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ARTICLE TYPE

Efficient Synthesis and Stabilization of Poly(propylene carbonate) from Delicately Designed Bifunctional Aluminum Porphyrin Complex

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Bifunctional aluminum porphyrin complexes were designed to synthesize poly(propylene carbonate) (PPC) from copolymerization of propylene oxide and carbon dioxide. The catalytic performance is adjustable via delicate control of the electronic environment of central Al by the number of methoxy group in the ligand framework as well as the length of alkyl chain in the quaternary ammonium cation.

The optimal catalyst having six methoxy groups in the ligand framework, two trihexylammonium cation linked to benzene via a six-methylene spacer, and NO₃⁻ as the axial ligand and quaternary ammonium anions, exhibited a TOF of 1320 h⁻¹ at 80 °C and 3 MPa, and PPC selectivity of 93%, and the TOF even reached 2824 h⁻¹ at 90 °C and 3 MPa, while the PPC selectivity could still remain 89%, the highest record in aluminum porphyrin complexes till now. In another concern, even though the bifunctional aluminum porphyrin complex has soil-compostable feature and can be left in PPC without separation, the depolymerization was very rapid even at 25 °C at ambient atmosphere, and over 50% decrease in number average molecular weight was observed in 8 days, which can be stabilized by treatment of aqueous HCl solution.

Introduction

Using carbon dioxide (CO₂) as an alternative feedstock to fossil fuels is becoming increasingly attractive,¹ however, currently only a limited number of chemical processes are successful, while most are facing challenges like energy balance or economic issue. The alternating copolymerization of epoxide and CO₂ has been considered to be a promising process, since the obtained polycarbonates was biodegradable in addition to melt processability, and the incorporation of CO₂ may provide a key cost-reduction effect to solve the low performance/price ratio long-term troubled in biodegradable industry since its birth.²

Although a variety of monomers can be employed in epoxides/CO₂ copolymerization, alternating copolymer of propylene oxide (PO) and CO₂ is particularly attractive from the viewpoint of industry, since the resultant poly(propylene carbonate) (PPC) is melt processable with most biodegradable polymers displaying suitable mechanical performance, which may create new applications in throw-away packages, biomedical materials and even in automotive parts.³

Since the first report by Inoue using ZnEt₂/H₂O as catalyst in the late 1960s,⁴ metal complexes with various combination of metal center and ligand have been investigated to improve the catalytic performance.² Previously reported active catalysts have typically been based on chromium⁵ and cobalt,⁶ but they are toxic and not soil-compostable, which limits their potential application in industry. Aluminum complex is a good choice considering environmentally benign metal complexes. Though aluminum-containing complexes have been reported as active catalysts, but

successful examples are still limited.⁷ The first single-site homogeneous catalyst based on aluminum was developed by Inoue in 1978, employing the tetraphenylporphyrin (TPPH₂) as the ligand framework.⁸ Copolymerization catalyzed by TPPAIX complex required long time (19 days) to achieve monomer completion, and the obtained poly(propylene carbonate) contained only 40% carbonate linkages with low number average molecular weight ($M_n = 3.9 \text{ kg mol}^{-1}$). In an effort to improve the catalytic activity, nucleophilic cocatalysts such as quaternary ammonium salts, phosphonium salts, and (4-dimethylamino) pyridine (DMAP) were added in the copolymerization system by Inoue, Ree and Chisholm, respectively.⁹ Though drastical increase in reaction rate and carbonate linkage of PPC was realized, the catalytic activity was generally low (TOF = 0.1~3.5 h⁻¹), and the obtained copolymer still showed low molecular weight ($M_n = 3.0\text{--}9.0 \text{ kg mol}^{-1}$). More recently, bifunctional catalysts displayed relatively high catalytic activity for the copolymerization of PO and CO₂ owing to the cooperative effects of the catalytic functional groups.^{6b-e, 6g} In previous work, we synthesized bifunctional aluminum porphyrin catalysts (**1a-i**, Fig. 1),¹⁰ which showed good catalytic performance because of the cooperative action of the Lewis acid metal centre and the quaternary ammonium salts. In this work, we will go further on design and synthesis of the aluminum porphyrin complex(**1j-o**, Fig. 1), focusing on adjusting the electronic environment of central Al and the length of alkyl chain in the quaternary ammonium cation. Furthermore, the effect of the length of the spacer linking ligand framework and quaternary ammonium units as well as quaternary ammonium anions and axial ligands on the

catalytic performance, were also investigated. An optimal bifunctional aluminum porphyrin complex gave PPC in TOF of 1320 h⁻¹ with 93% PPC selectivity at 80 °C and 3 MPa within 5 h, which was the highest record in this copolymerization for aluminum porphyrin complexes.

