Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Investigation of Green and Sustainable Solvents for Direct Arylation Polymerization (DArP)

Robert M. Pankow, Liwei Ye, Nemal S. Gobalasingham, Neda Salami, Sanket Samal and Barry C. Thompson*

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

*Email: barrycth@usc.edu

1. General

All reactions were performed under dry N_2 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. Cs_2CO_3 was ground into a fine powder and dried at 120 °C in a vacuum oven before use. Tetrahydrofuran (THF) was dried over sodium/benzophenone before distillation. 2-MeTHF was dried over CaH_2 and distilled onto activated molecular sieves (3 Å) prior to use. Diethylcarbonate (DEC) and γ-Valerolactone (GVL) were stirred with K_2CO_3 and distilled onto activated molecular sieves (3 Å) prior to use. 1,4-dibromo-2,5-bis[(2-hexyldecyl)oxy]-benzene (**S1**), 4,7-di-2-thienyl-2,1,3-benzothiadiazole (**S2**), and 2-bromo-3-hexyl-thiophene (**S3**) were prepared following literature procedures.[1–4] All NMR were recorded at 25 °C using $CDCl_3$ on either a Varian Mercury 400 MHz, Varian VNMRS-500 MHz, or a Varian VNMR-600 MHz. All spectra were referenced to $CHCl_3$ (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 70 °C HPLC grade 1,2-dichlorobenzene (*o*-DCB) as eluent at a flow rate of 0.6 mL/min on one 300 × 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 Kα radiation source ($\lambda = 1.54$ Å) in the reflectivity and 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. Polymer Synthesis

General procedure for PPDTBT synthesis using a high-pressure vessel:
An oven-dried 15 mL high pressure vessel equipped with a stir-bar was stoppered with a rubber-septum and cooled under a flow of N_2. S1 (0.25 mmol), S2 (0.25 mmol) Cs_2CO_3 (3 equiv.), and $P(o\text{-anisyl})_3$ (8 mol %) were added to the vessel. The solvent was then added to the vessel via syringe to achieve the appropriate monomers' concentration, and it was degassed for 15 min. using N_2. Pd_2dba_3 (2 mol %) was then added quickly and the rubber septum replaced with a Teflon screw-cap with a rubber o-ring. The vessel was then submerged in a pre-heated oil bath (120 °C). After the polymerization, the reaction mixture was cooled to room temperature, the product was dissolved in dichlorobenzene, and then precipitated into cold MeOH. The polymer product was filtered off and purified using Soxhlet extraction with MeOH, hexanes, and $CHCl_3$. The chloroform fraction was concentrated and precipitated into cold methanol, the solid filtered off, and then dried overnight under vacuum.

