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Syntheses, via precursor polymers, of polyethers containing 9,10-diacetoxyanthracene units or 9,10-anthraquinone units: chemical reactions of some of these polymers

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Abstract

Reaction of the bisphenol that is formally the Diels–Alder adduct of 2,6-dihydroxy-9,10-diacetoxyanthracene and dimethyl maleate with bis-acid chlorides and base in phase transfer catalysed reactions gives precursor polyethers. On heating the latter in a vacuum at 250–280°C retro-Diels–Alder reactions occur, with the loss of dimethyl maleate, to afford polymers containing 9,10-diacetoxyanthracene residues. Treating the precursor polyethers with sodium ethoxide in *N*,*N*-dimethylformamide converts them into soluble polymers containing units which are the disodium salts of the hydroanthraquinone. Aerial oxidation of these solutions gives polymers containing anthra-9,10-quinone (AQ) residues. Selected examples of the polymers containing 9,10-diacetoxyanthracene residues were similarly converted into the soluble polymers containing salt residues and thence into the corresponding AQ-containing polymers. Thus, we have shown that AQ-containing polymers can be prepared successfully by this novel type of precursor polymer approach.

Keywords: Polymers containing 9,10-diacetoxyanthracene units; Anthraquinone-containing polymers; Precursor polymers

1. Introduction

Polymers containing anthra-9,10-quinone (AQ) units, such as polymer **1** [1] are of interest for several reasons. First, AQs can take part in electron-transfer reactions that potentially may have applications in micro- and/or opto-electronics. Second, AQs are generally very stable both to heat and to oxidation. Third, whilst polymers containing a significant fraction of AQ units are likely to be very insoluble, they may possibly be solubilised reversibly using redox chemistry, i.e. by reduction to the quinol form or derivatives of this such as the salt **2**, which may be more soluble, and which may subsequently be oxidised back easily to the quinone form: see Scheme 1. Finally, we have shown that certain AQ derivatives and AQ-containing polymers have liquid crystal properties [2].

Despite these interesting features, only a few AQ-containing polymers have been synthesised. These include polymer **1** [1], poly(2-methylanthra-9,10-quinone-1,4-diyl) (**3**) [3,4] and poly(2-vinylanthra-9,10-quinone) (**4**) [5]. Several other quinone-containing polymers are known which serve as electron-exchange materials. Many of these, but not all [6–8], are crosslinked polymers that contain substituted benzoquinone units, or the corresponding hydroquinol units [9,10]. Closely related to AQ-containing polymers are polymers containing 9,10-diacetoxyanthracene units such as the polyesters **5** [11] and, at least potentially by oxidation, anthracene-containing polymers [12–20] such as poly(anthracene-2,6-diyl) (**6**) [12], polyester **7** [13] and polyamide **8** [14,15].

The present paper is concerned with the synthesis of several polyethers containing either 9,10-diacetoxyanthracene units or AQ units in the polymer backbone and chemical reactions of some of these polymers. Since polymers containing a significant fraction of such units are generally very insoluble [1,11] they need to be synthesised using a precursor polymer approach. We have previously shown [11] that the polyesters **5** can be prepared successfully by first reacting the bis-phenolic Diels–Alder adduct **9a**, prepared from commercial 2,6-dihydroxy-9,10-anthraquinone in four steps [11], with a range of bis-acid chlorides to give precursor polyesters **10**: see Scheme 2. On heating the latter at ca. 230°C retro-Diels–Alder reactions occur to give the polyesters **5** and dimethyl maleate. We have also shown that polymer **11**, prepared by a Ni[0]-catalysed coupling of Diels–Alder adduct **9b**, reacts with sodium

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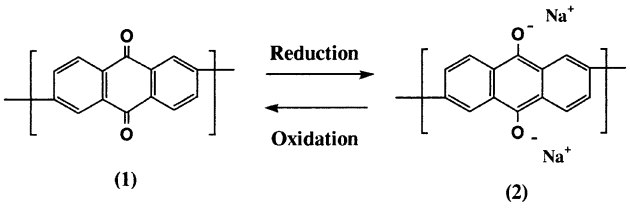
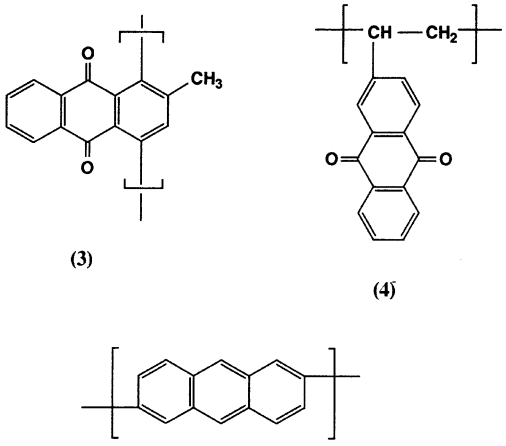
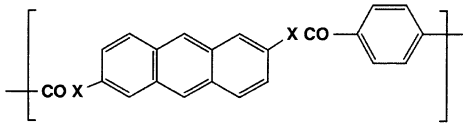