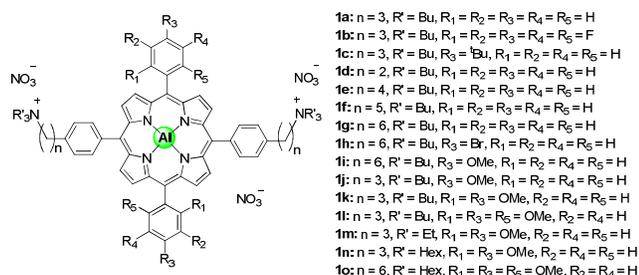


Fig. 1 Structure of the bifunctional aluminum porphyrin complex (**1a-o**).

In another issue, though aluminum porphyrin complexes could be left in PPC without extra separation, they lead to severe decomposition of PPC during storage, a common phenomenon in this kind of catalyst system.¹¹ Thus, how to stabilize the as-polymerized PPC is a key challenge for the practical application, which constitutes another topic in this work.

Experimental

Synthesis of bifunctional aluminum porphyrin complexes

Bifunctional aluminum porphyrin complexes **1j-1o** were synthesized according to the previously reported methods.¹⁰ The detailed procedures are given in the Supporting Information.

Table 1 Copolymerization results using catalysts **1j-1l**^a

Entry	Catalyst	TOF ^b (h ⁻¹)	Selectivity ^c (%PPC)	Carbonate linkage ^d (%)	M _n ^e (kg mol ⁻¹)	PDI ^e
1	1j	426	91	98	34	1.10
2	1k	671	93	98	41	1.08
3	1l	757	93	98	45	1.09
4	1a	306	87	98	25	1.09
5 ^f	--	152	19	96	10	1.18

^a Reaction conditions: PO (5 mL), [PO]/[catalyst] = 5000, 3 MPa CO₂ pressure, 70 °C, 2 h. ^b Turnover frequency of PO to products. ^c Selectivity for PPC over PC. ^d Determined by ¹H NMR spectroscopy. ^e Determined by gel permeation chromatography in CH₂Cl₂ at 25 °C, calibrated with polystyrene standards. ^f TPPAlNO₃ with 2 equivalent of tetrabutyl-ammonium nitrate as catalyst (Data from ref. 10b).

Adjusting Lewis acidity of central Al by tuning the substituents on the porphyrin ligand framework

The Lewis acidity of the central metal ion has significant influence on catalytic activity and PPC selectivity, which can be adjusted by introduction of specific ligand to change the electronic environment of the central metal.^{9c, 12} Our previous work clearly showed that aluminum porphyrin complexes bearing tertiary butyl or methoxy-functionalized aryl substituents exhibited significant improvement in catalytic activity and PPC selectivity.¹⁰ In an effort to further improve the catalyst performance, a series of bifunctional aluminum porphyrin complexes (catalysts **1j-1l**) bearing two, four and six electron donating methoxy groups were prepared. The copolymerization results by complexes **1j-1l** were listed in Table 1, and the result from unsubstituted complex **1a** was also listed as reference. All the copolymerization reactions were conducted at 70 °C under 3.0

General procedure for copolymerization

In a glove box free of oxygen and water, calculated aluminum porphyrin complex and PO were added to a 15 mL stainless-steel autoclave with a magnetic stirrer. CO₂ was pressurized to this mixture and the reaction was carried out at determined condition. After polymerization, the autoclave was cooled to room temperature, and the CO₂ pressure was released by opening the outlet valve. A small aliquot of the copolymerization mixture was taken out for ¹H NMR spectroscopy, and the resulting mixture was poured into a flask and dried in vacuum.

General procedure for the stabilization of copolymer

To a solution of the as-polymerized copolymer in dichloromethane, 2 mol L⁻¹ aqueous HCl solution (10 eq. of aluminum porphyrin complex) was slowly added. After stirred for 1 h, the mixture was dried in vacuum, which was used for the depolymerization reaction without other treatment.

Depolymerization of the copolymer

The copolymers (as-polymerized or HCl treated) were placed in a 25 °C thermostats at ambient atmosphere, and then small aliquots were periodically taken out to monitor the depolymerization process by ¹H NMR and GPC.

