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# Copolymerization of $CO_2$ and propylene oxide under rare earth ternary catalyst: design of ligand in yttrium complex

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**Abstract**

Copolymerization of carbon dioxide and propylene oxide was carried out employing $(RC_6H_4COO)_3Y$/glycerin/$ZnEt_2$ (R = –H, $-CH_3$, $-NO_2$, –OH) ternary catalyst systems. The feature of yttrium carboxylates (ligand, substituent and its position on the aromatic ring) is of great importance in the final copolymerization. Appropriate design of substituent and position of the ligand in benzoate-based yttrium complex can adjust the microstructure of aliphatic polycarbonate in a moderate degree, where the head-to-tail linkage in the copolymer is adjustable from 68.4 to 75.4%. The steric factor of the ligand in the yttrium complex is crucial for the molecular weight distribution of the copolymer, probably due to the fact that the substituent at 2 and 4-position would disturb the coordination or insertion of the monomer, lead the copolymer with broad molecular distribution. Based on the study of ultraviolet–visible spectra of the ternary catalyst in various solvents, it seems that the absorption band at 240–255 nm be closely related to the active species of the rare earth ternary catalysts.

*Keywords:* Carbon dioxide; Copolymerization; Ligand

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## 1. Introduction

Since the pioneering work of Inoue in 1969 [1], the synthesis of aliphatic polycarbonates from carbon dioxide and epoxides has been a long-standing interest as a potential way to carbon dioxide utilization. The catalyst design has been regarded as the driving force during the past decades, where a variety of promising catalysts have been developed to promote this copolymerization process. Several heterogeneous catalyst systems were employed to the copolymerization of $CO_2$ and epoxide [2,3], along with a homogeneous system derived from $ZnEt_2$/pyrogallol [4], aluminum porphyrin system [5], the well-defined diiminate/salen metal complexes [6,7], and Zn-fluoroalkly catalyst designed for supercritical polymerization [8]. Among all the catalysts reported, the rare earth coordination catalysts are known to produce high molecular weight aliphatic polycarbonates from carbon dioxide and epoxides in mild conditions [9,10]. Chen et al. [9] successfully synthesized a random poly(propylene carbonate) with a high molecular weight and a narrow molecular weight distribution by employing the catalyst "$Y(P_{204})_3$–Al(*i*-Bu)$_3$-glycerin" at 60 °C. Tan and Hsu [10] developed the rare earth-based catalyst system, by using the rare earth compound $Y(CF_3COO)_3$ and $ZnEt_2$ instead of $Y(P_{204})_3$ and Al(*i*-Bu)$_3$, respectively, the ternary catalyst exhibited a high catalytic activity of 4200 g/(mol Y h), and the carbonate content of the copolymer was beyond 95.6%. Considering the expensive and difficult synthesis of the $Y(CF_3COO)_3$, then the rare earth compound $Y(CF_3COO)_3$ was replaced by $Nd(CCl_3COO)_3$ in our recent work, which also exhibited high catalytic activity as well as high carbonate content [11].

Generally, the composition, regioregularity, molecular weight and its distribution are among the most important factors in determining the properties of the copolymer [12]. During the past two decades, much more attention was paid to the effect of ligands in the catalysts on the final polyolefin, and a suitable ligand design has been proved to be beneficial for a given purpose [13,14]. In the present work, the $(RC_6H_4COO)_3Y$-based ternary catalysts with different substituents were employed for the copolymerization of $CO_2$ and propylene oxide. Influences of the nature of

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ligand in the yttrium complex on the catalytic activity, polydispersity and regioregularity of the resultant copolymer will be discussed.

## 2. Experimental section

### 2.1. Materials

Propylene oxide, 1,4-dioxane, glycerin and other solvents used were dried over calcium hydride and distilled prior to use. The yttrium compounds and diethyl zinc were synthesized according to literature [15–17]. All the yttrium compounds were further dried under vacuum at 60–70 °C for 40 h before use. Commercial carbon dioxide (99.99% in purity) was used without further purification.

### 2.2. Preparation of rare earth ternary catalyst

To a pretreated two-necked flask bottle prefilled with $9.17 \times 10^{-4}$ mol of yttrium compound and 40 ml solvent, 0.68 ml of glycerin was added under carbon dioxide atmosphere to form a clear solution. After that 1.88 ml of diethyl zinc was dropped into the solution under vigorous stirring for 3 h, the white suspension was used directly in the following copolymerization.

