

Supporting Information for

**QUANTITATIVE COMPARISON OF THE COPOLYMERIZATION KINETICS IN
CATALYST-TRANSFER COPOLYMERIZATION TO SYNTHESISE
POLYTHIOPHENES**

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I. Instrumentation

NMR Spectroscopy: ^1H NMR spectra of all monomer consumption experiments were taken on Bruker AVANCE 300 or 500 MHz. ^1H NMR spectra of all homopolymer and copolymer samples were taken on 500 MHz of the AVANCE NEO series from Bruker, which is supported by grant NIH S10 OD030224-01A1. All solution samples were prepared in deuterated chloroform.

MALDI-TOF: MALDI-TOF spectra were taken from Bruker AutoFLEX II and Bruker TimsTOF flex with a 337 nm laser. 2,2':5'2''-terthiophene was used as the matrix for the samples.

GC-MS: GC-MS analyses were performed using an Agilent 5973 instrument with a HP-5MS 5% phenyl methyl column.

GPC: Dispersities of polymers were taken from the Viscotek TDA 305 GPC coupled with RI detectors, multi-angle light scattering detectors and viscometers. The eluent was tetrahydrofuran at 1 mL/min with the conventional calibration of polystyrene standard.

II. Monomer Synthesis Procedure

3-(4-octylphenyl)thiophene:

In an acid-washed and oven dried 250 mL round bottom flask, 3-thienylboronic acid (5 g, 39.1 mmol), 4-octyl-bromobenzene (8.46 g, 35.5 mmol) and tribasic potassium phosphate (10 g, 47.1 mmol) were degassed *in vacuo* for 30 min and switched to N_2 . Anhydrous n-butanol (78.1 mL) was subsequently added to dissolve the solid mixture. $\text{Pb}_2(\text{dba})_3$ (0.179 g, 0.195 mmol) and 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos, 0.0559 g, 0.117 mmol) were added to the mixture in one portion. The reaction was heated to 100 °C and run for overnight. The solvent was removed under reduced pressure and the mixture was passed through a silica plug with hexane. The solvent was further removed under reduced pressure to obtain white flaky solids. 6.77g, 70%

yield. ^1H NMR (500 MHz, CDCl_3) δ 7.53 – 7.50 (m, 2H), 7.41 (dd, $J = 2.6, 1.7$ Hz, 1H), 7.39 – 7.36 (m, 2H), 7.23 – 7.19 (m, 2H), 2.65 – 2.60 (m, 2H), 1.68 – 1.59 (m, 2H), 1.40 – 1.21 (m, 12H), 0.92 – 0.85 (m, 3H).

2-bromo-3-(4-octylphenyl)thiophene:

In a 100 mL three-neck round bottom flask, 3-(4-octylphenyl)thiophene (5 g, 18.3 mmol) was added and degassed *in vacuo* for 30 min. After switching to a N_2 environment, the monomer was dissolved in anhydrous THF (50 mL). The mixture was then placed in an ice bath and covered by aluminum foil. N-bromosuccinimide (NBS, 3.09 g, 17.4 mmol) was added into the mixture in one batch. The reaction mixture was left on the ice bath for 1 hour and brought back to the room temperature for an additional 1 hour. 1 M NaOH (10 mL) was used to quench the reaction. The mixture was extracted with hexane. The organic phase was later washed with brine and dried with Na_2SO_4 . After the solvent was removed under reduced pressure, the oily crude went through a silica gel column chromatography with hexane. 5.81 g, 95% yield, light yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 7.48 – 7.44 (m, 2H), 7.26 (d, $J = 5.6$ Hz, 1H), 7.25 – 7.21 (m, 2H), 7.01 (d, $J = 5.6$ Hz, 1H), 2.66 – 2.61 (m, 2H), 1.69 – 1.59 (m, 2H), 1.41 – 1.20 (m, 12H), 0.93 – 0.82 (m, 3H).

2-bromo-3-(4-octylphenyl)-5-iodothiophene:

In a 100 mL three-neck round bottom flask, 2-bromo-3-(4-octylphenyl)thiophene (5 g, 14.2 mmol) was added and degassed *in vacuo* for 30 mins. The flask was switched to N_2 environment and anhydrous DCM (50 mL) was added to dissolve the monomer. The mixture was placed on an ice bath. Iodine (1.98 g, 7.81 mmol) and iodobenzene diacetate (2.75 g, 8.52 mmol) were added to the solution in one batch. The reaction was brought back to the room temperature after the solution was stirred for 30 min. After for 4 h reaction time, the reaction was quenched with 10% aqueous

Na₂S₂O₃. The mixture was extracted with Et₂O. The extracted organic phase was washed with 10% aqueous Na₂S₂O₃ and dried with MgSO₄. The solvent was evaporated under reduced pressure and the crude was purified by a silica gel column chromatography with hexane. 6.44 g, 13.5 mmol, light yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.43 – 7.39 (m, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.19 (s, 1H), 2.67 – 2.61 (m, 2H), 1.69 – 1.60 (m, 2H), 1.41 – 1.22 (m, 10H), 0.89 (t, *J* = 6.8 Hz, 3H).

2-bromo-3-(6-bromohexyl)-5-iodothiophene

The monomer was prepared based on previously reported method in the literature.¹

¹H NMR (300 MHz, CDCl₃) δ 6.96 (s, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.59 – 2.46 (m, 2H), 1.93 – 1.78 (m, 2H), 1.64 – 1.23 (m, 6H).

