

# Copolymerizations of Carbon Dioxide and Epoxides in the Presence of Rare Earth Coordinate Catalyst

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**ABSTRACT:** Carbon dioxide (CO<sub>2</sub>) as a direct material was copolymerized with epoxides to synthesize new aliphatic polycarbonates, and the copolymerization was catalyzed by the coordinate catalyst composed of rare earth yttrium phosphonate and triisobutylaluminum [Y(P<sub>204</sub>)<sub>3</sub>-Al(i-Bu)<sub>3</sub>]. The epoxides used in this research included epichlorohydrin (ECH) and some new glycidol ether (GE) monomers prepared by the reaction of ECH and phenol or alcohol, such as  $\alpha$ -allyl glycidol ether,  $\beta$ -chloroethyl glycidol ether, benzene glycidol ether, *m*-tolyl glycidol ether, and

benzyl glycidol ether. The copolymers were characterized by infrared (IR), <sup>1</sup>H nuclear magnetic resonance (-NMR), and dynamic mechanical analysis. The results show that Y(P<sub>204</sub>)<sub>3</sub>-Al(i-Bu)<sub>3</sub> had better catalytic activity in the copolymerization of CO<sub>2</sub> with epoxide, and the copolymerization rate of aryl GE was distinctly higher than that of aliphatic GE. Dynamic mechanical analysis indicated the glass transition temperature *T*<sub>g</sub> of the copolymers GE-CO<sub>2</sub> were lower than that of ECH-CO<sub>2</sub>. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 2356–2359, 2003

## INTRODUCTION

Carbon dioxide (CO<sub>2</sub>) is a kind of precious carbon resource. Its storage on the earth is more than the sum of petroleum and coal. Synthesizing organics and polymers from CO<sub>2</sub> is an effective way to control environmental pollution and to ensure the circulation of carbon. Hence, the study of synthesis chemistry using CO<sub>2</sub> as raw material has broad developing prospects.<sup>1</sup> Over the past several years, large advances have been made in the development of CO<sub>2</sub> for polymer synthesis applications.<sup>2–10</sup> It is a new and important research area in C1 chemistry.

In order to develop new materials, in the present work a series of glycidol ethers (GE) was synthesized using ECH as raw material, and a rare earth coordinate catalyst was used in the copolymerization of epoxides with CO<sub>2</sub> to make a novel aliphatic polycarbonate. Characterization of this kind of copolymer was made in order to get a good performance polymer material.

## EXPERIMENTAL

### Raw materials and tests

Rare earth coordinate catalyst [Y(P<sub>204</sub>)<sub>3</sub>-Al(i-Bu)<sub>3</sub>] was made according to ref. 11.

CO<sub>2</sub>, >99.5% purity; ethanol, industrial; all other reagents are analytical grade.

Infrared spectra were determined as a solution coat on a Nicolet 5DX-FTIR Fourier transform infrared spectrometer. <sup>1</sup>H nuclear magnetic resonance (-NMR) and <sup>13</sup>C-NMR were determined on a Bruker AC-P 200 Fourier transform NMR spectra instrument. Dynamic mechanical analysis of copolymers were performed on a DDV-II-E viscoelastic analyzer of 110 Hz with a range of -150 ~ 100°C and a heating rate of 2°C/min. Intrinsic viscosities in cyclohexanone at 30.00 ± 0.05°C were determined with Ubbelohde viscometers and  $[\eta]$  was calculated.

### Monomer synthesis

#### Allyl GE

Allyl GE was synthesized according to ref. 12. An index of refraction and infrared (IR) test were made.

#### $\beta$ -chloroethyl GE

The amount of 0.25 mL BF<sub>3</sub>OEt<sub>2</sub> was injected into the reactor, which contained 88.6 g CH<sub>3</sub>CH<sub>2</sub>OCl. The solution was stirred and increased to 50°C. Then, 92.5 g ECH was dropped slowly and was finished in about 2 h. Stirring was continued for 1 h and the solution was cooled to room temperature. The amount of 112 g 60% KOH solution was dropped under stirring. After dropping, water was added to dissolve the generated salt and the organic layer was separated. It was decompressed distilled after the organic layer was dried by dried Na<sub>2</sub>SO<sub>4</sub>; the fraction of 88–90°C/1.427 kPa

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was collected. The yield was 47.0% and  $n_D^{25} = 1.4490$  (reference value<sup>13</sup>  $n_D^{25} = 1.4492$ ).

