

New routes to poly(4,4-dialkylcyclopentadithiophene-2,6-diyls)[†]

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Received 4th July 2002, Accepted 16th July 2002

First published as an Advance Article on the web 29th July 2002

Two new polymerisation routes to poly(4,4-dioctylcyclopentadithiophene-2,6-diyl) are reported. The polymer prepared by Kumada type cross-coupling showed significantly reduced molecular weight over that prepared by direct oxidative polymerisation using iron(III) chloride. The higher molecular weight polymer was shown to have extended conjugation by UV-visible spectroscopy.

The synthesis of poly(3-alkylthiophenes) has been extensively studied in the last decade and facile synthetic protocols to obtain high molecular weight, regioregular materials *via* Kumada type cross-coupling of heterofunctional monomers have been developed.^{1,2} Analogous regiorandom polymers are readily accessible by oxidative polymerisation of 3-alkylthiophenes using iron(III) chloride.³ This widely used procedure gives excellent yields of high molecular weight material and after extensive purification procedures iron impurity levels as low as 80 ppm can be achieved.⁴ Poly(3-alkylthiophenes) show great potential for use as the charge transporting layer in polymer based electronic devices such as FETs and PLEDs. However, it has been shown that the thickness and homogeneity of the thin films necessary for these devices are enhanced for higher molecular weight polymers ($\bar{M}_n > 10^4$).⁵

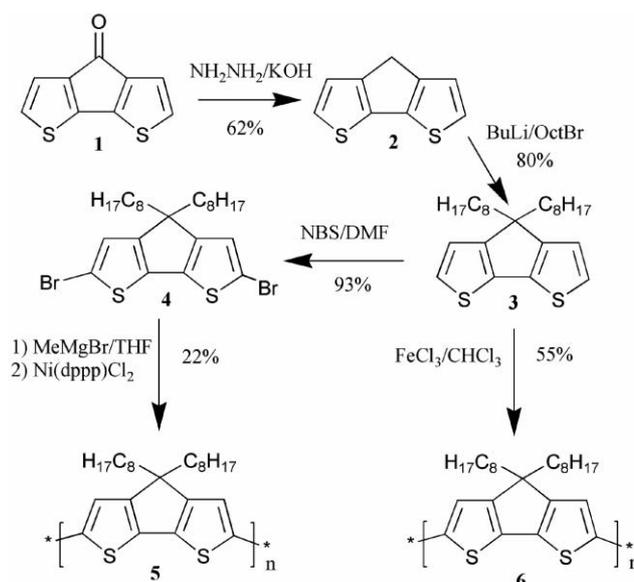
Poly(4,4-dialkylcyclopentadithiophene-2,6-diyls) are heterocyclic analogues of poly(dialkylfluorenes), which are currently the most commercially interesting conjugated polymers. Poly(cyclopentadithiophenes) exhibit high conductivity in the doped state⁶ and the low oxidation potentials (0.1–0.2 V) of these polymers are compatible with electronic devices where a low barrier to charge injection is required, such as double layer LEDs.^{5d} These polymers were initially prepared by electropolymerisation of 4,4-dialkylcyclopentadithiophenes.⁶ Only one report of a chemical approach to the synthesis of poly(dialkylcyclopentadithiophenes) has appeared. Polymers showing moderate molecular weights (\bar{M}_n 5000–9000) were prepared by nickel(0) catalysed coupling of 2,6-dibromo-4,4-dialkylcyclopentadithiophenes.⁷ In this report two novel synthetic approaches to the preparation of poly(cyclopentadithiophenes) are discussed. Polymers with a low degree of mislinkages, extensive conjugation and high molecular weight are presented.

The synthetic procedure is shown in Scheme 1. Dioctyl substituted 4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (**3**) was obtained by a modified literature procedure, involving a novel Huang–Minlon reduction of cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (**1**).^{6,8,9} Bromination at positions 2 and 6 occurred almost quantitatively on treatment of **3** with two equivalents of *N*-bromosuccinimide in DMF at room temperature in the dark. Compound **4** was polymerised by a Kumada type cross-coupling,

involving a metathesis with methylmagnesium bromide to generate a reactive thienyl Grignard monomer. The resulting purple polymer (**5**) was purified by precipitation into methanol and Soxhlet extraction with acetone. GPC against polystyrene standards showed the majority of the material to be of moderate molecular weight (see Table 1), however, a long tail to high molecular weight was observed (see Fig. 1). The molecular weight distribution was reproducible over several experiments, and is low when compared to the results obtained by application of the same protocol to the synthesis of poly(3-hexylthiophene) ($\bar{M}_n \sim 30000$).

