Synthesis of Polycarbonate Block Terpolymers Using Robust Cobalt Catalyst Systems

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Abstract   This contribution reports an efficient approach for preparing polycarbonate block terpolymers by immortal stepwise copolymerization of CO_2 with different epoxides in the presence of enol chain transfer, mediated by robust cobalt catalyst systems consisting of the fluorine substituted salenCo(III)NO_3 or biphenol-linker bimetallic Co(III) complex in conjunction with an ionic cocatalyst, PPNX (PPN = bis(triphenylphosphine)iminium, X = NO_3^- or 2,4-dinitrophenoxide). Various polycarbonate block terpolymers were obtained in perfectly unimodal distribution of their molecular weights with narrow polydispersity. They all possessed only one broad glass transition temperature, which could be adjusted by altering the length of different polycarbonate segments.

Keywords   Carbon dioxide (CO_2); Epoxides; Polycarbonates; Copolymerization; Block terpolymer

INTRODUCTION

The utilization of carbon dioxide (CO_2) in the production of degradable polycarbonates through copolymerization with epoxides has attracted much attention to both academic and industrial researchers over the past decade.[1−5] This chemistry has its roots in Inoue's discovery, where a heterogeneous catalyst derived from diethylzinc and water was active for this copolymerization reaction.[6] Following this discovery, numerous heterogeneous and homogeneous catalyst systems have been developed for this transformation.[7−10] Prominent among these systems for effectively coupling CO_2/epoxides are discrete *β*-diiminate zinc alkoxides,[11,12] and binary or bifunctional catalyst systems based on metal-Salen or Salan complexes.[9,13−15] Most of these studies focused on the copolymerization of CO_2 with aliphatic propylene oxide (PO) to give poly(propylene carbonate) (PPC) with low glass transition temperatures (T_g, 35−45 °C) and with alicyclic cyclohexene oxide (CHO) to produce brittle poly(cyclohexene carbonate) (PCHC) with a high T_g (~120 °C). The poor thermal property associated with PPC and the difficult processing of PCHC due to its brittle property is the predominant problem in their industrial utilization. Therefore, the adjustment of glass transition temperature (T_g) of the polycarbonates is necessary in order to make them suitable as structural materials in various fields.

Some scientists have attempted to achieve this goal by the

terpolymerization of CO_2 with PO and CHO.[16] The main problem is that the great difference in reactivity of CHO and PO during the terpolymerization of epoxides with CO_2 leads to difficulties in controlling the composition and the alternating nature of the resulting copolymer. Considering the fact that the relatively high basicity and coordination ability of CHO inhibit the reactivity of PO during the coordination polymerization, we first succeeded in synthesizing the CO_2/PO/CHO terpolymer with only one T_g and one thermolysis peak by using binary or bifunctional catalyst systems based on cobalt(III) salen complex.[17]

On the other hand, the block terpolymer consisting of two different polymer segments or atactic-isotactic stereoblock in one molecule is expected to show improved properties.[18] For example, thermoplastic elastomeric polypropylene is of immense commercial interest, ascribed to its atactic-isotactic stereoblock microstructure. As to the copolymerization of CO_2 with epoxides, it is very difficult to obtain block polycarbonates. The reasons are complicated. Because cyclic carbonates are thermodynamically more stable than polycarbonates, they are a common by-product during the coupling reaction of CO_2 with aliphatic epoxides, especially at high temperatures, low CO_2 pressures, and/or a prolonged reaction time. Also, the presence of ether linkages as a result of consecutive epoxide enchainment could be observed in the resultant copolymers. Furthermore, the dissociation of initiator from the propagating polymer chain at elevated temperature results in molecular weight discrepancy significantly, and thus makes it impossible to synthesize polycarbonate block copolymers.[19] In 2006, Nozaki and co-workers utilized a Salcy-type cobaltate complex with a piperidinium end-capping arm as catalyst for selectively synthesizing

aliphatic polycarbonates from CO_2 and terminal epoxides and first reported the synthesis of a novel PPC-*b*-poly-(1,2-hexene carbonate) terpolymer in the presence of an organic solvent.[13] However, the resultant copolymers gave bimodal traces, and their M_n values were lower than the calculated ones, which was attributed to the chain transfer by contaminant water.