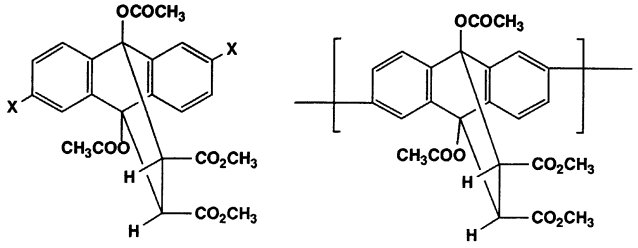
Scheme 1. Redox reactions of polyanthraquinone **1**.





(7) : X = O

(8) : X = NH

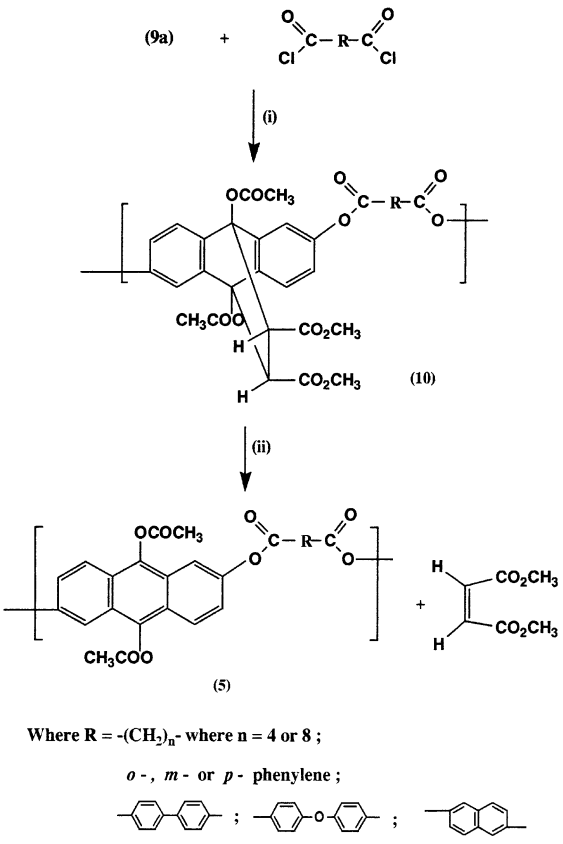


(9a): X = OH

(9b): X = Br

(9c): X = H

ethoxide in *N*-methylpyrrolidone and ethanol at 20°C under nitrogen to give a very dark olive-green solution of polymer **2**, see Scheme 1, which subsequently reacts with air at room temperature to give polymer **1** [1]. Clearly this novel synthetic approach to AQ-containing polymers cannot be applied to the precursor polyesters **10** in Scheme 2 because of the base-sensitive ester linkages in the polymer back-



Where R = -(CH$_2$)$_n$- where n = 4 or 8 ;

***o*-, *m*- or *p*- phenylene ;**

Reagents : (i) chloroform, aqu. $(C_4H_9)_4N^+OH^-$, 2hrs, 23°C;
(ii) heat at ca. 230°C

