

Synthetic Routes to Solution-Processable Polycyclopentadithiophenes

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ABSTRACT: Three synthetic protocols have been employed to prepare solution-processable poly(4,4-dialkylcyclopentadithiophenes). These polymers are fused-ring analogues of poly(3-alkylthiophenes) and structural analogues of the polyfluorenes. Oxidative polymerization of 4,4-dialkylcyclopenta[2,1-b;3,4-b']dithiophenes using iron (III) chloride gave high-molecular-weight polymers, whereas nickel-catalyzed polymerization of the 2,6-dibromo derivatives via in situ-generated thienylmagnesium and thienylzinc reagents gave moderate-molecular-weight polymers. The structures of the polymers were confirmed by NMR spectroscopy and MALDI-TOF mass spectrometry. In the polymerization using organomagnesium intermediates, some chain capping by methyl end groups was observed. This side reaction can be avoided by polymerization of the organozinc reagents. Post-functionalization of the halogen termini of these polymers can be readily achieved using a cross-coupling with an aryl Grignard reagent. The main chain conjugation in these polymers can be directly correlated to the length of the polymer backbone because the UV-vis spectra of fractionated samples show absorption maxima that increase with the average degree of polymerization as determined by GPC, up to a limiting value of ~20. UV-vis spectroscopy suggests that poly(4,4-dialkylcyclopentadithiophenes) do not self-assemble in the solid state, as has been previously observed for regioregular poly-3-alkylthiophenes.

Introduction

Conjugated polymers are emerging as the basis of major new technologies in organic optoelectronics and organic electronics.^{1–3} Consequently, there is tremendous interest in the preparation and the purification of these materials.^{4–6} Among the most interesting materials under investigation are the polyfluorenes and the poly(3-alkylthiophenes) and their copolymers.

The preparation of poly-3-alkylthiophenes has been extensively investigated in the past decade.⁴ Oxidative polymerization of 3-alkylthiophenes by FeCl₃ gives excellent yields of high-molecular-weight regiorandom polymer.^{7,8} Optimization of this procedure and extensive purification gives material with iron impurities as low as 80 ppm, compatible with their application in low performance electronic devices.^{9,10} Recently, efficient synthetic pathways using nickel-catalyzed cross couplings of heterofunctional monomers that give access to extremely pure materials with a high degree of control over the polymer regiochemistry have been developed.^{11–14} These materials have established new standards of performance for polymeric semiconductors in devices such as organic thin film transistors.^{15,16}

Given the interesting properties of polyfluorenes and poly(3-alkylthiophenes), recent work has focused on polycyclopentadithiophenes, as structural analogues of polyfluorenes based on thiophene.^{17–20} To date, very few preparative methods for the synthesis of soluble polycyclopentadithiophenes have been reported. Initial studies used anodic coupling of 4,4-dialkylcyclopenta[2,1-b;3,4-b']dithiophene to prepare poly(4,4-dialkylcyclopentadithiophenes). These polymers show extended conjugation and high electrical conductivity in the doped

state.²¹ Analogous polymers of moderate molecular weight (M_n 5000–9000) have been prepared by a Ni(0)-catalyzed reductive coupling of 2,6-dibromo-functionalized dialkylcyclopentadithiophenes.²² In this contribution, we report three novel approaches to the synthesis of solution-processable poly(4,4-dialkylcyclopentadithiophenes). The structural features and optical properties of the materials prepared by each approach are discussed, including an analysis of the polymer end groups and their subsequent reaction to remove undesirable halogen termini. Part of this work has been previously communicated.²³

Synthesis of the Polymers

Monomers **3a–c** were prepared from cyclopenta[2,1-b;3,4-b']dithiophen-4-one (**1**)^{24–26} by a new synthetic route, outlined in Scheme 1. Reduction of **1** according to a Huang-Minlon modification of the Wolff-Kischner procedure afforded **2** in satisfactory yield.²⁷ Compound **2** was dialkylated using procedures previously reported for fluorenes.^{28,29}

Oxidative polymerization of **3a–c** by FeCl₃ gave the oxidized polymers **5a–c** as black powders after precipitation. Dedoping treatment with hydrazine, followed by fractionation of the materials by multiple Soxhlet extractions, afforded the final polymers as blue solids that are soluble in chloroform (**5a–c**) and tetrahydrofuran (**5b–c**). Gel permeation chromatography against polystyrene standards showed these polymers to be of high molecular weight (See Table 1). Fractionation by Soxhlet extraction considerably reduced the polydispersity of polymers **5b–c**, but had little effect on that of polymer **5a**. The high polydispersity (pd) of this polymer may be due to the formation of aggregates in solution as a result of the lower solubility of **5a** when compared to polymers **5b–c**. In the examples reported, the molecular weight of the polymer decreases with increasing

