Synthesis of poly(anthra-9,10-quinone-2,6-diyl)

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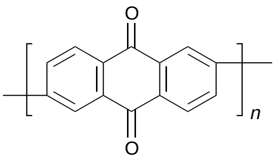
The synthesis, *via* a precursor polymer, of poly(anthra-9,10-quinone-2,6-diyl) 1 is described and some of its properties are reported.

Poly(anthra-9,10-quinone-2,6-diyl) **1** is of interest for several reasons. For example, it is expected to have novel redox properties and these might lead to applications of the polymer in electrochromic displays and/or as charge injection layers in electroluminescent displays. A previous attempt[1,2] to synthesise polymer **1** directly from 2,6-dichloroanthraquinone **2**, by nickel(0)-mediated couplings, led only to very small oligomers because of the extremely low solubilities of compounds of this general type in all common organic solvents. Even the dimer **3** has very low solubilities.[3] We now report a synthesis of polymer **1**, *via* the soluble precursor polymer **4**, which produces a product with a number average molecular weight corresponding to an average degree of polymerisation, $\overline{\mathrm{DP}}$, of 13.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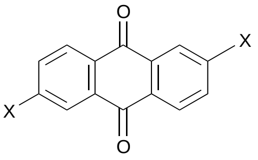
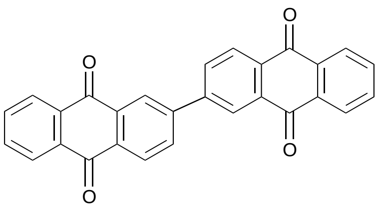

2 X = Cl
7 X = NH$_2$
8 X = Br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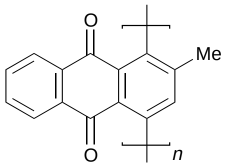
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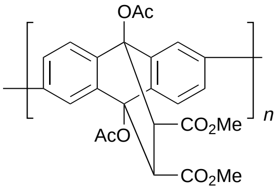
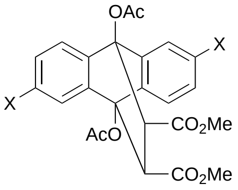
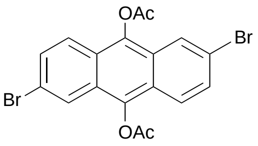

4

Quinone-containing polymers have been described before,[1,2,4] but most are electron-transfer polymers.[4] The latter are usually crosslinked polymers with quinone-containing pendant groups.[5] Very few quinone-containing polymers that have been described actually have the quinone moiety in the main chain and conjugated with the π-electron systems of the neighbouring units. The work most relevant to the present is the synthesis of poly(2-methylanthra-9,10-quinone-1,4-diyl) **5** and several very closely related polymers by nickel(0)-mediated couplings of dichloroquinones.[1,2] For steric reasons, the neighbouring anthraquinone moieties in these polymers are essentially orthogonal to each other.

The basic strategy of the present synthesis was to prepare Diels–Alder adduct **6**, carry out a nickel(0)-mediated coupling to give the soluble precursor polymer **4**, then, after characterisation of the latter, convert it into polymer **1**. Thus, commercial 2,6-diaminoanthraquinone **7** was converted into 2,6-dibromoanthraquinone **8**, mp 282–283 °C (lit.,[6] 289–290 °C) (60% yield) using a Sandmeyer reaction.[7,8] Reductive acetylation of quinone **8** by treatment with zinc dust, Ac$_2$O and NaOAc at reflux temperature gave the anthracene **9**, mp 310 °C (decomp.)‡ (81% yield), and treatment of this with an excess of maleic anhydride in xylene at reflux temperature for 18 h gave the Diels–Alder adduct. The latter was treated with MeOH at reflux temperature to give the half esters. These reacted smoothly with ethereal CH$_2$N$_2$ to give compound **6**, mp 195–200 °C (decomp.)‡, (35% overall yield of recrystallised product from compound **9**).


