Optically Active Physical Gels with Chiral Memory Ability: Directly Prepared by Helix-Sense-Selective Polymerization

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Table S1. Data for the gels and corresponding polymers. *

<table>
<thead>
<tr>
<th>Concentration of monomer (mol/L)</th>
<th>Mn</th>
<th>Mw/Mn</th>
<th>Yield (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 (without chiral additive)</td>
<td>93000</td>
<td>1.57</td>
<td>89</td>
</tr>
<tr>
<td>0.1 (R-PEA)</td>
<td>85200</td>
<td>1.56</td>
<td>88</td>
</tr>
<tr>
<td>0.05 (R-PEA)</td>
<td>83700</td>
<td>1.59</td>
<td>90</td>
</tr>
<tr>
<td>0.025 (R-PEA)</td>
<td>86100</td>
<td>1.54</td>
<td>90</td>
</tr>
<tr>
<td>0.017 (R-PEA)</td>
<td>79500</td>
<td>1.69</td>
<td>81</td>
</tr>
<tr>
<td>0.05 (S-PEA)</td>
<td>79400</td>
<td>1.58</td>
<td>88</td>
</tr>
</tbody>
</table>

* Preparation conditions: the ratio of [Rh]/[M] was 1/100 (mol/mol); the ratio of chiral PEAs/CHCl₃ was 1/100 (v/v).

b Determined by GPC with polystyrenes as standard, DMAC as eluent.

c Determined by weighing the solid product after freeze-dried.
Table S2. Comparison of the mass loss rate of the gels\textsuperscript{a} after heated at 200 °C for 30 min in vacuum.

<table>
<thead>
<tr>
<th>Dried gels</th>
<th>Synthesized without chiral additive\textsuperscript{b}</th>
<th>Synthesized with R-PEA\textsuperscript{b}</th>
<th>Synthesized with S-PEA\textsuperscript{b}</th>
<th>Synthesized with R-PEA\textsuperscript{c}</th>
<th>Synthesized with S-PEA\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight loss (%)</td>
<td>20.3</td>
<td>19.3</td>
<td>20.5</td>
<td>42.2</td>
<td>46.7</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Preparation conditions: monomer concentration [M] = 0.05 mol/L; [Rh]/[M] = 1/100 (mol/mol); chiral PEAs/CHCl\textsubscript{3} = 1/100 (v/v).

\textsuperscript{b} Dried at 50 °C after washing for 5 days in CHCl\textsubscript{3}.

\textsuperscript{c} Directly dried at 50 °C without washing.

Figure S1. Typical FT-IR spectra of the monomer and corresponding polymer (originate from the achiral gel).
**Figure S2.** NMR spectra of the monomer. A, $^1$H NMR; B, $^{13}$C NMR; measured in CDCl$_3$ at room temperature.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.38–7.02 (m, 15H, Ar−H), 4.93 (s, 1H, N−H), 3.72 (dd, 2H, CH$_2$N), 3.60 (s, 2H, CH$_2$CO), 2.09 (s, 1H, HC≡C).

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 170.2, 146.1, 129.2, 128.3, 126.6, 78.9, 71.2, 56.0, 48.6, 29.2.

**Figure S3.** Typical Raman spectra of the gels (freeze-dried for measurement) synthesized with (b) or without (a) chiral additive (R-PEA), and the monomer concentration for the gel preparations is 0.05 mol/L.

The calculated cis contents of (a) and (b) are 90.6% and 93%, respectively.
**Figure S4.** CD and UV-vis absorption spectra of the gel synthesized with both R- and S-PEA in identical amount. a, the resulting gel was directly pressed between two pieces of quartz glass for measurement; b, the polymer solution obtained by dissolving the gel in DMAC (10^{-4} \text{ mol/L}).

**Figure S5.** UV-vis absorption spectra of optically active physical gels synthesized in CHCl₃ ([M] = 0.05 mol/L) with R- (A, B) or S-PEA (C, D) and dissolved in DMAC with increasing (A, C) and decreasing (B, D) temperature. Concentration of the solutions, 10^{-4} \text{ mol/L} by monomer units.
Figure S6. CD(A, C, E) and UV-vis absorption (B, D, F) spectra of polymer gels (a, original gels) which had been immersed in a CHCl₃ solution of R-PEA (b) or S-PEA (c) for over 12 h. For A and B, the gels were directly pressed between two pieces of quartz glass for measurement; For C and D, the polymer (10⁻⁴ mol/L by monomer units) was dissolved in DMAC; For E and F, the polymer (10⁻⁴ mol/L by monomer units) was dispersed in CHCl₃ by ultrasonic. The ratio of chiral PEAs to CHCl₃ in the soak solution was 1/100 (v/v).
Figure S7. UV-vis absorption spectra of the eluates derived from immersing the optically active physical gel in CHCl₃. S-PEA was used as chiral additive for preparing the gel.

Figure S8. CD (A) and UV-vis absorption (B) spectra of the monomer (a), R-PEA (b) and S-PEA (c) dissolved in CHCl₃.
Figure S9. HPLC spectra of R-PEA (A), S-PEA (B), OAPG without washing off the chiral additive R-PEA (C), OAPG without washing off the chiral additive S-PEA (D), achiral gel after washing for 5 days in CHCl₃ (E), OAPG after washing off the chiral additive R-PEA for 5 days in CHCl₃ (F), and OAPG after washing off the chiral additive S-PEA for 5 days in CHCl₃ (G).

C18 column, 25 × 0.46 cm (i.d.); eluent, DMAC; elution flow rate, 0.5 mL/min; temperature, 25 °C; UV, 254 nm. Before measurement, all the gels were completely dried up at 50 °C in vacuum till constant weight.
Figure S10. CD spectra of the purified OAPGs dissolved in DMAC with increasing (A) and decreasing (B) temperature. Concentration of the solutions, $10^{-4}$ mol/L by monomer units.

Figure S11. UV-vis spectra of the purified OAPGs dissolved in DMAC with increasing (A, C) and decreasing (B, D) temperature. Concentration of the solutions, $10^{-4}$ mol/L by monomer units.