

Preparation of Poly(*p*-phenylene) via Processable Precursors

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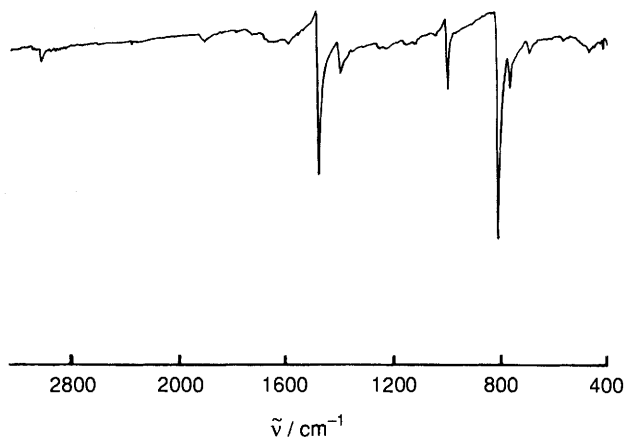
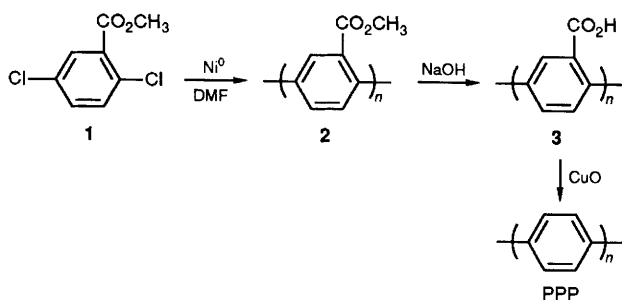
Starting with commercially available methyl 2,5-dichlorobenzoate, poly(*p*-phenylene) with a highly regular structure, which showed high conductivity after SbF_5 -doping, has been prepared by the decarboxylation of poly(2-carboxyphenylene-1,4-diyl); it is soluble in pyridine, quinoline and aqueous sodium hydroxide solution and has a degree of polymerization around 100.

Poly(*p*-phenylene) (PPP) is an interesting polymer in view of its high electrical conductivity and thermal resistivity. It is infusible and insoluble, and so it is intractable but it is desirable to prepare PPP in the form of a film or fibre. The electrochemical polymerization of benzene produced PPP films,¹⁻⁴ but their quality was not always high enough to give a high electrical conductivity and their degree of polymerization was inferred to be as low as 20 from IR studies. PPP films have also been prepared in a procedure from a processable precursor, but the starting material was produced using the genetically modified bacteria *Pseudomonium putida* as an oxidation catalyst for benzene, implying that this procedure is not easily accessible to polymer chemists.⁵ The preparation of structurally regular PPP with a high degree of polymerization starting with commercially available materials would be valuable.

The present route to PPP is as shown in Scheme 1. Commercially available methyl 2,5-dichlorobenzoate **1** (Aldrich) was recrystallized from methanol. The catalyst for the polymerization of **1** was prepared according to Colon's method.⁶ A mixture of nickel(II) bromide (0.654 g), triphenylphosphine (5.97 g) and zinc powder (6.06 g) was stirred in 30 ml of dimethylformamide (DMF) at 45°C under argon. After

the mixture had turned red, compound **1** (6.15 g) in DMF (15 ml) was added and the polymerization was performed at 80°C for 48 hr. The poly(2-methoxycarbonylphenylene-1,4-diyl) **2** obtained was white and soluble in chloroform. According to GPC, the molecular mass distribution of **2** was clearly monomodal and its degree of polymerization was 93. Although the previously reported **2** had a lower degree of polymerization and a bimodal molecular mass distribution, the ¹H NMR spectrum of the present polymer was identical to the reported one.⁷ Hydrolysis by refluxing **2** in methanolic sodium hydroxide for 1.5 h gave poly(2-carboxyphenylene-1,4-diyl) **3** which was white and soluble in aqueous sodium hydroxide as well as basic solvents such as pyridine and quinoline.

PPP was obtained by refluxing **3** (1.5 g) in quinoline (24 ml) in the presence of copper(II) oxide (0.14 g) for 3 h under argon. Powdery PPP was obtained in almost quantitative yield



(0.94 g) after thorough washing with acetone, hydrochloric acid and methanol and drying at 60 °C. The PPP thus obtained was green. Its IR spectrum (Fig. 1) did not show the peaks at 1700 and 1225 cm^{-1} due to the carboxy group and at 825 cm^{-1} due to the isolated 3-H which were present in the IR spectrum of **3**. A very strong peak occurred at 800 cm^{-1} , due to the C–H out-of-plane deformation of 1,4-disubstituted benzene. The peak at 1003 cm^{-1} is due to the corresponding in-plane deformation. The peaks at 1478 and 1403 cm^{-1} are due to the ring stretching and those at 774 and 690 cm^{-1} to the monosubstituted benzene termini. The peak at 3032 cm^{-1} may be assigned to the C–H stretching vibration. No other IR peaks are apparent, indicating that the present PPP has a very regular structure.

The maximum conductivity of an SbF_5 -doped PPP pellet was 18 S cm^{-1} . Since the conductivity of PPP is strongly dependent on dopants, this value should be compared with the previously reported conductivity of SbF_5 -doped PPP. The conductivities of an electrochemically prepared PPP film and chemically prepared PPP pellet are 6×10^{-4} and 4×10^{-2} S cm^{-1} , respectively.^{2,8} Taking these facts into account, the present polymer is highly conducting, consistent with it having a regular structure.

Heating a quinoline solution of **3** and copper(II) oxide for 15 min caused partial decarboxylation. This solution was cast on

a glass substrate and heated at 230 °C for 14 h under argon while small portions of quinoline were added to replenish the distilled-off solvent. This procedure yielded a film of PPP on a glass substrate. The IR spectrum of this PPP film is identical to that of powdery PPP.

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