxidants ( $I_2$ ,  $AsF_5$ ) had a small effect on the conductivity whereas reductants



| Polymer | Form       | Dopant  | Conductivity ( $\Omega^{-1} \text{cm}^{-1}$ ) |                    | Time  |
|---------|------------|---------|-----------------------------------------------|--------------------|-------|
|         |            |         | Initial                                       | Final              |       |
| A       | Film       | $I_2$   | $4 \times 10^{-12}$                           | $1 \times 10^{-2}$ | 23d   |
|         | Fiber(5%)  | $AsF_5$ | $1 \times 10^{-12}$                           | $8 \times 10^{-9}$ | 97.5h |
|         | (10%)      | "       | $4 \times 10^{-12}$                           | $6 \times 10^{-8}$ | 19d   |
|         | Fiber(5%)  | Na/Naph | $3 \times 10^{-12}$                           | $6 \times 10^{-3}$ | -     |
|         | (10%)      | "       | $4 \times 10^{-11}$                           | $1 \times 10^{-2}$ | 17h   |
|         | Fiber(5%)  | Na/anth | $2 \times 10^{-11}$                           | $1 \times 10^{-2}$ | 3h    |
|         | (10%)      | "       | $6 \times 10^{-12}$                           | $7 \times 10^{-1}$ | -     |
|         | (18%)      | "       | $6 \times 10^{-11}$                           | 8                  | 4h    |
| B       | Fiber(10%) | $AsF_5$ | $2 \times 10^{-12}$                           | $8 \times 10^{-6}$ | 19d   |
|         | Fiber(5%)  | Na/Naph | $1 \times 10^{-12}$                           | $1 \times 10^{-2}$ | 2h    |
|         | (10%)      | "       | $2 \times 10^{-11}$                           | $1 \times 10^{-3}$ | 5h    |
|         | Fiber(5%)  | Na/anth | $3 \times 10^{-11}$                           | $2 \times 10^{-2}$ | 3h    |
|         | (10%)      | "       | $2 \times 10^{-11}$                           | $6 \times 10^{-2}$ | 1.5h  |
| C       | Film       | $I_2$   | $2 \times 10^{-13}$                           | $6 \times 10^{-5}$ | 6.5d  |
|         |            | $AsF_5$ | $3 \times 10^{-12}$                           | $3 \times 10^{-7}$ | 147h  |
|         |            | Na/Naph | $2 \times 10^{-12}$                           | dissolved          | -     |
|         |            |         |                                               |                    |       |
| D       | Film       | $AsF_5$ | $1 \times 10^{-11}$                           | $3 \times 10^{-7}$ | 92.5h |
|         |            | Na/Naph | $2 \times 10^{-12}$                           | dissolved          | -     |
| E       | Fiber(5%)  | Na/anth | $5 \times 10^{-11}$                           | 11                 | 11h   |
|         |            | (18%)   | $4 \times 10^{-11}$                           | 3                  | 1h    |
| F       | Fiber(5%)  | Na/anth | $4 \times 10^{-10}$                           | $4 \times 10^{-2}$ | 1h    |
| G       | Fiber(5%)  | $I_2$   | $9 \times 10^{-8}$                            | $3 \times 10^{-2}$ | 341h  |
|         |            | $AsF_5$ | $6 \times 10^{-10}$                           | no change          | 7d    |
|         |            | Na/anth | $8 \times 10^{-10}$                           | $2 \times 10^{-2}$ | 1h    |

(Na/anth or Na/naph) had a much larger effect. Higher concentrations generally gave higher conductivities (A and B) but not in E, and incorporation of a vinyl group (A B) or a phenylene group (E F) lowered the conductivity as does adding a more electron donating group (E G). Polyquinoline E also has been subjected to ion implantation to yield a conducting material.

The foregoing research is described in the following publications:

J. K. Stille, *Contemporary Topics in Polymer Science*, **5**, 209 (1984); "New Developments in High Temperature and High Strength Polyquinolines."

G. E. Wnek, B. Wasserman, M. S. Dresselhaus, S. E. Tunney and J. K. Stille, *J. Polym. Sci.: Polym. Lett. Ed.*, **23**, 609 (1985); "Ion Implantation of a Polyquinoline."

S. E. Tunney, J. Suenaga and J. K. Stille, *Macromolecules*, in press; "Conducting Polyquinolines."

## List of Participating Scientific Personnel

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T. Takeichi

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M. Peña  
D. Rutherford  
S. Stoessel  
D. Sutherlin (Ph.D., Colorado State, May, 1985)  
S. Tunney (Ph.D., Colorado State, August, 1986)  
T. Upshaw  
E. Zimmerman (M.S., Colorado State, August, 1984)

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