Synthesis of regioblock copolythiophene by Negishi catalyst-transfer polycondensation using \( \text{tBu}_2\text{Zn} \cdot 2\text{LiCl} \)

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Synthesis

_Preparation of a THF solution of HH-monomer_

![Scheme S1. Synthesis of HH-monomer by zinc-iodine exchange reaction](image)

Table S1. Synthesis of HH-monomer by zinc-iodine exchange reaction using \( \text{tBu}_2\text{Zn·2LiCl} \) under varied conditions.

| Run | \(|\text{tBu}_2\text{Zn·2LiCl}|/|1|\)^a | \(|\text{LiCl}|/|1|\)^b | Conc. (M)^c | Conv. (%)^d |
|-----|-----------------|-----------------|-----------------|-----------------|
| S1  | 1.0             | 0.0             | 0.0242          | 61              |
| S2  | 2.0             | 0.0             | 0.0213          | 0               |
| S3  | 1.0             | 3.0             | 0.0239          | 37              |
| 3   | 1.0             | 0.0             | 0.107           | 95              |

^a Initial molar ratio of \( \text{tBu}_2\text{Zn·2LiCl} \) for 1. ^b Initial molar ratio of LiCl for 1. ^c Concentration (mol/L) of reaction mixture for synthesizing HH-monomer. ^d Conversion of zinc-iodine exchange reaction was evaluated by \(^1\)H NMR spectroscopy.

Preparation of a THF solution of HT-monomer as the second monomer

![Scheme S2. Synthesis of HT-monomer by zinc-iodine exchange reaction](image)

2-Bromo-3-hexyl-5-iodothiophene (185 mg, 0.496 mmol) was placed in a 5 mL two-necked flask purged with \( \text{N}_2 \). After dissolving 2-bromo-3-hexyl-5-iodothiophene in dehydrated THF (5 mL), a 0.184 M THF solution of \( \text{tBu}_2\text{Zn·2LiCl} \) (2.7 mL, 0.50
mmol) was added and stirred at room temperature for 30 min to afford the HT-
monomer.

**Synthesis of regiorandom P3HT**

![Scheme S3. Synthesis of regiorandom P3HT](image)

1 (112 mg, 0.207 mmol) and 2-bromo-3-hexyl-5-iodothiophene (154 mg, 0.413
mmol) were placed in a 20 mL two-necked flask purged with N₂. After dissolving
them in dehydrated THF (2 mL), a 0.184 M THF solution of tBu₂Zn·2LiCl (3.4 mL,
0.62 mmol) was added at 0 °C and stirred at room temperature for 1 h. Then, the
reaction mixture was diluted with 10 mL of dehydrated THF. The Ni catalyst (0.0092
mmol) solution (5 mL), which was prepared in another batch by mixing Ni(PPh₃)₂Cl₂
(6.0 mg, 0.0092 mmol) and dcpe (9.7 mg, 0.023 mmol) in THF (5 mL), was added to
start the polymerization. The polymerization was carried out at 60 °C for 30 min,
followed by quenching with 5 M HCl aq. (2 mL). The quenched solution was
extracted with chloroform, washed with water, and analyzed by SEC directly before
precipitation. The crude solution was poured into a large amount of methanol/water
(200 mL/100 mL) to precipitate the polymer. After filtrating and drying under
vacuum, the crude HHTT-P3HT was obtained as a dark red solid (91 mg, 66%). SEC:

\[ M_n = 11,200, \frac{M_w}{M_n} = 1.46. \]

\(^1H\) NMR (400 MHz, chloroform-\(d\)): \(\delta\) 7.10-6.91 (m, 1H), 2.88-2.68 (m, 1H), 2.66-2.42 (m, 1H), 1.78-1.50 (m, 2H), 1.49-1.15 (m, 6H), 0.99-0.80 (m, 3H). \(^{13}C\) NMR (101 MHz, chloroform-\(d\)) \(\delta\) 143.52, 143.00, 140.44, 140.02, 139.92, 137.11, 136.91, 135.82, 134.96, 133.89, 130.76, 130.62, 130.52, 129.75, 128.73, 128.44, 127.52, 127.28, 126.69, 125.94, 125.26, 31.99, 30.83, 30.66, 29.61, 29.41, 29.29, 22.93, 22.75, 14.27.
$^1$H and $^{13}$C NMR spectra

(a)

![NMR spectra](image)

(b)

![NMR spectra](image)

**Figure S1.** (a) $^1$H NMR and (b) $^{13}$C NMR spectra of HHTT-P3HT (Run 4).
Figure S2. (a) $^1$H NMR and (b) $^{13}$C NMR spectra of regioblock P3HT (HHTT$_{25}$HT)$_{75}$, Run 6).
Figure S3. (a) $^1$H NMR and (b) $^{13}$C NMR spectra of regioblock P3HT ($\text{HHTT}_{42}\text{HT}_{58}$, Run 7).
Figure S4. (a) $^1$H NMR and (b) $^{13}$C NMR spectra of regioblock P3HT (HHTT$_{69}$HT$_{31}$).
Figure S5. (a) $^1$H NMR and (b) $^{13}$C NMR spectra of regiorandom P3HT.
Figure S6. SEC UV traces of HHTT-P3HTs with (a) different ligands (Runs 1, 2 and 4) and (b) different [1]/Ni(PPh₃)₂Cl₂ (Runs 3-5).
Figure S7. SEC UV traces of HHTT-P3HT (1st block, orange) and regioblock P3HT (HHTT$_{25}$HT$_{75}$, Run 6, black) after the successive addition of the HT-monomer (2nd block).
Regioblock
P3HT
$M_n = 15,600$
$M_w/M_n = 1.19$

