Cathodic Oligomerisation of Bis(diazo) Compounds of the Indenofluorene Series. Part I. General Features

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Three bis(diazo) compounds of the indenofluorene series, 11,12-bis(diazo)-11,12-dihydroindeno[2,1-*a*]fluorene (**1b**), 10,12-bis(diazo)-10,12-dihydroindeno[2,1-*b*]fluorene (**2b**), and 6,12-bis(diazo)-6,12-dihydroindeno[1,2-*b*]fluorene (**3b**) have been prepared and decomposed by an electrochemically initiated chain process in dimethylformamide solution. The black solutions so obtained show single-line e.s.r. spectra and electronic absorption spectra extend into the near infra-red region of the spectrum. *in situ* electrochemical e.s.r. spectra of electrolysed solutions of (**1b**) and (**2b**) in CH_3CN are similar to spectra reported for lightly doped conjugated polymers. Chemical evidence is presented to show that the products are polyazines and the results of elemental and gel permeation chromatographic analysis suggest degrees of polymerisation in the range 2–5 for (**1b**) and *ca.* 17 for (**2b**) and (**3b**), although in the latter instances there is evidence for material of much greater molecular weight. The black solid materials isolated from the electrolysis solutions and containing supporting electrolyte (Me_4NBF_4) show specific conductivities of *ca.* 10^{-10} (**1b**), 10^{-9} (**2b**), and 10^{-6} (**3b**) ohm^{-1} cm^{-1}, all increasing to 10^{-4}–10^{-3} on exposure to gaseous SO_3.

Current interest in the preparation and investigation of novel fully conjugated polymers for electronic and other applications prompted us to examine the use of conjugated bis(diazo) compounds as monomers. It is well known[1] that aryldiazoalkanes $ArC(R)N_2$ such as phenyldiazomethane under a variety of conditions give rise to fully conjugated products, either alkenes $ArC(R)=N-N=C(R)Ar$ (by reaction, together, of two diazo molecules with loss of one molecule of nitrogen) or dimeric alkenes $ArC(R)=C(R)Ar$ (when two molecules of nitrogen are lost). If such reactions were induced in bis(diazo) compounds conjugated polymers would result.

Polymeric materials with rather low degrees of polymerisation have already been reported to result from photochemical,[2] acid-catalysed and thermal decompositions[3] of some bis(diazo) compounds. For example, bis(diazo)diarylmethanes on treatment with strong proton acids in dipolar aprotic solvents yield polyene-arylenes, $(CAr=CArC_6H_4)_n$, and with BF_3 in non-polar solvents polyazine-arylenes $(CAr=N=N=CArC_6H_4)_n$ with degrees of polymerisation in the range 12–20. The products are thus fully conjugated. Those cases where the conjugating linkages were mainly of the azine type are of special interest since heteroatoms are present in the conjugated backbone of the polymer. Polyazines have been prepared by other means, usually involving the action of hydrazine on dicarbonyl compounds such as terephthalaldehyde.[4,5] In this way products of higher molecular weight and lower solubility in organic solvents result. In the present work we have chosen to explore the use of an electropolymerisation technique based on our finding that 9-diazofluorene can be converted essentially quantitatively into the corresponding azine by cathodic reduction which initiates an electron-transfer chain reaction of high current efficiency.[6] The technique was seen as having the additional virtue of giving rise to polyazines in an n-doped form.

Polyazines are beginning to attract considerable interest.[5] The band gap is expected to be larger than for the corresponding all-carbon conjugated chain as in polyacetylene; a factor of two has been calculated for the simplest polyazine $(CH=N-N=CH)_n$ compared with poly(acetylene).[7] This sort of comparison provides theoretical interest while the possibility that, by suitable doping, materials of controllable conductivity may be produced, excites more practical interest.

We have previously shown that in 9-diazofluorene (FlN_2) reduction the rate-limiting step of the chain propagation is electron transfer to the reactant diazoalkane from fluorenone azine anion radical[6] or, based on more recent voltammetric studies,[8] a precursor $(FlN_2)_2^{+\bullet}$. Chain lengths of the order of 50 were observed and the coupling of the diazofluorene moieties has a second-order rate constant of the order of 10^5 dm^3 mol^{-1} s^{-1}, based on the measured value for $FlN_2^{+\bullet}$ dimerisation.[9] Accordingly bis(diazo)alkane structures for study were chosen that were of the diazofluorene type, namely bis(diazo) compounds derived from three dihydroindenofluorenes (**1a**), (**2a**), and (**3a**). The three bis(diazo)alkanes (**1b**),[10] (**2b**), and (**3b**) were prepared and subjected to cathodic reduction in dimethylformamide solution. In this paper we describe their preparation and the characterisation of the reduction products which turn out to be oligomeric polyazines. In a subsequent paper we shall describe the kinetic and mechanistic features of the oligomerisation process.

Results and Discussion

Preparation of the Monomeric Bis(diazo)alkanes.—The bis(diazo)alkanes were all prepared from the corresponding diketones [(**1c**), (**2c**), (**3c**)] *via* the hydrazones [(**1d**), (**2d**), (**3d**)]. The syntheses of the parent ketones has previously been described by *inter alia* Chardonnens and Deuschel and their co-workers using unambiguous routes.