#### Benzene GE

The amount of 18.4 g phenol, 120 mL ECH, 33.6 g KOH, and 6 g PEG-600 (PEG: polyethylene glycol) were added to a three-necked flask with stirrer, reflux condenser, and thermometer. The solution was stirred violently for 3 h at 40°C. Then 50–100 mL water was added to separate the organic layer. The water layer was extracted for twice by ether, and then mixed with the organic layer. Ether was evaporated after it was dried by dried Na<sub>2</sub>SO<sub>4</sub>. The fraction of 106–108°C/1.427 kPa was collected after decompressed distillation. The product was a colorless transparent liquid. The yield was 56.3%. The  $n_D^{20}$  equals to 1.5280, which corresponded to the documented<sup>14,15</sup> value.

#### Benzyl GE and *m*-Tolyl GE

Synthesis of benzyl GE and *m*-tolyl GE were similar to the synthesis of benzene GE.

#### Polymer synthesis

Y(P<sub>204</sub>)<sub>3</sub>-Al(*i*-Bu)<sub>3</sub>, epoxide and 1,4-dioxane were put into a 100 mL stainless steel high pressure reactor with electromagnetic stirrer. The amount of 3 ~ 4 MPa CO<sub>2</sub> was placed in the reactor and the reaction was made at 60°C for 24 h. The reactor was cooled to room temperature when the copolymerization was ended, and the unreacted CO<sub>2</sub> was released. The copolymer was washed with C<sub>2</sub>H<sub>5</sub>OH, which contained 5% chlorhy-

TABLE I  
Results of IR Spectra of Copolymers

Copolymer	Absorptive peaks (cm <sup>-1</sup> )
ECH-CO <sub>2</sub>	2928.1(m), 1757.3(vs), 1261.5(vs), 1111.1(vs), 752.2(m)
Allyl GE-CO <sub>2</sub>	3072.8(m), 3015.0(m), 1753.4(vs), 1645.4(m), 1263.5(vs), 1107.2(vs), 997.27(s), 923.97(s)
Benzyl GE-CO <sub>2</sub>	1753.4(vs), 1496.9–1599.1(vs), 1244.2(vs), 1080.2(vs), 752.29(vs), 697.95(vs)
Benzene GE-CO <sub>2</sub>	1750.5(vs), 1253.2(vs), 1097.6(vs), 783.3(vs), 697.95(vs)
<i>m</i> -Tolyl GE-CO <sub>2</sub>	1751.5(vs), 1456.4–1601(vs), 1257.7(vs), 1097.6(vs), 779.3(vs), 690.56(vs)
$\beta$ -Chloroethyl GE-CO <sub>2</sub>	1745.7(vs), 1455.3(m), 1431.3(m), 1257.7(vs), 1118.8(vs), 750.36(m)
Butyl GE-CO <sub>2</sub>	2959.0(vs), 2868.3(vs), 1753.4(vs), 1464.1(m), 1377.3(m), 1257.7(vs), 1118.8(vs), 748.43(m)

TABLE II  
Results of <sup>1</sup>H-NMR Spectra of Copolymers

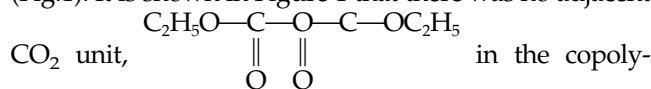
Copolymer	Chemical shifts of <sup>1</sup> H (ppm)
ECH-CO <sub>2</sub>	3.69(br, 2H, 1H, CH <sub>2</sub> , CH), 4.42(br, 2H, CH <sub>2</sub> ), 5.09(s, 1H, CH)
Benzyl GE-CO <sub>2</sub>	3.56(m, 2H, 1H, CH <sub>2</sub> , CH), 4.46(m, 2H, CH <sub>2</sub> ), 7.24(t, 4H, Ar)
Benzene GE-CO <sub>2</sub>	3.72–4.07(br, 2H, 1H, CH <sub>2</sub> , CH), 6.79(br, 4H, Ar), 7.15(br, 4H, Ar)
<i>m</i> -Tolyl GE-CO <sub>2</sub>	2.20(s, 3H, CH <sub>3</sub> ), 3.65–3.94(br, 2H, 1H, CH <sub>2</sub> , CH), 6.65(br, 4H, Ar), 6.94(br, 4H, Ar)
$\beta$ -Chloroethyl GE-CO <sub>2</sub>	3.60–3.71(br, 2H, 1H, CH <sub>2</sub> , CH)
Butyl GE-CO <sub>2</sub>	0.89(t, 3H, CH <sub>3</sub> ), 1.35(m, 2H, CH <sub>2</sub> ), 1.52(m, 2H, CH <sub>2</sub> ), 3.37–3.69(m, 2H, 1H, CH <sub>2</sub> , CH)

dric acid, then by C<sub>2</sub>H<sub>5</sub>OH only for three times. Finally, filtration and vacuum drying were done.