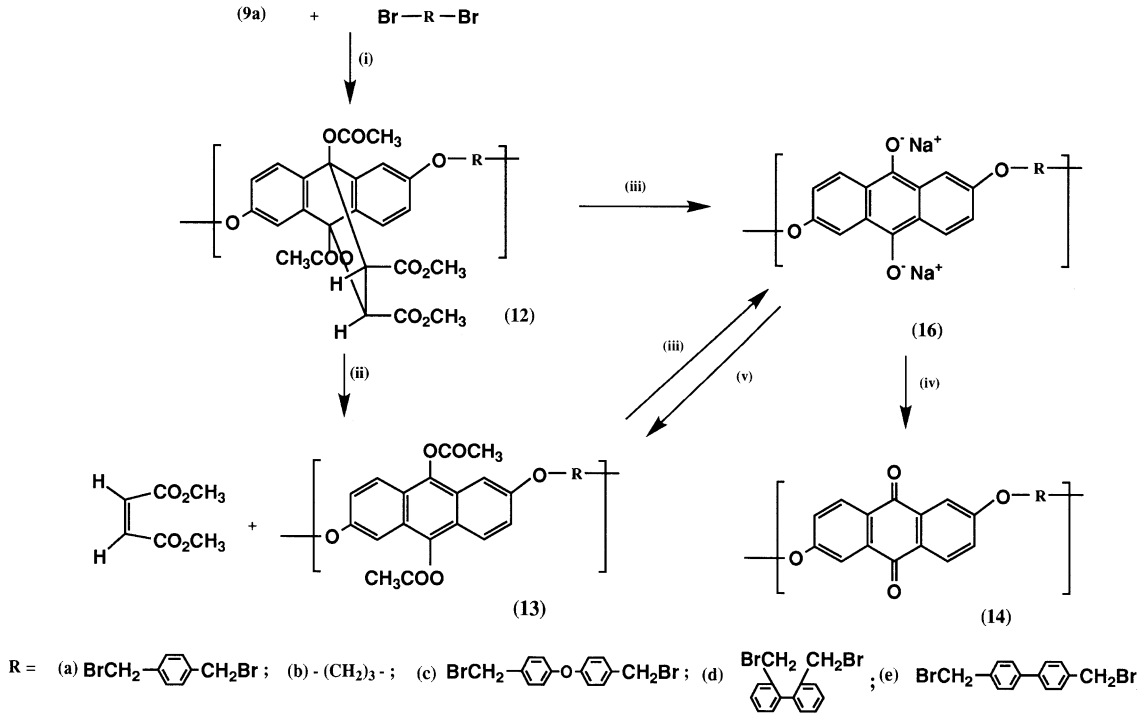
Scheme 2. Synthesis of polyesters **5** via precursor polymers **10**.

bone. This has prompted us to now prepare a range of precursor polyethers **12**, see Scheme 3, using the bis-phenolic Diels–Alder adduct **9a** and to study their conversion into polymers containing 9,10-diacetoxyanthracene units or AQ units. Other reactions of some of these polymers were also investigated.

2. Results and discussion

*2.1. Synthesis of precursor polyethers **12***

The precursor polyethers **12** were prepared in good yields, see Scheme 3, by vigorously stirring a mixture of the bis-phenolic Diels–Alder adduct **9a** in aqueous tetra-*n*-butylammonium hydroxide with a range of alkyl dibromides in *o*-dichlorobenzene at ca. 100°C for 3 or 4 days. The results are summarised in Table 1. It might have been anticipated that the ester groups in the Diels–Alder adduct monomer **9a**, and the corresponding moieties in the polymeric product, would be unstable under these reaction conditions, but this was not the case. It will be noted that the methyl ester groups are less reactive [11] than simple esters, because if they do react the tetrahedral intermediate formed closely approaches the neighbouring methyl ester group and

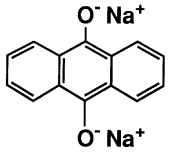


Reagents : (i) *o* - dichlorobenzene, aqu. $(C_4H_9)_4N^+OH^-$, 3 or 4 days, 100°C;
(ii) heat at ca.230°C;
(iii) sodium ethoxide in DMF;
(iv) H^+, air;
(v) acetic anhydride in DMF.

Scheme 3. Synthesis of polyethers **13** and **14** via precursor polymers **12**.

the latter has limited scope to manoeuvre to minimise the interactions, and that the acetate groups are only moderately reactive because they are esters of tertiary alcohols. The net effect is that whilst the ester groups can be reacted (see later for reactions involving the acetate groups), they react relatively sluggishly and are sufficiently stable to allow the syntheses of polyethers **12**. They are not, however, sufficiently stable to allow fully aromatic polyethers to be prepared successfully using 4,4′-dichlorodiphenylsulphone as the bis-halide [21].