Compounds (**1d**), (**2d**), and (**3d**) were prepared from the diketones by treating a suspension of the sparingly soluble diketones in refluxing ethanol with an excess of hydrazine hydrate. In the case of (**2d**) and (**3d**) a greater than tenfold excess was used and refluxing was continued for eighteen hours, affording the product, quantitatively, in essentially analytically

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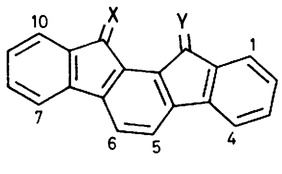
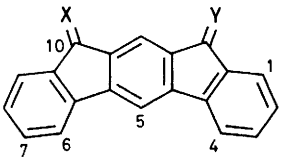


(1)



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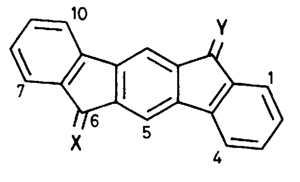

(3)

a, $X = Y = H_2$ **d**, $X = Y = NNH_2$
b, $X = Y = N_2$ **e**, $X = NNH_2, Y = H_2$
c, $X = Y = O$ **f**, $X = N_2, Y = H_2$

pure condition. Similar treatment of (**1c**) with a large excess of hydrazine hydrate and prolonged refluxing gave the monhydrazone (**1e**) of the parent hydrocarbon, indicating a half Wolff–Kishner reduction. Such reductions brought about by hydrazine have long been known,[10] although more powerful basic catalysts are normally used to effect the conversion of hydrazones into hydrocarbons. In the present instance (**1c**) could be efficiently converted into the bis(hydrazone) by refluxing with a twofold excess of hydrazine hydrate for thirty minutes, a procedure fortuitously used in an earlier preparation.[11] The divergent behaviour of (**1d**) on the one hand and (**2d**) and (**3d**) on the other when exposed for prolonged periods to treatment with hydrazine suggests an intramolecular interaction, although present evidence does not permit us to distinguish a simple effect of steric compression from one involving stereoelectronic elements.

Dehydrogenation of the bis(hydrazones) (**1d**) and (**2d**) was readily achieved using yellow mercuric oxide in ether, containing a few drops of saturated methanolic KOH, affording (**1b**) as green needles from THF with the characteristic double absorption maxima at 490 nm ($\varepsilon = 36$) and 568 nm ($\varepsilon = 16$), whereas (**2b**) crystallised as maroon platelets from the same solvent and showed broad absorption maximised at 540 nm ($\varepsilon = 73$). Oxidation of (**3d**) proved difficult to control and it was found impossible to obtain (**3b**) free from serious contamination by products of further oxidation which we were unable to remove by crystallisation or low-temperature column chromatography. The most successful procedure for oxidation used freshly prepared silver oxide in dry dichloromethane with addition of one drop of saturated KOH in methanol. The product, so obtained, was a purple amorphous solid with λ_{max} 547 nm (ε 1 790) with a shoulder at *ca.* 640 (ε 300) the mass spectrum and accurate mass of the parent ion being consistent with the bis(diazo)alkane. Elemental analysis and i.r. spectroscopy suggested only *ca.* 60% purity, however.

Each of the diazo compounds was characterised by conversion into its crystalline diacetate, a mixture of the (±)- and *meso*-diastereoisomers. These were formed in good yield [from (**1b**) 85%; (**2b**) 75%; (**3b**) 61%] by treatment of the diazo compound (*ca.* 25 mg) with excess acetic acid in dichloromethane solution and identified by elemental analysis and spectroscopically. Only in the case of the diacetates from (**1b**) could the diastereoisomers be separately detected in the ^1H n.m.r. spectrum (250 MHz). They were present in a 3:2 ratio, the less abundant component being assigned the *meso* structure from consideration of steric hindrance in the conversion of the second diazo group into the acetate and because the acetate methyl protons resonate at higher field than those of the other diastereoisomer. The latter observation is seen as a consequence of the proximity of the acetate groups which constrains one or other of the methyl groups to lie over the hydrocarbon nucleus where it experiences a shielding effect due to the anisotropy of the aromatic components.

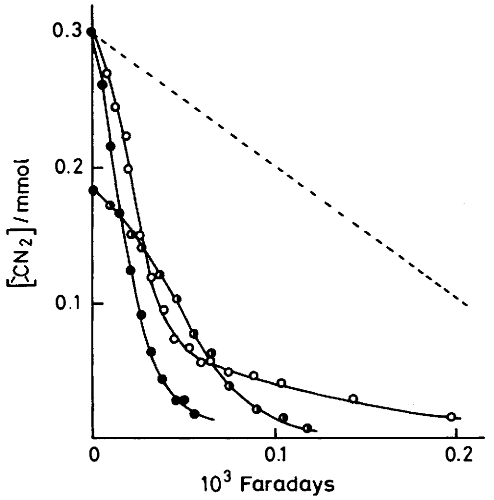

Figure 1. Constant-current electrolysis, at a Pt cathode, of bis(diazo)indenofluorenes (*ca.* 3 m mol dm^{-3}) in DMF solution at 30 °C. Diazo-functionality determined as a function of Faradays passed: ○, Compound (**1b**); ●, (**2b**); ◑, (**3b**). The dashed line indicates expectation if $n = 1$ Faraday mol^{-1}.

Cathodic Reduction of Compounds (**1b**), (**2b**), *and* (**3b**).—Reductions were carried out at constant current at a cylindrical smooth platinum cathode using solutions of the monomers in dimethylformamide (DMF) containing Me_4NBF_2 (0.1 mol dm^{-3}) as supporting electrolyte under purified nitrogen. A magnetically stirred divided electrolysis cell was used. Cyclic voltammetric experiments indicated that peak potentials for reduction of the monomers were *ca.* -1.2 V *vs.* Ag/Ag$^+$ (0.01 mol dm^{-3} in CH_3CN), but the cyclic voltammograms were all somewhat distorted; adsorption appears to be a serious problem and this prevented detailed study of the electrochemical kinetics of the initially generated monomer anion radicals.

On electrolysis, monomer solutions, initially green (**1b**), red (**2b**), or purple (**3b**) rapidly darkened becoming essentially black (see below). No particulate material could be detected visually nor was a product layer built up on the cathode surface. Thus, the reaction takes place in solution and yields DMF-soluble products. The progress of the reaction was followed by withdrawing samples at timed intervals and determining the concentration of diazo groups by i.r. spectroscopy using calibration curves based on the monomer and used on the assumption that the i.r. absorption would be the same for oligomeric/polymeric products containing the diazo function. No evidence of additional absorptions around 2 000 cm^{-1} that could be ascribed to intermediates or products was found.

