Supporting Information

Influence of an Ester Directing-Group on Defect Formation in the Synthesis of Conjugated Polymers via Direct Arylation Polymerization (DArP) using Sustainable Solvents

Robert M. Pankow, Liwei Ye, and Barry C. Thompson*

Department of Chemistry and Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089-1661

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1. General

All reactions were performed under dry N₂ in oven dried glassware, unless otherwise noted. Unless otherwise noted, all reagents were purchased and used as received from commercial sources. Solvents were purchased from VWR and used without purification, unless otherwise noted. Anhydrous, unstabilized cyclopentyl methyl ether (CPME) was purchased and used as received. Cs₂CO₃ was ground into a fine powder and dried at 120 °C in a vacuum oven before use. 5,5'-bis(trimethylstannyl)-2,2'-bithiophene was previously prepared following literature procedure.¹ All NMR were recorded at 25 °C using CDCl₃ on either a Varian Mercury 400 MHz, Varian VNMRS-500 MHz, or a Varian VNMR-600 MHz. All spectra were referenced to CHCl₃ (7.26 ppm), unless otherwise noted. Number average molecular weight (M_n) and polydispersity (Đ) were determined by size exclusion chromatography (SEC) using a Viscotek GPC Max VE 2001 separation module and a Viscotek Model 2501 UV detector, with 60 °C HPLC grade 1,2-dichlorobenzene (o-DCB) as eluent at a flow rate of 0.6 mL/min on one $300 \times$ 7.8 mm TSK-Gel GMHHR-H column (Tosoh Corp). The instrument was calibrated vs. polystyrene standards (1050-3,800,000 g/mol), and data were analysed using OmniSec 4.6.0 software. Polymer samples were dissolved in HPLC grade o-dichlorobenzene at a concentration of 0.5 mg ml-1, stirred at 65 °C until dissolved, cooled to room temperature, and filtered through a 0.2 µm PTFE filter.

For polymer thin-film measurements, solutions were spin-coated onto pre-cleaned glass slides from *o*-dichlorobenzene (*o*-DCB) solutions at 7 mg/mL. UV–vis absorption spectra were obtained on a Perkin-Elmer Lambda 950 spectrophotometer. Thicknesses of the samples and grazing incidence X-ray diffraction (GIXRD) measurements were obtained using Rigaku diffractometer Ultima IV using a Cu K α radiation source ($\lambda = 1.54$ Å) in the reflectivity and

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grazing incidence X-ray diffraction mode, respectively. Crystallite size was estimated using Scherrer's equation:

$$\tau = K\lambda/(\beta \cos\theta) \qquad (1)$$

where τ is the mean size of the ordered domains, K is the dimensionless shape factor (K = 0.9), λ is the x-ray wavelength, β is the line broadening at half the maximum intensity (FWHM) in radians, and θ is the Bragg angle.

2. Monomer Synthesis



Scheme S1. Monomer Synthesis.



Synthesis of 5-bromothiophene-3-carboxylic acid (2):

To an Erlenmeyer flask equipped with a stir-bar, 3-thiophene carboxylic acid (10 g, 78 mmol, 1 equiv) was dissolved in glacial acetic acid (60 mL). To this, a solution of bromine (5.61 g, 35.1 mmol, 0.9 equiv) in glacial acetic acid (30 mL) was added slowly. The mixture was allowed to stir for 1 hour and then it was poured in water (300 mL) and stirred for 15 minutes. The solid was filtered off and washed with water. It was then recrystallized from water (300 mL), filtered,

and dried in under vacuum (~100 mtorr) overnight. 5.83 g, 41%. ¹H-NMR 400 MHz (CDCl₃): δ (ppm) 8.11 (d, J = 1.6 Hz, 1H), 7.51 (d, J = 1.6 Hz, 1H). Consistent with literature reports.²



Synthesis of 2-butyloctyl-5-bromothiophene-3-carboxylate (3)

In an oven-dried 3-neck roundbottom flask equipped with a N₂ inlet and a stirbar **2** (4.00 g, 19.3 mmol, 1 equiv), DMAP (0.826 g, 23.16 mmol, 0.35 equiv), and DCC (4.78 g, 23.16 mmol, 1.2 equiv), were dissolved in anhydrous DCM (50 mL). This mixture was allowed to stir for 30 minutes. To this, 2-butyloctanol (5.39 g, 28.95 mmol, 1.5 equiv) was added dropwise via syringe. The mixture was then stirred for 48 hours. The precipitate was filtered off, it was diluted with water (50 mL), and it was extracted with DCM. The organic extracts were then washed with brine and dried with Na₂SO₄. The solvent was stripped and it was purified using column chromatography (15% DCM/hexanes). 6.30 g, 87%. ¹H-NMR 400 MHz (CDCl₃): δ (ppm) 7.97 (d, *J* = 1.6, 1H), 7.45 (d, *J* = 1.6 Hz, 1 H), 4.16 (d, *J* = 5.6 Hz, 2H), 1.74-1.69 (m, 1H), 1.35-1.28 (m, 16H), 0.91-0.86 (m, 6H). Consistent with literature reports.³