### 2.3. Preparation and purification of copolymers

The freshly produced ternary catalyst suspension and 50 ml of propylene oxide were introduced into a pretreated 500 ml autoclave free of oxygen and water. Copolymerization of $CO_2$ and PO was carried out at 60 °C. To terminate the copolymerization reaction, the autoclave was vented, and water was poured into the reactor. For purification, the extracted copolymer was dissolved in methylene dichloride, and precipitated by large quantity of methanol. The methanol-insoluble polymer was dried in vacuum at 40 °C till constant weight.

### 2.4. Characterization

The molecular weight and its polydispersity of the copolymer were determined by gel permeation chromatography (GPC) at 35 °C in polystyrene standard on a Waters 410 GPC instrument and the tetrahydrofuran was used as eluent. NMR spectra were recorded on a Bruker AV-300 NMR instrument at room temperature. The regioregularity of the copolymer was calculated from the corresponding signal intensity in the $^{13}C$ NMR spectra. The ultraviolet–visible (UV–Vis) spectra of the rare earth ternary catalyst were recorded under a dry $N_2$ atmosphere on a SHIMADZU UV-2401PC spectrometer.

## 3. Results and discussion

### 3.1. Influence of the benzoate-based yttrium compounds on the copolymerization

Rare-earth complexes $(RC_6H_4COO)_3Y$ (R = –H, –$CH_3$, –$NO_2$, –OH) in combination with glycerin and diethyl zinc were used for the copolymerization of $CO_2$ and propylene oxide at 60 °C under 4.0 MPa for 12 h. Influence of ligand in the yttrium compound on the copolymerization was summarized in Table 1. The catalytic activity of $(3\text{-}HOC_6H_4COO)_3Y$-based catalyst **a3** is 201.7 g polymer/(mol Zn h), and copolymer from **a3** has number average molecular weight of $9.6 \times 10^4$ and polydispersity of 9.6. By comparison, the catalytic activity of the $(2\text{-}HOC_6H_4COO)_3$-Y-based catalyst **a2** is 177.7 g polymer/(mol Zn h), the corresponding copolymer shows number average molecular weight and its distribution of $1.1 \times 10^5$ and 13.9, respectively. The catalytic activity of the $(4\text{-}HOC_6H_4COO)_3Y$-based catalyst **a4** decreases to 145.4 g polymer/(mol Zn h), and the corresponding copolymer shows number average molecular weight and its distribution of $5.7 \times 10^4$ and 16.0. Therefore, the 3-substituted catalyst gives highest catalytic activity, and the corresponding copolymer has much narrower molecular weight distribution than that from 2 or 4-substituted catalyst.

Similar phenomenon was observed in $(CH_3C_6H_4COO)_3$-Y-based catalysts **b2**, **b3**, **b4**, where catalytic activity of catalyst **b3** reaches 173.9 g polymer/(mol Zn h), higher than that of **b2** (154.9 g polymer/(mol Zn h)) or **b4** (143.9 g polymer/(mol Zn h)). The copolymer from catalyst **b3** has molecular weight distribution as low as 4.6, much narrower than that from **b2** (7.2) or **b4** (7.1). This is also true in the copolymer obtained from $(NO_2C_6H_4COO)_3Y$-based catalysts **c2**, **c3** and **c4**. The molecular weight distribution of the copolymer shows 6.6 for **c3**, 12.1 for **c2** and 11.4 for **c4**, respectively. However, the catalytic activity increase in the following sequence: **c2** < **c3** < **c4**, which is different from that of $(HOC_6H_4COO)_3Y$-based or $(CH_3C_6H_4COO)_3Y$-based catalysts. It seems that the steric factor of the substitution on the aromatic ring is very important for the molecular weight distribution of the final copolymer. One possible explanation is that the substituent at 3-position may inhibit the chain-transfer reaction, lead the final copolymer possess of a relatively narrow molecular weight distribution. On the other hand, the substituent at 2 and 4-position would disturb the coordination or insertion of the monomer, enhancing the chain-transfer reaction, gave the copolymer with broad molecular weight distribution.

