

Rare Earth Coordination Catalysts for the Polymerization of Alkylene Oxides I. Polymerization of Epichlorohydrin[†]

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ABSTRACT: Acetylacetonates of nine rare earth elements, combined with triisobutylaluminum and water, were used as catalysts for the polymerization of epichlorohydrin (ECH). It was found that the Nd(acac)₃-Al(iso-Bu)₃-H₂O system was a favourable catalyst for polymerization with respect to preparing polyepichlorohydrin (PECH) with high molecular weight and low crystallinity. The polymerization of ECH with Nd(acac)₃-Al(iso-Bu)₃-H₂O catalyst system was investigated concerning the dependence of polymerization catalyst composition, *i.e.*, Al/Nd and H₂O/Al molar ratios, polymerization time, and solvent, etc. THF polymerization catalyzed by Nd(acac)₃-Al(iso-Bu)₃-H₂O was also performed to check the character of the catalyst system. The bimetallic nature of the catalyst was proposed.

KEY WORDS Catalyst / Rare Earth Coordination Catalyst / Ring-Opening Polymerization / Epichlorohydrin / Polymerization of Epichlorohydrin

Because of the growing significance of epichlorohydrin (ECH) elastomers in practice, various catalysts for the polymerization of alkylene oxides have been developed in the recent decades, *e.g.*, the systems of AlR₃-H₂O-third component,^{1,2} AlR₃-strong phosphoric acid-Lewis base,³ and AlR₃-nitrogen containing organozinc.⁴ There are two important and necessary characteristics for ECH polymers to obtain useful elastomers: high molecular weight and low crystallinity. We first reported⁵⁻⁹ that rare earth compounds combined with alkylaluminum and water were highly effective catalysts for propylene oxide and/or ethylene oxide polymerization. A recent study showed that the ternary systems consisting of rare earth acetylacetonate RE(acac)₃, alkylaluminum, and water were favourable catalysts to prepare poly(epichlorohydrin) (PECH), with respect to the above points. This paper reports our extensive study on Nd(acac)₃-Al(iso-Bu)₃-H₂O catalyst sys-

tem for ECH polymerization.

EXPERIMENTAL

Materials

ECH and other monomers used in this paper, like propylene oxide (PO), allyl glycidyl ether (AGE), and tetrahydrofuran (THF), were refluxed over CaH₂ and distilled before use. Toluene of analytical reagent was dried with molecular sieve 4A overnight. Triisobutylaluminum Al(iso-Bu)₃ was used as purchased from Roth. Co. Rare earth acetylacetonates RE(acac)₃, were prepared and purified according to the reference.¹⁰

Catalyst Preparation and Polymerization

All procedures were carried out in an atmosphere of purified nitrogen. Water at a certain H₂O/Al molar ratio was added dropwise to a solution of Al(iso-Bu)₃ in toluene at 10°C. After alkane gas evolution had ceased,

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the solution was heated at 60°C for 2 h. The reaction mixture thus obtained was a colourless and transparent solution.

Al(iso-Bu)₃-H₂O solution was transferred with a tight syringe into a bottle in which a prescribed amount of RE(acac)₃ had been put. A homogeneous solution was soon formed. The resultant catalyst solution was aged for 1 h, and then toluene and ECH were added. The polymerization was terminated by adding excess methanol containing a small amount of HCl. The polymer precipitated was washed with methanol and dried in vacuum.

Measurements

Inherent viscosity of PECH was determined in cyclohexanone at 50°C by Ubbelohde-type viscometer. The viscosity-average-molecular weight \bar{M}_v was calculated by following equation¹¹:

$$[\eta] = 2.51 \times 10^{-5} \bar{M}_v^{0.87}$$

The crystallinity of PECH ($x_c\%$) was calculated as follows¹²:

$$x_c\% = 100 \times \Delta H_f / \Delta \bar{H}_f$$

where $\Delta \bar{H}_f = 27.27 \text{ cal g}^{-1}$, is the theoretical heat of fusion of PECH crystal, and ΔH_f is the heat of fusion of a given PECH sample which was measured with a CDR-1 Calorimeter. ¹H NMR spectrum of PECH was obtained on a JEOL FX-90Q NMR spectrometer, using CDCl₃ and TMS as the solvent and internal reference, respectively.