HHTT-P3HT
$M_n = 10,100$
$M_w/M_n = 1.23$

**Figure S8.** SEC UV traces of HHTT-P3HT (1\textsuperscript{st} block, orange) and regioblock P3HT (HHTT\textsubscript{69}HT\textsubscript{31}, Run 8, black) after the successive addition of the HT-monomer (2\textsuperscript{nd} block).
Figure S9. Schematic illustrations of plausible structures/mechanisms for (a) successful and (b) unsuccessful monomer addition sequences in NCTP and (c) unsuccessful and (d) successful monomer addition sequences in the conventional KCTP\(^1\) for the synthesis of regioblock copolythiophenes.
In-plane 1D GIWAXS profiles

Figure S10. In-plane 1D GIWAXS profiles of HT-P3HT, HHTT_{25}HT_{75}, HHTT_{42}HT_{58}, HHTT_{60}HT_{31}, and HHTT-P3HT. All of the films were spin-casted on a Si wafer and annealed at 150 °C for 1 h under vacuum.
2D GISAXS patterns

![2D GISAXS patterns](image)

**Figure S11.** 2D GISAXS patterns of (a) HT-P3HT, (b) HHTT$_{25}$HT$_{75}$, (c) HHTT$_{42}$HT$_{58}$, (d) HHTT$_{69}$HT$_{31}$ and (e) HHTT-P3HT. All of the films were spin-casted on a Si wafer and annealed at 150 °C for 1 h under vacuum.
Figure S12. Temperature dependency of in-plane 1D GISAXS profiles of regioblock P3HT (HHTT$_{42}$HT$_{58}$, Run 7). The film was spin-casted on a Si wafer and heated up and cooled down gradually.
TGA thermograms

Figure S13. TGA curves of HT-P3HT, HHTT_{25}HT_{75}, HHTT_{42}HT_{58}, HHTT_{69}HT_{31} and HHTT-P3HT at the heating scan rate of 10 °C/min in N_{2}.
DSC thermograms

Figure S14. DSC curves at the 2\textsuperscript{nd} cycle heating and 2\textsuperscript{nd} cycle cooling scans of HT-P3HT, HHTT\textsubscript{25}HT\textsubscript{75}, HHTT\textsubscript{42}HT\textsubscript{58}, HHTT\textsubscript{69}HT\textsubscript{31} and HHTT-P3HT at the heating and cooling rate of 10 °C/min in N\textsubscript{2}.

Table S2. Thermal properties of HT-P3HT, HHTT-P3HT and regioblock P3HTs measured by TGA and DSC.

<table>
<thead>
<tr>
<th></th>
<th>(T_{d5%}) (°C)\textsuperscript{a}</th>
<th>(T_m) (°C)\textsuperscript{b}</th>
<th>(\Delta H_m) (J/g)\textsuperscript{c}</th>
<th>(T_c) (°C)\textsuperscript{b}</th>
<th>(\Delta H_c) (J/g)\textsuperscript{c}</th>
<th>(X_c\textsuperscript{d})</th>
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</thead>
<tbody>
<tr>
<td>HT-P3HT</td>
<td>456</td>
<td>233.4</td>
<td>19.7</td>
<td>199.2</td>
<td>17.3</td>
<td>59.7</td>
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<tr>
<td>HHTT\textsubscript{25}HT\textsubscript{75}</td>
<td>448</td>
<td>213.8</td>
<td>12.5</td>
<td>172.8</td>
<td>10.5</td>
<td>37.9</td>
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<tr>
<td>HHTT\textsubscript{42}HT\textsubscript{58}</td>
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<td>8.57</td>
<td>163.9</td>
<td>4.98</td>
<td>26.0</td>
</tr>
<tr>
<td>HHTT\textsubscript{69}HT\textsubscript{31}</td>
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<td>160.4</td>
<td>2.74</td>
<td>107.9</td>
<td>2.40</td>
<td>8.30</td>
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<tr>
<td>HHTT-P3HT</td>
<td>432</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The 5\% weight-loss temperatures were evaluated by TGA at 10 °C/min in N\textsubscript{2}.  
\textsuperscript{b} The melting and crystallizing temperature were evaluated by DSC at 10 °C/min in N\textsubscript{2}.  
\textsuperscript{c} The melting and crystallizing enthalpies were evaluated from the integrated peaks of DSC.  
\textsuperscript{d} Crystallinities were calculated from the comparison between evaluated \(\Delta H_m\) and an ideal melting enthalpy (33 J/g)\textsuperscript{2}.
UV-vis absorption

Figure S15. UV-vis absorption spectra of HT-P3HT, HHTT$_{25}$HT$_{75}$, HHTT$_{42}$HT$_{58}$, HHTT$_{69}$HT$_{31}$ and HHTT-P3HT (a) dissolved in chloroform and (b) drop-casted from chloroform and annealed at 150 °C at 1 h under vacuum.
Reference
