Copolymerization

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A Highly Active and Recyclable Catalytic System for CO_2/Propylene Oxide Copolymerization[**]

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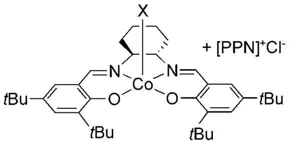
Copolymerization of CO_2 and epoxide catalyzed by metal complexes has drawn much attention recently.[1] In the initial report by Inoue and co-workers in 1969 the catalyst activity was poor (turnover number (TON): 6; turnover frequency (TOF): 0.12 h^{-1}),[2] but by the early 2000s it had been significantly improved by using binary catalytic systems of [Co(salen)][3] or [Cr(salen)] complexes[4] with an onium salt or base (**1**; salen = *N*,*N*′-bis(salicylidene)ethylenediamine, $[PPN]^+Cl^-$ = bis(triphenylphosphine)iminium chloride) or β-diketiminato zinc complexes.[5] It was proposed that the two components or the two zinc centers participated in the propagation reaction, and therefore binding of the two metal centers or the two components further improved catalysis to the maximum reported TON and TOF of 14500 and 4600 h^{-1}, respectively.[6,7] These values, which were achieved with **2** in the copolymerization of CO_2 and propylene oxide, are still low enough to warrant further improvement,[7] because low activity means higher catalyst cost and higher levels of catalyst-derived metal residue in the resin.[8] This metal residue either colors the resin or causes toxicity. For the TON of 14500 attained with **2**, the residual cobalt level in the resin reached 40 ppm unless it was removed.[9] Herein, we report a highly active catalytic system for CO_2/propylene oxide copolymerization and an efficient recovery strategy of the catalyst.



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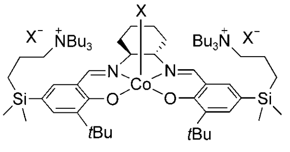
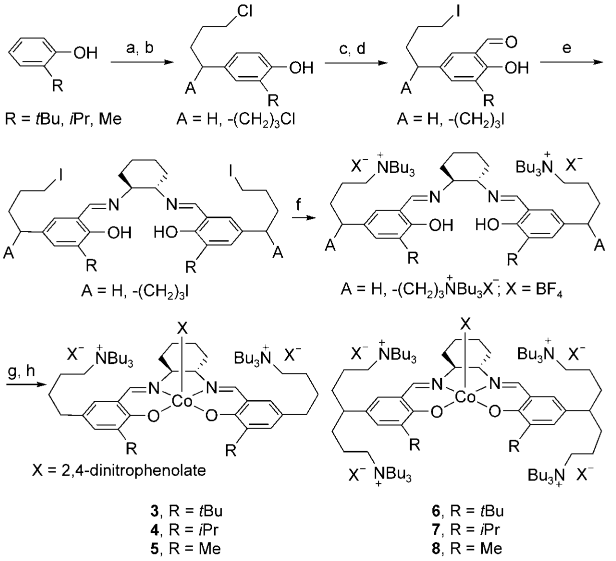


2, X = 2,4-dinitrophenolate

We prepared various cobalt–salen complexes by varying either the *ortho* substituent or the number of attached quaternary ammonium groups (Scheme 1). Thus, the Friedel–Crafts acylation of *ortho*-substituted phenol using 4-chlorobutyryl chloride and subsequent hydrogenation attached a $(CH_2)_4Cl$ group in the *para* position. In a similar manner, attack by 1,7-dichloroheptan-4-one on lithium 2-alkyl-4-lithiophenolate yielded a tertiary benzylic alcohol, and subsequent hydrogenation attached $CH[(CH_2)_3Cl]_2$. After formylation, the chloro substituent, that was not susceptible to nucleophilic substitution with tributylamine, was transformed into a more reactive iodo substituent. Formation of the quaternary ammonium salt occurred in nearly quantitative yields after generation of the salen-type ligand. Because the halide ion interfered with the metalation reaction, we replaced it with inert BF_4^-. Following metalation by a routine method, an active 2,4-dinitrophenolate anion replaced this BF_4^- ion.[3a]



