

Supporting information

Polyselenophenes with Distinct Crystallization Properties

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Experimental

General consideration: All reagents were used as received unless otherwise noted. Polyselenophene with different molecular weight were synthesized following our previously published protocol (ref 28 in the main text) with slight modification. Briefly, isopropylmagnesium chloride (0.42 mL, 2.0 M in THF, 0.84 mmol) was added drop-wise to a solution of 2,5-dibromo-3-hexylselenophene (300 mg, 0.81 mmol) in dry THF (4.5 mL) under a nitrogen atmosphere, stirred vigorously for 1 hour at room temperature, transferred to a nitrogen-filled flask containing Ni(dppp)Cl₂ (4.4 mg, 8.1 nmol; or 8.8 mg, 16.2 nmol; or 53 mg, 97nmol), and stirred vigorously overnight at 40°C, then quenched with dilute hydrochloric acid and precipitated into methanol. The precipitated solid was purified by Soxhlet extraction using methanol, hexanes, and chloroform. The chloroform fraction was concentrated to afford the polymers as deep purple solids. Isolated yields ranged from 35 – 80 mg, 20 – 46%), ¹H NMR (CDCl₃, 300 MHz): δ 7.12 (s, 1H), 2.73 (2H), 2.25(2H), 1.26-1.43 (6H), 0.91 (3H). $M_n = 5.9$ kg/mol, $M_w = 8.8$ kg/mol, PDI = 1.48; or $M_n = 9.9$ kg/mol, $M_w = 13.9$ kg/mol, PDI = 1.4 or $M_n = 19.0$ kg/mol, $M_w = 38.0$ kg/mol, PDI = 2.0. (Figures S1-S3). Polythiophene were synthesized by the same

procedure. ^1H NMR (CDCl_3 , 300 MHz): δ 6.98 (s, 1H), 2.78-2.83 (2H), 1.66-1.75 (2H), 1.31-1.46 (6H), 0.89-0.94 (3H). $M_n = 3.5 \text{ kg/mol}$, $M_w = 4.0 \text{ kg/mol}$, PDI = 1.14; or $M_n = 19.5 \text{ kg/mol}$, $M_w = 38.7 \text{ kg/mol}$, PDI = 1.98. (Figures S4 and S5)

Kiriy's polyselenophene synthesis (ref 36 in the main text): Ni(dppp)Cl₂ (1 mmol) was placed into 25 ml round bottom flask equipped with a magnetic stir bar, sealed with a rubber septum, and the atmosphere was replaced with argon. THF (20 mL) was add via syringe and the mixture was cooled to 0°C. o-Tolylmagnesium (1 mmol) was added drop-wise under stirring, resulting in dissolution of the initially present solid and in the formation of a clear yellow solution, which were then used for the initiation of the polymerization. In another flask, isopropylmagnesium chloride (0.28 mL, 2.0 M in THF, 0.56 mmol) was added drop-wise to a solution of 2,5-dibromo-3-hexylselenophene (200 mg, 0.54 mmol) in dry THF (2.0 mL) under a nitrogen atmosphere, and stirred vigorously for 1 hour at 0°C. To perform the polymerization, the solution of initiator in THF (1.2mL) was added in one portion to the activated monomer solution. The mixture was stirred at room temperature for 2h and then quenched with dilute hydrochloric acid and precipitated into methanol. The precipitated solid was purified by Soxhlet extraction using methanol, hexanes, and chloroform. The chloroform fraction was concentrated to afford the polymer as a deep purple solid 22 mg (30%), ^1H NMR (CDCl_3 , 300 MHz): δ 7.12 (s, 7H), 2.73 (12H), 2.48 (s, 3), 1.34-1.68 (70H), 0.91 (21H). $M_n = 4.5 \text{ kg/mol}$, $M_w = 5.9 \text{ kg/mol}$, PDI = 1.31. (Figure S6)

