Supporting Information

Asymmetric Michael Addition in an Aqueous Environment with the Assistance of Optically Active Hyperbranched Polymers

Hongli Zhang, Qijin Zhang, Chunyan Hong* and Gang Zou*

Author Affiliations
Key Laboratory of Soft Matter Chemistry, Department of Polymer Science and Engineering, iChEM, University of Science and Technology of China, Hefei, Anhui 230026, China.

*Corresponding author. Email: gangzou@ustc.edu.cn; hongcy@ustc.edu.cn
Figure S1. $^1$H NMR spectra recorded in situ for the reactions of POTC+DMPDA (molar feed ratio is 1:1.25) and thiol-click in DMSO-d$_6$ under irradiation of ultraviolet-light, the time of irradiation is 0 min (a), 30 min (b), 300 min (c).

Table S1. Optically active HPBs prepared from pure L-POTC, D-POTC, and the mixture with various molar ration of L-POTC and D-POTC.

<table>
<thead>
<tr>
<th>HPBs</th>
<th>n(L-POTC)/n(D-POTC) (molar feed ration)</th>
<th>specific rotation of the obtained HBPs (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPBs-1</td>
<td>1/0</td>
<td>-8.1</td>
</tr>
<tr>
<td>HPBs-2</td>
<td>0.75/0.25</td>
<td>-3.9</td>
</tr>
<tr>
<td>HPBs-3</td>
<td>0.5/0.5</td>
<td>0</td>
</tr>
<tr>
<td>HPBs-4</td>
<td>0.33/0.67</td>
<td>2.6</td>
</tr>
<tr>
<td>HPBs-5</td>
<td>0.25/0.75</td>
<td>4.2</td>
</tr>
<tr>
<td>HPBs-6</td>
<td>0/1</td>
<td>8.3</td>
</tr>
</tbody>
</table>
**Figure S2.** $^1$H NMR spectrum of the obtained hyperbranched polymers deviated from racemic POTC monomer.

branching degree (DB):

$$DB = \frac{I_b / 2 + I_c / 2}{I_a + I_b / 2 + I_c / 2}$$

$I$ denotes the integral values of protons.

---

**Figure S3.** Typical FT-IR spectra of (i) 1,2-ethanediol, (ii) quinine, (iii) HPBs-3 and (iv) HPBs-3-co-quinine (in KBr tablet).
Figure S4. (a) GPC curves and (b) The Mn, Mw, PDI and DB of six optically active HBPs.

Scheme S1. Synthesis route of HPBs-6-co-quinine.

Figure S5. UV-vis spectra of (i) quinine, (ii) HPBs-3 and (iii) HBPs-3-co-quinine in the acetonitrile solution.
Scheme S2. Schematically illustration of the asymmetric Michael addition reaction catalyzed by quinine.

Figure S6. $^1$H NMR spectrum of the Michael adduct catalyzed by the quinine and HPBs-6, measured in CDCl$_3$ at room temperature.

Figure S7. $^{13}$C NMR spectrum of the Michael adduct catalyzed by the quinine and HPBs-6, measured in CDCl$_3$ at room temperature.
**Figure S8.** Typical FT-IR spectra of (i) 2-carbethoxycyclopentanone, (ii) N-benzylmaleimid and (iii) the Michael adduct catalyzed by quinine and HPBs-6 (in KBr tablet).

**Figure S9.** (a) UV-vis and (b) CD spectra of the Michael adduct catalyzed by the quinine and HPBs-6.
Figure S10. HPLC spectrum of the Michael adduct catalyzed by the quinine and HPBs-6 in dichloromethane.

References