Results and Discussion

Delicate design of bifunctional aluminum porphyrin complexes

MPa for 2 h, with a [PO]/[cat.] ratio of 5,000. Complex **1j** with porphyrin framework bearing two methoxy-groups displayed an increased PO consumption and PPC selectivity in comparison with the unsubstituted catalyst **1a** (Entries 1 and 4, Table 1), indicating that the catalytic activity and PPC selectivity were significantly influenced by the electronic environment of the porphyrin. The incorporation of electronic donating substituents into the periphery of the ligand framework strongly modulated the electronic environment of the metal center, which was again proved in complex **1k** bearing more methoxy-fragments, by which both the catalytic activity and PPC selectivity further increased. Naturally, we synthesized complex **1l** bearing six methoxy groups to further decrease the Lewis acidity of the central aluminum. As expected, complex **1l** had a much higher catalytic activity (TOF = 757 h⁻¹) while the PPC selectivity still kept around 93%.

Improving catalytic performance by adjusting the length of alkyl chain in the quaternary ammonium cation

It is well-known that catalytic activity of metal porphyrin or salen-type catalysts can be improved upon the combination of organic salts as cocatalyst.¹³ Coates investigated the influence of cation and anion on the CO₂/PO copolymerization by altering the composition of the ionic cocatalyst,^{12d, 14} pointing out that an ideal cocatalyst should be composed of a bulky non-coordinating cation and a nucleophilic anion. A previous work by our group also indicated that the volume of the cocatalyst cation had strong influence on the copolymerization process,¹⁵ as far as TPPCoX/cocatalyst system was concerned, when *n*-Bu₄NCl was used as cocatalyst instead of PPNCl, a notable decrease in catalytic activity as well as PPC selectivity was observed.^{15a} Another work in our group indicated that NO₃⁻ was the best axial ligand and quaternary ammonium anions for these bifunctional aluminum porphyrin catalysts.¹⁰

Based on the above observations, we developed a series of

bifunctional aluminum porphyrin complexes (catalysts **1k**, **1m**, **1n**) using different tertiary amine sources to investigate the effect of ammonium cation volume on the catalytic performance. The copolymerization was conducted at 70 °C under 3.0 MPa for 2 h, with a [PO]/[cat.] ratio of 5,000, and the results were listed in Table 2. The catalytic performance of bifunctional aluminum porphyrin complexes were significantly influenced by tuning the tetraalkylammonium cation moiety. Complex **1k** with tributylammonium cation gave TOF of 671 h⁻¹ with PPC selectivity of 93%. However, triethylammonium cation (**1m**) gave slightly decreased TOF of 623 h⁻¹ with sharp decrease in PPC selectivity (75%). For complex **1n** with trihexylammonium cation, TOF reached 700 h⁻¹ with PPC selectivity of 95%, which was a very high value for aluminum porphyrin catalyst. These results were attributed to the improved nucleophilicity of NO₃⁻ where the bulky tetraalkylammonium cation in the catalyst can form a looser ion pair with NO₃⁻, consistent with the result in the literature.¹⁶

Table 2 Copolymerization results using Catalysts **1k**, **1m**, **1n**^a

Entry	Catalyst	TOF (h ⁻¹)	Selectivity (%PPC)	Carbonate linkage (%)	M _n (kg mol ⁻¹)	PDI
1 ^b	1k	671	93	98	41	1.08
2	1m	623	75	98	39	1.13
3	1n	700	95	98	44	1.10

^a Reaction conditions: PO (5 mL), [PO]/[catalyst] = 5000, 3 MPa CO₂ pressure, 70 °C, 2 h. ^b Entry 2 from Table 1 has been reproduced here for comparative purposes.

Optimization of bifunctional aluminum porphyrin complex

As shown above, adjusting electronic donating substituents and the length of alkyl chain in the quaternary ammonium cation could significantly change the catalytic performance of bifunctional aluminum porphyrin catalysts. To pursue better catalytic performance for the copolymerization of PO and CO₂,

complex **1o** was designed and prepared, which possessed six methoxy groups and two trihexylammonium cations linked to benzene via a six-methylene spacer in the meso-position of the porphyrin framework, and NO₃⁻ as axial ligand and quaternary ammonium anion.

