Highly Efficient One-pot/one-step Synthesis of Multiblock Copolymers from Three-Component Polymerization of Carbon Dioxide, Epoxide and Lactone

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Introduction: We report the first example of multiblock copolymer (MBC) with biodegradable polycarbonate and polyester blocks that were synthesized from highly efficient one-pot/one-step polymerization of cyclohexene oxide (CHO), CO_2 and ε-caprolactone (ε-CL) in the presence of zinc-cobalt double metal cyanide complex and stannous octoate. In this protocol, two cross chain exchange reactions (CCERs) occurred at two catalysts respectively and connected two independent chain propagation procedures (i.e., polycarbonate formation and polyester formation) simultaneously in a block-by-block manner, affording MBCs without tapering structure.

A one-pot/one-step synthesis of a new CO_2-based multiblock copolymer (MBC) without tapering from cyclohexene oxide (CHO), CO_2 and ε-caprolactone (ε-CL) via cross chain exchange reaction (CCER) that bridged two independent chain propagations catalyzed by two properly selected catalysts (Figure 1) simultaneously.

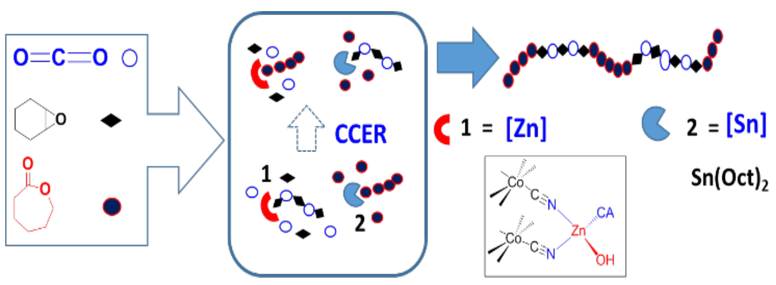


Figure 1. Proposed cross chain exchange polymerization of CO_2, CHO and ε-CL by using two selected catalysts: 1, Zn-Co(III) DMCC with Zn-OH group (Figure 2); and 2, stannous octoate [$Sn(Oct)_2$].

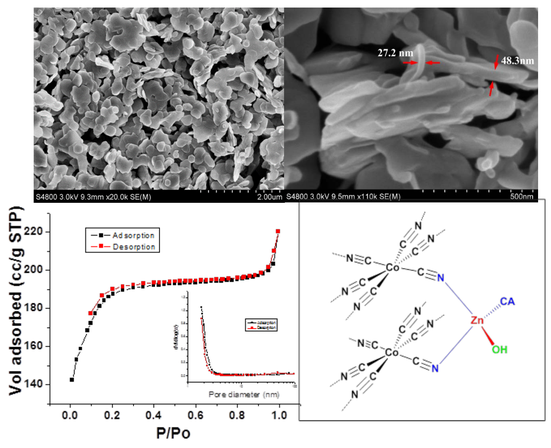
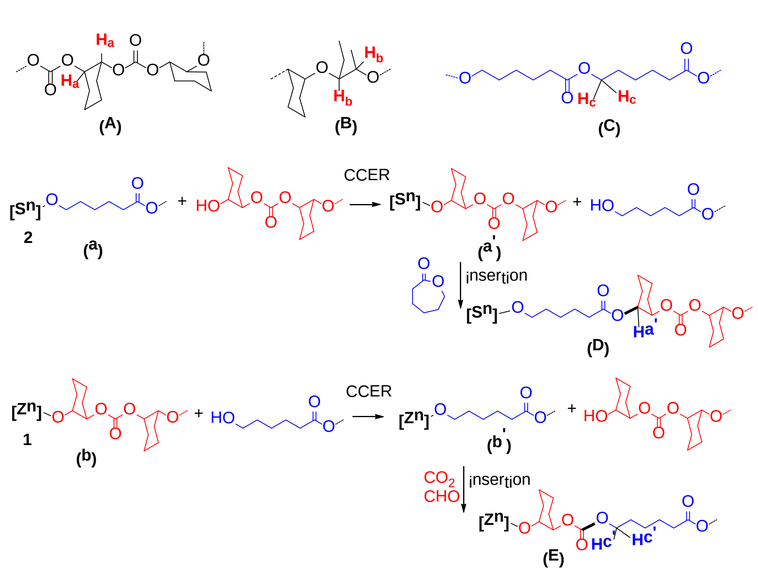


Figure 2. SEM images, N_2 absorption and desorption curves and the proposed ground-state structure of the active nano-lamellar Zn-Co(III) DMCC catalyst.