These results may be due to incomplete Grignard metathesis of the dibromocyclopentadithiophene and chain capping with unreacted methylmagnesium bromide. This suggestion is supported by the observation of several peaks in the ¹H NMR spectrum of **5** around 2.52 ppm (see inset in Fig. 2). This complex signal has been assigned to methyl groups at the polymer chain termini, the integration of which is consistent with the average degree of polymerisation determined by GPC (~15 units). MALDI-TOF mass spectrometry also confirmed the presence of these methyl end groups (see Supplementary Information[†]). Despite this end-capping process, the Kumada protocol afforded well-defined, highly soluble material with a UV-visible absorption in agreement with previous reports (λ_{\max} 560 nm, see Table 1 and Fig. 3).^{6,7}

Direct oxidative polymerisation of **3** was also investigated. Slow addition of **3** to a suspension of FeCl₃ in chloroform under an atmosphere of dynamic nitrogen gave oxidised poly(4,4-dioctylcyclopentadithiophene) (**6**). Polymer **6** was

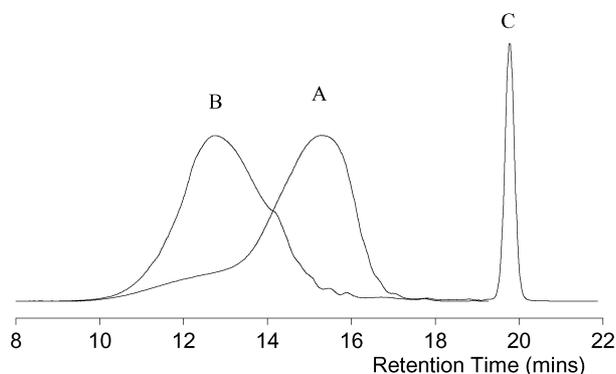
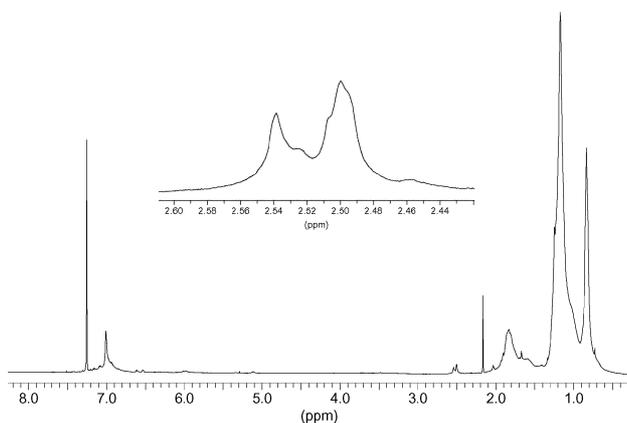


Scheme 1 Synthetic protocol to polymers **5** and **6**.

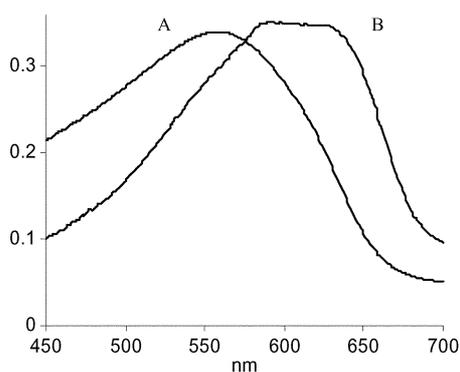
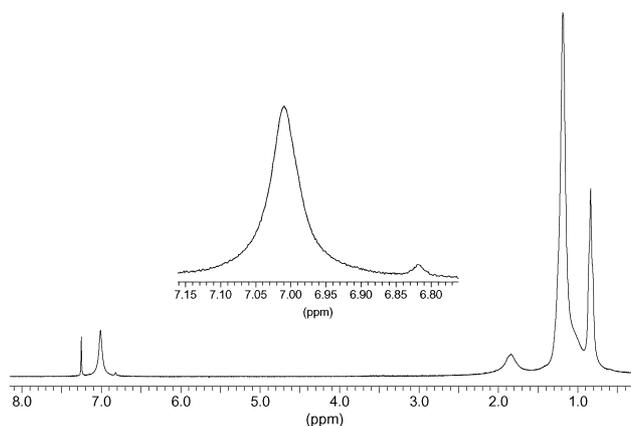
[†]Electronic supplementary information (ESI) available: partial MALDI-TOF mass spectrum of polymer **5**. See <http://www.rsc.org/suppdata/jm/b2/b206477d/>

Table 1 Yields, GPC molecular weights and absorption maxima for thin films of polymers **5** and **6**

Polymer	Yield (%)	λ_{max} /nm	Edge/band gap	\bar{M}_w/\bar{M}_n
5	22	560	670 nm/1.8 eV	41000/6000
6	55	595/625	700 nm/1.7 eV	121500/45000

**Fig. 1** GPC traces of **5** (A), **6** (B) and toluene (C) used as a flow standard.**Fig. 2** ^1H NMR spectrum of **5**, with an expansion of the signals associated with the methyl groups of the chain termini.

