Towards a new type of step growth polymerization: Synthesis of dehydro-oligomers of 2,6- and 2,7-dimethylanthraquinone

Ian Goodbody, Abderrazak Ben-Haida, Philip Hodge *

Department of Chemistry, University of Manchester, Oxford Road, Manchester M13 9PL, UK

Received 27 March 2007; received in revised form 4 July 2007; accepted 8 July 2007
Available online 18 July 2007

Abstract

Treatment of 2,6-dimethylanthraquinone and/or 2,7-dimethylanthraquinone with strong base affords, in good yields, oligomers consisting of anthraquinone units linked by ethylene or ethane units. These are formed by a new type of step growth oligomerization that can be summarized conveniently as the linking together of diradical–dianions, followed by air oxidation of the products.

Keywords: 2,6-Dimethylnaphthoquinone; 2,7-Dimethylnaphthoquinone; Oxidative polymerization; Dehydro-oligomers

1. Introduction

Several aromatic compounds with alkyl groups activated by electron-withdrawing substituents give dehydro- and/or bisdehydro-dimers when treated with base followed by exposure, during reaction work up, to acid and air. Thus, 2-methylnaphthoquinone (1) gives bisdehydrodimer 2 [1], anthraquinones 3 and 4 give the dehydrodimers [2], 2-methylnaphthoquinone gives both the dehydro- and bisdehydro-dimers [3], 3-methyl-4-nitropyridine-1-oxide gives the dehydro-dimer [4], 2-methylquinoline N-oxide gives the bisdehydrodimer [5], and 4-nitrotoluene gives the dehydrodimer [6,7].

It is not clear by what mechanism(s) these various reactions occur [3], but in the case of 2-methylnaphthoquinone the reaction almost certainly proceeds as outlined in Scheme 1 [1]. Initially base removes a proton from the methyl group, the latter being activated by the presence of the m- and p-carbonyl groups, to give anion 5. A canonical form of 5 which emphasises the radical character...
of the methylene site is shown in formula 6. Two of 5 may dimerize to form 7. Alternatively, one electron may transfer from 5 to another quinone molecule to give radical 8. This may then dimerize to give 9 or it may combine with 5. Repetition of these processes of proton removal and electron transfer continue to give ultimately tetra-anion 10 and other “dimeric” reduced species. During the reaction work up, treatment with acid and exposure to air oxidizes these reduced species back into quinones. For example, the species 10 oxidizes to bisdehydrodimer 2, and 7, if any is present, to dehydrodimer 9.

Since the electron-accepting properties of quinone-containing polymers [8–17] could lead to applications in electronics, for example in photovoltaic devices [18,19], we considered it of interest to investigate whether the above reactions of 2-methylantraquinone could be extended to the polymerization of 2,6-dimethylantraquinone (11) and/or 2,7-dimethylantraquinone (12). In this article, we report that the reactions lead to the formation in good yields of anthraquinone-containing oligomers 13a–13c with Mns of up to 2000. The latter are probably limited by the poor solubility of the intermediates. These oligomerizations can be conveniently summarized as a new type of step growth polymerization proceeding via the repeated linking together of diradical–dianion species 14.
Oligomers 13 clearly have structural similarities to the polyphenylenevinylene (PPVs), i.e., they are aromatic moieties linked together via olefinic moieties. PPVs are formed most commonly by base eliminations which give quinodimethanes. These are then polymerized by either radical [20] or anionic reactions [21]. Whilst the formation of oligomers 13 by a similar mechanism cannot be excluded, it seems unlikely given that 2-methylantraquinone readily undergoes dehydrodimerization [1].

Another family of polymers that were considered to be formed by radical reactions are the poly-2,6-dialkylphenols. The syntheses of these materials by catalytic oxidative polymerizations, were initially thought to involve aryloxy radicals as the key reactive species [22], but some recent work favours ionic intermediates [23].

