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13. ABSTRACT Processable precursor polymers to aramids, poly(imino-1,4-phenyleneiminocarbonyl-1,4 phenylenecarbonyl) and poly(imino-1,3-phenyleneiminocarbonyl-1,4-phenylenecarbonyl), were prepared and studied. The precursor polymers were made from the reaction of 2,5-dichlorobicyclo[2.2.2]octane-1,4-dicarbonyl chloride or 2,5-diacetoxycyclo[2.2.2]octane-1,4-dicarboxylic acid. The polymeric precursors were subsequently converted in approximately 98% - 100% yields, via dehydrohalogenation and retro Diels-Alder reactions to the corresponding aramids by refluxing in 1M solution of potassium hydroxide or sodium hydroxide, or by bulk pyrolysis using aromatization catalysts, such as, ZnCl ₂ and dichlorobenzene sulfonic acid. Only the p-phenylene precursor polymer exhibited liquid crystal characteristics in solution. Thermal properties were examined and tensile properties will be determined in a future study.					
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FINAL TECHNICAL REPORT

PROCESSABLE PRECURSORS TO HIGH PERFORMANCE LIQUID CRYSTALLINE POLYMERS

A. STATEMENT OF THE PROBLEM STUDIED

Desirable properties of main chain liquid crystalline aramids, such as, poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl) include high crystallinity, a high degree of orientation, high modulus and tensile properties, linear structures with angles approximately 180° between chain extending linkages, low solubilities in common organic and inorganic solvents, high glass transition temperatures, and relatively high melting points.

These properties are considered valuable for many applications, but impose serious limitations in processing and fabrication techniques. The high melting temperatures of aramids most often exceed the decomposition temperatures thereby eliminating melt processing as an option. Low solubilities in organic and inorganic solvents reduce solvent options to 98% sulfuric acid, N-methyl-2-pyrrolidone/ CaCl_2 , hexamethylphosphoramide/N-methyl-2-pyrrolidone/ LiCl , dimethylsulfoxide/ KOBu^t /methanol, and nitromethane/ Al_2Cl_6 among others.

In order to allow for easier processing and fabricating, it is imperative that the melting transitions of these rigid chain polymers be substantially depressed, and their solubility in common organic and inorganic solvents be increased.

Recently, intense synthetic efforts have been devoted to the development of more easily melt processable and more soluble liquid

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crystalline polymers which would nevertheless retain the remarkable properties associated with these polymers.¹⁻⁶ These approaches, although meritorious, are also to some extent self defeating, since two of the advantages of liquid crystalline polymers are the high heat performance and the solvent resistance. One approach that has not been tried, is to prepare liquid crystalline precursor polymers which are more processable, and which can be transformed to the desired high temperature liquid crystalline polymer after it has been processed into the desired shape. This concept which has gained wide acceptability in the preparation of preceramic polymers⁸, has not been explored for the preparation of intractable organic polymers. Preparation of pre-polyphenylene⁹ polymers is one of the few examples in the literature.

B. SUMMARY OF THE MOST IMPORTANT RESULTS

The structures of the polymer precursors prepared and studied are shown below.

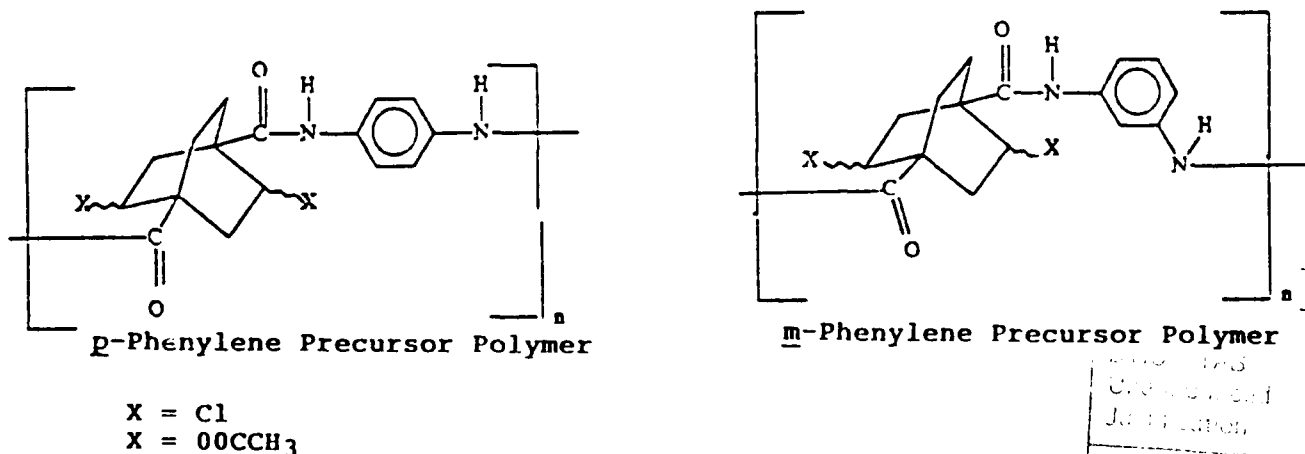


Figure 1. Structures of Precursor Polymers.

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The precursor polymers were subsequently converted to the corresponding aramid in 97 - 100% yields, via dehydrohalogenation and retro Diels-Alder reactions.

Generally, the polymers are soluble in dimethylformamide (DMF), N-methylpyrrolidone (NMP), and dimethylsulfoxide (DMSO). The inherent viscosities of the precursor polymers range from 0.79 - 0.65 dL/g at 30°C and the inherent viscosities aramids made from the precursor polymers range from 0.92 - 0.81 dL/g.

Solutions of the p-phenylene precursor polymers (25% w/w) in NMP or DMF under cross-polarized light resulted in the depolarization of plan-polarized light when thin layers were viewed at 32X magnification. The photomicrographs of the birefringent phase appears as threaded schlieren texture, characteristic of the nematic mesophase, typical of rigid-rod polymers.

X-ray diffraction shows that the p-phenylene precursor polymers are partially crystalline and the m-phenylene precursor polymers are noncrystalline.

C. LIST OF ALL PUBLICATIONS AND TECHNICAL

1. Precursor Polymers. 1. Synthesis and Characterization of Processable Precursors to Aramids.
-Submitted to Polymer Communications
2. Precursor Polymers. 2. Synthesis and Characterization of Processable Precursors to Aramids.
-Submitted to Polymer Preprints
3. Precursor Polymers
-to be presented at the American Chemical Society National Meeting, Spring 1993, Denver Colorado

D. List of all Participating Scientific Personnel Showing any Advanced Degrees Earned by Them while Employed on the Project

1. Dr. I.I. Harruna -Project Director/Principal Investigator

2. Ms. Agnes Thuo -Graduate Student (Clark Atlanta University)
3. Dr. K.B. Bota -Professor of Chemistry (Clark Atlanta University)
4. Ms. Sherita D. McLamore -Undergraduate student (Clark Atlanta University) earned B.S. Spring 1992
5. Ms. LaShawn Drew -Undergraduate (Spelman College) Earned B.S. Spring 1991
6. Ms. Rozalyn Strong -Undergraduate Student (Morris Brown College) Earned B.S. Spring 1992
7. Elve Jones -Undergraduate (Morris Brown College)
8. Sondra Paham -Undergraduate (Spelman College)
9. Tanya Scott -Undergraduate (Spelman College)

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