dedoped by treatment with hydrazine and purified by precipitation in methanol and Soxhlet extractions with acetone and hexane. GPC against polystyrene standards gave a monomodal distribution and showed the material to be of high molecular weight (see Table 1 and Fig. 1). The blue polymer was readily soluble in tetrahydrofuran and chloroform and at this stage of purification an ICP-AES analysis revealed 1060 ppm of iron

**Fig. 3** UV-visible spectra of thin films of polymers **5** (A) and **6** (B).**Fig. 4** ^1H NMR spectrum of polymer **6**, with an expansion of the signals associated with the aromatic protons in position 3 and the chain termini.

impurities. Further purification by filtration over silica considerably reduced the concentration of iron impurities to 145 ppm, consistent with the levels of metal impurities present in samples of conjugated polymers prepared by transition metal catalysed couplings. The polymerisation occurred with high selectivity towards 2,2 linkages (see Fig. 4). Despite the low oxidation potential reported for dialkylcyclopentadithiophenes (0.65 V) no mislinkages (2,3 and 3,3) were detected by ^1H NMR analysis as reported for the oxidative polymerisation of dialkylfluorenes.¹⁰ The small peak at δ 6.82 ppm (see inset in Fig. 4) can be assigned to the chain termini in position 3 as integration of this peak gave an average degree of polymerisation for **6** of 100 which compares favourably with that determined by GPC ($n = 112$). The absence of mislinkages in polymer **6** was confirmed by the UV-visible absorption spectrum. This showed a large red-shift (see Table 1 and Fig. 3) when compared to literature data^{6,7} and to polymer **5** obtained by Kumada cross-coupling in this work. The shift in the UV-visible absorption to a longer wavelength clearly indicates that the high molecular weight of polymer **6** enhances the conjugation length along the chain well above that of polymer **5** and also the extrapolated value for an infinite polythiophene chain (*ca.* 540 nm).¹¹ No significant bathochromic shifts due to polymer aggregation or solid state self-assembly were observed for polymers **5** and **6** as solutions in poor solvents (chloroform–methanol mixtures) or as thin films spin-coated from 1% chloroform solutions.

In summary, poly(dialkylcyclopentadithiophenes) have been prepared by two new polymerisation protocols. The polymer prepared by Kumada type cross-coupling showed significantly reduced molecular weight over that prepared by direct oxidative polymerisation using FeCl_3 . The higher molecular weight polymer **6** showed extended conjugation length and lower band gap. Further studies of the physical properties of these materials are under investigation.

Experimental

Oxidative polymerisation of **3**

Monomer **3** (1 g, 2.49 mmol) was dissolved in distilled chloroform (5 cm^3) and this solution was added dropwise to a suspension of FeCl_3 (1.62 g, 10 mmol) in distilled chloroform (40 cm^3). The mixture was vigorously stirred for 24 hours under a gentle stream of nitrogen. The oxidised polymer was precipitated into methanol, dedoped by heating a solution in chloroform–hydrazine hydrate at reflux for 24 hours and purified by Soxhlet extraction with acetone and hexane. Further precipitation into methanol and filtration over silica in chloroform solution afforded polymer **6** in 55% yield. ^1H NMR

(CDCl₃): δ 7.02 (s, 2H, aromatic), 6.82 (s, chain termini), 1.85 (m, 4H, CH₂), 1.19 (m, 24H, CH₂), 0.85 ppm (m, 6H, CH₃). ¹³C NMR (CDCl₃): δ 14.08 (CH₃), 22.62 (CH₂), 24.53 (CH₂), 29.32 (CH₂), 29.34 (CH₂), 30.07 (CH₂), 31.81 (CH₂), 37.86 (CH₂), 54.12 (CR₂), 117.04, 134.90, 138.55, 158.68 ppm. Elemental analysis: found (expected values) = C 74.12 (74.94); H 8.96 (9.06); S 15.41 (16.01); Cl 0.52% (0%).

Polymerisation of monomer 4

Monomer **4** (1.6 g, 2.85 mmol) was solubilised in anhydrous THF (40 cm³) under nitrogen. Methylmagnesium bromide (2.9 mmol, 1 ml of 3 M solution in diethyl ether) was added dropwise. The mixture was stirred at reflux for 3 hours, then 1% Ni(dppp)Cl₂ solubilised in anhydrous THF (2 cm³) was added. The purple mixture was stirred at reflux for 24 hours under nitrogen. The polymer was precipitated into methanol, purified by Soxhlet extraction with acetone, recovered with dichloromethane and precipitated into methanol to give polymer **5** in 22% yield. ¹H NMR (CDCl₃): δ 7.02 (m, 2H, aromatics), 2.48–2.56 (m, CH₃), 1.85 (m, 4H, CH₂), 1.19 (m, 24H, CH₂), 0.85 ppm (m, 6H, CH₃).

Acknowledgements

Avecia Limited, the EPSRC and The Royal Society are gratefully acknowledged for funding this project. Dr S. Stephen, Mrs I. Bartkowiak and Dr C. Zonta are gratefully acknowledged for their help in ICP-AES and NMR analyses.

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