2. Experimental

2.1. Methods and materials

Except where indicated otherwise experimental details are as given previously [24]. Potassium tert-butoxide (KtB), 1,2-dimethoxyethane (DME), N-methylpyrrolidone (NMP) and a solution of lithium bis(trimethylsilyl)amide (LBTSA) (1.0 M in THF) were obtained from Aldrich. The solvents were dried over calcium hydride before use. Solid products were dried in a vacuum (2 torr) oven at 70 °C overnight. Unless indicated otherwise FT infrared spectra were measured for KBr disks, ultraviolet–visible spectra for solutions in concentrated sulphuric acid, and 1H NMR spectra at 400 MHz for solutions in concentrated D2SO4.
2.2. Synthesis of 2,6-dimethylanthraquinone (11), 2,7-dimethyl anthraquinone (12) and a mixture of these two isomers

The syntheses of these materials and their characterization are described in the Supplementary material.

2.3. Reactions of 2-methylanthraquinone with base: synthesis of model compound 2 and model compound 9

2.3.1. 1,2-Di(anthraquinon-2-yl)ethylene (2) [1]
A mixture of DME (100 ml), KtB (5.60 g, 50 mmol), water (0.40 ml, 22 mmol) and 2-methylanthraquinone (1.00 g, 45 mmol) was stirred and heated under reflux. The mixture slowly became purple in colour [25] and after 3 h a brown precipitate began to form. The reaction was continued for a further 10 h and then allowed to cool. The cold mixture was poured, with stirring, over hydrochloric acid (1 M; 300 ml). After 30 min the greenish-yellow precipitate was filtered off and washed with water until neutral, and then with methanol to eliminate any starting material. The crude product was re-suspended in chloroform and the mixture heated under gentle reflux for 1 h. The yellow solid was filtered off and washed with hot chloroform until the washings were colourless. Recrystallization of the solid from nitrobenzene gave compound 2 (540 mg; 55% isolated yield) as bright yellow needles, m.p. 431 °C (by DSC) (lit. [1] 434 °C); \( \nu_{\text{max}} \) 1673 cm\(^{-1}\). Compound 2 dissolved in concentrated sulphuric acid to give a purple solution [26] with \( \lambda_{\text{max}} \) 251, 325, 417 and 566 nm (log \( \varepsilon \) 4.87, 4.73, 4.36 and 4.50, respectively): see Fig. 1. The product had \( m/z \) \( (E/I) \) [100%, \( (M) + \)] 441; \(^1\)H NMR: \( \delta \) 7.34 (s; 2H, aromatic H), 7.25 (d, \( J = 8.4 \) Hz, 2H, aromatic H), 7.20 (d, \( J = 8.5 \) Hz, 2H, aromatic H), 7.10 (d, \( J = 7.7 \) Hz, 2H, aromatic H), 6.95 (t, \( J = 8.8 \) Hz, 2H, aromatic H), 6.87 (t, \( J = 7.6 \), 2H, aromatic H), 6.79 ppm (t, \( J = 8.0 \) Hz, 2H, aromatic H) and 6.49 ppm (s; 2H, olefinic H). By \(^1\)H NMR spectroscopy the sample was >98% pure.

2.3.2. 1,2-Di(anthraquinon-2-yl)ethane (9)
A similar reaction to that described in Section 2.3.1 was carried out but with a reaction time of just 1 h. As before the crude product was suspended in chloroform and the mixture heated under gentle reflux for 1 h. The undissolved solid (compound 2) was filtered off and the filtrate was evaporated to dryness. The residue obtained was recrystallized repeatedly from a mixture of chloroform and hexane. This gave bright yellow needles of compound 9 (448 mg, 45% isolated yield), m.p. >350 °C (lit. [27] 330–332 °C); \( \nu_{\text{max}} \) 1674 cm\(^{-1}\). Compound 9 dissolved in concentrated sulphuric acid to give a dark solid...
Table 1
Reactions of anthraquinones 11 and 12 with base to give oligomers 13

