CHEMICAL AND ELECTROCHEMICAL SYNTHESES OF ELECTROACTIVE BENZENOID-HETEROAROMATIC POLYMERS

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Abstract The chemical synthesis and some properties of a variety of polyaromatics of defined structure are described. The polymers include some which are soluble in many organic solvents. Low current density electropolymerisation of some bithienylbenzenoids in dichloromethane gives electrochromic films of good mechanical stability and low electrochromic fatigue.

We have previously described[1] the synthesis of benzenoid-heteroaryl polymers of the poly(para-phenylene) (PPP) type in which the reaction between regiospecifically bismetallated diheteroarylbenzenes and dibromobenzenes provided unambiguous control of polymer constitution. We contrasted this approach with the difficulty in producing highly regular polyaromatics *via* electrochemical polymerisation.[2] The recent publication of a method for the synthesis of similar polymers, *via* the insertion of either sulphur or nitrogen into poly-1,4-diketones, under forcing conditions and during long periods, now prompts us to disclose some further results which greatly extend our previous observations. These include the production of the first readily processible organic soluble polyaromatics in which solubility is attained by benzene substitution.   Further, we emphasise that our methodology, which requires only mild conditions, obviates the risk of cross-linking which is present when diketones[3] or diynes[4] are used as polymer precursors.

Our general process, applied to the production of 1,4-linked polymers **3**, and which we have previously used[1] to produce **3af**, is shown in equation (1).

To show that the ratio of benzenoid to heteroaromatic units in **3** could be readily varied, **1a** was reacted with **2g** to give polymers **3ag** (Z=O,S) in good yields. Polymers **3ag** gave very sharply defined X-ray patterns similar to those given by **3af** and PPP.

We then introduced a repeated nitro-group into **3** by reacting **1b** with **2h** to give **3bh** (Z=S), as a stable and highly insoluble polynitro-polymer.

We were interested in introducing regularly spaced alkyl groups into **3** with a view to enhancing polymer solubility,[6] and we initially reacted **1c** with **2i**. The 2,5-disubstituted monomers were used in order to retain structural regularity in the polymer. In the event, **3ci** (Z=O,S) were obtained, in excellent yields, as insoluble polymers. When, however, **1e** was reacted with **2k** the polymer **3ek** (Z=S) that resulted was highly soluble in chloroform and dichloromethane, and was also soluble in warm toluene.

(a) X = Y = H
(b) X = NO$_2$, Y = H
(c) X = Y = Me
(d) X = Y = OMe
(e) X = Y = Bu

(f) Ar=
(g) Ar=
(h) Ar=

(i) Ar=
(j) Ar=
(k) Ar=
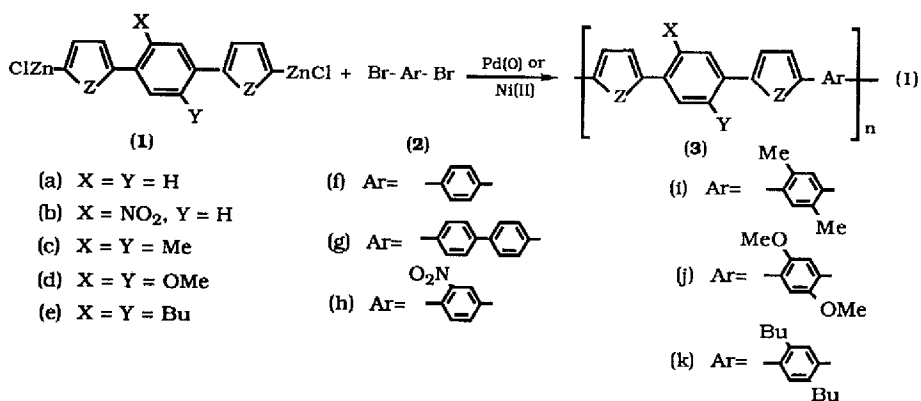
With the results of Miller's study[7] of poly-(3-methoxythienyl) in mind, we reacted **1d** with **2j** to give **3dj** (Z=O,S) which have a 1:1 ratio of methoxy to aromatic groups. The highly fluorescent polymers were readily soluble in all the organic solvents tried with the exception of petroleum and cyclohexane. Polymers **3ek** and **3dj** are apparently the first soluble aromatic-heteroaromatic polymers, and their properties are being studied.