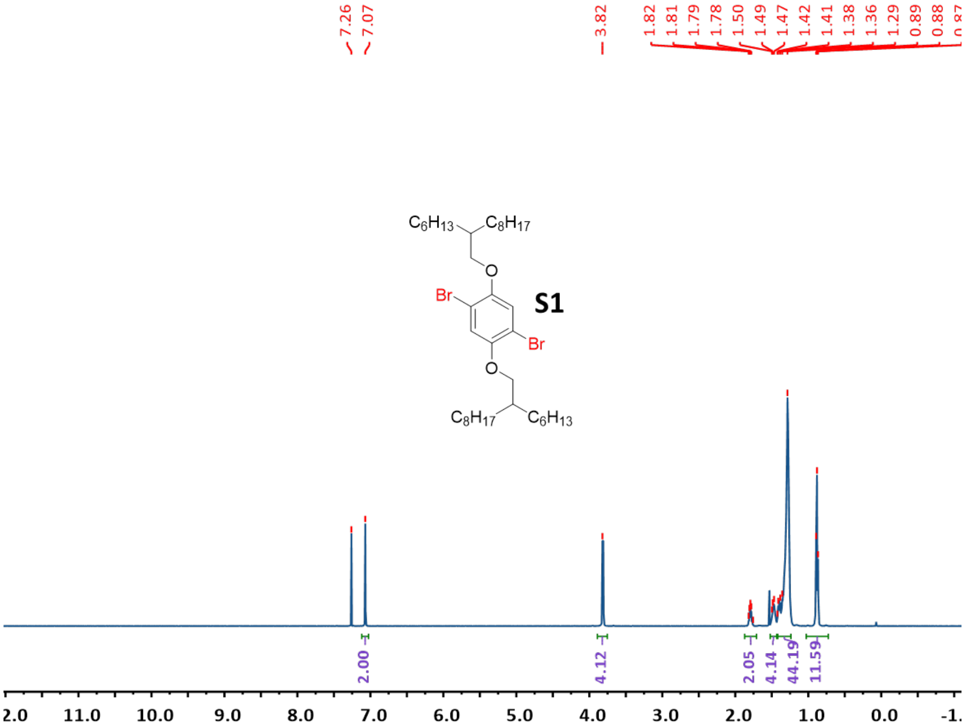
General procedure for PPDTBT synthesis using a Schlenk-tube:
An oven-dried 15 mL Schlenk-tube equipped with a stir-bar was stoppered with a rubber-septum and cooled under a flow of N_2. S1 (0.25 mmol), S2 (0.25 mmol) Cs_2CO_3 (3 equiv.), and $P(o\text{-anisyl})_3$ (8 mol %) were added to the vessel. The vessel was then vacuum-backfilled with N_2 3 times. The solvent was then added to the vessel via syringe to achieve the appropriate monomers' concentration, and it was degassed for 15 min. using N_2. Pd_2dba_3 (2 mol %) was then added quickly. The vessel was then submerged in a pre-heated oil bath (120 °C). After the polymerization, the reaction mixture was cooled to room temperature, the product was dissolved in dichlorobenzene, and then precipitated into cold MeOH. The polymer product was filtered off

and purified using Soxhlet extraction with MeOH, hexanes, and $CHCl_3$. The chloroform fraction was concentrated and precipitated into cold methanol, the solid filtered off, and then dried overnight under vacuum.

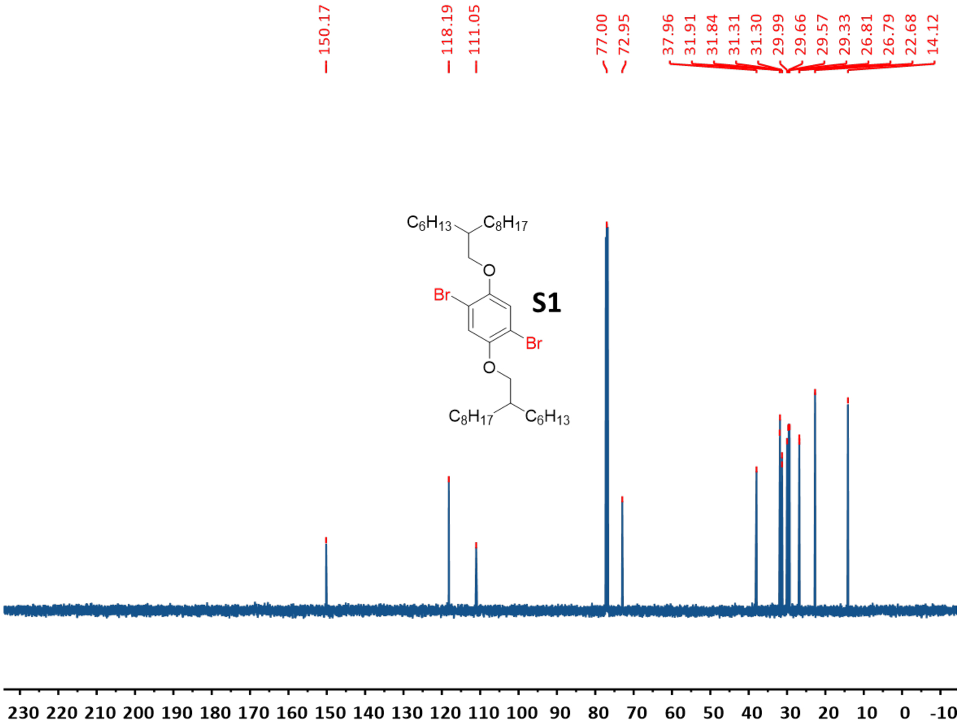
*Poly[(2,5-bis(2-hexyldecyloxy)phenylene)-alt-(4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole)](**P1-P3**)*. ^{1}H NMR (600 MHz, CDCl3, 25 °C): δ ppm 8.18 (br, 2H), 7.93 (br, 2H), 7.69 (br, 2H), 7.37 (br, 2H), 4.10 (br, 4H), 2.01 (br, 2H), 1.68 (br, 4H), 1.44−1.23 (m, 44H), 0.86−0.82 (br, 12H).