Herein, we report an efficient approach for preparing polycarbonate block terpolymers *via* immortal stepwise copolymerization of CO_2 with different epoxides in the presence of enol chain transfer (Fig. 1), mediated by robust cobalt catalyst systems consisting of the fluorine substituted salenCo(III)NO_3 (**1**) or biphenol-linker bimetallic Co(III) complex (**2**) in conjunction with an ionic cocatalyst, PPNX (PPN = bis(triphenylphosphine)iminium, X = NO_3^- or 2,4-dinitrophenoxide).

EXPERIMENTAL

Materials

All manipulations concerning air- and/or water sensitive compounds were carried out using standard Schlenk techniques under dry nitrogen. Epoxides were refluxed over a mixture of KOH/CaH$_2$ and fractionally distilled under a nitrogen atmosphere prior to use. Carbon dioxide (99.995%) was purchased from Dalian Institute of Special Gases and used as received. Toluene was distilled under nitrogen from sodium/benzophenone. Methylene chloride was distilled from calcium hydride under nitrogen. Bis(triphenylphosphine)iminium chloride (PPNCl) was purchased from Aldrich Chemicals Co. and recrystallized from dichloromethane/ether. PPNNO$_3$, PPNDNP (DNP = 2,4-dinitrophenoxide), and complexes **1** and **2** were synthesized according to our previously reported method.[20]

Analyses

^{1}H-NMR spectra were recorded on a Bruker 400 MHz type (^{1}H, 400 MHz) spectrometer, and their peak frequencies were referenced versus an internal standard (TMS) shift at 0 ppm. Molecular weights and polydispersity of polymers were determined by gel permeation chromatography (GPC) at 30 °C, with THF at a flow rate of 1.0 mL/min as the eluent on an Agilent 1260 instrument coupled with an Agilent RI detector and equipped with four PL gel columns. The sample concentration was about 0.1%, and the injection volume was 50 μL. The curve was calibrated using monodisperse polystyrene standards covering the molecular weight range from 580 Da to 4.60×10^5 Da. Differential scanning calorimetry (DSC) was carried out with a NETZSCH DSC 206 thermal analyzer.

Representative Procedure for the Synthesis of Polycarbonate Block Terpolymers

Synthesis of (CHO-alt-CO$_2$)$_x$-b-(PO-alt-CO$_2$)$_y$ (PCHC-b-PPC)

To a stirred mixture of complex **1** (0.0295 g, 0.05 mmol, 1 equiv.), PPNNO$_3$ (0.0300 g, 0.05 mmol, 1 equiv.), and 3-buten-1-ol (0.5mmol, 10 equiv.) were dissolved the mixture solution of CHO (25 mmol, 500 equiv.) and toluene (CHO/toluene = 1/2, *W/W*) to form a red-brown solution under nitrogen atmosphere. The resultant mixture solution was charged into a pre-dried 25 mL autoclave equipped with a magnetic stirrer under a CO_2 atmosphere. The autoclave was put into a bath of 25 °C and then pressurized to the appropriate pressure (2.0 MPa) with CO_2. After the allotted reaction time for complete conversion of CHO, a small amount of the resultant polymerization mixture was removed from the autoclave for ^{1}H-NMR analysis to quantitatively give the selectivity of polycarbonates to cyclic carbonate as well as carbonate linkages and also for GPC analysis. After the complete conversion of CHO, PO (50 mmol, 1000 equiv.) was added into the autoclave, and pressurized to 2.0 MPa with CO_2. After the allotted reaction time, the hydrogen chloride-diethylether solution (2 mol/L, 0.1 mL) was added dropwise before the crude polymer was dissolved in 5 mL CH$_2$Cl$_2$. The resulting solution was added to methanol to precipitate out the polymer. This process was repeated 3−5 times to completely remove the catalyst, and white polymer (PCHC-*b*-PPC capped with C═C chain end) was obtained by vacuum-drying.

