

Supporting Information

“In-Water” Direct Arylation Polymerization (DArP) under Aerobic Emulsion Conditions

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1. General

p-Cymene was purchased from Alfa Aesar (97%) and dried from CaH₂ followed by vacuum distillation to 3 Å sieves. Pd(OAc)₂ (Palladium(II) acetate trimer ≥ 99.98%) (BeanTown Chemical), PdCl₂(PPh₃)₂ (99.95%, BeanTown Chemical), tris(o-methoxyphenylphosphine) (Alfa Aesar) were purchased and used as received.

Preparation of the emulsions: (adapted from Beverina et al.¹) 2 wt% aqueous dispersion of K-EL was prepared by mixing 1.8 g of Kolliphor EL in 88.2 mL of deionized water. 100 mL of K-EL 2 wt% H₂O:toluene (9:1 v/v) or K-EL 2 wt% H₂O:p-cymene (9:1 v/v) emulsion was then prepared by stirring the 2 wt% K-EL aqueous solution with 10 mL of toluene/p-cymene overnight until a stable, milky dispersion is obtained.

9,9-Dioctyl-2,7-dibromofluorene was purchased from Combi-Blocks (98%) and recrystallized from EtOH to form a white solid prior to use. 2,2'-Bithiophene was purchased from Matrix Scientific (97%) and subjected to a short column chromatography followed by recrystallization from MeOH prior to use. 1,4-dibromo-2,5-bis[(2-hexyldecyl)oxy]-benzene,² 4,7-di-2-thienyl-2,1,3-benzothiadiazole,² were prepared previously following reported procedures.

Monomer NMR were recorded at 25 °C using CDCl₃ on a Varian Mercury Varian VNMR-500 MHz. Polymer NMR was obtained on a Varian VNMR-600 MHz. All spectra were referenced to CHCl₃ (7.26 ppm) and C₂D₂Cl₄ (6.03 ppm), unless otherwise noted.

Number average molecular weight (M_n) and polydispersity (\mathcal{D}) were determined by size exclusion chromatography (SEC) using a Agilent 1260 Infinity II High Temperature GPC and a Differential Refractive Index (DRI) detector, with 80 °C HPLC grade 1,2,4-trichlorobenzene (TCB) as eluent at a flow rate of 1.0 mL/min. The instrument was calibrated vs. polystyrene standards (1050–3,800,000 g/mol). Polymer samples were dissolved in HPLC grade TCB at a concentration of 0.5 mg/mL, stirred until dissolved, 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.

2. Visualization of emulsions and DArP in emulsion conditions

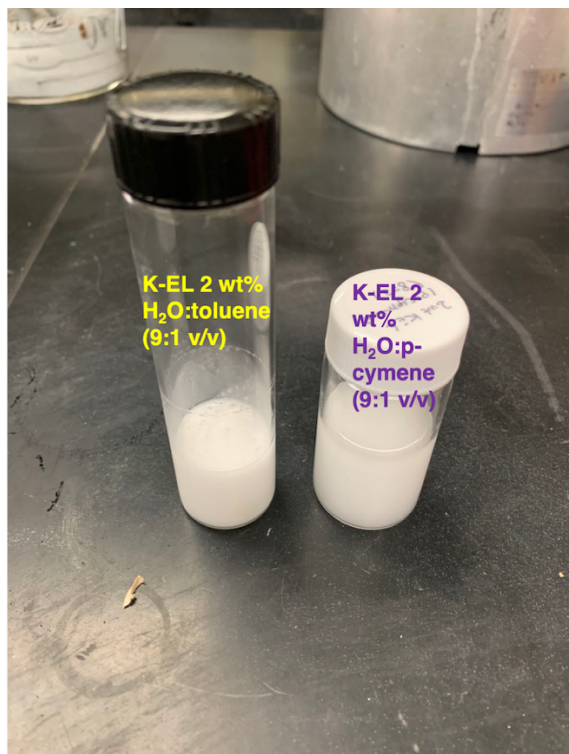


Figure S1. Comparison between K-EL 2 wt% H₂O:toluene (9:1 v/v) emulsion (left) and K-EL 2 wt% H₂O:p-cymene (9:1 v/v) emulsion (right).

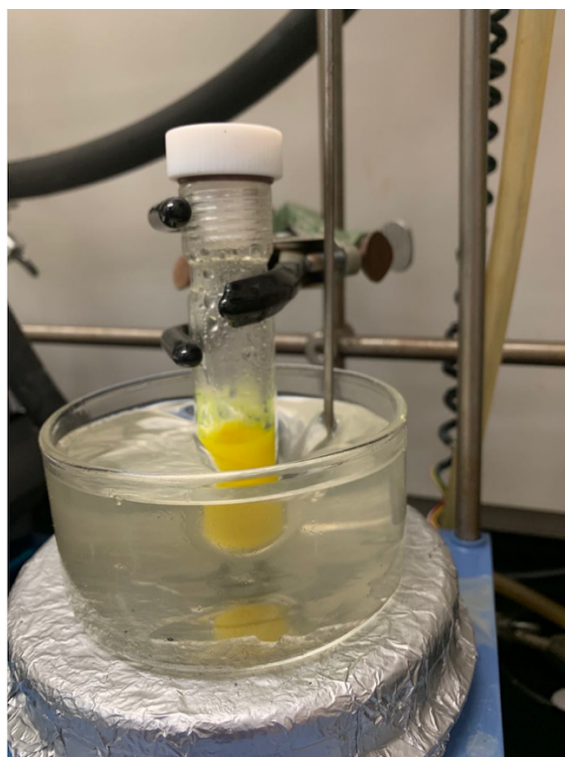


Figure S2. DArP conducted using K-EL 2 wt% H₂O:p-cymene (9:1 v/v) emulsion.