All the precursor polyethers **12** were obtained as off-white powders. They were readily soluble in chloroform, tetrahydrofuran, acetone, ethyl acetate and *N*,*N*-dimethylacetamide. The FT-IR and ^{1}H NMR spectra of the polymers were fully consistent with their assigned structures and they indicated that the Diels–Alder adduct moieties remained intact during the synthesis. The molecular weights of the polymers, determined by gel permeation chromatography (GPC) relative to polystyrene standards, were modest, see Table 1, corresponding to average degrees of polymerisation of only 7–26, but they were nevertheless considered to be adequate for the present studies of reactions. By differential scanning calorimetry (DSC) all the polymers were stable up to about 220°C, above which they began to decompose (see Section 2.2). None of the polymers showed glass transition temperatures below the decomposition temperatures.

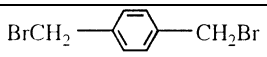
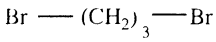
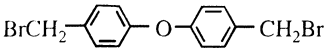
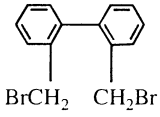
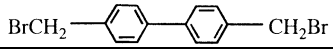


(15)

2.2. Conversion of precursor polymers *12* into polymers *13* containing 9,10-diacetoxyanthracene residues

Heating the precursor polyethers **12** was expected [1,22] to bring about retro-Diels–Alder reactions with the loss of dimethyl maleate and the formation polymers **13** containing 9,10-diacetoxyanthracene residues: see Scheme 3. By analogy with our previous work on the related polyesters **10**, the reactions were expected to occur at temperatures in the region of 210–250°C [11]. In the present work, two procedures were used to bring about the retro-Diels–Alder

Table 1
Synthesis (see Section 4 for general procedure. Unless indicated otherwise the reactions were carried out for 4 days) of precursor polyethers (**12**) using monomer (**9a**)

Polymer	Bis-bromide	Yield (%)	Molecular mass × 10^{-3} [a]		Degree of polymerisation [b]	Elemental analysis (%)				Reduced viscosity [c]
			M_n	M_w		C		H		
						Calc	Found	Calc	Found	
12a		85	6.5	13.2	23	67.1	67.1	4.9	4.2	0.32
12b		88	1.7	2.5	7	63.5	62.9	5.1	5.5	
12c		85	4.8	9.1	14	68.7	68.1	4.8	5.3	
12d		84[d]	7.3	16.0	23	70.4	70.3	4.9	5.0	0.29
12e		87[d]	8.3	17.4	26	70.4	70.0	4.9	5.2	0.35

[a] Estimated by GPC. System calibrated using polystyrene standards.
[b] Calculated from values of M_n.
[c] Reduced viscosity was measured for a 1% w/v solution in *N*,*N*-dimethylformamide.
[d] Reaction carried out for 3 days.

reactions. In both cases a major objective was to show that the weight changes that occurred were consistent with those expected for the loss of dimethyl maleate. In Procedure A carefully weighed samples of the precursor polymers **12** were heated in a vacuum (1 mm of Hg) in porcelain boats at 250°C for 6 h. Slowly the off-white powders became yellow/brown powders. In Procedure B thin films of the precursor polymers were cast from chloroform solutions on to pre-weighed quartz microscope slides. The weights of the films were noted and their UV spectra were recorded. The films were then heated in a vacuum (1 mm of Hg) from 250 up to 280°C and then held at this temperature for 2 h. Slowly the clear films darkened and became yellow/brown films. With both procedures the changes in the weights of the polymers were in close agreement with those expected for the loss of dimethyl maleate: see Table 2. The products also gave satisfactory elemental analyses. Infrared spectra were measured for KBr disks and found to be significantly different from those of the precursor polymers. For example, the carbonyl bands due to the 9- and 10-acetoxy groups shifted from ca. 1750 cm^{-1} to ca. 1765 cm^{-1}. The infrared spectrum of polymer **13a**, a typical product, is shown in Fig. 1. All the samples of polymers **13** were, unlike the precursor polymers, insoluble in chloroform, tetrahydrofuran, acetone and *N*,*N*-dimethylacetamide. The main purpose of using Procedure B was that the UV spectra of the final polymers could be determined. Whereas the initial films showed no significant absorption in the 300–450 nm region, the final films showed typical anthracene-like absorptions: see the λ_{max} values given in Table 2.

