## Supporting Information

# Molecular Weight-Dependent Physical and Photovoltaic Properties of Poly(3-alkylthiophene)s with Butyl, Hexyl, and Octyl Side-Chains

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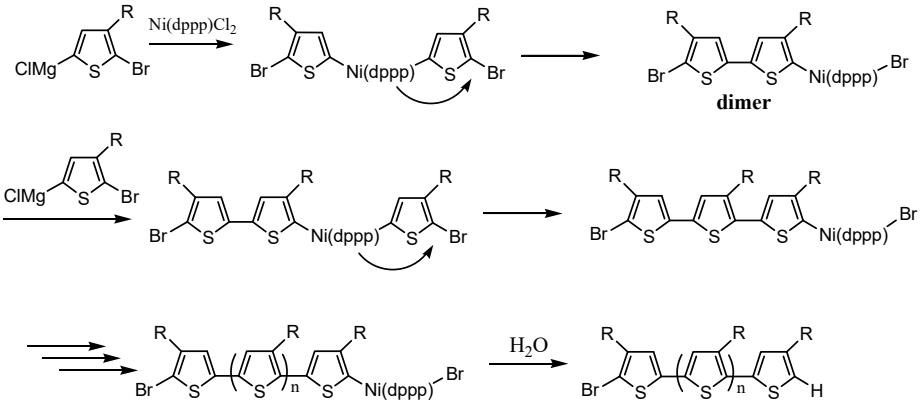