*Poly(3-hexylthiophene) (**P5**)*. ^{1}H NMR (600 MHz, CDCl3, 25 °C): δ ppm 6.98 (s, 1H), 2.81 (t, *J* = 7.8 Hz), 1.72-1.70 (m, 2H), 1.44-1.35 (m, 6H), 0.92 (t, *J* = 7.2 Hz, 3H).

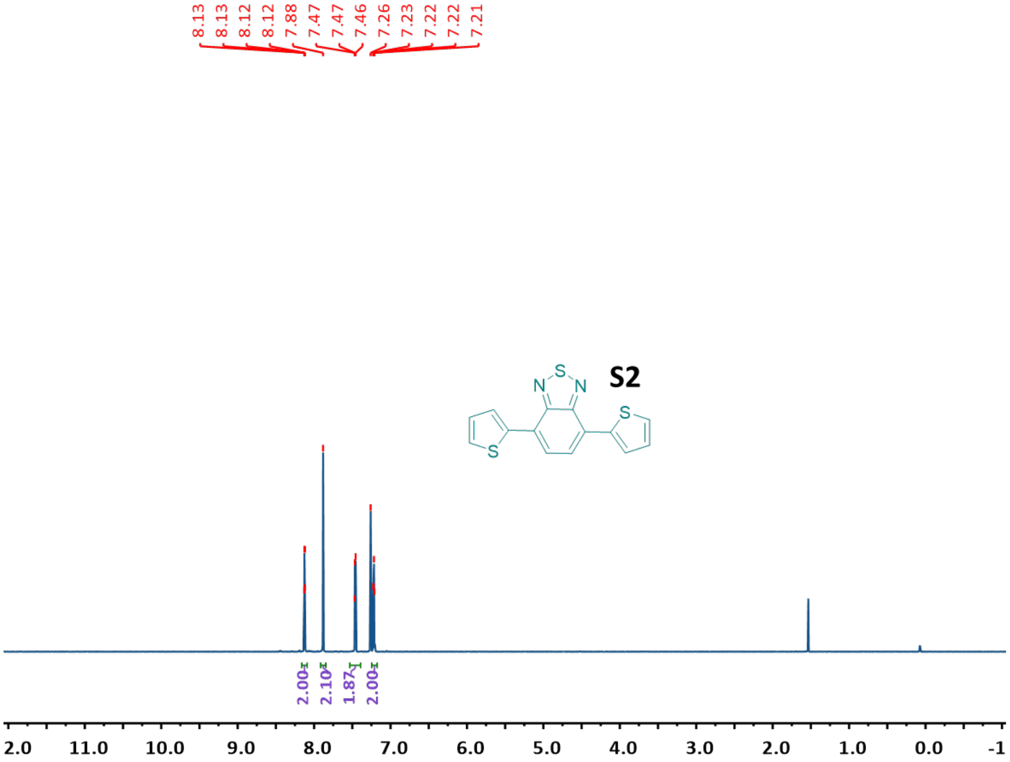