Scheme 1. Synthesis of catalysts. Reagents and conditions: a) $Cl(CH_2)_3C(O)Cl/AlCl_3$ for A = H; Br_2, then tBuLi (3 equiv)/$[Cl(CH_2)_3]_2C{=}O$ for A = $(CH_2)_3Cl$; b) H_2/Pd on C; c) paraformaldehyde/$MgCl_2$; d) NaI; e) *trans*-1,2-diaminocyclohexane; f) Bu_3N then $AgBF_4$; g) $Co(OAc)_2$ then O_2/2,4-$(NO_2)_2C_6H_3OH$; h) 2,4-$(NO_2)_2C_6H_3ONa$.

We screened the newly prepared complexes for CO_2/propylene oxide copolymerization under the following conditions: [propylene oxide (PO)]/[catalyst (cat.)] = 25000, 80 °C, and CO_2 pressure 2.0–1.7 MPa (Table 1). The polymerization was terminated before 25 % conversion was reached, because after this time the solution became highly viscous, thus making stirring and diffusion difficult. The identity of the *ortho* substituent strongly influenced the activity. Contrary to other reports,[3] the bulky *tert*-butyl group was not the best choice in this study, and replacing it with a small methyl group significantly enhanced TOF. The TOF also increased dramat-

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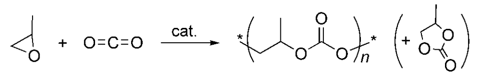
Table 1: CO_2/propylene oxide copolymerization.[a]



Entry	[PO]/[cat.] (cat.)	t [h]	TOF [h^{-1}]	TON	Selectivity[b]	$M_n \times 10^{-3}$	M_w/M_n[c]
1	25 000 (**3**)	6.0	270	1600	70	42	1.20
2	25 000 (**4**)	1.0	3100	3100	95	11	1.49
3	25 000 (**5**)	1.0	3000	3000	89	36	1.52
4	25 000 (**6**)	2.0	1300	2500	84	38	1.34
5	25 000 (**7**)	0.67	7900	5300	>99	76	1.32
6	25 000 (**8**)	0.25	26 000	6400	>99	114	1.29
7	50 000 (**8**)	0.50	26 000	13 000	>99	208	1.20
8[d]	100 000 (**8**)	1.0	22 000	22 000	>99	285	1.18
9[d]	100 000 (**8**)	1.5	18 000	27 000	92	225	1.28
10[d]	150 000 (**8**)	2.5	12 400	31 000	96	175	1.20
11[e]	25 000 (**2**)	1.0	3300	3300	94	71	1.25
12[f]	2000 (**1**)	0.70	1400	980	97	26	1.01

[a] Polymerization conditions: propylene oxide (10.0 g, 172 mmol), CO_2 pressure 2.0–1.7 MPa, 80 °C. [b] Selectivity for the polycarbonate over the cyclic carbonate in % units. [c] Molecular weight distribution: M_w = weight-average molecular weight; M_n = number-average molecular weight. [d] An induction time (ca. 30 min for entries 8 and 9, ca. 3 h for entry 10) was observed, which was excluded in calculating TOF. [e] Data from reference [7]. [f] Data from reference [3a].

