Synthesis of poly(anthracene-2,6-diyl) and a copolymer containing alternately anthracene-2,6-diyl and *p*-phenylene units

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The title polymers 1 and 2 are synthesised *via* precursor polymers assembled by organometallic couplings using a Diels–Alder adduct of 2,6-dibromoanthracene.

Polymers with extended π-electron systems have long been of interest for theoretical reasons and also for possible applications in micro- and opto-electronics.[1] The synthesis of such polymers is, however, often complicated by their insolubility. In several such cases syntheses *via* precursor polymers have been successful.[2,3] In this type of approach a soluble readily characterised precursor polymer is synthesised which on heating, for example, is converted into the insoluble target polymer. A classical example is the Durham synthesis of polyacetylene.[2] Polymers with extended π-electron systems which electroluminesce are now also of interest as they may form the basis of electroluminescent display devices.[4] Examples of such polymers are various poly-(phenylenevinylene)s.[5,6]

Many anthracene moieties are photoluminescent and polymers containing such units as part of a larger π-electron system are also likely to be electroluminescent. The only reported polymers where anthracene units are in the backbone and conjugated are some oligo(anthracene-9,10-diyl)s,[7] and some polyquinolines.[8] We now report syntheses, *via* precursor polymers 3 and 4 respectively, of poly(anthracene-2,6-diyl) 1 and a copolymer 2 containing alternately anthracene-2,6-diyl and *p*-phenylene units. The syntheses exploit the retro-Diels–Alder reaction. This has been exploited before, both in the synthesis of polymers with extended π-electron systems[2,8,9] and in the synthesis of polymers with nonconjugated anthracene moieties.[10,11]

The synthesis of the Diels–Alder adduct 5 was conveniently achieved as outlined in Scheme 1. Thus, commercially available 2,6-diaminoanthraquinone 6 was converted into 2,6-dibromo-anthraquinone 7 (60% yield) using a Sandmeyer reaction and the product 7 was reduced to 2,6-dibromoanthracene 8 (60% overall yield) by successive sodium borohydride reductions and acid catalysed dehydrations.[12] Treatment of compound 8 with an excess of maleic anhydride in xylene at reflux temperature gave the Diels–Alder adduct, which was then treated with methanol at reflux to give the half ester. The latter reacted smoothly with an Et_2O solution of diazomethane to give the diester 5 (59% overall yield from compound 8). This indirect route from compound 8 to diester 5 proved to be the most convenient route for obtaining a sufficient quantity of pure diester 5 for the subsequent synthetic work. Treatment of Diels–Alder adduct 5 in *N,N*-dimethylacetamide 80 °C with nickel(0)[13–15] gave precursor polymer 3 in 86% yield (Scheme 2). The infrared and ¹H NMR spectra of the product were consistent with structure 3. By gel permeation chromato-

graphy (GPC) the polymer had, relative to polystyrene standards, a number average molecular weight ($\overline{M}_n$) of 2700, a weight average molecular weight ($\overline{M}_w$) of 5400 and a peak molecular weight (M_p) of 5200. The $\overline{M}_w$ value corresponds to an average degree of polymerisation ($\overline{DP}$) of 17.

Copolymerisation of Diels–Alder adduct 5 and the 2,2-di-methylpropane-1,3-diol diester 9 of benzene-1,4-diboronic acid using a palladium(0) catalyst (Suzuki reaction)[16–18] gave precursor polymer 4 in 84% yield (Scheme 2). The infrared and ¹H NMR spectra were consistent with structure 4. By GPC the polymer had $\overline{M}_n$ 2300, $\overline{M}_w$ 5700 and M_p 3000. The $\overline{M}_w$ value corresponds to a ($\overline{DP}$) of 28.

The precursor polymers 3 and 4 were soluble in many common solvents including THF and chloroform.

Conversions of the precursor polymers 3 and 4 into the target polymers 1 and 2 were achieved by thermal retro-Diels–Alder reactions which eliminated dimethyl maleate and produced the desired anthracene moieties. The reactions were monitored by thermogravimetric and spectroscopic methods. Thermogravimetric analysis showed that for both precursor polymers the onset on dimethyl maleate loss was at around 220 °C. Isothermal heating at atmospheric pressure showed that dimethyl maleate loss was significantly faster from polymer 4 than from polymer 3. Heating polymer 3 at 260 °C for 3 h resulted in a weight loss corresponding to 73% of the theoretical maximum dimethyl maleate loss for this polymer. Similar treatment of polymer 4 at 240 °C for 1 h showed 95% of the theoretical maximum dimethyl maleate loss. It should be noted that these experiments were carried out at atmospheric pressure and that the observed weight losses would almost certainly be significantly greater for experiments carried out *in vacuo*. In all of these experiments both precursor polymers converted into the final polymers without melting.