3. Monomer NMR



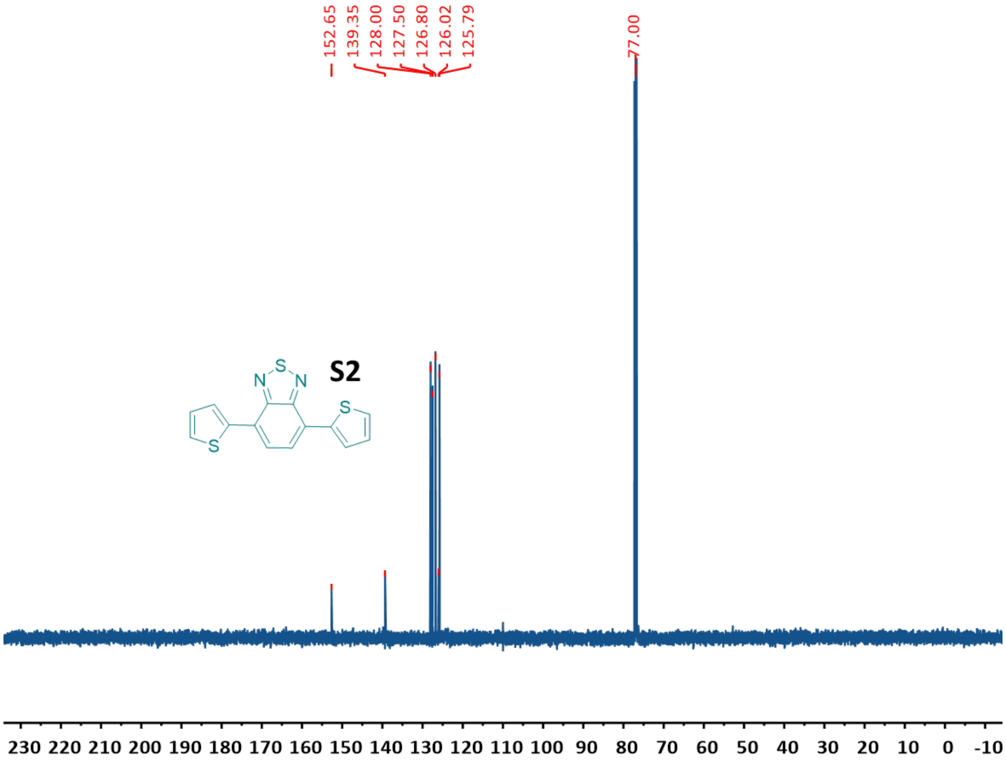
^{1}H NMR of S1 in $CDCl_3$ at 25 °C.



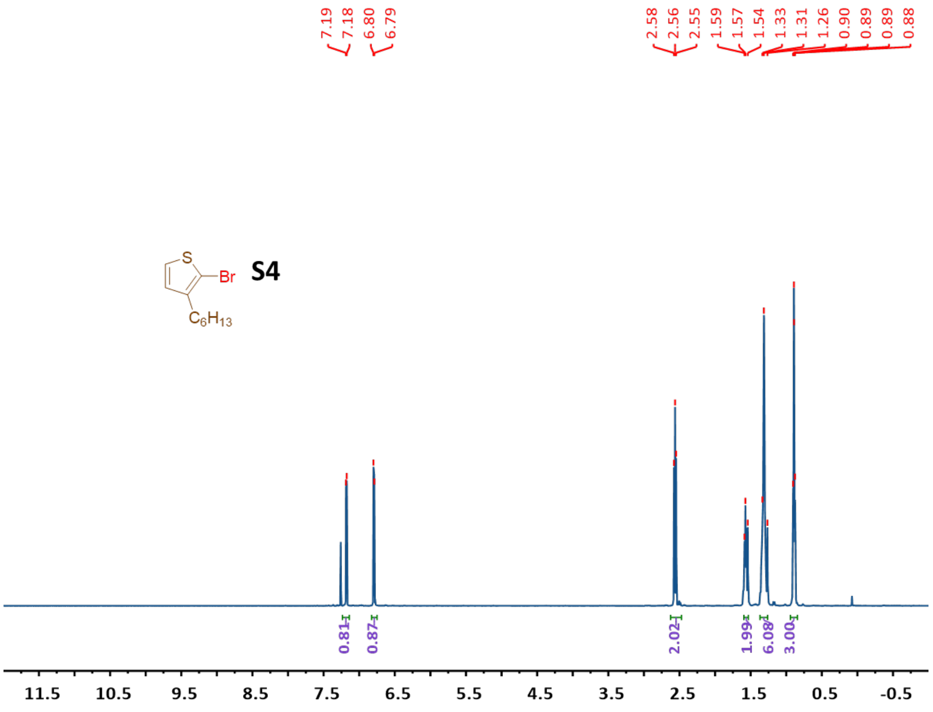
^{13}C NMR of S1 in $CDCl_3$ at 25 °C.