Table 2
Conversion of precursor polyethers (**12**) into polyethers (**13**)

Precursor polyether	Final polymer	Heating procedure [a]	Weight loss in TGA		λ_{max} of final polymer/nm [b]	Elemental analysis (%)				T_{dec}/°C [c]
			% Calc	% Found		C		H		
						Calc	Found	Calc	Found	
12a	**13a**	A	25	24		72.9	72.3	4.7	4.4	
12a	**13a**	B	25	24	331, 349, 395, 416	72.9	72.3	4.7	4.0	290
12b	**13b**	A	28	29		68.9	68.5	4.9	4.7	
12c	**13c**	A	22	27		73.8	74.1	4.6	4.8	
12d	**13d**	B	22	21	333, 350, 392, 416	76.2	75.8	4.8	4.6	305
12e	**13e**	B	22	20	333, 351, 392, 416	76.2	76.0	4.8	4.4	310

[a] In Procedure A the sample was heated in a porcelain boat at 250°C for 6 h and the weight loss recorded. In Procedure B the sample was heated as a thin film on a quartz microscope slide from 250–280°C at ca. 10°C/min and then at 280°C for a further 2 h.
[b] New absorption maxima.
[c] Determined by TGA.

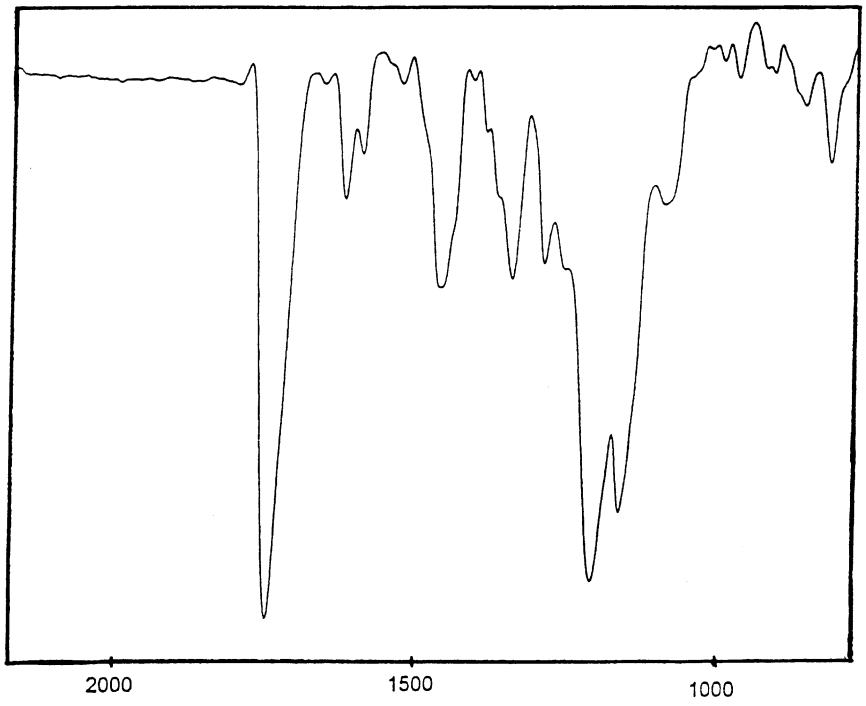


Fig. 1. The infrared spectrum for a KBr disc of polymer **13a**, containing 9,10-diacetoxyanthracene residues, in the region 800–2150 cm^{-1}.

Finally, for three samples (see Table 2) it was shown by thermogravimetric analysis (TGA) that the polymers **13** decomposed at temperatures in the range 290–310°C. Thus, there is a relatively narrow temperature window over which the retro-Diels–Alder reactions can be carried out satisfactorily.

*2.3. Conversion of precursor polymers **12** into polymers **14** containing 9,10-anthraquinone residues*

It has been shown previously that treating polymer **11** with sodium ethoxide and ethanol in *N*-methylpyrrolidone at 20°C under nitrogen gives a deep olive-