**Scheme S1.** Proposed living chain growth mechanism for the synthesis of rr-P3ATs by GRIM polymerization.

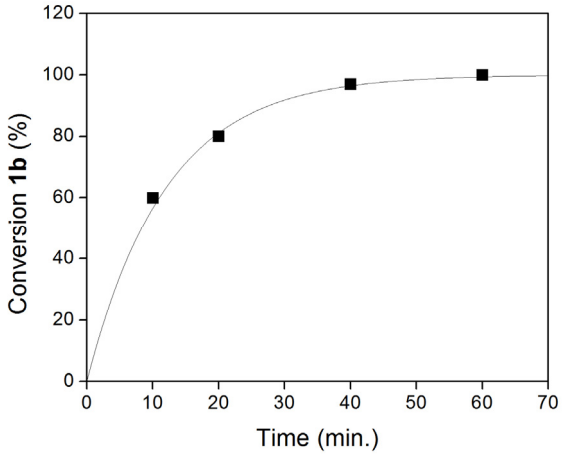


**Figure S1.** Conversion of 2-Bromo-3-hexyl-5-iodothiophene (**1b**) versus Grignard-exchanged reaction time.

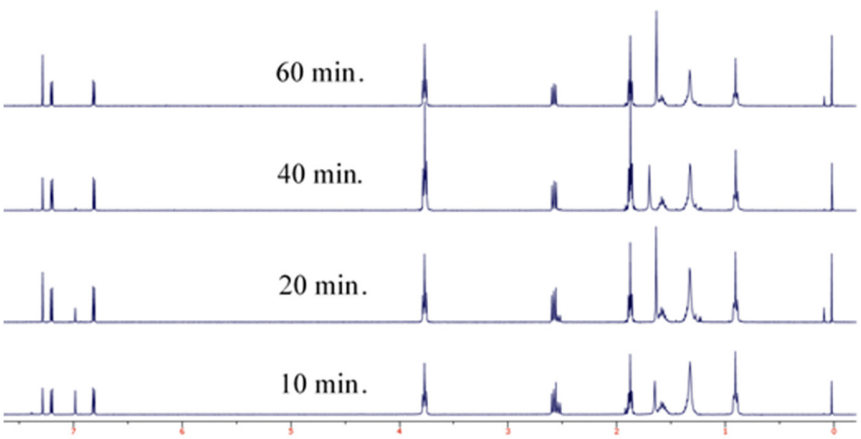


**Figure S2**. NMR spectra of 2-Bromo-3-hexyl-5-iodothiophene (**1b**) quenching with water at different time intervals.

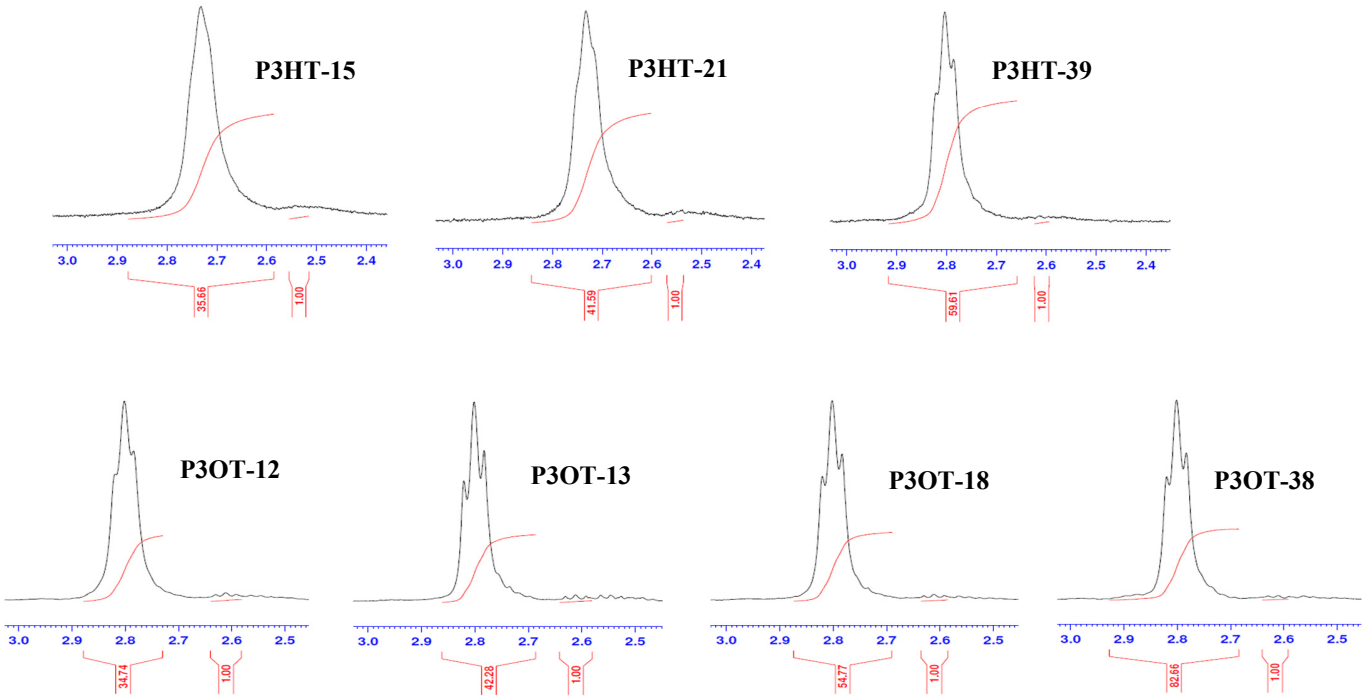


**Figure S3.** $^{1}$H-NMR used to calculate $M_n$ of P3HTs and P3OTs.

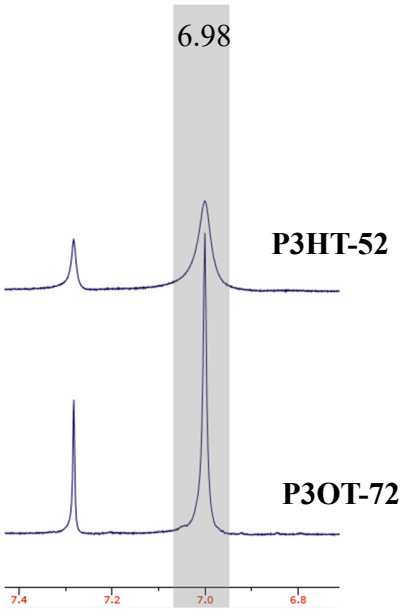


**Figure S4**. NMR spectra of P3HT and P3OT for calculated RR.

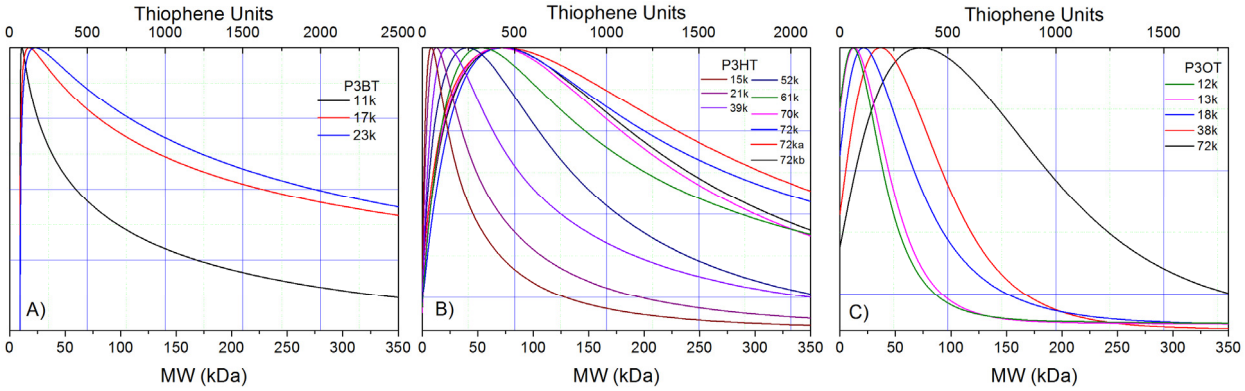


**Figure S5.** Normalized GPC curves of P3ATs.

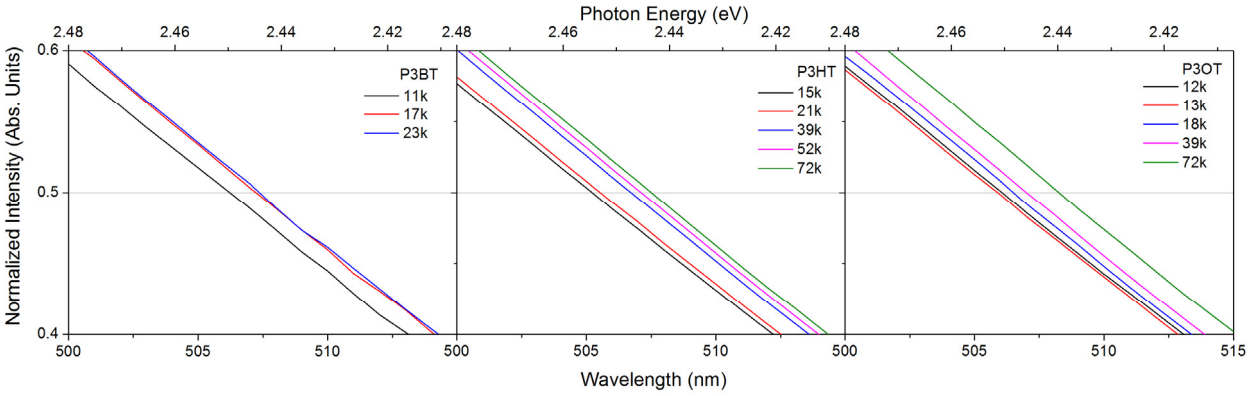


**Figure S6.** UV-Vis magnification of P3ATs.

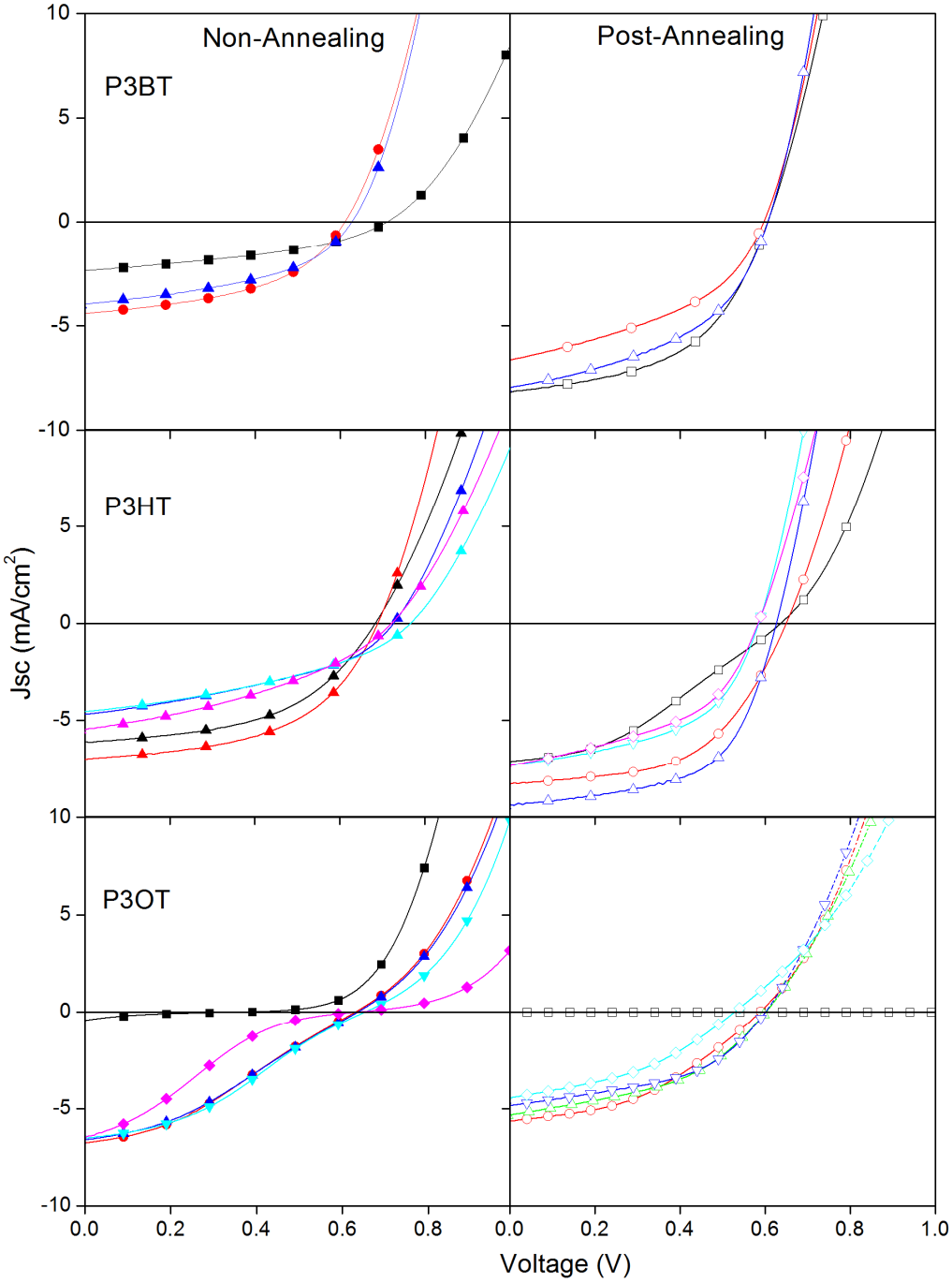