Table 3 Copolymerization of CO₂/PO catalyzed by catalyst **1o**^a

Entry	Catalyst	PO/Cat. ^b	T (°C)	P (MPa)	Time (h)	TOF (h ⁻¹)	Selectivity (%PPC)	Carbonate linkage (%)	M _n (kg mol ⁻¹)	PDI
1 ^c	1a	5000	70	3	2	306	87	98	25	1.09
2	1o	5000	70	3	2	809	95	98	49	1.11
3	1o	10000	80	3	2	1320	93	98	62	1.10
4	1o	10000	80	3	4	1260	92	98	97	1.12
5	1o	10000	80	3	6	1123	85	98	128	1.14
6	1o	20000	90	3	2	2824	89	98	58	1.13

^a Copolymerization was carried out in neat PO (5 mL), unless otherwise was specifically noted. ^b Molar ratio. ^c Entry 4 from Table 1 has been reproduced here for comparative purposes.

As expected, complex **1o** showed much improved catalytic performance for the copolymerization of PO and CO₂, giving TOF of 809 h⁻¹ and PPC selectivity of 95% at 70 °C and 3 MPa in 2 h, much higher than those achieved by bifunctional aluminum porphyrin complexes **1a-1m** in our previous work (e.g., TOF of 306 h⁻¹ and PPC selectivity of 87% for **1a**), and also the highest record for the bifunctional aluminum porphyrin complexes.

To optimize the copolymerization condition, the influences of reaction temperature, catalyst loading and reaction time were investigated. The reaction temperature had a strong influence on catalytic activity (Entries 2 and 3), and the activity increased

dramatically as the temperature increased from 70 °C to 80 °C, resulting in a dramatic increase of TOF from 809 h⁻¹ to 1320 h⁻¹. Generally, increase of reaction temperature led to decrease of PPC selectivity for the copolymerization of PO and CO₂, however, it was surprising that PPC selectivity only slightly decreased (from 95% to 93%) when the temperature increased from 70 °C to 80 °C, and the carbonate linkage and PDI kept nearly stable. Additionally, reaction time is an important factor for this copolymerization. In this catalyst system, the catalytic activity kept relatively high and varied slightly with increasing reaction time. It is interesting that the number average molecular

weight increased with the increasing reaction time, indicating that the copolymerization of PO and CO₂ showed some characteristics of living polymerization, and a high molecular-weight polymer (M_n up to 128 kg mol⁻¹) was obtained, which is the highest record in this copolymerization for aluminum porphyrin complexes. However, PPC selectivity decreased, and PDI was broadened, due to the increase viscosity of the reaction mixture. Importantly, the TOFs always remained relatively high even when the catalyst loading was reduced, which was an encouraging feature of this one-component bifunctional catalyst system compared to binary systems. Especially, at 90 °C and 3 MPa, when [PO]/[10] ratio was 20,000, the TOF reached 2824 h⁻¹, while the PPC selectivity could still remain 89%.

Depolymerization of the as-polymerized PPC

Though Bifunctional aluminum porphyrin complexes have exhibited good catalytic performance for the copolymerization of CO₂ and PO, and they could be left within PPC without any extra separation, metal residue in PPC could affect the performance of this copolymer significantly, especially the thermal stability. The degradation reaction of copolymer containing aluminum porphyrin complex is of key importance for its shelf life as well as the melt processing.

Depolymerization at ambient temperature

As-polymerized purple sample ([PO]/[11] = 5,000), P_{CO_2} = 3 MPa, T = 70 °C, t = 4 h) was used for this study, it had 97% carbonate linkage with number average molecular weight of 35.5 kg mol⁻¹ and a polydispersity of 1.16.

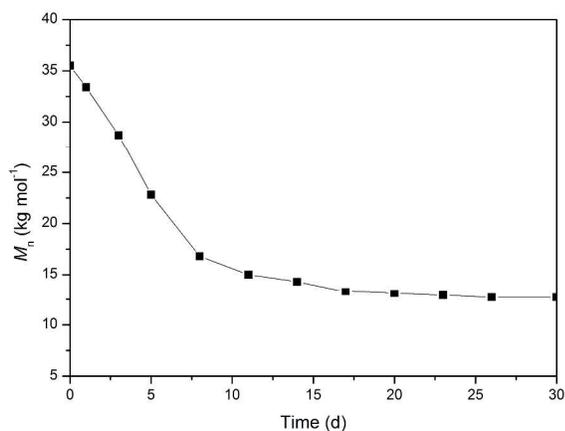


Fig. 2 Dependence of M_n of as-polymerized PPC at different time.

