Supporting Information

Ruthenium Catalyzed Equilibrium Ring-Opening Metathesis Polymerization of Cyclopentene

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**General information**

All reactions were conducted under Argon atmosphere. Ruthenium catalysts 1 and 2 (Materia), cyclopentene (Aldrich), ethyl vinyl ether (Aldrich), norbornene (Aldrich) toluene-$d_8$ (Cambridge Isotope or Aldrich) and other solvents, were used as received. Catalyst 3 was synthetized following literature procedures.\(^1\)

NMR experiments were performed at 25 °C. All NMR samples were stabilized at 25 °C for 5 min before data collection. All the screw capped, gas tight NMR tubes were flame dried and evacuated *in vacuo* in advance. The \(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker Avance II 400 spectrometer in Toluene-$d_8$ and referenced to residual internal toluene (δ = 2.09 ppm \(^1\)H and 20.4 ppm \(^{13}\)C). The quantitative \(^{13}\)C NMR spectra for *cis/trans* bond ratio determination were recorded with inverse gated decoupling at 10 s relaxation delay.

GPC analyses were carried out using a Viscotek GPC Max VE 2001 instrument with a Viscotek TDA 302 triple array detector and Viscotek Org Guard column with three (in series) Mixed Medium columns (LT5000L) at 35 °C and a flow rate of 1.0 mL/min. A 12-point Universal Calibration Standard calibration curve was recorded. From each sample three measurements have been carried out and the averages have been reported. A during the tests a second calibration curve has been recorded with polystyrene (PS) standards and the measured MW values of the samples were corrected with the multiplication of the measured values with 0.938.

![Figure S1. GPC calibration with PS standards, theoretical vs measured MW values (kDa).](image-url)

\(^1\) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *Organometallics*, **2001**, 20, 5314.
Investigation of the impact of reaction temperature on the ROMP of cyclopentene.

All the experiments were performed under the same conditions including vessel type, stirrer shape and size and concentration ranges at 0, 10, 20 and 30 °C. In a glove box, 10 mL, oven-dried round bottom flasks were charged with 4.2 mg (0.00495 mmol) 2 catalyst and 0.8 mL freshly opened toluene-$d_8$. The vessels were sealed with gas tight septa, taken out of the glovebox and cooled down to the target temperature under continuous stirring (500 rpm). Then 0.20 mL (2.17 mmol) cyclopentene was added by a 1.0 mL Hamilton glass syringe under inert atmosphere. After two hours, the reaction mixtures were quenched with 0.10 mL (1.044 mmol) ethyl vinyl ether. The solutions were stirred for an additional 15 minutes then 0.5 mL samples were transferred into sealable NMR tubes. $^1$H NMR spectra were recorded for each sample and the conversion was determined by the ratio of the integrals of the peaks at 5.70 ppm (cyclopentene, CH, s) and 5.45 ppm (polypentenamer, CH, br, s), ethyl vinyl ether was used as internal standard. The cis/trans ratio of the bonds was determined by quantitative $^{13}$C NMR spectra recorded in toluene-$d_8$ following the evaporation of the volatiles from the rest of the mixture remained in the reaction vessel. The cis/trans ratio was determined according to the integral of the peaks at 130.7 and 130.1 ppm. The solvents were then evaporated from the sample and the remaining rubber like residues were dissolved in THF to obtain 1.0 mg/mL polymer solution for GPC test (Figure S2-S6).
**Thermodynamic data calculation.** (See also Table 1. and Figure 1.) According to the equilibrium polymerization theory the thermodynamic data were calculated from the following relationships:

\[
\ln[M] = \frac{\Delta H}{RT} - \frac{\Delta S}{R}
\]

where \([M]\) is the monomer equilibrium concentration, \(\Delta H\) is the activation enthalpy (kJ mol\(^{-1}\)) during the polymerization, \(R\) is the universal gas constant (8.3144 J·mol\(^{-1}\)·K\(^{-1}\)), \(T\) is the absolute temperature in degrees Kelvin (K) and \(\Delta S\) is the activation entropy (J·mol\(^{-1}\)·K\(^{-1}\)). \(\Delta H\) can be calculated from the slope of the line in Figure 1. \((m = -2.80 \cdot 10^3 \text{ K})\) according to the following equation (1 kcal = 4.184 kJ):

\[
\Delta H = m \cdot R
\]

\[
\Delta H = -2.80 \cdot 10^3 K \cdot 8.31 J \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = -23.28 \text{ kJ} \cdot \text{mol}^{-1}
\]

\[
\Delta H = -5.56 \text{ kcal} \cdot \text{mol}^{-1}
\]

The standard entropy change can be calculated with the rearrangement of equation (1):

\[
\Delta S = \frac{\Delta H}{T} - R \cdot \ln[M]
\]

\[
\Delta S = \frac{-23268 J \cdot \text{mol}^{-1}}{273 K} - 8.31 \cdot \ln[0.385] = -77.30 J \cdot \text{mol}^{-1} \cdot \text{K}^{-1}
\]