<table>
<thead>
<tr>
<th>Entry</th>
<th>Monomer$^a$</th>
<th>Reaction conditions</th>
<th>Yield (%)</th>
<th>Intrinsic viscosity (dl/g)$^d$</th>
<th>DP$^e$</th>
<th>Mn$^f$</th>
<th>Fraction of linkages CH=CH=$^g$</th>
<th>MALDI$^g$</th>
<th>TGA$^h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2,6(7)-DMAQ</td>
<td>LBTSA NMP</td>
<td>75</td>
<td>0.62</td>
<td>3.3</td>
<td>768</td>
<td>0.62</td>
<td>8</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>2,6(7)-DMAQ</td>
<td>LBTSA NMP</td>
<td>73</td>
<td>0.71</td>
<td>4.2</td>
<td>976</td>
<td>0.82</td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td>3</td>
<td>2,6-DMAQ</td>
<td>LBTSA NMP</td>
<td>79</td>
<td>0.47</td>
<td>3.4</td>
<td>800</td>
<td>0.81</td>
<td>7</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>2,6-DMAQ</td>
<td>LBTSA NMP</td>
<td>78</td>
<td>0.96</td>
<td>4.4</td>
<td>1032</td>
<td>0.90</td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>2,7-DMAQ</td>
<td>LBTSA NMP</td>
<td>79</td>
<td>0.60</td>
<td>3.8</td>
<td>800</td>
<td>0.87</td>
<td>8</td>
<td>19</td>
</tr>
<tr>
<td>6</td>
<td>2,7-DMAQ</td>
<td>LBTSA NMP</td>
<td>72</td>
<td>0.67</td>
<td>4.2</td>
<td>976</td>
<td>0.92</td>
<td>8</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>2,6(7)-DMA</td>
<td>KtB DME</td>
<td>85</td>
<td>0.67</td>
<td>4.5</td>
<td>1046</td>
<td>0.92</td>
<td>11</td>
<td>25</td>
</tr>
<tr>
<td>8</td>
<td>2,7-DMAQ</td>
<td>KtB DME</td>
<td>75</td>
<td>0.55</td>
<td>8.7</td>
<td>2020</td>
<td>0.89</td>
<td>12</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ DMAQ = dimethylanthaquinone.
$^b$ LBTSA = lithium bis(trimethylsilyl)amide and KtB = potassium tert-butoxide.
$^c$ NMP = N-methylpyrrolidone and DME = 1,2-dimethoxyethane.
$^d$ Measured in concentrated sulphuric acid at 1.0 g/l and 25°C.
$^e$ Determined by $^1$H NMR spectroscopy. The DP is the average value of “$n$” and the fraction of CH=CH units is the average value of “$x$” in formula 13.
$^f$ Calculated from DP allowing for repeat unit = 232 and end groups = 2.
$^g$ MALDI-TOF mass spectrometry peaks seen from DP = 2 up to the value shown.
$^h$ TGA = thermogravimetric analysis. Figure given is the percentage of weight lost after heating the samples under nitrogen at 20°C/min up to 600°C.
$^i$ Reactions were carried out for 48 h. The crude reaction product was then mixed with 10% more monomer and retreated with base for 24 h.
$^j$ The MALDI-TOF MS is shown in Fig. 1. By calculation from the MS the average DP was 4.32.
yellow solution [26] with \( \lambda_{\text{max}} \) 277, 306, 416, and 569 nm (log \( e \) 5.25, 4.81, 4.66, 4.04, respectively): see Fig. 1. It had \( m/z \) \( E/I \) [100\%, (M\(^+\))] 443; \(^1\)H NMR: \( \delta \) 7.16 (d, \( J = 7.5 \) Hz, 2H, aromatic H), 7.12 (d, \( J = 8.0 \) Hz, 2H, aromatic H), 7.08 (d, \( J = 7.6 \) Hz, 2H, aromatic H), 6.99 (s, 2H, aromatic H), 6.83 (t, \( J = 7.6 \) Hz, 2H, aromatic H), 6.79 (t, \( J = 7.7 \) Hz, 2H, aromatic H), 6.63 (t, \( J = 9.2 \), 2H, aromatic H) and 2.01 ppm (s, 4H, 2 CH\(_2\)). By \(^1\)H NMR spectroscopy the sample was >98% pure.