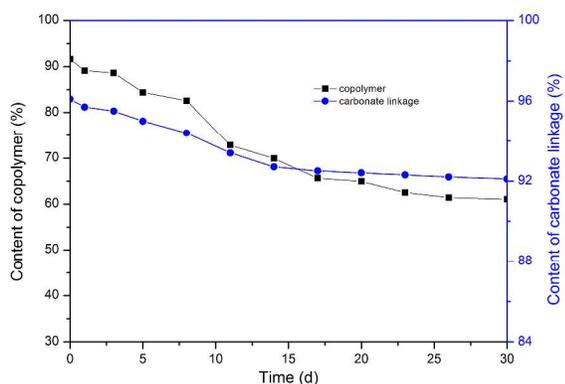
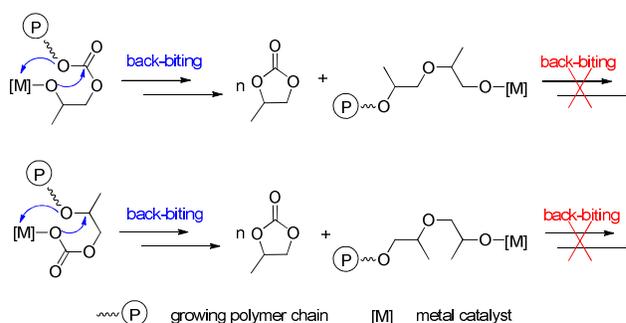


Fig. 3 Dependence of carbonate linkage content of as-polymerized PPC on time.

As shown in Fig. 2, depolymerization of PPC proceeded quickly in the initial stage, M_n decreased dramatically from 35.5 kg mol⁻¹ to 16.8 kg mol⁻¹ after 8 days, meanwhile, carbonate linkage CU% decreased to 94.4%. Late depolymerization reaction slowed down, and M_n remained almost unchanged at about 13 kg mol⁻¹ after 20 days. Moreover, in the initial stage, cyclic carbonate formed quickly and almost 35% PC was obtained after 20 days (Fig. 3), indicating that backbiting reaction happened. Consistent with the change of M_n , after 20 days, contents of copolymer and carbonate linkage remained almost unchanged at about 65% and 92.4%, respectively.

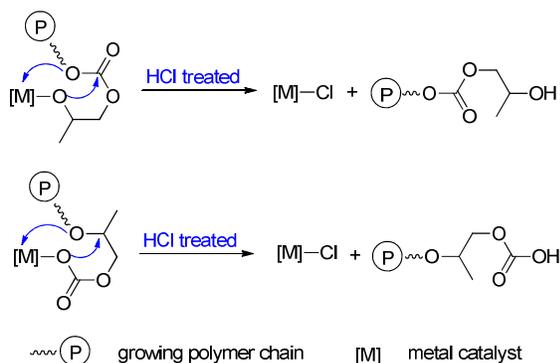
Because of the presence of bifunctional aluminum porphyrin complex, growing polymer chain mainly bound to the metal center. Plausible depolymerization pathways for PPC were described in Scheme 1. Two backbiting processes involving the polymer chain by metal-bound alkoxides and carbonates were described, by which the molecular weight was gradually reduced with concomitant formation of cyclic carbonate. The rate of this depolymerization was fast in the initial stage, but it was still much slower compared to the rate of metal-free polymer chain reported by Darensbourg,¹⁷ indicating that the metal-bound polymer degradation was sluggish. In the initial stage, the molecular weight of the copolymer decreased gradually, and the content of cyclic carbonate gradually increased. With the depolymerization proceeding, the content of carbonate linkage decreased gradually, and meanwhile the content of ether linkage increased. When depolymerization encountered the ether linkage in the copolymer, backbiting was inhibited due to the stability of the ether, leading to the termination of depolymerization after 20 days. Thus, in a manner, the presence of the ether linkage in the copolymer was beneficial to the stability of the CO₂ based copolymer.



Scheme 1 Plausible depolymerization pathways for PPC.