Instrumentation: NMR spectra were recorded on a Varian Mercury 300 spectrometer (300Hz). Polymer molecular weight was determined in 1,2,4-trichlorobenzene at 140°C using a Viscotek HT-GPC (high temperature gel permeation chromatography system) with narrow weight distribution polystyrene standards. Dark-field scanning transmission electron microscopy (STEM) imaging was carried out at 200kV using a Hitachi HD-2000 instrument. Wide-angle X-ray scattering (WAXS) spectra were recorded on a Bruker AXS D8 Discovery with a GADDS area detector. Absorption spectra were recorded using a Varian Cary 5000 spectrometer. MALDI measurements were obtained from a Waters Micromass Maldi MX mass spectrometer. Dithranol was used as the matrix. A

solution of approximately 10^{-4} M of polymer and 0.1 M dithranol was mixed in equal amounts in chloroform was spotted on the MALDI plate.

Thin film preparation: Polymer solutions (10 mg/mL) were drop coated on a carbon covered copper grid for dark-field STEM characterization. For WAXS characterization, solutions were drop coated onto a silicon substrate. For the absorption experiments, solutions were spin coated onto a quartz microscope slide at 500 rotations/min.

Additional Figures

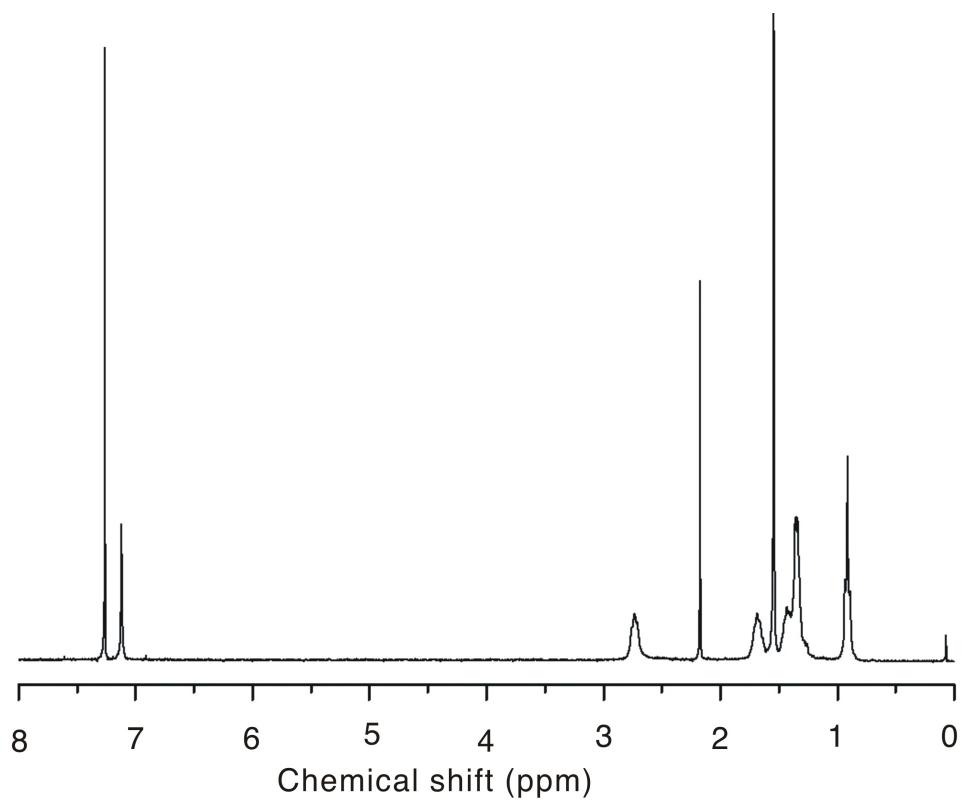


Fig. S1. ¹H NMR spectra of poly(3-hexyl)selenophene with $M_n=19.0\text{ kg/mol}$.

