Synthesis of novel conjugated polymers containing alternating hexa-1,3,5-triene and bi-*p*-phenylene or ter-*p*-phenylene segments

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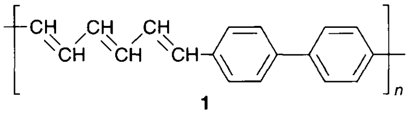
Novel conjugated polymers containing alternating hexa-1,3,5-triene and bi- or ter-*p*-phenylene segments are synthesised using a precursor polymer approach.

Polymers with extended π-electron systems have been extensively studied due to their interesting electrical and electro-optical properties.[1] However, the intractable nature of many polymers of this type makes their synthesis and characterisation difficult. The development of synthetic routes which involve the use of soluble precursor polymers has, however, resulted in well-characterised samples of polyacetylene,[2] poly(*p*-phenylene)[3] and poly(phenylene vinylene).[4,5] This has enabled thorough investigations of these important polymers which have led to their incorporation into electronic devices and displays.[5] Here we describe the synthesis, *via* a soluble precursor polymer route, of novel conjugated polymers **1** and **2**. They are well-defined copolymers of polyacetylene and poly(*p*-phenylene) comprised of hexa-1,3,5-triene segments separated by bi-*p*-phenylene or ter-*p*-phenylene segments.

The synthesis of conjugated polymer **1** is outlined in Scheme 1. It involves the aryl coupling of the anthracene-derived adducts **4a** or **4b** using nickel(0) catalysis. This gives the soluble precursor polymer **5**. The latter readily undergoes a retro-Diels–Alder reaction at temperatures above 200 °C to give anthracene and the final insoluble target polymer **1**.



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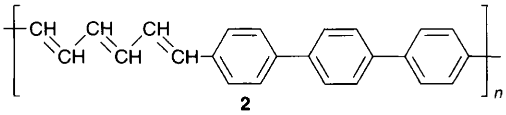

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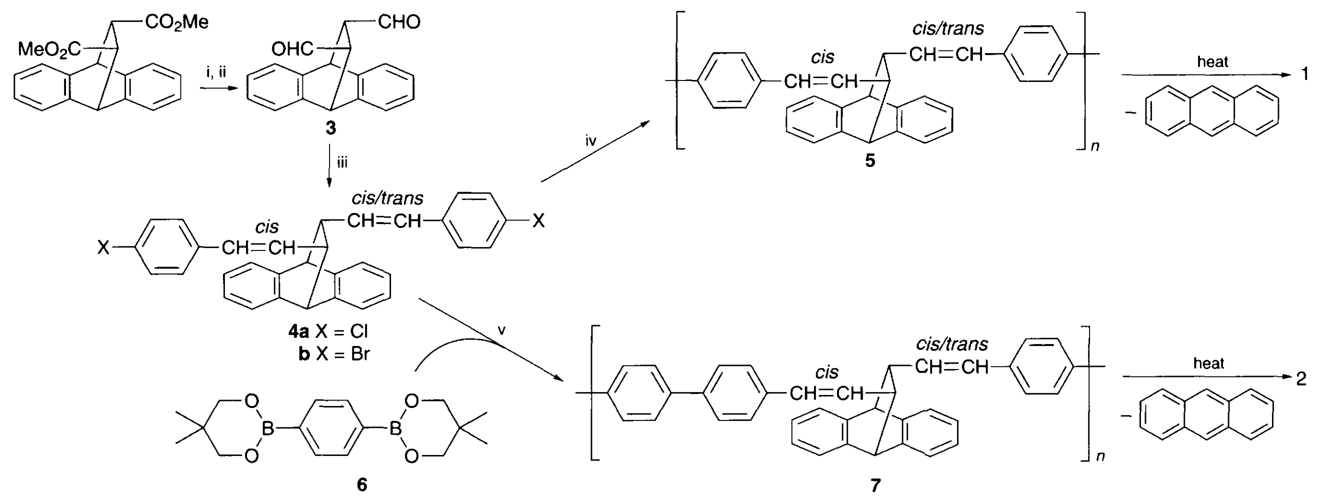
The synthesis of conjugated polymer **2**, also outlined in Scheme 1, involves a palladium(0)-catalysed coupling reaction between adduct **4b** and the diester **6** of benzene-1,4-diboronic acid. This gives the soluble polymer **7**. The latter readily undergoes a retro-Diels–Alder reaction at temperatures above 200 °C to give anthracene and the final insoluble polymer **2**.

