Supplementary information for “Development of H$_3$PW$_{12}$O$_{40}$/CeO$_2$ catalyst for bulk ring-opening polymerization of cyclic carbonate”

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Table S1. Effect of the pre-calcination temperature of CeO$_2$

<table>
<thead>
<tr>
<th>Pre-calcination temperature / ºC</th>
<th>BET surface area / m$^2$ g$^{-1}$</th>
<th>Conv. a) / %</th>
<th>Ether linkage a) / %</th>
<th>$M_{n,\text{theo}}$ b) / g mol$^{-1}$</th>
<th>$M_{n,\text{GPC}}$ c) / g mol$^{-1}$</th>
<th>$M_{w}/M_{n}$ c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>119</td>
<td>12</td>
<td>0</td>
<td>3,700</td>
<td>3,600</td>
<td>1.21</td>
</tr>
<tr>
<td>500</td>
<td>109</td>
<td>18</td>
<td>0</td>
<td>5,700</td>
<td>5,100</td>
<td>1.31</td>
</tr>
<tr>
<td>600</td>
<td>73</td>
<td>20</td>
<td>0</td>
<td>6,300</td>
<td>6,200</td>
<td>1.41</td>
</tr>
<tr>
<td>700</td>
<td>62</td>
<td>15</td>
<td>0</td>
<td>4,700</td>
<td>4,500</td>
<td>1.35</td>
</tr>
<tr>
<td>800</td>
<td>43</td>
<td>4</td>
<td>0</td>
<td>1,300</td>
<td>1,400</td>
<td>1.19</td>
</tr>
<tr>
<td>900</td>
<td>26</td>
<td>0</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tbody>
</table>

Reaction conditions: 1 wt% H$_3$PW$_{12}$O$_{40}$/CeO$_2$ 20 mg (pretreated by drying under reduced pressure, 180 ºC, 0.5 h), TMC 3 mmol, methyl iodide 0.01 mmol, reaction temperature 60 ºC, reaction time 2 h.

a) calculated by $^1$H NMR, b) calculated by $[\text{TMC}]_0/[\text{CH}_3\text{I}]_0 \times (\text{conv.}) \times (\text{molecular weight of TMC}) + (\text{molecular weight of CH}_3\text{I})$, c) determined by GPC in chloroform relative to polystyrene standards.

Table S2. Effect of the pretreatment temperature

<table>
<thead>
<tr>
<th>Pretreatment temperature / ºC</th>
<th>Conversion a) / %</th>
<th>Ether linkage a) / %</th>
<th>$M_{n,\text{theo}}$ b) / g mol$^{-1}$</th>
<th>$M_{n,\text{GPC}}$ c) / g mol$^{-1}$</th>
<th>$M_{w}/M_{n}$ c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>7</td>
<td>0</td>
<td>2,100</td>
<td>660</td>
<td>1.29</td>
</tr>
<tr>
<td>100</td>
<td>8</td>
<td>0</td>
<td>2,700</td>
<td>2,000</td>
<td>1.30</td>
</tr>
<tr>
<td>120</td>
<td>8</td>
<td>0</td>
<td>2,700</td>
<td>3,500</td>
<td>1.31</td>
</tr>
<tr>
<td>140</td>
<td>11</td>
<td>0</td>
<td>3,500</td>
<td>3,400</td>
<td>1.33</td>
</tr>
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<td>15</td>
<td>0</td>
<td>4,600</td>
<td>4,600</td>
<td>1.40</td>
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<tr>
<td>180</td>
<td>20</td>
<td>0</td>
<td>6,300</td>
<td>6,200</td>
<td>1.41</td>
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<td>200</td>
<td>8</td>
<td>0</td>
<td>2,700</td>
<td>2,800</td>
<td>1.30</td>
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</tbody>
</table>

Reaction conditions: 1 wt% H$_3$PW$_{12}$O$_{40}$/CeO$_2$ 20 mg (pretreated by drying under reduced pressure, 0.5 h), TMC 3 mmol, methyl iodide 0.01 mmol, reaction temperature 60 ºC, reaction time 2 h.

a) calculated by $^1$H NMR, b) calculated by $[\text{TMC}]_0/[\text{CH}_3\text{I}]_0 \times (\text{conv.}) \times (\text{molecular weight of TMC}) + (\text{molecular weight of CH}_3\text{I})$, c) determined by GPC in chloroform relative to polystyrene standards.