In Figure 1 the consumption of diazo groups is shown as a function of time (being proportional to coulombs) for cathodic reduction. A constant current, giving a low current density (25 μA cm^{-2}), was chosen to encourage high degrees of polymerisation. The dashed line in Figure 1 shows the expected disappearance of diazo groups if one electron were required to consume each group ($n = 1$). It can be seen that several diazo

Table 1. Parameters of e.s.r. spectra of electrolysis solutions (transference experiments).

Compound	% Decomposition	g-Value	Line width/mT
(**1b**)	68	2.002 41 ± 0.000 03	0.8
(**2b**)	83	2.002 38 ± 0.000 04	0.3
(**3b**)	33	2.002 68 ± 0.000 04	0.5

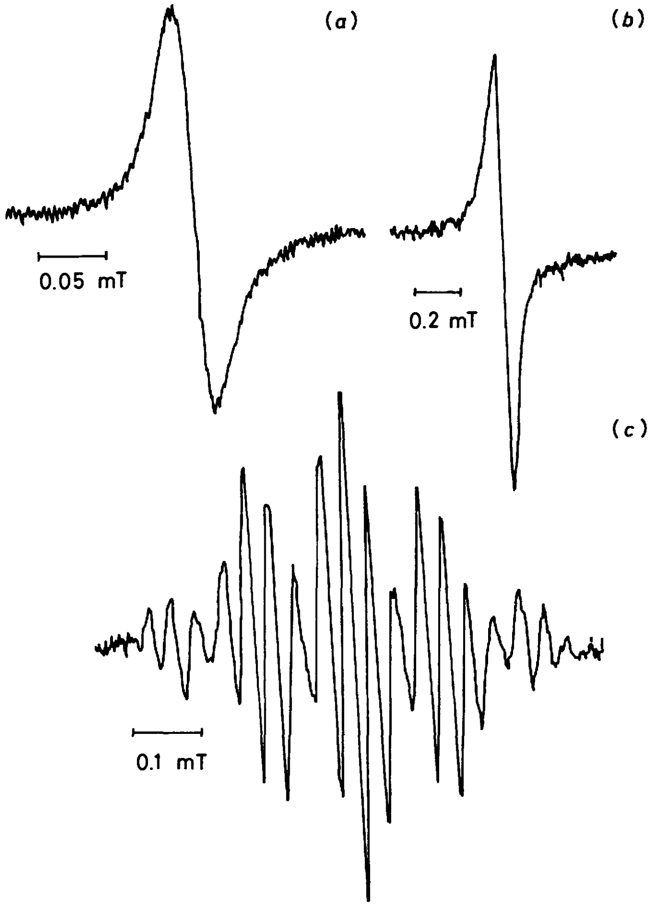

Figure 2. *in situ* e.s.r. spectra observed on reduction of CH_3CN solutions of (*a*) (**1b**), (*b*) (**2b**), and (*c*) (**3b**) at −1.5 V (*vs.* Ag/Ag$^+$).

groups are destroyed for each electron introduced [*ca.* 5 for (**1b**), 10 for (**2b**), and 2 for (**3b**)], indicating that an electron-transfer chain process is involved. This is confirmed by our observation that diazo groups continue to be consumed when the electrodes are disconnected after partial electrolysis, a process that continues for several hours. These observations will be analysed in more detail in a later paper, but it is emphasised now that the degree of polymerisation is related in a rather complex way to the electrochemical chain length because of the competition for chain carriers between chain extension and electron transfer to monomer and oligomeric diazo compounds.

When the i.r. absorption due to diazo groups was no longer detectable, the reduction products were isolated in one of two ways, either by simple removal of the solvent under reduced pressure of nitrogen (whereafter the amorphous black powder was stored in sealed glass tubes under vacuum) or by quenching of solutions with glacial acetic acid which led to precipitation of a brown, amorphous, air-stable solid which was insoluble in a wide range of organic solvents. Glacial acetic acid converts diazo groups into secondary alkyl acetates quantitatively in aprotic solvents, and this quenched product was used for characterisation of the product chemically and by elemental analysis after treatment with boiling water to remove residual supporting electrolyte.

Electron Spin Resonance and Electronic Spectroscopy of Electrolysis Solutions.—E.s.r. spectroscopy was used to investigate the radical species generated in the course of cathodic reduction of (**1b**), (**2b**), and (**3b**). In preliminary experiments, samples of the electrolysis solution in DMF after partial reaction were transferred by syringe to a nitrogen-purged e.s.r. tube. The signals, so observed, were weak and their intensity decreased on exposure of the solution to air. Each spectrum consisted of a single, broad line, the intensity corresponding to *ca.* 10^{-6} mol dm^{-3} radicals; g-values and peak-to-peak line widths are in Table 1. All the signals had g-values above the free-electron value, but not so large as to suggest substantial spin densities on nitrogen. The line widths were large enough to obscure any hyperfine splitting.

in situ electrochemical e.s.r. spectroscopy was also used in an effort to obtain further information. The facilities were kindly made available by Dr. R. G. Compton and made use of a Coles–Compton silica channel unit incorporating a planar platinum electrode located in the e.s.r. cavity.[12] The experiments involved the use of stationary acetonitrile solutions of the bis(diazo) compounds (saturated = *ca.* 1 mmol dm^{-3}) with Me_4NBF_4 (sat.) as supporting electrolyte. The choice of solvent was dictated by the method of construction of the channel unit. Reductions were carried out at a constant potential close to −1.5 V (*vs.* Ag/Ag$^+$). The spectra in this case were somewhat different from those observed in the preliminary transference experiments. Both (**1b**) and (**2b**) again yielded single-line spectra but these were now very much narrower, *ca.* 0.06 mT peak-to-peak for both (**1b**) and (**2b**). The appearance of these signals [Figure 2(*a*), (*b*)] suggests that they were due to radicals in the solid phase,[13] perhaps on the electrode surface. The line shape is very similar to those in reported spectra of lightly p-doped polyacetylene[14a] and polyphenylenevinylene,[14b] but falls short of the Dysonian line shape associated with metallic-type conductors.

in situ electrochemical e.s.r. experiments on (**3b**) yielded the spectrum shown in Figure 2(*c*), the only one showing hyperfine coupling, although the resolution is not very good. The spectrum appears to be that of the anion radical of (**3c**) since the same spectrum could be generated by similar treatment of the diketone. It is worth noting, however, that reduction of analytically pure fluorenone azine *in situ* at −1.5 V under the same conditions gives a well-resolved spectrum identical with that of the anion radical of fluorenone[15a] rather than that reported for the azine anion radical.[15b] These transformations of azine in to ketone are presumed to depend on the presence of traces of molecular oxygen in the solutions.

