

COPOLYMERIZATION OF CARBON DIOXIDE AND CYCLOHEXENE OXIDE CATALYZED BY ALUMINUM PORPHYRIN-QUATERNARY AMMONIUM SALT IN THE PRESENCE OF BULKY LEWIS ACID*

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Abstract Chloro(5,10,15,20-tetraphenyl-porphyrinato)-aluminum/tetraethylammonium bromide (Et_4NBr) in combination with bulky Lewis acid was used for the copolymerization of CO_2 and cyclohexene oxide (CHO). Bulky Lewis acid having substituents at the ortho positions of the phenolate ligands, like methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate), significantly shortened the induction period and raised the catalytic activity, the corresponding turnover frequency reached 44.9 h^{-1} in 9 h, which was 23.8% higher than that from (TPP)AlCl/ Et_4NBr binary catalyst. The resulting polycarbonate has carbonate linkage over 93% with number average molecular weight of $(4.5\text{--}6.5) \times 10^3$ and polydispersity index below 1.10.

Keywords: Carbon dioxide; Aluminum porphyrinate; Bulky Lewis acid; Copolymerization; Poly(cyclohexenylene carbonate).

INTRODUCTION

CO_2 is an ideal synthetic feedstock because it is abundant, inexpensive, and nontoxic. One growing area in CO_2 chemistry is the development of catalysts for the alternating copolymerization of CO_2 and epoxides to form polycarbonates, a field pioneered by Inoue and co-workers in the late 1960s^[1]. In the following years a variety of heterogeneous catalyst systems have been developed with limited success, generally suffering from low catalytic activity, low molecular weight, and significant amounts of the undesired cyclic carbonate byproduct^[2–6]. Recently, several kinds of well-defined single site catalysts have been reported which demonstrate much improvement in activity and selectivity^[7–13].

Inoue and coworkers developed the first single site catalyst in 1978 for copolymerization of CO_2 and epoxide based on metal tetraphenylporphyrin (TPP) ligand^[14, 15], where aluminum porphyrinates such as (TPP)AlCl and (TPP)AlOMe acted as initiators for copolymerization of CO_2 and epoxide, or phthalic anhydrides and propylene oxide^[16–18]. When propylene oxide (PO) and CO_2 copolymerized using (TPP)AlOMe as catalyst at 20°C under 0.8 MPa, poly(propylene carbonate) (PPC) with 40% carbonate linkage was obtained after 19 days^[16], the carbonate linkage content reached 99% once EtPh_3PBr or Et_4NBr was used as cocatalyst. In another case, (TPP)AlCl in combination with a quaternary salt (EtPh_3PBr) was used for copolymerization of CO_2 and cyclohexene oxide (CHO)^[19], where poly(cyclohexenylene carbonate) (PCHC) with number average molecular weight (M_n) of 6.2×10^3 and polydispersity index (PDI) of 1.06 was obtained, but the turnover frequency (TOF) was only 0.30 h^{-1} . Kruper developed a catalyst consisted of chromium porphyrin complex ((TPP)CrCl) and 4–10 equivalents of 1-methylimidazole (MeIm) or (4-dimethylamino)pyridine (DMAP) for the cyclization of epoxides and CO_2 to produce cyclic carbonates^[20]. Holmes used a CO_2 -soluble