Nickel(0)[6–8] and palladium(0)[9–11] couplings of the above type have been used before in polymer synthesis including the synthesis of poly(*p*-phenylene).[8] They do not, however, normally lead to polymers with a very high average degree of polymerisation ($\overline{DP}$). An attractive feature of the present syntheses is that the modest $\overline{DP}$s obtained are substantially offset by the fact that the monomers **4** contain what would normally be regarded in the context of conjugated polymers such as polyacetylene and poly(*p*-phenylene) as five repeat units, *viz* three alkenic groups and two *p*-phenylene units. The concept of exploiting the reversible Diels–Alder reactions of anthracene in precursor-based polymer syntheses has been exploited previously by us[12] and by other researchers.[13–15]

Monomers **4a** and **4b** were prepared from compound **3**, which is formally the Diels–Alder adduct of anthracene and fumaraldehyde. Compound **3** was, however, best prepared indirectly by the reduction of the dimethyl fumarate–anthracene adduct,[16] followed by controlled oxidation of the diol. The Wittig reaction between compound **3** and an excess of *p*-chlorobenzyltriphenylphosphonium chloride or *p*-bromobenzyltriphenylphosphonium bromide gave a complex mixture from which monomers **4a** and **4b**, respectively, were isolated in modest yields using column chromatography. The structures of monomers **4a** and **4b** were confirmed by accurate mass



Scheme 1 *Reagents and conditions*: i, LiAlH$_4$, THF; ii, PCC, CH$_2$Cl$_2$; iii, 4-chlorotriphenylphosphonium chloride for the synthesis of **4a** or 4-bromotriphenylphosphonium bromide for the synthesis of **4b**, Bu^{t}OK, 18-crown-6; CH$_2$Cl$_2$; iv, Ni^0, Zn, Ph$_3$P, 2,2′-bipyridyl, DMAc, 70 °C; v, Pd^0, toluene–aq. NaHCO$_3$, reflux, 24 h

spectrometry and elemental analysis. Standard and COSY ^1H NMR spectra (500 MHz) revealed that the samples obtained in each case were a mixture of the *cis–cis* and *cis–trans* isomers, as defined by the configuration of the two carbon–carbon double bonds, in the ratio of 7 : 3.† Subsequent polymerisations were carried out using the isomeric mixtures of **4a** or **4b**.

Aryl–aryl couplings of monomer **4a** in *N*,*N*-dimethylacetamide (DMAc) in the presence of triphenylphosphine, 2,2′-bipyridyl, nickel(II) chloride and zinc powder under various conditions gave the THF-soluble precursor polymer **5** in 60–90% yields. Molar mass averages obtained by gel permeation chromatography (GPC), against polystyrene standards, indicated that the number averages ($\overline{M}_n$), weight averages ($\overline{M}_w$) and peak molecular weights ($\overline{M}_{peak}$) were respectively in the ranges 4.5–5.7 × 10^3, 11.7–14.0 × 10^3 and 11.2–13.2 × 10^3. The latter corresponds to $\overline{DP}$s of *ca.* 30 and to final polymers **1** containing *ca.* 150 alkenic or phenylene units. Light scattering experiments on a sample of polymer **5** gave a value of $\overline{M}_w$ very similar to that obtained by GPC. The ^1H NMR spectrum (500 MHz) of polymer **5** showed broadened peaks with chemical shifts similar to those present in the spectrum of monomer **4a**. elemental analysis of polymer **5** prepared from the monomer **4a** indicated that only *ca.* 30% of the polymer end groups contained chlorine. This suggests that side reactions involving chloride displacement are mainly responsible for the modest $\overline{DP}$ obtained.