RESULTS AND DISCUSSION

Combinations of nine rare earth acetylacetonates RE(acac)₃, with Al(iso-Bu)₃ and H₂O, were used as polymerization catalysts for ECH, as shown in Table I. The results of polymerization with Al(iso-Bu)₃-H₂O (1:0.5) catalyst system are also listed in Table I for comparison. It was found that with the addition of RE(acac)₃ to the catalyst system, the yield and molecular weight of PECH increased largely Nd(acac)₃-Al(iso-Bu)₃-H₂O system was the most outstanding catalyst among the combinations examined. So the study was focused on the Nd catalyst system.

Polymerization of ECH with Nd(acac)₃-Al(iso-Bu)₃-H₂O

The composition ratios of Nd(acac)₃-Al(iso-Bu)₃-H₂O catalyst system are the most important factors influencing ECH polymerization. Table II shows the effects of the H₂O/Al molar ratio on the molecular weight, yield, and crystallinity of PECH. It was seen that the inherent viscosity $[\eta]$ and yield of PECH increased greatly by the addition of a small amount of water into the catalyst system. The amount of water is not critical in the range of H₂O/Al = 0.1—0.5 for obtaining PECH with high molecular weight and high yield. The crystallinity (10—20%) of PECH so prepared was much lower than that of polymer produced by zinc catalyst system.²

At a H₂O/Al molar ratio of 0.5, the influence of the Al/Nd molar ratio on polymerization was investigated in two ways: varying Al mole

Table I. ECH polymerization with RE(acac)₃-Al(iso-Bu)₃-H₂O^a

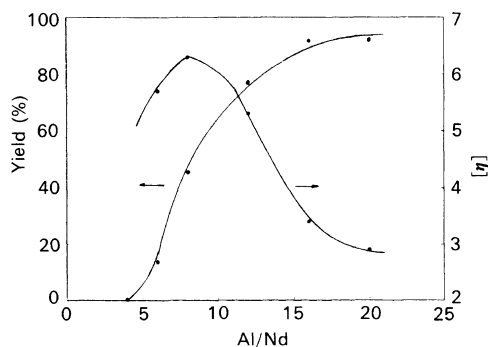
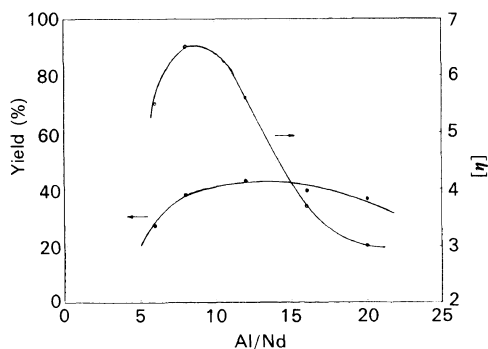
RE	La	Pr	Nd	Sm	Eu	Gd	Dy	Yb	Y	^b
Yield/wt%	30	43	51	53	21	55	57	60	60	23
$[\eta]$	4.4	4.1	6.5	4.5	3.4	3.6	4.0	3.7	4.1	0.9
$\bar{M}_v / \times 10^5$	10.7	9.8	16.5	10.9	7.9	8.6	9.6	8.8	9.8	1.7

^a Al/RE = 8; H₂O/Al = 0.5; RE, $8 \times 10^{-3} \text{ mol l}^{-1}$, 80°C, 2 h; ECH, 1.2 g; toluene, 5 ml (amounts of ECH and solvent are the same in the following tables and figures).

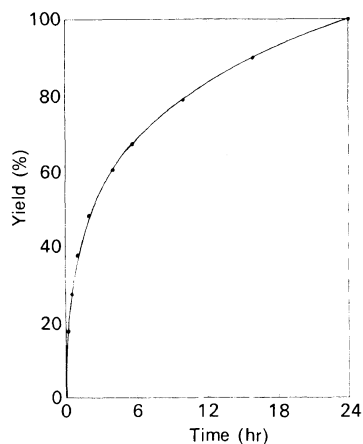
^b Al(iso-Bu)₃-H₂O (1:0.5) catalyst system at the corresponding condition.

