Supramolecular multi-nuclear cluster catalysts for alternating copolymerization of epoxide and CO_2: unique telomerization by carboxylate anions

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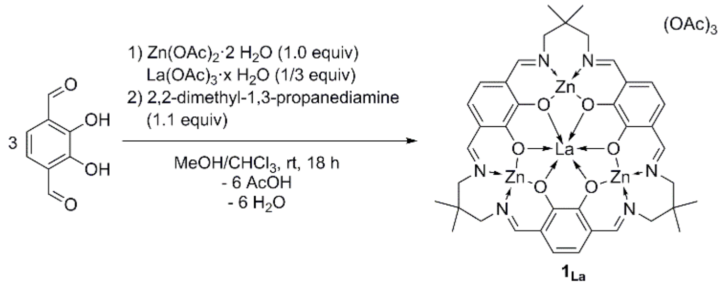
Abstract: We prepared and characterized heterometallic supramolecular catalysts based on trimetallated macrocyclic tris(salen) ligands that bind to rare earth metal and show unique catalytic performance toward alternating copolymerization of cyclohexene oxide (CHO) and CO_2 with a high carbonate linkage. Among lanthanide metals, the $CeZn_3$ system exhibited the highest catalytic activity with TOF over 370 h^{-1}. The acetate ligands coordinated to the $LaZn_3$ unit showed dynamic behavior, rapidly fluxional within a molecular but also between the coordinated anions and outer sphere carboxylate anions added as ammonium carboxylates, leading to the unique telomerization by adding excess amounts of ammonium carboxylates.

Keywords: Supramolecular catalyst, Cluster complexes, Alternating copolymerization, Telomerization.

1. Introduction

Alternating copolymerization of epoxides with CO_2 has been catalyzed by several heterogeneous and homogeneous catalyst systems. Among homogeneous systems, Coates first demonstrated that zinc β-diiminate complexes were associated into dimers during copolymerization,[1] leading to the deliberate preparation of various bimetallic zinc catalysts.[2] Williams recently reported that a heterodinuclear complex having a magnesium atom and a zinc atom exhibited higher activity toward alternative copolymerization of epoxide and CO_2 than either magnesium or zinc homodinuclear complexes.[3] We have been especially interested in supramolecular complexes bearing three zinc atoms and one lanthanide atom supported by macrocycles made of salen units.[4] Herein, we report that heterometallic Zn_3Ln catalysts for alternating copolymerization of CHO and CO_2. Furthermore, we found the first example of the telomerization of polycarbonate by adding ammonium salts as chain transfer reagents to control the molecular weight while retaining the catalytic activity.[5]



2. Experimental

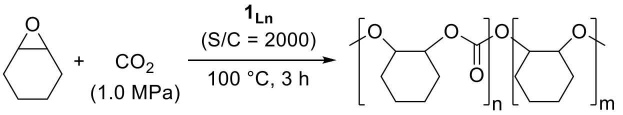
A complex $[LaZn_3(OAc)_3L^1]$ ($\mathbf{1}_{\mathbf{La}}$), where L^1 is the hexa-anion of the macrocyclic tris(salen)-based ligand, was prepared by the template reaction of 1,4-diformyl-2,3-dihyroxylbenzene with 2,2-dimethyl-1,3-propanediamine in the presence of 1.0 equiv of $Zn(OAc)_2 \cdot 2H_2O$ and 1/3 equiv of $La(OAc)_3 \cdot xH_2O$ according to the literature procedure.[6] Copolymerization of CHO and CO_2 was conducted in pressured glass apparatus under the conditions of S/C = 2000, 100 °C, 3 h, 1.0 MPa of CO_2.

3. Results and discussion

We examined variations of $\mathbf{1_{Ln}}$ using lanthanide elements for co-polymerization, and the results are summarized in Table 1. Complexes of larger lanthanides, such as La, Ce, Pr, and Nd, resulted in higher catalytic activities compared with middle or late lanthanide elements with very high carbonate linkage and a narrow molecular weight distribution, indicating that living polymerization proceeded even though these have three acetate ligands coordinated over the Zn_3Ln unit. Thus, we selected complex $\mathbf{1_{Ce}}$ as the optimal catalyst precursor.

Next, we tried to conduct the telomerization of polycarbonate by adding excess amounts of carboxylate anions since we observed fluxional behaviour of acetates in not only an intramolecular but also intermolecular manner as evident from NMR measurements. Addition of $[^{n}Bu_4N][OAc]$ (1.0 equiv to $\mathbf{1_{Ce}}$) decreased molecular weight during alternative copolymerization of CHO and CO_2. The polymer was characterized by ^{1}H NMR spectroscopic analysis and MALDI-TOF-MS.

Table 1. Catalytic activity and selectivity of $\mathbf{1_{Ln}}$ for alternating copolymerization of CHO and CO_2.



Entry	Ln	TOF$^{a)}$ /h^{-1}	Carbonate linkage$^{b)}$ /%	$M_n$$^{c)}$ /g·mol^{-1}	PDI$^{c),d)}$
1	La	230	99	10000	1.2
2	Ce	370	> 99	14000	1.3
3$^{e)}$	Ce	330	> 99	14000	1.2
4$^{f)}$	Ce	300	> 99	15000	1.2
5	Pr	310	> 99	14000	1.3
6	Nd	320	> 99	18000	1.2
7	Sm	290	> 99	21000	1.2
8	Eu	250	> 99	11000	1.2
9	Gd	200	> 99	11000	1.2
10	Dy	100	98	6600	1.2

a) Turn Over Frequency = mole [CHO] consumed per mole catalyst per hour.
b) Determined by the relative integrals of the ^{1}H NMR resonances at $\delta = 3.45$ (polyether) and $\delta = 4.65$ ppm (polycarbonate).
c) Determined by GPC in THF, using polystyrene standards as the calibrant.
d) Bimodal molecular weight distribution in GPC was observed.
e) The pressure of CO_2 was 0.6 MPa. f) The pressure of CO_2 was 0.3 MPa.

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