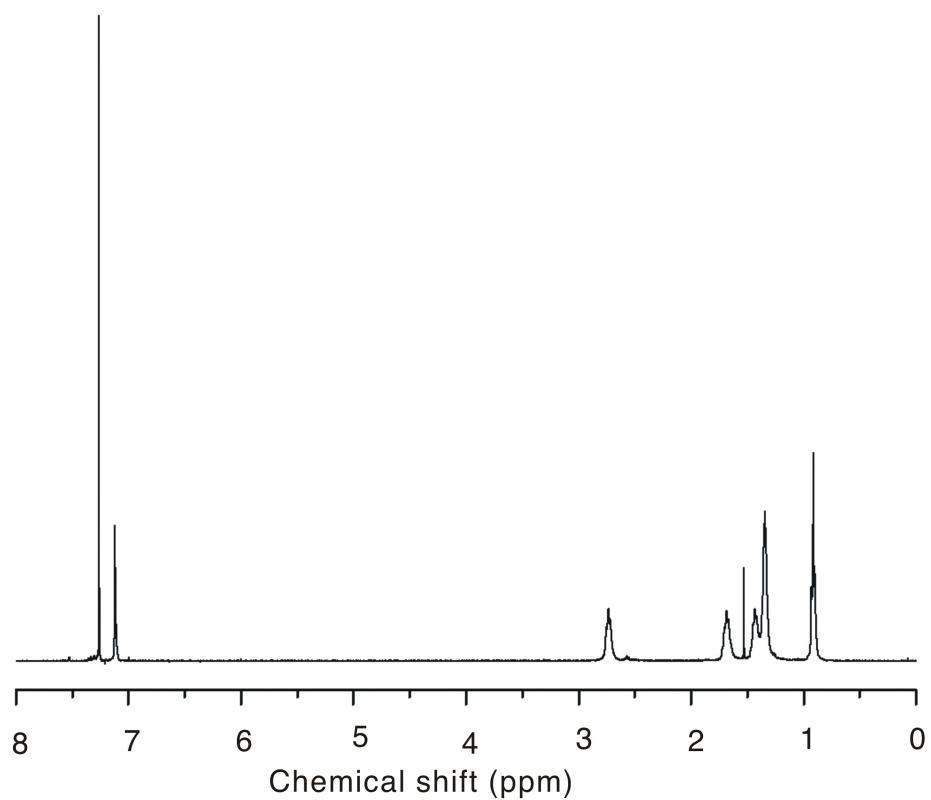


Fig. S2. ¹H NMR spectra of poly(3-hexyl)selenophene with $M_n = 9.9$ kg/mol.