Other polycarbonate di- or tri-block terpolymers were prepared with the similar procedure described above. Biphenol-linker bimetallic Co(III) complex **2** in conjunction with PPNDNP was applied to the copolymerization of CO_2 and meso-epoxides, such as CHO, *cis*-2,3-butene oxide (CBO), and cyclopentene oxide (CPO), by their stepwise addition, producing polycarbonate block terpolymers, including (CBO-*alt*-CO$_2$)$_m$-*b*-(CPO-*alt*-CO$_2$)$_n$ (PCBC-*b*-PCPC) and (CHO-*alt*-CO$_2$)$_x$-*b*-(CBO-*alt*-CO$_2$)$_y$-*b*-(CHO-*alt*-CO$_2$)$_x$ (PCHC-*b*-PCBC-*b*-PCHC).
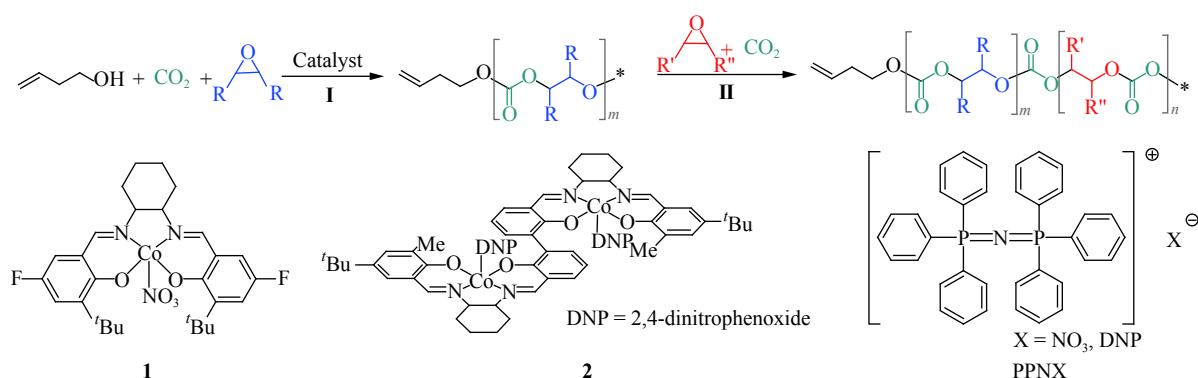

Fig. 1 The procedure for preparing polycarbonate block terpolymers *via* immortal stepwise copolymerization of CO_2 with different epoxides mediated by cobalt complex-based catalyst systems

RESULTS AND DISCUSSION

Previously, binary catalyst systems consisting of salen Co-(III)X/PPNX (X = nucleophilic anion) were demonstrated to be highly active in catalyzing CO_2/PO copolymerization, as well as CO_2/CHO copolymerization to selectively give the corresponding polycarbonates with more than 99% carbonate linkages at ambient temperature.[21] Further study found that the quantitative conversion of epoxide was achieved without sacrificing polymer selectivity in the presence of an organic solvent such as 1,2-dimethoxyethane. These results stimulate us to explore the synthesis of polycarbonate block copolymer with the use of these binary catalyst systems. Since complex **1** with electron-withdrawing substituents on the salen framework possesses more redox stable Co(III) species and longer catalyst lifetime,[22] the complex **1**/PPNNO$_3$ binary system was used as catalyst and 3-buten-1-ol as the chain transfer for preparing (PCHC-*b*-PPC) diblock copolymer, as well as PCHC-*b*-PPC-*b*-PCHC triblock polycarbonates capped with C=C chain ends. MALDI-TOF MS analysis confirmed the resulting polycarbonates from CO_2/CHO copolymerization in the presence of 3-buten-1-ol possessing C=C chain ends $(C_4H_7O + (CO_2\text{-}alt\text{-}CHO)_n + H + Na^+)$ (Fig. 2).
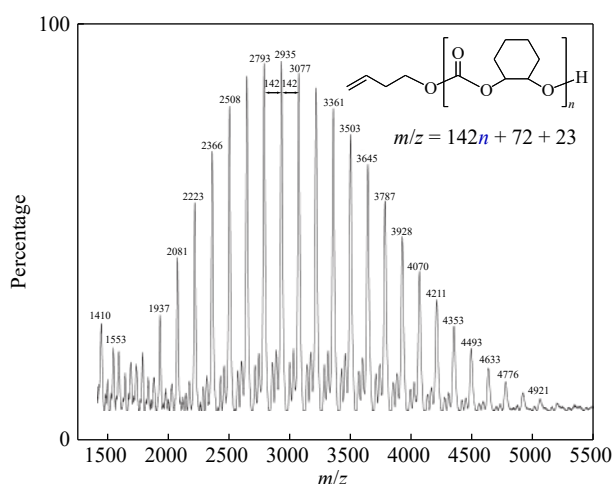