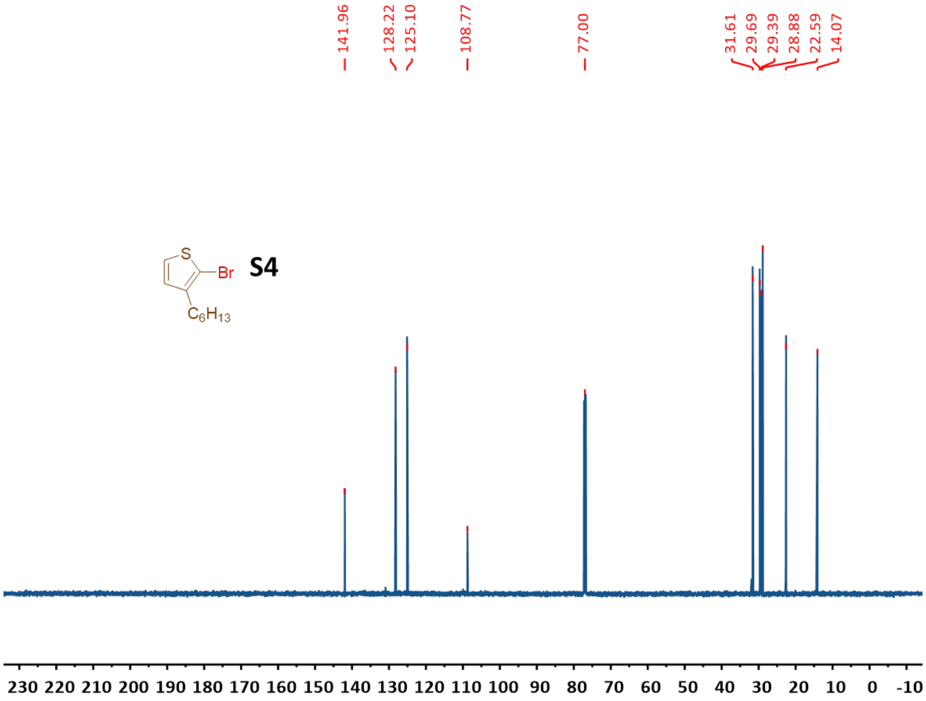
^{1}H NMR of S2 in $CDCl_3$ at 25 °C.



^{13}C NMR of S2 in $CDCl_3$ at 25 °C.