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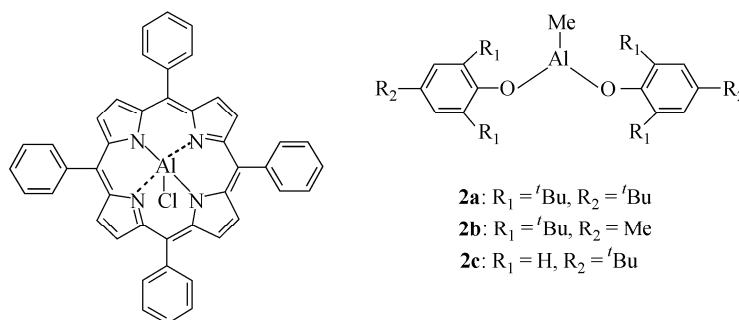
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tetra(pentafluorophenyl)porphyrin chromium chloride (TFPP)CrCl catalyst for copolymerization of CHO and CO₂ under supercritical CO₂. The polymer was obtained with yield up to 75% for 18 h at temperature between 95–110°C^[21]. Inoue utilized manganese porphyrin ((TPP)MnOAc) for copolymerization of CHO and CO₂^[22], PCHC with TOF of 16.3 h⁻¹ was prepared at 80°C under 5 MPa, but the existence of additives such as PPh₃, pyridine, or MeIm reduced the carbonate content. Interestingly, (TPP)MnOAc was used as catalyst for copolymerization of CHO and CO₂ at 80°C even under 0.1 MPa, though the TOF was only 3.3 h⁻¹.

Copolymer from the metal porphyrinates generally displayed narrow molecular weight distribution^[20–22]. Moreover, the metalloporphyrin catalysts were tolerant toward water and air, and sometimes “immortal polymerizations” was mentioned^[23, 24], though it had limitation considering the slow polymerization process.

It is well-known that ring-opening polymerization of epoxide with aluminum porphyrin can be dramatically accelerated once a bulky Lewis acid such as methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2b** in Scheme 1) was added^[25], where epoxide was activated upon coordinating with bulky Lewis acid and polymerization proceeded rapidly by continuing nucleophilic attacking of the growing species on the activated epoxide, and attacking of nucleophiles on the Lewis acid leading to termination was suppressed due to the large steric barrier between the bulky porphyrin ligand and the bulky substituents of the Lewis acid.



Scheme 1 Structure of (TPP)AlCl and Lewis acid

In this report, the bulky Lewis acid idea was used for the copolymerization of CHO and CO₂, employing aluminum porphyrinate and quaternary ammonium salt as catalyst in the presence of bulky Lewis acid, poly(cyclohexylene carbonate) with narrow molecular weight distribution was prepared in high yield within a short time.

EXPERIMENTAL

Materials

Diethylaluminum chloride (Et₂AlCl) and trimethylaluminum (Me₃Al) were provided by Aldrich. Dichloromethane (CH₂Cl₂), chloroform, *n*-hexane, and methanol were of analytical purity and used without further purification. 2,4,6-Tri-*tert*-butylphenol, 2,6-*tert*-butyl-4-methylphenol and 4-*tert*-butyl-phenol were recrystallized from hexane prior to use. Cyclohexene oxide (CHO) was refluxed over calcium hydride under nitrogen protection and distilled before use.

5,10,15,20-Tetraphenylporphyrin (TPPH₂) was synthesized by the reaction of pyrrole and benzaldehyde in propionic acid, it was recrystallized from chloroform/methanol (1/2, V/V) before use^[26].

Preparation of Chloro(5,10,15,20-tetraphenylporphinato)aluminum ((TPP)AlCl)

To a round-bottom three neck flask (100 mL) prefilled with TPPH₂ (1 mmol) was subsequently added CH₂Cl₂ (20 mL) and Et₂AlCl (0.16 mL, 1.2 mmol) under dry nitrogen protection. After the mixture was stirred for 2 h, the volatile fractions were removed from the reaction mixture under reduced pressure to give (TPP)AlCl (Scheme 1) as purple powder^[27].