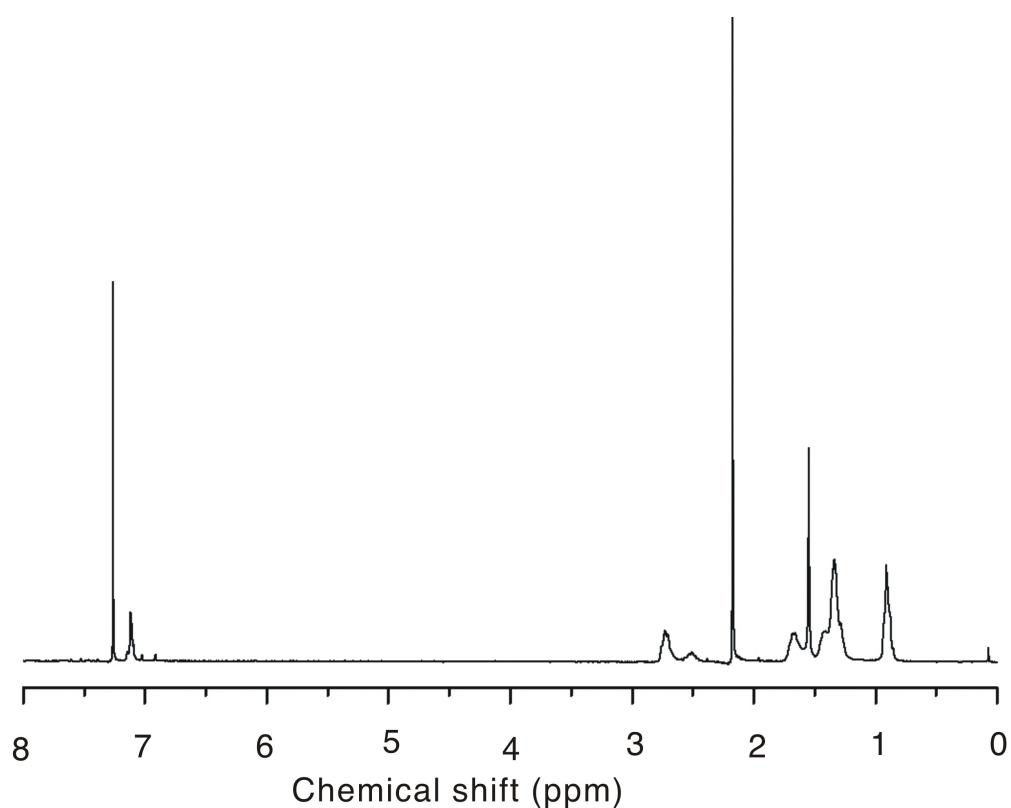


Fig. S3. ¹H NMR spectra of poly(3-hexyl)selenophene with $M_n = 5.9$ kg/mol.

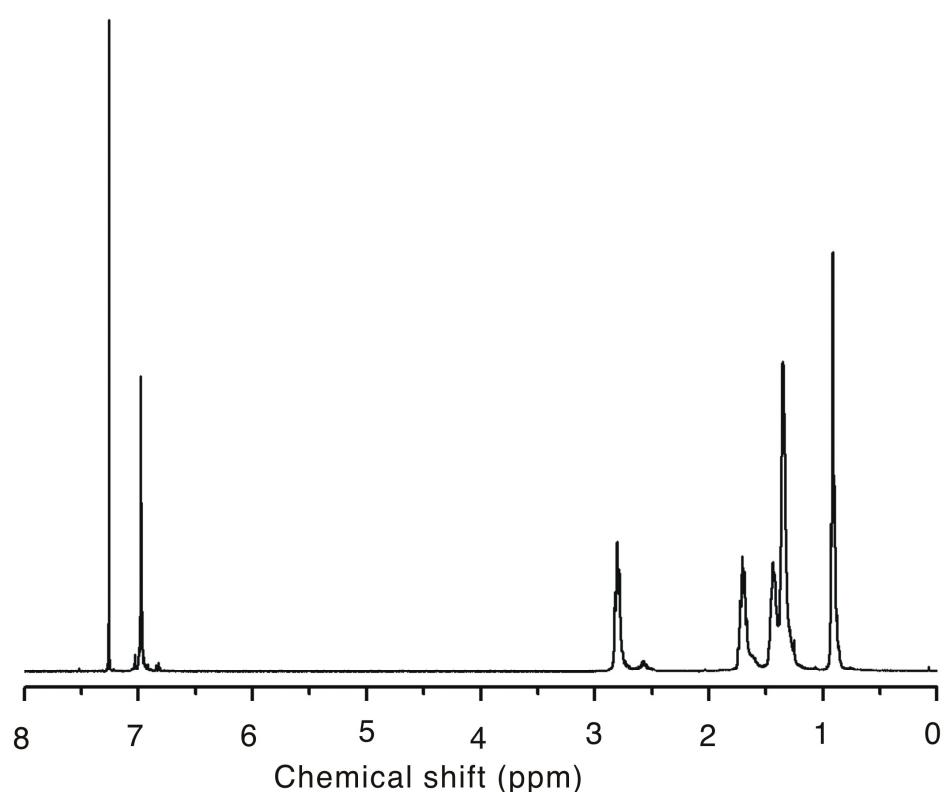


Fig. S4. ¹H NMR spectra of poly(3-hexyl) thiophene with $M_n = 19.5$ kg/mol.