The substituents in the yttrium complexes are categorized into electron-donating and electron-withdrawing ones. As listed in Table 1, the introduction of electron-donating substituent like methyl or hydroxyl group leads to a catalytic activity increase in the similar tendency: **b4** < **b2** < **b3**, **a4** < **a2** < **a3**, which is different from that of electron-withdrawing substituent like nitro group (**c2** < **c3** < **c4**). It

Table 1
Influence of yttrium-based catalysts on the copolymerization of $CO_2$ and propylene oxide

| | Ligand in the rare earth compound | CU % (NMR) | Catalyst activity (g/(mol Zn h)) | H–T (%) | $M_n$ ($\times 10^{-4}$) | $M_w/M_n$ |
|---|---|---|---|---|---|---|
| **a** | $C_6H_5COO^-$ | 98.2 | 173.6 | 72.9 | 9.6 | 5.7 |
| **a2** | $2\text{-}HOC_6H_4COO^-$ | 97.5 | 177.7 | 71.5 | 11.0 | 13.9 |
| **b2**[a] | $2\text{-}CH_3C_6H_4COO^-$ | 97.6 | 154.9 | 68.4 | 7.0 | 7.2 |
| **c2** | $2\text{-}NO_2C_6H_4COO^-$ | 98.2 | 149.5 | 73.0 | 9.2 | 12.1 |
| **a3** | $3\text{-}HOC_6H_4COO^-$ | 97.8 | 201.7 | 72.6 | 9.6 | 9.6 |
| **b3**[a] | $3\text{-}CH_3C_6H_4COO^-$ | 97.7 | 173.9 | 75.4 | 9.6 | 4.6 |
| **c3** | $3\text{-}NO_2C_6H_4COO^-$ | 97.2 | 187.7 | 72.3 | 9.1 | 6.6 |
| **a4** | $4\text{-}HOC_6H_4COO^-$ | 98.2 | 145.4 | 72.0 | 5.7 | 16.0 |
| **b4**[a] | $4\text{-}CH_3C_6H_4COO^-$ | 98.1 | 143.9 | 73.6 | 5.9 | 7.1 |
| **c4** | $4\text{-}NO_2C_6H_4COO^-$ | 98.5 | 194.0 | 73.7 | 11.8 | 11.4 |

[a] Reaction time: 10 h, pressure of $CO_2$: 3.0 MPa. Copolymerization conditions: molar ratio of [Zn]/[glycerin] = 2, [Zn]/[Y] = 20, PO: 50 ml, $ZnEt_2$: 1.88 ml, 1,4-dioxane: 40 ml, 4.0 MPa, 12 h at 60 °C.

is supposed that the electronic factor of ligands in the yttrium complex affect the progress of copolymerization greatly.

The typical IR and $^1H$ NMR spectra of the resultant copolymers from the $(C_6H_5COO)_3Y$-based ternary catalysts are shown in Figs. 1 and 2. The strong absorption signals located at 1250 and 1750 $cm^{-1}$ in Fig. 1 are attributed to the C–O and C=O stretching vibrations of carbonate units in the copolymer. The $^1H$ NMR spectrum of the methanol-insoluble polymer displays chemical signals at 1.3 ppm attributed to $CH_3$, very weak signals centered at 3.5–3.8 ppm to CH and $CH_2$ in the polyether, 4.2 and 5.0 ppm attributed to $CH_2$ and CH in the carbonate unit, respectively. Based on the $^1H$ NMR spectrum, the carbonate content in the copolymer (CU%) could be calculated from the relative intensity of peaks at 5.0 and 4.2 ppm to those at 3.5–5.0 ppm according to the literature [9]. As listed in Table 1, the carbonate content in all the copolymers obtained was found to be more than 97.2%, indicating that the rare earth ternary catalyst is quite efficient for preparing the highly alternating copolymer from $CO_2$ and propylene oxide, which is consistent with the earlier reports [10,11].

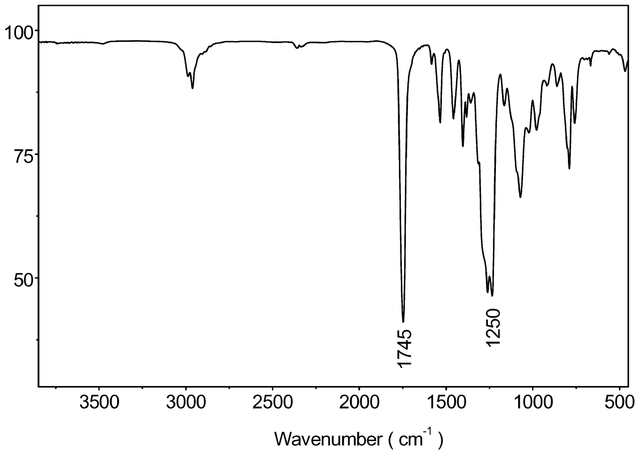


Fig. 1. The IR spectra of the poly(propylene carbonate) produced by the $(C_6H_5COO)_3Y$-based ternary catalyst. Copolymerization conditions: see in Table 1.