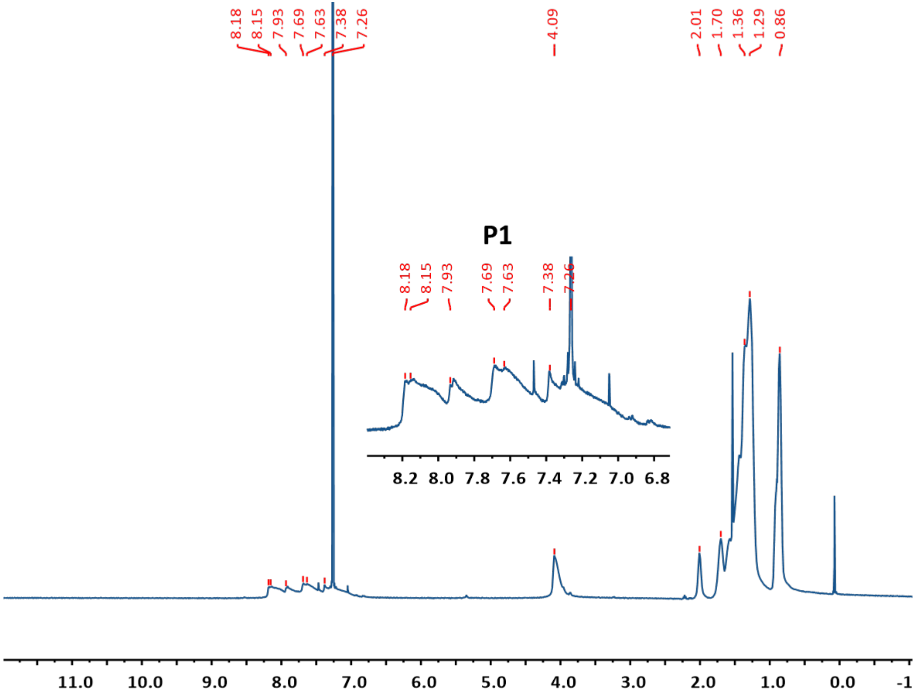


^{1}H NMR of S4 in $CDCl_3$ at 25 °C.

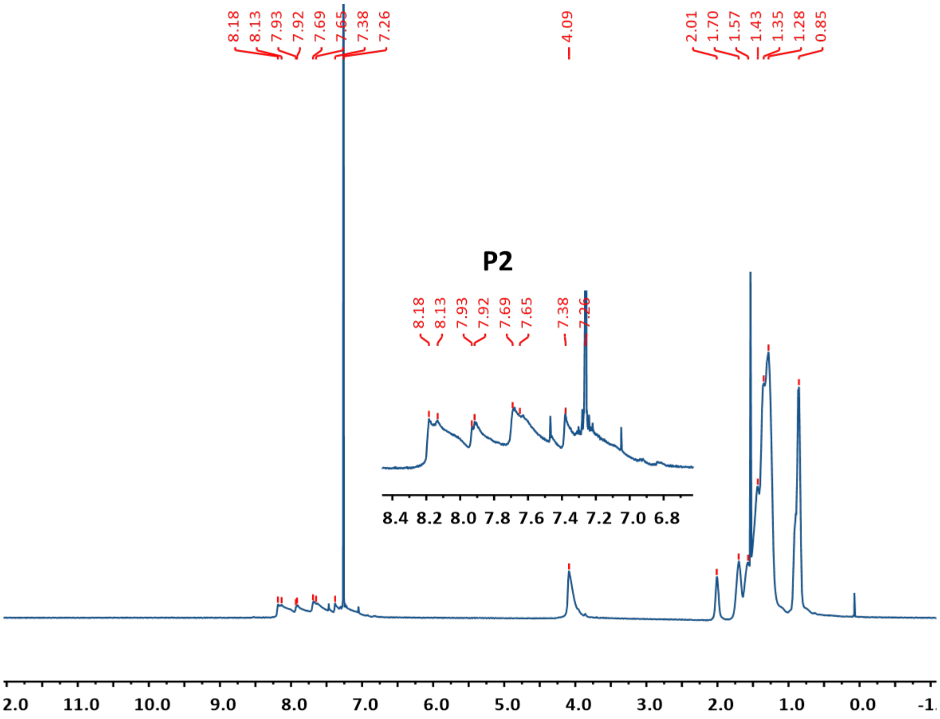


^{13}C NMR of S4 in $CDCl_3$ at 25 °C.