After completion of cathodic reductions, the electronic spectra of the resultant DMF solutions were examined in the visible and near i.r. regions. The spectra are shown in Figure 3(*a*), (*b*), in which it can be seen that intense absorption extended well beyond 1 000 nm, particularly for the product from (**2b**). The product of reduction of (**3b**) gave even more intense absorption which, under the experimental conditions used for the other products, gave 100% absorption up to 1 400 nm and a further broad maximum centred around 2 000 nm with a sharp cut-off at 2 140 nm. On exposure to the air, all the solutions lightened and eventually showed no detectable absorption beyond 700 nm. In their appearance the spectra of the products of reduction of all three monomers are reminiscent of the spectra of polyaniline and related materials described by McDiarmid *et al.*[16]

Table 2. Representative elemental analytical data for reduction products treated with CH_3CO_2H.

	Observation (%)				Theory (%)			
Reactant	C	H	N	n	C	H	N	M_w
(1b)	80.53	3.64	8.12	2	81.47	4.35	4.32	649
(2b)	83.64	3.60	9.12	5	84.19	3.94	7.55	1 484
(3b)	84.98	3.74	8.53	10	85.22	3.79	8.77	2 875
				17	85.66	3.72	9.29	4 823
				∞	86.31	3.62	10.07	

[a] Calculated for a linear polyazine with secondary acetate end groups: $(CH_3CO_2)H(C_{20}H_{10}N_2)_{n-1}(C_{20}H_{10})H(O_2CCH_3)$.

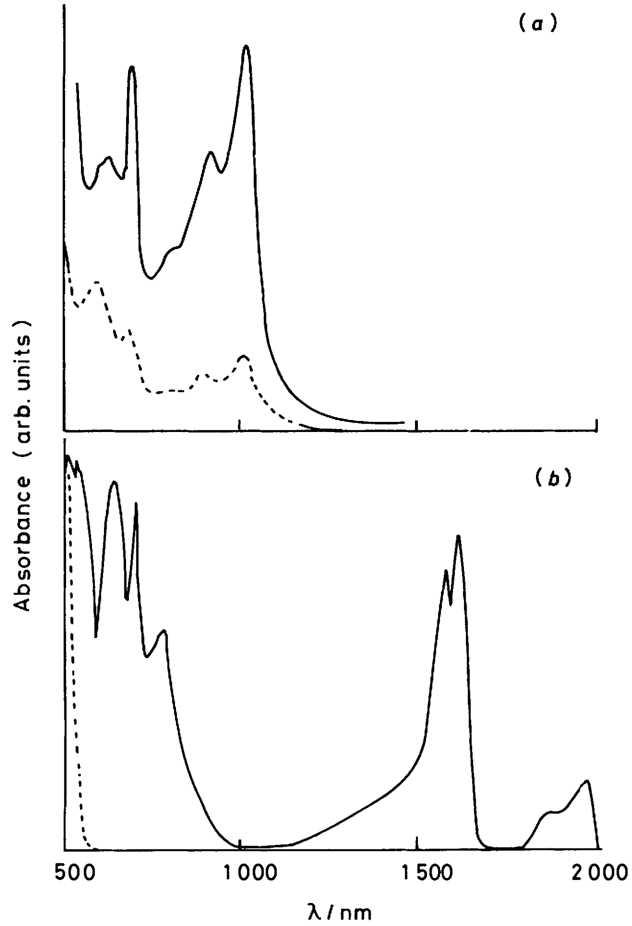

Figure 3. Electronic spectra of products of electrochemical reduction of (*a*) (**1b**) and (*b*) (**2b**) each initially 3 mmol dm^{-3} in DMF solution at 30 °C. Dotted curves show spectra after exposure to air until no further change occurred.

These results and those from e.s.r. spectroscopy are consistent with extended conjugation in a negatively charged polymer containing some unpaired electrons.

Characterisation of the Reduction Products of (**1b**), (**2b**), *and* (**3b**).—Solutions from constant-current electrolysis of the three bis(diazo) compounds were treated with excess glacial acetic acid and the precipitated material washed with boiling water to remove as far as possible any trapped supporting electrolyte. The insolubility of the amorphous brown solids so obtained precluded end-group analysis by n.m.r. spectroscopy. The materials were subjected to elemental analysis and were also degraded by treatment with bromine and aqueous acetic acid, a procedure that converts ketazines into the parent ketone.[17]

Representative analytical data are in Table 2, together with percentages of carbon, hydrogen, and nitrogen calculated for linear polyazines with acetate end groups and a selection of degrees of polymerisation. Significantly C, H, and N constitute over 95% of the product from (**2b**) and (**3b**) but only about 92% of that from (**1b**) suggesting that shorter chain lengths are achieved in the last case. The results for the product from (**3b**) fit quite well for a product with a degree of polymerisation of 10 (M_w = 2 875) although this is a lower degree of polymerisation than results from gel-permeation chromatography (see below).

In the other two instances, the percentage of carbon fell short of that expected on the basis of the percentage of nitrogen, assuming the linear polyazine structure. This suggests contamination with some other material of low carbon content, possibly traces of supporting electrolyte trapped within the very insoluble product. For example, the observed elemental analysis for the product from (**2b**) is compatible with $n = 17$ if it is assumed to contain 3.6% of Me_4NBF_4.