Table S3. Effect of the loaded amount of H$_3$PW$_{12}$O$_{40}$ on CeO$_2$

<table>
<thead>
<tr>
<th>Loaded amount of H$<em>3$PW$</em>{12}$O$_{40}$ / wt%</th>
<th>BET surface area / m$^2$ g$^{-1}$</th>
<th>Conversion a) / %</th>
<th>Ether linkage a) / %</th>
<th>$M_{n,\text{theo}}$ b) / g mol$^{-1}$</th>
<th>$M_{n,\text{GPC}}$ c) / g mol$^{-1}$</th>
<th>$M_{w}/M_{n}$ c)</th>
</tr>
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<td>66</td>
<td>19</td>
<td>0</td>
<td>5,900</td>
<td>19,000</td>
<td>1.26</td>
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<tr>
<td>0.5</td>
<td>70</td>
<td>20</td>
<td>0</td>
<td>6,300</td>
<td>14,000</td>
<td>1.29</td>
</tr>
<tr>
<td>1</td>
<td>73</td>
<td>20</td>
<td>0</td>
<td>6,300</td>
<td>6,200</td>
<td>1.41</td>
</tr>
<tr>
<td>2</td>
<td>70</td>
<td>3</td>
<td>0</td>
<td>1,000</td>
<td>470</td>
<td>1.39</td>
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<tr>
<td>5</td>
<td>68</td>
<td>2</td>
<td>0</td>
<td>750</td>
<td>250</td>
<td>1.36</td>
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</table>

Reaction conditions: H$_3$PW$_{12}$O$_{40}$/CeO$_2$ 20 mg (pretreated by drying under reduced pressure, 180 ºC, 0.5 h), TMC 3 mmol, methyl iodide 0.01 mmol, reaction temperature 60 ºC, reaction time 2 h.

a) calculated by $^1$H NMR, b) calculated by $[\text{TMC}]_0/[\text{CH}_3\text{I}]_0 \times (\text{conv.}) \times (\text{molecular weight of TMC}) + (\text{molecular weight of CH}_3\text{I})$, c) determined by GPC in chloroform relative to polystyrene standards.
weight of CH$_3$I), c) determined by GPC in chloroform relative to polystyrene standards.

Table S4. Catalyst recycle test

<table>
<thead>
<tr>
<th>Usage time</th>
<th>Conversion a) / %</th>
<th>Ether linkage a) selectivity / %</th>
<th>$M_{n,\text{theo}}$ b) / g mol$^{-1}$</th>
<th>$M_{n,\text{GPC}}$ c) / g mol$^{-1}$</th>
<th>$M_{w}/M_{n}$ c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21</td>
<td>0</td>
<td>6,400</td>
<td>6,200</td>
<td>1.41</td>
</tr>
<tr>
<td>2</td>
<td>17</td>
<td>0</td>
<td>5,100</td>
<td>690</td>
<td>1.18</td>
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<tr>
<td>2$^{b)}$</td>
<td>17</td>
<td>0</td>
<td>5,100</td>
<td>1,300</td>
<td>1.23</td>
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</table>

Reaction conditions: H$_3$PW$_{12}$O$_{40}$/CeO$_2$ 20 mg (pretreated by drying under reduced pressure, 180 °C, 0.5 h), TMC 3 mmol, initiator 0.01 mmol, reaction temperature 60 °C, reaction time 2 h.

a) calculated by $^1$H NMR, b) calculated by [TMC]$_0$/[CH$_3$I]$_0$×(conv.)×(molecular weight of TMC) + (molecular weight of CH$_3$I), c) determined by GPC in chloroform relative to polystyrene standards, d) calcined at 200 °C for 0.5 h.