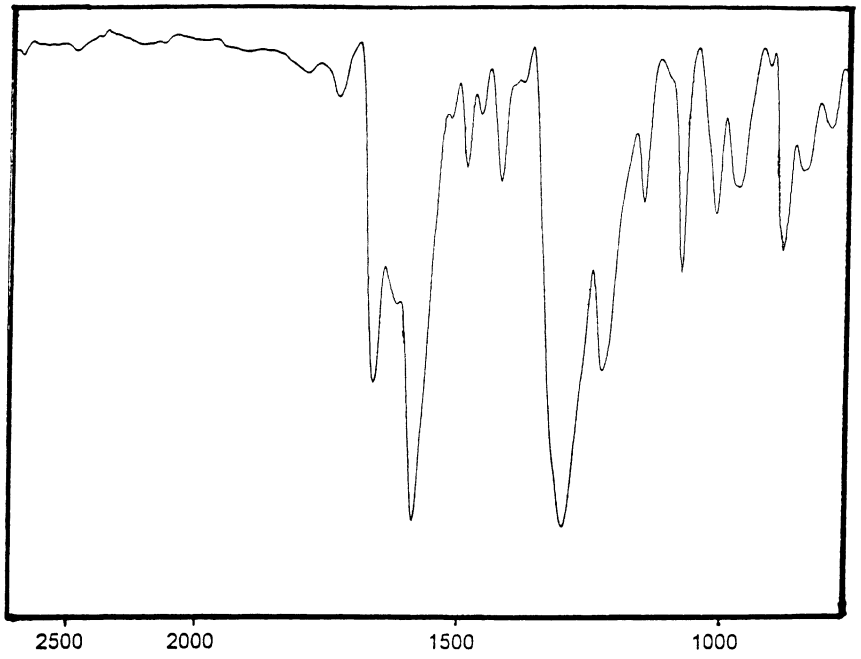


Fig. 2. The infrared spectrum for a KBr disc of polymer **14a**, containing 9,10-anthraquinone residues, in the region 750–2700 cm^{-1}.

green solution of the polymeric sodium salt **2**, which, on exposure to acid and air, is oxidised to give polyanthraquinone **1** [1]: see Scheme 1. The Diels–Alder adduct **9c** behaves analogously except that due to the reduced conjugation relative to that in polymer **2**, the solution of the intermediate **15** is blood red [1]. It is not clear by what mechanism this novel interconversion takes place, but it almost certainly [1] involves a retro-Diels–Alder reaction of the alkoxide formed by an initial esterolysis of an acetoxy group. It is known that retro-Diels–Alder reactions proceed very rapidly from such anions [23].

The precursor polymers **12a**–**12c** were similarly treated with sodium ethoxide, but in *N*,*N*-dimethylformamide. As expected this afforded blood-red polymer solutions of polymers **16a**–**16c** which, on exposure to acid and air, gave pale-yellow coloured precipitates in high yields. These were characterised as the AQ-containing polymers **14a**–**14c**. Thus, the elemental analyses were satisfactory and in the infrared spectra the ester carbonyl bands which were evident ca. 1750 cm^{-1} in the spectra of the precursor polymers had now been replaced by the characteristic anthraquinone carbonyl stretch at ca. 1665 cm^{-1}: see Fig. 2 for a typical spectrum. As expected, the precipitates were too insoluble to allow UV and ^1H NMR spectra to be obtained.

*2.4. Conversion of polymers **13** into polymers **14** containing 9,10-anthraquinone residues*

An alternative route to the AQ-containing polymers appeared to be to treat polymers **13**, which contain 9,10-diacetoxyanthracene residues, with sodium ethoxide under the conditions described above. Such treatment of polymers **13a**–**13c** rapidly afforded blood-red solutions which on aerial oxidation as before gave the AQ-containing polymers **14a**–**14c** (identical infrared spectra to the original samples) in >95% yields. It was also shown (identical infrared spectrum) that quenching the blood-red solution of polymer **16a** with acetic anhydride regenerated polymer **13a**.

3. Conclusions

We have shown that the precursor polyethers **12** can be prepared by reacting the bis-phenolic Diels–Alder adduct **9a** with bis-acid chlorides and base in phase transfer catalysed reactions. The polyethers **12** can be converted into polymers **13**, which contain 9,10-diacetoxyanthracene residues, by heating them in a vacuum at 250–280°C under which conditions retro-Diels–Alder reactions occur with the loss of dimethyl maleate. Treating the precursor polymers **12** with sodium ethoxide converts them into the soluble polymers **16**, containing units which are the disodium salts of the hydroanthraquinone, and these on aerial oxidation give polymers **14**, containing AQ residues, Examples of polymer **13** were also converted into soluble polymers **16** and thence into the corresponding AQ-containing polymers **14**. In the case of the soluble polymer **16a** it was shown that quenching with acetic anhydride reformed polymer **13a**.

Thus we have shown that further AQ-containing polymers can be prepared successfully by this particular precursor polymer approach. Future work will be concerned with the synthesis of other AQ-containing polymers, using the precursor approach discussed here, and a detailed study of their electron transfer properties.

4. Experimental

Experimental notes are as given previously [11].

*4.1. Monomer (**9a**)*

This compound was prepared from 2,6-dihydroxyanthraquinone (anthraflavic acid; Aldrich Chemical Company) in four steps as described previously [11].