III. GC-MS Calibration

A series of aliquots containing constant concentration of TDC (8.47×10^{-6} M) and varied concentrations of (A) to (E) were prepared in DCM and analyzed by Agilent 5973 (**Figure S12**). With known concentrations of TDC and analytes in the calibration samples, the response factor of

each analyte could be calculated by the equation below. The response factors are the slopes calculated from the linear fitting of the calibration samples.

$$\text{Analyte peak area} = \text{Response Factor} \times \frac{\text{TDC peak area}}{[\text{TDC}]} \times [\text{Analyte}]$$

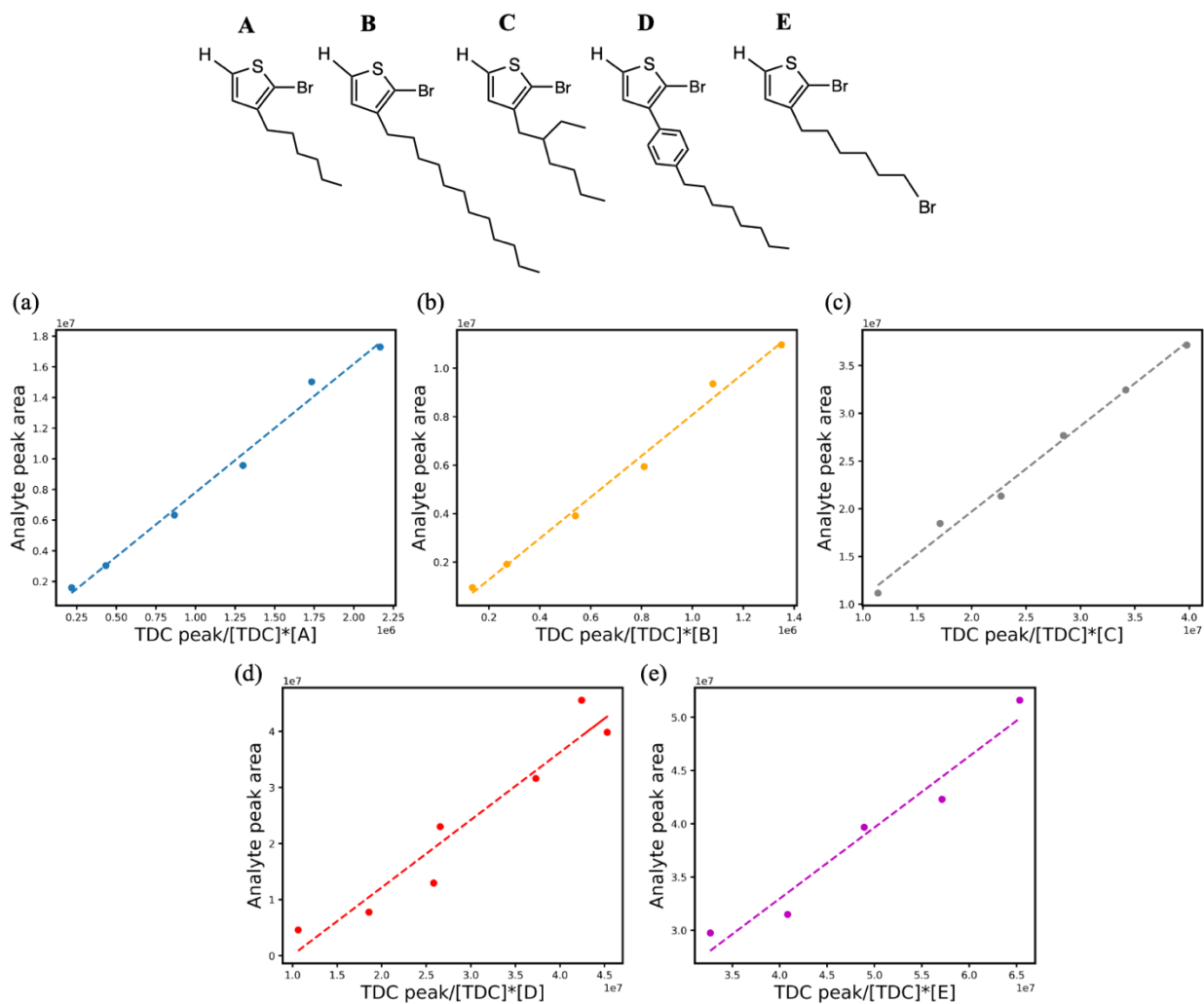


Figure S1. GC-MS calibration curve of quenched monomers with TDC.