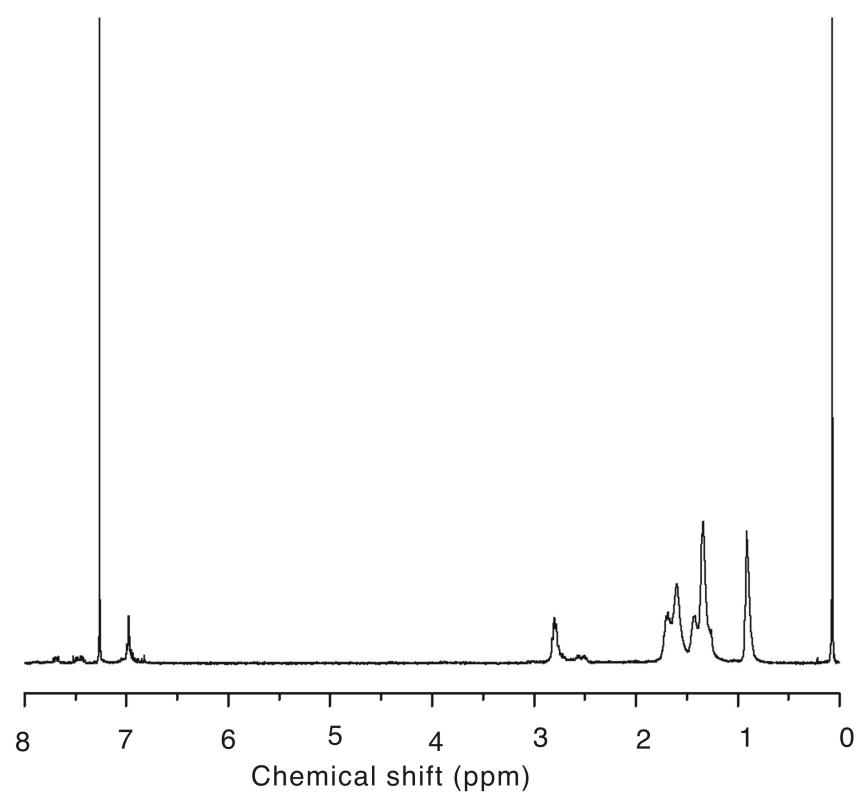


Fig. S5. ¹H NMR spectra of poly(3-hexyl)thiophene with $M_n = 3.5$ kg/mol.

