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Synthesis and Properties of Carbon Dioxide - Epoxides Copolymers from Rare Earth Metal Catalyst

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Summary: Ternary rare earth metal coordinate was used to the copolymerization of epoxides and carbon dioxide. Rare earth compound is crucial in raising the catalytic activity and improving the micro-structure of the aliphatic polycarbonates. The Tg of the aliphatic polycarbonate is adjustable by controlling the relative molar ratio of the comonomers.

Keywords: aliphatic polycarbonate; carbon dioxide; copolymerization; glass transition temperature; rare earth compound

Introduction

In the past several years, the utilization of carbon dioxide as raw material for chemical industry is becoming increasingly attractive. One of such interest is employing carbon dioxide as comonomer to make bio- or light degradable aliphatic polycarbonates as first disclosed by Inoue *et al.* in the late 1960's.[1] Inoue's creative work is to realize copolymerization of carbon dioxide and epoxide with organic zinc catalyst under elevated pressure and temperature. This technique is further developed by Kuran to make various kinds of copolymers.[2] Currently, there are at least four kinds of relatively effective catalysts for this purpose: zinc based catalysts, metallic porphyrins, and rare earth coordinate catalyst.[3,4] Organozinc compound needs co-catalyst having active hydrogen like water, di- or tri-hydroxybenzene to obtain alternate copolymer, but the reaction time is generally long accompanied by relatively low epoxide conversion rate. A recent improvement is made by Darensbourg *et al* using Zn(II) bisphenol(base)$_2$ catalyst which is very effective on the copolymerization of epoxide and CO_2.[5] Beckman *et al* employed fluorinated Zinc(II) compound to carry copolymeriztion of propylene oxide and CO_2 in supercritical liquid.[6]

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More recently, Coates *et al* developed bulky β-diimine ligands chelated Zinc(II) complexes, which are of high activity.[7] Metallic porphyrin catalyst, though has catalyst activity of about 10^4g polymer/mol catalyst, the polymerization time needs to be shortened and the molecular weight of the resulted polymer to be raised. Though the rare earth coordinate catalyst can give high molecular weight of copolymer, the carbon dioxide fixation rate is below 30mol%[4]. Recently, Tan *et al.* developed a rare-earth metal coordination catalyst to obtain carbon dioxide-propylene oxide copolymer with relatively high yield and molecular weight.[8] This catalyst was also effective to the ter-polymerization of cyclohexene oxide, propylene oxide and CO_2.[9] However, the catalytic activity needs further increase, the microstructure of the obtained polymers need further clarification, and the glass transition temperature (T_g) of the copolymer should be adjustable in order to be suitable as structural material in various fields. These are the main concerns in this report, where the rare earth coordinate-organozinc-glycerine ternary catalysts are prepared and used as copolymerization and terpolymerization of epoxide and CO_2, the structure properties of the polycarbonates will be discussed.

Experimental

Diethylzinc was prepared according to the literature,[10] other organozinc compounds were synthesized in similar procedure to that of diethyl zinc, except that the iodoethane and bromoethane were replaced by corresponding iodides and bromides. Di-i-propylzinc, di-n-propylzinc, di-n-butylzinc, di-i-butylzinc were prepared with the purity of over 98%.

To make the ternary rare earth metal coordinate, glycerine and corresponding rare earth compounds were stirred in 1,3-dioxane to give a clear solution, and stoichiometric organozinc was then added, the mixture was stirred for 12 hours under CO_2 atmosphere before polymerization reaction.

Copolymer or terpolymer was prepared according to following procedure. The obtained ternary catalyst and epoxides(propylene oxide, cyclohexene oxide, or ethylene oxide) were put into the autoclave in the absence of oxygen, and then CO_2 was quickly filled in till 3.5-4.0MPa. The copolymerization was carried out at 65-70℃ for 12 hrs. The reaction was terminated by addition of 5% HCl/methanol solution, and the precipitate was dried under vacuum till constant weight.[11] For purification, the dried polymer was re-dissolved in

CH_2Cl_2 to make 5wt% of solution. The solution was filtered to remove the insoluble part, and it was then precipitated by methanol. The precipitate was collected and dried under vacuum till constant weight. It was then subjected to spectra experiments like ^{13}C-NMR, ^1H-NMR, FTIR, as well as thermal analysis and rheological experiments.