IV. Polymer Characterization

4.1. Homopolymer Characterization

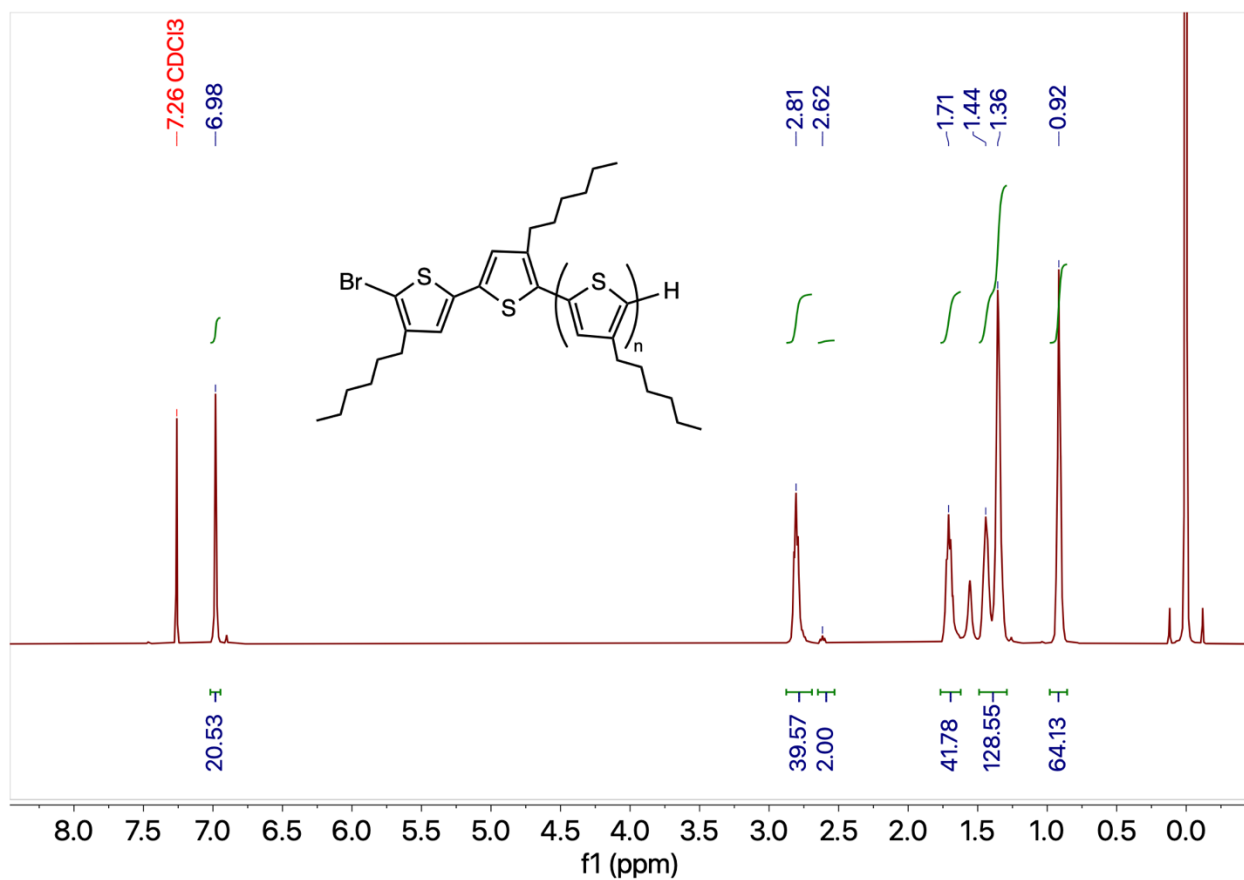


Figure S2. ¹H NMR spectrum of P3HT. The M_n from DP is 7100 g/mol. The estimated M_n from the monomer conversion and targeted DP was 8200 g/mol.

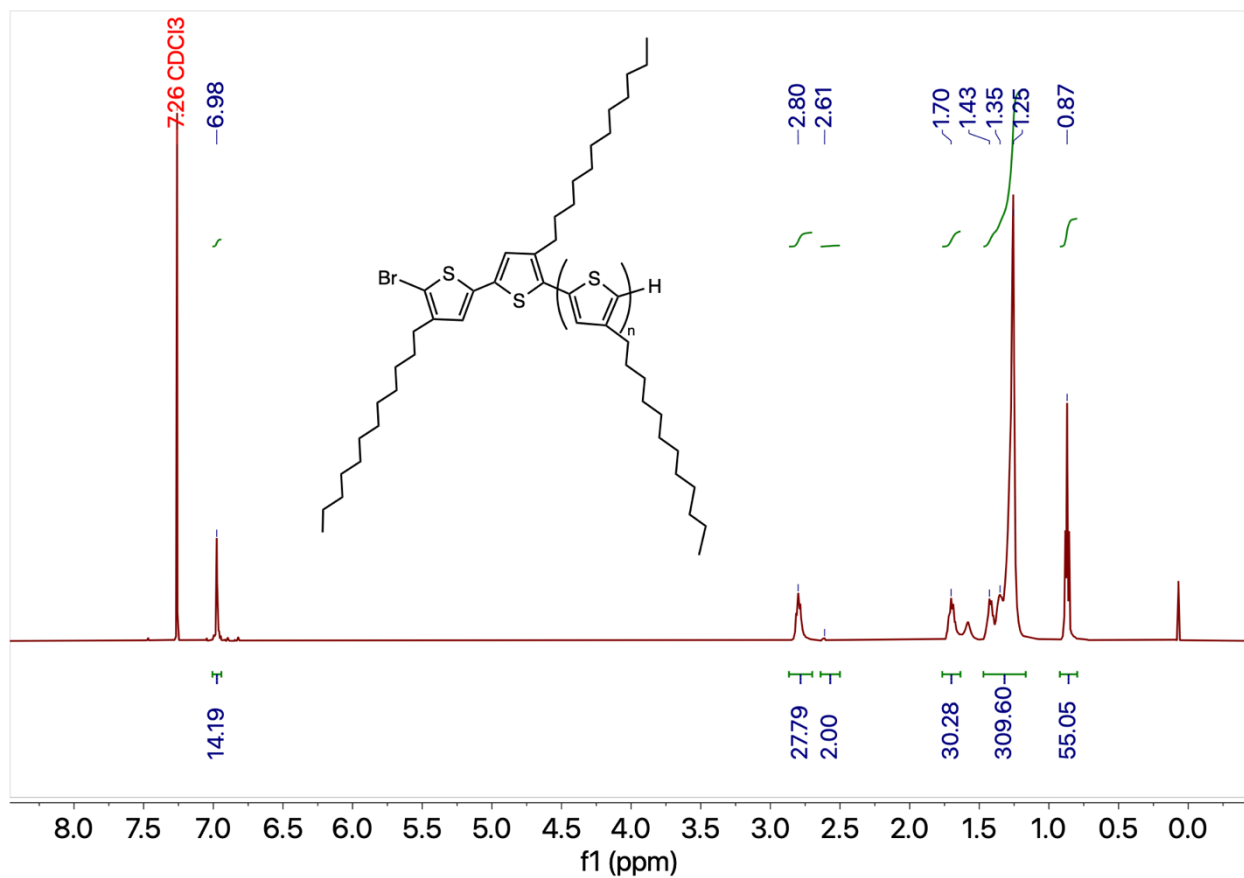


Figure S3. ^1H NMR spectrum of P3DDT. The estimated M_n from DP is 7600 g/mol. The estimated M_n from the monomer conversion and targeted DP was 9000 g/mol.