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Scheme 1. Synthetic Route to Monomer 3 and Polymers 5–7 (a, R = Hexyl; b, R = Octyl; c, R = Hexadecyl)

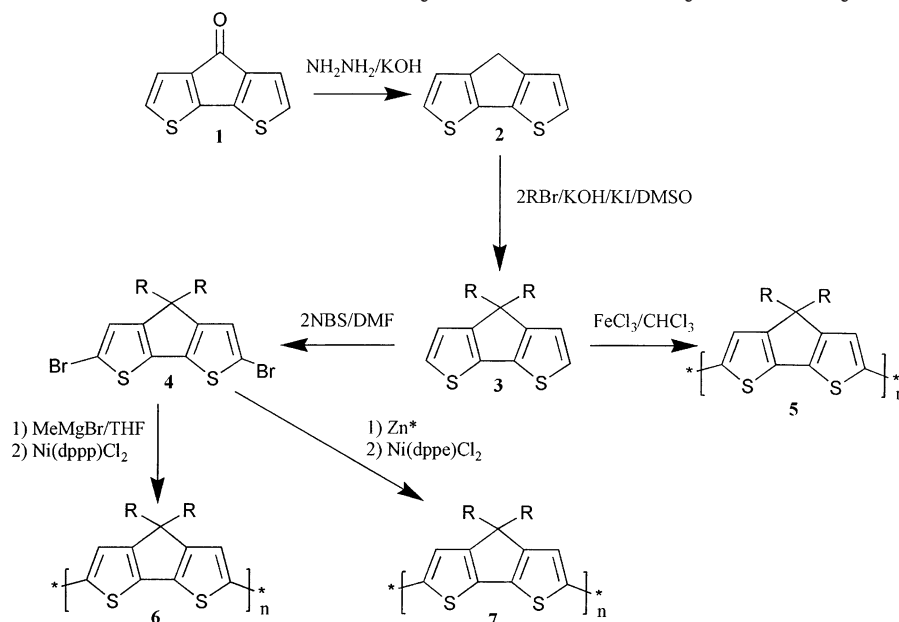


Table 1. Spectroscopic and GPC Data for Polymers 5–7

polymer	yield (%)	M_w/M_n	pd	UV-vis _{max} (nm)	UV-vis _{edge} (nm)/band gap (eV)
5a	15 ^a	1 390 000/168000	8.3	590	700/1.7
5b	55	121500/45000	2.7	595	700/1.7
5c	36	100000/30000	3.3	592	700/1.7
6a	19	28000/6200	4.5	561	670/1.8
6b	22	41000/6000	6.8	560	670/1.8
7a	21	10200/7000	1.5	582	675/1.8
7b	25	11800/8200	1.4	583	675/1.8

^a The polymer was obtained in 67% yield; 15% represents the fraction soluble in chloroform.

alkyl chain length (see Table 1). Purification of polymer **5b** by multiple Soxhlet extraction gave material containing 1000 ppm of iron impurities according to ICP-AES analysis. Further purification by filtration of a chloroform solution of **5b** over a silica gel layer lowered the iron content to 145 ppm, a value in line with the best results previously obtained for poly-3-alkylthiophenes.^{9–10}

Dibromination of **3a,b** with *N*-bromosuccinimide at room temperature in the dark gave **4a,b** in nearly quantitative yield (see Scheme 1). Monomers **4a,b** were polymerized by a nickel-catalyzed Kumada-type cross-coupling,³⁰ which is shown in Scheme 1, and involved a Grignard metathesis from methylmagnesium bromide to generate the active thienyl-Grignard intermediate.^{12,31} Low yields of polymers **6a–b** of moderate molecular weight were isolated, and the GPC traces showed a long tail to high molecular weight (see Table 1). These results can be contrasted with the high molecular weights and low polydispersities achieved in an analogous preparation of poly(3-hexylthiophene) (M_n 30 000, pd 1.4) using the same source of magnesium (3 M solution of MeMgBr in diethyl ether) on a similar scale. The lower molecular weights of polymers **6a,b** were attributed to incomplete Grignard metathesis and chain capping by residual methylmagnesium bromide (see Figures 1 and 3), competing with the polymerization reaction, as discussed in the following section.

