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A novel zinc diimide catalyst for copolymerization of CO_2 and cyclohexene oxide

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Summary

A novel catalyst (AMDA)ZnOAc was firstly prepared and applied to catalyze the copolymerization of carbon dioxide and cyclohexene oxide, showing efficiency as high as 3.84×10^4g polymer/ mol. The resulting polycarbonate was found not to consist of cyclohexene carbonate by-product and possess a glass transition temperature of 120°C and a temperature of thermal decomposition up to 5wt% of 177°C and that up to 50wt% of 273°C respectively.

Introduction

The Synthesis of aliphatic polycarbonates via copolymerization of CO_2 and epoxides has been extensively investigated as effective way for the utilization of CO_2. Catalysts for the reaction include Et_2Zn/H_2O, Et_2Zn/polyphenol, metalloporphyrins, Zinc dicarboxylate, polymer chelated bimetal cyanides (PBM), rare earth complex/$Al(i\text{-}Bu)_3$ etc. The most effective catalyst so far is chelating diamide complexes[1], developed for the copolymerization of CO_2 and cyclohexene oxide in 1998 by Ming Chen et al. One mol of the diimide complex was reported to produce 4.94×10^4g of the polycarbonate, which had narrow molecular weight distribution. Sterically hindered aromatic groups were involved in the complex and thought to be important for the high catalytic efficiency.

This paper describes the synthesis, characterization and application of a novel catalyst, in which the high sterohindrence was provided by polymeric structure instead of the expensive reagents. The catalyst can be quite easily prepared, and has been found to be very active for the copolymerization of CO_2 and cyclohexene oxide.

Experimental

Materials

4,4’-methylenedianiline(MDA) (Acros, purity over 98%). Acetylactone (analysis reactant) was distilled under reduced pressure. Cyclohexene oxide (Acros, purity over 98%) was treated over calcium hydride, as to reduce the water content, less than 200 ppm determined by Kart Fisher titration. Other solvents (methylene chloride, anhydrous alcohol, methnol) were dried with routine methods. CO_2 was commercially obtained without further purification. Nitrogen with 99.99% purity was applied as the system atmosphere.

Instruments

IR spctrum was obtained using RFX-65A FTIR instrument (Analect). ^1H NMR and ^{13}C NMR spectra were recorded using DRX-400 (Bruker). Thermogravimetry (TG) diagrams were obtained from DT-30B Shimatzu thermal analysis instrument at a heating rate of 10°C/min in static air. Differential Scanning Calorimetry (DSC) samples were run on a DSC-2C (Perkin-Elmer) instrument. Instrinsic viscosity $[\eta]$ was measured in chloroform at 30°C using an Ubbelohde viscosity meter. Molecular weight of polymers was recorded by gel permeation chromatography in THF using polystyrene standards.

Synthsis of diimide polymer (AMDA)

Acetylacetone (1g, 10mmol) was added to a solution of 4,4’-methylenedianiline (1.98g, 10mmol) in ethanol (30ml). The reaction mixture was heated at reflux for 64 hours and then concentrated to a viscous brown residue. The IR, ^{13}C NMR and ^1H NMR of AMDA were given in figure 1, 2, 3. ^1H NMR (AMDA): δ2.0(a, e, 6H), 5.1(c, 1H), 12.3(f, 1H), 6.6-7.1(g, h, i, j, 8H), 3.8(k, 2H); ^{13}C NMR (AMDA): δ160.1(b, d), 28.7(a), 97.0(c), 19.4(e), 144.0(g), 130.1(h), 115.0(i), 124.0(j), 40.1(k). In above the symbols a□k were corresponding to the assignments denoted in Scheme 1 and Figure 2 □ 3. The molecular weight of AMDA was estimated to be about 1000 by evaluation of the ^1H NMR intensities of $-NH_2$ and -NH- signals.