2.3.3. Treatment of 2-methylanthraquinone with lithium bis(trimethylsilyl)amide

A solution of the mixture of 2-methylanthraquinones (1000 mg, 4.50 mmol) in NMP (150 ml) was stirred under a nitrogen atmosphere at 20°C. LBTSA (45.0 ml of 1.0 M solution in THF) was added. The reaction mixture was heated gradually to 120°C until all the THF had been distilled out. The reaction was continued for a further 48 h. The mixture was then allowed to cool and poured over acidified water (400 ml). The precipitate was filtered off and washed thoroughly first with hot water and then with hot methanol, and dried. The yellow product was extracted with hot chloroform for 48 h using a Soxhlet apparatus, then dried under vacuum (961 mg, 97% yield). It had \( \mu_{\text{max}} \) 1673 cm\(^{-1}\). The \(^1\)H NMR spectrum indicated the product was a mixture of compounds 2 and 9 (see above for the spectra of separate pure compounds) in a mole ratio 96:4.

2.4. Typical polymerization

The results of the main polymerization experiments are summarized in Table 1. The following procedure is typical of that used for the polymerizations and for the re-treatments. The starting materials for the latter were the crude products from the initial (48 h) experiments plus a further portion (10% by weight) of the appropriate monomer(s).

**Entry 2:** A solution of the mixture of 2,6- and 2,7-dimethylanthraquinones (500 mg, 2.12 mmol) in NMP (100 ml) was stirred under a nitrogen atmosphere at 20°C. LBTSA (22.0 ml of 1.0 M solution in THF) was added. The reaction mixture was heated gradually to 120°C until all the THF had been distilled out. The solution turned a very intense purple [25]. The reaction was continued for a further 48 h, during which time a brown precipitate formed. The mixture was then allowed to cool and poured over acidified water (200 ml). The precipitate was filtered off and washed thoroughly first with hot water and then with hot methanol, and dried. The crude dark yellow product was extracted with hot chloroform for 48 h using a Soxhlet apparatus, then dried under vacuum (360 mg, 73% yield). It had \( \mu_{\text{max}} \) 1671 cm\(^{-1}\). No thermal transition was observed by differential scanning calorimetry (DSC) up to 350°C. The product dissolved in concentrated sulphuric acid to give a blue solution [26]. It had \( \lambda_{\text{max}} \) 253, 326, 420, and 600 nm (log \( e \) 4.80, 4.76, 4.30 and 4.40, respectively), see Fig. 1, and \( \eta_{\text{inh}} \) 0.71 dl/g (conc. H\(_2\)SO\(_4\)). Integration of the signals in the \(^1\)H NMR spectrum due to the aromatic and vinyl protons (ca. 6.5–7.4 ppm), CH\(_2\)CH\(_2\) groups (ca. 2.0 ppm) and methyl groups (ca. 1.4 ppm), indicated the polymer had the composition summarized in Table 1, entry 2. A typical \(^1\)H NMR spectrum is shown in Fig. 2 and a typical MALDI ToF MS is shown in Fig. 3.
3. Results and discussion

The object of the present work was to investigate the reactions of \( \beta,\beta' \)-dimethylanthraquinones with bases as a means to synthesize anthraquinone-containing oligomers and/or polymers. The selected starting materials were 2,6-dimethylanthraquinone (11), 2,7-dimethylanthraquinone (12) and a readily-prepared mixture of these isomers. The syntheses and characterization of these materials are described in the Supplementary material.