\[
\Delta S = -18.47 \text{ cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}
\]
Figure S2. $^1$H NMR spectrum (top) of the reaction mixture quenched at 2 hour in toluene-$d_8$ at 0 °C. Quantitative $^{13}$C spectrum (middle) and a representative GPC plot (bottom) of the isolated polymer.
Figure S3. $^1$H NMR spectrum (top) of the reaction mixture quenched at 5 hour in toluene-$d_8$ at 0 °C. Quantitative $^{13}$C spectrum (middle) and a representative GPC plot (bottom) of the isolated polymer.
Figure S4. $^1$H NMR spectrum (top) of the reaction mixture quenched at 2 hour in toluene-$d_8$ at 10 °C. Quantitative $^{13}$C spectrum (middle) and a representative GPC plot (bottom) of the isolated polymer.
Figure S5. $^1$H NMR spectrum (top) of the reaction mixture quenched at 2 hour in toluene-$d_8$ at 20 °C. Quantitative $^{13}$C spectrum (middle) and a representative GPC plot (bottom) of the isolated polymer.
**Figure S6.** $^1$H NMR spectrum (top) of the reaction mixture quenched at 2 hour in toluene-$d_8$ at 30 °C. Quantitative $^{13}$C spectrum (middle) and a representative GPC plot (bottom) of the isolated polymer.
Investigation of the impact of catalyst loading on the ROMP of cyclopentene.

All the experiments were performed in the same conditions including vessel type, stirrer shape and size at 0 °C. In the glove box a 10 mL, oven-dried round bottom flasks were charged with 2.2 mg (0.00259 mmol), 4.2 mg (0.00495 mmol), 10.3 mg (0.01213 mmol), 20.5 mg (0.02415 mmol) catalyst 2 and 0.8 mL freshly opened toluene-$d_8$. The vessels were sealed with gas tight septa, taken out of the glovebox and cooled down to 0 °C under continuous stirring (500 rpm). Then 0.20 mL (2.17 mmol) cyclopentene was added by a 1.0 mL Hamilton glass syringe under inert atmosphere. After two hours the reaction mixtures were quenched with 0.10 mL (1.044 mmol) ethyl vinyl ether. The solutions were stirred for additional 15 minutes then 0.5 mL samples were transferred into a sealable NMR tubes. $^1$H NMR spectra were recorded for each sample and the conversion was determined by the ratio of the integrals of the peaks at 5.70 ppm (cyclopentene, CH, s) and 5.45 ppm (polypentenamer, CH, br, s), ethyl vinyl ether was used as internal standard. Then the volatiles were evaporated from the rest of the mixture remained in the reaction vessel. The remaining rubber like residues was dissolved in THF to obtain 1.0 mg/mL polymer solution for GPC test.
**Table S1.** Cyclopentene conversion at different catalyst loading. Toluene-$d_8$ solution; [M] = 2.17 M; catalyst: 2; t = 0 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>[2] (mM)</th>
<th>$t_r$ (h)</th>
<th>Conversion (%)</th>
<th>$\text{MW}_{\text{theoretical}}$ (kDa)</th>
<th>$\text{MW}_{\text{theoretical Corrected with conversion}}$ (kDa)</th>
<th>$\text{MW}_{\text{measured}}$ (kDa)</th>
<th>PDI</th>
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<tbody>
<tr>
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<td>2</td>
<td>34.5</td>
<td>59.44</td>
<td>20.51</td>
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<tr>
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<td>3</td>
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**Figure S7.** Cyclopentene conversions obtained at different catalyst 2 loading. Toluene-$d_8$ solution; [cyclopentene] = 2.17 M; catalyst 2; t = 0 °C; $t_r$ = 2h (red), 5h (orange).
Investigation of the impact of different Ru catalyst systems on the ROMP of cyclopentene.

All the experiments were performed in the same conditions including vessel type, stirrer shape and size at 0 °C. In a glove box, a 10 mL, oven-dried round bottom flasks were charged with 2.0 mg (1, 0.00486 mmol), 2.2 mg (2, 0.00259 mmol) and 4.4 mg (3, 0.00497 mmol) catalysts and 0.8 mL freshly opened toluene-$d_8$. The vessels were sealed with gas tight septa, taken out of the glovebox and cooled down to 0 °C under continuous stirring (500 rpm). Then 0.20 mL (2.17 mmol) cyclopentene was added by a 1.0 mL Hamilton glass syringe under inert atmosphere. After two hours the reaction mixtures were quenched with 0.10 mL (1.044 mmol) ethyl vinyl ether. The solutions were stirred for additional 15 minutes then 0.5 mL samples were transferred into sealable NMR tubes. $^1$H NMR spectra were recorded for each sample and the conversion was determined by the ratio of the integrals of the peaks at 5.70 ppm (cyclopentene, CH, s) and 5.45 ppm (polypentenamer, CH, br, s), ethyl vinyl ether was used as internal standard. Then the volatiles were evaporated from the rest of the mixture remained in the reaction vessel. The remaining rubber like residues was dissolved in THF to obtain 1.0 mg/mL polymer solution for GPC test.
Table S2. Cyclopentene conversion with different catalyst systems. Toluene-$d_8$ solution; [M] = 2.17 M; 
$t = 0 \, ^\circ\text{C}; \ t_r = 2h$ (entry 3: $t_r = 5h$).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>[Catalyst] (mM)</th>
<th>Conversion (%)</th>
<th>MW\text{theoretical} (kDa)</th>
<th>MW\text{theoretical Corrected with conversion} (kDa)</th>
<th>MW\text{measured} (kDa)</th>
<th>PDI</th>
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<tbody>
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Figure S8. Cyclopentene conversion with different catalyst systems. Toluene-$d_8$ solution; [M] = 2.17 
M; $t = 0 \, ^\circ\text{C}; \ t_r = 2h$ (red), $5h$ (orange).