To avoid the undesirable chain-capping reaction, monomers **4a,b** were polymerized by an initial metathesis with Rieke zinc to generate the thienyl-bromozinc intermediate,¹⁴ and a Negishi-type polymerization³² catalyzed by Ni(dppe)Cl₂ led to the synthesis of polymers

7a,b (see Scheme 1). Purification by precipitation and repeated Soxhlet extraction gave polymers with moderate molecular weights (see Table 1) that are generally lower than those achieved in an analogous preparation of poly-3-hexylthiophene (M_n 12 000, pd 1.3). However, the degrees of polymerization for polymers **7a,b** are higher than those of **6a,b**, suggesting that metathesis with Rieke zinc is more suitable for the polymerization of 4,4'-dialkylcyclopentadithiophenes.

Structural Characterization of the Polymers

NMR spectroscopy is extremely useful for the elucidation of backbone regiochemistry and for the identification of structural defects in conjugated polymers. MALDI-TOF mass spectrometry gives valuable information on the repeat unit and the end groups of the polymer, potentially giving useful information about the polymerization mechanism.^{33,34} Polymers **5a–c**, obtained by oxidative polymerization, were shown to have very low levels of mislinkages in the polymer backbone by NMR spectroscopy. This can be compared with the significant levels of defect linkages reported for the analogous polyfluorenes prepared by the same method.³⁵ The intense signal at δ 7.02 ppm can be assigned to the protons in position 3 of the cyclopentadithiophene rings. A weak broad signal at δ 6.82 ppm in the spectrum of polymer **5b** (see Figure 1) can be attributed to a proton in position 3 of the terminal thiophene ring. This assignment is consistent with its integration (~2% of the peak at δ 7.02 ppm) given the average degree of polymerization determined by GPC (~112 units) and the fact that molecular weights determined by GPC, calibrated against polystyrene standards, are known to be

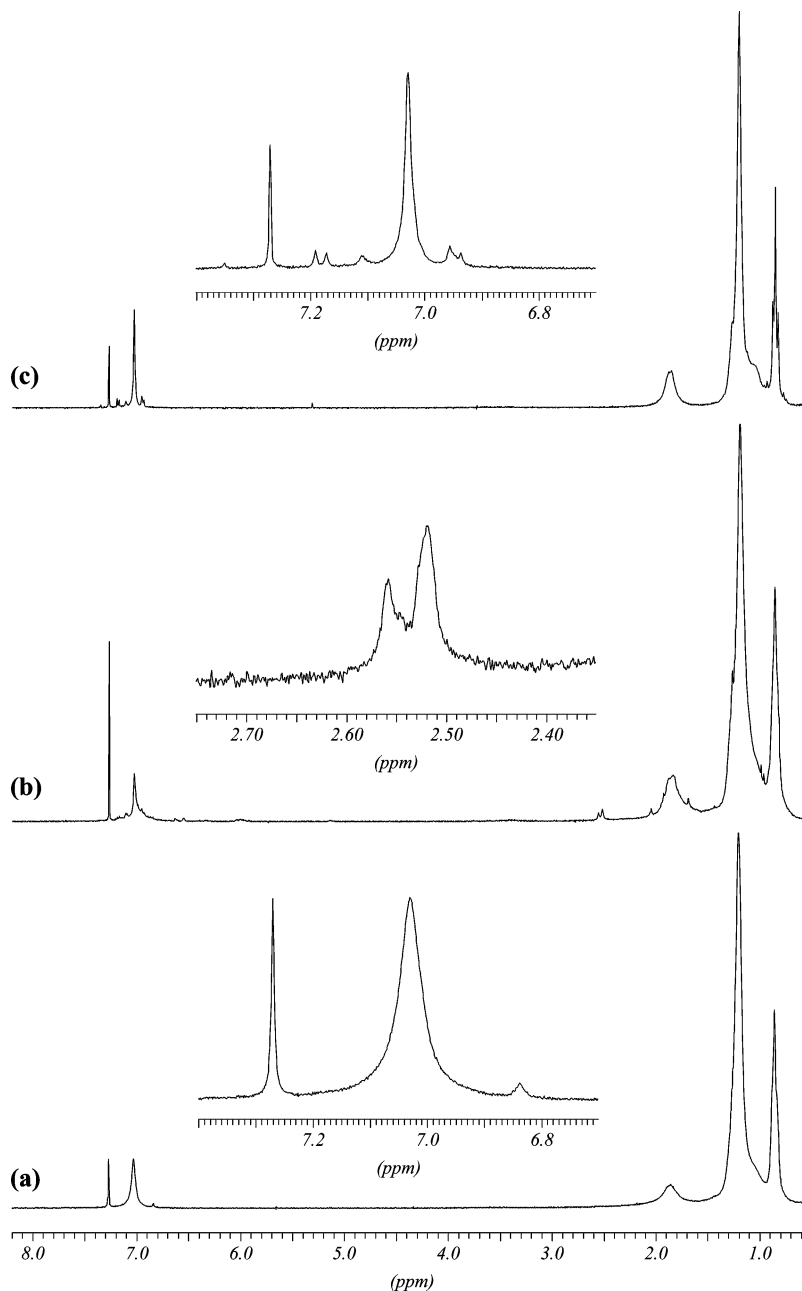


Figure 1. ^1H NMR spectra (in CDCl_3 solution at 250.133 MHz) of: (a) Polymer **5b** (inset expansion of the aromatic region), (b) polymer **6b** (inset expansion of the signal at δ 2.52 ppm), and (c) polymer **7b** (inset expansion of the aromatic region).