*4.2. Synthesis of precursor polyethers from monomer (**9a**)*

The following reaction procedure is typical. Several details of the reactions and the products are summarised in Table 1.

*Synthesis of polymer (**13a**).* Monomer (**9a**) (3.08 g, 6.6 mmol) was dissolved in aqueous tetra-*n*-butylammonium hydroxide solution (13.2 mmol: 8.52 g of a 40% w/v solution). α,α'-Dibromo-*p*-xylene (1.65 g, 6.2 mmol) was dissolved in hot *o*-dichlorobenzene (30 ml) and added to the reaction flask. The reaction mixture was then heated at 100°C under nitrogen for 4 days with vigorous stirring. At the end of the reaction period the dark solution was cooled. The organic layer was separated off, washed with water and then added dropwise into acidic methanol to precipitate the product. The latter was collected, dissolved in chloroform (15 ml) and re-precipitated into methanol. The final product (3.18 g, 85%) was obtained was a pale brown solid. It had ν_{max} (evaporated film): 1754 (s) (overlapped ester carbonyl bands), 1216 (s) (Ph–O stretch) and 1018 (m) cm^{-1} (aliphatic-O stretching absorption); δ (500 MHz, $CDCl_3$) 2.36 (6H, s, 9- and 10-acetates), 3.43 (6H, s, two CO_2CH_3 groups), 4.61 (2H, s, two bridgehead CH), 4.95 (4H, s, two benzylic CH_2) and 6.6–7.5 ppm (10H, m, ArH). See Table 1 for elemental and GPC analyses.

*Polymer (**13b**)* was synthesised similarly except that all the precipitations were carried out using petroleum ether (60/80). It had ν_{max} (evaporated film): 1755, 1217 and 1017 cm^{-1}; δ (200 MHz, $CDCl_3$) 2.16 (2H, m, $-CH_2-CH_2-$), 2.35 (6H, s, 9- and 10-acetates), 3.45 (6H, s, two CO_2CH_3 groups), 4.07 (4H, m, $-CH_2-CH_2-CH_2-$), 4.64 (2H, s, two bridgehead CH), 4.75 (4H, s, two benzylic CH_2) and 6.5–7.5 ppm (14H, m, ArH).

*Polymer (**13c**)* was synthesised similarly (for the preparation of the appropriate dibromide starting material see Ref. [24]) except that all the precipitations were carried

out using petroleum ether (60/80). It had ν_{max} (evaporated film): 1756, 1215 and 1016 cm^{-1}; δ (200 MHz, $CDCl_3$) 2.41 (6H, s, 9- and 10-acetates), 3.48 (6H, s, two CO_2CH_3 groups), 4.67 (2H, s, two bridgehead CH), 4.98 (4H, s, two benzylic CH_2) and 6.5–7.5 ppm (6H, m, ArH).

*Polymer (**13d**)* was synthesised similarly. It had ν_{max} (evaporated film): 1758, 1217 and 1018 cm^{-1}; δ (200 MHz, $CDCl_3$) 2.35 (6H, s, 9- and 10-acetates), 3.45 (6H, s, two CO_2CH_3 groups), 4.60 (2H, s, two bridgehead CH), 4.75 (4H, s, two benzylic CH_2) and 6.7–7.6 ppm (14H, m, ArH).

*Polymer (**13e**)* was synthesised similarly. It had ν_{max} (evaporated film): 1753, 1216 and 1019 cm^{-1}; δ (200 MHz, $CDCl_3$) 2.34 (6H, s, 9- and 10-acetates), 3.44 (6H, s, two CO_2CH_3 groups), 4.61 (2H, s, two bridgehead CH), 4.77 (4H, s, two benzylic CH_2) and 6.7–7.6 ppm (14H, m, ArH).

*4.3. Retro-Diels–Alder reactions of precursor polyethers (**12**) to give polymers (**13**) containing 9,10-diacetoxyanthracene units*

Several details of the reactions and the products are summarised in Table 2. The following procedures are typical.

*Procedure A: Synthesis of polymer (**13a**).* An accurately weighed sample of precursor polyether (**12a**) (35 mg) was placed in a preweighed porcelain boat and heated under vacuum (1 mm of Hg) at 250°C until a constant weight was achieved. This took 5 h. Heating was then continued for a further hour. The sample was finally weighed and the percentage weight-loss calculated. The percentage weight-loss and the elemental analyses are given in Table 2. The FTIR spectrum of the product is shown in Fig. 1. It had ν_{max} (KBr disk) 1765 cm^{-1} (s) (ester carbonyl band).

