

NEW CATALYTIC SYSTEMS FOR THE FIXATION OF CO₂ III. INFLUENCE OF ADDITIVES AND REACTION MEDIUM ON THE COPOLYMERIZATION OF CARBON DIOXIDE-EPICHLOROHYDRIN IN THE PRESENCE OF Nd(P₂₀₄)₃-Al(i-Bu)₃*

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ABSTRACT

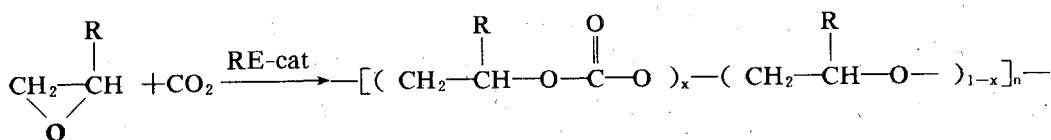
Copolymerization of carbon dioxide with epichlorohydrin was successfully carried out by using Nd(P₂₀₄)₃-Al(i-Bu)₃ as catalyst (P₂₀₄) = (RO)₂POO-, R = CH₃(CH₂)₃CH(C₂H₅)CH₂-). Addition of carbonyl compounds into the catalyst decreased the carbon dioxide content of the copolymer to some extent. Compared to nonpolar solvents, ethereal and moderate polar solvents were favourable to obtaining higher carbon dioxide content copolymer. The coincidence of these results with the assumed copolymerization scheme clearly indicated that the copolymerization proceeds via coordinate anionic mechanism.

INTRODUCTION

Copolymerization of epoxides with carbon dioxide is one of the effective way for chemical fixation of carbon dioxide. The catalysts reported so far include organozinc-additives^[1-4], (TPP)AlCl or related compounds^[5]; zinc salts^[6]. However, all of these catalysts could hardly catalyze the copolymerization of CO₂ with epichlorohydrin (ECH). We had reported in detail that the copolymerization of propylene oxide (PO) with carbon dioxide by using rare earth coordination catalysts composed of RE(P₂₀₄)₃-Al(i-Bu)₃-glycerine (RE = rare earth elements) to give high molecular weight PO-CO₂ copolymer with narrow molecular weight distribution and high thermal stability^[7].

Furthermore, introducing of functional group-containing epoxide into copolymer is in favour of the modification of polymer. Recently, we have found that the rare earth catalysts were very effective for the copolymerization of epichlorohydrin with carbon dioxide.

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In this paper, the copolymerization of epichlorohydrin and CO₂ catalyzed by Nd(P₂₀₄)₃-Al(i-Bu)₃ has been reported, with emphasis on the influence of additives and reaction medium on the copolymerization reaction. And also, a possible mechanism scheme of the copolymerization is suggested.

EXPERIMENTAL

Materials

Epichlorohydrin (ECH) was refluxed over CaH₂ and distilled before use. High purity commercial carbon dioxide (purity > 99.9%) was used without further purification. Maleic anhydride was recrystallized from chloroform and dried under reduced pressure. All solvents and additives were analytical reagents purified by the usual methods.

Synthesis of catalyst

The rare earth complex and the solution of rare earth coordination catalyst were prepared by the previously described method^[8].

Copolymerization of CO₂-ECH

The copolymerization reaction was carried out in 80 ml stainless steel autoclave under the carbon dioxide pressure of 30–40 atm by using Nd(P₂₀₄)₃-Al(i-Bu)₃ as catalyst. After 24 hours, the reaction mixture was precipitated by ethanol containing 5% HCl. The resultant polymer was washed several times with ethanol and then dried under vacuum at room temperature.

¹H-NMR measurements

¹H-NMR spectra of the ECH-CO₂ copolymers in CDCl₃ solution were recorded on a JEOL FX-90Q apparatus at room temperature.

Measurements of intrinsic viscosity

The intrinsic viscosities of the copolymer were measured in CHCl₃ solution at 30°C with Ubbelohde-type viscometer.