Role of Rare Earth Compound on the Copolymerization

Parts of the H^1-NMR spectra of a typical propylene oxide-carbon dioxide(PO/CO_2) copolymer obtained from $Y(OOCCCl_3)_3/ZnEt_2$/glycerine ternary catalyst is shown in Fig.1. The absorption peaks at 1.3ppm, 4.2ppm and 5.0ppm have been assigned to the hydrogens in CH_3, CH_2 and CH in the carbonate units of the copolymer, respectively. The absorption peaks ranging from 3.5ppm to 3.7ppm are characteristics of ether linkage of more than two propylene oxide units.[1] As shown from Figure 1a to Figure 1c, the 3.5-3.7ppm absorption peaks decreased with increasing rare earth compound loading in the ternary catalyst. When the diethyl zinc concentration was fixed, once the rare earth compound reached 1.2×10^{-3} mol in the catalyst, the peaks ranging from 3.5ppm to 3.7ppm nearly disappeared, indicating that the copolymer was nearly alternative. Thus the rare earth compounds in the catalysts play a positive role to reduce the ether linkage in the copolymers.[11]

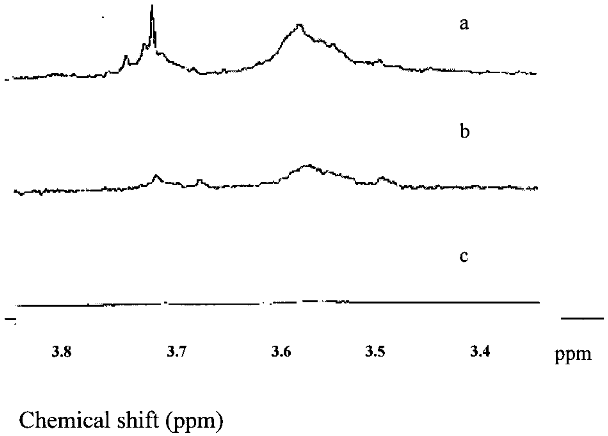


Figure 1. ^1H-NMR(400MHz) spectra of PO/CO_2 copolymer obtained by $Y(OOCCCl_3)_3/ZnEt_2$/glycerine ternary catalyst with changing [Y]. a) binary $ZnEt_2$/glycerine system, [Y]=0mol; b) $[Y]=5.1x10^{-4}mol$; c) $[Y]=1.2x10^{-3}mol$.

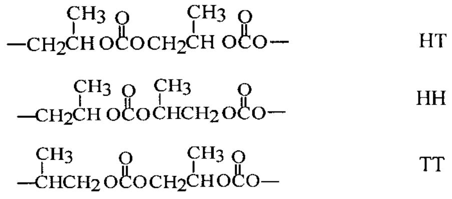
Intrinsic viscosities of four typical PO/CO_2 copolymers are measured in their benzene solution at 35^{0}C and listed in Table 1. The intrinsic viscosity of the copolymer increased dramatically when rare earth compound was added. It was only 0.48dl/g for the copolymer from binary catalyst, and increased by 25% to 0.60dl/g at 1.3×10^{-4}mol of rare earth compound. It was further raised by 31% to 0.64dl/g at 5.1×10^{-4}mol of rare earth compound. Moreover, the intrinsic viscosity was raised by 60% to 0.77dl/g for 1.2×10^{-3}mol of rare earth compound, compared with the $ZnEt_2$-glycerine binary system. It is clear that addition of rare earth compound is effective to raise the molecular weight of the copolymer.

Table 1. Influence of [Y] concentration on the molecular weight of copolymer.

[Y], mol	η(dl/g)	$\bar{M}n^{a}$	$\bar{M}n^{b}$	$\bar{M}w/\bar{M}n$
0	0.48	35067	32241	18.5
1.3×10^{-4}	0.60	46348	39120	18.3
5.1×10^{-4}	0.64	50243	46679	14.7
1.2×10^{-3}	0.76	62282	73412	13.7

a: Data calculated from the equation according to literature,[12] $[\eta](dL/g)=1.11\times10^{-4}\ \bar{M}n^{0.80}$;
b: Data from GPC.

The micro-structure of the propylene oxide-carbon dioxide copolymer is important on their thermal and mechanical properties. As shown in Scheme 1, there exists tail-to-tail(TT), head-to-tail(HT), and head-to-head(HH) structure in the copolymer, corresponding to the three groups of peaks located at 154.7ppm, 154.2ppm and 153.6-153.8ppm,[13] respectively. Copolymer obtained from $ZnEt_2$/glycerine binary generally has about 70% HT structure.[13]



$-CH_2\overset{CH_3}{\overset{|}{C}}H\,O\overset{O}{\overset{\|}{C}}O\,CH_2\overset{CH_3}{\overset{|}{C}}H\,O\overset{O}{\overset{\|}{C}}O-$ HT

$-CH_2\overset{CH_3}{\overset{|}{C}}H\,O\overset{O}{\overset{\|}{C}}O\,\overset{CH_3}{\overset{|}{C}}HCH_2\,O\overset{O}{\overset{\|}{C}}O-$ HH

$-\overset{CH_3}{\overset{|}{C}}HCH_2\,O\overset{O}{\overset{\|}{C}}O\,CH_2\overset{CH_3}{\overset{|}{C}}H\,O\overset{O}{\overset{\|}{C}}O-$ TT

Scheme 1. Microstructure of the obtained copolymer.

