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ELECTRIDE DOPING OF SOLUBLE HIGH TEMPERATURE POLYMERS

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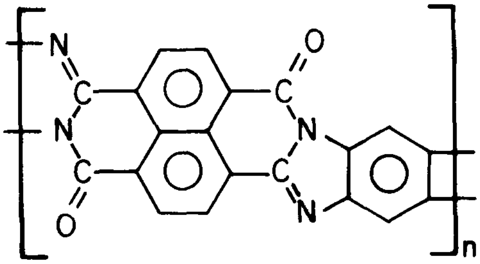
We report on the conductivity of two new Pyrrones and a polyphenylquinoxaline. A new and novel material, cesium electride, was used as the doping agent.

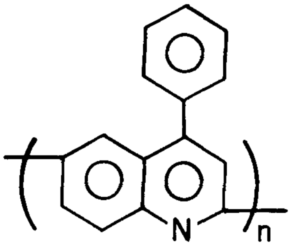
INTRODUCTION

A new development in the electrically conducting polymers field is the emergence of conducting [$\sigma > 1$ $(\Omega\ \mathrm{cm})^{-1}$], soluble, high temperature polymers as a class of materials. Many of these polymers possess molecular order due to their rigid, planar, ladder chain structure. The first report on an n-doped Pyrrone, prepared from naphthalene-1,4,5,8-tetracarboxylic acid and 2,3,5,6-tetra-aminobenzene,

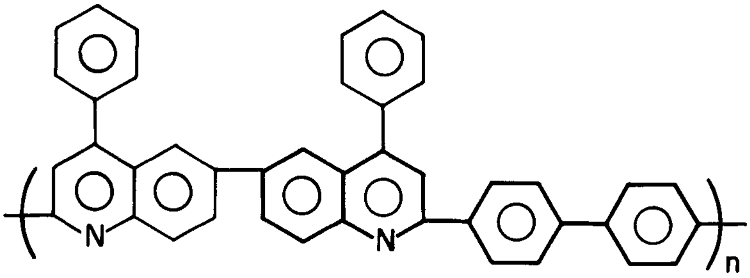


is that of Kim reporting a conductivity of 1 $(\Omega\mathrm{cm})^{-1}$ for the potassium naphthalide doped material.[1] Soon after this report, Chevron Research Co. announced at the

Gordon Research Conference on Polymers[2] the preparation of processable and conducting polyquinolines with conductivities as high as 50 $(\Omega cm)^{-1}$. Subsequently this information was put in print as the Electrochemical Society, Inc. Annual meeting abstract[3] and then as the Polymer Division of the American Chemical Society Fall Meeting preprint.[4] The polyquinoline that had the highest conductivity was poly-2,6-(4-phenyl)-quinoline,



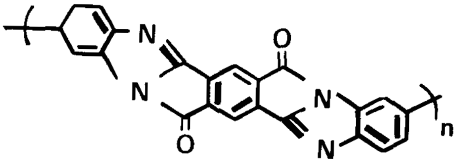
Similar work on polyquinolines was being done by another group and was reported at about the same time in a communication.[5] In this work the conductivities of three polyquinolines, two of which as fibers, were reported: poly-2,6-(4-phenyl)-quinoline fiber, 11 $(\Omega cm)^{-1}$ and



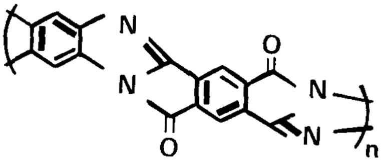
8 $(\Omega cm)^{-1}$

The doping agents used in these three studies were: elemental potassium, and potassium naphthalide in THF,[1] sodium and potassium naphthalides and anthracides in THF or dimethoxyethane,[2-4] and sodium naphthalide and anthracide in THF.[5]

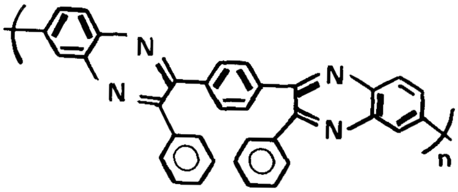
We are reporting here on the conductivity of two new Pyrrones and a new conducting polymer-polyphenylquinoxaline:



PYRRONE I



PYRRONE II



POLYPHENYLQUINOXALINE

Furthermore, we have used a new and novel material as the doping agent, cesium electride, in our studies.

EXPERIMENTAL

Polymer Preparation

These polymers and films were prepared in 1968.

Pyrrone I. Pyromellitic dianhydride (Princeton Chemical Research) was sublimed through a fiberglass fabric onto a cold finger in a sublimator at 200°/0.05 mm. A colorless sublimate, mp 286-287°C was obtained.

3,3'-Diaminobenzidine (Burdick and Jackson Laboratories, Inc.) was recrystallized from a 2:1 mixture of water and acetonitrile after treatment with charcoal to yield a light tan powder, up 176°C, after vacuum drying for two days.

Dimethylacetamide (E.I. duPont de Nemorus and Co., Inc.) was received under N_2 and distilled from pyromellitic dianhydride before use.

The polymer was prepared by adding 95 ml of dimethylacetamide solution of pyromellitic dianhydride (12.9 g in 100 ml, 0.04M) to a stirred, hot (∿ 60°C) dimethylacetamide solution of 3,3' diaminobenzidine (8.56 g. in 100 ml, 0.04M) in a preheated high-speed blender under N_2. After 30 minutes of stirring the remainder (5 ml) of the dimethylacetamide solution of pyromellitic dianhydride was added. The stirring and heating were continued for one hour and then the polymer dope was centrifuged. The supernatant was decanted off and stored under N_2 in a refrigerator. The intrinsic viscosity of the polymer dope was 1.0 dl/g in dimethylacetamide.