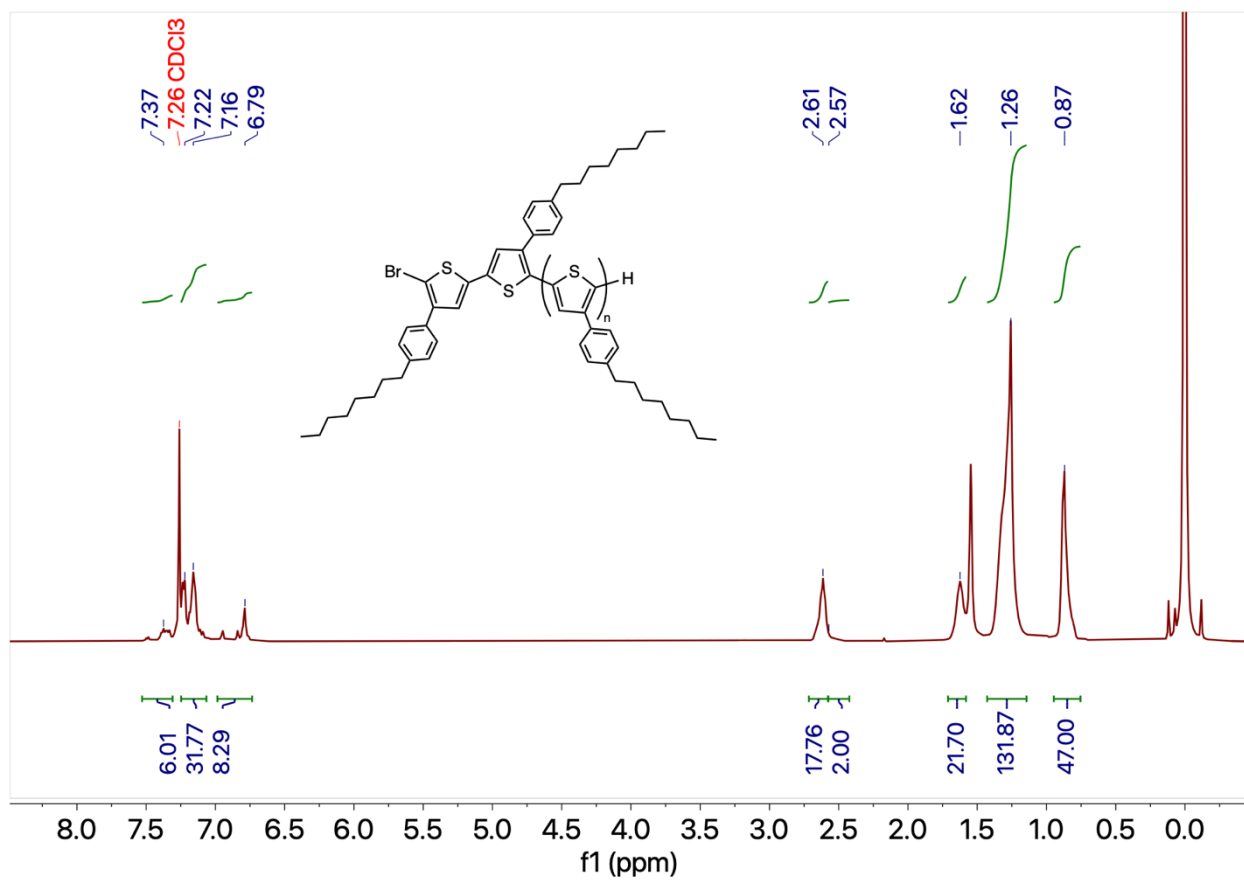


Figure S4. ¹H NMR spectrum of P3OPT. The estimated M_n from DP is 5500 g/mol. The estimated M_n from the monomer conversion and targeted DP was 8700 g/mol.