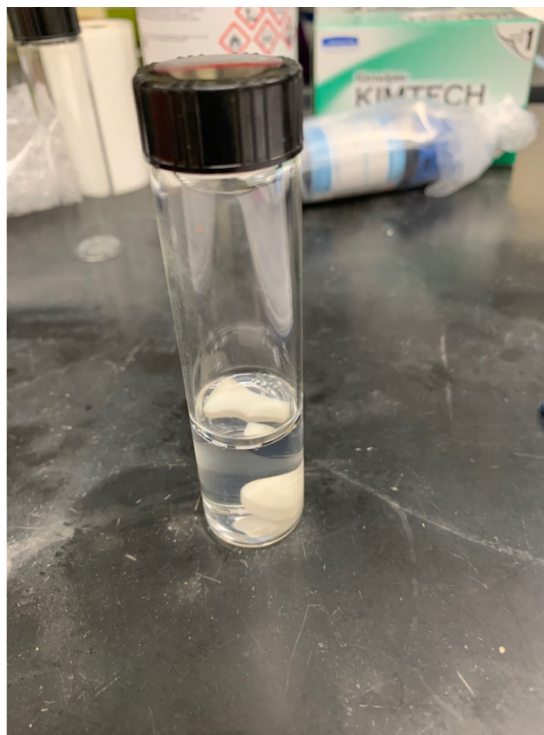


Figure S3. The breakage of emulsion (separated into two layers) as a result of increasing the loading of K_2CO_3 to 40 equiv., which increases the density of the aqueous solution (Table 1, entry 9).

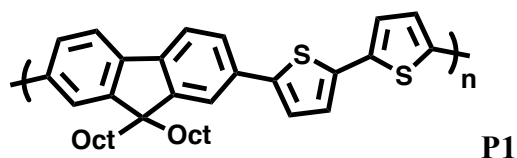
3. General polymerization procedures

For the synthesis of P1 under emulsion, aerobic conditions (Table 1, entry 7 as an example):

An 15 mL pressure vessel equipped with a stir-bar was added 9,9-dioctyl-2,7-dibromofluorene (0.4 mmol, 1.0 equiv.), 2,2'-bithiophene (0.4 mmol, 1.0 equiv.), K_2CO_3 (1.28 mmol, 3.2 equiv.), neodecanoic acid (0.4 mmol, 1.0 equiv.), tris(o-methoxyphenylphosphine) (0.064 mmol, 0.16 equiv), $\text{PdCl}_2(\text{PPh}_3)_2$ (0.016 mmol, 0.04 equiv), were added in air. 1.6 mL of the prepared K-EL 2 wt% H_2O :p-cymene (9:1 v/v) emulsion was added in air to give the desired concentration of 0.25 M. The vessel was then sealed with a Teflon screw-cap with a rubber o-ring and submerged in a pre-heated oil bath at 130 °C for 48 hours. The reaction was then cooled to room temperature and the mixture was diluted with 2 mL of CHCl_3 and then precipitated into a cold 10% (v:v) NH_4OH /methanol solution with high-stirring (100 mL). The solids were then filtered into a Soxhlet thimble and purified via Soxhlet extraction (methanol, hexanes, and CHCl_3). The CHCl_3 fraction was concentrated to ~1-2 mL, and re-precipitated into cold methanol with vigorous stirring. The polymer was then filtered and further dried overnight under vacuum (~100 mtorr).

For the synthesis of P1 under emulsion, N₂ conditions (Table 1, entry 8):

An oven-dried 15 mL pressure vessel equipped with a stir-bar was stoppered with a rubber-septum and cooled under a flow of N₂. 9,9-dioctyl-2,7-dibromofluorene (0.4 mmol, 1.0 equiv.), 2,2'-bithiophene (0.4 mmol, 1.0 equiv.), K₂CO₃ (1.28 mmol, 3.2 equiv.), neodecanoic acid (0.4 mmol, 1.0 equiv.), tris(o-methoxyphenylphosphine) (0.064 mmol, 0.16 equiv), PdCl₂(PPh₃)₂ (0.016 mmol, 0.04 equiv), were added under N₂. 1.6 mL of the prepared K-EL 2 wt% H₂O:p-cymene (9:1 v/v) emulsion through the rubber septum to give the desired concentration of 0.25 M. The vessel was further sparged with N₂ (5 min.) and was then quickly sealed with a Teflon screw-cap with a rubber o-ring. The vessel was then submerged in a pre-heated oil bath at 130 °C for 48 hours. The reaction was then cooled to room temperature and the mixture was diluted with 2 mL of CHCl₃ and then precipitated into a cold 10% (v:v) NH₄OH/methanol solution with high-stirring (100 mL). The solids were then filtered into a Soxhlet thimble and purified via Soxhlet extraction (methanol, hexanes, and CHCl₃). The CHCl₃ fraction was concentrated to ~1-2 mL, and re-precipitated into cold methanol with vigorous stirring. The polymer was then filtered and further dried overnight under vacuum (~100 mtorr).

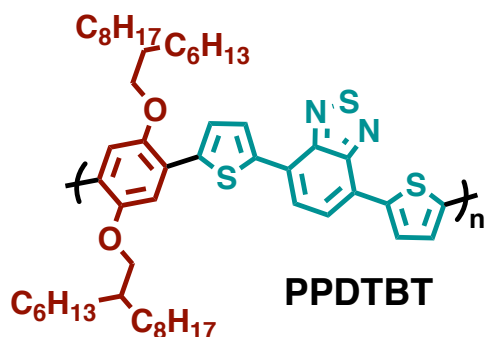


Poly(9,9-dioctyl-2,7-fluorene-alt-2,2'-bithiophene) (P1). ¹H NMR (600 MHz, C₂D₂Cl₄, 100 °C) δ 7.89 – 7.57 (m, 6H), 7.48 – 7.26 (m, 4H), 2.21-2.03 (br, 4H), 1.40-1.09 (m, 20H), 1.02-0.82 (m, 10H). Consistent with literature report.³

For the synthesis of PPDTBT under emulsion, aerobic conditions (Scheme 3):

An 15 mL pressure vessel equipped with a stir-bar was added 1,4-dibromo-2,5-bis[(2-hexyldecyl)oxy]-benzene (0.4 mmol, 1.0 equiv.), 4,7-di-2-thienyl-2,1,3-benzothiadiazole (0.4 mmol, 1.0 equiv.), K₂CO₃ (1.28 mmol, 3.2 equiv.), neodecanoic acid (0.4 mmol, 1.0 equiv.), tris(o-methoxyphenylphosphine) (0.064 mmol, 0.16 equiv), PdCl₂(PPh₃)₂ (0.016 mmol, 0.04 equiv), were added in air. 1.6 mL of the prepared K-EL 2 wt% H₂O:p-cymene

(9:1 v/v) emulsion was added in air to give the desired concentration of 0.25 M. The vessel was then sealed with a Teflon screw-cap with a rubber o-ring and submerged in a pre-heated oil bath at 130 °C for 48 hours. The reaction was then cooled to room temperature and the mixture was diluted with 2 mL of CHCl₃ and then precipitated into a cold 10% (v:v) NH₄OH/methanol solution with high-stirring (100 mL). The solids were then filtered into a Soxhlet thimble and purified via Soxhlet extraction (methanol, hexanes, and CHCl₃). The CHCl₃ fraction was concentrated to ~1-2 mL, and re-precipitated into cold methanol with vigorous stirring. The polymer was then filtered and further dried overnight under vacuum (~100 mtorr).