RESULTS AND DISCUSSION

1. Copolymerization of ECH-CO₂ in different solvents

It has been found that the copolymerization of epichlorohydrin and carbon dioxide can be carried out in benzene, 1, 4-dioxane, chlorobenzene, CH₂Cl₂ or CH₃OCH₂CH₂OCH₃ by using Nd(P₂₀₄)₃-Al(i-Bu)₃ as catalyst. As seen from the data in Table 1, the copolymer yield was affected by the electron-donor property as well as the polarity of solvent. Non-polar solvent (benzene) gave higher copolymer yield accompanied with lower carbon dioxide content ($f(\text{CO}_2)$) in the copolymer chain. But for 1, 4-dioxane, it gave a high $f(\text{CO}_2)$ copolymer even though its dielectric constant was close to that of benzene because the solvent itself was a kind of ethereal compound competing with epichlorohydrin during the copolymerization reaction, thus inevitably caused the decrease of copolymer yield. Moderate polar solvent (chlorobenzene) was favourable to be used for synthesizing higher $f(\text{CO}_2)$ copolymer. Figure 1 shows the ¹H-NMR spectrum of the copolymer No. 2 in Table 1 having absorption peaks at 5.1 ppm and 4.5 ppm from TMS besides the peak observed in the epichlorohydrin homopolymer (appeared at 3.7 ppm). These two new peaks were assigned to methine and methylene protons adjacent to the carbonate linkage respectively. The carbonate unit content and the carbon dioxide content of the copolymer were determined from the peak area ratio. It can also be found 2.6 ppm and 0.8–1.3 ppm absorptions in Figure 1 which were due to the end groups of —CH₂OH and —CH₂CH(CH₃)₂ respectively.

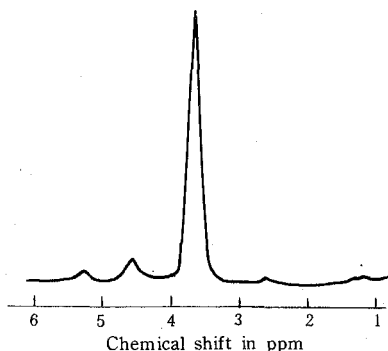


Fig. 1 ¹H-NMR spectrum of ECH-CO₂ copolymer

Table 1 Copolymerization of ECH-CO₂ in different solvents^{a)}

No.	Solvent	Dielectric constant	Yield(g/mol Nd)	[η](dl/g)	$f(\text{CO}_2)$
1	benzene	2.27	3064	0.774	12%
2	1, 4-dioxane	2.24	1552	0.212	24%
3	C ₆ H ₅ Cl	5.61	1670	0.076	23%
4	CH ₃ OCH ₂ CH ₂ OCH ₃	7.20	723	0.364	11%
5	CH ₂ Cl ₂	9.14	2118	0.559	9%

a) Al/Nd 8; Nd = 4.75×10^{-2} mol/L; [ECH] = 2.8 mol/L; 60°C

2. Effect of the additives

In order to improve the activity of catalyst, the third components have been attempted to be used in the catalyst system. The results are summarized in Table 2. It was notable that anhydrides increased the catalytic activity in terms of copolymer yield remarkably but decreased the carbon dioxide content of the copolymer obtained. This might suggest that the addition of anhydrides to the catalyst formed new active species which inhibited the complexation of carbon dioxide with the catalyst to some extent. Comparing the results of experiment No. 3 with No. 4 and No. 6 with No. 7, it seemed that the bulk of III affected the catalytic activity.