Doping of all our polymers with either I_2 or $FeCl_3$ gave lustrous black materials with enhanced electrical conductivities (Table).

TABLE
CONDUCTIVITY Ω^{-1} cm^{-1}

Structure	Undoped	Doped Minimum	Doped Maximum
3af (Z = S)	4 x 10^{-11}	4 x 10^{-4}	12 x 10^{-4} (FeCl$_3$)
3ci (Z = S)	1.3 x 10^{-10}	4.6 x 10^{-6}	1.9 x 10^{-4} (FeCl$_3$)
3bh (Z = S)	3.3 x 10^{-9}	2.73 x 10^{-5}	1.4 x 10^{-4} (FeCl$_3$)
3dj (Z = S)	1.0 x 10^{-7}	3.5 x 10^{-4}	1.6 x 10^{-3} (I$_2$)
3ek (Z = S)	3.6 x 10^{-11}	5.0 x 10^{-4}	1.3 x 10^{-3} (FeCl$_3$)
3ag (Z = S)	2.0 x 10^{-11}	1.9 x 10^{-5}	1.9 x 10^{-4} (FeCl$_3$)
7	2.0 x 10^{-11}	1.7 x 10^{-5}	2.0 x 10^{-4} (FeCl$_3$)
3af (Z = O)	1.0 x 10^{-10}	2 x 10^{-4}	3.24 x 10^{-4} (FeCl$_3$)
3ci (Z = O)	6.8 x 10^{-10}		4.5 x 10^{-2} (FeCl$_3$)
3dj (Z = O)	5.0 x 10^{-6}		1.6 x 10^{-3} (I$_2$)
3ag (Z = O)	6.2 x 10^{-11}	1.7 x 10^{-7}	5.9 x 10^{-5} (FeCl$_3$)

Notwithstanding the structural inhomogeneity which is associated with polymer films obtained *via* electrochemical polymerisation of small aromatic molecules,[1,2] the films themselves often possess excellent mechanical properties and offer many potential and actual applications.[2] The structural homogeneity of these films may be enhanced by the use of small chemically preformed oligomers as electrochemical precursors, in preference to the monomers themselves. Thus, for example, polythiophenes obtained *via* electrochemical polymerisation of thiophene, 2,2'-bithienyl and 2,2':5',2"-terthienyl have differing electrical properties[2,8] which may be associated with the increasing proportion of α, α'-linkages in the respective polymers. With these facts in mind, and in view of the ready availability to us of a range of diheteroarylbenzenes, prepared as precursors in the

chemical polymer syntheses described above, we decided to investigate the electrochemical polymerisation of examples of this class of precursor. We now report our preliminary results in this area. Specifically, we describe the electrochemical polymerisation of dithienylbenzenes **4, 5** and **6**; the polymerisation of other members of this class, together with the polymerisation of larger molecules, will be described elsewhere.
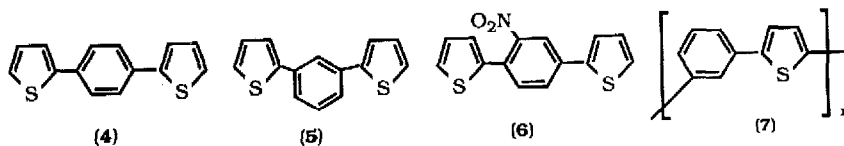

The anodic polymerisation of **4**, with acetonitrile as solvent and at a current density of 1 mA cm^{-2}, is reported[9] to give a 'black film' which becomes 'spongy and rubbery during growth'. Under similar conditions, but with dichloromethane as solvent, we find that **4** polymerises rapidly to give fragile dark blue dendrites of mm dimensions. Even at 100 μA cm^{-2} we obtained a dark blue powdery deposit rather than a mechanically stable film.