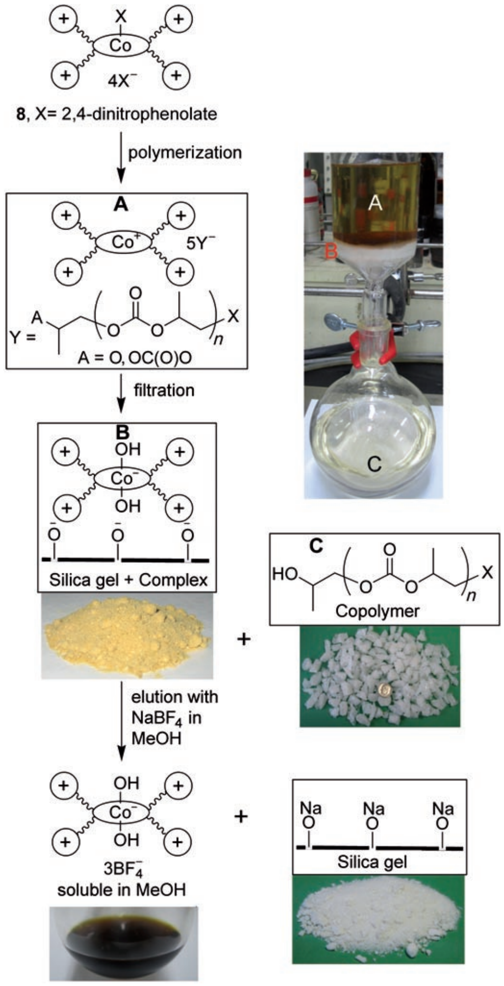
ically as more ammonium salt units were attached. By applying these principles, we obtained the best catalytic performance with **8** (Scheme 1), for which about 25% conversion was obtained in 15 min at [PO]/[cat.] = 25 000 (Table 1, entry 6). This result corresponds to TOF = 26 000 h^{-1} or 2.7×10^6 (g polymer) $mol^{-1} h^{-1}$, one order of magnitude higher than the values obtained with **1** and **2** (1400 and 3300 h^{-1}, respectively; Table 1, entries 11 and 12).

Another advantage of **8** was its high selectivity for copolymer formation over cyclic carbonate (>99%). In contrast, **2**–**6** exhibited selectivities below 95%, and the binary [Co(salen)]/PPNCl system (**1**) produced exclusively cyclic carbonate under the same conditions of [PO]/[cat.] = 25 000 and 80 °C.[7] Our results also demonstrated that binding the quaternary ammonium salts to the salen unit crucially affected activity and selectivity, because the catalytic system of **5**/2 $[NBu_4]^+[2,4\text{-}(NO_2)_2C_6H_3O]^-$ exhibited significantly lower activity (TOF, 4300 h^{-1}) and selectivity (75%) than **8** (TOF, 26 000 h^{-1}; selectivity, >99%). All copolymers obtained with **3**–**8** were strictly alternating copolymers that did not contain any ether linkages.

To increase the TON, we should be able to reach the same level of conversion (ca. 25%) at a higher [PO]/[cat.] ratio by running the polymerization for a longer time. Doubling the [PO]/[cat.] ratio from 25 000 to 50 000 did not reduce the catalytic performance of **8** (TOF, 26 000 h^{-1}), and we could double the TON (13 000) by doubling the polymerization time from 15 to 30 min (Table 1, entry 7). The system was also highly active even at [PO]/[cat.] = 100 000 (TOF, 22 000 h^{-1}; TON, 22 000), under which conditions **2** completely lost its activity. We observed some induction time (ca. 30 min) in this extreme condition. Through realizing such a high TON as 22 000, we obtained a very high molecular weight copolymer (M_n = 285 000), one order of magnitude higher than that obtained with the binary system **1** (M_n = 26 000; Table 1, entry 12). The molecular weight distribution was narrow (M_w/M_n = 1.18). When polymerization was carried out for an additional 30 min (90 min total) at [PO]/[cat.] = 100 000, the TON increased to 27 000 (27% conversion), but with concomitant formation of cyclic carbonate (92% selectivity; Table 1, entry 9). We attributed the lowering of the selectivity to a possible back-bite mechanism in the highly viscous polymerization solution at a later stage in the run. At [PO]/[cat.] = 150 000, we did not observe CO_2 consumption until 3 h after CO_2 injection. After that, the polymerization started and the TOF (12 400) was also reduced (Table 1, entry 10).

Even at a TON as high as 22 000, which corresponds to 38 (kg polymer) $(g\,Co)^{-1}$, the cobalt level in the isolated polymer reached 26 ppm unless the catalyst was separated; the residual cobalt complex made the isolated polymer a light yellowish color. When the light yellow polymerization solution prepared with **8** was passed through a short pad of silica gel (230–400 mesh, Merck), the top layer of the pad trapped the colored catalyst, thus yielding a colorless polymer solution (Scheme 2). Importantly, this simple separation was possible because the quaternary ammonium salts were bound to the salen unit. When the polymerization solution prepared with an unbound binary catalytic system [Co(salen)]/PPN^+Cl^- (**1**) was filtered through the silica-gel pad, the [Co(salen)] complex passed through it, which gave the filtrate a deep red color. It was proposed that the 2,4-dinitrophenolate anion attacking the coordinated epoxide initiated polymer-chain growth. If this scenario was the case, after polymerization the 2,4-dinitrophenolate anion would become a carbonate anion or alkoxide anion attaching a polymer chain, either of which might be protonated on a silica surface. This protonation allowed it to pass through the silica-gel pad while leaving the cobalt complex on the silica surface.