3.1. Preparation and characterization of model compounds 2 and 9

In anticipation of preparing oligomers and/or polymers containing anthraquinone moieties linked by ethane or ethylene moieties, to assist in their characterization model compounds 2 and 9 were prepared by treating 2-methylanthraquinone (1) with KtB in DME at 85 °C [1]. When the reaction was carried out for 1 h compound 9 was the main isolated product (45% yield); after 13 h compound 2 was the main isolated product (55% yield). The former was sparingly soluble in all common organic solvents, but 2 was only soluble in hot nitrobenzene. However, both compounds dissolve in concentrated \( \text{H}_2\text{SO}_4 \); 9 to give a deep yellow solution [26], 2 a purple solution [26]. In the UV–vis spectrum of compound 9 in concentrated \( \text{H}_2\text{SO}_4 \) the longest wavelength maximum was at 569 nm whilst with compound 2 it was at 566 nm: see Fig. 1. However, with compound 2 the band was more intense (\( \varepsilon \) 31,600 \( \nu \) 11,000) [28]. The \( ^1\text{H} \) NMR spectrum of compound 9 in concentrated \( \text{D}_2\text{SO}_4 \) shows the signal due to the methylene units at 2.01 ppm and the signals due to the aromatic protons between 7.1 and 6.7 ppm. In the \( ^1\text{H} \) NMR spectrum of compound 2 the signal due to the olefinic protons is present at 6.49 ppm, and those due to the aromatic protons between 7.3 and 6.6 ppm. The appearance of the olefinic protons as a sharp singlet suggests that only one geometrical isomer is present, almost certainly the less hindered \( E \)-isomer.

3.2. Oligomerizations/polymerizations

In an attempt to identify a better base for these reactions than a mixture of potassium \( \text{tert} \)-butoxide and water (10 M equivalents to 3), as was used in the early work and which has the problem of a small but significant side reaction (accounting for ca. 3% of the 2-methylanthraquinone) resulting in cleavage of the quinone ring [1,29], 2-methylanthraquinone was treated with LBTS in NMP at 120 °C for 48 h. This afforded a mixture of compounds 2 and 9 in 97% yield, so indicating that LBTS is a satisfactory base for carrying out polymerizations. Accordingly the chosen dimethylanthraquinone was treated with either LBTS in NMP or KtB in DME at the chosen temperature and for the chosen time. The experiments are summarized in Table 1. In all cases the reaction mixtures turned a very intense purple colour [25]. At the end of the reaction period the mixture was cooled and added to a large volume of dilute acid. The purple colour faded rapidly. As the mixture was stirred vigorously in air a yellow precipitate formed. This was collected and dried, then unreacted starting quinone was removed by exhaustive extraction with chloroform using a Soxhlet apparatus. The final products were pale yellow powders.

Initial experiments (not summarized in Table 1) were carried out by treating the mixture of quinones 11 and 12 with either KtB in DME at 85 °C or LBTS in NMP at 100 °C for 4 h. In all cases the yields of insoluble product were <40%, suggesting that more vigorous reaction conditions were required. The conditions then selected were LBTS in NMP at 120 °C for 48 h and the mixture of quinones 11 and 12 and the pure isomers were all treated under these conditions. The results are summarized in Table 1, entries 1, 3 and 5. In a further set of experiments the initial crude products were retreated with fresh base for 24 h, see Table 1, entries 2, 4 and 6, in an attempt to raise the molecular weight and the fraction of CH=CH linkages. Finally, KtB was used as the base in DME at 85 °C for 72 h, see entries 7 and 8. It is evident from the data in Table 1 that the different base-solvent combinations give very similar results with no obvious trends, possibly because the limiting factor is the solubility of the initial polymeric product.

3.3. Characterization of the products

2,6-Dimethylanthraquinone (11) has m.p. 236 °C and 2,7-isomer (12) m.p. 169 °C. In contrast all the polymerization products had m.p.s >320 °C. The products were insoluble in all common organic solvents, but they did dissolve in concentrated sulphuric acid [26] and so were not crosslinked. They were characterized using a range of spectroscopic techniques. Together these indicate that the products
were oligomers with the general structure 13. Clearly from reactions starting with 2,6-dimethylanthaquinone (11) the product is 13b, whilst from reactions starting with quinone 12 it is 13c. Starting with a mixture of these quinones gives product 13a.

