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

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Abstract: It is a long-standing challenge to combine mixed monomers into multiblock copolymer (MBC) in a one-pot/one-step polymerization manner. We report the first example of 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 (CCER) occurred at dual catalysts respectively and connected two independent chain propagation procedures (i.e., polycarbonate formation and polyester formation) simultaneously in a block-by-block manner, affording MBC without tapering structure. The multiblock structure of MBC was determined by the rate ratio of CCER to the two chain propagations and could be simply tuned by various kinetic factors. This protocol is also of significance due to partial utilization of renewable CO$_2$ and improved mechanical properties of the resultant MBC.

Introduction

The big concerns on the global energy and environmental issues prompt us to develop efficient methods to prepare new polymeric materials that can be derived from renewable resources. Aliphatic polycarbonates (APCs) and polyesters are two classes of biodegradable polymers with bright future because of their practical advantages. APCs can be synthesized by copolymerization of epoxide with carbon dioxide (CO$_2$), which is one of the most attractive renewable C1 resources and abundant, non-toxic and low-cost, while polyesters can be prepared by ring-opening polymerization of lactones that can also be obtained from the renewable resources. In contrast to the most of commercialized polycarbonates and polyesters via condensation polymerization, which requires long reaction time as well as high energy supply and releases small molecules as by-products, both CO$_2$/epoxide copolymerization and ring-opening polymerization of lactone are addition polymerizations and undergo a sustainable and environmentally benign process, which meets the principle of the atom economy.

Another virtue of both ring-opening polymerization of lactone and CO$_2$/epoxide copolymerization is that they could be used to make CO$_2$-based di- and tri-block copolymers, which were rarely reported. Generally, polycarbonate with one or two hydroxyl (–OH) end groups was at first synthesized by copolymerization of epoxide with CO$_2$ and then used as the macroinitiator for ring-opening polymerization of lactone. For example, Daresbourg and co-workers reported the syntheses of di- and tri-block copolymers from CO$_2$, epoxide and lactone via macroinitiator intermediate by tandem using a (Salen)Co(III) complex plus an organic base [5.4.0] undec-7-ene. Williams et al synthesized a di-block copolymer from epoxide, CO$_2$ and lactone by using a dizinc catalyst, which could be reversibly switched from a polycarbonate catalyst to a polyester catalyst by adding switching reagents. These works elegantly provided di- and tri-block copolymers by multi-step or sequential operations. In this context, we present 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 generated by two properly selected catalysts (Figure 1) simultaneously.

Figure 1. Proposed cross chain exchange polymerization of CO$_2$, CHO and ε-CL by using Zn-Co(III) DMCC (1, Scheme S1) and stannous octoate [2, Sn(Oct)$_2$] together.
CCER is a kind of chain transfer reaction in which the propagating chain exchanged with a dormant chain with different structures. Indeed, many metal-catalyzed ring-opening polymerizations of lactone and CO₂-epoxide copolymerizations are chain transfer agents (Table S3, runs S4-S5). When polymerization of three monomers with catalysts either polycarbonate exchanged with (Zn–OH, Scheme S1), which could afford poly(cyclohexene carbonate) with two hydroxy end groups (HO–PCHC–OH) resulted from Zn–OH initiation and chain transfer reaction, respectively. 2-catalyzed ring-opening polymerization of ε-CL is a typical chain transfer polymerization at 80–130 °C. When CO₂/CHO copolymerization and ring-opening polymerization of ε-CL were combined into one reactor in the presence of the two catalysts presented high efficiency towards CHO/ε-CL terpolymerization. 2× Determined by gel permeation chromatography (GPC) of the purified product calibrated with polystyrene standards in THF; 1H NMR spectroscopy of CHO/ε-CL terpolymerization.

**Results and discussion**

To this end, two catalysts, zinc-cobalt double metal cyanide complex (Zn–Co(II) DMCC, 1) and stannous octoate [Sn(Oct)₂, 2], were screened out (Figure 1). A nanomolar Zn–Co(III) DMCC [Figure S1, its synthesis and characterization are seen in the supporting information] is a highly active catalyst for CO₂-epoxide copolymerization without producing the byproduct of cyclic carbonate at 50–110 °C. The initiating site of 1 is zinc-hydroxyl group (Zn–OH, Scheme S1), which could afford poly(cyclohexene carbonate) with two hydroxy end groups (HO–PCHC–OH) from Zn–OH initiation and chain transfer reaction, respectively. 

The prerequisite for the formation of MBC is that 1-catalyzed CO₂/CHO copolymerization and 2-catalyzed ring-opening polymerization of ε-CL could occur independently with matched polymerization rates. 

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

**Table 1.** Results of CHO/CO₂ copolymerization, ring-opening polymerization of ε-CL and CHO/CO₂/ε-CL terpolymerization.