Preparation of Bulky Lewis Acids (Methylaluminum Diphenolates)

Methylaluminum bis(2,6-di-*tert*-butyl-4-methylphenolate) (**2b**) (Scheme 1) was prepared by the reaction of 2,6-*tert*-butyl-4-methylphenol with Me₃Al. To a 50 mL round-bottom three neck flask containing 2, 6-*tert*-butyl-4-methylphenol (20 mmol) was successively added *n*-hexane (15 mL) and Me₃Al (0.95 mL, 10 mmol) at 0°C. Upon stirring at room temperature, the reaction mixture gradually became turbid with evolution of methane. The temperature was raised to 60°C after 1 h, and the resulting solution was cooled to room temperature, affording **2b** as white crystal (3.0 g, 63% yield), it was then dried under reduced pressure at room temperature^[28, 29]. Methylaluminum bis(2,4,6-tri-*tert*-butylphenolate) (**2a**) was prepared in the same manner. Methylaluminum bis(4-*tert*-butyl-phenolate) (**2c**) was prepared by the reaction of Me₃Al and 4-*tert*-butyl-phenol in CH₂Cl₂ under nitrogen protection. All the methylaluminum diphenolates (MADs) were used in CH₂Cl₂ solution (0.1 mol/L) in the context. The structure of (TPP)AlCl and Lewis acid (**2a**, **2b**, and **2c**) were shown in Scheme 1.

Catalyst Preparation

The (TPP)AlCl-Et₄NBr-MAD catalyst was prepared under nitrogen atmosphere. Bulky Lewis acid (**2a**, **2b**, and **2c**) solution (0.1 mol/L) was added dropwise to (TPP)AlCl and Et₄NBr solution of CH₂Cl₂ at room temperature, the mixture was then stirred at room temperature for 0.5 h.

Copolymerization

The catalyst and CHO were added into the autoclave free of oxygen and water, and CO₂ was pressurized into the autoclave, the system was then heated to the polymerization temperature and maintained at this temperature under vigorous stirring for certain period. The polymerization was terminated by adding an excess of methanol, and the resulting copolymer was precipitated by adding more methanol to the solution. The precipitated copolymer was purified by dichloromethane dissolving and hydrochloride/methanol precipitating process.

RESULTS AND DISCUSSION

Table 1 lists the results of copolymerization of CO₂ and CHO using different catalysts. (TPP)AlCl-Et₄NBr-**2b** catalyst provided the highest TOF of 44.9 h⁻¹, the obtained copolymer had carbonate linkage content of 96.7% with PDI of 1.07. (TPP)AlCl-Et₄NBr-**2a** showed similar results, showing 23.5% catalytic activity higher than (TPP)AlCl-Et₄NBr binary catalyst. While for the Lewis acid having no ortho substituents (**2c**), the catalyst activity was 7.8% lower than corresponding binary catalyst. Thus, the presence of bulky Lewis acid having substituents at the ortho positions of the phenolate ligands (**2a** and **2b**) significantly raised the catalytic activity. Only polyether was obtained using (TPP)AlCl and Lewis acid as catalyst, indicating that homopolymerization of cyclohexene oxide occurred rather than copolymerization. When the catalyst consisted of only Et₄NBr and Lewis acid used, neither polyester nor polyether was obtained. Therefore, the active center for copolymerization of CHO/CO₂ might be on the aluminum complex formed between (TPP)AlCl and Et₄NBr. Bulky Lewis acid was only an accelerator in this system.

Table 1. Copolymerization of CO₂ and CHO by various catalysts^a

Catalyst component			Yield (%) ^b	TOF (h ⁻¹) ^c	Carbonate linkage (%) ^d	<i>M_n</i> ^e	PDI ^e
I	II	III					
(TPP)AlCl	Et ₄ NBr		65.5	36.1	97.9	6100	1.08
(TPP)AlCl		2b	— ^f				
	Et ₄ NBr	2b	Trace				
(TPP)AlCl	Et ₄ NBr	2a	81.1	44.6	95.8	5600	1.04
(TPP)AlCl	Et ₄ NBr	2b	81.8	44.9	96.7	5800	1.07
(TPP)AlCl	Et ₄ NBr	2c	60.5	33.3	96.1	6100	1.09

^a The reaction was performed in CH₂Cl₂ (20 mL) at 60°C for 9 h, *P*_{CO₂} = 4.0 MPa, *V*(CHO) = 50 mL (0.495 mol), *n*((TPP)AlCl) = 1 mmol, molar ratio of (TPP)AlCl/Et₄NBr/Lewis acid = 1:1:0.125; ^b Yield (%) = Product (g)/[{CO₂ (44 g/mol) + CHO (98 g/mol)} × 0.495 (mol)] × 100; ^c Turnover frequency of CHO to PCHC; ^d Determined by using ¹H-NMR spectroscopy; ^e Determined by gel permeation chromatography in THF, calibrated with polystyrene standards; ^f Polyether was the main product.