The FT-IR spectra of all the products showed very strong carbonyl bands at 1671–1673 cm\(^{-1}\). The spectra were very similar to each other and to those of the starting materials, suggesting that the anthraquinone moieties were largely, if not entirely, retained in the products. The UV–vis spectra, see Fig. 1, recorded for solutions in concentrated H\(_2\)SO\(_4\), show the longest wavelength maximum at 600 nm (log \(\varepsilon\) 4.40). This suggests the formation of new extended conjugated systems [28].

The \(^1\)H NMR spectra of the products, for solutions in concentrated D\(_2\)SO\(_4\), were the most informative spectra. A typical spectrum is shown in Fig. 2. The spectra show signals near 1.3 ppm due to CH\(_3\) end groups, near 2.2 ppm due to CH\(_2\)=CH\(_2\) linkages and near 6.5 ppm due to CH=CH linkages. The latter signals overlap with those in the region 6.5–8.2 ppm due to aromatic protons. Thus, one of the signals near 6.5 ppm is due to olefinic protons and one is due to aromatic protons. The shift values are in excellent agreement with those of the corresponding protons in the model compounds 2 and 9, and the starting quinones 11 and 12 (see Supplementary material). The integrals allow the DP (i.e., the average value of “\(n\)” in 13) and the fraction of linkages that are olefinic (\(x\)) to be calculated: see Table 1. It is evident that the products are oligomers with DPs ranging from 3.3 to 8.7 and hence Mn values from ca. 750 to ca. 2000. Since these products are obtained from step growth polymerizations, the Mw are expected to be approximately twice the Mn values [30], i.e., ca. 4000. Attempts to raise the molecular weights by retreating the initial products with base were only moderately successful, for example, comparing entries 1 and 2 it is apparent that the average degree of polymerization (DP) only increased from 3.3 to 4.2. The major reason for the modest DPs is almost certainly the poor solubility of the initially formed polyanion salts.

The products in concentrated sulphuric acid had intrinsic viscosities in the range 0.47–0.96 dl/g at 20 °C, suggesting significantly higher Mw than 4000. This is perhaps due to strong interactions between the oligomers and the solvent, for example, many of the quinone moieties may be protonated, and/or some type of association. Unfortunately the products were too insoluble for GPC analysis with the equipment available.

Consistent with structures 13, the MALDI-TOF MS of the products showed a series of mass peaks spaced at intervals of approximately 234 amu indicating that the products contained anthraquinone units linked by two-carbon units: a typical spectrum is shown in Fig. 2. The observed mass peaks correspond to the various samples having values of “\(n\)” (see formula 13) from 2 up to at least 8 to 11: see Table 1. As discussed above, the \(^1\)H NMR spectra indicate that both ethylene and ethane types of linkages were present. The fact these two types of linkage only differ in mass by 2 amu, plus the complications caused by the presence of isotopes means estimating the proportions of these linkages by mass spectrometry is difficult. The mass values are consistent with the end groups being methyls as shown in 13 (see Fig. 3.)

By DSC the products displayed no phase transitions up to 350 °C. By thermogravimetric analysis (TGA) the polymers were stable up to ca. 350 °C above which temperature they gradually lost mass. For several samples the char yield up to 600 °C was 66–81%: see Table 1.