Table II. Effect of H₂O/Al molar ratio on ECH polymerization^a

H ₂ O/Al	Yield/wt%	$[\eta]$	Crystallinity/%
0	1	2.1	24
0.1	43	5.6	12
0.2	46	5.2	15
0.4	50	5.3	18
0.5	51	6.5	21
0.6	27	5.0	21
0.8	10	3.5	21

^a Al/Nd=8, 80°C, 2 h.**Figure 1.** Influence of the Al/Nd molar ratio on ECH polymerization. Nd: $8 \times 10^{-3} \text{ mol l}^{-1}$, 80°C, 2 h.**Figure 2.** Influence of the Al/Nd molar ratio on ECH polymerization. Al: $6.6 \times 10^{-2} \text{ mol l}^{-1}$, 80°C, 2 h.

while keeping Nd and a constant and *vice versa*. The results are shown in Figures 1 and 2. It was found that the yield of PECH increased with Al concentration in catalyst system (Figure 1); on the other hand, the yield of PECH decreased with decreasing Nd

**Figure 3.** The rate of ECH polymerization with Nd(acac)₃-Al(iso-Bu)₃-H₂O (1:8:4) catalyst system at 80°C.

concentration (Figure 2). It was notable that the molecular weight of PECH largely depended on Al/Nd molar ratio. The optimum Al/Nd molar ratio for high $[\eta]$ is 8. Similar results were observed for other rare earth coordination catalysts. Since Al(iso-Bu)₃-H₂O (1:0.5) could initiate ECH polymerization to give PECH with much lower molecular weight (10^4 — 10^5), we postulated that rapid decreasing of $[\eta]$ in the high Al/Nd ratio region might be caused by the coexistence of active species produced by excess Al(iso-Bu)₃-H₂O (1:0.5) in the catalyst system. It seems that a kind of bimetallic catalyst species, involving Al and Nd in certain molar ratio, was responsible for the high polymerization degree of PECH obtained at Al/Nd=8.

The rate of ECH polymerization with Nd(acac)₃-Al(iso-Bu)₃-H₂O (1:8:4) can be seen from Figure 3. The polymerization rate was fairly high in the first hour, and decreased gradually with time. The declination of the polymerization rate may be caused by reduction of the active center number, or/and insufficient diffusion of ECH molecules to the propagation species due to the increasing viscosity of the polymerization solution. Further kinetic study is described elsewhere.¹³

The polymerization was greatly influenced

by the solvent used. A solution polymerization of ECH took place either in toluene or in dichloromethane. But, PECH was precipitated during polymerization with aliphatic hydrocarbon as solvent. Toluene appeared more preferable for the polymerization, as shown in Table III. The activity order was toluene \gg dichloromethane $>$ *n*-hexane $>$ acetone. The Nd(acac)₃-Al(iso-Bu)₃-H₂O catalyst system showed no activity for ECH polymerization in acetone, because the solvent itself coordinated with the catalyst and thus prohibited the coordination of ECH with the active species, which was one of the key steps for ring-opening

polymerization of alkylene oxide catalyzed by coordination catalyst. Using toluene as the polymerization solvent, the effect of polymerization temperature on the polymerization was examined and the results are summarized in Table IV.

PECH so prepared was characterized by ¹H NMR spectroscopy, as shown in Figure 4. The three different kinds of hydrogens in PECH (-CH₂Cl, -CH-, and -CH₂-) gave an overlapping signal at $\delta = 3.6$ – 3.8 ppm.

Character of the Nd(acac)₃-Al(iso-Bu)₃-H₂O Catalyst System

Al(iso-Bu)₃-H₂O (1:0.5), acting as a Lewis acid, can be used to catalyze the polymerization of tetrahydrofuran (THF), which is known to be polymerized only by a cationic mechanism.¹⁴ In order to check the character of the Nd(acac)₃-Al(iso-Bu)₃-H₂O catalyst system, the polymerization of THF with this catalyst was studied and the results are shown in Table V. The polymerization was carried out at 5°C for 24 h with ECH as a promoter by Saegusa's method.¹⁴ The catalyst system with Al/Nd $>$ 10 showed the same activity as that of Al(iso-Bu)₃-H₂O (1:0.5); when Al/Nd \leq 8. However, only a trace of polymer was obtained. The trace polymer was determined as PECH because it was insoluble in the solvent of poly(tetrahydrofuran), *i.e.*, benzene.

Table III. Effect of solvent^a

Solvent	Toluene	Dichloromethane	<i>n</i> -Hexane	Acetone
Yield/wt%	66	26	15	0

^a Al/Nd = 8, H₂O/Al = 0.5, 35°C, 16 h.