As shown in Table 2, TOF increased from 30.1 h⁻¹ to 44.9 h⁻¹ when molar ratio of Et₄NBr to (TPP)AlCl increased from 0.5 to 1, and TOF decreased when molar ratio of Et₄NBr to (TPP)AlCl was over 1, for example, when molar ratio of Et₄NBr to (TPP)AlCl was 2, the catalytic activity dropped to 34.5 h⁻¹. Therefore, the presence of Et₄NBr was critical for obtaining high catalytic activity, the optimum ratio providing the highest catalytic activity was 1, with the TOF reaching 44.9 h⁻¹ (**2b**/TPPAICl = 0.125). The resulting polycarbonate has M_n of 5.8×10^3 and PDI of 1.09 with carbonate linkage over 96%.

Table 2. Effect of the molar ratio of Et₄NBr to (TPP)AlCl on copolymerization of CO₂ and CHO under (TPP)AlCl-Et₄NBr-**2b** ternary catalyst^a

Molar ratio of Et ₄ NBr to (TPP)AlCl	Yield (%)	TOF (h ⁻¹)	Carbonate linkage (%)	M_n	PDI
0.5	54.8	30.1	96.2	6100	1.08
1	81.8	44.9	96.7	5800	1.07
2	62.8	34.5	95.1	5900	1.09
5	59.7	32.8	93.6	5800	1.08

^a The reaction was performed in CH₂Cl₂ (20 mL) at 60°C for 9 h, P_{CO_2} = 4.0 MPa, V(CHO) = 50 mL, $n((TPP)AlCl)$ = 1 mmol, molar ratio of TPPAICl/**2b** = 1:0.125; See Table 1 for all the measurements.

The influence of the molar ratio of Lewis acid to (TPP)AlCl on copolymerization was summarized in Table 3. For convenience, the content and ratio of (TPP)AlCl to Et₄NBr was kept constant ((TPP)AlCl/Et₄NBr = 1). The catalytic activity was only 14.9 h⁻¹ when the ratio of **2b** to (TPP)AlCl was 2, and it increased to 44.9 h⁻¹ when the ratio of **2b** to (TPP)AlCl dropped to 0.125. Therefore, the bulky Lewis acid played a key role in improving the catalytic activity.

Table 3. Effect of the molar ratio of **2b** to (TPP)AlCl on copolymerization of CO₂ and CHO^a

Molar ratio of 2b /(TPP)AlCl	Yield (%)	TOF (h ⁻¹)	Carbonate linkage (%)	M_n	PDI
2	27.1	14.9	93.4	6100	1.07
1	69.4	38.1	93.8	6000	1.06
0.5	70.9	38.9	94.5	6400	1.08
0.25	77.1	42.3	94.2	6200	1.08
0.125	81.8	44.9	96.7	5800	1.07
0.1	76.6	42.1	95.8	5800	1.05
0	65.5	36.1	97.9	6100	1.08

^a The reaction was performed in CH₂Cl₂ (20 mL) at 60°C for 9 h, P_{CO_2} = 4.0 MPa, V(CHO) = 50 mL, $n((TPP)AlCl)$ = 1 mmol, molar ratio of TPPAICl/ Et₄NBr = 1:1; See Table 1 for all the measurements.

Figure 1 showed dependence of copolymer yield on reaction time for ternary and binary catalysts, respectively. For the ternary catalyst, the copolymer yield reached 86.7% after 11 h, which was 23.8% increase in comparison with that for binary catalyst. The induction period for the ternary catalyst was below 30 min, whereas it was 1 h for the binary catalyst. Apparently, the polymerization induction period was shortened using the ternary catalyst containing bulky Lewis acid compound.