Poly[(2,5-bis(2-hexyldecyloxy)phenylene)-alt-(4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)](PPDTBT).
1 H NMR (600 MHz, CDCl₃, 25 °C): δ ppm 8.18 (br, 2H), 7.93 (br, 2H), 7.69 (br, 2H), 7.37 (br, 2H), 4.10 (br, 4H), 2.01 (br, 2H), 1.68 (br, 4H), 1.44–1.23 (m, 44H), 0.86–0.82 (br, 12H). Consistent with literature report.

4. Polymer NMR

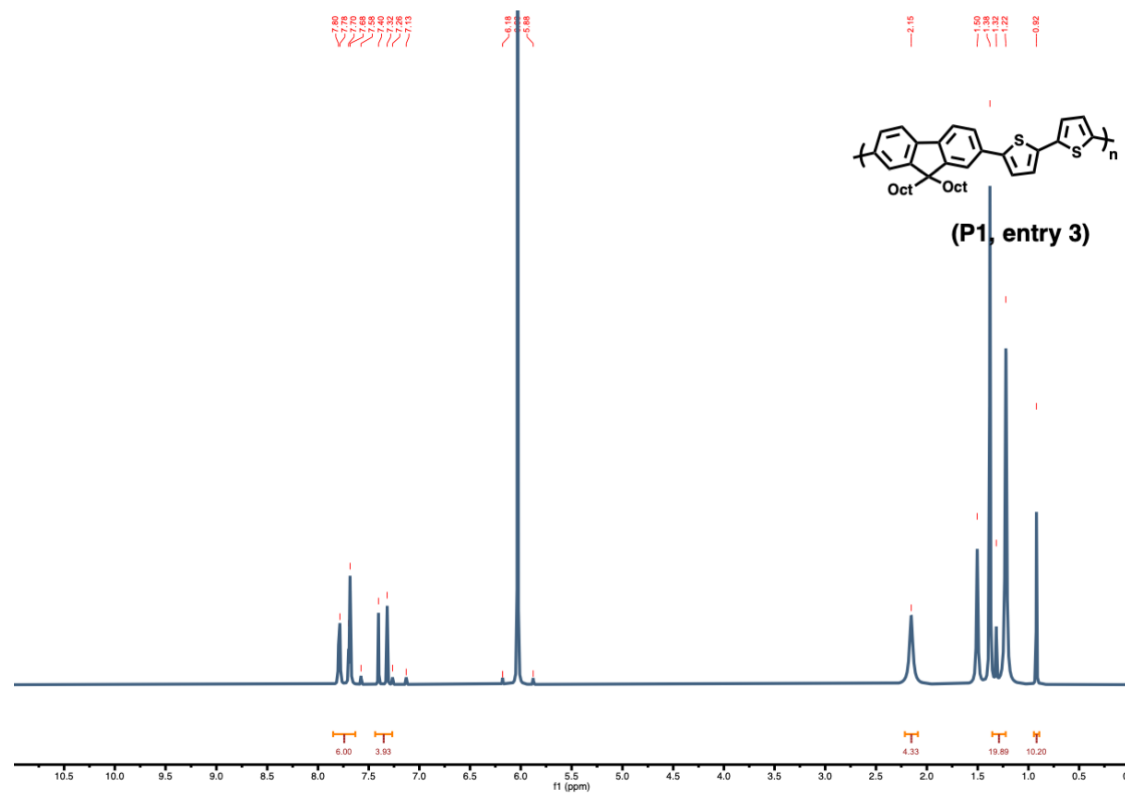


Figure S4. ¹H NMR of P1 synthesized using the conditions in Table 1 (entry 3). Collected in C₂D₂Cl₄ at 100 °C and 600 MHz. Referenced to previous reports.^{3,4}