## RESULTS AND DISCUSSION

### Structure of copolymer epoxide-CO<sub>2</sub>

IR analyses were made for the synthesized copolymer. It was found that there were characteristic absorption peaks for carbonyl and C—O of the carbonate group for every polymer around 1750 and 1260 cm<sup>-1</sup>. This indicated that CO<sub>2</sub> as a monomer was copolymerized with epoxide. At the same time, it was also strongly proved by IR spectrum that there was structure unit that came from GE and ECH in the copolymer. Data of every characteristic absorption peaks are listed in Table I. <sup>1</sup>H-NMR spectra of every GE-CO<sub>2</sub> and ECH-CO<sub>2</sub> copolymer were determined respectively by using CDCl<sub>3</sub> as solvent. <sup>1</sup>H-NMR analysis results are shown in Table II. The <sup>13</sup>C-NMR spectrum was measured by taking benzene glycidol ether-CO<sub>2</sub> copolymer as an example (Fig. 1). It is shown in Figure 1 that there was no adjacent



mers. It was reported in literature<sup>16</sup> that the chemical displacement of this structure is 148.3 and 158.7 ppm, which corresponds to the carbon of carbonate group in copolymers. The location of every spectrum peak related to the structural distribution of polymers is shown in Figure 1.

### Dynamic mechanical analysis of copolymer

Dynamic mechanical properties were performed using *m*-tolyl GE-CO<sub>2</sub> copolymer as an example, and the spectrum is shown in Figure 2. There was only one wide glass transition peak corresponding to 26.6°C.

