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Tailored Living Block Copolymerization: Multiblock Poly(cyclohexene carbonate)s with Sequence Control

Jeung Gon Kim,[†] **Christina D. Cowman,**[†] **Anne M. LaPointe,**[†] **Ulrich Wiesner,**[‡] **and Geoffrey W. Coates***[,†]

[†]*Department of Chemistry and Chemical Biology and*
[‡]*Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853, United States*

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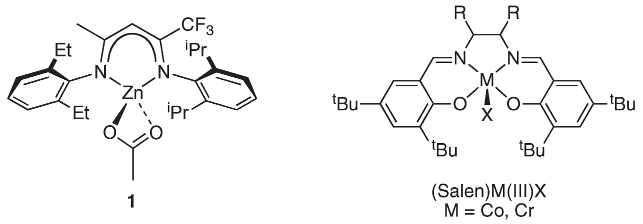
Block copolymers have found use in many applications, including thermoplastic elastomers, information storage, drug delivery, antifouling agents, microelectronics, and optics.[1] A wide range of synthetic methods has been developed to access new types of well-defined block copolymers and novel polymer architectures.[2] Living polymerizations allow precise syntheses of well-defined block copolymers.[3] In theory, it is possible to produce as many blocks as desired by sequential monomer addition. However, only a few reports describe the use of living polymerization to produce polymers containing four or more discrete blocks.[4]

Several studies investigated the effect of block sequence on the behavior of triblock copolymers. The sequence of the blocks influenced the polymer properties and morphologies.[5] Microphase separation calculations have suggested that block terpolymers may form more than 30 different complex morphologies,[6] but improved synthetic methodologies are required to systematically access a wider range of the compositional space and fully probe the effect of changes in the Flory–Huggins interaction parameter (χ). Ideally, such routes would be one-pot and would enchain monomers containing a wide range of functionalized side chains with precise control of block length and sequence.

A variety of synthetic strategies have been used to prepare multiblock copolymers. These include the use of macroinitiators, one-pot syntheses and variations thereof, and modification of macromonomers (e.g., coupling reactions or postfunctionalization). In an example of the macroinitiator approach, Matyjaszewski and co-workers reported the synthesis of ABC triblocks, $X(ABC)_3$ star polymers, and ABCBA pentablocks by atom transfer radical polymerization (ATRP) of styrene (A), *tert*-butyl acrylate (B), and methyl methacrylate (C). Each block or multiblock was isolated and purified prior to the initiation of the next block.[7] Hadjichristidis and co-workers used anionic polymerization to prepare tri-, tetra-, and pentablocks of styrene (A), isoprene (B), dimethylsiloxane (C), vinylpyridine (D), and ethylene oxide (E).[4a,8] In this one-pot synthesis, monomers were added via vacuum transfer and reaction conditions were adjusted accordingly for each monomer. However, the order of monomer addition was determined by the relative nucleophilicity of the propagating center, so it was not possible to vary the block sequence. In an example of postpolymerization functionalization, macromonomers may be coupled to yield multiblocks. For instance, Paik et al. used ATRP to prepare diblock polymers of poly(styrene)-*b*-poly(butyl acrylate) (AB) and poly(methyl methacrylate)-*b*-poly(methyl acrylate) (CD), which were then functionalized and linked via click chemistry to form ABCD tetrablocks.[9] However, to our knowledge, a convenient, one-pot synthesis in which the block sequence and length could be readily varied has not been reported.



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(Salen)M(III)X
M = Co, Cr

Figure 1. Selected catalysts for the living alternating copolymerization of epoxides and CO_2.

In this Communication, the living block copolymerization of functionalized cyclohexene oxides and CO_2 is described, yielding multiblock poly(cyclohexene carbonate)s [p(CHC)s] with a diverse range of functionality on the side chains and good control of block sequence and length. Unlike prior systems that contain stable vinyl backbones, the carbonate backbones of polymers reported herein are degradable, allowing possible applications where removable templates are required.