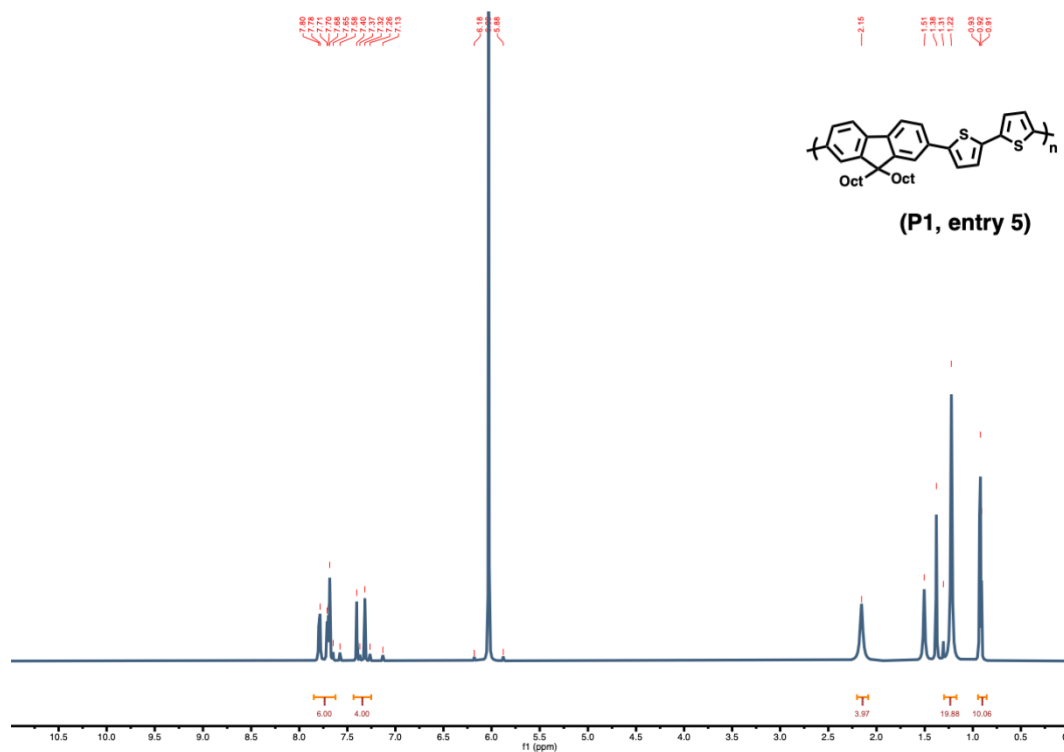


Figure S5. ^1H NMR of P1 synthesized using the conditions in Table 1 (entry 5). Collected in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100°C and 600 MHz. Referenced to previous reports.^{3,4}

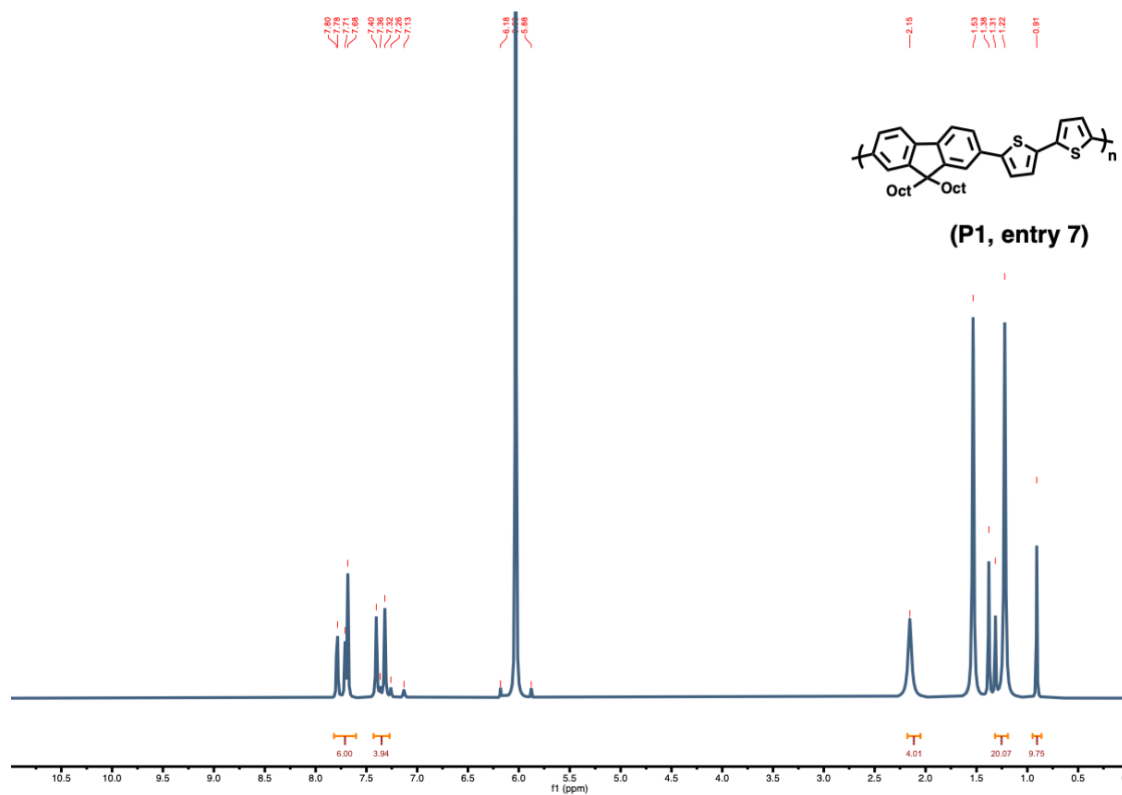


Figure S6. ^1H NMR of P1 synthesized using the conditions in Table 1 (entry 7). Collected in $\text{C}_2\text{D}_2\text{Cl}_4$ at 100°C and 600 MHz. Referenced to previous reports.^{3,4}