Table S5. Effect of initiator

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Conversion a) / %</th>
<th>Ether linkage a) selectivity / %</th>
<th>$M_{n,\text{theo}}$ b) / g mol$^{-1}$</th>
<th>$M_{n,\text{GPC}}$ c) / g mol$^{-1}$</th>
<th>$M_{w}/M_{n}$ c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-I</td>
<td>21</td>
<td>0</td>
<td>6,400</td>
<td>6,200</td>
<td>1.41</td>
</tr>
<tr>
<td>2</td>
<td>-I</td>
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<td>3,300</td>
<td>1.38</td>
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<tr>
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<td>1.56</td>
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<td>0</td>
<td>140</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>-I</td>
<td>15</td>
<td>0</td>
<td>4,600</td>
<td>2,400</td>
<td>1.18</td>
</tr>
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<td>1,000</td>
<td>1,600</td>
<td>1.12</td>
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<td>430</td>
<td>1.55</td>
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<td>1.77</td>
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<tr>
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<td>3</td>
<td>0</td>
<td>-</td>
<td>640</td>
<td>1.36</td>
</tr>
</tbody>
</table>

Reaction conditions: H$_3$PW$_{12}$O$_{40}$/CeO$_2$ 20 mg (pretreated by drying under reduced pressure, 180 °C, 0.5 h), TMC 3 mmol, initiator 0.01 mmol, reaction temperature 60 °C, reaction time 2 h.

a) calculated by $^1$H NMR, b) calculated by [TMC]$_0$/[initiator]$_0$×(conv.)×(molecular weight of TMC) + (molecular weight of initiator), c) determined by GPC in chloroform relative to polystyrene standards.
Figure S1. $^1$H NMR spectra of 4-methyl-1,3-dioxan-2-one

Figure S2. $^{13}$C NMR spectra of 4-methyl-1,3-dioxan-2-one

Figure S3. FTIR spectra of 4-methyl-1,3-dioxan-2-one
Figure S4. MS spectra of 4-methyl-1,3-dioxan-2-one

Figure S5. $^1$H NMR spectra of 5-methyl-1,3-dioxan-2-one

Figure S6. $^{13}$C NMR spectra of 5-methyl-1,3-dioxan-2-one
Figure S7. FTIR spectra of 5-methyl-1,3-dioxan-2-one

Figure S8. MS spectra of 5-methyl-1,3-dioxan-2-one

Figure S9. $^1$H NMR spectra of 5,5-dimethyl-1,3-dioxan-2-one
Figure S10. $^{13}$C NMR spectra of 5,5-dimethyl-1,3-dioxan-2-one

Figure S11. FTIR spectra of 5,5-dimethyl-1,3-dioxan-2-one

Figure S12. MS spectra of 5,5-dimethyl-1,3-dioxan-2-one
Figure S13. $^1$H NMR spectra of 4,6-dimethyl-1,3-dioxan-2-one

Figure S14. $^{13}$C NMR spectra of 4,6-dimethyl-1,3-dioxan-2-one

Figure S15. FTIR spectra of 4,6-dimethyl-1,3-dioxan-2-one
Figure S16. MS spectra of 4,6-dimethyl-1,3-dioxan-2-one

Figure S17. Raman spectra of 30 wt% H$_3$PW$_{12}$O$_{40}$/CeO$_2$ pretreated at different temperature
Figure S18. XRD profile of WO$_3$, H$_3$PW$_{12}$O$_{40}$ and H$_3$PW$_{12}$O$_{40}$/CeO$_2$

Figure S19. Raman spectra of WO$_3$, H$_3$PW$_{12}$O$_{40}$ and H$_3$PW$_{12}$O$_{40}$/CeO$_2$
Figure S20. FTIR spectra of 1 wt% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{CeO}_2$ catalyst before and after the reaction.

Figure S21. Differential FTIR spectra of $\text{CeO}_2$. 

Before the reaction

After the reaction
Figure S22. DSC profiles of (a) entries 1-4 (b) entries 5, 6 in Table 5

Figure S23. TG-DTA profiles of entries 1-6 in Table 5
Figure S24. $^1$H NMR spectra of (a) poly(5-Methyl TMC)s in DMSO-$d_6$ and (b) poly(5,5-dimethyl TMC)s in CDCl$_3$

(a) 220 °C (corresponds to 3% degradation)  
(b) 330 °C (corresponds to 99% degradation)

Figure S25. The chromatograms of Py-GCMS of poly(TMC-ether)