Similar polymerisation reactions using **4b** produced samples of polymer **5** of lower molar mass ($\overline{M}_n$ = 3.0–3.5 × 10^3; $\overline{M}_w$ 6.0–8.7 × 10^3; M_{peak} 5.7–7.6 × 10^3). This is consistent with some other studies which have compared the relative efficiency of aryl chloride *vs.* aryl bromide in direct couplings.[6,17,18]

The preparation of polymer **7** was attempted using the palladium(0)-catalysed reaction between monomer **4b** and benzene-1,4-diboronic acid, but no significant polymeric material was formed. This failure was attributed to the instability of the boronic acid functionality under the reaction conditions. Cyclic esters of boronic acids are known to be more stable.[19] Accordingly the cyclic ester **6** was prepared, by reaction between benzene-1,4-diboronic acid and 2,2-dimethylpropane-1,3-diol, and used as the comonomer. In this case with an aqueous potassium carbonate/toluene mixture as the reaction medium, tetrakis(triphenylphosphine) palladium as the catalyst and a reaction temperature of 100 °C, polymer **7** was obtained in 80% yield. It had, by GPC, $\overline{M}_n$, $\overline{M}_w$ and M_{peak} values of 4.5, 11.0 and 10.9 × 10^3 respectively. The latter value corresponds to a $\overline{DP}$ of *ca.* 23 and to a final polymer **2** containing *ca.* 138 alkenic or phenylene units.

Thermogravimetric analysis of polymer **5** revealed that the retro-Diels–Alder reaction begins at *ca.* 180 °C and that by 240 °C it is complete, the total mass loss corresponding to a > 90% yield. A similar result was obtained for polymer **7**. When a thin film of precursor polymer **5**, cast from a solution in THF, was heated under vacuum at 240 °C for 30 mins the mass loss was 100 ± 3% of the expected loss. The weight of anthracene recovered from the cooler parts of the apparatus corresponded to a similar yield.

Films of the precursor polymers **5** and **7** were cast on quartz microscope slides from solutions in THF. The films were pale yellow. They were heated at 240 °C *in vacuo* to give films of polymers **1** and **2**. At this temperature any *cis*-alkenic bonds in the hexa-1,3,5-triene segments would be expected to isomerise to give the all *trans*-configuration.[2] The films were dark orange. Exposure to ambient conditions did not bring about any colour change. UV–VIS spectra were measured within 10 mins and compared to those of the precursor polymer films. It was evident that the benzenoid absorption was greatly reduced, that the absorption shifted to longer wavelengths and that there was no evidence for the presence of anthracene (strong absorption at 250 nm with a series of subsidiary maxima between 300 and 400 nm[20]). After exposure to ambient conditions for a further 24 h the UV–VIS spectra were unchanged. The films were insoluble in *N*,*N*-dimethylformamide and *N*-methylpyrrolidone. The films had electrical conductivities of $< 10^{-8}$ S cm^{-1}, but after doping with a saturated solution of ferric chloride in dichloromethane, polymer **1** had a conductivity of 0.2 S cm^{-1} and polymer **2** a conductivity of 1 × 10^{-3} S cm^{-1}.

The synthetic methodology outlined above has been extended to produce polymers which contain 2,5-dithienyl units in place of some of the phenylene units.[21] The resultant polymers show enhanced conductivity on doping.

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Footnote

† *Spectroscopic data* for **3a** δ_H (500 MHz, $CDCl_3$): *cis,cis*-isomer: 4.07 (2 H, d, *J* 1.5 Hz), 2.78 (2 H, dd, *J* 10.3 and 1.5 Hz), 5.02 (2 H, m), 6.33 (2 H, d, *J* 11.75 Hz) and 7.02–7.16 (16 H, m); *cis,trans*-isomer: 4.08 (H, d, *J* 2.0 Hz), 4.16 (H, d, *J* 2.0 Hz), 2.74 (H, ddd, *J* 2.0, 4.8, 11.4 Hz), 2.36 (H, ddd, *J* 2.0, 4.8, 9.4 Hz), 5.02 (H, m) 5.55 (H, dd, *J* 5.7, 9.5 Hz), 6.33 (H, d, *J* 11.75 Hz), 6.29 (H, d, *J* 5.8 Hz) and 7.02–7.16 (16 H, m).

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