Exhaustive treatment of the electrolysis products with bromine in acetic acid containing a little water[17] led to degradation and the isolation of analytically pure parent diketones (**1c**), (**2c**), and (**3c**) in yields of 60, 40, and 35%. As a check on the method, fluorenone azine when treated in the same way afforded fluorenone in 80% isolated yield. The lower yields from the electrolysis products may be in part a result of their very insoluble nature but might be taken to indicate the presence of some linkages between indenofluorene units that are not of the azine type (see below).

Molecular weight distributions of the products were examined by gel-permeation chromatography (g.p.c.). For reasons of solubility, products were isolated by removal of the solvent and redissolved immediately before g.p.c. analysis. In each case, a little material did not redissolve and this was removed by filtration prior to analysis. Only the product from (**1b**) could be dissolved in THF, the preferred solvent for the analysis; the products from (**2b**) and (**3b**) were examined in DMF solution. The results are displayed graphically in Figure 4 in which elution volumes for the monomer and a number of polystyrene markers of known molecular weight are also indicated. With the assumption that the markers are an adequate guide to the behaviour of the present extensively conjugated materials, the results indicate that (**1b**) gives rise to products with degrees of polymerisation in the range 2–4, whereas (**2b**) and (**3c**) give materials of much higher molecular weight, most material apparently centred on a molecular weight around 4 800 which would correspond to chains of *ca.* 17 monomer units. Both, however, showed evidence of material of much higher molecular weight. This would not be unexpected for a step-growth polymerisation (condensation polymerisation). The mechanistic aspects of these observations and their implications for classification of the polymerisation will be discussed elsewhere. The practically important corollary, however, is that prolonging electrolysis after the apparent disappearance of the diazo

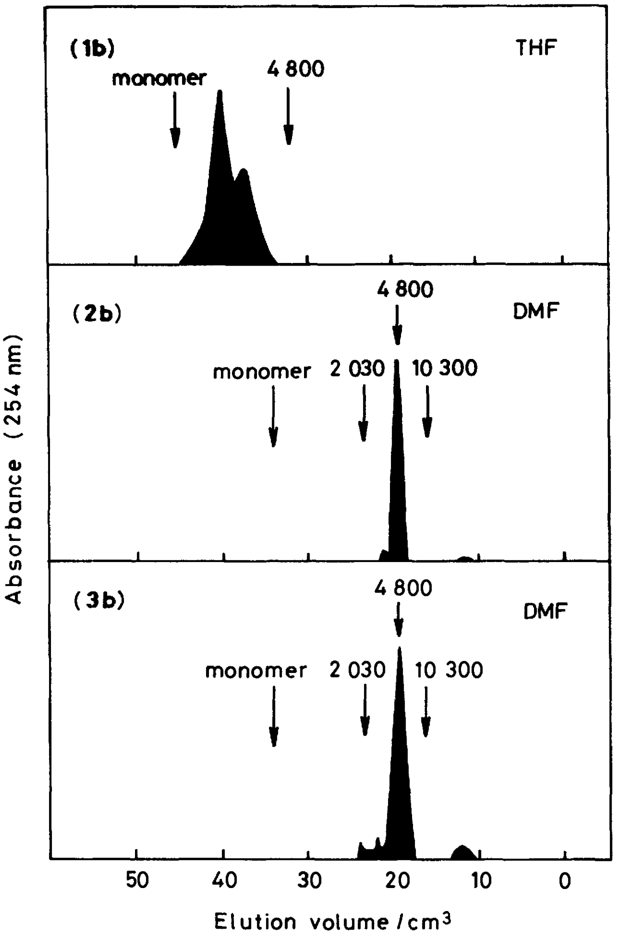

Figure 4. Gel-permeation chromatographic analysis of products of reduction of (*a*) (**1b**) in THF solution; (*b*) (**2b**) in DMF solution; (*c*) (**3b**) in DMF solution. Arrows indicate elution volumes of polystyrene markers.

Table 3. Specific conductivities of solid products from electrolysis of (**1b**), (**2b**), and (**3b**) in the pristine state and after SO_3-doping.

	σ/ohm^{-1} cm^{-1}	
Reactant	Pristine	SO_3-Doped
(**1b**)	2.3×10^{-10}	1.2×10^{-4}
(**2b**)	1.3×10^{-9}	2.0×10^{-3}
(**3b**)	3.0×10^{-6}	1.3×10^{-4}
9-Diazofluorene[a]	1.4×10^{-10}	6.4×10^{-7}

[a] Product is fluorenone azine.

functionality might have given much higher proportions of the higher molecular weight material; further work is clearly desirable.

Electrical/Electrochemical Studies on the Reduction Products.—The d.c. conductivity at room temperature *in vacuo* of samples of the reduction products in the pristine state compressed into a pellet was examined in a preliminary way using a van der Pauw four-terminal probe.[18] Values of the specific conductivity are in Table 3. For comparison, fluorenone azine was also investigated.

It should be borne in mind that all samples contained a substantial amount of supporting electrolyte (Me_4NBF_4) and this may explain why the observed values of σ are all substantially higher than those previously reported for polyazines.[4] Values of σ increased in all cases on exposure of the samples to SO_3, a readily available p-dopant; this was particularly marked in the case of the product of reduction of (**1b**) and (**2b**), but all showed rather similar specific conductivities of 10^{-4} to 10^{-3} ohm^{-1} cm^{-1} after exposure to SO_3. Visual examination of the compressed samples after SO_3 treatment showed that they were darkened on the surface, the interior being apparently unaffected.