Synthesis of catalyst (AMDA)ZnOAc

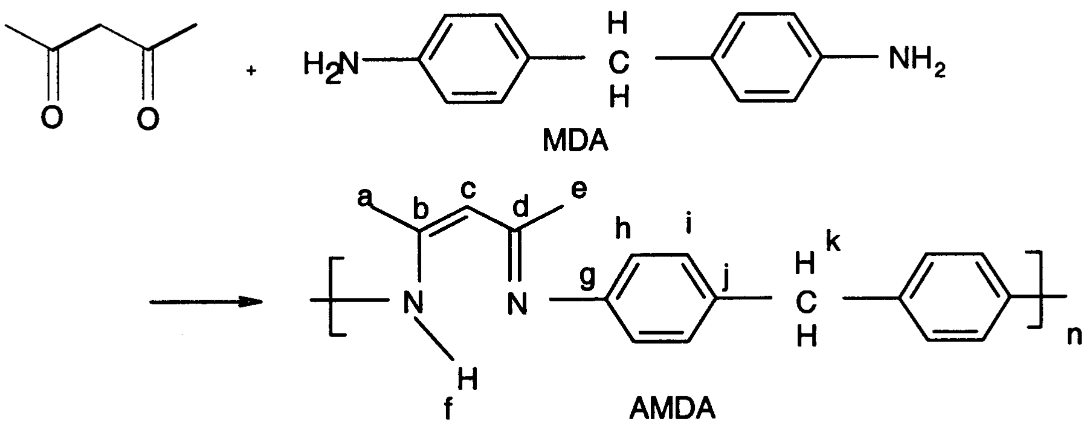
To a solution of AMDA (0.327g, 1 mmol) in toluene (10ml) was slowly added diethyl Zinc (0.61ml, 5.9mmol) at 0°C. After stirring overnight at 80°C, acetic acid (0.34ml, 5.9mmol) was added to the reaction mixture at room temperature. After stirring for another hour at RT, the catalyst was obtained as a clear solution in toluene.

Copolymerization of CO_2 and cyclohexene oxide

A 130 ml autoclave was evacuated and flushed with nitrogen, and then charged with the catalyst solution (1ml, 0.1mmol). The solution was evacuated to remove the toluene and then flushed with nitrogen. Cyclohexene oxide and CO_2 was added to the autoclave. The reaction was carried out at desired temperature for a certain period. The crude product was redissolved in methylene chloride and precipitated from methanol and dried in vacuo at 70°C for 4 hours until the weight reached constant.

Results and discussion

The synthesis of diimide polymer was accomplished by a ketone - amine condensation reaction (Scheme 1).



Scheme 1. Polycondensation of MDA and acetylacetone

The product was characterized spectrumetrically to have a polymeric diimide structure as shown in the equation. Figure 1 illustrates the comparison of IR spectra of the obtained AMDA with the raw material MDA. Disappearance of the amine signals at 3443 and 3414 cm^{-1} in the AMDA spectrum indicated the complete conversion of MDA. The ^{13}C NMR (Figure 2) and ^{1}H NMR (Figure 3) also showed that the produced AMDA has the expected structure (as assignments of the peaks in the figures corresponding to the groups in Scheme 1).