Synthesis of Bis(2-butyloctyl)[2,2'-bithiophene]-4,4'-dicarboxylate (4): To a 3-neck round bottom flask equipped with a stir-bar, nitrogen inlet, glass-stopper, Teflon septum, and condenser was added potassium carbonate (9.1 g, 66 mmol, 4 equiv) and bispinacolatodiboron (2.09 g, 8.23 mmol, 0.5 equiv). The flask was evacuated and refilled with N₂ 3 times. Compound 3 (6.18 g, 16.46 mmol, 1 equiv) and a 50 mL mixture of THF:H₂O (3:1) was then added, and the mixture was degassed for 20 minutes. Pd(PPh₃)₂Cl₂ (693 mg, 0.99 mmol, 0.06 equiv) was quickly added and the mixture degassed for an additional 20 minutes. The Teflon septum was replaced with a glass stopper, and the mixture was then heated at 80 °C for 24 hours. The reaction was cooled and extracted with DCM. The extracts were washed with brine, dried with Na₂SO₄, and chromatographed using a solvent gradient of 10% DCM/hexanes to 30% DCM/hexanes to afford a pale yellow, viscous oil (69% yield). ¹H-NMR 400 MHz (CDCl₃): δ (ppm) 7.98 (d, *J* = 1.2 Hz, 2H), 7.57 (d, *J* = 1.2 Hz, 2H), 4.19 (d, *J* = 6.0 Hz, 4H), 1.77-1.73 (m, 2H), 1.39-1.27 (m, 32H), 0.93-0.86 (m, 12H). Consistent with literature reports.³



Synthesis of Bis(2-butyloctyl)[2,2'-bithiophene]-4,4'-dicarboxylate (5):

To a scintillation vial equipped with a screw cap and stir bar was added 4 (267 mg, 0.45 mmol, 1 equiv.), CHCl₃ (2 mL), and trifluoroactetic acid (0.5 mL). The vial was wrapped with foil to shield it from light, and NBS (160.2 mg, 0.9 mmol, 2 equiv.) was added portion wise and it was allowed to stir for 16 hours. In order to reach completion, an additional 16 mg, 0.2 equiv, of NBS and 1.5 mL of TFA were added and it was allowed to stir for an additional 4 hours. The reaction mixture was then diluted with water (10 mL) and extracted with CHCl₃. The organic extracts were then washed with brine and dried with Na₂SO₄. Purification was performed using column chromatography (20% DCM/hexanes). 197 mg, 59%. ¹H-NMR 500 MHz (CDCl₃): δ (ppm) 7.35 (s, 2H), 4.21 (d, *J* = 5.5 Hz, 4H), 1.75-1.73 (m, 2H), 1.41-1.27 (m, 32H), 0.91-0.86 (m, 12H). Consistent with literature reports.^{2,3}



Synthesis of 5,5'-dibromo-2,2'-bithiophene (7):

To 3-neck roundbottom flask equipped with a N₂ inlet and a stirbar **6** (2.0 g, 12.0 mmol, 1 equiv) was added and dissolved in DMF (50 mL). The mixture was then cooled to 0 °C and NBS (4.28 g, 24.06 mmol, 2 equiv.) was added in one portion. This was allowed to slowly warm-up to room temperature with stirring overnight. The mixture was then poured into water (250 mL) and recrystallized from a mixtures of hexanes/CHCl₃. 2.84 g, 73%. ¹H-NMR 400 MHz (CDCl₃): δ (ppm) 6.96 (d, *J* = 4.0 Hz), 2H), 6.85 (d, *J* = 4.0 HZ, 2H). Consistent with literature reports.⁴



Synthesis of 2,5-dibromothieno[3,2-b]thienothiophene (9):