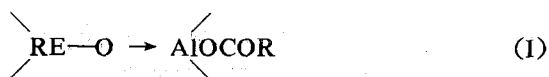
Table 2 Effect of the third component (III) on the catalytic activity of rare earth coordination catalyst^{a)}

No.	III	Yield(g/mol Nd)	<i>f</i> (CO ₂)(mol-%)
1	none	1552	24
2	benzoylacetone	649	5
3	maleic anhydride(MAN)	3327	11
4	phthalic anhydride	2025	2
5	acetylacetone	675	3
6	methyl benzoate	1683	17
7	dibutyl phthalate	1420	13
8	pyrrole	618	2
9	DMSO, NEt ₃ or imidazole	0	0

a) III/Al=0.5; Al/Nd=8; [Nd]=4.75×10⁻²mol/L; [ECH]=2.8mol/L; in 1,4-dioxane; 60°C

3. Assumed copolymerization mechanism

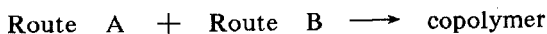
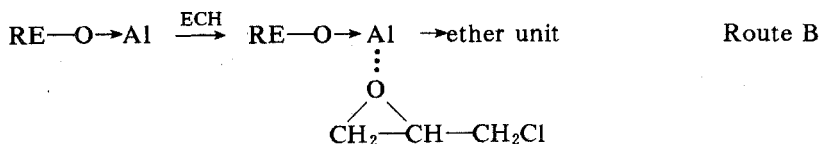
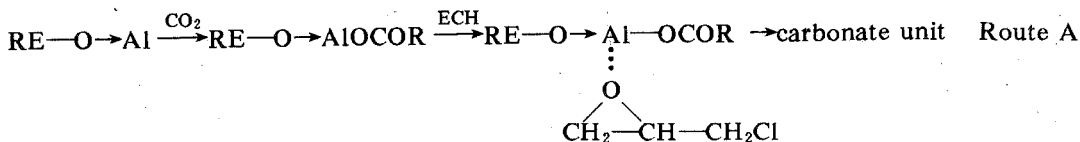
We have reported that the copolymerization of epoxides with carbon dioxide by rare earth catalysts proceeds through the coordinate anionic mechanism. Carbon dioxide may insert into Al—R bond in the initiation step.



RE=rare earth elements

Considering the structure of the end group described above, the following scheme of copolymerization could be assumed.

The copolymer composition would be determined by the relative reactivity of the two reaction routes A and B. According to this copolymerization scheme, at least two methods were reasonable for the purpose to increase the carbon dioxide content of the copolymer; (1) Using moderate polar solvents to enhance the reactivity of carbon dioxide toward the rare earth catalyst. The results shown in Table 1 were in agreement with this assumption.



tion; (2) Using ethereal compounds which can not be homopolymerized by the catalysts used to restrict the coordination of ECH with catalyst site. Therefore, the copolymerization was carried out with THF as a competing monomer. As shown in Table 3, THF gave a significant effect on the carbon dioxide content of the copolymer obtained. The decrease of $f(\text{CO}_2)$ of experiment No. 4 in Table 3 was related to the too high polarity of reaction medium caused by THF in which the volume ratio of THF to benzene was 2:1.

Table 3 Effect of THF on the copolymerization^{a)}

No.	Catalyst system	THF/ECH	Yield(g/mol Nd)	$f(\text{CO}_2)$
1	Nd(P204) ₃ -Al(i-Bu) ₃	0.0	3064	12
2	Nd(P204) ₃ -Al(i-Bu) ₃	0.5	1643	24
3	Nd(P204) ₃ -Al(i-Bu) ₃	1.0	842	20
4	Nd(P204) ₃ -Al(i-Bu) ₃	2.0	658	10
5 ^{b)}	Nd(P204) ₃ -Al(i-Bu) ₃ -MAn	0.5	1854	15
6 ^{c)}	Nd(P204) ₃ -Al(i-Bu) ₃ -MAn	0.5	1315	18

a) Al/Nd=8; [Nd]=4.75×10⁻²mol/L; [ECH]=2.8mol/L; in benzene; 60°C;

b) MAn/Al=0.5; in 1,4-dioxane; c) MAn/Al=0.125; in 1,4-dioxane

Keywords:

Carbon dioxide fixation; Rare earth coordination catalyst; Epichlorohydrin

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