It is evident from Table 1 that the fraction of linkages which are CH=CH, i.e., “\(x\)” in formulae 13, were initially in the range 0.62–0.87. Retreating the initial products with base gave slightly improved values of \(x\) (see entries 2, 4 and 6). Good values of “\(x\)” were obtained when KtB was used as the base in DME (see entries 7 and 8). As the oxidation required in the polymerization is initially provided by the quinone units themselves and as each quinone unit only has the oxidizing ability to form just one C—C bond, if the CH=CH linkages in the product resulted only from the quinone units in the product, then since in an oligomer/polymer there are DP – 1 linkages, the maximum fraction of CH=CH linkages possible is 1/(DP – 1). With DP = 5, for example, the maximum fraction of CH=CH linkages is 0.25. The fact that in the 48 h polymerizations, i.e., Table 1 entries 1, 3 and 5, much higher fractions of olefinic linkages than this are present in the products indicates that many of the monomer molecules served simply as an oxidant. Once a quinone unit has accepted electrons the CH\(_3\) groups are, of course, no longer activated for proton removal and unless they are reconverted into the quinone play they no further part in the polymerization. During the work up reduced starting material is reoxidized and is extracted from the product by
washing. This explains why the yields of oligomers 13, based on the starting quinone, were only ca.70–80%. It suggests that better yields would be obtained by including an appropriate oxidant in the reaction mixture. However, attempts to do this by adding anthraquinone to the reaction mixture resulted in little or no improvement. In those polymerizations where the initial crude product was retreated with base, Table 1 entries 2, 4, 6–8, not only was 10% w/w of fresh monomer added but the original product contained many quinone residues which would also help to generate more CH=CH linkages.

4. Conclusions

The results presented indicate that treatment of 2,6-dimethylanthraquinone (11) and/or 2,7-dimethylanthraquinone (12) with base produces the expected types of products 13, i.e., anthraquinone units linked by CH=CH and CH₂CH₂ units. The products had, by ¹H NMR spectroscopy, average DPs of up to 8.7 units corresponding to Mns of ca. 2000. It is likely than with the current substrates the DPs were limited by the solubility of the intermediate polyanion salts which are, in the work up, oxidized to oligomers 13. Higher DPs can probably be obtained by using more soluble starting materials, for example, α,α’-dialkoxy-β,β’-dimethylanthraquinones. The oligomerizations can be conveniently summarized as a new type of step growth polymerization proceeding via the repeated linking together of diradical–dianion species 14.

Products such as oligomers 13 may find applications as electron acceptors in electronic devices [8–19]. It should be noted that even products with 100% ethylene linkages would not be expected to have extensive electron delocalization because the two benzene rings in each anthraquinone unit are linked via two carbonyls and so are only cross-conjugated. However, when the anthraquinone units are reduced to anions and so become substituted anthracenes units the situation may well change.

Acknowledgement

We thank the EPSRC Carbon-based Electronics Programme for financial support for this project (Grant No. GR/S02297/01).

Appendix A. Supporting material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.reactfunctpolym.2007.07.007.
References

[25] The intense colour is not surprising as it is well known that reduction of anthraquinone itself with sodium hydrosulphite gives intensely coloured blood-red solutions of the sodium salt of anthrahydroquinone. In the present reactions the reduced species present, for example of analogues of 10 and the related diradical–dianion, generally have more extended π-electron systems.
[26] Anthraquinones generally dissolve in concentrated sulphuric acid to give coloured solutions, see, for example: F. Feigl, Spot Tests, Elsevier, Amsterdam, 1954, Vol. II, p. 111. In the case of hydroxyanthraquinones the substitution pattern can often be deduced from the colour. No structures have been proposed for the coloured species.
[28] Detailed interpretation of the UV–vis spectra is complicated because in concentrated sulphuric acid it is not clear which species are present and in what proportions. For example, with compound 2 significant proportion of the C=C may be protonated.
学霸图书馆
www.xuebalib.com

本文献由“学霸图书馆-文献云下载”收集自网络，仅供学习交流使用。

学霸图书馆（www.xuebalib.com）是一个“整合众多图书馆数据库资源，提供一站式文献检索和下载服务”的24小时在线不限IP图书馆。
图书馆致力于便利、促进学习与科研，提供最强文献下载服务。

图书馆导航：
图书馆首页 文献云下载 图书馆入口 外文数据库大全 疑难文献辅助工具