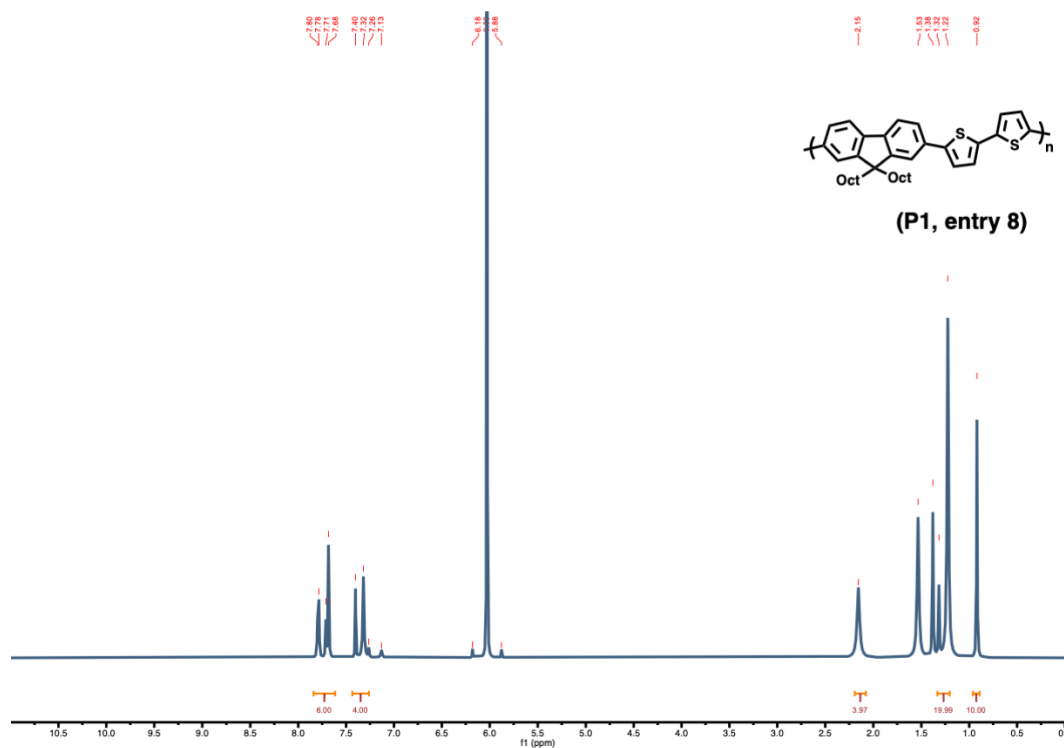


Figure S7. ^1H NMR of P1 synthesized using the conditions in Table 1 (entry 8). Collected in $\text{C}_2\text{D}_2\text{Cl}_4$ at $100\text{ }^\circ\text{C}$ and 600 MHz. Referenced to previous reports.^{3,4}

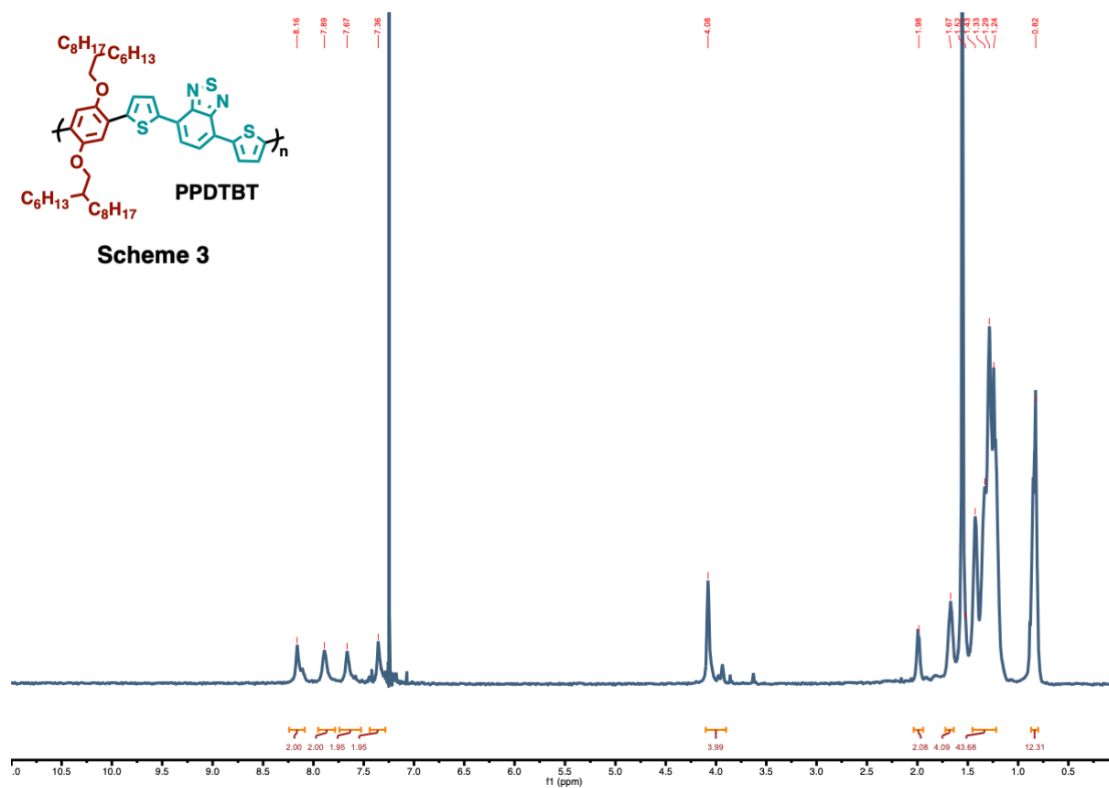


Figure S8. ^1H NMR of P1 synthesized using the conditions in Scheme 3. Collected in CDCl_3 at $25\text{ }^\circ\text{C}$ and 600 MHz. Referenced to previous reports.^{2,5}