Table IV. Effect of polymerization temperature^a

Temp./°C	Yield/wt%	$[\eta]$
30	12	5.9
50	32	7.0
60	35	6.9
70	40	6.3
80	50	6.3
100	55	4.1

^a Al/Nd = 8, H₂O/Al = 0.5, 2 h, toluene.

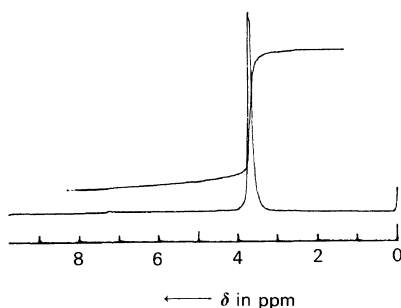


Figure 4. The ¹H NMR spectrum of PECH. Solvent, CDCl₃; internal reference, TMS.

Table V. The polymerization of THF^a

Catalyst system	Al/mol	Nd/mol	Al/Nd	Yield/wt%
Al(iso-Bu) ₃ -H ₂ O (1:0.5)	1.23	0	—	76
Nd(acac) ₃ -Al(iso-Bu) ₃ -H ₂ O (H ₂ O/Al=0.5)	1.23	0.031	40	76
	1.23	0.062	20	74
	1.23	0.082	15	71
	1.23	0.123	10	29
	1.23	0.154	8	^b
	1.23	0.205	6	^b

^a Using ECH as promoter: ECH, 0.11 g (ECH/Al = 1); THF, 5 ml, 5°C, 24 h.

^b A trace of polymer which was insoluble in benzene.

It was indicated that the cationic character of $\text{Al}(\text{iso-Bu})_3\text{-H}_2\text{O}$ system became a coordination anionic one gradually with the addition of $\text{Nd}(\text{acac})_3$. A complete coordination anionic feature was shown by $\text{Nd}(\text{acac})_3\text{-Al}(\text{iso-Bu})_3\text{-H}_2\text{O}$ ($\text{H}_2\text{O}/\text{Al}=0.5$) at $\text{Al}/\text{Nd}=8$.

The coordination anionic feature of the $\text{Nd}(\text{acac})_3\text{-Al}(\text{iso-Bu})_3\text{-H}_2\text{O}$ (1 : 8 : 4) catalyst system was further demonstrated by the results of ECH-AGE and PO-AGE copolymerization ratios. Values obtained were $r_1(\text{PO})=2.0$, $r_2(\text{AGE})=0.5$; and $r_1(\text{ECH})=0.5$, $r_2(\text{AGE})=0.4$. The monomer reactivity order was $\text{PO} > \text{ECH} > \text{AGE}$. The values of $r_1(\text{PO})=0.6$ and $r_2(\text{ECH})=1.8$ were reported¹⁵ by Ishida for $\text{FeCl}_3\text{-PO}$ catalyst. Since the ferric chloride catalyst generally has a cationic nature, the opposite results obtained by $\text{Nd}(\text{acac})_3\text{-Al}(\text{iso-Bu})_3\text{-H}_2\text{O}$ (1 : 8 : 4) catalyst system support the idea that this rare earth catalyst is a coordination anionic system.

Based on the above polymerization results, it is proposed that one kind of active species in $\text{Nd}(\text{acac})_3\text{-Al}(\text{iso-Bu})_3\text{-H}_2\text{O}$ catalyst system, comprising of Al and Nd with certain molar ratio, and exhibiting the coordination anionic character, is responsible for the outstanding catalytic behaviour in the polymerization of ECH.

CONCLUSIONS

The rare earth coordination catalysts, consisting of rare earth acetylacetonate $\text{RE}(\text{acac})_3$, triisobutylaluminum, and water, can catalyze the polymerization of ECH. The

system of $\text{Nd}(\text{acac})_3\text{-Al}(\text{iso-Bu})_3\text{-H}_2\text{O}$ is the most outstanding catalyst among the nine combinations examined, with which PECH of high molecular weight and low crystallinity is prepared. The cationic character of $\text{Al}(\text{iso-Bu})_3\text{-H}_2\text{O}$ system becomes a coordination anionic one gradually with the addition of $\text{Nd}(\text{acac})_3$. A kind of bimetallic active species involving Al and Nd is proposed.

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