Communication

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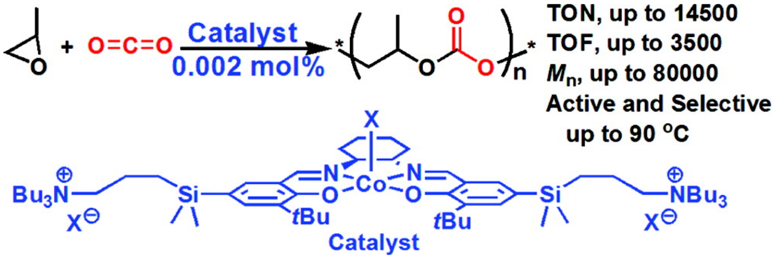

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Two Components in a Molecule: Highly Efficient and Thermally Robust Catalytic System for CO$_2$/Epoxide Copolymerization

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Recently, a significant progress has been achieved in the area of catalyst development for CO$_2$/epoxide copolymerization. Among the representative examples of this progress are the binary system of [(Salen)Co[1] or (Salen)Cr complex[2]]/(onium salt or base) and the β-diketiminatoZn complex.[3] As a propagation mechanism for the (Salen)Co-based binary system, it was proposed that the Lewis acidic metal center activates the epoxide attacked by the carbonate anion derived from the onium salt or the bulky amine base (Figure 1).[4] A bimolecular propagation mechanism in which a Zn-bound carbonate attacks a Zn-bound epoxide was proposed for the β-diketiminatoZn catalyst (Figure 1).[5]

Under these propagation mechanisms, the binary catalytic system and the mononuclear β-diketiminatoZn catalyst may have some drawbacks that will prevent them from being commercially viable. It is conceptually difficult to achieve a high turnover number (TON) because the catalytic systems cannot be highly active at a high [monomer]/[catalyst] ratio under these mechanisms. For the steps shown in Figure 1, the $\Delta S^{\ddagger}$ is negative and, consequently, the reaction is unfavorable at a high temperature. Most of commercial polymerizations are run at a high temperature, which enables us to remove the generated heat using ambient water or air. By running the process at a high temperature, the productivity per unit volume of the reactor can be maximized by the reduced viscosity of the polymerization solution. So, development of a thermally robust catalyst has been an issue.[6]

We reported a bimetallic Zn catalyst where the two metal centers are anchored on well-separated positions to efficiently operate the bimetallic propagation mechanism shown in Figure 1 even at a high [monomer]/[catalyst] ratio.[7] It provides a high molecular-weight polymer with a high TON up to 10000, but it works only for CO$_2$/(cyclohexene oxide) copolymerization and not for a more industrially viable CO$_2$/(propylene oxide) copolymerization. In this paper, we report a catalytic system **1** which bears two components in a molecule (Chart 1). In this complex, the chain-growing carbonate unit always hangs around the metal center through Coulombic interaction between the quaternary ammonium cation anchored on the ligand framework and the chain-growing anion, and so we can expect a high activity even at a condition of high [monomer]/[catalyst] ratio or high temperature.

Very recently, a (Salen)cobaltate complex containing a piperidinium unit as a pendant group (**3**) was reported which was designed to enhance the selectivity for polycarbonate over cyclic carbonate.[8] The high selectivity was achieved based on the proposal that the anionic propagating species is protonated by the proton on the piperidinium unit and then released from the cobalt center. With the complex, we cannot expect the same advantages that are expected for **1**, where the propagating group always hangs around the metal center and is not released far away from it.