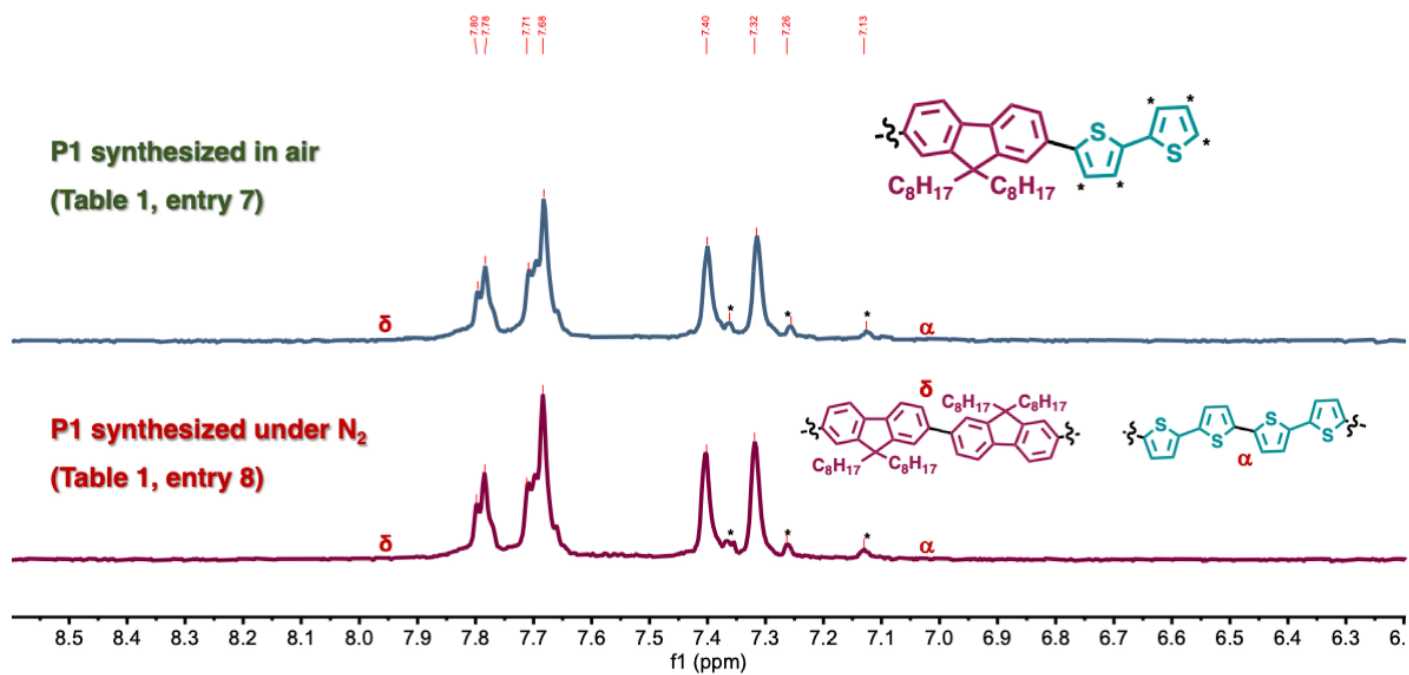


Figure S9. ¹H NMR analyses of P1 synthesized using H₂O/p-cymene 9:1 (v:v) emulsion in air and under N₂ atmosphere (Table 1, entry 7 and 8, respectively). Potential resonances and corresponding structures for end groups (*) and potential defects (δ , α) are denoted. Collected in C₂D₂Cl₄ at 100 °C and 600 MHz.

5. UV-vis spectra

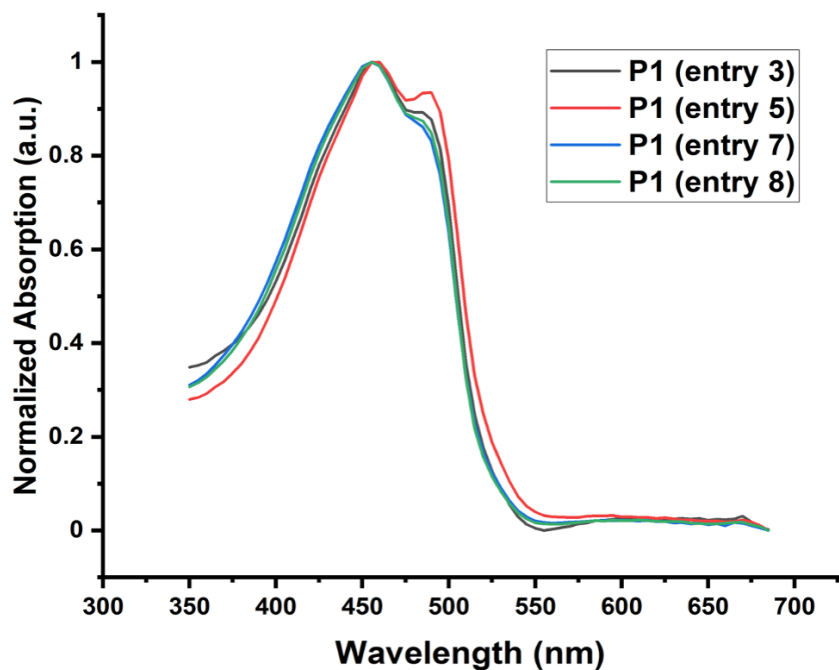


Figure S10. UV-vis spectra of P1 (Table 1, entry 3, 5, 7, 8) synthesized by using emulsion conditions.

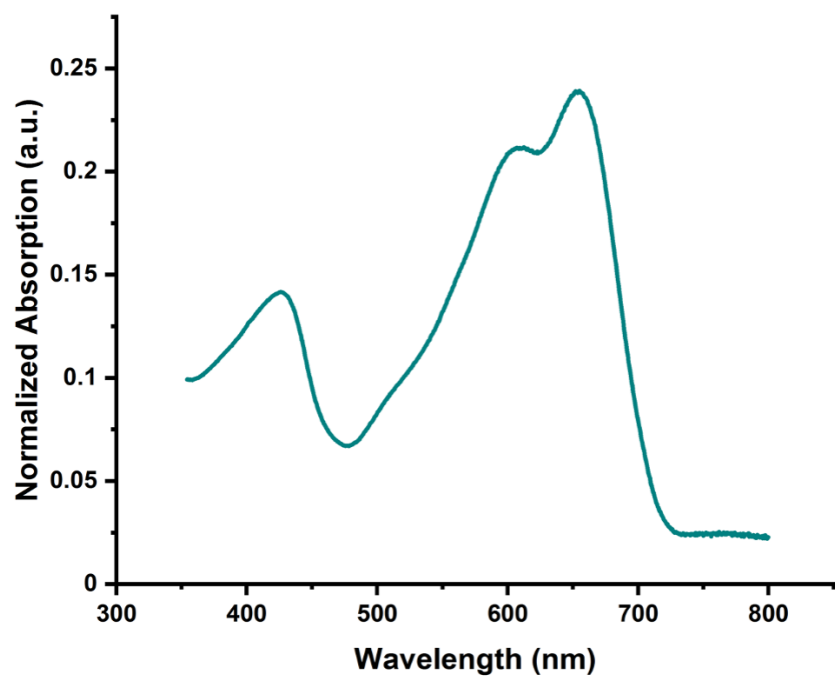


Figure S11. UV-vis spectra of PPDTBT (Scheme 3) synthesized by emulsion conditions.