### 3.2. Effect of ligand on the microstructure of the copolymer

Propylene oxide has one asymmetric carbon atom, as shown in Scheme 1, two kinds of ring opening, α and β openings are possible depending on the nature of attacking reagent [18]. Therefore, the selective incorporation of propylene oxide monomer is a determining factor to influence the microstructure of the copolymer. The $^{13}C$ NMR spectrum of carbonyl region are shown in Fig. 3, the signals located at 155.1, 154.6 and 154.3–154.1 ppm, have been assigned to tail-to-tail (T–T), head-to-tail (H–T) and head-to-head (H–H) structures in the copolymer, respectively [19]. The existence of the three signals indicated that β opening is accompanied by α opening during the coupling reaction of $CO_2$ and propylene oxide. Statistically, as shown in Scheme 2, the selective insertion of propylene oxide during the propagating reaction would give a copolymer with T–T:H–T:H–H of 1:2:1. Therefore, the value of (H–T)/[(H–H) + (H–T) + (T–T)] could be chosen to evaluate the regioselective insertion of propylene oxide in the copolymerization. As shown in Table 1, the content of H–T unit in the copolymer varies from 68.4 to 75.4%, indicating that the bond cleavage of propylene oxide occurs

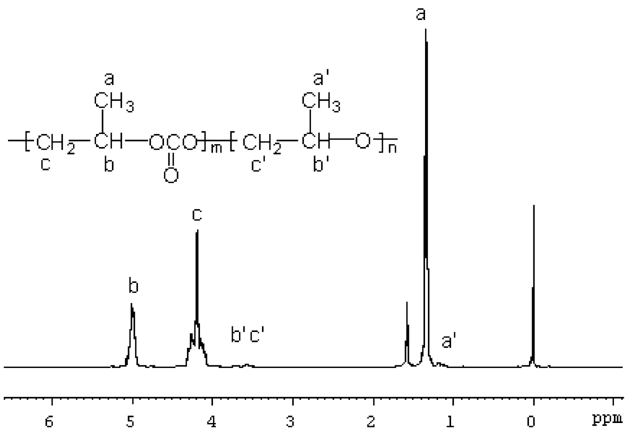
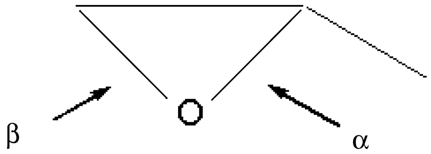


Fig. 2. The $^1H$ NMR spectrum of the poly(propylene carbonate) produced by $(C_6H_5COO)_3Y$-based ternary catalyst. Copolymerization conditions: see in Table 1.



Scheme 1. Bond cleavage of propylene oxide in the copolymerization of $CO_2$ and epoxide.

with certain regioselectivity during the formation of polycarbonate. The H–T unit in the copolymer from catalyst **b2** and **b3** varies from 68.4 to 75.4%. By comparison, the copolymers from series **a** and **c** have insignificant change in head-to-tail structure (less than 3%). It is plausible that the suitable choice of ligand in the rare-earth compounds might adjust the regioregularity of the copolymer in a moderate degree. The influence on the coordination or insertion of the monomers to the propagation chain ends might be attributed to the different feature of the yttrium compounds.

### *3.3. Influence of the solvent on the copolymerization*

The polarity of the solvent plays an important role during the process of the copolymerization due to the possible coordination between the active species and solvent [20,21]. Therefore, solvents with varying dipole moment were selected as the medium for the copolymerization of $CO_2$ and propylene oxide. As listed in Table 2, the polarity of the solvent has little influence on the regioregularity of the copolymer, but it is important for the catalytic activity and molecular weight of the copolymer. When the $(3\text{-HOC}_6H_4\text{-COO})_3Y$-based catalyst was used, the catalytic activity in different solvents decreased in the following sequence: 1,4-dioxane (251.5 g polymer/(mol Zn h)), ethyl acetate (221.5 g polymer/(mol Zn h)), ethylene glycol dimethyl ether (177.2 g polymer/(mol Zn h)), chloroform (65.4 g polymer/(mol Zn h)), and no polymer was obtained when the strong polar basic solvent like pyridine was chosen. Therefore, the stronger polarity of the solvent was employed, the less copolymer was obtained. The copolymer produced from 1,4-dioxane gave the highest number average molecular weight of $10.2 \times 10^4$, whereas those from ethylene glycol dimethyl ether and ethyl acetate exhibited high polydispersity of 11.5 and 11.4, and relatively lower number average molecular weight of $4.98 \times 10^4$ and $3.01 \times 10^4$, respectively. It seems that the relatively low molecular weight and broad polydispersity of the copolymer arisen from the chain transfer to the solvents.

