Efficient Synthesis of a Highly Active Catalyst for CO_2/Epoxide Copolymerization

Jaeki Min, Jong Eon Seong, Sung Jae Na, Anish Cyriac, and Bun Yeoul Lee*

Department of Molecular Science and Technology, Ajou University, Suwon 443-749, Korea
**E-mail: bunyeoul@ajou.ac.kr*
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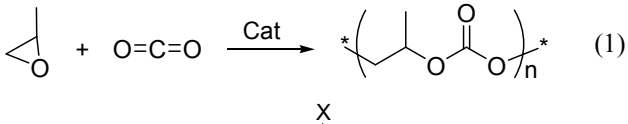
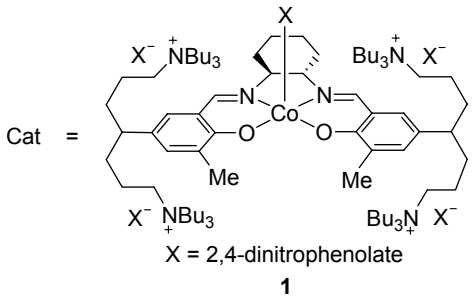
The carbon dioxide/propylene oxide (CO_2/PO) copolymer is attractive in many aspects and so has attracted much interest.[1] The copolymer, which consists of alternating CO_2 and PO subunits, has 44% by weight CO_2. The CO_2 gas is abundant and cheap, making the copolymer economical to prepare. The copolymer burns gently in air without emission of toxic materials, decomposes at a relatively low temperature of approximately 250 °C without an ash residue, and adheres strongly to a cellulosic substrate. These merits have been blunted by the lack of commercial quantities of the polymer due to the absence of a satisfactory catalytic system. We recently reported a highly active catalyst (**1**) that has the potential to be applied in a commercial process (equation 1).[2] A key to the catalyst is the binding of two components-Salen-cobalt(III) unit and quaternary ammonium salt-in proximity regardless of either low catalyst concentration or high polymerization temperature, which consequently allows a high turnover number (TON) and a high molecular weight (M_n) of the resulting polymer. With the conventional binary systems of [(Salen)Co[3] or (Salen)Cr complex[4]]/(onium salt or base), where the two components are not bound, catalytic performance is not observed at a low catalyst concentration and/or high polymerization temperature. Thus, a high TON and a high molecular weight could not be attained. Using the compound detailed in **1** a TON exceeding 20,000 and turnover frequency (TOF) more than 20,000 h^{-1} were achieved, and a strictly alternating copolymer of a high M_n up to 300,000 was provided with a high selectivity (> 99%). The highly active catalyst **1** was prepared through a rather lengthy synthetic route (Scheme 1), which might be a bottleneck for commercial utilization of the catalyst. In this work, we report a shortened synthetic route.



(1)



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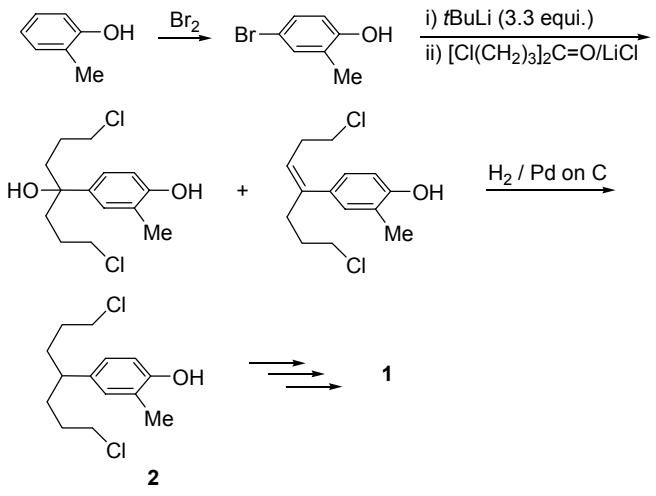
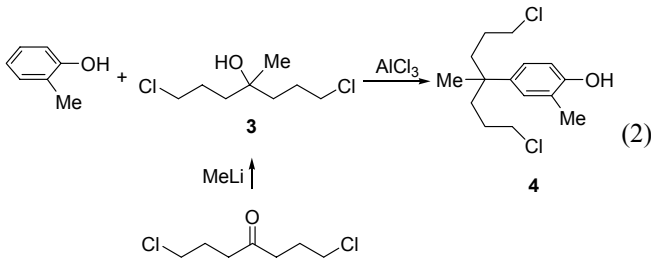
In the previous synthetic route, there were problems in the early steps to prepare a key intermediate **2** from *ortho*-cresol (Scheme 1). A *para*-regioselective bromination of *o*-cresol was reported in 96% isolated yield using *N*-bromosuccinimide (NBS).[5] The product was isolated from a side product of succinimide by column chromatography using silica gel, which hampers scale-up of this step. When Br_2 was employed instead of NBS, some side reactions such as benzylic bromination or dibromination, were concomitant and the yield was lowered to 80%. To remove the side products, the crude product should also be purified by column chromatography using silica gel. We experienced a more severe problem in the second step of Scheme 1. We added 3.3 equivalents of *t*-BuLi under an inert atmosphere using a rigorously dried solvent at a low temperature (-78 °C). The product was a mixture of a benzylic *tertiary*-alcohol and its H_2O-eliminated alkene compound contaminated with some *o*-cresol. *o*-Cresol might be generated through deprotonation of the α-proton in 1,7-dichloro-4-heptanone by the action of the lithiated compound. This protonation side reaction was inevitable even though we added LiCl in the reaction to facilitate carbonyl attack.[6] The mixture of products was isolated through an exhaustive silica gel column chromatography. Hydrogenation of the mixture of *tertiary*-alcohol and alkene produced the desired compound (**2**) in fairly good yield, but the crude product should also be purified by silica gel column chromatography. The overall yield from 3-bromo-2-methylphenol to **2** moderately fluctuated from batch-by-batch (52-67%). In subsequent steps from **2** to



