Efficient ternary catalyst system for the copolymerization of lactide, epoxides and CO$_2$: new insights into the cooperative mechanism

Xiang Li$^a$, Chen-yang Hu$^b$, Ran-long Duan$^b$, Zhuang-zhuang Liang$^b$, Xuan Pang$^b$, and Ming-xiao Deng$^a$

$^a$ Institute of Chemistry, Northeast Normal University, Changchun, 130024, PR China.
$^b$ Key Laboratory of Polymer Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China.
Figure S1. The $^1$H NMR spectra of SalenCo$^4$. 
As known, the SalenCo$^{II}$ complexes were paramagnetic.\textsuperscript{1, 2} \textbf{c} and \textbf{b} were synthesized via the same reported method.\textsuperscript{3} Although the Co atoms were supposed to be oxidized to Co(III) completely, showed paramagnetic features in its $^1$H NMR spectrum, some peaks were obviously shifted.\textsuperscript{3} This result was in accord with the conclusion by Coates.\textsuperscript{4, 5}
### Table S1. The copolymerization of PO, CO$_2$ and LLA.$^{(a)}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Cat$^{(b)}$</th>
<th>Ratio$^{(c)}$</th>
<th>Time (h)</th>
<th>Con. 1$^{(d)}$</th>
<th>Sel.$^{(e)}$ (%)</th>
<th>Con. 2$^{(f)}$</th>
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</thead>
<tbody>
<tr>
<td>1</td>
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<td>7</td>
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<tr>
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<td>7</td>
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(a) The reactions were performed with 2 mL neat PO in 25 mL autoclave at 60 $^\circ$C, with oxygen and PPNCl as cocatalyst, 2 MPa CO$_2$. (b) Molar ratio. (c) [Cat]:[PPNCl]:[LLA]:[PO]. (d) The results based on the amount of converted PO (Con. 1) and converted LLA (Con. 2) by $^1$H NMR spectroscopy. (e) Selectivity for polycarbonates over cyclic carbonate, determined by $^1$H NMR spectroscopy. (f) Adding 0.1 Mpa oxygen. (g) Adding oxygen first, then oxygen was released and CO$_2$ was added.
Figure S3. The influence of oxygen (0.1 MPa) to the selectivity (a) and activity (b) of SalenCo<sup>III</sup> with different loading of PPNCl.

As we have reported in previous work, the loading of PPNCl is decisive for the probability of di- and mononuclear mechanism (Table 1, Entries 11-14). For TCS<sub>III</sub> (Table 1, Entries 15-18), the similar tendency was also observed as shown in Figure 3a and 3b, which indicated adding oxygen could intervene the collaboration of SalenCo<sup>III</sup> and PPNCl. When the loading of PPNCl is as the half as the loading of SalenCo<sup>III</sup>, adding oxygen makes up the shortage of PPNCl and leads to enhanced activity via the dinuclear mechanism. When the loading of PPNCl is equal with SalenCo<sup>III</sup>, adding oxygen makes slight effect. If the amount of PPNCl outnumber SalenCo<sup>III</sup>, the mononuclear mechanism is in charge, adding surplus oxygen would consolidate the probability of mononuclear mechanism.
Figure S4. The HHCOSY NMR spectrum of PLAPC$_1$ in CDCl$_3$. 
Figure S5. HHCOSY NMR spectrum of PLAPC$_{3a}$ in DMSO-D$_6$. 
Figure S6. The HHCOSY NMR spectrum of PLAPC$_{3b}$ in CDCl$_3$. 
Figure S7. The $^{13}$C NMR spectrum of PLABC$_{14}$. 
Figure S8. The HMQC NMR spectrum of PLABC$_{3a}$ ($^1$H 600 MHz, $^{13}$C 150 MHz).
Figure S9. The HHCOSY spectrum of PLABC$_{3a}$. 
Figure S10. The $^1$H NMR spectrum of PLABC$_1$. 
Figure S11. The HHCOSY spectrum of PLABC$_1$. 