**Figure S7**. J-V characteristics of all P3ATs before annealing (solid symbols) and after annealing (open symbols).

**Table S1**. Solubility of P3ATs in common organic solvents.

| P3AT | Hexane | $CH_2Cl_2$ | THF | $CHCl_3$ | Toluene | CB | ODCB |
|---|---|---|---|---|---|---|---|
| P3HT-15 | MS[a] | MS[a] | S | S | S | S | S |
| P3HT-21 | I | MS[a] | S | S | S | S | S |
| P3HT-39 | I | MS[a] | S[a] | S[a] | S | S | S |
| P3HT-52 | I | I | S[a] | S[a] | S | S | S |
| P3HT-61 | I | I | S[a] | S[a] | S[a] | S[a] | S[a] |
| P3HT-70 | I | I | S[a] | S[a] | S[a] | S[a] | S[a] |
| P3HT-72a | I | I | S[a] | S[a] | S[a] | S[a] | S[a] |
| P3OT-12 | MS[a] | S[a] | S | S | S | S | S |
| P3OT-13 | MS[a] | S[a] | S | S | S | S | S |
| P3OT-18 | MS[a] | MS[a] | S | S | S | S | S |
| P3OT-38 | I | MS[a] | S | S | S | S | S |
| P3OT-72 | I | MS[a] | S | S | S | S | S |