Fig. 2 MALDI-TOF mass spectrum of PCHC capped with C=C chain ends

Although the complex **1**/PPNNO$_3$ binary system shows high activity for CO_2/epoxides copolymerization, a prolonged reaction time is necessary for quantitative conversion of the epoxides at various steps. In the presence of toluene, quantitative conversion of the epoxide was achieved with high polymer selectivity. All the resulting copolymers exhibited unimodal distribution and narrow polydispersity of lower than 1.1 (Fig. 3, top). Of importance, the chain transfer does not result in chain termination, and the dissociated chain can re-propagate when activated on a catalyst center. Moreover, the polymer molecular weight is linearly proportional to the conversion, and its polydispersity is lower than 1.1. This is consistent with an immortal polymerization (a living polymerization that involves rapid and reversible chain transfer),[23] which allows for the production of block terpolymers by stepwise addition of two different epoxides.

The PCHC-*b*-PPC-*b*-PCHC triblock terpolymer was produced from the alternating copolymerization of CO_2 with epoxides in the presence of 3-buten-1-ol by stepwise addition of CHO, PO, and CHO in the presence of toluene at ambient temperature (Fig. 3, bottom). The conversion of epoxides is higher than 99% with excellent polymer selectivity in each step, which was determined by ^{1}H-NMR spectroscopy. The polydispersity indexes of the resulting polymers at various steps are very close and remain narrow (1.06−1.09). Similarly, the PPC-*b*-PCHC-*b*-PPC triblock terpolymer was prepared by stepwise addition of PO, CHO, and PO into polymerization system. From ^{1}H-NMR analysis (Fig. 4), the resulting triblock terpolymer (Fig. 4c) shows more than 99% carbonate linkages and contains 38% PCHC and 62% PPC segments based on the molar ratio of cyclohexene carbonate units to propylene carbonate units.
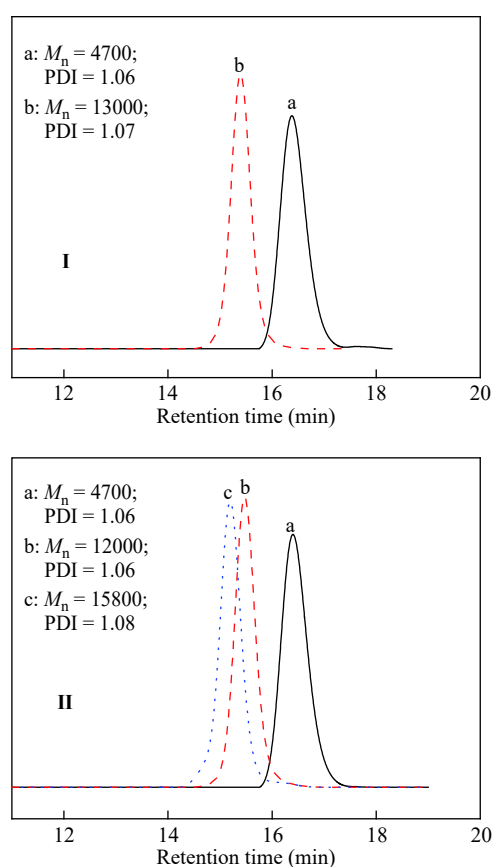