an overestimate as a result of the rigid rod behavior of thiophene polymers.³⁶ It is clear that no 2–3 or 3–3 mislinkages are present in the polymer backbone, because these structural defects can be detected by the presence of signals for position 2 of the thiophene ring at a chemical shift downfield of that for the polymer main chain (δ 7.02 ppm).

The ^1H NMR spectra of polymers **6a,b** obtained by Kumada cross-coupling are more complex. The major signal at δ 7.01 ppm (see Supporting Information for an expansion of this signal) can be assigned to position 3 on the cyclopentadithiophene ring. However, a broad signal consisting of several overlapping resonances is detectable at δ 2.52 ppm (see Figure 1). These resonances can be assigned to a methyl end group at position 2 of the terminal thiophene ring from the chemical shift³⁷ and the integration (20% of the main chain at δ 7.01 ppm). The integration is consistent with an average

degree of polymerization of 15 determined by GPC. The presence of several overlapping resonances for methyl end groups at δ 2.52 ppm is related to the wide polydispersity of these polymers (see Table 1). The MALDI-TOF mass spectrum of **6b** (see Figure 3) shows the presence of polycyclopentadithiophene polymers with a repeat unit of 400 capped by a wide variety of end groups, including H, Me, Br, and Cl. The presence of methyl groups at the chain termini is presumably the result of a nickel-catalyzed coupling between the unreacted methylmagnesium bromide and the cyclopentadithienyl bromide, as reported previously for polyalkylthiophenes.³⁶

^1H NMR spectroscopy indicated that structural defects were absent in polymers **7a,b** obtained by the Rieke polymerization method. The chain termini at positions 2 and 3 were clearly identified as doublets at δ 7.16 and 6.92 ppm, showing a coupling constant of 4

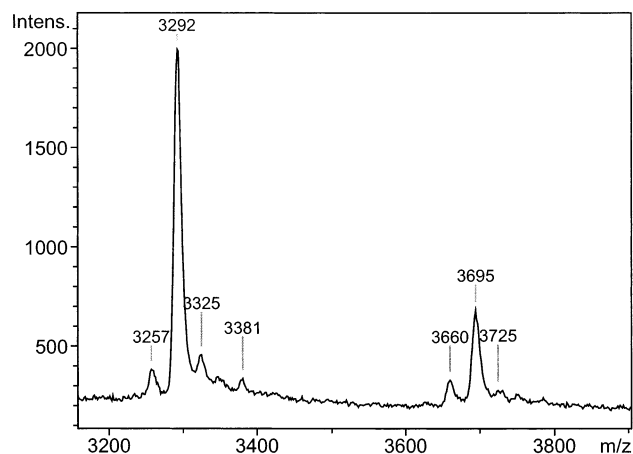


Figure 2. MALDI-TOF mass spectrum of polymer **5b** (hexane extraction) showing the octamer and the nonamer.

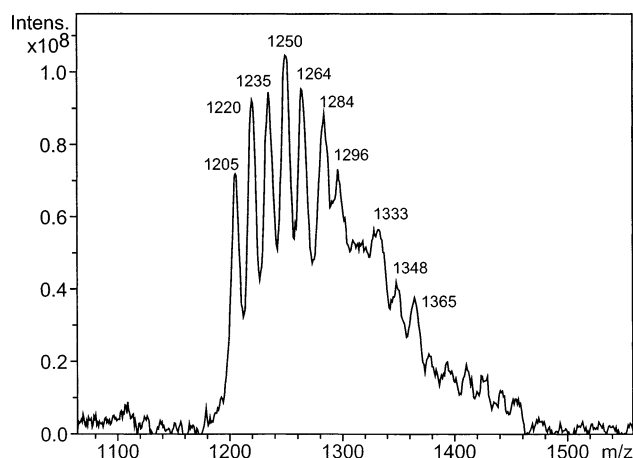


Figure 3. MALDI-TOF mass spectrum of polymer **6b**, showing the trimer with a wide distribution of chain termini.