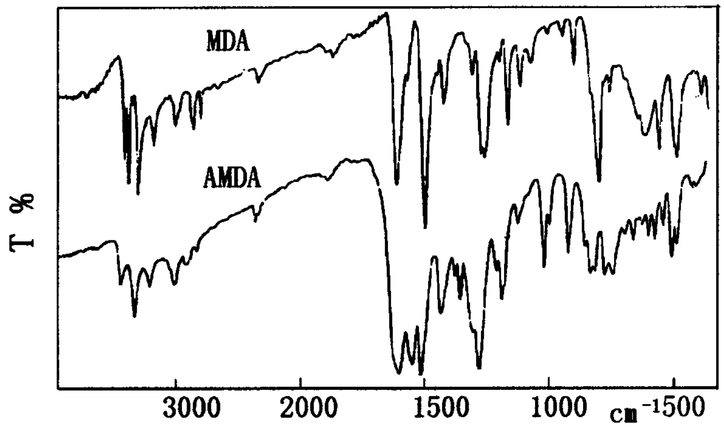


Figure 1. IR Spectra of MDA and AMDA

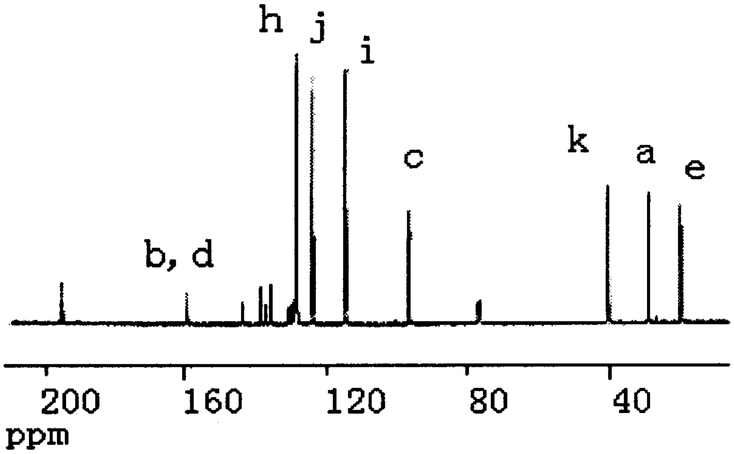


Figure 2. ^{13}CNMR Spectrum of AMDA

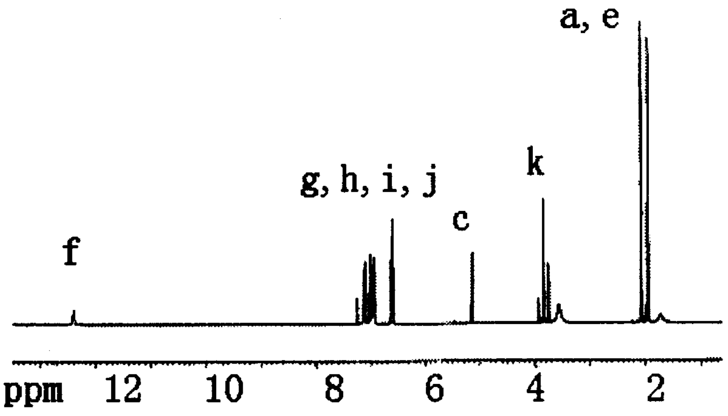
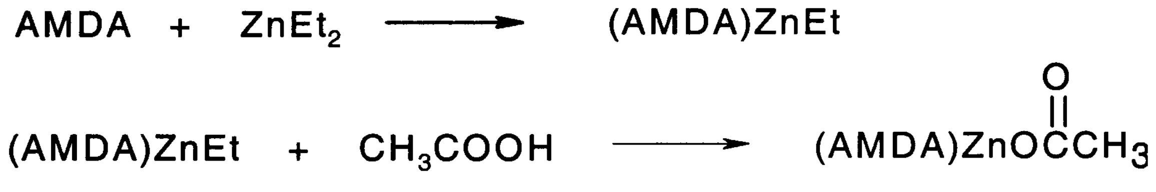


Figure 3. ^{1}HNMR Spectrum of AMDA

To the imide AMDA, -ZnEt groups were introduced upon treatment with diethyl zinc, while ethane evolved. These groups were further converted to those consisting of Zn - acetate bonds by reaction with acetic acid to release more ethane (Scheme 2). The zinc complex so obtained is useful for CO_2 activation.

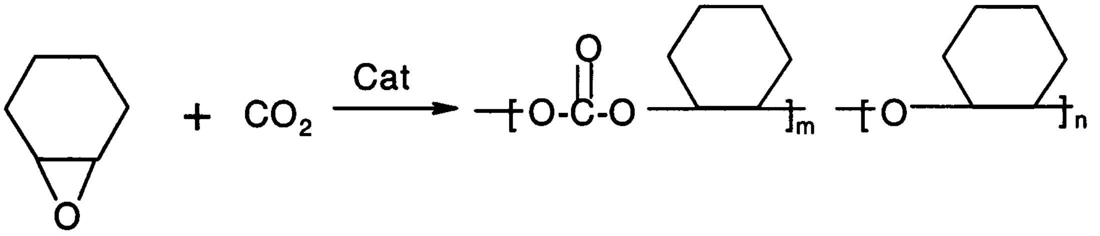


$$\text{AMDA} + \text{ZnEt}_2 \longrightarrow \text{(AMDA)ZnEt}$$

$$\text{(AMDA)ZnEt} + \text{CH}_3\text{COOH} \longrightarrow \text{(AMDA)ZnO}\overset{\overset{\displaystyle O}{\|}}{\text{C}}\text{CH}_3$$

Scheme 2. Preparation of (AMDA)ZnOAc

The above prepared complex (AMDA)ZnOAc was successfully applied to catalyze the copolymerization of CO_2 and cyclohexene oxide to form poly(cyclohexene carbonate) (Scheme 3).