Fig. 3 GPC plots of PCHC-*b*-PPC diblock polymer (**I**, (a) the 1st segment, (b) the 2nd segment), and PCHC-*b*-PPC-*b*-PCHC triblock polymer (**II**, (a) the 1st segment, (b) the 2nd segment, (c) the 3rd segment)

Interestingly, in the present study, we notice that the resulting PCHC-*b*-PPC diblock polymer containing 46 mol% PCHC segment has only one T_g of 65.8 °C (Fig. 5a), but the baseline shift is significantly broader than that of the CO_2/PO/CHO terpolymer in random distribution (Fig. 5b). On the contrary, the thermogram of the PCHC/PPC blend shows two baseline shifts (Fig. 5c), one T_g at 41.6 °C (attributable to PPC) and the other T_g at 117.1 °C (attributable to PCHC). This result suggests that PPC and PCHC segments
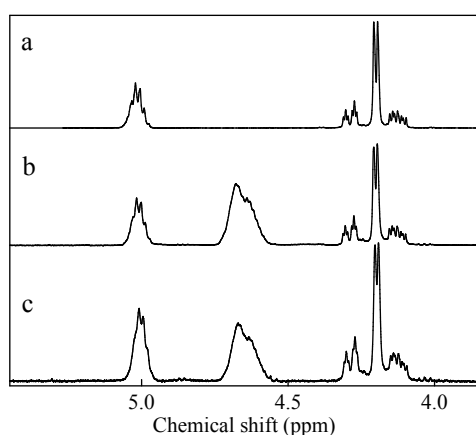
Fig. 4 ^{1}H-NMR spectra of (a) the 1st block PPC copolymer, (b) the 1st block + the 2nd block [PPC-*b*-PCHC] diblock polymer, and (c) the 1st block + the 2nd block + the 3rd block [PPC-*b*-PCHC-*b*-PPC] triblock polymer
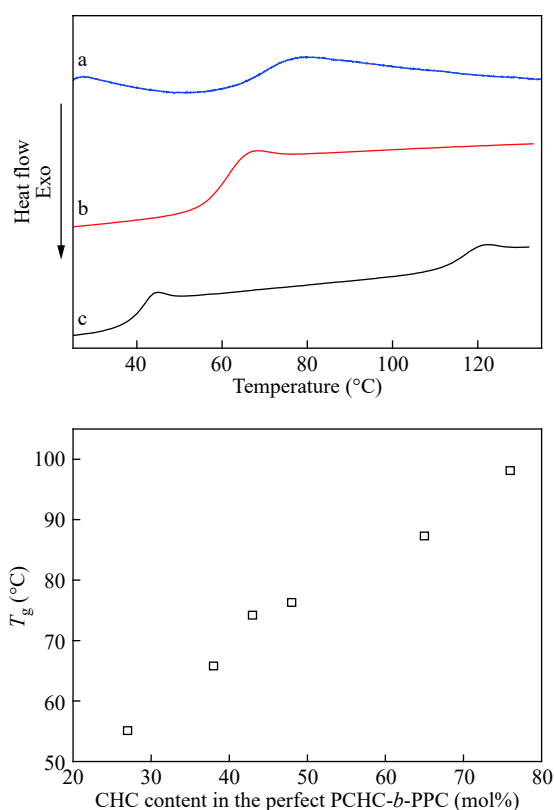

Fig. 5 DSC thermograms (top) of (a) PCHC-*b*-PPC diblock polymer containing 46 mol% PCHC segment, (b) the PO/CHO/CO$_2$ terpolymer containing 30 mol% CHC units, and (c) the blend of PPC and PCHC (1/1 molar ratio in carbonate unit), respectively; A plot (bottom) of T_g versus cyclohexene carbonate (CHC) unit content in the PCHC-*b*-PPC diblock polymers

in the diblock copolymer have enhanced miscibility in comparison with that of the PCHC/PPC blend.