Hz (see Figure 1). Integration of these signals relative to those of the main chain at δ 7.01 ppm compared favorably with the average degree of polymerization determined by GPC (1:16 vs $n \sim 20$, Table 1). The integration indicates that most of the material is H-capped on both sides of the polymer chain, presumably as a result of reduction of thienyl bromide end groups by unreacted Rieke zinc. MALDI-TOF analysis (Figure 4) revealed that $\sim 80\%$ of the material is doubly H-capped; 14% is monobrominated, as expected for a polymerization of this type; and 6% is capped with bromine on both sides.

The presence of halogen termini in polymers for electronic applications can be detrimental to device performance because they can act as traps in the charge transport process.³⁸ It was therefore desirable to replace the bromide end groups with a suitable aromatic capter. This was achieved by reacting purified polymer **7a** with an excess of *p*-tolylmagnesium bromide under Kumada conditions. The resulting polymer, **8a**, showed optical properties analogous to those of the precursor **7a** (see Table 1). MALDI-TOF mass spectrometry (Figure 5) for **8a** showed the postfunctionalization to be extremely efficient, as the signals attributed to the brominated materials have been replaced by the signals of the tolyl-capped derivatives.

Optical Characterization of the Polymers

Poly(4,4-dialkylcyclopentadithiophenes) have been reported to show extended main chain conjugation with

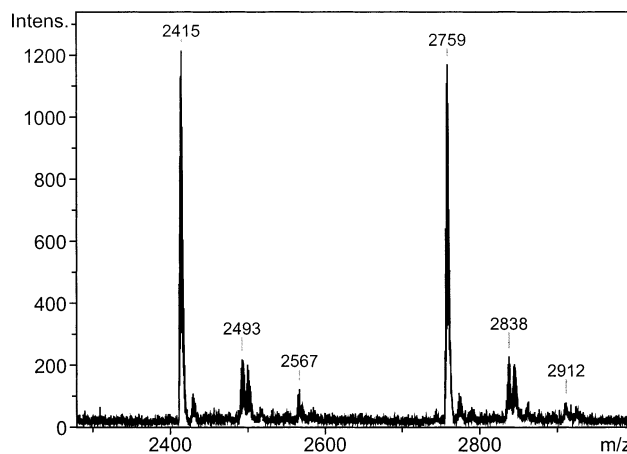


Figure 4. MALDI-TOF mass spectrum of polymer **7a**, showing the heptamer and the octamer, with H-H, H-Br, and Br-Br end groups.

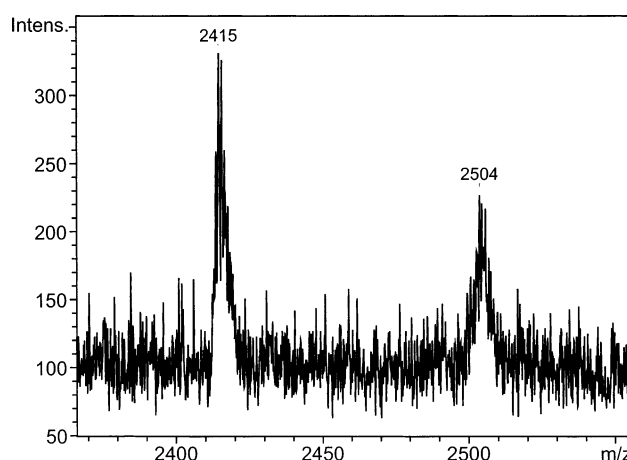


Figure 5. MALDI-TOF mass spectrum of polymer **8a**, showing the heptamer with H-H and H-tolyl end-groups.

solution absorption maxima in the range 550–610 nm.^{21,22} This is significantly longer than the conjugation of the related poly(3-alkylthiophenes) (430–450 nm).⁴ Polymers **5a–c** obtained by the FeCl_3 oxidative method show higher molecular weights and extended conjugation ($\lambda_{\text{max}} \sim 595$ nm) when compared to polymers **6–8** obtained by transition-metal-catalyzed polymerization (see Figure 6: **6** $\lambda_{\text{max}} \sim 560$ nm; **7** $\lambda_{\text{max}} \sim 582$ nm; **8** $\lambda_{\text{max}} = 580$ nm). For these polymers, the main chain conjugation can be directly correlated to the length of the polymer backbone. Extraction of polymers **5b** and **7b** using solvents of varying solubilizing power led to fractions with increasing molecular weight. A typical sequence of extractions involved acetone, pentane, hexane, petrol (80–100 °C), dichloromethane, and chloroform. UV-vis spectra of the fractions show absorption maxima (see Figure 7) that increase with the average degree of polymerization as determined by GPC (see inset of Figure 7), up a limiting value of ~ 20 . This behavior is in good agreement with similar experiments reported for other conjugated polymers.³⁹