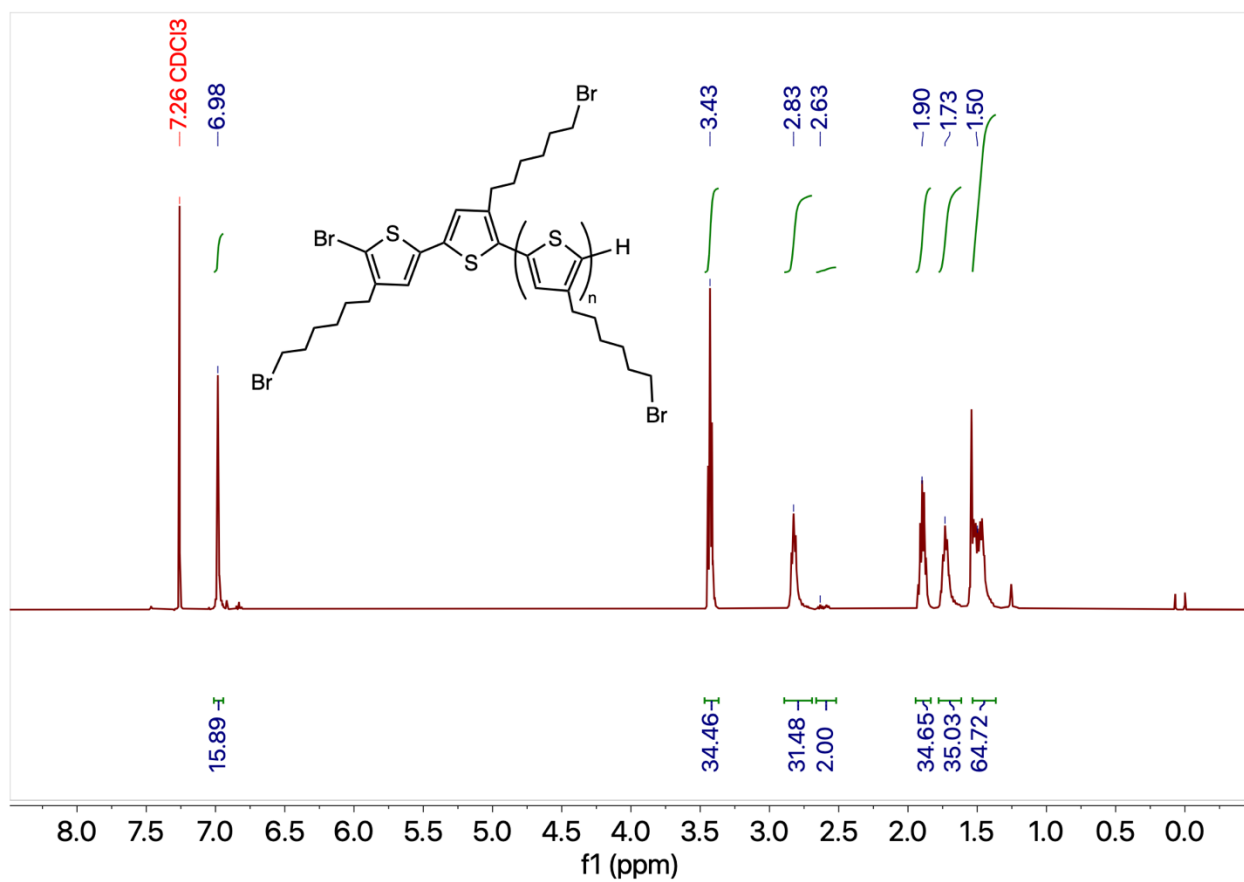


Figure S5. ¹H NMR spectrum of P3BrHT. The estimated M_n from DP is 8900 g/mol. The estimated M_n from the monomer conversion and targeted DP was 10000 g/mol.

4.2. Copolymer Characterization

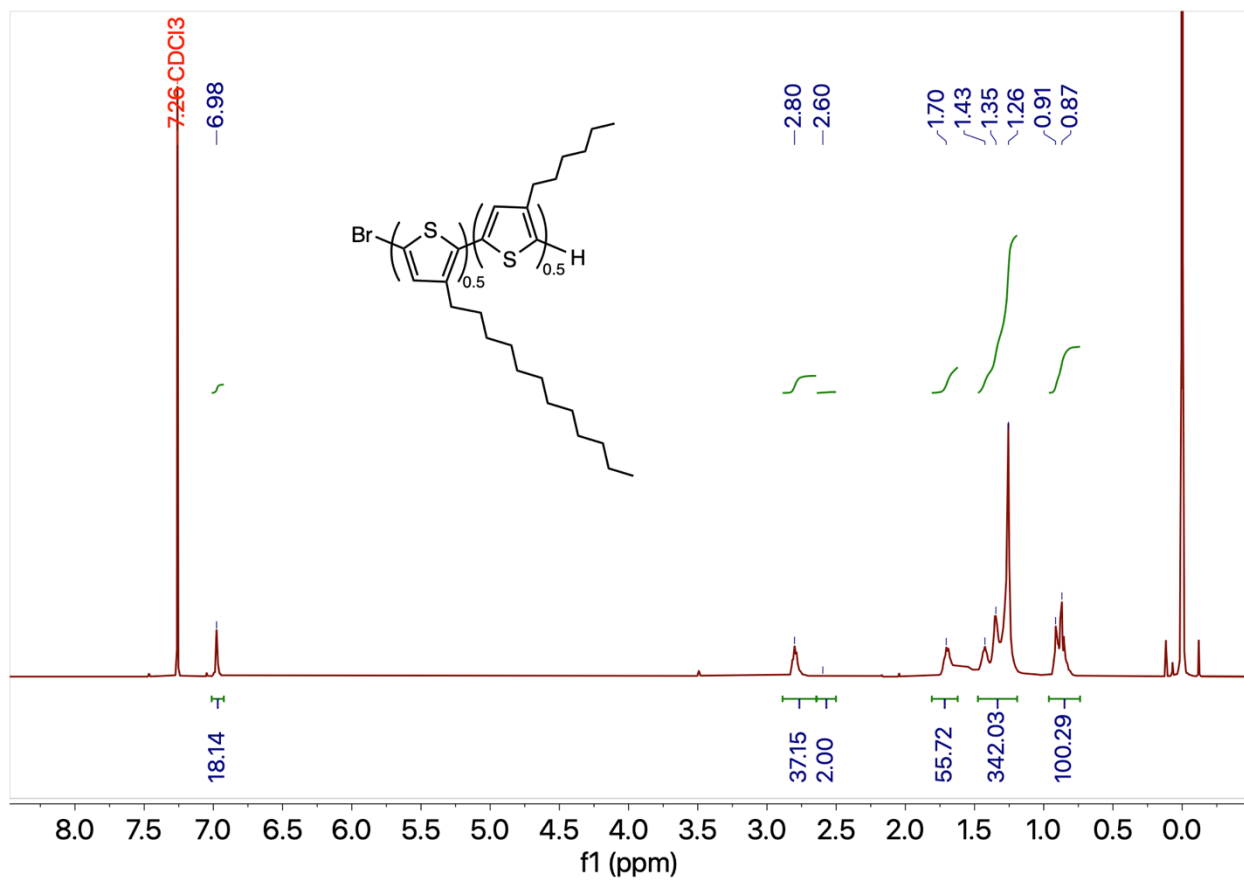


Figure S6. Representative ¹H NMR spectrum of P(3HT-co-3DDT). The estimated M_n from DP is 8200 g/mol. The estimated M_n from the monomer conversion is 8800 g/mol.