The series of one-pot polymerizations with mixed monomers of CHO, CO₂, and ε-CL in the presence of 1 and 2 were carried out (runs 3-6, Table 1) under mechanical stirring with 500 rpm. GPC results showed that the resultant MBCs had single elution curves (Figure 2) with PDIs of 1.8-2.0. The number-average molecular weights (Mₙ) increased from 9.7 to 35.2 kg/mol with decreasing the [BnOH]/[ε-CL] molar ratios from 1.40 to 0.40. Note that BnOH could initiate ring-opening polymerization of ε-CL and be used to tune the molecular weights of the resultant MBCs. 97-99% CHO and 94-96% ε-CL were converted within 4.0 h according to the ¹H NMR spectra of the crude products, indicating that two catalysts presented high efficiency towards this ring-opening polymerization. Moreover, the ether units of MBCs
be attributed to the solvent-assisted depression effect (herein, ε) block, the possible junction units linked with consecutive ether peaks could be ascribed to the proton signals of 4.07 ppm and 4.79 ppm were clearly observed in Figure 3-A. Both when H0>OPCHC>OH with a chain exchange reaction of H0>OPCL>OH on Zn site. Moreover, CCERs with two catalysts were clearly disclosed by the observation that two junction units D and E were produced at Zn and Sn sites, respectively. Firstly, HO>PCL-OH with a Mₙ of 1700 (run-S10 in Table S3, Figure S6) was introduced into the 1-catalyzed CO₂/CHO copolymerization system, 1H,13C HSQC NMR spectrum of the resultant polymers (Figure S5-D) showed only one junction unit E {4.12 ppm, 67.83 ppm}, which was solely caused by the chain exchange reaction of HO-PCL-OH on Zn site. Moreover, when HO-PCHC-OH with a Mₙ of 700 was introduced into the 2-catalyzed ring-opening polymerization of ε-CL system under 4.0 MPa CO₂ pressure (run-S11 in Table S3, Figure S6), 1H,13C HSQC NMR spectrum of the product showed only one junction unit D {4.80 ppm, 73.52 ppm} (Figure S5-E). This result confirmed that the CCER only occurred on Sn site.

In order to form multiblocks, the total rates of two CCERs should be smaller than those of corresponding propagation processes. The rate percentage of two CCERs to two propagations (N) could be estimated by the ratio of the integral area of D and E to the total carbonate (including small amounts of ether unit) and ester units based on 1H NMR spectra. N of runs 3-5 MBCs in Table 1 was calculated to be ca. 3–10%, indicating that the total formation rate of the junction units D and E were ca. 3–10% of the MBC formation. Such rate difference between CCER and chain propagations led to the formation of polycarbonate and polyester multiblocks. Moreover, the rate ratio of D formation to the polycarbonate formation was approximately equal to that of E formation to the polyester formation based on the 1H NMR spectra (Figure S3), suggesting that CCERs at Zn site and Sn site had nearly the same reactivity.

The evolution of the block structure of MBC was further monitored by the apparent kinetic study of the terpolymerization (Figure 4, Figure S7-S10 and Table S4). Figure 4 shows the semi-logarithmic plots of the conversions of CHO and ε-CL (Table S4) versus the reaction time with the assumption of the first order dependence on monomer concentration for two polymerizations. The rate ratio of
CHO/CO₂ copolymerization to ring-opening polymerization of ε-CL was estimated to be ca. 3, suggesting that the rate constant of CHO/CO₂ copolymerization was three times than that of ring-opening polymerization of ε-CL. As a result, the average block length of PCHC block was longer than that of PCL block. NMR spectrum kept in the range of 11-14% (Table S4) in the whole polymerization time, which ensured the continuous production of multiblocks at nearly stable rate. Moreover, \( M_n \) increased with the conversion of CHO and ε-CL in a nearly linear manner (Figure S9). In this sense, the obtained MBCs are statistical multiblock copolymers.

There are only a few examples of MBC synthesized by using two catalysts.\(^{5,14}\) In the previous reports, two catalysts of the same type were used to catalyze two monomers with same functionality (e.g., double bond)\(^{13}\) or one monomer with R and S enantiomers.\(^{14}\) In these cases, the transition of one block to another via chain shuttling obeyed the same propagation manner, which might cause tapering structure in the resultant multiblock copolymers. Our example reported in the present work provides a novel CCER route between different types of catalysts for three monomers with different functionalities in a one-pot/one-step way, affording MBCs without tapering.