6. Representative GPC Traces

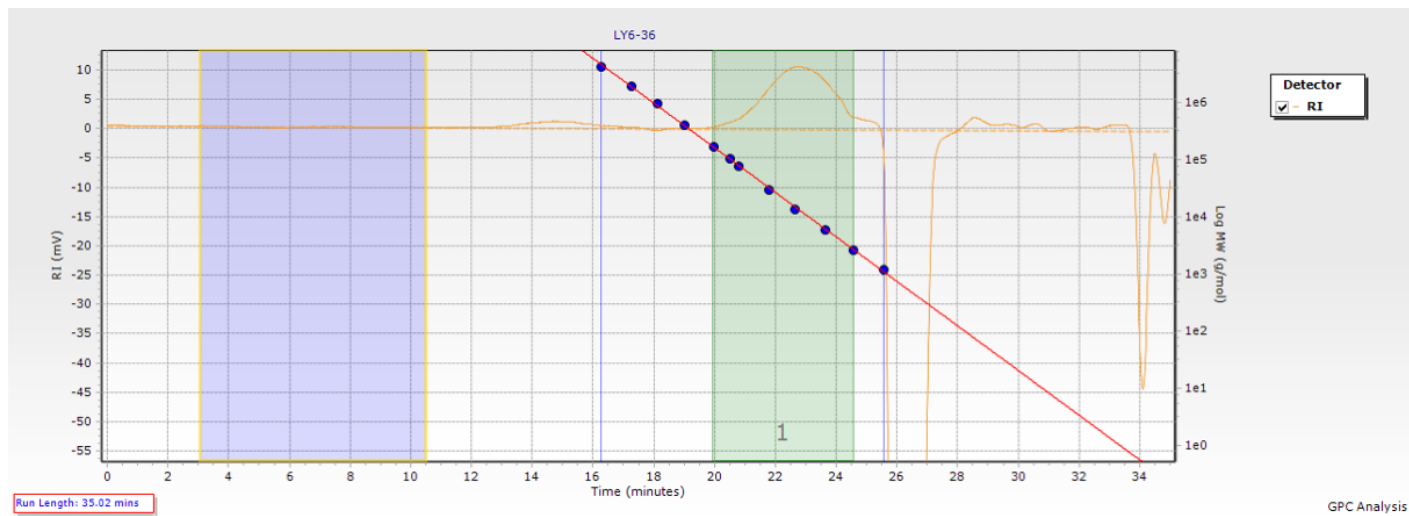


Figure S12. GPC trace of P1 (Table 1, entry 3): $M_n = 10.3$ kg/mol, $\bar{D} = 2.01$.

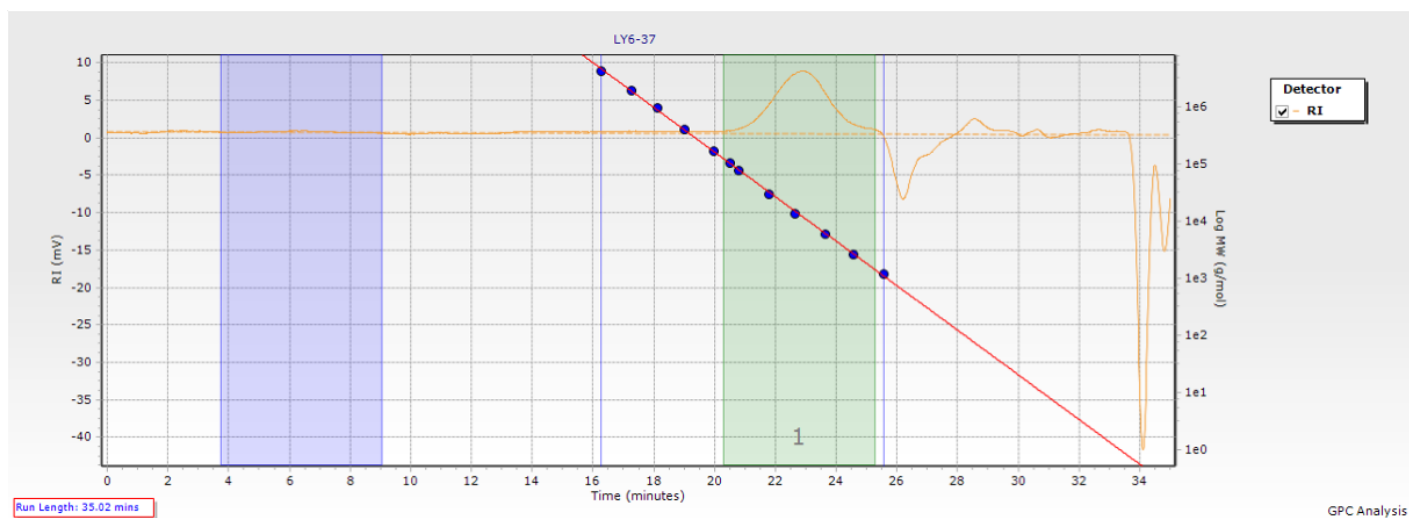


Figure S13. GPC trace of P1 (Table 1, entry 5): $M_n = 11.9$ kg/mol, $\bar{D} = 3.17$.

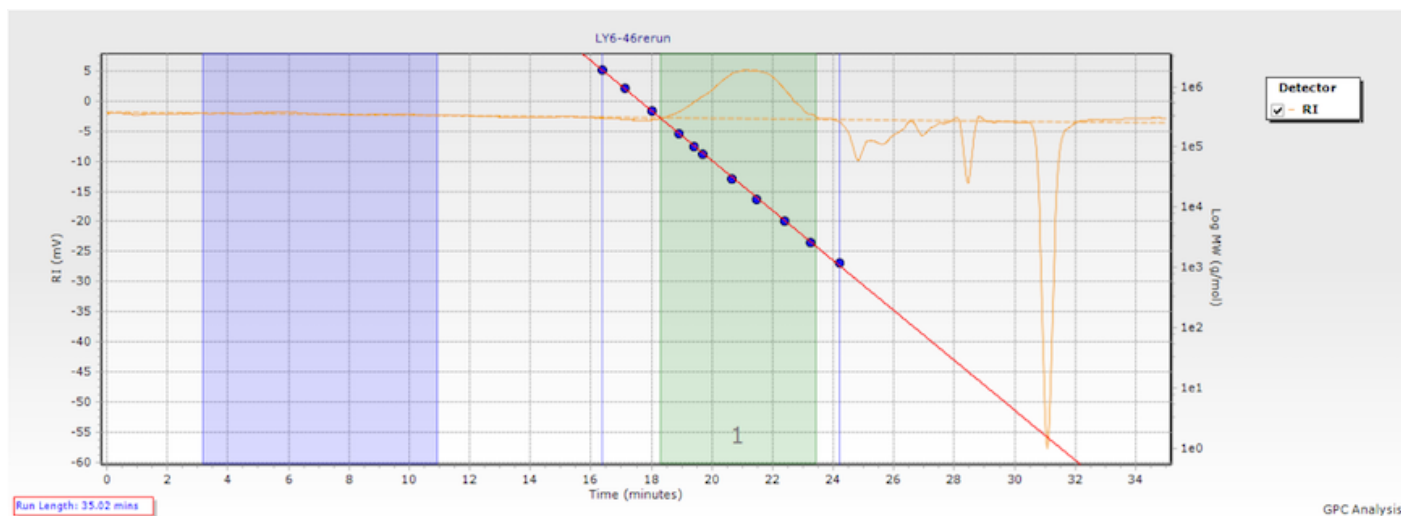


Figure S14. GPC trace of P1 (Table 1, entry 7): $M_n = 13.6$ kg/mol, $\bar{D} = 3.03$