Scheme 1. Synthetic Route for a Highly Active Catalyst for CO_2/PO Copolymerization

reach the target complex **1**, we did not have any significant problems; the yield for each step was almost quantitative and the product for each step could be used for the subsequent next step without the need of extensive purification.

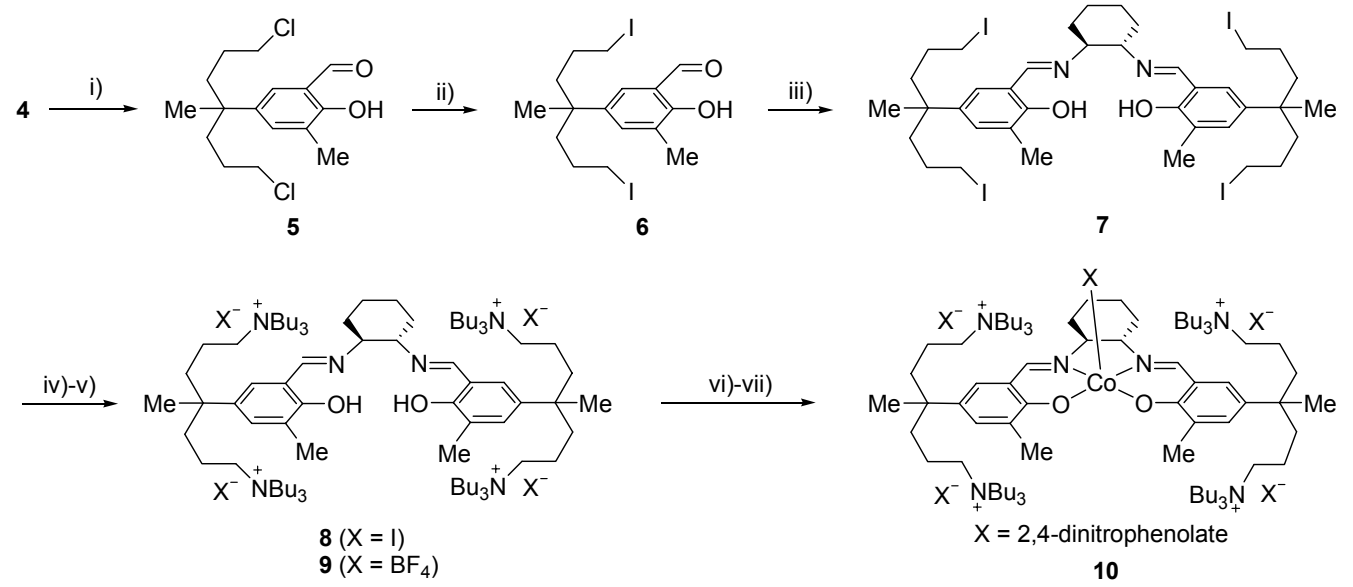
We developed a very simple route that attaches -CMe[$(CH_2)_3$-Cl]$_2$, instead of -CH[$(CH_2)_3$Cl]$_2$ in **2**, at the *para*-position of *o*-cresol (equation 2). Thus, Friedel-Craft alkylation of *o*-cresol using 1,7-dichloro-4-methylheptan-4-ol (**3**) in the presence of $AlCl_3$ produced the desired compound **4** in 97% yield. In this reaction, *o*-cresol was used as both a reactant and a solvent, and no additional solvent was required. The excess *o*-cresol was recovered by vacuum distillation (45°C/2 mmHg) and the remaining residue was pure **4** as determined by ^{1}H and ^{13}C{^{1}H} NMR, and was amenable for the next reaction without further purification. We could prepare **4** in a 25 g scale with a 250 mL scale glassware. The reactant **3**, 1,7-dichloro-4-methylheptan-4-ol, was prepared in 95% yield through MeLi treatment of 1,7-dichloro-4-heptanone, which can be easily prepared using inexpensive γ-butyrolactone in large scale in one-step reaction.[7] The MeLi addition reaction is also very clean, yielding a crude product that can be used without further purification in the Friedel-Craft alkylation reaction.



