Supporting Information

Toward Perfect Regiocontrol for β-Selective Cyclopolymerization Using a Ru-Based Olefin Metathesis Catalyst

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Table of Contents

1. General experimental ........................................................................................................... S3
2. Experimental procedures for the preparation of the monomers ........................................... S4
3. General procedure for the cyclopolymerization .................................................................. S5
4. Polymerization results in Table 1 ....................................................................................... S5
5. $^1$H and $^{13}$C NMR characterization of the polymers ........................................................ S6
6. $^{13}$C NMR spectra of the polymers in Table 1 ................................................................. S7–S11
7. In situ NMR experiment: procedure and data ................................................................. S12
8. Physical and thermal properties of the polymers .............................................................. S13
9. UV-Vis and PL spectra of the polymers ............................................................................. S13–S14
10. Cyclic voltammograms of the polymers ........................................................................... S15–S16
11. TGA and DSC curves of the polymers ............................................................................. S16–S23
12. $^1$H and $^{13}$C NMR spectra of the monomers ................................................................. S24
13. SEC traces of the polymers in Table 1 ............................................................................. S25–S31
14. Calculation of the regioselectivity for P1 using $^1$H NMR ................................................... S32
15. References ......................................................................................................................... S33
1. General experimental

Materials
All reagents which are commercially available from Sigma-Aldrich®, Tokyo Chemical Industry Co. Ltd., Acros Organics, Alfa Aesar®, without additional notes, were used without further purification. Ru2 was provided from Materia Inc. (C633, CAS# 1352916-84-7), and is also commercially available from Sigma-Aldrich®. Dichloromethane for the polymerization were purified by Glass Contour Organic Solvent Purification System, and degassed further by Ar bubbling for 10 minutes before performing reactions. Thin-layer chromatography (TLC) was carried out on MERCK TLC silica gel 60 F254 and flash column chromatography was performed using MERCK silica gel 60 (0.040~0.063 mm).

Characterization
1H-NMR and 13C-NMR were recorded by Varian/Oxford As-500 (500 MHz for 1H and 125 MHz for 13C) and Agilent 400-MR (400 MHz for 1H and 100 MHz for 13C) spectrometers. 13C NMR for the polymers were mainly recorded by Bruker (600 MHz for 1H and 150 MHz for 13C) spectrometers in the National Instrumentation Center for Environmental Management (NICEM) at SNU. High resolution mass spectroscopy (HRMS) analyses were performed by the ultrahigh resolution ESI Q-TOF mass spectrometer (Bruker, Germany) in the Sogang Centre for Research Facilities. Size exclusion chromatography (SEC) analyses were carried out with Waters system (1515 pump, 2414 refractive index detector) and Shodex GPC LF-804 column eluted with THF (GPC grade, Honeywell Burdick & Jackson®) and filtered with a 0.2 μm PTFE filter (Whatman®). Flow rate was 1.0 mL/min and temperature of column was maintained at 35 °C. UV-Vis spectra were obtained by Jasco Inc. UV/vis Spectrometer V-650. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out under N2 gas at a scan rate of 10 °C/min with Q50 and Q10 model devices, respectively, from TA Instruments. Cyclic voltammetry (CV) measurements were carried out on a CHI 660 Electrochemical Analyzer (CH Instruments, Insc., Texas, USA).
2. Experimental procedures for the preparation of the monomers

Ru1, Ru3, M1-M4, M5, M6, M7, M9, M10, and M11 were prepared by literature methods.

M8 (3,3,9,9-tetraisopropyl-2,10-dimethyl-6,6-di(prop-2-yn-1-yl)-4,8-dioxo-3,9-disilaundecane)

To a solution of 4,4-Bis(hydroxymethyl)-1,6-heptadiyne (460 mg, 3.0 mmol) in dichloromethane (9 mL), 2,6-lutidine (1.4 mL, 12 mmol) was added and the mixture was cooled down to 0 °C, followed by the addition of triisopropylsilyl trifluoromethanesulfonate (1.1 mL, 6 mmol). After stirring overnight at room temperature, the mixture was quenched by aqueous NH₄Cl solution. Product was extracted with ethyl acetate and organic layer was washed with brine. The organic layer was dried with MgSO₄ and concentrated to give a yellow colored solid. It was purified by flash column chromatography on silica gel (Hexane 100%) to afford compound M8 as a colorless liquid (1.2 g, 84%).