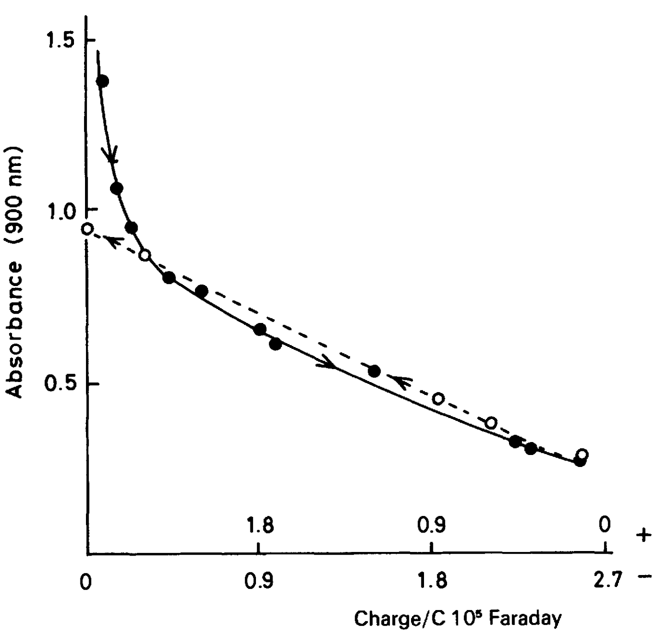

Figure 5. Absorbance changes at 900 nm of solution of products of reduction of (**1b**) (3 mmol dm^{-3}) in DMF on oxidation at constant current ●. The dotted line and open circles indicate first re-reduction at constant current.

A cyclic-voltammetric study of the product solution from reduction of (**1b**) showed quasi-reversible behaviour with $E^{\mathrm{P}}_{\mathrm{R}} = -1.39 E^{\mathrm{P}}_{\mathrm{O}} = -1.26$ V [*vs.* Ag/Ag$^+$ (0.01 mol dm^{-3} in CH_3CN)]. The absorbance of the solution in the reduced form in the solution taken directly from the electrolysis cell was monitored at 900 nm while it was oxidised at constant current. The observations are summarised in Figure 5 and it can be seen that there is a bimodal decrease in absorbance. The initial decrease corresponded to the passage of only about one-sixth of the total charge needed to minimise the absorbance (corresponding to one electron for every five monomer molecules originally present). Thereafter there is a roughly linear decrease of absorbance with charge passed. Re-reduction of the solution restored the absorbance but only to the value expected by extrapolation of this linear portion of the curve, suggesting that about half of the initial absorbance is attributable to species where oxidation is irreversible. The remainder is associated with a species which will undergo repeated cycles of oxidation and reduction in the absence of air.

Conclusions

The present exploratory work has shown that bis(diazo) compounds (**1b**), (**2b**), and (**3b**) do indeed undergo electropolymerisation on cathodic reduction in DMF solution. The process is a chain reaction of the same general form as that observed in the reduction of 9-diazofluorene which gives fluorenone azine, but the chain length, the number of diazo groups consumed per electron, is much smaller.

The products appear to be conjugated and these are produced in solution in reduced form, as judged by the intense absorption, stretching into the near i.r. region, and the detection of e.s.r. signals. This also explains this discharge of the colour on electrochemical oxidation, exposure to air, or by treatment with acetic acid.

Molecular-weight determinations, though not very precise, indicate that short chain (n = 10–17) polymers are mainly produced from (**2b**) and (**3b**), although there is evidence of some material of higher molecular weight. Monomer (**1b**) seems to give short chain oligomers (n = 2–5).

All the materials as produced are effectively n-doped and show modest specific conductivities in the range associated with semiconductors. Exposure of solid samples to gaseous SO_3 leads to increases of σ by factors up to 10^6-fold. However, more detailed investigation is necessary (*e.g.*, variable-temperature studies) to confirm these observations and inferences. In particular the possibility that SO_3 reacts with the oligomers chemically (*i.e.*, by sulphonation) rather than as a p-dopant needs to be considered.

Experimental

Preparation of the Bis(*diazo*) *Compounds*.—11,12-*Dioxo*-11,12-*dihydroindeno*[2,1-a]*fluorene bis*(*hydrazone*) (**1d**). The parent ketone[19] (4.00 g), prepared by two-stage intramolecular Friedel–Crafts acylation from 3,6-diphenylphthalic anhydride, was suspended in absolute ethanol (100 cm^3) and the mixture heated to boiling. Hydrazine hydrate (2.56 g) was added and heating under reflux continued for 30 min. After being cooled the yellow crystalline suspension was filtered and the solid washed with cold ethanol. Recrystallisation from ethanol gave the bis(hydrazone) (4.2 g) m.p. 188–190 °C (Found: C, 77.2; H, 4.65; N, 18.25. $C_{20}H_{14}N_2$ requires C, 77.42; H, 4.52; N, 18.06%).

11-*Oxo*-11,12-*dihydroindeno*[2,1-a]*fluorene Hydrazone* (**1e**). Treatment of parent diketone (**1c**) (0.556 g) suspended in ethanol (15 cm^3) with hydrazine hydrate (10.3 g) followed by heating under reflux for 8 h yielded a clear solution. After being cooled a yellow crystalline product precipitated (0.526 g), m.p., 200–203 °C (Found: C, 84.95; H, 5.35; N, 9.25. $C_{20}H_{14}N_2$ requires C, 85.08; H, 5.00; N, 9.92%; δ[$(CD_3)_2SO$; 220 MHz] 3.90 (2 H, s), 7.35 (4 H, m), 7.62 (1 H, d), 7.83 (5 H, m), and 8.24 (2 H, br s).