(2)

Starting from **4**, we prepared the corresponding Salen-cobalt(III) complex (Scheme 2). Formylation of **4** using paraformaldehyde, triethylamine, and magnesium chloride yielded **5** with good efficiency.[8] Because tributylamine cannot attack chloroalkane, the chloro-group is transformed into a more reactive iodo-group. The yield for this step was almost quantitative, but at this stage the product needs to be purified by passage through a short pad of silica gel. Formation of a quaternary ammonium salt at this salicylaldehyde stage is unsatisfactory. An accompanying side reaction occurred, which might represent an attack of the phenolate anion generated by the action of tributylamine base on phenolic proton, onto the iodo-group. When formation of the quaternary ammonium salt was carried out after the formation of Salen-type ligand **7**, the side reaction was negligible and formation of the desired compound occurred in a near quantitative yield. Because iodide anion intervenes in the metallation reaction, it was replaced with an inert BF_4^- through the treatment of $AgBF_4$. Metallation was carried out by a routine method involving the treatment of $Co(OAc)_2$ in ethanol and oxidation using O_2 in the presence of an equivalent amount of 2,4-dinitrophenol. Finally, the inert BF_4^- was replaced with an active 2,4-dinitrophenolate anion by stirring the solution of cobalt complex over a slurry of excess sodium 2,4-dinitrophenolate in CH_2Cl_2. ^{1}H and ^{13}C{^{1}H} NMR spectra signals produced by complex **10** were broad at room temperature, but became sharp enough to be assignable by raising the temperature. Complex **10** also displayed excellent polymerization performance for CO_2/PO copolymerization at the conditions of [PO]/[Cat] = 50000, 80 °C, and CO_2 pressure = 2.0-1.7 MPa (TON, 6200; TOF, 9200 h^{-1}, the selectivity for the formation of polymer over the cyclic carbonate of 96%; M_n of the obatined polymer of 89000; molecular weight distribution (M_w/M_n) of 1.21).

In summary, we developed a shortened synthetic route for a highly active catalyst for CO_2/PO copolymerization. This route allows the scaleable synthesis of the potential catalyst, which will encourage the commercialization of these CO_2/PO copolymers.



Scheme 2. i) Paraformaldehyde/NEt_3/$MgCl_2$; ii) NaI in CH_3CN; iii) 1,2-*Trans*-diaminocyclohexane in CH_2Cl_2; iv) Bu_3N in CH_3CN; v) $AgBF_4$; vi) $Co(OAc)_2$ in ethanol; vii) O_2 and 2,4-dinitrophenol in CH_2Cl_2, then sodium 2,4-dinitrophenolate.

Experimentals

General remarks. All manipulations were performed under an inert atmosphere using standard glove box and Schlenk techniques. THF and diethyl ether were distilled from benzophenone ketyl. Ethanol was dried as previously described using sodium and diethyl phthalate.[9] CH_3CN, CH_2Cl_2, and $CDCl_3$ were dried by stirring over CaH_2, and were subsequently vacuum-transferred to reservoirs. *o*-Cresol was dried over molecular sieves. 1,7-Dichloroheptan-4-one was prepared as previously described.[7] CO_2 gas (99.999% purity) was dried by storing in a column of molecular sieves 3A at a pressure of 30 bar. Propylene oxide (PO) was dried by stirring over CaH_2 for several days and was vacuum-transferred to a reservoir. The ^{1}H NMR (400 MHz) and $^{13}C\{^1H\}$ NMR (100 MHz) spectra were recorded on a Varian Mercury Plus 400. Elemental analyses were carried out at the Analytical Center, Kyunghee University. Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Gel permeation chromatograms (GPC) were obtained at room temperature in THF using a Waters Millennium apparatus with polystyrene standards.

