Electronic Supplementary Information

Precise synthesis of rod-coil type miktoarm star copolymer containing poly(n-hexyl isocyanate) and aliphatic polyester

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**Table S1.** Synthesis of PHIC macroinitiators (PHIC-OH, PHIC-(OH)$_2$, and PHIC-(OH)$_3$) via CuAAC reaction of PHIC-N$_3$ with ethynyl alcohol derivatives.$^a$

<table>
<thead>
<tr>
<th>PHIC-N$_3$</th>
<th>PHIC macroinitiators</th>
<th>$M_{n,\text{NMR}}$$^b$</th>
<th>$M_w/M_n$$^c$</th>
<th>Structure</th>
<th>$M_{n,\text{NMR}}$$^b$</th>
<th>$M_w/M_n$$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3,000</td>
<td>PHIC-OH</td>
<td>1.07</td>
<td>PHIC-OH</td>
<td>3,100</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>5,000</td>
<td></td>
<td>1.06</td>
<td></td>
<td>5,100</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>10,300</td>
<td></td>
<td>1.13</td>
<td></td>
<td>10,300</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>11,400</td>
<td></td>
<td>1.18</td>
<td></td>
<td>11,400</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>3,000</td>
<td>PHIC-(OH)$_2$</td>
<td>1.07</td>
<td>PHIC-(OH)$_2$</td>
<td>3,100</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>5,000</td>
<td></td>
<td>1.06</td>
<td></td>
<td>5,100</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>10,900</td>
<td></td>
<td>1.10</td>
<td></td>
<td>10,900</td>
<td>1.13</td>
<td></td>
</tr>
<tr>
<td>11,300</td>
<td></td>
<td>1.18</td>
<td></td>
<td>11,300</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>3,000</td>
<td>PHIC-(OH)$_3$</td>
<td>1.07</td>
<td>PHIC-(OH)$_3$</td>
<td>3,200</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>5,000</td>
<td></td>
<td>1.07</td>
<td></td>
<td>5,200</td>
<td>1.06</td>
<td></td>
</tr>
<tr>
<td>9,600</td>
<td></td>
<td>1.16</td>
<td></td>
<td>9,600</td>
<td>1.16</td>
<td></td>
</tr>
<tr>
<td>11,300</td>
<td></td>
<td>1.19</td>
<td></td>
<td>11,300</td>
<td>1.18</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Synthesis conditions: solvent, dry THF; catalyst, CuCl, PMDETA; [ethynyl derivatives]/[PHIC-N$_3$]/[CuCl]/[PMDETA] = 3.5/1.0/3.0/6.0; reaction time, 48 h; temp., r.t. $^b$ Determined by $^1$H NMR spectrum in CDCl$_3$. $^c$ Determined by SEC in THF using PST standards.
Table S2. Solubility of PHIC-\textit{b}-PLLA$_{1-3}$, PHIC-\textit{b}-PCL$_{1-3}$, and homopolymers$^a$