\[
\text{\textsuperscript{1}H NMR (500 MHz, CDCl}_3\text{)} \delta 3.71 (s, 4H), 2.37 (d, J = 2.7 Hz, 4H), 1.95 (t, J = 2.6 Hz, 2H), 1.07 (s, 42H);
\text{\textsuperscript{13}C NMR (125 MHz, CDCl}_3\text{)} \delta 81.6, 70.5, 64.1, 44.2, 21.4, 18.2, 12.2.;}
\text{HR-MS (ESI) m/z for } \text{C}_{27}\text{H}_{52}\text{NaO}_2\text{Si}_2\text{ [M+Na]}^+, \text{calcd. 487.3398, found: 487.3399.}
3. **General procedure for the cyclopolymerization**

A 5-mL sized screw-cap vial with septum was flame dried and charged with monomer and a magnetic bar. The vial was purged with argon four times, and degassed anhydrous dichloromethane was added. After the Ar-purged catalyst (Ru1-Ru3) in another 5-mL vial was dissolved in dichloromethane, the solution was rapidly injected to the monomer solution at experimental temperature (RT) under vigorous stirring. The reaction was quenched by excess ethyl vinyl ether after desired reaction time, and partially precipitated in hexane at -78 °C, remaining small amount of crude mixture (~10%). Obtained solid was filtered and dried in vacuo. Monomer conversion was calculated from the $^1$H NMR spectrum of the remaining crude mixture.

4. **Polymerization results in Table 1**

<table>
<thead>
<tr>
<th>No.</th>
<th>Additive</th>
<th>M/I/Add</th>
<th>conv$^a$</th>
<th>yield$^b$</th>
<th>$M_n$(Da)$^c$</th>
<th>PDI$^c$</th>
<th>6:5 ($^1$H)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>30/1/-</td>
<td>76%</td>
<td>58%</td>
<td>6.8k</td>
<td>1.58</td>
<td>5.9:1</td>
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<tr>
<td>2</td>
<td>Pyridine</td>
<td>30/1/10</td>
<td>83%</td>
<td>46%</td>
<td>6.6k</td>
<td>1.48</td>
<td>6.1:1</td>
</tr>
<tr>
<td>3</td>
<td>3-ClPy</td>
<td>30/1/10</td>
<td>85%</td>
<td>76%</td>
<td>7.1k</td>
<td>1.63</td>
<td>8.8:1</td>
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<tr>
<td>4</td>
<td>3-BrPy</td>
<td>30/1/10</td>
<td>45%</td>
<td>37%</td>
<td>6.0k</td>
<td>1.43</td>
<td>12.5:1</td>
</tr>
<tr>
<td>5</td>
<td>3-IPy</td>
<td>30/1/10</td>
<td>73%</td>
<td>15%</td>
<td>5.3k</td>
<td>1.43</td>
<td>13.8:1</td>
</tr>
<tr>
<td>6</td>
<td>3,5-Cl$_2$Py</td>
<td>30/1/10</td>
<td>91%</td>
<td>65%</td>
<td>8.1k</td>
<td>1.62</td>
<td>11.6:1</td>
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<tr>
<td>7</td>
<td>3,5-Br$_2$Py</td>
<td>30/1/10</td>
<td>6.1%</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>8</td>
<td>3,5-Me$_2$Py</td>
<td>30/1/10</td>
<td>29%</td>
<td>29%</td>
<td>6.4k</td>
<td>1.46</td>
<td>4.3:1</td>
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<td>9</td>
<td>4-MeOPy</td>
<td>30/1/10</td>
<td>18%</td>
<td>11%</td>
<td>3.5k</td>
<td>1.31</td>
<td>1.9:1</td>
</tr>
<tr>
<td>10</td>
<td>4-MePy</td>
<td>30/1/10</td>
<td>4.5%</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>4-IPy</td>
<td>30/1/10</td>
<td>74%</td>
<td>22%</td>
<td>5.4k</td>
<td>1.48</td>
<td>14.3:1</td>
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<tr>
<td>12</td>
<td>4-CF$_3$Py</td>
<td>30/1/10</td>
<td>6.2%</td>
<td>-</td>
<td>-</td>
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<td>-</td>
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</table>