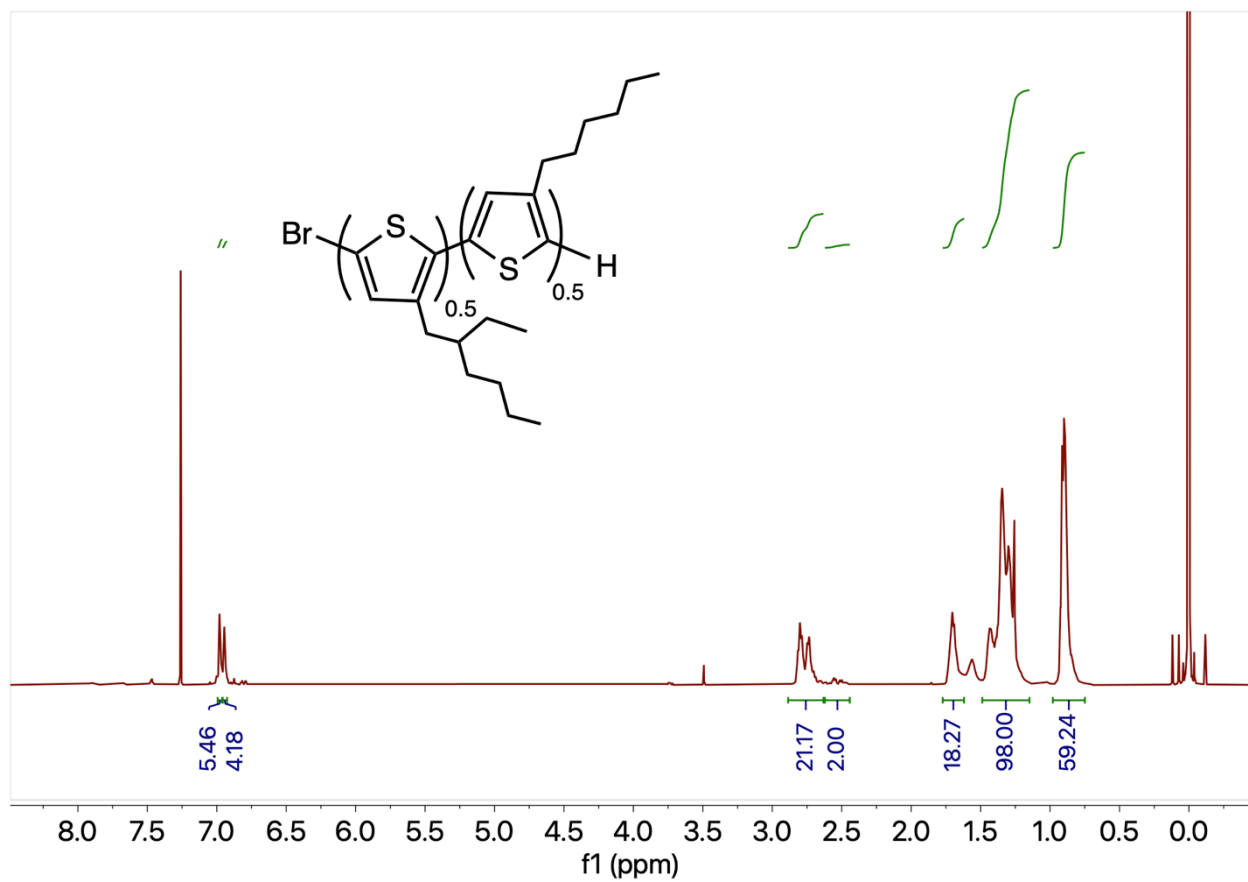


Figure S7. Representative ¹H NMR spectrum of P(3HT-co-3EHT). The estimated M_n from DP is 4300 g/mol. The estimated M_n from the monomer conversion is 5000 g/mol.