UV-vis spectra of polymers **5–8** recorded in good solvents (chloroform, THF) and poor solvents (chloroform/methanol mixtures) were identical. The absence of a significant bathochromic shift on going from a good solvent to a poor solvent suggests that these polymers do not assemble into ordered structures in solution, as has been previously observed for regioregular poly(3-alkylthiophenes).⁴

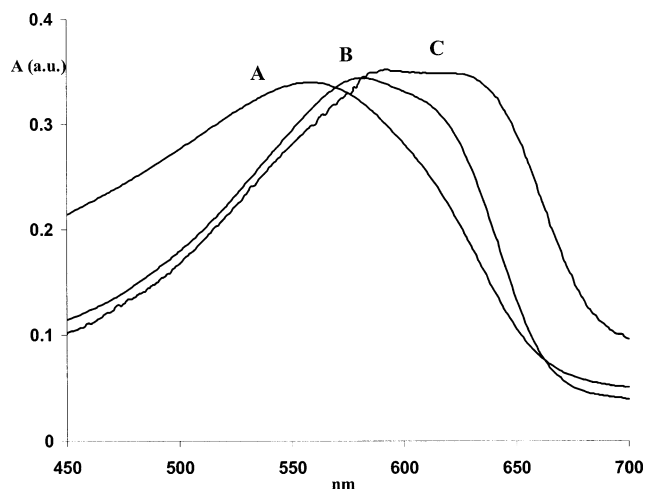


Figure 6. UV-vis spectra of polymers **6b** (A), **7b** (B), and **5b** (C).

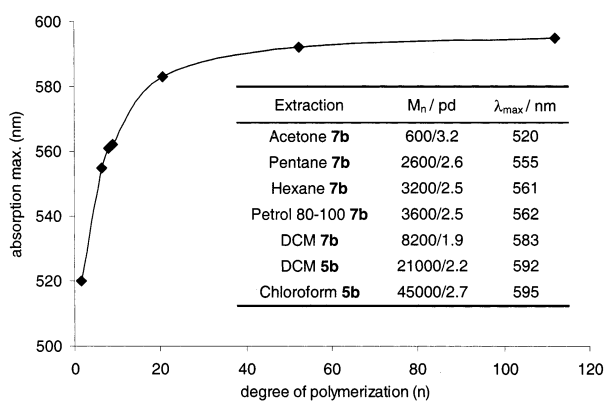


Figure 7. Correlation between the degree of polymerization determined by GPC (n) and the UV-vis absorption maxima for poly(4,4-dioctylcyclopentadithiophene) obtained by Soxhlet extractions from polymers **5b** and **7b**.

The UV-vis spectra of thin films of **5–7** spin-coated from chloroform solution and annealed at 100 °C for 2 h were recorded. The thin film spectra show an increase in the vibronic structure, but the position of the absorption maxima was unchanged. It appears that these polymers do not self-assemble in the solid state in a fashion similar to that reported for regioregular poly-3-alkylthiophenes.⁴⁰ This observation is consistent with the absence of any mesophase behavior for polymers **5–7** observable by DSC or optical microscopy for temperatures up to their decomposition.

Conclusions

Three protocols for the preparation of poly(4,4-dialkylcyclopentadithiophenes) have been investigated. All three methods afford soluble materials, free of mislinkages and showing extended conjugation in solution. Polymers obtained by an oxidative protocol show a higher molecular weight than those prepared by transition-metal-catalyzed polymerization. NMR spectroscopy and MALDI-TOF mass spectrometry showed that the moderate degree of polymerization (15–20 units) achieved by Kumada- and Negishi-type polymerization is probably due to incomplete formation of the organometallic intermediate. It has been shown that halogen termini of the initial polymers can be efficiently scav-

enged by postfunctionalization using a cross-coupling with an aryl Grignard reagent.

