Novel Catalytic Dehydrogenative Polymerization for Polyquinoline Synthesis

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Quinoline oligomers can be prepared by a novel one-step dehydrogenative polymerization of tetrahydroquinoline using rhenium sulphide as a catalyst.

In recent years there has been enormous interest in using fully conjugated linear polymers and aromatic heterocyclic polymers as precursors for low-dimensional conducting materials[1] or high-strength–high-modulus fibres.[2] One class of such polymers is polyquinoline and its derivatives. Surprisingly, to date the unsubstituted polyquinoline has not yet been made in spite of the fact that many substituted polyquinoline derivatives have been successfully synthesized[3] and studied.[4,5]

In this communication we report a novel one-step synthesis of polyquinoline by a method of catalytic dehydrogenative polymerization. Traditionally, polyquinoline derivatives can be prepared by an acid-catalysed Friedländer synthesis.[6] This method is most suitable for the synthesis of substituted polyquinolines, but presents difficulties for the preparation of unsubstituted polyquinoline.[3] We found that the unsubstituted polyquinoline can be prepared by a dehydrogenative polymerization of tetrahydroquinoline (1) in the presence of a rhenium sulphide catalyst at the refluxing temperature of (1) giving a high yield (>90%). The rhenium sulphide catalyst was synthesized by the reported procedure[7] as a poorly crystalline powder of composition ReS_x ($2 \leqslant x \leqslant 4$) with a surface area of 2—30 m^2/g. In a typical reaction, tetrahydroquinoline (25 ml) was charged with a fine powder of rhenium sulphide (500 mg). The stirred mixture was maintained under argon at atmospheric pressure and heated at 200 °C for 12 hours initially and then at 270 °C for one week. The product was cooled to room temperature, giving a mixture of dark solids, which was separated into fractions of differing solubility in sequence using diethyl ether, methylene chloride, acetic acid, and conc. hydrochloric acid–water (1 : 1). The combined fractions of the soluble polymer product gave polyquinolines (2) in a total yield of ≥90%. The final insoluble black solid (560—650 mg) was recovered as an organic polymer containing rhenium sulphide (ReS_2). Elemental analysis led to formulation of the polymer as $C_9H_{5+x}N$, where x varied with the degree of polymerization, close to the expected polyquinoline composition. Vapour-pressure osmometric measurements led to an estimate of the molecular weight of the acetic acid-soluble fraction of ~10^3. The acetic acid-insoluble fraction is believed to have a higher molecular weight than the soluble one. The

structure of the polymer was characterized mainly based on the organic solvent-soluble oligomer isolated from the bulk polymer product.

The mass spectrum (electron impact) of the methylene chloride-soluble oligomer showed a clear consecutive m/z loss of 127 which matched with the m/z value of the quinoline unit in the polymer. It also showed ion fragmentations of m/z 128, 255, 383, 510, etc., corresponding to the monomeric, dimeric, trimeric, and tetrameric polyquinoline fragments. The i.r. spectra of both oligomer and bulk polymer, compared with that of tetrahydroquinoline itself, showed a new band at 821 cm^{-1} in addition to a band at 746 cm^{-1} corresponding to the aromatic C–H out-of-plane deformation. This, along with the disappearance of a band at 2800—2930 cm^{-1} in the i.r. spectrum of the polymer, which corresponds to the aliphatic C–H stretch in the monomer (1), indicated that the heterocyclic ring moiety of the polymer had been fully dehydrogenated.

The highly aromatic nature of the polymer was further confirmed by n.m.r. spectroscopy. Both ^{1}H and ^{13}C n.m.r. spectra of the polymer contained either no, or only a trace of, aliphatic hydrogen and carbon signals. The most characteristic ^{1}H peaks were three groups of peaks below δ 8.8, one of which corresponds to the α proton adjacent to the nitrogen atom in the quinoline unit. The much lower intensity of this peak relative to the combined intensity of the rest of the aromatic protons indicated that one of the ring conjunctions had occurred at the α carbon next to the nitrogen atom in the polymer.

The reaction of tetrahydroquinoline apparently occurs on the surface of rhenium sulphide. A highly crystalline, low

(1) $ReS_x (2 \leqslant x \leqslant 4)$ (2)
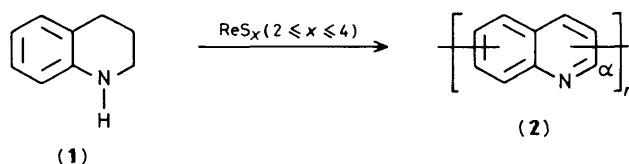
surface area rhenium sulphide gave a much less satisfactory result with a lower yield of polymer. We found that 2—4 wt% is the optimum proportion of poorly crystalline catalyst required for complete reaction. Upon decreasing the catalyst concentration, both the yield and the aromaticity decline. For example, at a catalyst concentration of 0.4 wt %, only a 10% yield of soluble polymers was observed, which showed aliphatic hydrocarbon ^{1}H n.m.r. peaks of relatively high intensity. No polymer was obtained with a concentration of 0.04 wt % of catalyst.

In conclusion, we have observed a novel dehydrogenative polymerization of tetrahydroquinoline catalysed by rhenium sulphide,[8] to give a novel polyquinoline in high yield. This simple one-step catalytic conversion offers a good insight into the synthesis of polyquinoline and its derivatives since complicated monomer synthesis is unnecessary and tetra-hydroquinoline is readily available on a commercial scale.

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