S: soluble, I: insoluble, MS: marginally soluble, a: only possible in hot solvents.

**Table S2**. Thermal properties and crystallinity of P3ATs.

| P3ATs | $T_m$ (°C) | $T_c$ (°C) | $\Delta H_f$ (J/g) | X (%) |
|---|---|---|---|---|
| P3BT-11 | 245 | 165 | 21.7 | - |
| P3BT-17 | 250 | 170 | 19.8 | - |
| P3BT-23 | 249 | 168 | 25.2 | - |
| P3HT-15 | 212 | 174 | 3.2 | 3.2 |
| P3HT-21 | 220 | 159 | 4.2 | 4.2 |
| P3HT-39 | 219 | 182 | 8.6 | 8.7 |
| P3HT-52 | 225 | 189 | 16.4 | 16.6 |
| P3HT-72a | 225 | 180 | 12.1 | 12.2 |
| P3OT-12 | 173, 184 | 145 | 11.2 | 14.5 |
| P3OT-13 | 183, 189 | 155 | 17.5 | 22.7 |
| P3OT-18 | 186, 191 | 162 | 14.1 | 18.3 |
| P3OT-38 | 194 | 165 | 17.6 | 22.9 |
| P3OT-72 | 198 | 162 | 19.7 | 25.6 |

**Table S3**. Overview of P3ATs' device parameters.

| P3ATs | $V_{oc}$ (V) | | $J_{sc}$ (mA/cm$^2$) | | FF (%) | | PCE (%) | |