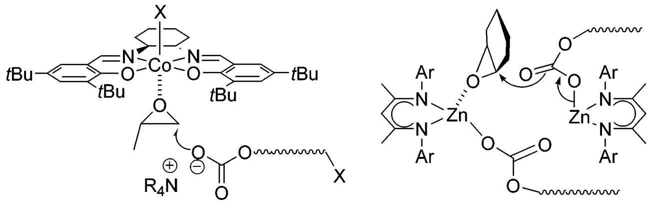
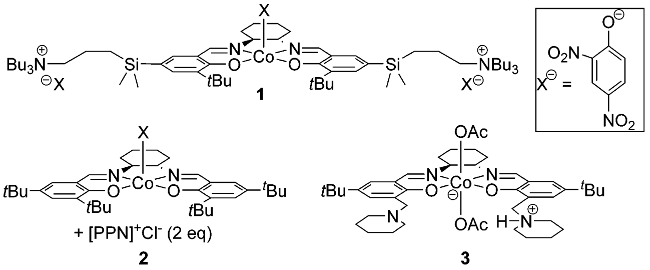
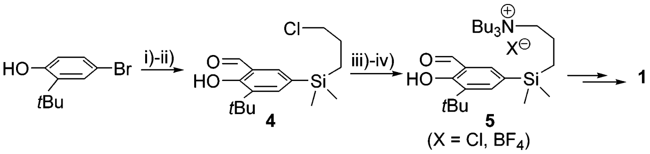


Figure 1. Propagation mechanisms for CO$_2$/epoxide copolymerization.

Chart 1



Scheme 1 [a]



[a] Conditions: (i) *t*BuLi (3 equiv) then ClMe$_2$Si(CH$_2$)$_3$Cl; (ii) paraformaldehyde/MgCl$_2$; (iii) Bu$_3$N/NaI; (iv) AgOAc then LiCl (X = Cl) or AgBF$_4$ (X = BF$_4$).

Complex **1** is prepared by the route described in Scheme 1. The chloride ion intervenes in the metalation reaction, and the desired complex **1** (X = Cl) is not afforded from the corresponding Salen-type ligand containing the chloride ion. However, the ligand containing BF$_4^-$ affords cleanly the desired complex **1** (X = BF$_4$). Because the binary system of (Salen)Co(III)X/[R$_4$N][BF$_4$] was reported not to be active,[1a] the BF$_4^-$ is replaced with 2,4-dinitrophenolate after metalation.

As expected, complex **1** is highly active for CO$_2$/[propylene oxide (PO)] copolymerization at a high [PO]/[catalyst] ratio of 25 000 (Table 1). The activity increases dramatically as the temperature increases to 90 °C, and the TOF up to 3500 h^{-1} is achieved at 90 °C, the highest record in this copolymerization (entry 4). It loses its activity at 100 °C by the decomposition of the catalyst. We can achieve a high TON, such as 14 500, also the highest record, by realizing the catalytic activity at such a high [PO]/[catalyst] ratio of 50 000 (entry 5). We can run the polymerization in 100 g scale using a bomb reactor equipped with a mechanical stirrer (entry 6). The attainable maximum conversion at this condition is 33%, which corresponds to furnishing a very viscous 46 wt % polymer solution.[9]

The binary system (**2**) composed of (Salen)Co(2,4-(NO$_2$)$_2$C$_6$H$_3$O) and PPNCl, which was reported to be highly active at a condition of the relatively low [PO]/[catalyst] ratio of 2000 and low temperature of 45 °C (TON, 980; TOF, 1400; entry 8),[1a] forms no

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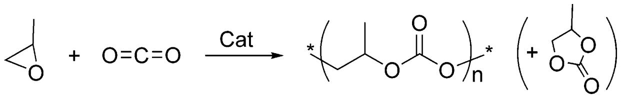
Table 1. CO_2/(Propylene Oxide) Copolymerization Results[a]



entry	cat; [PO]/[cat]	*T* (°C)	*t* (h)	TOF[b] (h^{-1})	TON[b]	selectivity[c]	M_n[d] ($\times 10^{-3}$)	M_w/M_n
1	**1**; 25000	50	7.0	650	4600	100	75	1.23
2	**1**; 25000	70	1.0	2400	2400	94	61	1.19
3	**1**; 25000	80	1.0	3300	3300	94	71	1.25
4	**1**; 25000	90	1.0	3500	3500	90	80	1.32
5	**1**; 50000	80	4.5[f]	3200	14500	84	53	1.35
6[e]	**1**; 25000	80	6.0[f]	1400	8300	88	95	1.46
7[g]	**2**; 25000	80	1.0	0	0	0		
8[h]	**2**; 2000	45	0.7	1400	980	97	26	1.01
9	**3**; 25000	80	3.0	370	1100[i]	60	nd[i]	nd
10[j]	**3**; 2000	60	1.0	610	610	90	7	1.22

