Reductive Electropolymerization of 2,5-Dichlorobenzonitrile

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Reductive electropolymerization of 2,5-dichlorobenzonitrile gives an electroactive polymer showing n-doping, which suggests that the polymer may be useful as a charge storage material; the polymer is identified as poly(benzonitrile-2,5-diyl).

Conductive polymeric films can be obtained conveniently on the surface of electrodes in one step. For example, polythiophene,[1,2] polypyrrole,[3,4] and polyphenylene[5,6] have been prepared by electrochemical polymerization under oxidative conditions to facilitate formation of a cation radical initiator.[7] There are few reports of reductive electropolymerization however, although Schiavon *et al.*[8] have used dihalopyridines as starting materials. The types of monomers that can be used for reductive electropolymerization are limited but a C–C bond formation at the original carbon atoms substituted by two halogens implies that this method could be used to obtain regular polymers. In this communication, we report the first reductive electropolymerization of 2,5-dichlorobenzonitrile. By introducing an electron-withdrawing cyano group, dichlorobenzene can be easily reduced electrochemically to produce a free-standing film, which shows n-doping clearly.

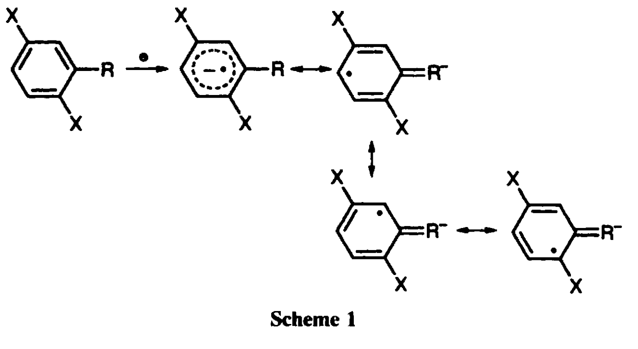
THF and MeCN were distilled from CaH_2. DMF was distilled *in vacuo* from CaH_2. Monomers (2,5-dichlorobenzonitrile, 2,5-dichloronitrobenzene, and *p*-dichlorobenzene) and Bu_4NBF_4 were used without further purification.

Electropolymerization was carried out under a constant potential (Ag wire reference electrode) with constant Ar bubbling. A platinum plate or indium–tin oxide (ITO) glass was used as the working electrode. The concentrations of monomer and electrolyte were 0.05 and 0.1 mol dm^{-3}, respectively.

FTIR spectra were recorded on a Perkin-Elmer 1720-X spectrophotometer. Cyclic voltammograms were measured by using a Hokuto-Denko HA-501 potentio-galvanostat and a HB-104 function generator.

Although the reductive electropolymerization of *p*-dichlorobenzene gave no polymer at −3.0 V for 1–17 h in THF, 2,5-dichlorobenzonitrile and 2,5-dichloronitrobenzene gave soluble or insoluble polymers respectively under more positive potentials. A smooth, yellow film was obtained on the surface of an electrode in the case of 2,5-dichlorobenzonitrile. Apparently, introducing electron-withdrawing groups to a benzene ring facilitates reductive electropolymerization, presumably by stabilization of a charged aromatic ring, as shown in Scheme 1.

Oxidative polymerization of thiophene and pyrrole was reported to start with the removal of an electron from the aromatic ring to give a cation radical, which would couple with each other. In the case of reductive electropolymerization, formation of an anion radical is considered to be the first step of the polymerization. Usually, this radical would be unstable; but when an electron-withdrawing group is introduced the negative charge could be delocalized on this group.



Scheme 1

In acetonitrile and DMF, polymerization of 2,5-dichlorobenzonitrile also gave films on the surface of electrode. Film quality was highest when DMF was used as solvent. Current efficiency was about 30%, which was lower than that observed in the oxidative electropolymerization of thiophenes.[1,9]

A FTIR spectrum of the polymer showed three bands at 806, 1460, and 2230 cm^{-1}, assignable to the out-of-plane deformation vibration of a 1,2,4-trisubstituted benzene ring, the skeletal vibration of benzene, and the antisymmetric stretching vibration of a C≡N bond, respectively. These bands were also observed in the spectrum of the monomer, 2,5-dichlorobenzonitrile. The monomer had a band at 703 cm^{-1}, assignable to a C–Cl bond, which was absent in the polymer. These results indicate that the polymer can be identified as poly(benzonitrile-2,5-diyl). However, there was the additional band at 1720 cm^{-1}, attributable to the stretching vibration of a C=O bond. Oxygen was detected despite the polymerization being carried out under argon. We assume that the solvent (DMF) is somehow involved: radical anion polymer may behave as a nucleophile attacking a DMF carbonyl carbon atom producing a C=O group at the end of the polymer.

Fig. 1 shows the CV of poly(benzonitrile) measured in THF. Clear reduction and oxidation peaks were observed at −2.1 and −1.4 V, respectively, indicating that the polymer was a π-conjugated system. There was no peak at positive potential regions. The n-doped state would be stabilized by the charge delocalization as described above. From the calculation of the peak areas, it can be estimated that the n-doping level is *ca.*

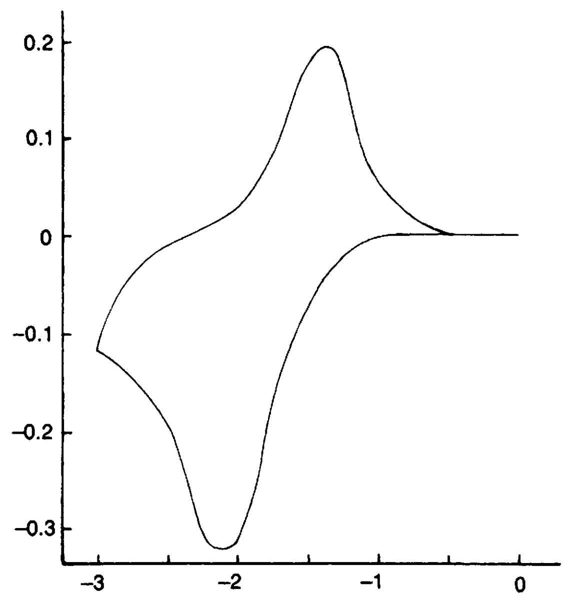


Fig. 1 CV of poly(benzonitrile). Sweep rate: 100 mV s^{-1}. Electrolyte: Bu_4NBF_4.

4% per repeating unit. This value could be improved by obtaining the polymer without a C=O bond.

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