Afterward, we were able to recover the catalyst from the silica-gel pad and reuse it. Nothing was extracted when the collected composite of silica gel and salen–cobalt complex was dispersed in CH_3OH, but the color of the solution rapidly became reddish brown when excess $NaBF_4$ was added to the dispersion (Scheme 2). A possible salt exchange reaction between the surface siloxy anion and the inert BF_4^- might have solubilized the complex in the CH_3OH phase. We did not observe 2,4-dinitrophenolate signals in the ^1H NMR spectrum of the recovered BF_4^- salt of the cobalt complex; furthermore, the white color of the recovered silica gel indicated that it did not contain 2,4-dinitrophenolate anions, which would yield a yellowish color. These observations implied that all five 2,4-dinitrophenolate anions originally present in **8** were used up during polymerization. Treatment of the extracted



Scheme 2. Strategy for catalyst separation and recovery.

complex with two equivalents of 2,4-dinitrophenol and excess sodium 2,4-dinitrophenolate in CH_2Cl_2 afforded a recovered complex, with a ^{1}H NMR spectrum (see the Supporting Information) and catalytic performance (TOF = 24 000 h^{-1}; selectivity > 99% at [PO]/[cat.] = 50 000) that were almost identical to those of fresh, virgin **8**. We presume that the extract is a dihydroxycobaltate complex bearing three BF_4^- groups (Scheme 2), because two equivalents of 2,4-dinitrophenol were required to convert the extract back to an active catalyst.

In the scale-up reaction, the copolymer could be prepared on the 90 g scale at [PO]/[cat.] = 100 000 (95 mg **8**/250 g PO) with almost the same catalytic performance as that attained in a small-scale reaction (first run in Table 2). Again, we repeatedly used the recovered catalyst without significant loss in catalytic activity. In the repeated polymerizations, some reductions of the selectivity from > 99% to 97–98% and of the molecular weights from 300 000 to about 200 000 were observed. The recovery yields were 85–89%; we attributed some of this loss to the necessarily incomplete transfer of the polymerization solution from the reactor to the filtration apparatus. We supplemented the lost catalyst with fresh material for each subsequent batch.

Table 2: CO_2/propylene oxide copolymerization on the 90 g scale using recovered catalyst **8**.[a]

Run	t [min]	TON	Selectivity	$M_n \times 10^{-3}$	M_w/M_n	Recovery yield [%]
1st	65	21 000	> 99	296	1.19	88
2nd	85	21 000	98	172	1.41	89
3rd	85	21 000	97	176	1.34	87
4th	80	21 000	98	190	1.22	85
5th	90	20 000	97	210	1.21	86

[a] Polymerization conditions: propylene oxide (250 g), [PO]/[cat.] = 100 000, 70–77 °C, CO_2 pressure 2.0 MPa.

To isolate the copolymer, the propylene oxide was simply removed from the filtrate by distillation. The distillate was pure propylene oxide, which could also be reused for subsequent polymerization after drying with CaH_2. The isolated polymer was white, and inductively coupled plasma mass analysis indicated that it contained negligible amounts of cobalt residue (1–2 ppm).

In conclusion, we have presented a highly active catalytic system (TON > 20 000; TOF > 20 000 h^{-1}) for CO_2/propylene oxide copolymerization to selectively produce a very high molecular weight copolymer (M_n = 300 000). The catalyst can be readily separated by filtration through a short pad of silica gel to yield a resin containing negligible amounts of metal residue (1–2 ppm). The separated catalyst can be reused without significant loss of catalytic performance. All these features will encourage the commercialization of these CO_2/propylene oxide copolymers.

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