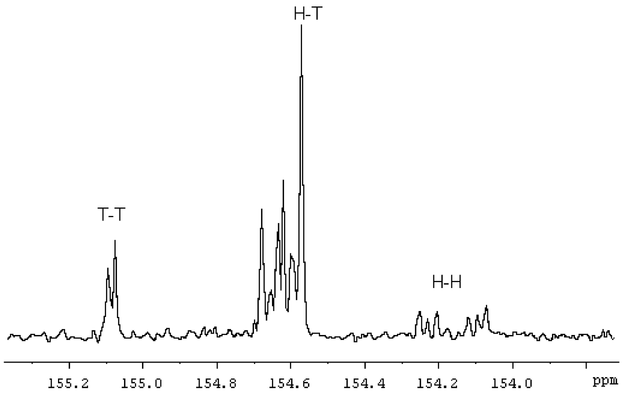
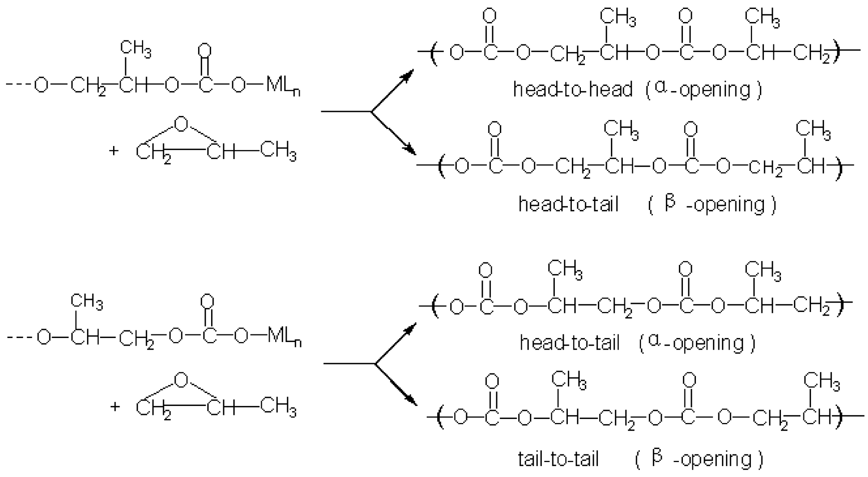


Fig. 3. $^{13}C$ NMR spectrum of the carbonyl region. Copolymerization conditions: produced by $(C_6H_5COO)_3Y$-based ternary catalyst, see other conditions in Table 1.

In the previous publication, the influence of solvent on the copolymerization had been attributed to the solubility of $CO_2$ in the solvent [9]. However, it is noteworthy that the coordination between the active species and the solvent plays an important role, due to the nucleophilic or electrophilic feature of the solvent used [21]. The highest conversion of the poly(propylene carbonate) obtained from 1,4-dioxane might be related to the existence of more electronic deficient active species in the non-polar medium. In all cases of the stronger polar solvent used, the coordination between the polar solvent and active species may weaken or inhibit the coordination and activation of monomer, leading the rate of chain propagation decrease.

To gain further insight into the preceding coordination between the solvent and active species, UV–Vis absorption spectra of the $(3\text{-HOC}_6H_4COO)_3Y$-based ternary catalyst prepared in chloroform, ethyl acetate, pyridine and 1,4-dioxane, were recorded and shown in Fig. 4. In addition to the maximum absorption band centered at 241 and 251 nm respectively, both the UV–Vis spectra in chloroform and ethyl acetate were quite similar to each other, and a hypsochromic shift of 10 nm was observed in chloroform corresponding to an increase in dipole moment of 0.1. In the case of 1,4-dioxane, apart from the absorption band located at 247 nm, a new shoulder-like peak at 303 nm appeared. For the ternary catalyst prepared in pyridine, the absorption band around 240–255 nm disappeared completely and a new one centered at 320 nm appeared. Therefore, the absorption band at 320 nm might be related to the formation of the inactive complex. It is thus deduced that the absorption band at 240–255 nm might be related to the formation of the active species in the $(HOC_6H_4COO)_3Y$-based ternary catalyst.