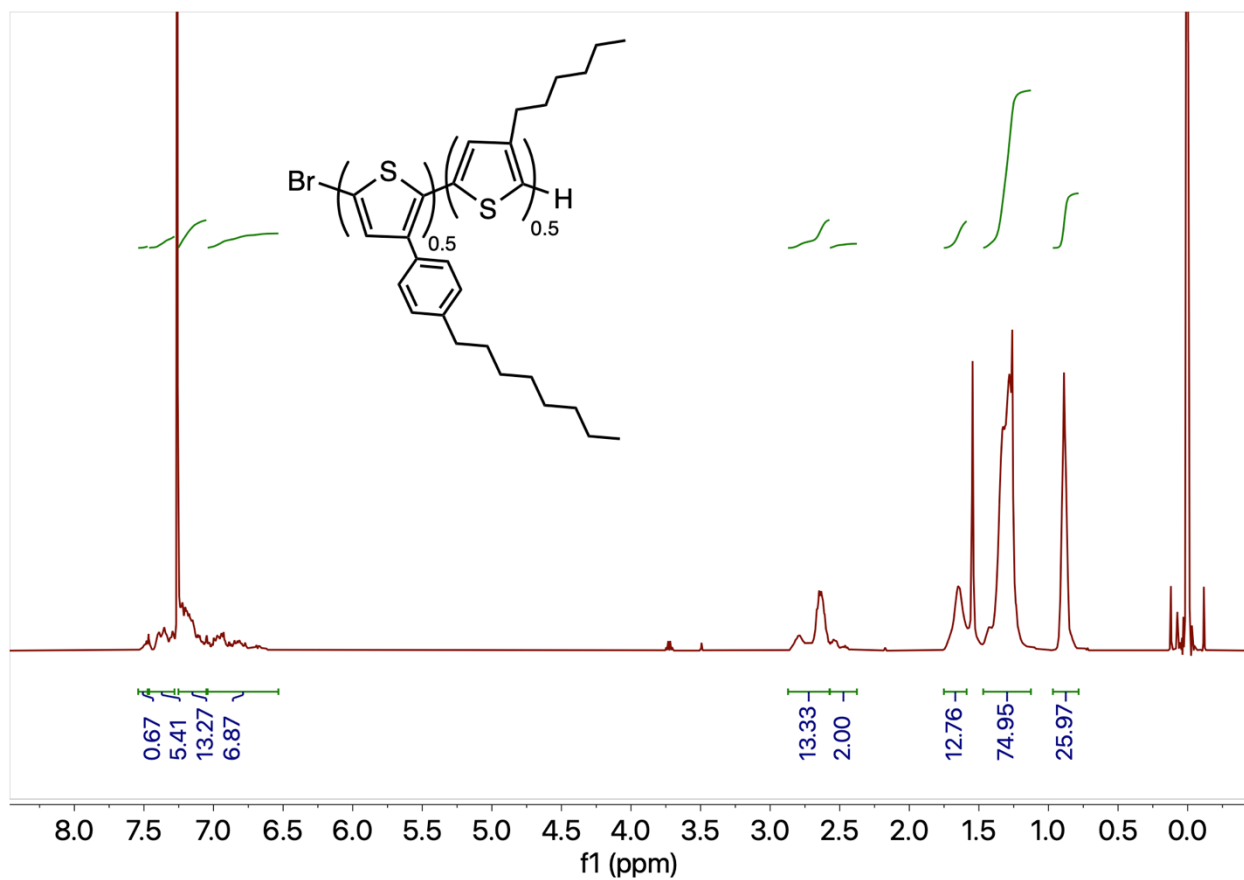


Figure S8. Representative ¹H NMR spectrum of P(3HT-co-3OPT). The estimated M_n from GPC is 6600 g/mol. The estimated M_n from the monomer conversion is 9600 g/mol.

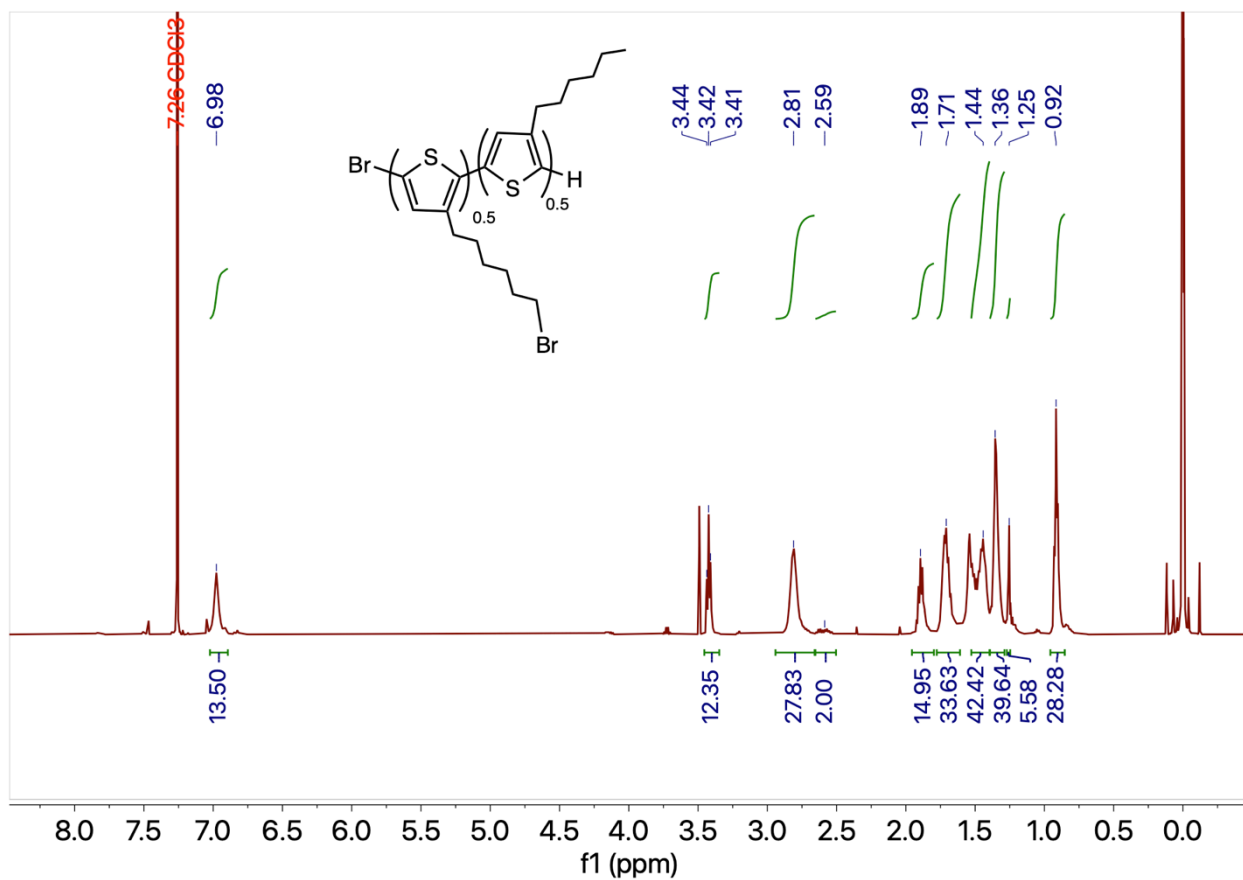


Figure S9. Representative ¹H NMR spectrum of P(3HT-co-3BrHT). The estimated M_n from DP is 6300 g/mol. The estimated M_n from the monomer conversion is 5800 g/mol.