11,12-*Bis*(*diazo*)-11,12-*dihydroindeno*[2,1-a]*fluorene* (**1b**). The bishydrazone (**1d**) (4.20 g) was finely ground with freshly prepared yellow mercuric oxide (14.67 g) and suspended in dry ether (200 cm^3), together with a few drops of alcoholic potassium hydroxide. After being stirred for 3 h, the mixture was filtered, the ether removed under reduced pressure, and the residue crystallised from boiling THF to give green needles (2.61 g), m.p. 140 °C (decomp.) (Found: C, 78.5; H, 3.25; N, 18.35%; M^+, 306.0905. $C_{20}H_{10}N_4$ requires C, 78.43; H, 3.27; N, 18.30%; M^+, 306.0903); m/z 278, 250, and 69 (base); δ(CD_2Cl_2; 250 MHz) 7.35 (2 H, td, J 6.5, 2.0 Hz, 2-, 9-H), 7.37 (2 H, dd, J 6.5, 2.0 Hz, 1-, 10-H), 7.44 (2 H, td, J 6.5, 2.0 Hz, 3-, 8-H), 7.92 (2 H, s, 5-, 6-H), and 7.97 (2 H, dd, J 6.5, 2.0 Hz, 4-, 7-H); ν_{max}(Nujol) 2 050 cm^{-1}; λ_{max}(THF) 480 nm (ε 36 dm^3 mol^{-1} cm^{-1}) and 568 (16).

11-*Diazo*-11,12-*dihydroindeno*[2,1-a]*fluorene* (**1f**). Similar treatment of the monohydrazone (**1e**) (282 mg) yielded a product after removal of the ether solvent from which the diazo compound was extracted with cold THF. Crystallisation occurred when the extract was concentrated to a small volume to yield scarlet prisms (154 mg), m.p. 184 °C (decomp.) (Found: C, 85.7; H, 4.18; N, 10.44%; M^+, 280.0996. $C_{20}H_{12}N_2$ requires C, 85.71; H, 4.29; N, 10.00%); m/z 252 and 40 (base); δ(CD_2Cl_2; 250 MHz) 4.05 (2 H, s, 12-H), 7.33 (4 H, m, 2-, 3-, 8-, 9-H), 7.41 (1 H, d, J 7.5 Hz, 1-H), 7.50 (1 H, d, J 7.5 Hz, 10-H), 7.56 (1 H, d, J 7.5 Hz, H-4), 7.62 (1 H, d, J 7.5 Hz, 5-H), and 7.97 (2 H, d, J 7.5 Hz, 6-, 7-H); ν_{max}(CH_2Cl_2 solution) 2 030 cm^{-1}; λ_{max}(THF) 534 nm (ε 33 dm^3 mol^{-1} cm^{-1}).

10,12-*Dioxo*-10,12-*dihydroindeno*[2,1-b]*fluorene bishydrazone* (**2d**). Hydrazine hydrate (1.73 g) was added to a refluxing suspension of the diketone[20] (**2c**) (1.00 g) in ethanol (30 cm^3) which, after being refluxed for a further 18 h and then cooled, gave the yellow microcrystalline bis(hydrazone) which needed no further purification; m.p., 188–190 °C (Found: C, 77.3; H, 4.6; N, 17.84%; M^+, 310.1213. $C_{20}H_{14}N_4$ requires C, 77.42; H, 4.52; N, 18.06%; M, 310.1218); m/z 280, 250, and 43 (base).

10,12-*Bis*(*diazo*)-10,12-*dihydroindeno*[2,1-b]*fluorene* (**2b**). Oxidation of the bis(hydrazone) with a tenfold excess of yellow mercuric oxide in dry ether as for (**1b**) yielded, after filtration, repeated washing of the residue with THF, and removal of the solvent, a maroon solid. Recrystallisation of this from boiling THF gave maroon crystals in 74% yield, m.p. 180 °C (decomp.) (Found: C, 78.6; H, 3.25; N, 18.07%; M^+, 306.0901. $C_{20}H_{10}N_4$ requires C, 78.43; H, 3.27; N, 18.30%; M, 306.0903); m/z 278, 250, and 69 (base); δ(CD_2Cl_2; 250 MHz) 7.34 (2 H, td, J 6.7, 2.0 Hz, 2-, 8-H), 7.36 (1 H, s, 11-H), 7.38 (2 H, td, J 6.7, 2.0, 3-, 7-H), 7.50 (2 H, ddd, J 6.7, 2.0, 0.8 Hz, 1-, 9-H), 8.03 (2 H, ddd, J 6.7, 2.0, 0.8 Hz, 4-, 6-H), and 8.47 (1 H, s, 5-H); ν_{max}(Nujol mull) 2 050 cm^{-1}; visible (THF); λ_{max} 540sh nm (ε 55 dm^3 mol^{-1} cm^{-1}).

6,12-*Dioxo*-6,12-*dihydroindeno*[1,2-b]*fluorene Bis*(*hydrazone*) (**3d**). A suspension of the diketone[21] (**3c**) (2.25 g) in ethanol (50 cm^3) was refluxed for 18 h. The yellow–orange bishydrazone was filtered from the reaction mixture, washed with cold ethanol and recrystallised from ethanol; 2.25 g; m.p., 240 °C (decomp.) (Found: C, 77.55; H, 4.5; N, 17.95%; M^+, 310.1226. $C_{20}H_{14}N_4$ requires C, 77.42; H, 4.52; N, 18.06%; M, 310.1218); m/z 280, 278, 250, and 43 (base).

6,12-*Bis*(*diazo*)-6,12-*dihydroindeno*[1,2-b]*fluorene* (**3b**). The bishydrazone (**3d**) (2.00 g) was finely ground with freshly prepared silver oxide (14.95 g) and the solid suspended in dry CH_2Cl_2 (200 cm^3). On addition of a drop of ethanolic KOH the bis(hydrazone) was consumed (t.l.c.) after being stirred for 30 min. The reaction mixture was filtered and the solids washed with further CH_2Cl_2. Evaporation of solvent from the combined CH_2Cl_2 solutions afforded a dark-purple solid (1.24 g), m.p. 170 °C (decomp.) (Found: C, 79.15; H, 3.35; N, 14.65%. M^+, 306.0904. $C_{20}H_{10}N_4$ requires C, 78.43; H, 3.27; N, 18.30%; M, 306.0905); m/z 278, 250, and 69 (base); ν_{max}(Nujol mull) 2 050 cm^{-1}. Spectrophotometry in DMF solution indicated that the intensity of the absorption at 2 050 cm^{-1} was 60% of that expected by comparison with analytically pure samples of (**1b**) and (**2b**).