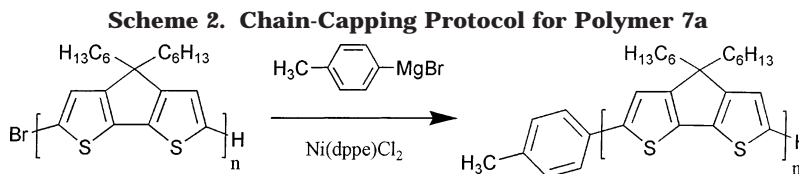
Experimental Section

All experiments were carried out under nitrogen, except those involving Rieke zinc, which were performed under an argon atmosphere using established procedures¹⁴ (method 2). Anhydrous tetrahydrofuran and diethyl ether were obtained by distillation over sodium/benzophenone ketyl. All other reagents were used as received. ¹H and ¹³C NMR spectra were recorded using a Bruker AC 250 MHz spectrometer operating at 250.133 MHz for ¹H NMR spectroscopy and Bruker AMX 400 MHz spectrometer operating at 100.624 MHz for ¹³C NMR spectroscopy. The spectra were referenced to the resonance of the solvent as internal standard. Molecular weight determination was carried out in chloroform solution on an HP1090 liquid chromatograph using Polymer Laboratories Mixed C or Mixed E chromatography columns that were calibrated against narrow molecular weight polystyrene calibration standards.

4H-Cyclopenta[2,1-b:3,4-b']dithiophene (2). Compound **1** (5.0 g, 26 mmol) was suspended in 100 cm³ of ethylene glycol. Finely ground potassium hydroxide (5.0 g) was added under nitrogen. The resulting slurry was heated to 180 °C and hydrazine hydrate (10 cm³) was added dropwise by means of a syringe. The mixture was stirred at 180 °C for 8 h. The resulting brown solution was then allowed to cool to room temperature. Water was added (100 cm³), and the organic phase was extracted twice with diethyl ether (100 cm³); washed three times with water, brine, and saturated ammonium chloride solution; and dried with magnesium sulfate. The solvent was removed under reduced pressure, and the title compound was obtained as a brown oil. Purification by flash chromatography over silica/hexane afforded pure **2** as white crystals. Yield 3.0 g, 65%. Analytical data were consistent with previously reported values.⁴¹ ¹H NMR (CDCl₃): δ 7.18 (d, J = 5 Hz, 2H, aromatics), 7.09 (d, J = 5 Hz, 2H, aromatics), 3.54 ppm (s, 2H, CH₂). mp 73–74 °C.

4,4-Dioctyl-cyclopenta[2,1-b:3,4-b']dithiophene (3b). Compound **2** (2.0 g, 11.2 mmol) was solubilized in 50 cm³ of dimethyl sulfoxide. Octyl bromide (4.3 g, 22.4 mmol) was added, followed by potassium iodide (50 mg). The mixture was flushed with nitrogen and cooled in an ice bath, and finely ground potassium hydroxide (2.0 g) was added in portions. The resulting green mixture was vigorously stirred overnight at room temperature. The reaction vessel was then cooled in an ice bath, and water (50 cm³) was added. The organic phase was extracted twice with diethyl ether; washed with water, brine and ammonium chloride; and dried with magnesium sulfate. Evaporation of the solvent afforded the title compound as a yellow oil. Purification by chromatography over silica/hexane was performed to eliminate traces of monoalkylated product and unreacted octyl bromide. The title compound was obtained as a clear oil. Yield 3.84 g, 85%. Analytical data were consistent with previously reported values:²¹ ¹H NMR (CDCl₃): δ 7.13 (d, J = 5 Hz., 2H, aromatics); 6.91 (d, J = 5 Hz, 2H, aromatics), 1.81 (m, 4H, CH₂), 1.13 (m, 20H, CH₂), 0.94 (m, 4H, CH₂), 0.84 ppm (t, J = 7 Hz, 6H, CH₃).

2,6-Dibromo-4,4-dioctylcyclopenta[2,1-b:3,4b']dithiophene (4b). Compound **3b** (2.0 g, 4.97 mmol) was solubilized in 50 cm³ of distilled dimethylformamide under nitrogen in the dark. NBS (1.8 g, 9.94 mmol) was added portionwise. The resulting yellow solution was stirred at room temperature under nitrogen overnight. Water (50 cm³) was then added, and the organic phase was extracted with diethyl ether (100 cm³) twice, washed with water and with 1% HCl, and dried with magnesium sulfate. The solvent was removed under reduced pressure to obtain the title product as a yellow oil. Impurities of succinimide were removed by filtration over silica/hexane. The title compound was obtained as a pale yellow oil, yield 2.31 g, 83%. ¹H NMR (CDCl₃): δ 6.92 (s, 2H, aromatics); 1.74 (m, 4H, CH₂), 1.14 (m, 20H, CH₂), 0.90 (m, 4H, CH₂); 0.84 ppm (t, J = 7 Hz, 6H, CH₃). ¹³C NMR (CDCl₃): δ 14.10 (CH₃), 22.63 (CH₂), 24.41 (CH₂), 29.25 (CH₂), 29.29



(CH₂), 29.92 (CH₂), 31.80 (CH₂), 37.53 (CH₂), 55.02 (C), 111.06 (C), 124.58 (CH); 136.28 (C), 155.94 ppm (C).