We believe that high current densities, though previously suggested to lead to particularly homogenous polymers *via* polymer film formation at a large number of nucleation centres[10] may, in fact, be deleterious to high polymer formation. High current densities *may* lead to higher potentials at the working electrode, and hence to significant oxidation of relatively small oligomers to give oligomers with dication character. These will not participate in further polymerisation and are precipitated as highly coloured salts at the working electrode. This hypothesis would seem to be confirmed by our own observations, and by those of others.[9]

We therefore subjected a 10^{-2} $\underline{M}$ dichloromethane solution of **4**, containing Bu$_4$NPF$_6$ (0.1 $\underline{M}$), to controlled current (i = 12 μA cm^{-2}) conditions during 8 min at a gold wire working electrode. A potential of *ca*. 1.1 V (*vs* a silver wire pseudo-reference[11]) was maintained during this time. We obtained a lustrous coppery film, with a bluish tint, that turned golden yellow on switching to 0.0 V. The film was resistant to scratching with a finger nail, and it showed no tendency whatever to drop from the electrode, and no obvious mechanical fragility. Cyclic voltammetry (Figure 1) revealed an anodic peak at 1.15 V, with the cathodic part of the wave showing the double-humped and rather flatish characteristic seen in a number of other thiophene derivatives.[12] The film could be cycled between its yellow reduced form, and its blue oxidised form, many tens of times with only a small reduction in the peak current.

Electropolymerisation of **5**[1,13] was carried out as for **4** and gave a similarly tough film. The cyclic voltammogram of the film was similar to that of the film derived from **4**, and it had an anodic peak at 1.05 V. Peak currents were reduced by <10% after 500 cycles (Figure 2). When the electropolymerisation of **5** was carried out at a 2 x 2 cm platinum electrode, repeated cycling of the polymer film caused the solution to become yellow, suggesting a release of oligomers from the film. This might explain the small reductions in peak currents between consecutive voltammetric cycles. Failure

to observe this phenomenon previously is attributable to the small quantities of material involved in the gold wire electropolymerisation.
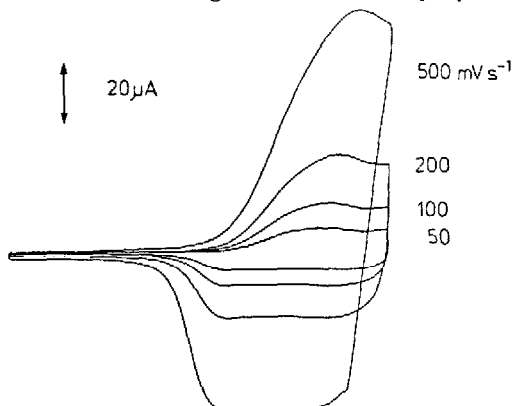
Figure 1: Cyclic voltammograms (0-1.3V vs "Ag")of the electrochromic film formed *via* anodic oxidation of (4)
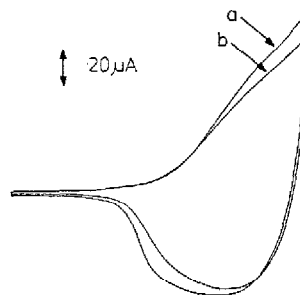
Figure 2 : Cyclic voltammograms (0 -1.0V vs "Ag" 100mV/s) , below the anodic peak , of the electrochromic film formed *via* anodic oxidation of (5) ; (a) 1st cycle . (b) 500th cycle.

Electropolymerisation of nitro-derivative **6** required the higher current density of 25 μA cm^{-2} which gave a working potential of 1.4 V. A mechanically stable film was formed, and it appeared greenish-yellow when reduced and coppery-blue when oxidised. Cyclic voltammetry was carried out below 1.4 V and an anodic peak was not observed below this limit. Thus both **6** and its polymer are more difficult to oxidise than the unsubstituted materials. The film showed an electrochromic fatigue similar to that for the non-functionalised polymers.

In order to obtain polymer films *via* anodic polymerisation of small aromatic compounds, low current densities are recommended. The solvent may play an important role and the choice of dichloromethane seems to be particularly advantageous. Even at the low current densities that have been utilised there is some evidence for oligomer formation and resulting electrochromic fatigue. Nevertheless, the films that result look promising for electrochromic display purposes.

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