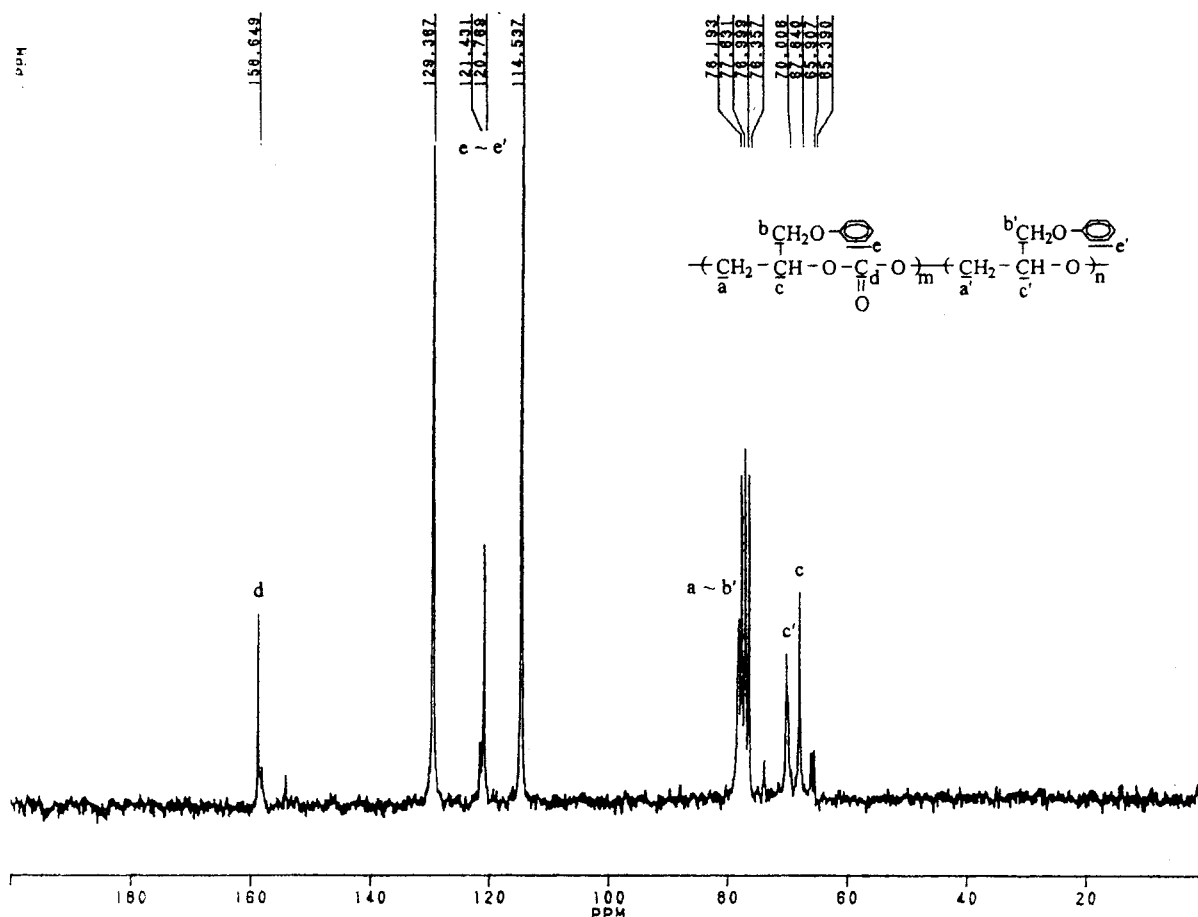


Figure 1  $^{13}\text{C}$ -NMR spectrum of benzene GE- $\text{CO}_2$  copolymer.

Glassy relaxation in the heat mechanical spectrum indicated *m*-tolyl glycidol ether- $\text{CO}_2$  copolymer is amorphous. The glass transition  $T_\beta$  occurred around

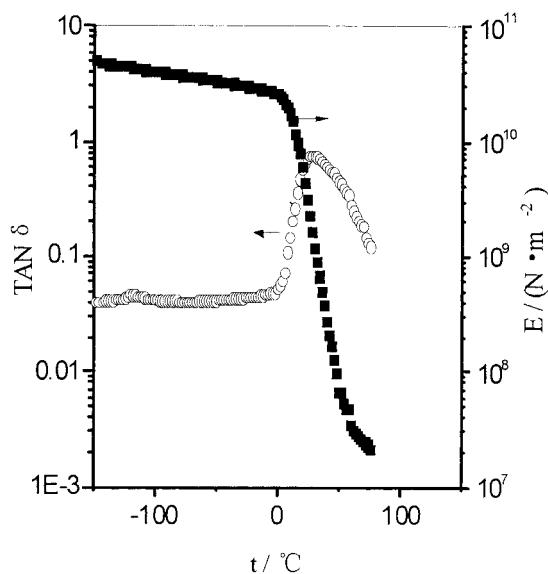


Figure 2 Dynamic mechanical spectrum of *m*-tolyl GE- $\text{CO}_2$  copolymer.

$-123^\circ\text{C}$ , which was caused by short chain movement in the pendent group and polymer chain.

The  $T_g$  of *m*-tolyl GE- $\text{CO}_2$ , benzene GE- $\text{CO}_2$ , ECH- $\text{CO}_2$ , and aryl polycarbonate (bisphenol A polycarbonate) are shown in Table III. The  $T_g$  of the aryl polycarbonate was higher than that of the aliphatic polycarbonate because of the stiff benzene group in the main chain. But as to aliphatic polycarbonate, the  $T_g$  of ECH- $\text{CO}_2$  was higher than that of GE- $\text{CO}_2$ . This is because the flexibility of the pendent group in GE is better than  $-\text{CH}_2\text{Cl}$ . The existence of this kind of flexible pendent group played the role of plasticizer, decreasing the glass temperature.

It is shown in Table III that the  $T_\beta$  relaxation of bisphenol A polycarbonate occurred at  $-100^\circ\text{C}$ .<sup>17</sup> This

TABLE III  
Transition Temperatures of Copolymers

Copolymer	$T_g$ ( $^\circ\text{C}$ )	$T_\beta$ ( $^\circ\text{C}$ )
<i>m</i> -Tolyl GE- $\text{CO}_2$	26.6	-123
Benzene GE- $\text{CO}_2$	46.6	-121
ECH- $\text{CO}_2$	59	-118
Bisphenyl A polycarbonate	150	-100

is attributed to the movement of the carbonate group,  
 $\begin{array}{c} \text{—O—C—O—} \\ || \\ \text{O} \end{array}$  which is connected with the benzene

ring. And after the benzene ring was replaced by the methylene group, the flexibility of the main chain increased and the energy barrier was decreased. Hence, the  $T_{\beta}$  of copolymer GE-CO<sub>2</sub> was decreased.