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_{n,NMR}^{b}$</th>
<th>$f_{PHIC}^{d}$</th>
<th>CHCl$_3$</th>
<th>THF</th>
<th>DMF</th>
<th>Hexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLLA</td>
<td>10,200 (1.08)</td>
<td></td>
<td>○</td>
<td>○</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>PCL</td>
<td>10,500 (1.04)</td>
<td></td>
<td>○</td>
<td>○</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>PHIC</td>
<td>10,400 (1.11)</td>
<td>1.00</td>
<td>○</td>
<td>○</td>
<td>×</td>
<td>○</td>
</tr>
<tr>
<td>PHIC-\textit{b}-PLLA</td>
<td>19,200 (1.07)</td>
<td>0.59</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>×</td>
</tr>
<tr>
<td>PHIC-\textit{b}-PLLA$_2$</td>
<td>20,700 (1.12)</td>
<td>0.59</td>
<td>○</td>
<td>○</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>PHIC-\textit{b}-PLLA$_3$</td>
<td>19,700 (1.08)</td>
<td>0.54</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>×</td>
</tr>
<tr>
<td>PHIC-\textit{b}-PCL</td>
<td>20,900 (1.07)</td>
<td>0.53</td>
<td>○</td>
<td>○</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>PHIC-\textit{b}-PCL$_2$</td>
<td>22,200 (1.17)</td>
<td>0.53</td>
<td>○</td>
<td>○</td>
<td>×</td>
<td></td>
</tr>
<tr>
<td>PHIC-\textit{b}-PCL$_3$</td>
<td>20,600 (1.09)</td>
<td>0.50</td>
<td>○</td>
<td>○</td>
<td>×</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Conditions: temp., r.t.; concentration, 0.1 (g·L$^{-1}$); ○, soluble; ×, insoluble. $^b$ Determined by $^1$H NMR spectrum in CDCl$_3$. $^c$ Determined by SEC in THF using PST standards. $^d f_{PHIC} = (M_{n,NMR, PHIC} \times d_{PLLA \text{ or } PCL})/(M_{n,NMR, PHIC} \times d_{PLLA \text{ or } PCL} + M_{n,NMR, PLLA \text{ or } PCL} \times d_{PHIC})$, $d_{PHIC} = 1.0$, $d_{PLLA} = 1.20$, and $d_{PCL} = 1.15$. 
Figure S1. SEC traces of PHIC-(OH)\textsubscript{2} (a, $M_{n,NMR} = 5,100$, $M_{w,SEC} = 6,100$, $M_w/M_n = 1.06$) and PHIC-(OH)\textsubscript{3} (b, $M_{n,NMR} = 5,200$, $M_{w,SEC} = 5,900$, $M_w/M_n = 1.06$) (flow rate, 1.0 mL·min\textsuperscript{-1}; solvent: THF).
Figure S2. FT-IR spectra of PHIC-N$_3$ (upper), PHIC-(OH)$_2$ (middle) and PHIC-(OH)$_3$(lower).
Figure S3. SEC traces detected by RI detector (eluent, THF; flow rate, 1.0 mL·min\(^{-1}\)).

a) PHIC-\(b\)-PLLA\(_2\) (solid line, \(M_{n,NMR} = 20,000, M_{w,SEC} = 23,300, M_w/M_n = 1.09\)) and PHIC-(OH)\(_2\) (dashed line, \(M_{n,NMR} = 5,100, M_w/M_n = 1.06\)), b) PHIC-\(b\)-PLLA\(_3\) (solid line, \(M_{n,NMR} = 20,200, M_{w,SEC} = 22,800, M_w/M_n = 1.08\)) and PHIC-(OH)\(_3\) (dashed line, \(M_{n,NMR} = 5,200, M_w/M_n = 1.06\)).
Figure S4. SEC traces detected by RI detector (eluent, THF; flow rate, 1.0 mL·min⁻¹).

a) PHIC-b-PCL₂ (solid line, $M_{n,NMR} = 21,700$, $M_{n,SEC} = 35,700$, $M_w/M_n = 1.06$) and PHIC-(OH)₂ (dashed line, $M_{n,NMR} = 5,500$, $M_w/M_n = 1.10$), b) PHIC-b-PCL₃ (solid line, $M_{n,NMR} = 23,600$, $M_{n,SEC} = 37,600$, $M_w/M_n = 1.09$) and PHIC-(OH)₃ (dashed line, $M_{n,NMR} = 5,600$, $M_w/M_n = 1.11$).
Figure S5. DSC results of PCL and PHIC-b-PCL₁₋₃, which were measured during heating run with a rate of 10.0 °C min⁻¹ after quenched to −100 °C from the melt: (a) PCL ($M_n = 10,000$); (b) PHIC-b-PCL ($M_{n,NMR} = 22,200$, $M_w/M_n = 1.17$, $f_{PHIC} = 0.55$); (c) PHIC-b-PCL₂ ($M_{n,NMR} = 23,000$, $M_w/M_n = 1.12$, $f_{PHIC} = 0.53$); (d) PHIC-b-PCL₃ ($M_{n,NMR} = 22,200$, $M_w/M_n = 1.14$, $f_{PHIC} = 0.54$).
Figure S6. DSC results of PCL and PHIC-b-PCL1-3, which were measured during quenching from the melts: (a) PCL ($M_n = 10,000$); (b) PHIC-b-PCL ($M_{n,NMR} = 22,200$, $M_w/M_n = 1.17$, $f_{PHIC} = 0.55$); (c) PHIC-b-PCL2 ($M_{n,NMR} = 23,000$, $M_w/M_n = 1.12$, $f_{PHIC} = 0.53$); (d) PHIC-b-PCL3 ($M_{n,NMR} = 22,200$, $M_w/M_n = 1.14$, $f_{PHIC} = 0.54$).