Characterisation of the Bis(*diazo*) *Compounds*.—A small sample (*ca.* 25 mg) of each of the bis(diazo) compounds was characterised by conversion into the corresponding diacetate (mixture of diastereoisomers), by treatment with excess acetic acid (*ca.* 5 g) in CH_2Cl_2 (25 cm^3) in the dark for several days. The mixture was quenched by being poured into water, extracted with CH_2Cl_2, washed free of acetic acid, and dried (Na_2SO_4). Details for the compounds so characterised are in Table 4, which includes the chemical shifts of the methyl protons of the acetoxy groups.

Constant Current Electrolysis.—Experiments were conducted at a smooth platinum cathode in a divided cell under purified nitrogen as previously described.[6a] The solvent, dimethylformamide, was purified by leaving it to stand for 24 h over calcium hydride followed by double distillation *in vacuo* with rejection of the first 10% of the distillate. Solutions of the supporting electrolyte, Me_4NBF_4 (0.1 mol dm^{-3}) were further dried immediately prior to use by passage through a short column of activated alumina (Woelm, Super N). The monomer

Table 4. Characterisation of diazo compounds by conversion into the acetates.

Compound	Yield(%)	M.p./°C	Analysis[a]			$\delta_H(CH_3CO_2)$
			%C	%H	m/z (M^+)	
(1b)	85	181.5	77.69	5.06	370.1210	2,13, 2.19
(2b)	75	185–186	77.86	4.93	370.1210	2.19
(3b)	61	189–190	77.57	5.10	370.1210	2.20
(1f)	90	152–153	84.33	5.14	312.1133	2.36

[a] For the diacetates from **(1b**, **(2b)**, and **(3b)** $C_{24}H_{18}O_4$ requires C 77.84, H 4.86%; m/z 370.1205. For the monoacetate from **(1f)** $C_{22}H_{16}O_2$ requires C 84.59, H 5.16%; m/z 312.1150.

concentration was 3 mmol dm^{-3}. The constant current used was typically 2.5 mA. Samples removed at timed intervals were analysed for diazo groups by i.r. spectroscopy at 2 050 cm^{-1} using monomer solutions for calibration; these showed excellent Beer–Lambert behaviour over the whole concentration range.

Product Isolation and Degradation.—After completion of the electrolysis, the solvent was removed *in vacuo*. The black, amorphous residue was then either transferred, in an atmosphere of purified nitrogen, to a glass tube in which it was sealed to await further examination; or it was treated with glacial acetic acid at room temperature for a period of 24 h to destroy residual diazo end groups, filtered, washed with boiling water, and dried *in vacuo* at 80 °C.

Oxidative degradation of the air-stable but highly insoluble material obtained after the acetic acid treatment was based on a method described by Still *et al.*[17] The product (100 mg) was suspended in aqueous acetic acid (15 cm^3; AcOH:H_2O = 12:3 v/v) and bromine (5 cm^3) and potassium bromide (0.5 g) added. The mixture was heated under reflux until the bromine colour was discharged. Five further portions of bromine (each 1 cm^3) were added and heating was continued for 24 h. The reaction mixture was poured into water and extracted repeatedly with CH_2Cl_2. The solution was washed with aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and evaporated to leave a residue which was recrystallised and identified by i.r. spectroscopy and elemental analysis.

Spectroscopic Studies.—Electronic absorption spectra were recorded on a Perkin-Elmer 330 spectrophotometer. E.s.r. spectra on samples transferred from the electrolysis cell were obtained on a Varian E4 spectrometer. *in situ* electrochemical e.s.r. experiments made use of apparatus described by Coles and Compton[12] involving a Bruker ER200D spectrometer. For these experiments saturated solutions of the bis(diazo) compounds in CH_3CN were used, the supporting electrolyte again being Me_4NBF_4 (0.07 mol dm^{-3}).

Gel-permeation Chromatography.—Measurements were made by Dr. P. G. James (BP Research Centre, Sunbury-on-Thames). Only the product from **(1b)** was sufficiently soluble in THF for the chromatography to be run in this solvent. The products from **(2b)** and **(3b)** were, therefore, examined in DMF solution. In all cases traces of insoluble material were removed by filtration prior to chromatography. No attempt was made at this stage to protect the solutions from oxygen. The analyses were made on Microstyrogel columns (Waters: M 600 pump, U6K injector, Model 440 u.v. absorption detector). In some cases an R401 refractive-index detector was used, but this proved too insensitive.

Electrical Conductivity.—Measurements were made using the van der Pauw four-terminal procedure.[18]

Samples (*ca.* 350 mg) of the solid electrolysis product obtained by removal of solvent from the electrolysed solution *in vacuo* were transferred in a glove box to an air-tight die and compressed into a pellet (applied force 10 tons). The die was returned to the glove box, the pellet removed and its thickness (d) measured. Four gold contacts (A, B, C, D) were attached at roughly equal intervals around its edge, contact being made across the whole thickness of the pellet to ensure that the bulk conductivity was determined. The method requires the measurement of the resistance (R_1) between adjacent contacts (C, D) when a current is passed between the other pair (A, B) and resistance (R_2) between D and A when current flows between B and C, the specific resistivity (φ) is then given by

$$\rho = \frac{\pi d}{2 \ln 2}(R_1 + R_2) f(R_1/R_2) = \frac{1}{\sigma}$$

where the function $f(R_1/R_2)$ is obtained by an iterative procedure from the expression:

$$f(R_1/R_2) = \frac{\ln 2}{\ln\left[2 \cosh\left\{\frac{R_1 - R_2}{R_1 + R_2} \frac{\ln 2}{f(R_1/R_2)}\right\}\right]}$$

The measurements were made at room temperature in an evacuated glass cell using a Keightley 606 electrometer.

Doping was carried out at liquid-nitrogen temperature by passing SO_3 in a stream of dry nitrogen through the cell for a period of 120 min. The cell was then evacuated, allowed to reach room temperature and the measurements were repeated.

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