[a] Polymerization condition: Propylene oxide (10.0 g), CO_2 (initial pressure, 2.0 MPa). [b] Calculated based on the weight of the isolated polymer not including the cyclic carbonate. [c] Selectivity for the polycarbonate over the cyclic carbonate in unit of % determined by the ^1H NMR spectroscopy of the crude product. [d] Determined on GPC using the polystyrene standard. [e] Scale-up reaction: Propylene oxide (200 g), CO_2 pressure (2.0−1.7 MPa). [f] Enough time is given to maximize TON. [g] Only the cyclic carbonate was obtained with a TOF of 1950 h^{-1}. [h] Data from ref 1a. [i] Isolation of the polymer by precipitating in methanol failed by nature of its low molecular weight, and the TOF and the TON were calculated from the ^1H NMR spectra of the crude product. [j] Data from ref 8.

polymer at all by the increase of both the ratio to 25 000 and the temperature to 80 °C (entry 6).

The high selectivity (90%) achieved with **3** at the condition of low [PO]/[catalyst] ratio of 2000 and low temperature of 60 °C (entry 10) is not preserved by the increase of the [PO]/[catalyst] ratio and the temperature (60% at 80 °C and [PO]/[catalyst] =25 000, entry 9). Furthermore, the TOF (370 h^{-1}) observed for **3** is significantly lower than those (∼3000 h^{-1}) observed for **1** at a condition of high [PO]/[catalyst] ratio of 25 000.

High selectivity (>90%) for the copolymer over the cyclic carbonate even at a high [PO]/[catalyst] ratio and a high temperature is another merit of **1** in addition to the high TOF, high TON, and thermal robustness. The comparison catalytic system **2** gives only the cyclic carbonate (entry 7), and complex **3** shows very poor selectivity (60%) at our standard condition ([PO]/[catalyst] = 25 000, 80 °C).

Producing high molecular-weight polymers is another advantage of **1**. Because most of the catalysts for this copolymerization show some living characteristics, the molecular weight is basically dependent on the attained TON. Complex **1** is capable of providing high molecular-weight polymers (M_n = 53 000−95 000) because it is able to provide high TONs. The average molecular weight increases as the TON increases in case the polymerization time is the same (entries 2−4), but the increase of TON by increasing the polymerization time in the diluted condition is not accompanied by an increase of the molecular weight (entries 3 and 5). This indicates that some chain transfer reactions operate when the polymerization reaction is carried out for a long time in a diluted condition.[10] Fairly narrow molecular-weight distributions (M_w/M_n = 1.19−1.35) are observed for the copolymers obtained with **1**, even though the GPC traces of the polymers exhibit a narrow bimodal shape, which might be attributed to the presence of more than one chain-growing unit in **1** (see Supporting Information). The molecular weights (M_n) reported with the binary catalytic system such as **2** have rarely exceeded 30 000 because it shows high activity only at a low [PO]/[catalyst] ratio.[1a] Complex **3** provides only oily oligomers at 80 °C (entry 8), even thought it was able to give a high molecular-weight polymer (M_n = 84 000) at 25 °C.[8]

The ^1H NMR spectra of the polymers obtained with **1** indicate perfectly alternating copolymers not containing any ether linkage. The ^{13}C NMR spectra indicate mostly head-to-tail linkage (94−83%).

Conclusively, a catalytic system containing a Lewis acidic metal center and a quaternary ammonium salt unit in a molecule is prepared, which shows activity even at a condition of high temperature and high [epoxide]/[catalyst] ratio. A very high TOF (up to 3500 h^{-1}) and TON (up to 14 500) are achieved, which have never been attained with other catalytic systems. The high selectivity and the high molecular weight of the obtained polymers are the other merits of the catalyst.

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Supporting Information Available: Details of the syntheses and characterization of the compounds, polymerization procedure, and polymer characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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