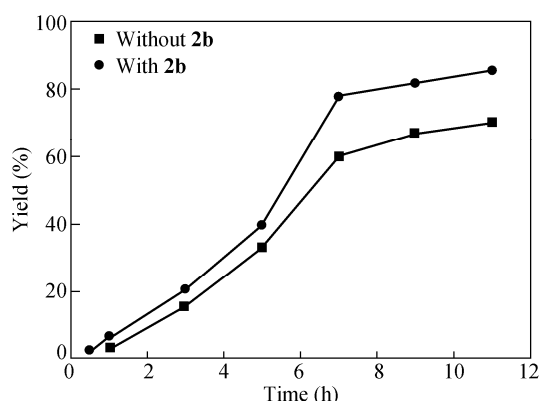
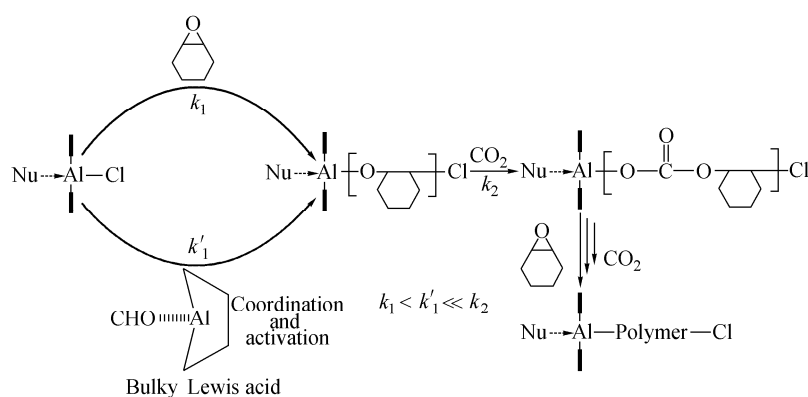


Fig. 1 Dependence of copolymer yield on reaction time for ternary and binary catalysts
 Reaction conditions: molar ratio of (TPP)AlCl/Et₄NBr/**2b** = 1:1:0.125; Solvent: 20 mL CH₂Cl₂; CHO: 50 mL; P_{CO₂}: 4.0 MPa; Temperature: 60°C

Chisholm discussed the copolymerization of CO₂ and epoxide catalyzed by (TPP)AlCl/4-(*N,N*-dimethylamino)pyridine(DMAP)^[30], the ring-opening reaction of PO happened at first to give (TPP)Al(PO)-Cl, and subsequently CO₂ inserted rapidly into the aluminum alkoxide to generate the aluminum carbonate. Therefore, the initial copolymerization rate exhibited a pronounced dependence on the ring-opening reaction of epoxide. The role of the bulky Lewis acid was to accelerate the ring-opening reaction of CHO, which was consistent with Inoue's suggestion of "high-speed polymerization" of epoxides^[25, 31]. When the copolymerization of CHO and CO₂ was carried out under (TPP)AlCl/Et₄NBr catalyst in the presence of bulky Lewis acid, as shown in Scheme 2, the ring-opening reaction of CHO initiated by (TPP)AlCl was accelerated by the bulky Lewis acid such as **2a** and **2b**, while the Lewis acid without ortho bulky substituents such as **2c** caused slower or termination of the ring-opening reaction of CHO. Therefore, the induction period of copolymerization initiated by (TPP)AlCl/Et₄NBr was shortened using ternary catalyst containing bulky Lewis acid.