Table 1. Results of CHO/CO_2 copolymerization, ε-CL ROP and CHO/CO_2/ε-CL terpolymerization[a].

Run	[OH]/[ε-CL]	M_n/PDI [b] kg/mol	Composition(%)[c]			N [d]	Conv.%[e] CHO/ε-CL
			C	A	B		
1[f]	-	29.9/1.8	-	81.0	19.0	-	99 / -
2[g]	1:150	22.7/1.7	100	-	-	-	- / 84
3	1:40	9.7/2.0	52.1	38.1	9.9	9	97 / 94
4	1:150	18.7/1.8	49.5	46.6	3.9	7	99 / 95
5	0	35.2/1.9	49.2	47.5	3.4	5	98 / 96
6[h]	1:125	14.9/3.7	50.2	40.4	9.4	10	99 / 92

[a]Reaction conditions of runs 3-5: 100°C, 4.0 MPa; 35.0mg of Zn-Co(III) DMCC, [OH]: $[Sn(Oct)_2]$ = 2:1, 4.0h, 30.0mL CHO, 30.0mL ε-CL, 20.0mL THF, [OH] was benzyl alcohol (Bzl-OH) for ε-CL ROP .



Scheme 1. The main units (**A-C**), CCERs and the possible junction units of (**D**) and (**E**) in MBCs.

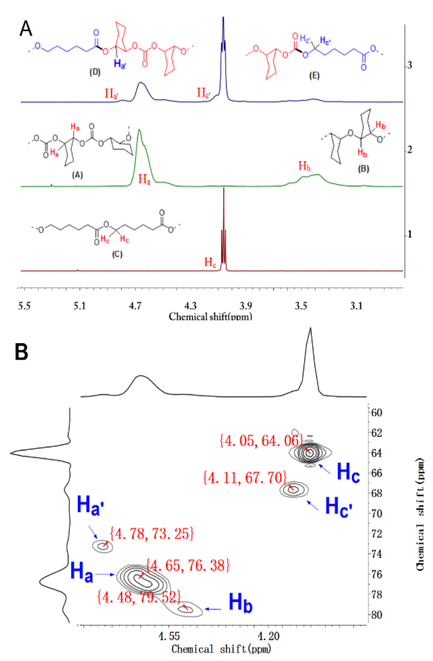


Figure 3. (A): curves 1, 2 and 3 are ^1H NMR spectrum of PCL, PCHC and the resultant terpolymer of run-3 in Table 1; (B) ^1H-^{13}C HSQC spectrum of the terpolymer of run-3 in Table 1.

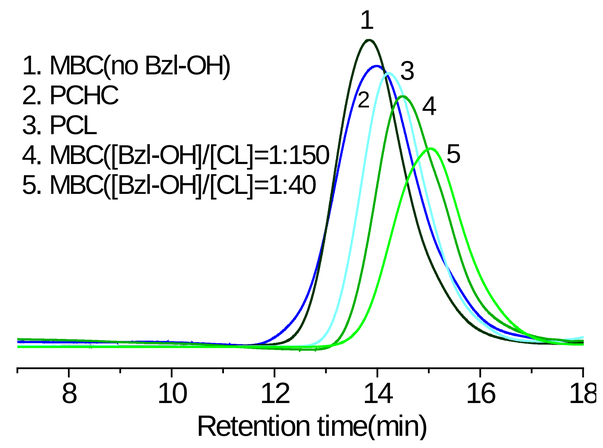


Figure 4. GPC curves of the purified PCHC (run-1), PCL (run-2), and the resultant terpolymers from runs 3-5 in Table 1.

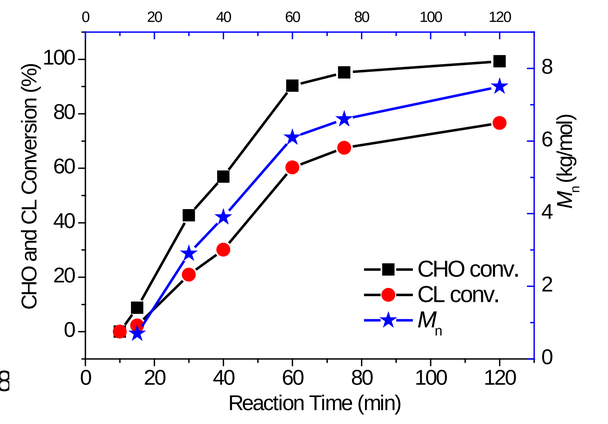


Figure 5. The conversion of CHO, ε-CL and Mn of the resultant product versus polymerization time. $[Sn(Oct)_2]$: [Bzl-OH]: [ε-CL] = 0.5 :1: 40; 101°C±2°C (from ca.20-125min), 4.0MPa.

