Efficient ternary catalyst system for the copolymerization of lactide, epoxides and CO₂: 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 S2. The ¹H NMR spectra of SalenCo^{III}-DFTP.

As known, the SalenCo^{II} complexes were paramagnetic.^{1, 2} **c** and **b** were synthesized via the same reported method.³ Although the Co atoms were supposed to be oxidized to Co(III) completely, showed paramagnetic features in its ¹H NMR spectrum, some peaks were obviously shifted.³ This result was in accord with the conclusion by Coates.^{4, 5}

Table S1. The copolymerization of PO, CO2 and LLA. ^(a)											
Entry	Cat ^(b)	Ratio ^(c)	Time (h)	Con. 1 ^(d)	Sel. ^(e) (%)	Con. 2 ^(d)					
1	а	1:1:0:2000	12	7	0	-					
2 ^(f)	а	1:1:0:2000	12	88	6	-					
3 ^(g)	а	1:1:0:2000	12	7	0	-					
4 ^(f)	а	1:1:20:2000	24	10	7	100					

(a) The reactions were performed with 2 mL neat PO in 25 mL autoclave at 60 °C, with oxygen and PPNCI as cocatalyst, 2 MPa CO_2 . (b) Molar ratio. (c) [Cat]:[PPNCI]:[LLA]:[PO]. (d) The results based on the amount of converted PO (Con. 1) and converted LLA (Con. 2) by ¹H NMR spectroscopy. (e) Selectivity for polycarbonates over cyclic carbonate, determined by ¹H 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^{III} with different loading of PPNCI.

As we have reported in previous work, the loading of PPNCI is decisive for the probability of di- and mononuclear mechanism (Table 1, Entries 11-14).³ For TCS III_b (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^{III} and PPNCI. When the loading of PPNCI is as the half as the loading of SalenCo^{III}, adding oxygen makes up the shortage of PPNCI and leads to enhanced activity via the dinuclear mechanism. When the loading of PPNCI is equal with SalenCo^{III}, adding oxygen makes slight effect. If the amount of PPNCI outnumber SalenCo^{III}, 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-D₆.



Figure S6. The HHCOSY NMR spectrum of $PLAPC_{3b}$ in $CDCI_3$.



Figure S7. The $^{\rm 13}C$ NMR spectrum of $\mathsf{PLABC}_{3a}.$



Figure S8. The HMQC NMR spectrum of $PLABC_{3a}$ (¹H 600 MHz, ¹³C 150 MHz).



Figure S9. The HHCOSY spectrum of PLABC_{3a}.



Figure S10. The 1 H NMR spectrum of PLABC₁.



Figure S11. The HHCOSY spectrum of PLABC₁.



Figure S12. The ¹H DOSY spectrum (Table 3, Entry 21).



Figure S13. The ¹H DOSY spectrum (Table 3, Entry 17).



Figure S14. The ¹H NMR spectra of PLAPC₁ in different solvents.

As shown above, the ¹H NMR spectra of PLAPC₁ showed obvious difference in CDCl₃ and DMSO-d₆. Notably, the alternative linkages (LA-CO₂ and PO-LA) showed significant signals in DMSO-d₆ (blue arrow). In CDCl₃, there is distinct signal at 4.35 ppm (red arrow), which is regarded as the end group. In DMSO-d₆, 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 ¹H NMR spectrum of PLAPC₁.

For simplified calculation, we regard the amounts of "LA-CO₂" and "PO-LA" linkages to be equal $(i_a=i_d)$. As shown in Figure S10-15, i_i , which should be $0.5*i_{i_k}$ is less than $0.5*i_{(l+g)}$ for the extra methylene signal of g. Meanwhile, i_i , which should be $1/3*i_{k_k}$ is less than $1/3*i_{(k+f)}$. The average chain length of PPC blocks is 6 $(2i_j + i_{(a+d)})/i_{(a+d)})$, and the average chain length of PLA blocks is 8 $(2i_h + i_{(a+d)})/i_{(a+d)})$. The calculation results are approximate, as the peak h is not completely characteristic.



e S16. The ¹H NMR spectrum of $PLACHC_1$.

The average chain length of PCHC blocks is 3, and the average chain length of PLA blocks is 7.



e S17. The ¹H NMR spectrum of $PLAPC_2$.

The average chain length of PCHC blocks is 7, and the average chain length of PLA blocks is 7.



Figure S18. The ¹H NMR spectrum of $PLAPC_{3a}$.

The average chain length of PPC blocks is 7, and the average chain length of PLA blocks is 3.



e S19. The ^1H NMR spectrum of $\text{PLAPC}_{3a}.$

The average chain length of PPC blocks is 2, and the average chain length of PLA blocks is 9.



e S20. The $^1\!H$ NMR spectrum of $\mathsf{PLAPC}_{3b}.$

The average chain length of PPC blocks is 2, and the average chain length of PLA blocks is 14.



Figure S21. The $^{\rm 13}{\rm C}$ NMR spectrum of ${\rm PLAPC}_{\rm 3a}$ (150 Mhz).



Figure S22. Assigned HMQC NMR spectrum of PLAPC_{3a} (¹H 600 MHz, ¹³C 150 MHz).



e S23. The ¹H 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 PLAPC₂.

The average chain length of PPC blocks is 18 [IA''/(Ia+Ia')], the average chain length of PLA blocks is 8 [IA'/(Ia+Ia')].



Figure S25. The 1 H NMR spectrum of PLAPC₂.

The DSC curve of $PLAPC_2$, the second heat route.



Figure S26. The conjectural chain propagation circle for TCS_1 in previous article.

Table S2. The polymerization of LA.

Step	Cat⁵	PPNCI ^b	PO ^b	LLA ^b	Time (h)	Con.₁(%) ^c	Sel. (%)°	Con. ₂ (%) ^c
1	1	1	3500	350	6	-	-	47
2 ^d	1	1	3500	350	18	-	-	47

(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

¹H 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 CO₂.

Reference

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