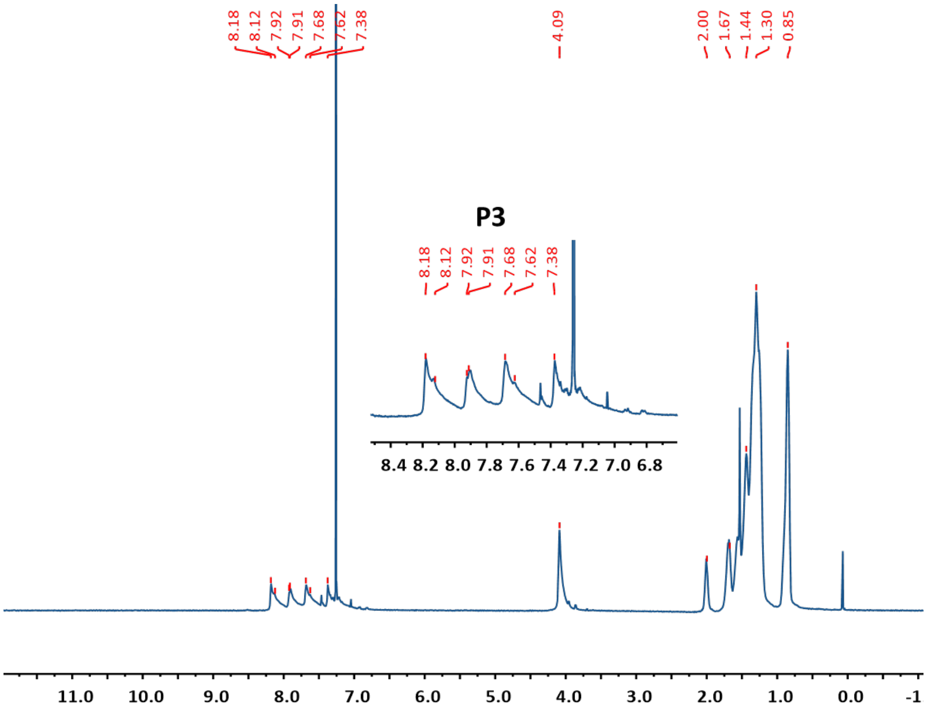
4. Polymer NMR



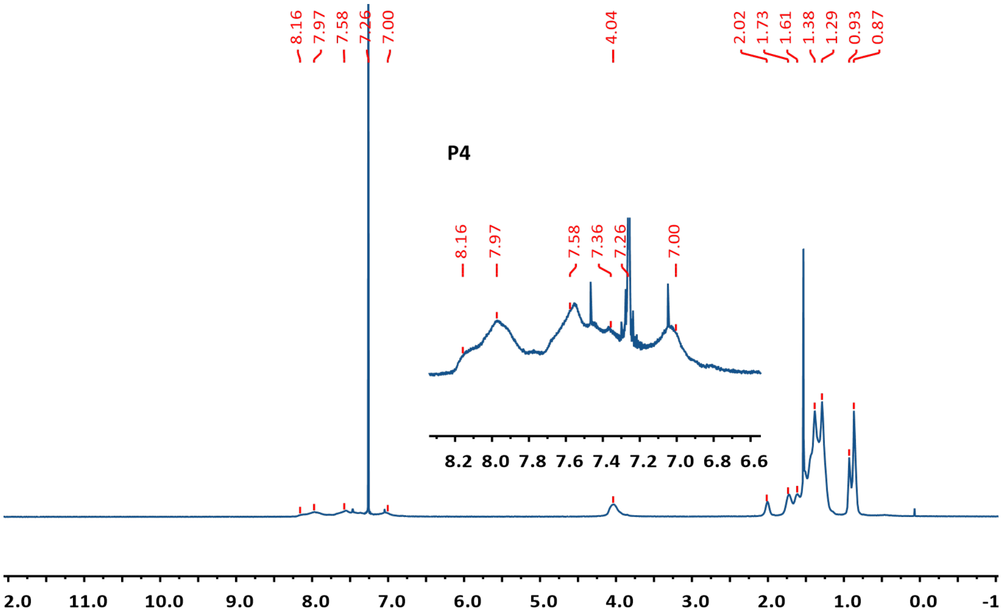
^{1}H NMR of PPDTBT (P1) in $CDCl_3$ at 25 °C.