Synthesis of 1,7-dichloro-4-methylheptan-4-ol (3). To a flask containing 1,7-dichloroheptan-4-one (17.40 g, 95.04 mmol) in diethyl ether (285 mL) was added MeLi (81.0 g, 143 mmol, 1.5 M in diethyl ether) dropwise at -78 ^{o}C under nitrogen. After stirring at -78 ^{o}C for two hours, the reaction was quenched by addition of water (170 mL) at -78 ^{o}C. The organic phase was collected and the water phase was further extracted with the addition of diethyl ether (3 × 300 mL). After the combined diethyl ether was dried over anhydrous $MgSO_4$, the solvent was removed with a rotary evaporator to give an oily residue, which is used for the next reaction without further purification (18.0 g, 95%). The compound slowly decomposed during storage and was used for the next step immediately following preparation. ^{1}H NMR ($CDCl_3$): δ 3.59 (t, J = 6.4 Hz, 4H, CH_2Cl), 1.90-1.86 (m, 4H, CH_2), 1.65-1.61 (m, 4H, CH_2), 1.23 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 72.32, 45.88, 39.51, 27.61, 27.23 ppm.

Synthesis of 4. *o*-Cresol (78.17 g, 722.8 mmol), 1,7-dichloro-4-methylheptan-4-ol (17.99 g, 90.35 mmol), and $AlCl_3$ (13.25 g, 99.39 mmol) were mixed and the mixture was stirred overnight under an atmosphere of N_2. The reaction was quenched by the addition of diethyl ether (500 mL) and water (300 mL). The organic phase was collected and the water phase was further extracted with additional diethyl ether (3 × 300 mL). After the combined diethyl ether was dried over anhydrous $MgSO_4$, the solvent was removed with a rotary evaporator. The excess *o*-cresol was recovered by vacuum distillation (45^{o}C/2 mmHg). ^{1}H and ^{13}C NMR analysis indicated that the oily residue was pure enough to be used for the next reaction without further purification (25.40 g, 97%). IR (KBr): 3528 (OH) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.01 (d, J = 2.0 Hz, 1H, *m*-H), 6.97 (dd, J = 8.0 Hz, 2.0 Hz, 1H, *m*-H), 6.72 (d, J = 8.0 Hz, 1H, *o*-H), 4.85 (s, 1H, OH), 3.45 (t, J = 6.4 Hz, 4H, CH_2Cl), 2.27 (s, 3H, CH_3), 1.86-1.44 (m, 8H, CH_2), 1.30 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 151.79, 138.67, 129.06, 125.02, 123.45, 114.85, 46.20, 41.12, 39.95, 28.09, 24.22, 16.58 ppm. HRMS (EI): *m/z* calcd (M^+ $C_{15}H_{22}Cl_2O$) 288.1046, found 288.1048.

Synthesis of 6. Compound **4** (25.40 g, 87.83 mmol) was dissolved in anhydrous THF (650 mL). Paraformaldehyde (10.55 g, 351.3 mmol), triethylamine (37.31 g, 368.9 mmol) and magnesium chloride (33.52 g, 351.3 mmol) were added under a N_2 atmosphere. The reaction mixture was heated to reflux for 5 hours and cooled to room temperature. The solvent was removed with a rotary evaporator. Water (300 mL) and CH_2Cl_2 (500 mL) were added to the residue, and the mixture was filtered over Celite. The organic phase was collected, and the aqueous phase was further extracted using CH_2Cl_2 (2 × 300 mL). The combined organic phase was dried over anhydrous $MgSO_4$. The solvent was removed with a rotary evaporator to give an oily residue that was evacuated further to remove some residual triethylamine. The residue was dissolved in CH_3CN (110 mL) and NaI (126.4 g, 843.2 mmol) was added. After the resulting mixture was refluxed for 20 hours, it was cooled to room temperature. After water (300 mL) was added, the product was extracted using diethyl ether (3 × 300 mL). After the collected organic phase was dried over anhydrous $MgSO_4$, all volatiles were removed with a rotary evaporator to give a yellow oil. The product was purified by column chromatography on silica gel, eluting with hexane and toluene (v/v; 5:1). The yield was 83% (22.2 g). IR (KBr): 3448 (OH), 1650 (C=O) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 11.14 (s, 1H, OH), 9.87 (s, 1H, CH=O), 7.33 (d, J = 2.4 Hz, 1H, *m*-H), 7.25 (d, J = 2.4 Hz, 1H, *m*-H), 3.14-3.09 (m, 4H, CH_2I), 2.30 (s, 3H, CH_3), 1.87-1.43 (m, 8H, CH_2), 1.34 (s, 3H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 196.85, 158.20, 137.51, 136.09, 128.85, 126.93, 119.62, 44.28, 39.95, 28.66, 24.16, 15.81, 7.99 ppm. Anal. Calcd. ($C_{16}H_{22}I_2O_2$): C, 38.42; H, 4.43 %. Found: C, 38.46; H, 4.24 %.