Several groups have reported the living alternating copolymerization of epoxides and CO_2[10] by (BDI)ZnOAc (BDI = β-diiminate)[11] or (Salen)M(III)X (M = Co[12] or Cr[13]; X = halide or carboxylate) catalysts (Figure 1). These catalysts produce polycarbonates from propylene oxide (PO) and cyclohexene oxide (CHO) with high selectivity and relatively narrow molecular weight distribution ($M_w/M_n < 1.5$). A recent report by Lu and Darensbourg et al. describes the first selective copolymerization of styrene with CO_2 using a modified Co(Salen) complex.[14] The living nature of these catalyst systems has allowed for the preparation of "immortal" catalysts by addition of diprotic initiators.[15] However, to date there have been few reports of block copolymer synthesis by sequential epoxide addition using the Zn or Co catalysts. One potential problem is incomplete conversion of some epoxides; to avoid tapering, it is necessary to remove or completely consume each epoxide prior to the formation of the next block. Nozaki and co-workers reported the synthesis of poly(propylene carbonate)-*b*-poly(1-hexene carbonate).[16] A modified (Salen)Co(III) catalyst was able to completely convert PO into poly(propylene carbonate) in the presence of CO_2, and the subsequent addition of 1-hexene oxide (HO) resulted in formation of a diblock copolymer. However, incomplete conversion of HO was observed and would present a problem for syntheses of block copolymers with three or more blocks. Darensbourg and co-workers recently reported the synthesis of a well-defined triblock copolymer by sequential reaction of PO, CHO, and 4-vinyl-1,2-cyclohexene oxide (V-CHO) with CO_2.[17] At the end of each step, residual monomers were removed prior to the addition of the next monomer to minimize tapering.

β-Diiminate zinc catalysts have been used to copolymerize cyclohexene oxide derivatives with CO_2 to produce polycarbonates with narrow molecular weight distributions.[11] We hypothesized that this living catalyst might produce well-defined multiblock copolymers, as it tolerates a number of functional groups and shows complete epoxide consumption.

To test this hypothesis, a number of functionalized cyclohexene oxides (CHOs) were prepared which contained substituents at the 4-position, which is well separated from the propagating species during the copolymerization with CO_2 (Scheme 1). The substituted CHOs were copolymerized with CO_2 by catalyst **1**

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*Corresponding author. E-mail: coates@cornell.edu.

Scheme 1. Synthesis of Functionalized p(CHC)s

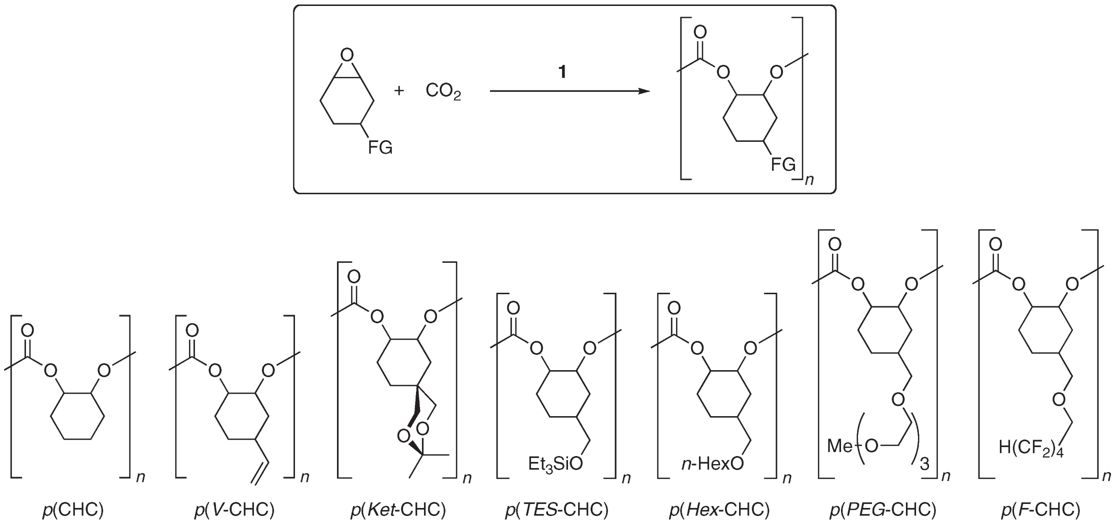


Table 1. Copolymerization of Functionalized Cyclohexene Oxides with CO_2 Using 1[a]