The spectrum shows correlations between different chemical shifts, with peaks at specific points indicated by coordinates [5.04, 1.59].
Figure S12. The $^1$H DOSY spectrum (Table 3, Entry 21).
Figure S13. The $^1$H DOSY spectrum (Table 3, Entry 17).
As shown above, the $^1$H NMR spectra of PLAPC showed obvious difference in CDCl$_3$ and DMSO-d$_6$. Notably, the alternative linkages (LA-CO$_2$ and PO-LA) showed significant signals in DMSO-d$_6$ (blue arrow). In CDCl$_3$, there is distinct signal at 4.35 ppm (red arrow), which is regarded as the end group. In DMSO-d$_6$, there is no peak at corresponding location, by contrast, there is new signal at 5.5 ppm (black arrow). As the signals at black and red arrow showed similar integration value, we regard they are both from the end groups (start end and finish end), which is also supported by the HHCOSY result (Figure S5).
Figure S15. The $^1$H NMR spectrum of PLAPC$_2$.

For simplified calculation, we regard the amounts of “LA-CO$_2$” and “PO-LA” linkages to be equal ($i_j = i_d$). As shown in Figure S10-15, $i_j$, which should be 0.5*$i_l$, is less than 0.5*$i_{lg}$ for the extra methylene signal of g. Meanwhile, $i_d$, which should be 1/3*$i_k$, is less than 1/3*$i_{km}$.

The average chain length of PPC blocks is 6 ($2i_j + i_{jkl}/i_{jkl}$), and the average chain length of PLA blocks is 8 ($2i_d + i_{klm}/i_{klm}$). The calculation results are approximate, as the peak h is not completely characteristic.
Figure S16. The $^1$H NMR spectrum of PLACHC$_2$.

The average chain length of PCHC blocks is 3, and the average chain length of PLA blocks is 7.
The average chain length of PCHC blocks is 7, and the average chain length of PLA blocks is 7.
Figure S18. The $^1$H NMR spectrum of PLAPC$_{3a}$.

The average chain length of PPC blocks is 7, and the average chain length of PLA blocks is 3.
The average chain length of PPC blocks is 2, and the average chain length of PLA blocks is 9.
Figure S20. The $^1$H NMR spectrum of PLAPC$_{3b}$.

The average chain length of PPC blocks is 2, and the average chain length of PLA blocks is 14.
Figure S21. The $^{13}$C NMR spectrum of PLAPC$_{3a}$ (150 MHz).
Figure S22. Assigned HMOC NMR spectrum of PLAPC$_3a$ ($^1$H 600 MHz, $^{13}$C 150 MHz).
**Figure S23.** The $^1$H NMR spectrum of PLABC$_{3a}$.

The average chain length of PBC blocks is 3, and the average chain length of PLA blocks is 7.
Figure S24. The $^1$H NMR spectrum of PLAPC$_2$.

The average chain length of PPC blocks is $18 \left[ I_{A''}/(I_a+I_{a''}) \right]$, the average chain length of PLA blocks is $8 \left[ I_{A'}/(I_a+I_{a''}) \right]$. 
Figure S25. The $^1$H NMR spectrum of PLAPC$_2$.

The DSC curve of PLAPC$_2$, the second heat route.
Figure S26. The conjectural chain propagation circle for TCS₃ in previous article.
<table>
<thead>
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<th>Step</th>
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<th>PPNCl(^b)</th>
<th>PO(^b)</th>
<th>LLA(^b)</th>
<th>Time (h)</th>
<th>Con.(_1) (%)(^c)</th>
<th>Sel. (%)(^c)</th>
<th>Con.(_2) (%)(^c)</th>
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</table>

(a) The reactions were performed in 2 mL neat PO in 5 mL autoclave at 60 °C, employing b as Cat. (b) Molar ratio. (c) Results based on the \(^1\)H NMR spectroscopy. Con.\(_1\) is for PO and Con.\(_2\) is for LA; Sel. is for polycarbonates over all converted PO. (d) Adding 2 Mpa CO\(_2\).
Reference