Synthesis of 7. Compound **6** (20.67 g, 41.33 mmol) and (±)-*trans*-1,2-diaminocyclohexane (2.360 g, 20.66 mmol) were weighed into a one-neck flask, and then CH_2Cl_2 (240 mL) was added. The solution was stirred overnight under a N_2 atmosphere. The solvent was removed under vacuum to give a pure compound (21.84 g, 98%). IR (KBr): 3432 (OH), 1629 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 13.44 (s, 2H, OH), 8.31 (s, 2H, CH=N), 7.04 (d, J = 1.6 Hz, 2H, *m*-H), 6.91 (d, J = 1.6 Hz, 2H, *m*-H), 3.38-3.35 (m, 2H, cyclohexyl-CH), 3.08-3.03 (m, 8H, CH_2I), 2.25 (s, 3H, CH_3), 1.96-1.89 (m, 4H, cyclohexyl-CH_2), 1.96-1.43 (m, 20H, cyclohexyl-CH_2 and CH_2), 1.26 (s, 6H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ. 165.01, 157.31, 136.12, 131.35, 126.93, 125.54, 117.67, 72.94, 44.47, 39.79, 33.73, 28.72, 24.57, 24.32, 16.28, 8.38, 8.26 ppm. Anal. Calcd. ($C_{38}H_{54}I_4N_2O_2$): C, 42.32; H, 5.05; N, 2.60%. Found: C, 42.63; H, 5.21; N, 2.41 %.

Synthesis of 8. Compound **7** (21.08 g, 19.55 mmol) and tributylamine (15.22 g, 82.10 mmol) were weighed into a one-neck flask, and CH_3CN (210 mL) was added. The solution was refluxed for 2 days under a N_2 atmosphere. After the solution was cooled to room temperature, the solvent was removed under vacuum to give a residue that was subsequently triturated three times in diethyl ether (20 mL) to give a light yellow powder in 96% yield (34.13 g, 18.76 mmol). IR (KBr): 3413 (OH), 1627 (C=N) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ. 13.50 (s,

2H, OH), 8.52 (s, 2H, CH=N), 7.25(s, 2H, *m*-H), 7.24 (s, 2H, *m*-H), 3.53 (br, 2H, cyclohexyl-CH), 3.27 (br, 32H, NCH_2), 2.23 (s, 6H, CH_3), 1.93-1.80 (br, 4H, cyclohexyl-CH_2), 1.57-1.33 (br, 74H), 0.91-0.88 (t, 36H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ. 164.72, 157.54, 135.30, 131.09, 127.10, 125.46, 117.62, 71.96, 59.88, 59.02, 40.27, 37.81, 37.56, 25.87, 25.78, 24.26, 23.92, 19.81, 18.30, 15.97, 13.84 ppm. Anal. Calcd. ($C_{86}H_{162}B_4F_{16}N_6O_2$): C, 56.76; H, 8.97; N, 4.62 %. Found: C, 56.86; H, 9.13; N, 4.65 %.