entry	[CHO]/[**1**]	polymer	M_n (kg/mol)[b]	M_w/M_n[b]	yield (%)[c]
1	100[d]	p(CHC)	16.6	1.10	82
2	100[d]	p(V-CHC)	23.8	1.07	99
3	100[e]	p(Ket-CHC)	16.6	1.07	79
4	100[e]	p(TES-CHC)	24.5	1.07	66
5	100[e]	p(Hex-CHC)	30.4	1.07	83
6	60[e]	p(PEG-CHC)	18.0	1.09	99
7	50[e]	p(F-CHC)	18.5	1.06	99

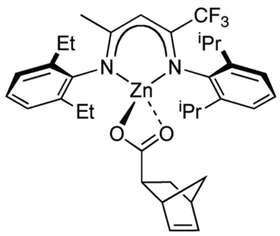
[a] Polymerization conditions: 50 °C, 1 h, toluene, 100 psi CO_2. [b] Determined by GPC calibrated with polystyrene standards in tetrahydrofuran at 40 °C. [c] Isolated yield. [d] [**1**] = 0.02 M. [e] [**1**] = 0.01 M.

(Table 1). Polycarbonate derivatives containing vinyl [p(V-CHC)], ketal [p(Ket-CHC)], triethylsiloxy [p(TES-CHC)], hydrophilic [p(PEG-CHC)], lipophilic [p(Hex-CHC)], and fluorophilic [p(F-CHC)] groups were prepared and exhibited narrow molecular weight distributions (M_w/M_n = 1.07−1.10). Full conversion in comparable reaction times was observed by ^{1}H NMR spectroscopy for all of the CHOs suggesting that the system might be suitable for living multiblock copolymerizations.

The living nature of CHO/CO_2 copolymerization catalyzed by the β-diiminate zinc complex was confirmed by the observation that M_n (measured by GPC and ^{1}H NMR) increases linearly as aliquots of CHO are added ([CHO]/[**2**] = 25, 50, 75, and 100) (Figure 2). For M_n determinations by NMR spectroscopy, a modified catalyst (**2**) containing a norbornenyl acetate initiator was used due to its distinct ^{1}H NMR signals.[18]

A series of multiblock copolymers were prepared using catalyst **1** (Scheme 2). Reaction progress was monitored by CO_2 uptake, and completion of each step was confirmed by ^{1}H NMR spectroscopy prior to addition of subsequent monomer. Di-, tri-, tetra-, and heptablock polymers containing alternating blocks of p(CHC) and p(V-CHC) were prepared (Table 2, entries 1−4). Complete monomer consumption was observed, and the resulting polymers had narrow molecular weight distributions. Catalyst **1** showed no loss of activity during the transition of p(CHC) to p(V-CHC) and vice versa.

Different combinations of monomers were then investigated, yielding multiblock copolymers with consistent molecular weight growth and narrow molecular weight distributions (entries 5−11). Pentablock (entry 7) and hexablock (entry 8) copolymers are novel examples of well-defined block copolymers prepared by a living polymerization which contain more than four nonequivalent blocks.[2]



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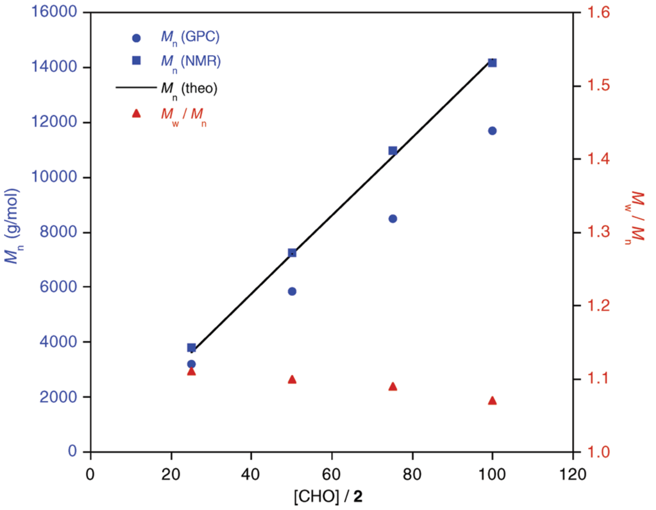