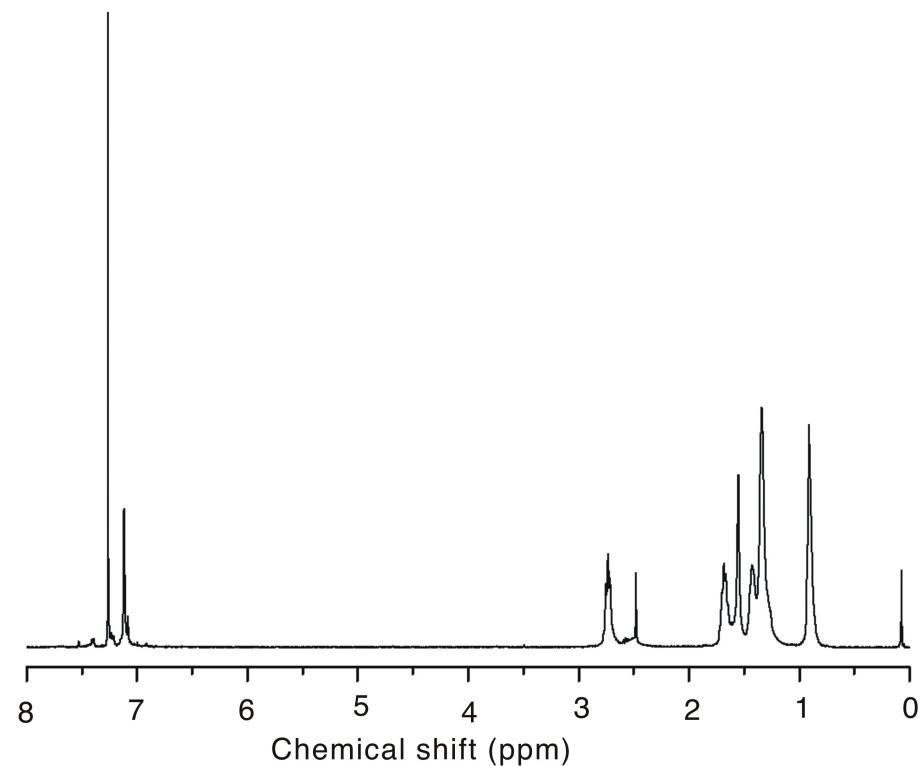


Fig. S6. ¹HNMR spectra of poly(3-hexyl)selenophene synthesized by Kiriy's method with $M_n = 4.5$ kg/mol

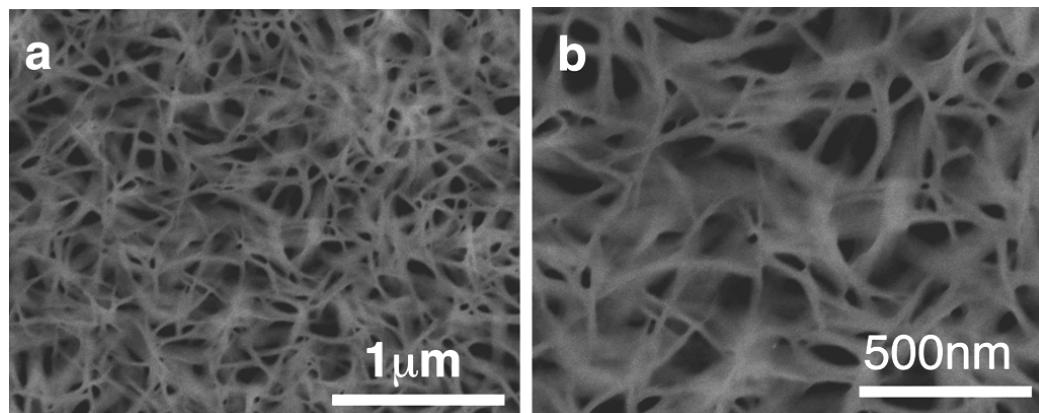


Fig. S7. STEM images of P3HS samples synthesized by Kiriy's method (ref 36 in the main text) with $M_n = 4.5 \text{ kg/mol}$.

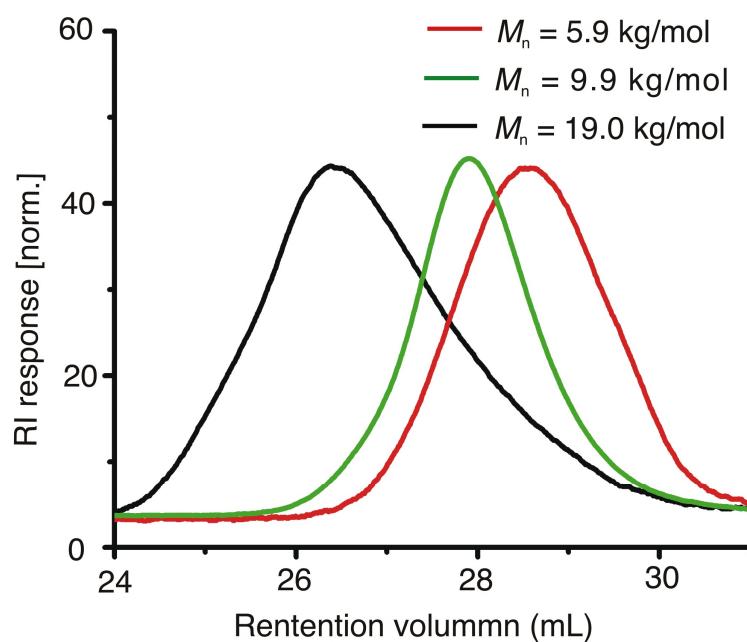


Fig. S8. GPC traces of the three P3HS samples with different molecular weight.