Synthesis of 9. To a flask containing **8** (5.0 g, 2.75 mmol) and $AgBF_4$ (2.14 g, 11 mmol), CH_2Cl_2 (50 mL) was added rapidly with stirring. Black precipitates were observed as soon as ethanol was added and stirring was ceased due to the formation of a lump of light yellow solid. The lump was broken down with a spatula to facilitate the stirring. The solution was stirred for a day in the dark. After the generated AgI was filtered off over Celite inside a glove box, the solvent was immediately removed under vacuum to give a residue that was redissolved in CH_2Cl_2 (~ 6 mL). The solution was filtered again over Celite, and the solvent was removed under vacuum to yield a yellow residue that was subsequently purified by column chromatography on a short pad of silica gel, eluting with ethanol and CH_2Cl_2 (v/v, 1:5). The yield was 3.25 g (71%). IR (KBr): 3413 (OH), 1627 (C=N) cm^{-1}. ^1H NMR ($CDCl_3$): δ. 13.55 (s, 2H, OH), 8.42 (s, 2H, CH=N), 7.12 (s, 2H, *m*-H), 7.08 (s, 2H, *m*-H), 3.38 (br, 2H, cyclohexyl-CH), 3.06 (br, 32H, NCH_2), 2.20 (s, 6H, CH_3), 1.88-1.84 (br, 4H, cyclohexyl-CH_2), 1.68-1.26 (br, 74H), 0.87-0.86 (br, 36H, CH_3) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ. 165.23, 157.79, 135.21, 131.17, 127.18, 125.76, 117.91, 72.05, 59.17, 58.63, 40.16, 38.10, 37.71, 26.45, 24.91, 23.90, 20.31, 19.80, 17.30, 16.01, 13.97, 13.80, 13.79 ppm. Anal. Calcd. ($C_{86}H_{162}B_4F_{16}N_6O_2$): C, 62.24; H, 9.84; N, 5.06 %. Found: C, 62.03; H, 10.00; N, 5.15 %.

Synthesis of 10. Cobalt(II) acetate (0.221 g, 1.247 mmol) and ligand **9** (2.07 g, 1.247 mmol) were dissolved in ethanol (50 mL) inside a glove box. The solid precipitated in approximately 5 minutes. The resulting slurry was stirred for 3.0 hours at room temperature. The solvent was removed under vacuum to give a red solid that was subsequently triturated two times in diethyl ether (30 mL) to remove acetic acid that had been generated. The solid was dissolved in CH_2Cl_2 (50 mL) containing 2,4-dinitrophenol (0.229 g, 1.247 mmol), and the solution was stirred under an O_2 atmosphere for 3 hours. Sodium-2,4-dinitrophenolate (1.28 g, 6.21 mmol) was added. After the solution was stirred overnight at room temperature, it was filtered over Celite. The solvent was removed under vacuum to give a dark brown powder that was pure enough to be used for polymerization. Yields were quantitative (2.84 g). ^1H NMR (DMSO-d_6, 38 °C): δ. 8.65 (br, 4H, $(NO_2)_2C_6H_3O$), δ. 7.88 (br, 6H, $(NO_2)_2C_6H_3O$, CH=N), 7.31 (br, 4H, *m*-H), 6.39 (br, 4H, $(NO_2)_2C_6H_3O$), 3.38 (br , 2H, cyclohexyl-CH), 3.08 (br, 32H, NCH_2), 2.64 (s, 6H, CH_3), 2.06-1.85 (br, 4H, cyclohexyl-CH_2), 1.50-1.15 (br, 74H), 0.86 (br, 36H, CH_3) ppm.

CO_2/PO copolymerization. Into a bomb reactor (50 mL), inside a glove box, the complex (8.0 mg for [PO]/[Cat] = 50000) and propylene oxide (10.0 g, 172 mmol) were added. The bomb reactor was assembled and immersed in an 80 °C oil bath. It was stirred for 15 minutes to allow the solution temperature to reach the bath temperature. The CO_2 gas was pressurized to 20 bar and the valve was closed. Thirty minutes later, a pressure drop started, indicating commencement of polymerization. The CO_2 valve was opened and CO_2 was continuously fed for 1 hours. The reactor was cooled to room temperature by immersion in an ice bath. After the CO_2 gas was released, the reactor was opened. An aliquot was taken and dissolved in $CDCl_3$. ^1H NMR analysis of the solution indicated that the the selectivity for the formation of polymer over the cyclic carbonate is 96% and a strictly alternating copolymer was formed. The viscous solution was diluted with 10.0 g of PO and the viscous solution was filtered over a short pad of silica gel to give a colorless solution. Volatiles were removed using a rotary evaporator to give a white residue. The polymer lump was taken out of the flask and then broken manually to pieces. After the polymer pieces were placed in a hood overnight to evaporate some residual PO, they were completely dried in an oven at approximately 150 °C for 30 minutes. The yield was 2.15 g (TON = 6100; TOF = 9200 h^{-1} excluding induction time). Averaged molecular weight (M_n) and molecular weight distribution (M_w/M_n) measured on GPC and calculated based on polystyrene standard were 89000 and 1.21, respectively.

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