Electronic Supplementary Information

Heterogeneous Catalyst Based on Built-in N-Heterocyclic Carbenes with High Removability, Recoverability and Reusability for Ring-opening Polymerization of Cyclic Esters

Wen Liu, Guo-Qiang Tian, Dan-Dan Yang, Gang Wu, Si-Chong Chen,* Yu-Zhong Wang*

National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), State Key Laboratory of Polymer Materials Engineering, College of Chemistry, Sichuan University, Chengdu, 610064, China.

*Corresponding Author: chensichong@scu.edu.cn (S. C. Chen) and yzwang@scu.edu.cn (Y. Z. Wang)
**Diameter distribution of PS-CH₂Cl and PS-PrIm⁺Cl⁻ microsphere**

![Graph A](#)  
**A** mean diameter = 159.2 ± 53.8 (µm)

![Graph B](#)  
**B** mean diameter = 160.3 ± 52.3 (µm)

**Fig. S1** Diameter distribution of PS-CH₂Cl and PS-PrIm⁺Cl⁻ microsphere. (The number of microspheres exceeds 500).

---

**The separation of catalyst and product by filtration**

**HCl**  
**Recycled PS-PrIm⁺Cl⁻**

**Filtration**

**Precipitate in methanol**

**PCL**

---

**Fig. S2.** The purification of ROP products and recycling of the catalysts.
**The whiteness of samples**

**Table S1.** The whiteness of PCL prepared with different catalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>termination agent</th>
<th>L*&lt;sup&gt;a&lt;/sup&gt;</th>
<th>a*&lt;sup&gt;b&lt;/sup&gt;</th>
<th>b*&lt;sup&gt;c&lt;/sup&gt;</th>
<th>R457&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>NHCs</td>
<td>HCl</td>
<td>96.09</td>
<td>-0.46</td>
<td>2.41</td>
<td>87.44</td>
</tr>
<tr>
<td>NHCs</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>97.45</td>
<td>-0.36</td>
<td>1.57</td>
<td>91.22</td>
</tr>
<tr>
<td>NHCs</td>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>94.49</td>
<td>-1.45</td>
<td>10.1</td>
<td>75.39</td>
</tr>
<tr>
<td>PS-NHCs</td>
<td>HCl</td>
<td>98.01</td>
<td>-0.07</td>
<td>0.57</td>
<td>94.15</td>
</tr>
<tr>
<td>Sn(Oct)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>--</td>
<td>97.83</td>
<td>-0.53</td>
<td>1.26</td>
<td>93.22</td>
</tr>
<tr>
<td>Commercial PCL (DG-COH150)</td>
<td></td>
<td>93.85</td>
<td>-0.1</td>
<td>0.61</td>
<td>81.90</td>
</tr>
</tbody>
</table>

<sup>a</sup> The brightness of the sample.

<sup>b</sup> The red and green phase of the samples.

<sup>c</sup> The yellow and blue phase of the samples.

<sup>d</sup> The whiteness of samples.
Thermal stability of microspheres

Fig. S3. The TG curves of microspheres.
**N₂ sorption isotherms of recycled PS-PrIm⁺Cl⁻ microsphere**

![N₂ sorption isotherms of recycled PS-PrIm⁺Cl⁻ microsphere](image)

**Fig. S4.** N₂ sorption isotherms of 1st (A) and 5th (B) recycled PS-PrIm⁺Cl⁻ microspheres

<table>
<thead>
<tr>
<th>Sample</th>
<th>S⁰/m²g⁻¹</th>
<th>Vᵇ/cm³g⁻¹</th>
<th>Pore size c/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st recycled PS-PrIm⁺Cl⁻</td>
<td>155</td>
<td>0.33</td>
<td>5.89</td>
</tr>
<tr>
<td>5th recycled PS-PrIm⁺Cl⁻</td>
<td>149</td>
<td>0.29</td>
<td>4.83</td>
</tr>
</tbody>
</table>

*a Surface area calculated from the nitrogen adsorption isotherm using the BET method.*

*b Single point pore volume calculated at relative pressure P/P₀ of 0.99.*

*c BJH method from desorption branch.*