6 X = Br
11 X = H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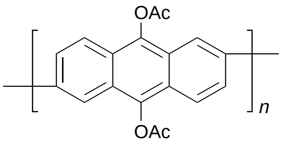
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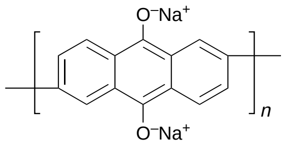
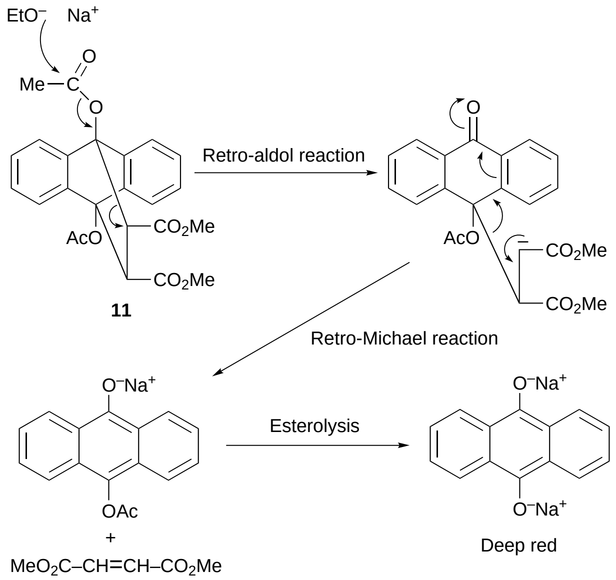

12 Very dark green

Treatment of compound **6** in DMA at 80 °C with 1.2 equiv. of Ni^0[cod]$_2$ in the presence of cod (1.0 equiv.) and 2,2′-bipyridyl (1.2 equiv.)[2,8–11]gave precursor polymer **4**‡ in 82% yield. The polymer was highly soluble in many organic solvents including CHCl$_3$ and THF. The infrared and ^{1}H NMR spectra of the product were consistent with structure **4**. By gel permeation chromatography polymer **4** had, relative to polystyrene standards, a number average molecular weight $\overline{M}_n$, of 5690, a weight average molecular weight $\overline{M}_w$, of 8980 and a peak molecular weight M_p, of 6830. The $\overline{M}_n$ value corresponds to a DP of 13.

Heating polymer **4** to 240 °C did not bring about a clean retro-Diels–Alder reaction to give polymer **10** even though analogous reactions in syntheses of related polymers proceed cleanly.[8,12] However, model studies showed that the dimethyl maleate-9,10-diacetoxyanthracene Diels–Alder adduct **11**‡ reacts readily with 5 equiv. of NaOEt and EtOH in NMP at 20 °C under nitrogen to give a deep red solution of the disodium salt of 9,10-dihydroxyanthracene, and that exposure of this to air rapidly gives anthra-9,10-quinone in essentially 100% yield. We suggest that the key steps in this overall conversion are, successively, (i) a retro-aldol reaction, (ii) a retro-Michael reaction and (iii) an esterolysis (see Scheme 1). Treatment of polymer **4** with NaOEt under similar conditions to those used above gave a very dark green *solution* which we attribute to the formation of polymer **12**. Passage of air through the green solution precipitated polymer **1**, as a pale brown solid, in 95% overall yield from the precursor polymer **4**.



Scheme 1

Polymer **1**, like most anthraquinones, is soluble in concentrated sulfuric acid and trifluoromethanesulfonic acid but it is insoluble in all common organic solvents. The product had an elemental analysis consistent with structure **1**. The FT-IR spectrum of polymer **1** displayed the expected bands at 1679 and at 1592 cm^{-1}: there were no bands which could be attributed to the presence of either maleate or aryl acetate groups. Thermogravimetric analysis of the polymer in air showed no significant weight loss up to 175 °C, then a steady weight loss up to 480 °C by which temperature 35% of the weight had been lost. There was no further significant loss up to 600 °C, the temperature limit of the instrument. A very similar pattern of weight loss was observed when the polymer was heated under nitrogen.

These results demonstrate a practical synthesis of polymer **1**. They also indicate how closely related polymers with these or other anthraquinone moieties might be prepared. Optimisation of the synthesis to obtain a higher $\overline{DP}$ and a more detailed study of the properties of polymer **1**, including its redox properties, are currently under investigation.

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Notes and References

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‡ All new compounds had satisfactory FT-IR and ^{1}H NMR spectra and elemental analyses.

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