From the results mentioned above, as-polymerized PPC containing residual bifunctional aluminum porphyrin complex had low thermal stability. Due to high cost and energy demands for removing the residual metal from products, it is therefore highly desirable to develop a method that can improve the thermal stability of PPC containing residual metal. As mentioned above, the copolymer containing bifunctional aluminum porphyrin complex was still degradable and M_n decreased significantly from 35.5 to 13.1 kg mol⁻¹ in 20 days. As reported in the literature, the depolymerization rate of metal-bound polymer chain alkoxides and carbonates were much slower than that of metal-free analogs, due to the reduced nucleophilicity of terminal oxygen atom.¹⁸ Thus, reducing the nucleophilicity of the copolymers' terminal oxygen atoms may be effective to improve the stability of the copolymer. Here, aqueous HCl solution was

used to treat the copolymer, and the copolymer chain was dissociated from the metal center and capped with protons, reducing the nucleophilicity of the terminal oxygen atoms (Scheme 2). As shown in Fig. 4 and Fig. 5, M_n and carbonate linkage in the copolymer kept nearly constant, indicating that the degradation process was significantly retarded. Thus, the treatment of as-polymerized PPC with aqueous HCl solution was an effective method to improve the stability of PPC containing metal residue.



Scheme 2 Reaction of the metal-bound polymer upon treated with aqueous HCl solution.

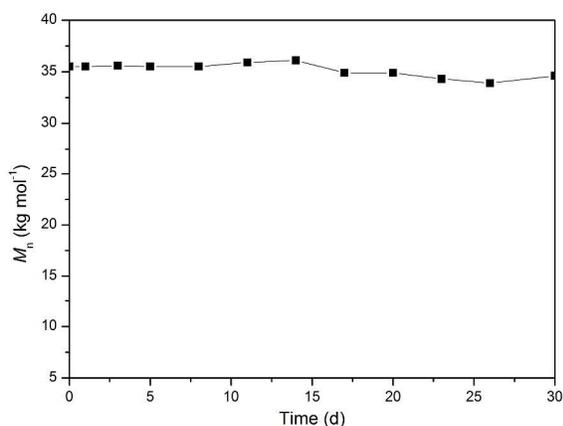


Fig. 4 Dependence of M_n on time for HCl treated PPC.

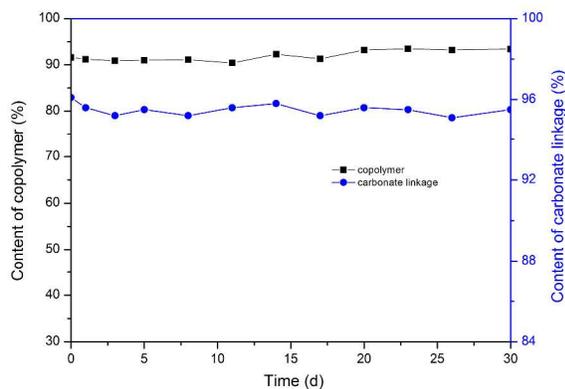


Fig. 5 Dependence of carbonate linkage content of PPC (HCl treated) on time.

Conclusions

Bifunctional aluminum porphyrin complexes have been designed and synthesized. A delicate design in electronic and space

environment of central Al may be realized by the substituents and the pendent tetraalkylammonium cation on the porphyrin ligand, the length of the spacer linking ligand framework and quaternary ammonium units, the axial ligand and quaternary ammonium anions, which may provide an optimal catalyst for the copolymerization of PO and CO₂, showing TOF of 1320 h⁻¹ at 80 °C and 3 MPa, and PPC selectivity of 93%, the highest record in this copolymerization for aluminum porphyrin complexes. Furthermore, the depolymerization and stability of copolymer containing bifunctional aluminum porphyrin complexes was also investigated. The PPC containing residual aluminum depolymerized rapidly in the initially stage at 25 °C in ambient atmosphere, but this PPC can be stabilized by treatment of aqueous HCl solution.

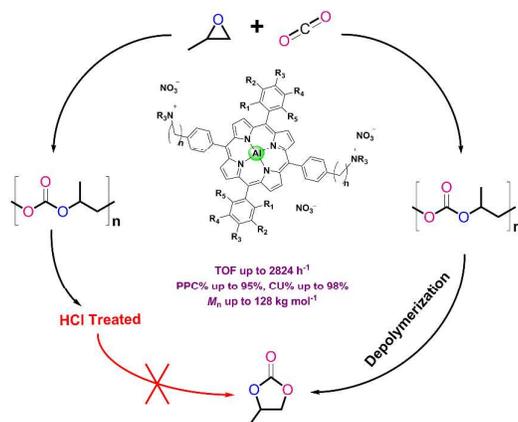
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Notes and references

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Bifunctional aluminum porphyrin complexes were prepared, which showed good catalytic performance for copolymerization of propylene oxide and carbon dioxide, and the resultant poly(propylene carbonate) could be stabilized by treatment of aqueous HCl solution.