

Novel Organic Polymer Films with High Intrinsic Conductivity Derived from the Vapour-phase Thermolysis of Polyquinoline

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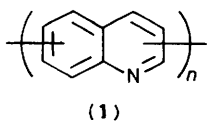
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Novel organic polymer films with high intrinsic conductivity have been synthesized by the vapour-phase thermolysis of polyquinoline at 900–1000 °C; the resulting flexible films exhibit a conductivity (σ) of higher than 400 S/cm at room temperature without doping and a good stability under ambient conditions.

Organic conjugated polymers have been systematically developed in recent years, with the goals of improving their transport properties and processability.¹ Success has been achieved in conversion of insulating organic polymers into semiconducting or conducting materials by various chemical dopings or thermal treatments. In the area of thermal treatment, the method of vapour-phase polymerization at elevated temperatures has been particularly successful in the preparation of conductive poly-peri-naphthalene^{2,3} from the corresponding molecular perylene tetraradical. However, this thermal method has not been used in the synthesis of polymers from organic conjugated aromatic polymers owing to their extremely low volatility at the thermal condensation temperature. In such cases, the pyrolytic reactions of the polymers most often occur without even passing through a liquid phase. Here I report vapour-phase polymerization of the fully conjugated polyquinoline (PQ) to produce a novel highly intrinsic conducting film referred to as pyrolytic product of polyquinoline (PPQ). This organic flexible film exhibits a room temperature conductivity of higher than 400 S/cm making it one of the highest intrinsic conducting organic materials^{2–7} known to date.

Polyquinoline (1) used in this study was synthesized by the catalytic dehydrogenative polymerization of tetrahydroquinoline⁸ and had an average molecular weight of roughly 10^3 . The thermolysis of this oligomer was carried out in a vacuum sealed quartz tube in a Lindberg furnace. The temperature of the furnace was raised to a predetermined pyrolytic temperature (T_p , 700–1200 °C) and held there for one hour. During the heating process, the PQ oligomer was observed to liquify and then vapourize to a pale brown gas. The vapourization occurred below 500 °C, in keeping with the vapourization temperature (405 °C) of the oligomer measured by thermogravimetric analysis (T.G.A.). After the tube had been cooled to room temperature, shiny black films were found to have been deposited on the surface of tube. The thickness of film can be varied in the range 80 nm to 30 μ m, depending upon the amount of PQ used. In general, films thicker than 10 μ m could be isolated from the surface as free-standing films. The yield was found to be 86 and 81% at $T_p = 700$ and 900 °C, respectively, with a weight loss of <20%. This is much lower than that (40–50%) normally observed in the thermolysis of known systems such as polyimide,⁵ preoxidized polydivinylbenzene,⁶ and polyacrylonitrile.⁷

Elemental analysis led to formulation of the 700, 900, and 1200 °C treated PPQ product as $C_9H_{3.0}N_{0.9}$, $C_9H_{1.0}N_{0.5}$, and $C_9H_{0.3}N_{0.5}$, respectively. These data suggest that the quinoline moiety in the polymer product remains to a large extent intact during the pyrolytic process below 700 °C. Above



700 °C, the loss of nitrogen increases and levels off at 50%. As shown in Figure 1, the solid-state ^{13}C n.m.r. spectrum of PPQ (T_p 700 °C) gives a broad peak centred at δ 125, in the same chemical shift range observed for PQ. The n.m.r. and elemental analysis results agree with the proposed cross-linked polyquinoline structure for the thermal product resulting from the originally linear PQ chain. Transmission electron microscopy (T.E.M.) of PPQ thin films generated at temperatures below 1200 °C showed an amorphous structureless appearance without any obvious features of graphitic layer structure. This was confirmed by a powder X-ray diffraction study. For a sample of PPQ prepared at 700 °C, only a very weak and diffuse peak centred at 3.56 Å was observed. However, the centre of this peak shifts towards 3.35 Å and the width becomes narrower for PPQ made at higher T_p , indicating an increased ordering in going from $T_p = 700$ to 1200 °C.

The conductivity of the thin films (200–800 nm) was measured in terms of sheet resistivities using the in-line four-point-probe technique. The room temperature conductivities of the black PPQ films prepared at 700, 800, 900, and 1000 °C were found to be 10, 60, 400, and 450 S/cm, respectively, without doping. The observed high intrinsic conductivities in this system are believed to derive from the increase in number of charge carriers *via* the formation of stable free radicals and the increase of charge carrier mobilities resulting from the highly extended charge carrier delocalization through a condensed aromatic structure. This condensed aromatic structure is thought to be a highly cross-linked polyquinoline network formed through direct

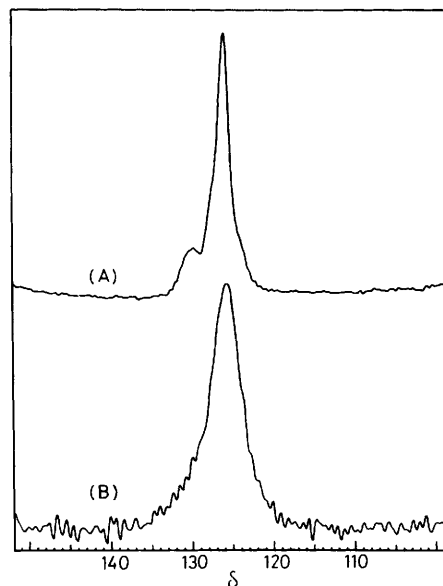


Figure 1. Solid state ^{13}C n.m.r. spectrum of (A) polyquinoline (1) and (B) pyrolytic polymer PPQ (T_p 700 °C).

free radical condensations between adjacent linear host polymers.

In conclusion, novel polymer films with high intrinsic conductivity can be synthesized by a vapour-phase condensation reaction between vapourized quinoline oligomers. The resulting films are found to be among the most conductive and thermally stable organic materials known under ambient conditions. Since the reaction was tailored to occur in the vapour phase of the host polymer, it has a great advantage over the traditional pyrolytic fabrication process of conducting polymers, in terms of the direct surface coating on many different substrates.

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