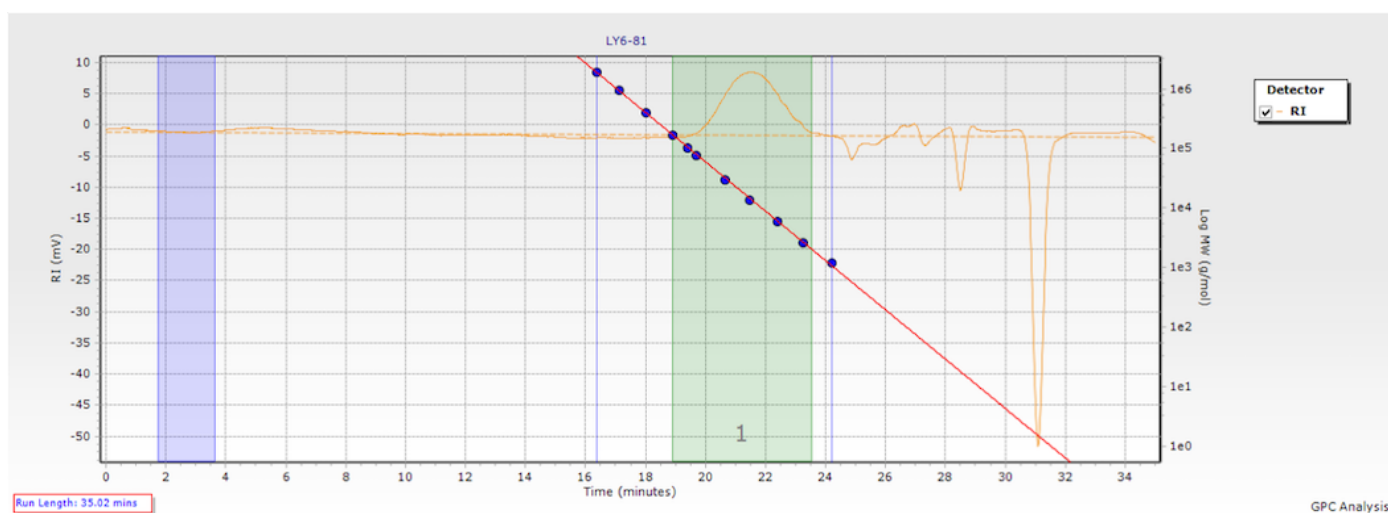


Figure S15. GPC trace of P1 (Table 1, entry 8): $M_n = 12.9$ kg/mol, $\bar{D} = 2.63$.

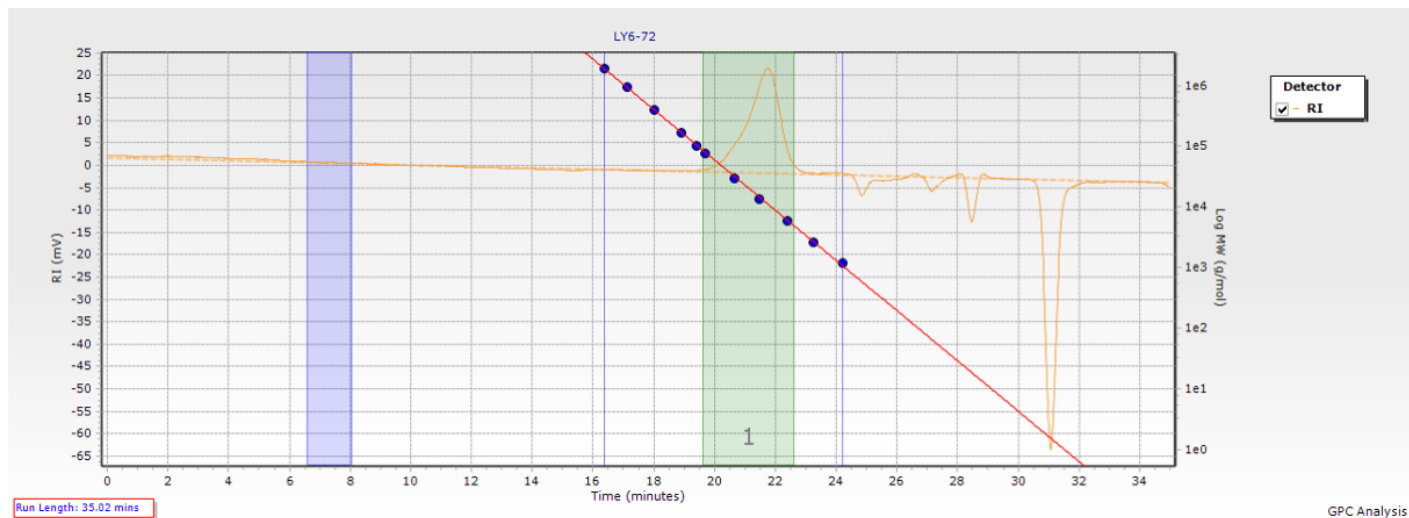


Figure S16. GPC trace of PPDTBT (Scheme 3): $M_n = 14.5$ kg/mol, $\mathcal{D} = 2.5$.

7. References

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- (3) Morin, P.-O.; Bura, T.; Sun, B.; Gorelsky, S. I.; Li, Y.; Leclerc, M. Conjugated Polymers à La Carte from Time-Controlled Direct (Hetero)Arylation Polymerization. *ACS Macro Lett.* **2015**, *4* (1), 21–24. <https://doi.org/10.1021/mz500656g>.
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