Figure 2. Plot of p(CHC) M_n (GPC) (●), M_n (NMR) (■), and M_w/M_n (▲) vs the equivalents of monomer added (toluene, 50 °C, 100 psi CO_2, initial catalyst loading [**2**] = 0.02 M).

To confirm the living behavior and the lack of tapering between blocks in the hexablock (entry 8), GPC and ^{1}H NMR data[19] were collected for each block during the polymerization. GPC data from each sequential block showed that M_n increased steadily and the polydispersity remained narrow (~1.10) (Figure 3), thus confirming that this system maintained its living character during the course of the multiblock copolymerization. We have noted a small, low-molecular-weight tail on the diblock copolymer; to date, we have been unable to determine the origin of this undesirable feature.

Fluorine-enriched polymers have drawn much attention due to their high stability, low surface energy, low refractive index, low

Scheme 2. Preparation of Cyclohexene Carbonate Multiblock Copolymers

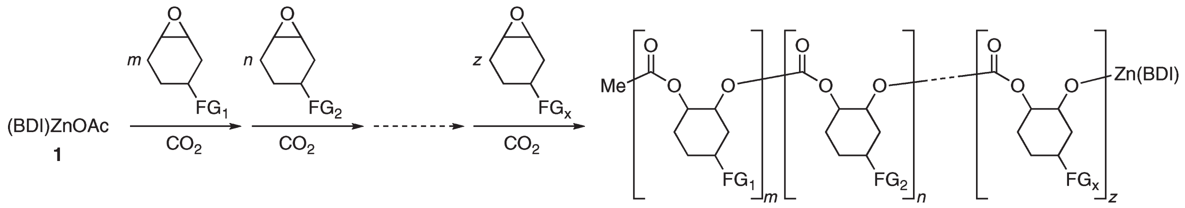

Table 2. Multiblock Copolymerizations of Functionalized Cyclohexene Oxides and CO_2[a]

entry	block copolymer	reaction time (min)	M_n[b] (kg/mol)	M_w/M_n[b]	yield (%)[c]
1[d]	$p(CHC)_{50}$-$p(V\text{-}CHC)_{50}$	20−20	15.9	1.06	99
2[d]	$p(CHC)_{50}$-$p(V\text{-}CHC)_{50}$-$p(CHC)_{50}$	15−15−15	22.8	1.05	98
3[d]	$[p(CHC)_{31}$-$p(V\text{-}CHC)_{31}]_2$	20−20−20−20	18.9	1.07	91
4[d]	$[p(CHC)_{30}$-$p(V\text{-}CHC)_{30}]_3$-$p(CHC)_{30}$	20−20−20−20−20−20−20	29.8	1.09	94
5[d]	$p(CHC)_{50}$-$p(V\text{-}CHC)_{50}$-$p(TES\text{-}CHC)_{25}$	15−15−30	23.5	1.05	99
6[e]	$p(CHC)_{50}$-$p(V\text{-}CHC)_{50}$-$p(TES\text{-}CHC)_{25}$-$p(F\text{-}CHC)_{25}$	15−15−20−30	32.4	1.09	99
7[e]	$p(TES\text{-}CHC)_{50}$-$p(CHC)_{100}$-$p(F\text{-}CHC)_{50}$-$p(V\text{-}CHC)_{100}$-$p(Ket\text{-}CHC)_{50}$	45−30−30−30−540	53.2	1.11	94
8[e]	$p(Hex\text{-}CHC)_{70}$-$p(TES\text{-}CHC)_{50}$-$p(F\text{-}CHC)_{30}$-$p(Ket\text{-}CHC)_{30}$-$p(CHC)_{70}$-$p(V\text{-}CHC)_{60}$	30−30−45−90−45−540	47.4	1.12	87
9[d]	$p(Hex\text{-}CHC)_{30}$-$p(F\text{-}CHC)_{30}$-$p(PEG\text{-}CHC)_{30}$	20−20−30	25.8	1.12	98
10[e]	$p(Hex\text{-}CHC)_{30}$-$p(PEG\text{-}CHC)_{30}$-$p(F\text{-}CHC)_{30}$	20−20−30	25.4	1.11	96
11[e]	$p(PEG\text{-}CHC)_{30}$-$p(Hex\text{-}CHC)_{30}$-$p(F\text{-}CHC)_{30}$	20−20−30	24.9	1.11	95