Scheme 3. Copolymerization of CO_2 and cyclohexene oxide

The IR spectrum of the copolymer shows a strong absorption at 1750 cm^{-1}. It's a typical C=O vibration in carbonate linkage. No signal around 1800 cm^{-1} was observed, indicating no cyclohexene carbonate byproduct contained in the polymer. The fraction of ether and carbonate linkages can be estimated by the intensities of signals at δ3.45 and 4.60 in ^1H NMR spectra. The results of calculation were listed in Table 1.

Table 1 The results of copolymerization using (AMDA)ZnOAc catalyst[a]

Run.	t(h)	monomers[b]/(ml)	CO_2(g)	[η](dL/g)	Yield (g polymer/mol)	f_c[c]
1	6	CHO/3	5	0.550	11200	0.449
2[d]	24	CHO/3	5	0.782	24700	0.466
3	24	CHO/5	5	0.674	38400	0.484
4	24	PO/10	5	/	0	/

[a] All polymerization was carried out at 80°C using 1.24mmol catalyst. [b] CHO = cyclohexene oxide, PO = propylene oxide. [c] f_c is molar fraction of CO_2 in copolymer. For alternative copolymer f_c is 0.5. [d] M_w=37532, M_n=19250, M_w/M_n=1.95.

As indicated in Table 1, the yield, intrinsic viscosity [η] and f_c of the obtained copolymers were enhanced with increasing time of copolymerization (Run. 1-3). A decreased concetration of catalyst led to a higher yield but a lower intrinsic viscosity [η] (Run. 2-3). The highest catalytic efficiency was 3.84×10^4 g polymer/ mol catalyst (Run. 4). The polymeric catalyst consisted of mutiple active centers, which worked associatively and somewhat differently. This may be responsible for the M_w/M_n value as big as 1.95.

Propylene oxide (PO) was also attempted to be copolymerized with CO_2 instead of cyclohexene oxide (CHO) in the presence of (AMDA)ZnOAc. The catalyst was found not effective for PO (Run.4 in Table 1) although it did well for CHO (Run. 1□3 in Table 1). Some other reported catalysts containing amine ligands behaved similarly [1,2]. The observation implies that some different mechanism were involved for these two epoxides to copolymerize with CO_2. This may be a topic of further study.

Thermal properties of poly (cyclohexene carbonate)

Recently much attention has been paid to poly (cyclohexene carbonate) because it is superior to convenient aliphatic polycarbonates such as poly(propylene carbonate) [3]. For comparison, glass transition temperature T_g, 5% and 50% decomposition temperatures ($t_{5\%}$, and $t_{50\%}$) were measured by differential scanning Calorimetry (DSC) and thermogravimetry (TG). The obtained data were listed in table 2. Obviously, poly (cyclohexene carbonate) is thermally more stable, easier to process, and is more suitable to be applied as a plastic material than poly (propylene carbonate).

Table 2 Thermal property of Poly(cyclohexene carbonate) and Poly(proplene carbonate)

Copolymer	T_g(°C)	$t_{5\%}$(°C)	$t_{50\%}$(°C)
Poly(propylene carbonate)[a]	38	173	210
Poly(cyclohexene carbonate)	120	177	273

[a] Data from references[4,5].

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References

1. Cheng M, Lobkovsk EB, Coates GW (1998) J Am Chem Soc 120:11018
2. Darensbourg DJ, Holtcamp MW, Struck GE, Zimmer MS, Niezgoda SA et al (1999) J Am Chem Soc 121:107
3. Zhang NY, Chen LB, Yang SY, Yu AF, He SJ (2000) Acta Polymerica Sinica 6:718
4. Liu BY, Zhao XJ, Zhao DQ, Wang XH, Wang FJ (1999) 6th Pacific Polymer Conference 67
5. Yang SY, Peng H, Huang B, Chen LB(1993) Petrochemicals 22:730