Pyrrone II. Tetraaminobenzene tetrahydrochloride (Burdick and Jackson Laboratories, Inc.) was purified by dissolving in the minimum amount of water, treated with charcoal, and reprecipitated with concentrated hydrochloric acid. Since 1,2,4,5-tetraaminobenzene is extremely susceptible to air oxidation, polymers from this tetramine were prepared using the tetrahydrochloride salt. Dimethylformamide was purified by distillation from phosphorus pentoxide.

The polymer was prepared by adding a dimethylformamide solution of pyromellitic dianhydride (4.36 g, 0.04M in 40 ml) dropwise to a stirred slurry of tetraaminobenzene tetrahydrochloride in dimethylforamamide and pyridine (5.68 g, 0.02M; 35 ml DMF and 6.32 g, 0.08M pyridine) in a high-speed blender under N_2. The stirring was then continued for half an hour. The polymer was precipitated with aqueous ethanol and washed with acetone to remove pyridine hydrochloride. The polymer was then redissolved in dimethylformamide or hexamethylphosphoramide for intrinsic viscosity determination and film casting. Typical intrinsic viscosity in dimethylformamide was 0.60 dl/g.

Polyphenylquinoxaline. Para-bis(phenylglyoxalyl) benzene was prepared according to the literature procedure.[6,7] The polymer was prepared by adding the para-bis(phenylglyoxaxlyl) benzene powder (10.27 g, 0.03M) to a stirred (high-speed blender) slurry of 3,3'-diaminobenzidine (5.36 g, 0.025M) in a 1:1 mixture of m-cresol and xylene (40 ml). Additional solvent (13 ml) was used to wash down the residual tetracarbonyl reactant and the mixture was stirred at R.T. for 16 hours. For viscosity determination a portion of the solution was poured into methanol in a high-speed blender, the precipitated solid was boiled in methanol and dried at 130°C in a vacuum oven overnight. Typical inherent viscosity in sulfuric acid was 2.0 dl/g.

Film Preparation

Pyrrone Films. Typical film preparation consisted of diluting the polymer dope solutions to 5-10% solids content, casting the solution on an optical glass plate in a laminar flow hood. After the films were cast, gentle heat was applied from a hot plate for about two hours. After that the plates were placed in a vacuum oven (∿ 1 hour) at 45°C/12 hours, then at 100°C/3 hours and then 250°C/4 hours. The films were stripped from the glass plates by submerging them in a water bath. The films were then dried in air at 250°C for four hours.

Polypenylquinoxaline Films. The polymer dope solutions were diluted to 10-15% solids content and cast on optical glass plates in a laminar flow hood. The films were dried overnight at ∿ 70°C in air and then at 130°C/16 hours in a vacuum oven. The films were stripped from glass plates by submerging them in a water bath.

Doping Procedure

The doping procedure is conducted in a high vacuum (at least 10^{-5} torr) glass system. The doping solution is prepared by dissolving an equimolar amount of cesium, lithium, and the crown ether, 18C6, in liquid methylamine.[8] The methylamine is distilled under vacuum from the cylinder into a glass container, is degassed and then distilled over the metals and the crown ether. The solution is kept at -20°C or lower so that the methylamine is in the liquid phase. The deep blue color, characteristic of electrides, is noticed immediately upon the distillation of the solvent over the solid components. Before the polymer films were dipped into the doping solution they were dried under dynamic vacuum at ∿ 100°C for about half an hour and then kept in a dry box in a highly purified Ar atmosphere for three days. The films were then dipped into the electride solution for one hour at -20°C. Then the doping solution was decanted, the films were rinsed with methylamine and dried in the vacuum system.

Conductivity Measurements

The conductivity measurements were conducted in a dry box using a two-probe technique.

RESULTS AND DISCUSSION

The synthetic procedures for the polymers were similar to those reported in the literature.[9-11] The Pyrrone films before the curing step are soluble in such solvents as dimethylformamide, dimethylacetamide, hexamethylphosphoramide and dimethylformamide. The molecular weight for the Pyrrones ranges from 7,000 to 20,000 by osmotic pressure measurements. The films have a tensile strength of 10-15 kpsi and elongaton of 25-35%. The color of the cured films is typically brown-red. The polyphenylquinoxaline polymer formed a tough, flexible, transparent yellow colored film. After doping the color of all the films changed to black with a metallic luster to it.

The doping and conductivity measurements were also performed on a Shirakawa catalyst prepared polyacetylene for comparison pruposes. The film thickness and conductivity data are given in Table I.

Table I

Conductivities of Cesium Electride Doped Polymers

Polymer	Film Thickness µm	Conductivity $(\Omega cm)^{-1}$	Color of Doped Film
Polyacetylene	100 µm	200	Bright Purple
Pyrrone I cured at 250°	50 µm	20	Black
Pyrrone I cured at 350°	50 µm	0.2	Black
Pyrrone II	100 µm	2	Black
Polyphenylquinoxaline	100 µm	20	Black

Curing of the Pyrrone films at higher temperature (350°C) in air leads to a decrease in conductivity by some two orders of magnitude. Chemically, the polymer would be expected to be highly crosslinked under these oxidizing curing conditions.

Currently, we are evaluating other high temperature polymers for their conductivity properties, other electrides for their doping characteristics and are conducting more detailed conductivity measurements using the 4-probe measurement technique. The results of these studies will be reported elsewhere.

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