It is well known that the location of the $\lambda_{max}$ absorption band in the UV–Vis spectra may be related to the energy transfer of the 'ligand to metal charge transfer' (LMCT), which varies with the electron density of the metal [22–24]. Therefore, it may provide valuable information on the structure of the yttrium-based ternary catalyst formed in solvents with various dipole moments. According to the literature [25,26], the neutral solvent molecule may act as ligand to form adducts with rare earth compounds. The observed bathochromic shift of $\lambda_{max}$ and different UV–Vis profile indicates the existence of the coordination between the polar/non-polar solvent and the active species. As shown in Fig. 4, the electron transfer from the neutral ligand to metal center is very sensitive to the polarity of solvent. The replacement of non-polar solvent like 1,4-dioxane by



Scheme 2. Selective incorporation of the propylene oxide into the propagating chain ends.

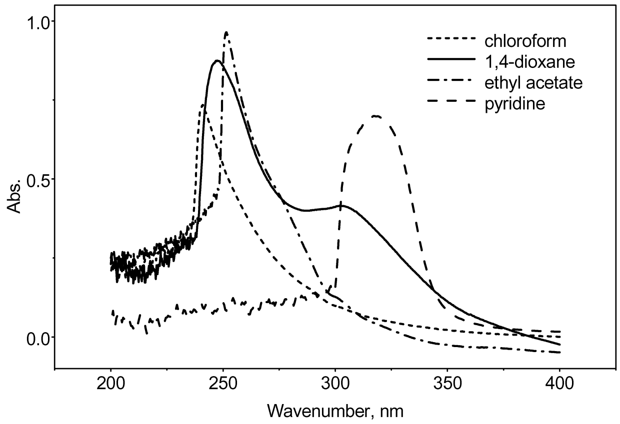


Fig. 4. The UV–Vis spectra of the (3-$HOC_6H_4COO)_3Y$-based catalyst prepared in solvents with different polarity. Reaction conditions: $ZnEt_2$: 1.88 ml, molar ratio of [Zn]/[Y] = 20, [Zn]/[glycerin] = 2, solvent: 50 ml, aging time: 3 h.

stronger polar solvent like ethyl acetate or chloroform, may cause a hypsochromic shift of the maximum absorption band from 303 to 241 nm, except for the strong basic polar solvent pyridine, where inactive complex is formed.

## 4. Conclusions

A series of rare earth ternary catalysts $(RC_6H_4COO)_3$-Y/glycerin/$ZnEt_2$ were employed in the copolymerization of $CO_2$ and propylene oxide. The catalytic activity, molecular weight and its distribution as well as the regioregularity of the resultant copolymer significantly depend on the substitution feature and its position on the aromatic ring. The steric factor of the ligand determines the molecular weight distribution of the copolymer, i.e. the substituent at 2 or 4-position disturbed the coordination of the monomer, lead the final copolymer with broad molecular weight distribution. H–T unit in the copolymer is dominant, and adjustable from 68.4 to 75.4% by choosing the ligand in yttrium compounds. Depending on the dipole moments of the reaction medium, the coordination between solvent molecule and central metal in the ternary catalyst may change the electron density of the active species. Higher electron deficiency of the active species leads to the increase in catalytic activity.

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Table 2
Influence of the solvent on the coupling reaction of $CO_2$ and propylene oxide

| Run | Solvent | Dipole moment (D) | Catalyst activity (g/(mol Zn h)) | $M_n$ ($\times 10^{-4}$) | $M_w/M_n$ | H–T (%) |
|---|---|---|---|---|---|---|
| **$s_1$** | 1,4-Dioxane | 0 | 251.5 | 10.20 | 9.3 | 72.3 |
| **$s_2$** | Ethylene glycol dimethyl ether | – | 177.2 | 4.98 | 11.5 | 72.4 |
| **$s_3$** | Ethyl acetate | 1.8 | 221.5 | 3.01 | 11.4 | 72.2 |
| **$s_4$** | Chloroform | 1.9 | 65.4 | 2.19 | 2.6 | 71.8 |
| **$s_5$** | Pyridine | 2.2 | No polymer | – | – | – |

Pressure of $CO_2$: 3.0 MPa, time = 8 h, see other reaction conditions in Table 1.

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