The multiblock structure of MBCs was also evidenced by the differential scanning calorimetry (DSC) results of the runs 3-5 MBCs from Table 1 with heating and cooling rates of 20 °C/min (Figure 5) and 10 °C/min (Figure S11). As shown in Figure 5-A, the melting temperatures (\( T_m \)) of the PCL block of runs 3-5 MBCs were observed because all samples were kept at 0 °C for at least 24 h before testing and complete crystallization. Since MBC with smaller \( N \) had a longer average block length, \( T_m \)s of runs 3-5 MBCs increased from 45.7 °C to 54.2 °C with decreasing \( N \) value and were lower than that of the PCHC/PCL blend (58.8 °C, Figure 5-A).\(^{13}\) \( T_m \) of the run-5 and run-4 MBCs were found to be 79.3 °C and 71.8 °C (see inserted chart in Figure 5-A), respectively. Both were lower than that of the PCL/PCHC blend (115.0 °C). However, no \( T_g \) was observed for the run-3 MBC (Figure 5-A), in which the glass transition of the run-3 MBC might be neutralized by the melting process with strong enthalpy of the PCL block. The subsequent DSC measurements were further carried out for the samples with heat treatment at 160 °C for 10 min. As shown in Figure 5-B, the cooling curves of the PCL/PCHC blend and run-5 MBC presented the crystallization temperatures (\( T_s \)) at 29.4 °C and 5.5 °C, and \( T_s \)s at 117.3 °C and 80.0 °C, respectively. The low \( T_c \) of run-5 MBC was caused by the restricted crystallization of PCL blocks, which are covalently linked with PCHC block with relatively high \( T_g \).\(^{15}\) However, no \( T_c \) and \( T_m \) were observed for runs 3-4 MBCs. The disappearance of crystallization and melting peaks in the rapidly cooled runs 3-4 MBCs suggested that the crystallization rate of these two samples was very slow. This is also one of the characteristics of the restricted crystallization, which is frequently observed in semicrystalline block copolymers.\(^{15}\) \( T_s \)s of runs 3-4 MBCs could be observed at ca. 69.0 °C when their DSC curves were magnified and subtracted the base line (Figure S12). It is reasonable that both MBCs had nearly the same chain compositions (Table 1). Moreover, when DSC measurement was carried out for runs 3-5 and the PCL/PCHC blend with a heating and cooling rate of 10°C/min, \( T_s \)s...
The restricted crystallization behavior of PCL blocks in MBCs was also confirmed by the comparative study of small-angle X-ray scattering (SAXS) profiles of run-5 MBC in Table 1 and PCL/PCHC blend. As seen in Figure 6-A, run-5 MBC presented a lamellar crystal thickness ($l_c$) of 3.4 nm, which was smaller than that of PCL/PCHC blend (4.6 nm). Due to the multiblock structure, the run-5 MBC in Table 1 showed improved elongation at break of 22.8% relative to those of PCHC (3.3%)\(^{16}\) and PCHC/PCL blend (1.8%) (Figure 6-B), which meant that the run-5 MBC was tougher than the pure PCHC and PCHC/PCL blend.

We also examined the effect of CO\(_2\) pressure, CHO/ε-CL feeding ratio, reaction temperature, the type as well as the amount of the initiator on the structure of the resultant MBCs (Table 1, Table S6-S7). With the fixed molar ratios of 1 to CHO and 2 to ε-CL, the variation of CHO/ε-CL ratio had a strong impact on the chain composition of the resultant polymers. When CHO/ε-CL volume ratio was 1/4 (run-S26 in Table S7), a MBC with shorter PCHC block was obtained with a $T_m$ of 56.9 °C that was less than that of the PCL/PCHC blend (58.4 °C, Figure S13), indicating that even very short PCHC block in MBC could result in restricted crystallization of PCL block. The suitable temperatures and CO\(_2\) pressure for synthesizing MBCs were 90-110 °C and $\geq 2.0$ MPa, respectively. PCL block in MBCs in Table S6 kept nearly in the range of 44.7-51.9%. Remarkably, the average block lengths of MBCs could be tuned by changing the type and amounts of the initiator. MBCs from run-3 and run-5 (thickness of 2.0 mm, Table 1) were semi-transparent and non-transparent, respectively (Figure 6-C). Larger amount of initiator caused shorter average block lengths, which formed relatively thinner PCL lamellar crystals in the sample. When pentaerythritol was used as the initiator (run-6, Table 1), soft and transparent sample was obtained, suggesting that the crystallization of PCL blocks in the armed MBCs was more severely restricted.

**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.

**Experimental**

Typical terpolymerization of CHO, CO\(_2\) and ε-CL in a one-pot/one-step procedure: the terpolymerization was conducted in a Büchi autoclave, which had been pre-dried at 80 °C under vacuum for 2 h. Desired amounts of Zn-Co(III) DMCC, Sn(Oct)\(_2\) (in dried THF), BnOH, CHO and ε-CL were transferred into the autoclave equipped with a mechanical stirrer (500 rpm) and a pressure gauge. CO\(_2\) was then pressurized to the target pressure. The autoclave was heated by a cyclic oil heating bath with designed temperature (e.g., 100 °C) and kept stirring for a certain time (e.g., 4 h). After reaction, the autoclave was cooled down to room temperature and CO\(_2\) was slowly vented. A small amount of the crude product was taken out for \(^1^H\) NMR measurement. The remaining sample was dissolved in the CH\(_2\)Cl\(_2\) and precipitated from methanol. This process was repeated for 3 times to give the purified polymers.
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9 Catalyst pairs of (Salen)Co(or Cr) complexes/Sn(Oct)2(PPNCl, TBD and DBU) and zinc glutarate/Sn(Oct)2, were applied to the terpolymerization of CO2, CHO and ε-CL, but failed to get MBCs because of the unmatched polymerization rates, poisoning of catalysts.