$^a$Determined from $^1$H NMR. $^b$Precipitated in Hex at -78 °C. $^c$Determined by THF SEC calibrated using polystyrene standards.
5. $^1$H and $^{13}$C NMR characterization of polymers

Poly($M_1$)
$^1$H (500 MHz, CDCl$_3$): $\delta$ 7.04 – 5.73 (br m, 2H), 4.40 – 3.88 (br s, 4H), 3.62 – 2.69 (br m, 4H), 1.50 – 1.01 (br s, 6H); $^{13}$C (125 MHz, CDCl$_3$): $\delta$ 171.9, 170.0, 134.5, 134.1, 133.1, 131.8, 61.7, 58.1, 54.7, 35.1, 32.4, 14.2.

Poly($M_2$)
$^1$H (500 MHz, CDCl$_3$): $\delta$ 6.94 – 5.69 (br m, 2H), 5.22 – 4.82 (br s, 2H), 3.62 – 2.60 (br m, 4H), 1.50 – 0.97 (br s, 12H); $^{13}$C (125 MHz, CDCl$_3$): $\delta$ 171.4, 170.3, 136.5, 134.4, 134.1, 133.1, 131.9, 69.0, 57.9, 54.5, 32.2, 21.6.

Poly($M_3$)
$^1$H (500 MHz, CDCl$_3$): $\delta$ 6.93 – 5.71 (br m, 2H), 3.56 – 2.46 (br m, 4H), 1.74 – 1.07 (br m, 12H); $^{13}$C (125 MHz, CDCl$_3$): $\delta$ 171.1, 170.1, 134.6, 134.3, 133.3, 131.9, 81.4, 59.1, 55.7, 35.3, 32.4, 27.7.

Poly($M_4$)
$^1$H (500 MHz, CDCl$_3$): $\delta$ 6.85 – 5.63 (br m, 2H), 3.71 – 2.52 (br m, 4H), 1.30 – 0.66 (br m, 18H); $^{13}$C (125 MHz, CDCl$_3$): $\delta$ 171.8, 170.7, 135.1, 135.0, 132.4, 65.3, 40.6, 33.5, 30.6, 26.2, 18.4, -5.3.

Poly($M_5$)
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.06 – 5.47 (br m, 2H), 4.01 – 3.21 (br s, 2H), 3.21 – 1.47 (br m, 4H), 1.12 – 0.57 (br s, 9H), 0.37 – -0.40 (br s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 137.0, 134.6, 130.9, 67.3, 37.2, 32.6, 29.8, 26.1, 18.5, -5.2.

Poly($M_6$)
$^{13}$C (125 MHz, CDCl$_3$): $\delta$ 136.4, 133.8, 132.4, 66.4, 66.0, 41.3, 33.6, 31.0, 18.3, 12.2.

Poly($M_7$)
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.46 – 6.99 (br m, 10H), 4.63 – 4.19 (br s, 4H), 3.61 – 3.10 (br s, 4H), 2.86 – 2.21 (br m, 4H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 139.2, 135.6, 135.2, 133.3, 132.3, 128.3, 127.3, 73.3, 73.3, 39.6, 34.4, 31.4.

Poly($M_8$)
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.92 – 5.62 (br m, 2H), 3.40 (br d, 8H), 2.80 – 2.07 (br m, 4H), 1.39 – 0.92 (br s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 135.9, 135.4, 133.0, 132.0, 74.2, 73.7, 73.6, 67.0, 66.8, 39.4, 34.1, 31.2, 15.3.

Poly($M_9$)
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 6.92 – 5.62 (br m, 2H), 3.40 (br d, 8H), 2.80 – 2.07 (br m, 4H), 1.39 – 0.92 (br s, 6H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 135.9, 135.4, 133.0, 132.0, 74.2, 73.7, 73.6, 67.0, 66.8, 39.4, 34.1, 31.2, 15.3.