Having established the temperatures at which the retro-Diels–Alder reaction occurred, films of precursor polymers 3 and 4 were cast on sodium chloride discs and quartz discs in order to follow the reactions by FTIR and UV spectroscopy, respectively. On heating *in vacuo* for 12 h and 260 °C the clear polymer films were seen to change from colourless to an intense
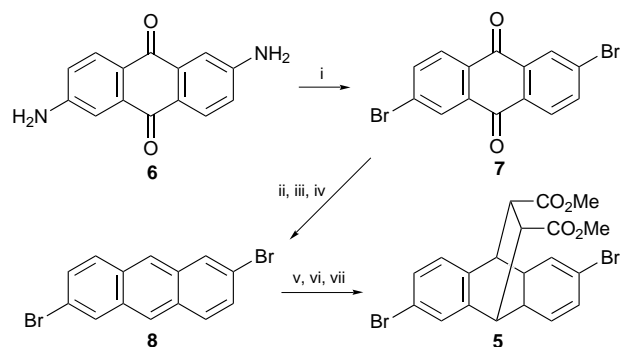
Scheme 1 *Reagents and conditions*: i, *tert*-butyl nitrite, copper(ii) bromide, MeCN, 80 °C; ii, NaBH₄, MeOH; iii, 5 **m** HCl, 90 °C, 6 h; iv, NaBH₄, Pr^iOH; v, maleic anhydride, *p*-xylene, 132 °C, 18 h; vi, MeOH, 56 °C, 16 h; vii, CH₂N₂, Et₂O, 20 °C
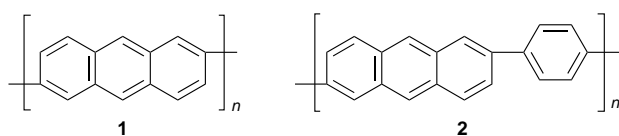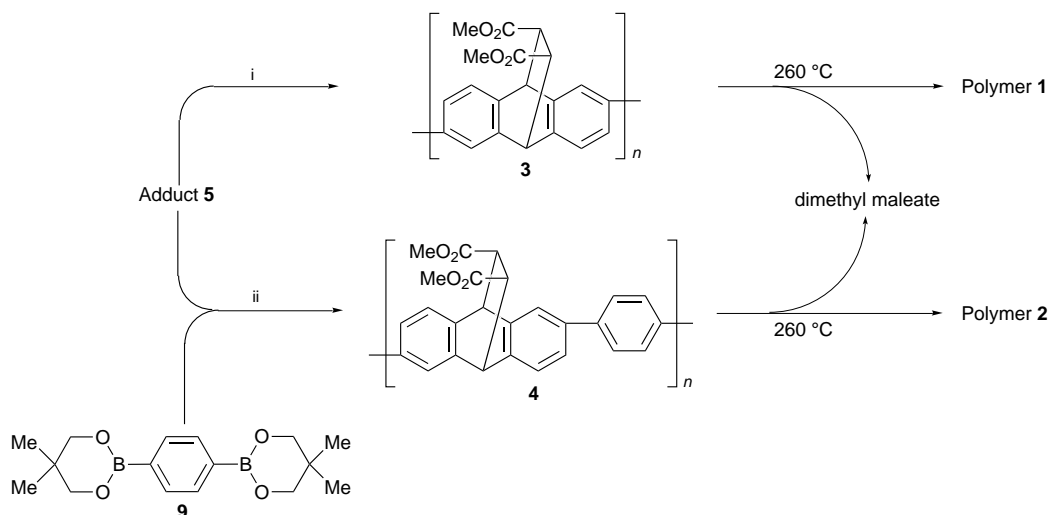
Scheme 2 *Reagents and conditions*: i, [Ni(PPh$_3$)$_2$Cl$_2$], PPh$_3$, Zn, 2,2′-bipyridyl, *N,N*-dimethylacetamide, 80 °C; ii, [Pd(PPh$_3$)$_4$], toluene, aqueous potassium carbonate (2 **m**)

yellow. The final films were transparent and free from cracks. With both precursor polymers **3** and **4** the ester carbonyl stretch at 1747 cm^{-1} was completely lost on heating and new bands due to anthracene moieties appeared respectively at 1623 cm^{-1} and 1635 cm^{-1}. The UV spectrum of polymer **3** shifted from λ_{max} 267 nm (absorbance arbitrarily assigned 1.00) to λ_{max} 315 and 442 nm (relative absorbances 1.76 and 0.67). For polymer **4** there was a shift from λ_{max} 294 nm (absorbance arbitrarily assigned 1.00) to λ_{max} 322 and 427 nm (relative absorbances 1.48 and 0.62). This data is consistent with the formation of the desired final polymers **1** and **2**.

The electrical conductivities of polymers **1** and **2**, measured as thin films, were $<10^{-4}$ S cm^{-1}, but both showed significant conductivities after n- or p-type doping. Thus, after doping with potassium naphthalenide polymers, **1** and **2** had conductivities of 4.0×10^{-2} and 1.4×10^{-3} S cm^{-1} respectively, and after doping with ferric chloride they had conductivities of 1.2×10^{-1} and 5.5×10^{-2} S cm^{-1}. It is evident that for a given dopant polymer **1** has the greater conductivity. When thin films were irradiated with UV light (366 nm), both polymers **1** and **2** gave a yellow–green luminescence.

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