Scheme 2 Copolymerization of CHO and CO₂ under (TPP)AlCl and Et₄NBr catalyst in the presence of bulky Lewis acid

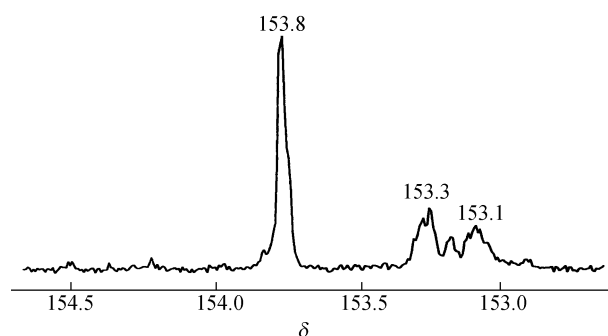
The influence of temperature and pressure on the copolymerization of CHO and CO₂ was summarized in Table 4. When reaction temperature was raised from 40°C to 80°C, TOF rapidly increased from 22.7 h⁻¹ to 53.8 h⁻¹, and *M_n* of the copolymer increased from 4500 to 6100. However, a decrease in the CO₂ pressure from 4.0 MPa to 2.0 MPa did not cause significant decrease in TOF. This was consistent with the assumption that the insertion of CO₂ into aluminum alkoxide bonds was not the rate-determining step.

Table 4. Effect of temperature and pressure on copolymerization of CO₂ and CHO^a

Run	Pressure (MPa)	Temperature (°C)	Yield (%)	TOF (h ⁻¹)	Carbonate linkage (%)	<i>M_n</i>	PDI
1	4.0	80	98.1	53.8	93.4	6100	1.07
2	4.0	70	91	48.5	95.3	5700	1.06
3	4.0	60	81.8	44.9	96.7	5800	1.07
4	4.0	40	41.2	22.7	95.7	4500	1.06
5	3.0	60	79.2	43.5	94.2	5000	1.05
6	2.0	60	77.4	42.5	94.6	5100	1.07

^a The reaction was performed in CH₂Cl₂ (20 mL) in a 500 mL autoclave for 9 h; V(CHO) = 50 mL; *n*((TPP)AlCl) = 1 mmol, molar ratio of TPPAlCl/Et₄NBr/**2b** = 1:1:0.125; See Table 1 for all the measurements.

The copolymer obtained had a narrow molecular weight distribution (PDI = 1.04–1.10), but its *M_n* was approximately an order of magnitude lower than those calculated for a initiator based on the ratio of [monomer] to [catalyst], indicating that severe chain transfer process occurred. Generally, the chain transfer reaction causes broadening of molecular weight distribution of the polymer, however, when the chain transfer reaction is rapid enough compared with the propagation reaction, the molecular weight distribution of the polymer may remain narrow. Of course, more convincing explanation should come from qualitative data of the two reactions.

**Fig. 2** ¹³C-NMR spectrum of the poly(cyclohexenylene carbonate) copolymer

The ¹³C-NMR spectrum of the poly(cyclohexenylene carbonate) obtained from (TPP)AlCl-Et₄NBr-**2b** catalyst was shown in Fig. 2, the signal at $\delta = 153.8$ in ¹³C-NMR was assigned to the chemical shift of equivalent m-centered tetrads ([mmm], [mmr] and [rmr]) (For convenience, —SS—RR— diad is defined as racemo diad [r], —SS—SS—(or —RR—RR—) diad is defined as meso diad [m]), and the signals at higher field ($\delta = 153.3$ – 153.1) of the copolymer were assigned to the central carbonyl carbons of r-centered tetrads ([mrm], [rrr] and [mrr])^[32]. The ratio of m-centered tetrads to r-centered tetrads was 52:48, indicating a lack of stereocontrol in the ring-opening step, which was similar to the copolymer obtained by the salen chromium chloride catalyst^[33, 34].

CONCLUSIONS

Compared with Et₄NBr/(TPP)AlCl binary catalyst, ternary catalyst with bulky Lewis acid having substituents at the ortho positions of the phenolate ligands could significantly shortened induction period and raised catalytic activity. The optimal yield was obtained with TOF of 44.9 h⁻¹ at 60°C when the molar ratios of Et₄NBr/(TPP)AlCl and Lewis acid/(TPP)AlCl were of 1 and 0.125, respectively. The copolymer obtained had carbonate content of 96% with PDI around 1.07.

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