A series of one-pot polymerizations with mixed monomers of CHO, CO_2 and ε-CL in the presence of 1 and 2 were carried out (Table 1). GPC results showed that the resultant MBCs had single elution curves.(Figure 4) with PDIs of 1.8-2.0. The number-average molecular weights (Mns) increased from 9.7 to 35.2 kg/mol with decreasing the [Bzl-OH]/ [ε-CL] molar ratios from 1:40 to 0.

The plots of Figure 5 shows that the conversion of CHO and ε-CL (and Mn) increased with increasing the reaction time. Mn was also increased with the conversion of CHO and ε-CL in a nearly linear manner.

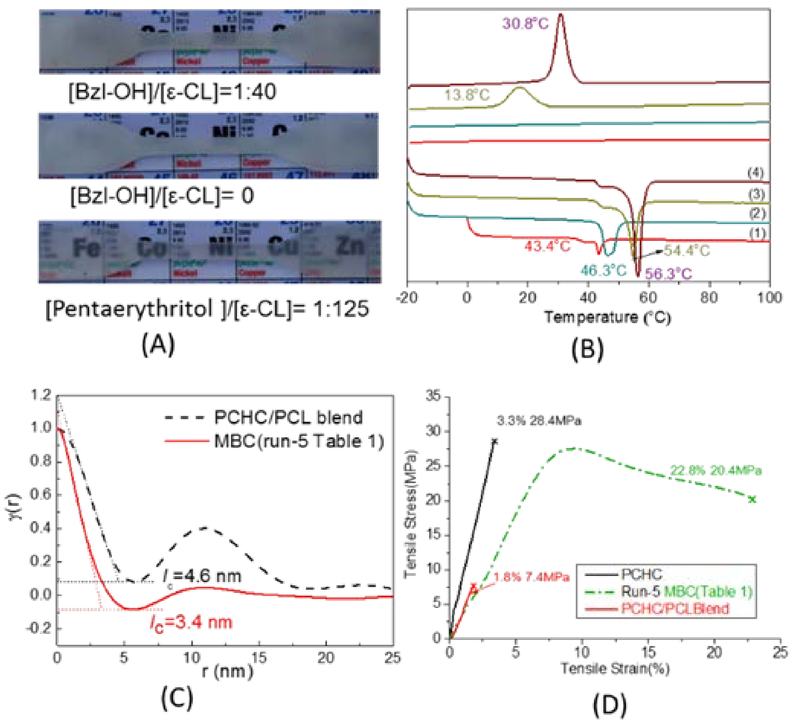


Figure 6. (A) Images of MBCs synthesized under different conditions; (B) DSC curves of MBCs from runs 3-5 (curves 1-3) and PCL/PCHC blend (curve 4, Mn: 26.4kg/mol), T_gs of MBCs were not clearly observed because the melted PCL block could dissolve PCHC block; (C) SAXS results: one-dimensional correlation functions for run-5 MBC in Table 1 (solid line) and PCL/PCHC blend (dash line). (D) Stress-strain curves of run-5 MBC, PCL/PCHC blend and PCHC (Mn: 37.4kg/mol) at room temperature and 10mm/min, * Denotes failure point.

The multiblock structure of MBCs was also evidenced by the crystallization behavior from the differential scanning calorimetry (DSC) result. Due to the multiblock structure, the run-5 MBC showed improved elongation at break of 22.8% relative to those of PCHC (3.3%) and PCHC/PCL blend (1.8%) (Figure 6D), which meant that run-5 MBC was tougher than the pure PCHC and PCHC/PCL blend.

Conclusions

In summary, we described a convenient method to synthesize MBCs with high efficiency from a one-pot/one-step polymerization of CO_2, CHO and ε-CL by bridging two independent chain propagations via CCER in one system. This reaction is also of significance because it produced multiblock copolymers without tapering by partially using renewable CO_2. Such MBCs with improved mechanical properties have a CO_2 uptake up to 15 mol% when [CHO]/[ε-CL] feeding ratio was 1.0. The ongoing work will be directed towards MBCs with tunable properties by precise kinetic control.

Acknowledgement

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References

(1) Yang Li, Jiali Hong, Renjian Wei, Yingying Zhang, Zaizai Tong, Xinghong Zhang*, Binyang Du, Junting Xu, Zhiqiang Fan, Highly Efficient One-pot/one-step Synthesis of Multiblock Copolymers from Three-Component Polymerization of Carbon Dioxide, Epoxide and Lactone. (Submitted)