*Procedure B: Synthesis of polymer (**13d**).* A film of precursor polyether (**12d**) (35 mg) was cast on a quartz microscope slide from a chloroform solution. The UV spectrum was recorded. The film was then placed in a Büchi oven at 250°C and heated under vacuum (1 mm of Hg) up to 280°C. It was held at this temperature for 2 h. The sample was finally weighed and the percentage weight-loss calculated. The percentage weight-loss and the elemental analyses are given in Table 2. The UV spectrum was again measured. The results are presented in Table 2. The product had ν_{max} (KBr disk) 1765 cm^{-1} (s) (ester carbonyl band).

*4.4. Conversion of polyethers (**12**) into polymers (**14**) containing 9,10-anthraquinone units*

*Synthesis of polymer (**14a**).* Precursor polyether (**12a**) (200 mg, 0.35 mmol), sodium ethoxide (50 mg, 0.73 mmol) and ethanol (0.05 ml, 0.73 mmol) were stirred in *N,N*-dimethyl formamide (10 ml) under an atmosphere of nitrogen. A deep red colour formed rapidly. The mixture was left stirring for approximately 0.5 h. The deep red solution was then syringed into aerated hydrochloric acid (50 ml of 1 M). A dull yellow solid precipitate formed. It was filtered off, washed with water and dried under vacuum. The product (**14a**) (145 mg, 96%) had ν_{max} 1667 cm^{-1} (s) (characteristic anthraquinone carbonyl stretch); see Fig. 2 for the spectrum; (Found: C, 77.4; H, 3.7. Calcd for $C_{22}H_{14}O_4$: 77.2; H, 4.1 %).

*Synthesis of polymer (**14b**).* Precursor polyether (**12b**) was converted into product (**14b**) (92%) using the above procedure. The pale yellow product had ν_{max} 1666 cm^{-1} (s) (Found: C, 72.1; H, 4.0. Calcd for $C_{17}H_{12}O_4$: 72.85; H, 4.3 %).

*Synthesis of polymer (**14c**).* Precursor polyether (**12c**) was converted into product (**14c**) (91%) using the above procedure. The pale yellow product had ν_{max} 1667 cm^{-1} (s) (Found: C, 76.9; H, 4.1. Calcd for $C_{28}H_{18}O_5$: 77.4; H, 4.1%).

*4.5. Conversion of polymers (**13a**)–(**13c**) into polymers (**14a**)–(**14c**)*

The following procedure is typical.

*Synthesis of polymer (**14a**).* A suspension of polyether (**13a**) containing 9,10-diacetoxyanthracene units (75 mg, 0.18 mmol), sodium ethoxide (25 mg, 0.37 mmol) and ethanol (0.025 ml, 0,37 mmol) were stirred together in *N,N*-dimethylformamide (10 ml) under an atmosphere of nitrogen. The solid slowly dissolved and the mixture was stirred for approximately 3 h. At the end of this time the deep red solution was syringed into aerated hydrochloric acid (50 ml of 1 M). A dull yellow solid precipitate formed. It was filtered off, washed with water and dried under vacuum. The product (**16a**) (59 mg, 98%) had an infrared spectrum (including ν_{max} 1667, 1216 and 1018 cm^{-1}) superimposable on that of polymer (**14a**) obtained directly from polymer (**12a**).

*4.6. Reaction of polyether (**13a**) with sodium ethoxide and then acetic anhydride*

A suspension of polyether (**13a**) (200 mg, 0.35 mmol), sodium ethoxide (50 mg, 0.73 mmol) and ethanol (0.05 ml, 0.73 mmol) were stirred together in *N,N*-dimethylformamide (10 ml) under an atmosphere of nitrogen. The solid slowly dissolved and a blood-red solution formed. The mixture was stirred for approximately 3 h. At the end of this time acetic anhydride (1 ml) was syringed into the reaction flask. The deep red solution faded and a yellow/brown material precipitated from the solution. This was filtered off, washed with water and dried under vacuum at 40°C. The product (**13a**) (142 mg, 95% yield) had an infrared spectrum (including ν_{max} 1760, 1216 and 1018 cm^{-1}) superimposable on that of polymer (**13a**) obtained directly from polymer (**12a**).

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