Poly($M_{10}$)
$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.00 – 5.58 (br m, 2H), 4.35 – 3.79 (br s, 2H), 3.79 – 2.14 (br m, 4H), 1.65 – 0.82 (br d, 9H), 0.56 – -0.22 (br s, 9H); $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$ 174.2, 137.5, 136.5, 134.2, 131.7, 130.3, 76.4, 60.4, 56.8, 56.6, 56.3, 56.2, 35.9, 33.7, 32.7, 30.2, 26.8, 14.2, 2.7.

S6
6. $^{13}$C NMR spectra of the polymers in Table 1

Those spectra were used for the determination of the ratio between five- and six-ring on the polymer backbone.
<Figure S5. $^{13}$C NMR spectra of polymer from entry 5 in Table 1>

<Figure S6. $^{13}$C NMR spectra of polymer from entry 6 in Table 1>

<Figure S7. $^{13}$C NMR spectra of polymer from entry 7 in Table 1>

<Figure S8. $^{13}$C NMR spectra of polymer from entry 8 in Table 1>
Figure S9. $^{13}$C NMR spectra of polymer from entry 9 in Table 1

Figure S10. $^{13}$C NMR spectra of polymer from entry 10 in Table 1

Figure S11. $^{13}$C NMR spectra of polymer from entry 11 in Table 1

Figure S12. $^{13}$C NMR spectra of polymer from entry 12 in Table 1
Figure S13. $^{13}$C NMR spectra of polymer from entry 13 in Table 1

Figure S14. $^{13}$C NMR spectra of polymer from entry 14 in Table 1

Figure S15. $^{13}$C NMR spectra of polymer from entry 16 in Table 1

Figure S16. $^{13}$C NMR spectra of polymer from entry 18 in Table 1
<Figure S17. $^{13}$C NMR spectra of polymer from entry 19 in Table 1>

<Figure S18. $^{13}$C NMR spectra of polymer from entry 20 in Table 1>

<Figure S19. $^{13}$C NMR spectra of polymer from entry 21 in Table 1>

<Figure S20. $^{13}$C NMR spectra of polymer from entry 22 in Table 1>
7. *In situ* NMR experiment: procedure and data

**Ru3** (0.003 mmol, 1 eq) and hexamethyldisilane (internal standard, 5 μl) were dissolved in DCM-\(d_2\) (400 μl). Initial benzylidene was measured by integral ratio of **Ru3** to hexamethyldisilane in \(^1\)H NMR spectrum. (After the addition of 7 eq of the pyridine additive,) Monomer (0.06 mmol, 20 eq) solution in DCM-\(d_2\) (200 μl) was added to the **Ru3** solution and mixed by shaking NMR tube for 5 sec. The reaction was monitored by \(^1\)H NMR over time. The \(k_i\) or \(k_p\) values were obtained from the slope of linear – \(\ln [\text{Ru3}]/[\text{Ru3}]_0\) or – \(\ln [\text{M}]/[\text{M}]_0\) vs. time graphs, respectively.

<table>
<thead>
<tr>
<th>M/I/Add</th>
<th>(k_i)</th>
<th>(k_p)</th>
<th>(k_i/k_p)</th>
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<tr>
<td>20/1/-</td>
<td>0.4847</td>
<td>0.4584</td>
<td>1.0574</td>
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<tr>
<td>20/1/7</td>
<td>0.4432</td>
<td>0.1263</td>
<td>3.5091</td>
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8. Physical and thermal properties of the polymers

