

A Biotech Route to Polyphenylene

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Starting from benzene and oxygen and using the genetically modified bacteria *Pseudomonium putida* as an oxidation catalyst compound (6) is readily obtained; derivatives of the latter are soluble in organic solvents and polymerise to give a soluble precursor (5) which can be used to make fibres and films which on heating are converted into polyphenylene fibres and films.

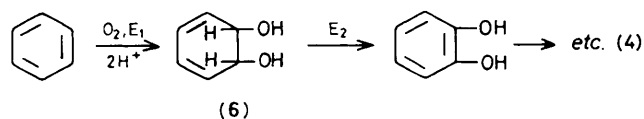
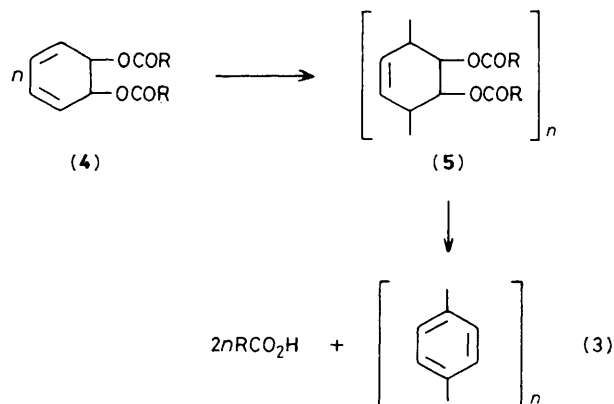
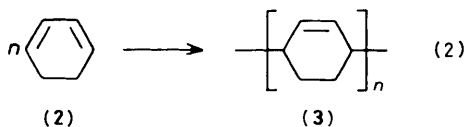
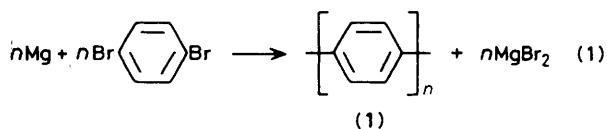
Poly(*p*-phenylene) (1) is of interest to scientists concerned with relationships between molecular structure and properties such as modulus, thermal stability, and in the doped condition, electrical conductivity. However, because the polymer is infusible and insoluble in known solvents only limited studies of these properties have been possible.

The accepted method of preparing polymers containing the aromatic nuclei as part of the main chain is to use condensation polymerisation techniques.¹ One of the better routes to polyphenylene is given in equation (1). Our study of the chemistry of this process shows that, although a strictly linear compound is obtained, only oligomers are formed. Owing to its insolubility in known solvents it is doubtful if high molecular weight polyphenylene has ever been previously obtained. Moreover the material produced by reaction (1) is only capable of fabrication by sintering and compression at high temperatures. Continuous fibres and films are difficult to obtain using this type of technology.

A number of attempts^{2,3} have been made to produce polyphenylene by routes which do not involve polycondensation, for example, polymerisation of cyclohexa-1,3-diene (2) to give poly(cyclohexene) (3) using organometallic catalysts [equation

(2)]. Various attempts to aromatise (3) to give pure polyphenylene have failed because of the poor solubility of the partially aromatised product. Moreover the conditions of aromatisation were severe enough to cause fracture of the main chain.

We report a novel route to polyphenylene based on the discovery that derivatives (4) of 5,6-dihydrocyclohexa-1,3-diene (6) are readily polymerised, using radical initiators, to high molecular weight polymers (5) which are very soluble in simple organic solvents. These solutions can be used to cast film, coat substrates, or spin fibres of the precursor polymers (5). In this form, on heating to 140–240 °C a smooth conversion into polyphenylene occurs [equation (3)].



Electron microscopic studies show that the fibres and films obtained are coherent. X-Ray analysis of unorientated material shows that crystallisation up to 60% is possible and that there are three principle reflections at 4.5, 3.9, and 3.2 Å. These are close to those observed for the linear terphenyl molecule which also has three Bragg reflections at 4.4, 3.89, and 3.0 Å.⁴ The derivatives (4), include those where R is OMe, Me, and Ph. The aromatisation of the methyl carbonate polymer at 220 °C gives a half-life for the precursor polymer of 30 s. Molecular weight measurements have been made on solutions of the precursor polymer using laser light scattering and small angle neutron scattering (S.A.N.S.). Results show 600–1000 cyclohexenyl units. Using a fully deuteriated equivalent of (5) S.A.N.S. enables the aromatisation process to be followed in the solid state. Such studies are in progress and information of the size and shape of the polyphenylene molecule will be obtained along the lines previously described for polypropylene.⁵

Monomer (4) can also be copolymerised with vinyl and diene monomers which on heating give phenylene copolymers.

We have found that the simplest route to (6) is the bacterial oxidation of benzene [equation (4)].⁶ The organism *Pseudomonas putida* is able to utilise benzene as a carbon source by converting it into catechol *via* (6) by a reaction in which enzymes within the cell E_1 , E_2 , *etc.* are utilised. Genetic

manipulation of this organism is possible so that enzyme E_2 is not active. With organisms of this type the exclusive oxidation product of benzene is the dihydrodiol (6). This is excreted by the cell, isolated by solvent extraction, and purified by crystallisation. Suitable bacteria are available from various sources. Moreover, studies show that these organisms accumulate in soils which have been exposed to benzene for several decades. They are modified using chemical mutagens by applying well established microbiological techniques.

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