The influence of the rare earth content in the ternary catalyst on the micro-structure is studied, where the ternary catalyst is $Y(m\text{-}NO_2C_6H_4COO)_3/ZnEt_2$/glycerine. As shown in Figure 2, the HH structure is almost constant with changing [Y]/[Zn] ratio, whereas the content of TT structure experiences a valley located at 0.04, and that of HT structure shows a peak at similar position. The highest value for HT structure approaches 77%, corresponding to Tg of 42^{0}C. For comparison, the copolymer with HT value of 70-72% shows Tg of 36-37^{0}C.

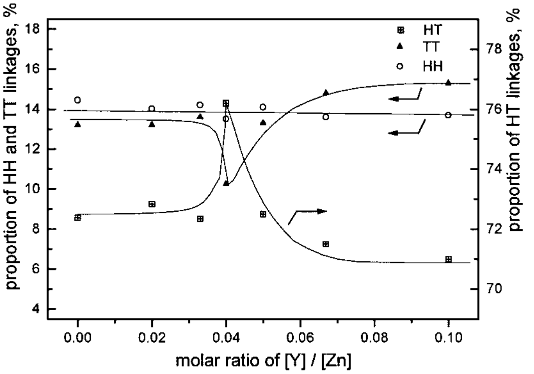


Figure 2. Influence of rare earth compound content on the microstructure of the propylene oxide-carbon dioxide copolymer. Catalyst: Y(*m*-$NO_2C_6H_4COO)_3/ZnEt_2$/glycerine; Reaction pressure: 3.5-4.0Mpa; reaction time:12h; solvent: 1,3-dioxane.

Terpolymerization of Epoxides and Carbon Dioxide

The Tg of the PO/CO_2 copolymer is around 35-42^{0}C, adjusting Tg of the copolymer is necessary for various applications. Therefore, Employing Y($CCl_3COO)_3/ZnEt_2$/gylcerine ternary catalyst, ter-polymerization of cylcohexene oxide(CHO), proplyene oxide(PO) with CO_2 is carried out for this purpose. As listed in Table 2, in addition to very high catalytic activity, the ternary catalyst is very effective to tune the Tg of the ter-polymer, where two Tg phenomenon is observed, which is important for good mechanical property of the polymer. Ter-polymerization of ethylene oxide(EO), PO with CO_2 is also realized by the same ternary catalyst. It is interesting to observe that EO is very effective to tune the Tg of the ter-polymer. Low Tg polymer is obtained, where its Tg varies from 36^{0}C to 9^{0}C when the EO/PO weight ratio changes from 0/100 to 12/88.

In conclusion, the ternary catalyst has very important influence on the microstructure of aliphatic polycarbonate. In addition to high activity to the ter-polymerization of epoxides and carbon dioxide, the ternary catalyst is also very effective to tune the Tg of the ter-polymer.

Table 2. Ter-copolymerization of cylcohexene oxide, proplyene oxide with CO_2.

PO/CHO (w/w)	Yield (g/mol Zn)	Yield (g/mol Y)	Mn	Mw	Mw/Mn	Tg(°C)
100/0	4.9x10^{3}	1.0x10^{5}	9.7x10^{4}	5.2x10^{5}	5.4	37.2
95/5	5.1x10^{3}	1.1x10^{5}	5.0x10^{4}	3.2x10^{5}	6.4	40.6
						76.8
90/10	6.1 x10^{3}	1.2 x10^{5}	5.4x10^{4}	3.8x10^{5}	7.0	41.8
						81.2
80/20	6.6 x10^{3}	1.3x10^{5}	1.1x10^{4}	1.4x10^{4}	1.3	42.9
			1.6x10^{5}	5.8x10^{5}	3.6	83.2
50/50	7.9 x10^{3}	1.7 x10^{5}	1.0x10^{4}	1.5x10^{4}	1.5	42.8, 83.8
			2.0x10^{5}	7.2x10^{5}	3.6	
25/75	9.4 x10^{3}	1.9 x10^{5}	9.8x10^{3}	1.4x10^{4}	1.4	45.6
			1.8x10^{5}	5.9x10^{5}	3.3	106.3
0/100	1.2 x10^{4}	2.4x10^{5}	9.3x10^{3}	1.3x10^{4}	1.4	125.8
			1.7x10^{5}	6.3x10^{5}	3.7	

Reaction condition: Catalyst ratio: $Y(CCl_3COO)_3/ZnEt_2$/gylcerine=1/20/10 in mole ratio; polymerization pressure: 3.5-4.0Mpa; reaction temperature: 65-70°C

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