Moreover, T_g can be easily adjusted by controlling the proportion of PCHC and PPC segments in the block copolymer. T_g is directly proportional to the content of cyclohexene carbonate linkages in the block polycarbonates (Fig. 5, bottom). For example, an increase in the content of

cyclohexene carbonate units in the block polymers from 27 mol% to 76 mol% results in the significant increase of T_g from 55.1 °C to 98.1 °C.

Similarly, with the same synthetic strategy, we succeeded in producing CO$_2$-based di- or tri-block polymers from the copolymerization of CO$_2$ and different *meso*-epoxides by stepwise addition (Fig. 6), using the previously reported catalyst system based on bimetallic complex **2**.[20] As anticipated, the PCBC-*b*-PCPC diblock polycarbonate possesses only one T_g with a broad baseline shift, which is between the T_g values of PCBC and PCPC (Fig. 7).
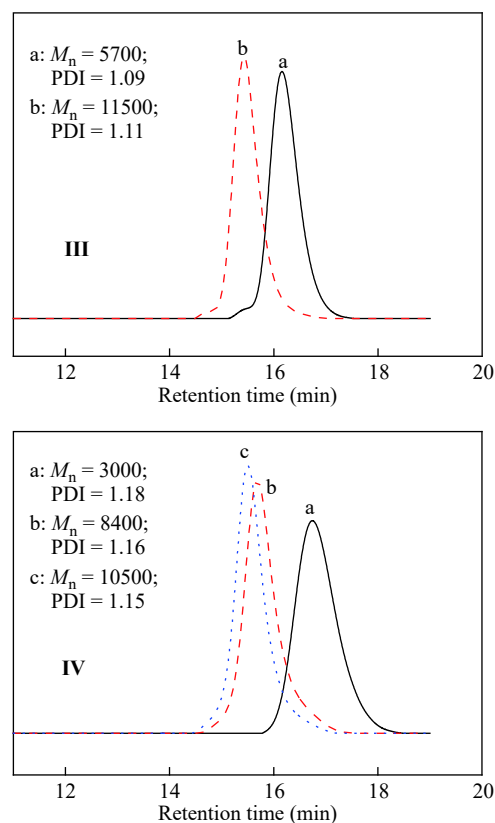

Fig. 6 GPC plots of PCBC-*b*-PCPC diblock (**III**, (a) the 1st segment, (b) the 2nd segment), and PCHC-*b*-PCBC-*b*-PCHC triblock (**IV**, (a) the 1st segment, (b) the 2nd segment, (c) the 3rd segment) copolymers
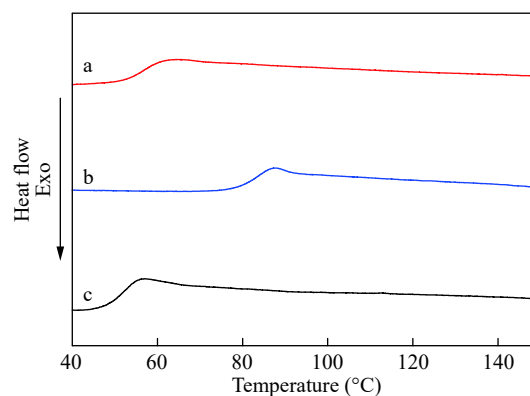

Fig. 7 DSC thermograms of (a) PCBC-*b*-PCPC containing 50 mol% PCPC segment, (b) PCPC, and (c) PCBC, respectively

CONCLUSIONS

In summary, we have reported an efficient approach for synthesizing polycarbonate block terpolymers *via* immortal stepwise copolymerization of CO_2 with different epoxides in the presence of enol chain transfer, mediated by robust cobalt catalyst systems. Various di- or tri-block polycarbonates, including PCHC-*b*-PPC, PCHC-*b*-PPC-*b*-PCHC, PPC-*b*-PCHC-PPC, PCBC-*b*-PCPC, and PCHC-*b*-PCBC-*b*-PCHC, were obtained in perfectly unimodal distribution and narrow polydispersity. The resultant block copolymers have only one broad T_g, which could be adjusted by altering the length of different polycarbonate segments.

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