[a] Polymerization conditions: toluene, 50 °C, 100 psi CO_2. [b] Determined by GPC calibrated with polystyrene standards in tetrahydrofuran at 40 °C. [c] Isolated yield. [d] $[\mathbf{1}]_{initial} = 0.02$ M. [e] $[\mathbf{1}]_{initial} = 0.01$ M. All polymerizations proceeded to >99% conversion by ^1H NMR spectroscopy.

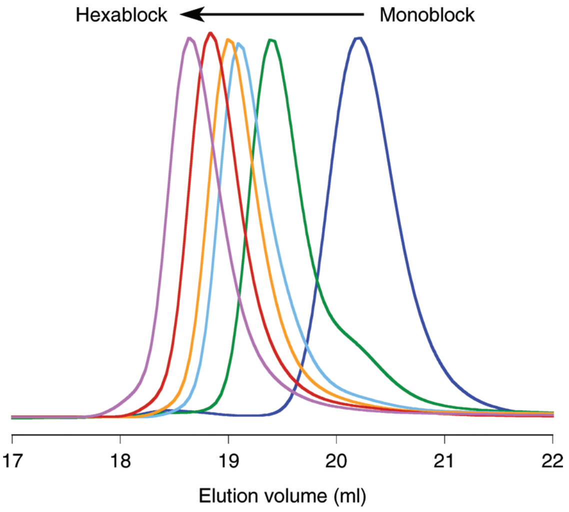

Figure 3. GPC traces of polymers sampled during the formation of a hexablock copolymer (Table 2, entry 8).

dielectric constant, and good solubility in supercritical CO_2.[20] In many cases, fluorinated block copolymers are prepared via multistep syntheses such as postpolymerization modification[21] or chain growth from a macroinitiator.[22] Using our system, fluorine-enriched blocks with tunable block size could be placed at any location within the chain in a one-pot procedure (entries 6−11). Since catalyst **1** successfully polymerized lipophilic (Hex-CHO), hydrophilic (PEG-CHO), and fluorophilic monomers (F-CHO), three sequentially isomeric triblock copolymers containing these blocks were prepared (entries 9−11). The three polymers exhibited similar molecular weights and narrow molecular weight distributions. To our knowledge, this is the first example of monodisperse block copolymers having lipophilic, hydrophilic, and fluorophilic blocks in one linear chain with interchangeable sequences. The increased immiscibility between blocks may facilitate good microphase separation and yield interesting nanostructures.

In summary, we report a method for the living multiblock copolymerization of functionalized cyclohexene oxides and CO_2. Catalyst **1** is suitable for the enchainment of many different polycarbonate blocks. The minimal influence of monomer variations on chain propagation permits the synthesis of various block copolymers with functionalities including protected alcohol, lipophilic, hydrophilic, and fluorophilic groups in a single chain. In addition, the interchangeability of blocks makes this method well-suited for controlled block copolymer synthesis so that it is now possible to prepare polycarbonates with a wide range of block combinations. Studies on phase separation, self-assembly, and postpolymerization modification are currently in progress.

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Supporting Information Available: Experimental details, catalyst synthesis, polymer synthesis and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) The ^{1}H NMR signal of the acetate end group of catalyst **1** overlapped with some peaks from the growing polymer.

(19) The complete consumption of each epoxide was confirmed by ^{1}H NMR spectroscopy. More details can be found in the Supporting Information.

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