<Table S2. Comparison of the properties (five- vs. six-membered rings)>

<table>
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<tr>
<th>Monomer</th>
<th>Cat</th>
<th>Solution</th>
<th>Film</th>
<th>$E_{\text{HOMO}}$ (eV)</th>
<th>PL (nm)</th>
<th>Stokes shift (nm)</th>
<th>$T_d$ (°C)</th>
<th>$T_g$ (°C)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$E_g$ (eV)</td>
<td>$\lambda_{\text{max}}$ (nm)</td>
<td>$E_g$ (eV)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M3</td>
<td>Ru1</td>
<td>588, 547</td>
<td>2.02</td>
<td>515</td>
<td>2.01</td>
<td>-4.98</td>
<td>643</td>
<td>96</td>
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<tr>
<td></td>
<td>Ru3</td>
<td>519</td>
<td>1.92</td>
<td>477</td>
<td>1.93</td>
<td>-4.73</td>
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<td>640</td>
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<tr>
<td></td>
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<td>1.91</td>
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<td>M6</td>
<td>Ru1</td>
<td>586, 546</td>
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<td>548</td>
<td>1.94</td>
<td>-4.77</td>
<td>645</td>
<td>99</td>
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<tr>
<td></td>
<td>Ru3</td>
<td>508</td>
<td>1.94</td>
<td>503</td>
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<td>644</td>
<td>124</td>
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<td>M7</td>
<td>Ru1</td>
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<td>1.97</td>
<td>572, 529</td>
<td>2.02</td>
<td>-5.12</td>
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<td>1.97</td>
<td>598, 551</td>
<td>1.94</td>
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<td>Ru3</td>
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<td>496</td>
<td>1.86</td>
<td>-4.52</td>
<td>641</td>
<td>104</td>
</tr>
</tbody>
</table>

9. UV-Vis and PL spectra of the polymers
10. Cyclic voltammograms of the polymers

Cyclic voltammetry (CV) measurement was carried out at the room temperature on a CHI 660 Electrochemical Analyzer (CH Instruments, Inc., Texas, USA) using a degassed acetonitrile solution of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M). Polymer solution was prepared by dissolving the polymer in dichloromethane (10 mg/ml). Cyclic voltammogram was recorded using the glassy carbon working electrode and a reference electrode of Ag/Ag⁺ (0.1 M AgNO₃ in acetonitrile) with a platinum wire counter electrode at a scan rate of 50 mV/s. The absolute energy level was obtained using ferrocene/ferrocinium as an internal standard. The oxidation potential of ferrocene was regarded as -4.8 eV.
11. TGA and DSC curves of the polymers

TGA and DSC data for Poly(M3) synthesized using Ru1 catalyst were reported previously.3

<Figure S21, TGA curves of Poly(M3) synthesized using Ru3 catalyst>
Figure S22. TGA curves of Poly(M5) synthesized using Ru1 catalyst.

Figure S23. TGA curves of Poly(M5) synthesized using Ru3 catalyst.
<Figure S24. TGA curves of Poly(M6) synthesized using Ru1 catalyst>

<Figure S25. TGA curves of Poly(M6) synthesized using Ru3 catalyst>
<Figure S26. TGA curves of Poly(M7) synthesized using Ru1 catalyst>

<Figure S27. TGA curves of Poly(M7) synthesized using Ru3 catalyst>
<Figure S28. TGA curves of Poly(M11) synthesized using Ru1 catalyst>

<Figure S29. TGA curves of Poly(M11) synthesized using Ru3 catalyst>
<Figure S30. DSC thermogram of Poly(M3) synthesized using Ru3 catalyst>

<Figure S31. DSC thermogram of Poly(M5) synthesized using Ru1 catalyst>

<Figure S32. DSC thermogram of Poly(M5) synthesized using Ru3 catalyst>
<Figure S33. DSC thermogram of Poly(M7) synthesized using Ru1 catalyst>

<Figure S34. DSC thermogram of Poly(M7) synthesized using Ru3 catalyst>

<Figure S35. DSC thermogram of Poly(M11) synthesized using Ru1 catalyst>
Figure S36. DSC thermogram of Poly(M11) synthesized using Ru3 catalyst.
12. $^1$H and $^{13}$C NMR spectra of the monomers

**M8 ($^1$H, 400 MHz, CDCl₃)**

![M8 $^1$H NMR spectrum](image1)

**M8 ($^{13}$C, 100 MHz, CDCl₃)**

![M8 $^{13}$C NMR spectrum](image2)
13. SEC traces of the polymers in Table 1
14. Calculation of the regioselectivity for P1 using $^1$H NMR

Monomer conversion $= 1 - \frac{H_{\text{alkyne}}}{2.0}$

Composition of five-membered ring $= \frac{2 \times H_{\text{C,5}}/H_{\text{originated from propargylic}}}{\text{Monomer conversion}}$

e.g. (entry 2 in Table 1)

Composition of five-membered ring $= \frac{2 \times 0.15/3.83}{0.91} = 0.086$ (6-ring:5-ring=11.6:1)
15. References