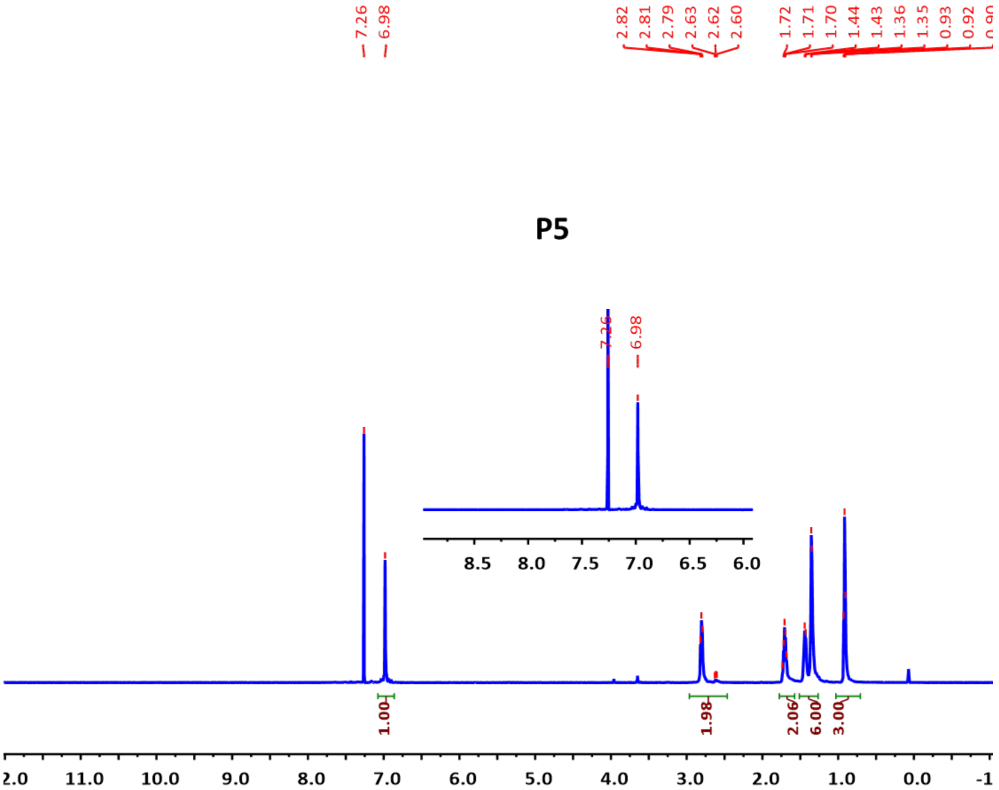
^{1}H NMR of PPDTBT (P2) in $CDCl_3$ at 25 °C.



^{1}H NMR of PPDTBT (P3) in $CDCl_3$ at 25 °C.



^{1}H NMR of PPDTBT-Stille (P4) in $CDCl_3$ at 25 °C.



^{1}H NMR of P3HT (P5) in $CDCl_3$ at 25 °C.

5. Polymer GIXRD

Polymer	2θ (degrees)	d_{100} (Å)	Height	FWHM (degrees)	Crystallite size (nm)
P1	4.695	18.8060	7652	0.540	14.7
P2	4.653	18.9775	8673	0.518	15.3
P3	4.700	18.7844	16346	0.453	17.5
P4	4.650	18.9863	6362	0.514	15.5
P5	5.249	16.8228	14028	0.467	17.0

6. References

1. R. M. Pankow, N. S. Gobalasingham, J. D. Munteanu and B. C. Thompson, *J. Polym. Sci. A Polym. Chem.*

2 F. Livi, N. S. Gobalasingham, B. C. Thompson and E. Bundgaard, *J. Polym. Sci., Part A*, 2016, **54**, 2907–2918.

3 Y. Qiu, J. C. Worch, A. Fortney, C. Gayathri, R. R. Gil and K. J. T. Noonan, *Macromolecules*, 2016, **49**, 4757–4762.

4 B. Burkhart, P. P. Khlyabich, T. Cakir Canak, T. W. LaJoie and B. C. Thompson, *Macromolecules*, 2011, **44**, 1242–1246.