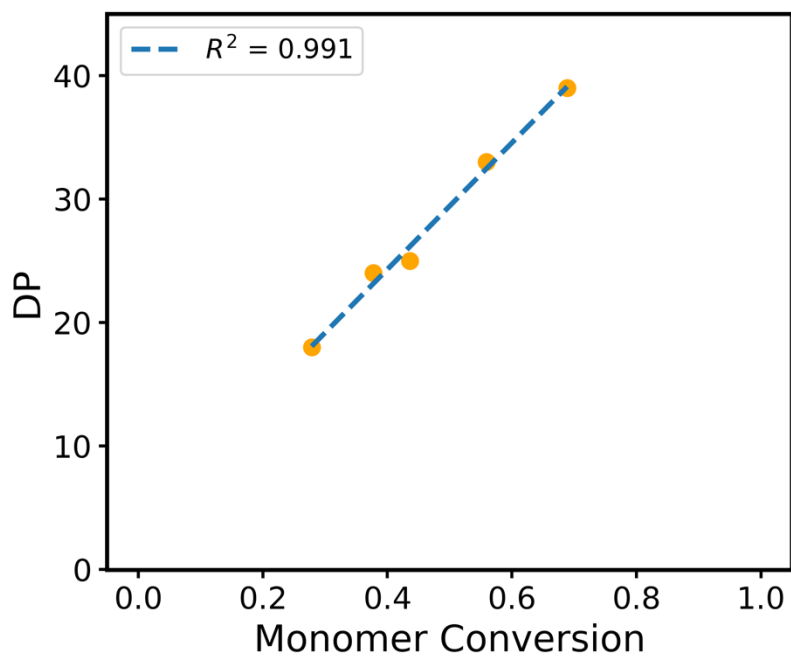


Figure S10. DP vs. monomer conversion of the copolymerization of P(3HT-co-3DDT).

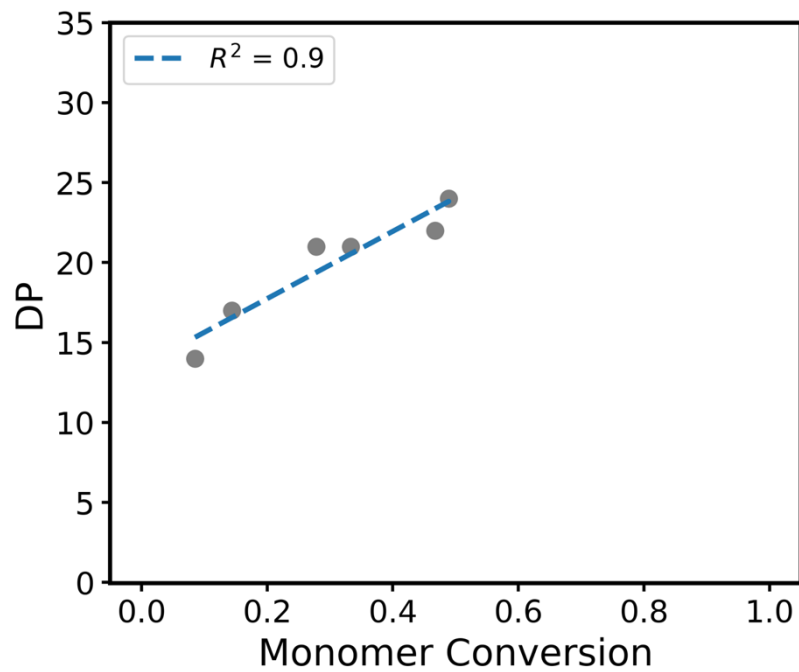


Figure S11. DP vs. monomer conversion of the copolymerization of P(3HT-co-3EHT).

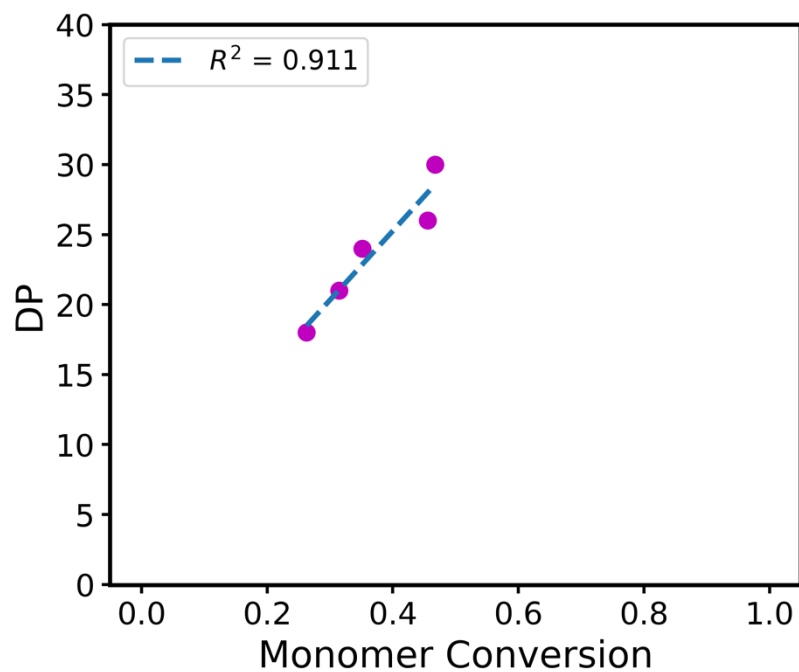


Figure S12. DP vs. monomer conversion of the copolymerization of P(3HT-co-3BrHT).