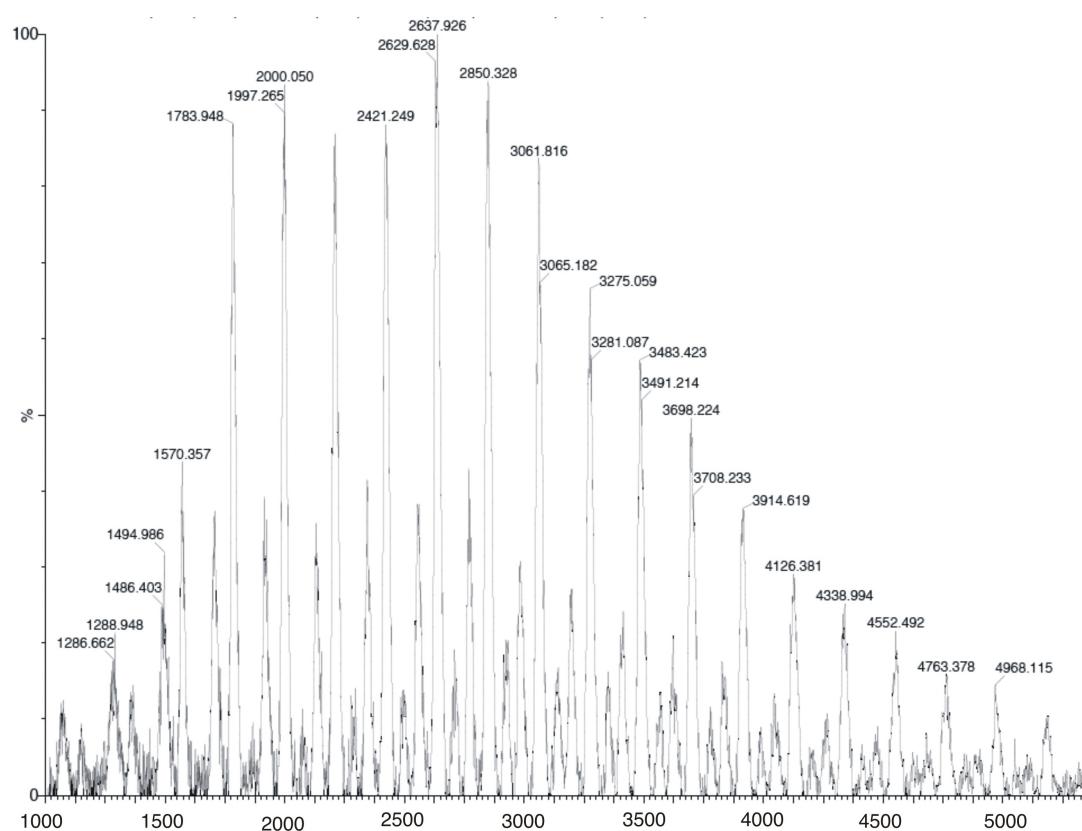


Fig. S9. MALDI spectra of the P3HS samples with $M_n = 5.9\text{kg/mol}$.

Table S1: Summary of GPC and NMR measurements of P3HS and P3HT polymers.

	$M_n/\text{kg mol}^{-1}$	$M_w/\text{kg mol}^{-1}$	PDI	regioregularity
Low- M_n P3HS	5.9	8.8	1.48	76%
Low- M_n P3HS by Kiriy's method	4.5	5.9	1.31	
Medium- M_n P3HS	9.9	13.9	1.40	88%
High- M_n P3HS	19.0	38.0	2.00	100%
Low- M_n P3HT	3.5	4.0	1.14	76%
High- M_n P3HT	19.5	38.7	1.98	87%