|---|---|---|---|---|---|---|---|---|
| | NA | PA | NA | PA | NA | PA | NA | PA |
| P3BT-11 | 0.70 | 0.60 | 2.6 | 8.2 | 41.6 | 51.3 | 0.8 | 2.4 |
| P3BT-17 | 0.62 | 0.60 | 4.9 | 7.8 | 47.3 | 42.8 | 1.5 | 2.0 |
| P3BT-23 | 0.63 | 0.61 | 4.4 | 7.7 | 46.4 | 45.4 | 1.3 | 2.0 |
| P3HT-15 | 0.69 | 0.65 | 7.1 | 7.9 | 53.0 | 40.0 | 2.4 | 2.0 |
| P3HT-21 | 0.69 | 0.65 | 7.1 | 8.9 | 51.8 | 56.1 | 2.6 | 3.3 |
| P3HT-39 | 0.74 | 0.63 | 5.0 | 9.5 | 44.0 | 61.3 | 1.4 | 3.6 |
| P3HT-52 | 0.77 | 0.61 | 5.3 | 9.7 | 40.9 | 56.4 | 1.5 | 3.4 |
| P3HT-72a | 0.72 | 0.60 | 5.2 | 8.2 | 38.0 | 47.0 | 1.6 | 2.3 |
| P3OT-13 | 0.63 | 0.57 | 7.0 | 5.5 | 32.4 | 41.3 | 1.4 | 1.4 |
| P3OT-18 | 0.63 | 0.58 | 6.7 | 4.7 | 33.7 | 40.5 | 1.4 | 1.3 |
| P3OT-38 | 0.65 | 0.60 | 6.7 | 5.3 | 35.9 | 46.6 | 1.6 | 1.5 |
| P3OT-52 | 0.53 | 0.64 | 4.5 | 6.5 | 39.5 | 22.8 | 0.9 | 0.9 |

NA: non-annealed, PA: post-annealed.