### Copolymerization of epoxides with CO<sub>2</sub>

Aliphatic polycarbonates were copolymerized by epoxide with CO<sub>2</sub> using the rare earth coordinate catalyst Y(P<sub>204</sub>)<sub>3</sub>-Al(i-Bu)<sub>3</sub> in the same condition as above. The effect of catalyst concentration on catalytic activity of copolymerization and molecular weight of the product was investigated. The effect of catalyst concentration on copolymerization of *m*-tolyl GE with CO<sub>2</sub> is shown in Figure 3. The effect of catalyst concentration on copolymerization of other GEs with CO<sub>2</sub> was similar to this one.

The experimental results indicated that catalytic activity and the molecular weight increased with the increasing of the catalytic concentration. But when the concentration was over a certain value, the catalytic activity and the molecular weight decreased with the increase of the catalytic concentration. Within a certain range of catalytic concentration, the increase of the concentration was favorable to the copolymerization of CO<sub>2</sub> with GE, while if the concentration were too high, it would lead to the depolymerization of the generated aliphatic polycarbonate, which is not favorable to the copolymerization. Under the condition of this experiment, the suitable concentration of Y(P<sub>204</sub>)<sub>3</sub>-Al(i-Bu)<sub>3</sub> was  $2.7 \times 10^{-2} \sim 5.0 \times 10^{-2}$  mol(Y)/L. The comparison of every GE-CO<sub>2</sub> copolymerization was made and is listed in Table IV. The results show that the copolymerization rate of aryl GE was distinctly higher than that of aliphatic GE.

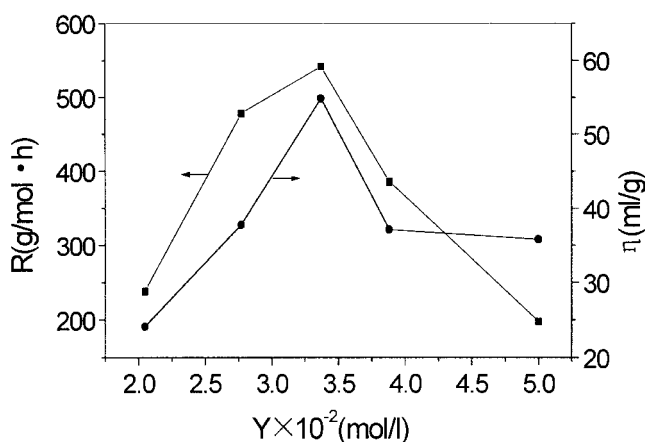


Figure 3 The effect of catalyst concentration on *m*-tolyl GE-CO<sub>2</sub> copolymerization.

TABLE IV  
Comparison of Copolymerization of CO<sub>2</sub> and Different Monomers

Monomer	R (g/ml h)	[η] (mL/g)	State
ECH-CO <sub>2</sub>	272.32	75.03	White solid
<i>m</i> -Tolyl GE-CO <sub>2</sub>	385.85	37.08	White solid
Benzene GE-CO <sub>2</sub>	311.07	37.44	White solid
Benzyl GE-CO <sub>2</sub>	301.99	30.00	White soft solid
β-Chloroethyl GE-CO <sub>2</sub>	265.21	41.46	White elastic solid
Butyl GE-CO <sub>2</sub>	213.20	31.39	White elastic solid
Allyl GE-CO <sub>2</sub>	100.71	/	White brittle solid

Reaction condition: Y(P<sub>204</sub>)<sub>3</sub>-Al(i-Bu)<sub>3</sub> =  $3.88 \times 10^{-2}$  mol(Y)/L; Al/Y = 8, 60°C; 24 h; 3 ~ 4 MPa; monomer = 10 mL. Solvent: 1,4-dioxane.

### CONCLUSION

A series of GE monomers and some new aliphatic polycarbonates were prepared. Y(P<sub>204</sub>)<sub>3</sub>-Al(i-Bu)<sub>3</sub> had better catalytic activity in the copolymerization of CO<sub>2</sub> with epoxide and the preferred amount of catalyst was  $2.7 \times 10^{-2} \sim 5.0 \times 10^{-2}$  mol(Y)/L. The copolymerization rate of aryl GE was distinctly higher than that of aliphatic GE.

Dynamic mechanical analysis indicated the glass transition temperature  $T_g$  of the copolymer GE-CO<sub>2</sub> was lower than that of ECH-CO<sub>2</sub>.

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