Oxidative Polymerization of 3b. Monomer **3b** (1.0 g, 2.49 mmol) was dissolved in distilled chloroform (5 cm³), and this solution was added dropwise to a suspension of FeCl₃ (1.6 g, 10 mmol) in distilled chloroform (40 cm³). The mixture was vigorously stirred for 24 h at room temperature under a gentle stream of nitrogen. The oxidized polymer was precipitated into methanol (400 cm³); dedoped by heating a suspension in chloroform/hydrazine hydrate at reflux for 24 h; and purified by Soxhlet extraction with acetone, pentane, hexane, and petrol 80–100. Further precipitation into methanol (300 cm³) and filtration of a chloroform solution over silica gel afforded polymer **5b** (0.55 g, 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 (9.16); S, 15.41 (16.01); Cl, 0.52 (0).

Kumada Polymerization of Monomer 4b. Monomer **4b** (1.6 g, 2.85 mmol) was solubilized in anhydrous THF (40 cm³) under nitrogen atmosphere. Methylmagnesium bromide (2.9 mmol, 1 cm³ of 3 M solution in diethyl ether) was added dropwise. The mixture was stirred at reflux for 3 h, then 1% w/w Ni(dppp)Cl₂ solubilized in anhydrous THF (2 cm³) was added. The purple mixture was stirred at reflux for 24 h under nitrogen. The polymer was precipitated into methanol (300 cm³), purified by Soxhlet extraction with acetone, recovered with dichloromethane and precipitated into methanol to give polymer **6b** (0.25 g, 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). ¹³C NMR (CDCl₃): δ 14.07 (CH₃), 22.61 (CH₂), 24.52 (CH₂), 29.32 (CH₂), 29.32 (CH₂), 30.06 (CH₂), 31.80 (CH₂), 37.84 (CH₂), 54.10 (CR₂), 117.03, 134.90, 138.55, 158.67 ppm.

Negishi Polymerization of Monomer 4b. A black suspension of Rieke zinc (2.85 mmol) in THF (20 cm³) was cooled to –78 °C and **4b** (1.6 g, 2.85 mmol), solubilized in 5 cm³ of anhydrous THF, was added dropwise by means of a syringe. The reaction mixture was allowed to warm to room temperature over a period of 3 h, and the polymerization catalyst, Ni(dppe)Cl₂ (1% w/w in 2 cm³ of anhydrous THF), was then added. The mixture was stirred at room temperature for 24 h, and the resulting purple polymer was precipitated into methanol (300 cm³), purified by Soxhlet extraction with acetone and hexane, and then reprecipitated into methanol (200 cm³) to give polymer **7b** (0.29 g, 25% yield). ¹H NMR (CDCl₃): δ 7.16 (d, *J* 4 Hz, chain termini pos. 2), 7.01 (s, 2H, aromatics), 6.93 (d, *J* 4 Hz, chain termini pos. 3), 1.85 (m, 4H, CH₂), 1.19 (m, 24H, CH₂), 0.84 ppm (t, *J* 7 Hz, 6H, CH₃). ¹³C NMR (CDCl₃): δ 14.09 (CH₃), 22.62 (CH₂), 24.54 (CH₂), 29.33 (CH₂), 29.34 (CH₂), 30.07 (CH₂), 31.82 (CH₂), 37.86 (CH₂), 54.14 (CR₂), 117.04, 134.90, 138.56, 158.68 ppm.

Chain-Capping on Polymer 7a. Polymer **7a** (100 mg) was solubilized in anhydrous THF (10 cm³) under nitrogen. *p*-Tolylmagnesium bromide (0.33 cm³ of a 1 M solution in THF) was added together with Ni(dppp)Cl₂ (1% w/w in 2 cm³ of anhydrous THF). The mixture was heated at reflux under nitrogen for 24 h. The resulting polymer was precipitated into methanol (50 cm³) and then washed with hot acetone in a Soxhlet apparatus to give **8a** (77 mg, 76% yield) as a blue-purple material. ¹H NMR (CDCl₃): δ 7.16 (d, *J* 4 Hz, chain termini pos. 2), 7.01 (s, 2H, aromatics), 6.93 (d, *J* 4 Hz, chain termini pos. 3), 1.86 (m, 4H, CH₂), 1.19 (m, 16H, CH₂), 0.85 ppm (t, *J* 7 Hz, 6H, CH₃).

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Supporting Information Available: One figure showing the ¹H NMR spectra (in CDCl₃ solution at 250.133 MHz) of polymer **6b** with an expansion of the aromatic region. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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