Thineno[3,2-b]thiophene (500 mg, 3.57 mmol, 1 equiv) was added to a 3-neck round bottom flask equipped with a stir-bar, which was then vacuum-backfilled with N₂ three times. DMF (7 mL) was added and the solution was degassed for 15 minutes. It was then cooled to 0 °C and NBS (1.27 g, 7.13 mmol, 2 equiv.) was added in one portion. The mixture was then stirred for 3 hours, allowing it to warm to room temperature. Water was added (15 mL) and a precipitate formed that was then filtered, washed with water, and dried under high-vacuum. The crude product was then recrystallized using a mixture of EtOH/CHCl₃. 460 mg, 43%.¹H-NMR 400 MHz (CDCl₃): δ (ppm) 7.17 (s, 2H). Consistent with literature reports.⁵



Synthesis of 2,2'-bithiazole (11):

To an oven-dried 3-neck round-bottom flask cooled under N₂ was added Bu₄NBr. The flask was then vacuum-backfilled three times with N₂. 2-bromothiazole (2.60 g, 16 mmol, 1 equiv), Et(*i*-Pr)₂N (2.07 g, 16 mmol, 1 equiv.), and toluene (6 mL) were added to the flask. It was then degassed with N₂ for 30 minutes. Pd(OAc)₂ (359 mg, 1.6 mmol, 0.1 equiv.) was quickly added and the flask was heated at 105 °C overnight. The reaction mixture was cooled, H₂O (25 mL) was added, and it was extracted with CHCl₃. The combined organics were washed with brine and dried with Na₂SO₄. Purification was performed using column chromtagoraphy (20% EtOAc/hexanes). 587 mg, 43%. ¹H-NMR 400 MHz (CDCl₃): δ (ppm) 7.90 (d, *J* = 3.2 Hz, 2H), 7.44 (d, *J* = 3.2 Hz, 2H). Consistent with literature reports.⁶



Synthesis of 5,5'-dibromo-2,2'-dithiazole (12):

To an oven-dried 3-neck round-bottom flask cooled under N₂ was added 2,2'-dithiazole (11) (500 mg, 2.97 mmol, 1 equiv.) and anhydrous DMF (15 mL). NBS (2.14 g, 12 mmol, 4 equiv.) was added in one portion, and the reaction mixture was heated at 60 °C overnight. After cooling to room temperature, H₂O (25 mL) was added and the mixture was stirred for 15 minutes. The precipitate was filtered off, and it was then recrystallized with MeOH/CHCl₃. 571 mg, 59%. ¹H-NMR 400 MHz (CDCl₃): δ (ppm) 7.17 (s, 2H). Consistent with literature reports.⁶

3. ¹H-NMR for Compounds 2-12.







Figure S2. ¹H NMR of compound 3 in CDCl₃ at 25 °C and 400 MHz.



Figure S4. ¹H NMR of Compound 5 in CDCl₃ at 25 °C and 400 MHz.



¹³ ¹² ¹¹ ¹⁰ ⁹ ⁸ ⁷ ⁶ ⁵ ⁴ ³ ² ¹ ⁰ ⁻¹ Figure S6. ¹H-NMR of monomer 9 in CDCl₃ at 25 °C and 400 MHz.



Figure S8. ¹H-NMR of monomer 12 in CDCl₃ at 25 °C and 400 MHz.



Figure S9. ¹H-NMR of monomer 13 in CDCl₃ at 25 °C and 500 MHz.



Figure S10. ¹H-NMR of PDCBT (Stille) collected in CDCl₃ at 25 °C and 500 MHz.



Figure S11. ¹H-NMR of PDCBT prepared via DArP (entry 3 of Table 1). Collected in CDCl₃ at 25 °C and 500 MHz.



Figure S12. ¹H-NMR of PDCTT (entry 8 of Table 1) collected in CDCl₃ at 25 °C and 500 MHz. (*)Denotes potential end-group.



Figure S13. ¹H-NMR of PDCBTz (entry 9 of Table 1) collected in CDCl₃ at 25 C and 600 MHz. (*) Denotes potential end-group.



•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
1.75	7.74	7.73	7.72	7.71	7.70	7.69	7.68	7.67	7.66	7.65	7.64	7.63	7.62	7.61	7.60	7.59

Figure S14. Expanded view of the region δ (ppm)7.75-7.55 in the ¹H-NMR spectra for PDCBT prepared by DArP (top) and Stille (bottom). Detailing what are likely penultimate protons for the respective DArP and Stille polymers.

5. Polymer GIXRD

Polymer	20	$d_{100}(Å)$	Height	FWHM (degrees)	Crystallite size
	(degrees)				(nm)
PDCBT- Stille	4.250	20.7729	12801	0.531	14.96546
PDCBT-DArP	4.151	21.2673	2430	0.593	13.40035
PDCBTz	4.251	20.7714	5016	0.691	11.50024

6. GPC Traces



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