

Ring-Opening Polymerization of Tetrahydrofuran with Rare Earth-Contained Catalysts

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SYNOPSIS

Rare earth trifluoroacetates, $\text{Ln}(\text{CF}_3\text{CO}_2)_3$ (Ln = thirteen rare earth elements), combined with $\text{R}_n\text{AlH}_{3-n}$ (R = methyl, octyl, $n = 3$; R = ethyl, *i*-Butyl, $n = 2, 3$) were used as catalysts for the polymerization of tetrahydrofuran (THF). The activity increased by adding propylene oxide (PO), as a promoter, to the polymerization system, producing high molecular weight polytetrahydrofuran (PTHF). The effects of Ln , PO/Ln , and Al/Ln , and others on the polymerization of THF were also studied. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The ring-opening polymerization of tetrahydrofuran (THF) was first reported by Meerwein,^{1,2} who used a trialkyloxonium salt as a catalyst. Since then, various catalyst systems have been found.³⁻⁸ Shen and coworkers^{9,10} reported the polymerization of propylene oxide, ethylene oxide, and epichlorohydrin with the catalysts of rare earth complexes, combined with alkylaluminum. No rare earth catalyst, however, was found in literature for THF polymerization. In this article, we will report the polymerization of THF with the catalysts of rare earth trifluoroacetates, $\text{Ln}(\text{CF}_3\text{CO}_2)_3$ ($\text{Ln} = \text{Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Tm}$), combined with alkylaluminums, $\text{R}_n\text{AlH}_{3-n}$ ($\text{R} = \text{methyl, octyl, } n = 3; \text{R} = \text{ethyl, } i = \text{Butyl, } n = 2, 3$).

EXPERIMENTAL

Materials

THF was refluxed over a Na—K alloy and benzophenone under argon and was distilled before use. PO was dried over CaH_2 and was distilled under argon. All $\text{R}_n\text{AlH}_{3-n}$ were Fluka products. $\text{Ln}(\text{CF}_3\text{CO}_2)_3$ was prepared according to Ref. 11, and was dissolved in THF with the concentration

of 1×10^{-4} mol/mL THF. PO and $\text{R}_n\text{AlH}_{3-n}$ were all diluted in THF with certain concentrations before use.

Measurements

The inherent viscosity of polytetrahydrofuran (PTHF) was determined in benzene at 30° by an Ubbelohde-type viscometer. The viscosity-average-molecular weight, M_n , was calculated by the following equation.¹²

$$[\eta] = 2.9 \times 10^{-4} M_n^{0.74}$$

The UV spectrum of PTHF was determined in CH_2Cl_2 .

Polymerization

Polymerization procedures were all carried out in an atmosphere of purified argon. Components of polymerization were syringed into polymerization bottles in a certain order. The polymerization was terminated by adding an excessive amount of water, containing a small amount of HCl. The polymer precipitated was washed with water and was dried in vacuum.

$\text{C}_6\text{H}_5\text{O}$ -end-contained PTHF was prepared, according to Ref. 13, by the reaction of the $\text{Y}(\text{CF}_3\text{CO}_2)_3 - (i\text{-Bu})_2\text{AlH} - \text{PO} - \text{THF}$ ($\text{Al}/\text{Y} = 4, \text{PO}/\text{Y} = 1$, molar ratio) polymerization system with $\text{Pho Na} - \text{THF}$.

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Table I Bulk Polymerization of THF

Catalysts	Conversion (%)
Ce(CF ₃ CO ₂) ₃ + Et ₃ Al	22.5
Pr(CF ₃ CO ₂) ₃ + Et ₃ Al	5.6
Sm(CF ₃ CO ₂) ₃ + Et ₃ Al	50.0

Conditions: [Ln] = 1×10^{-1} mol/L THF, Al/Y = 5 (molar ratio); room temperature for 5 months.

RESULTS AND DISCUSSION

Ln(CF₃CO₂)₃—Et₃Al Catalyst System

Ln(CF₃CO₂)₃ (Ln = Ce, Pr, and Sm), combined with Et₃Al, was found to polymerize THF (Table I). Five months later, the highest yield was 50% under sealed conditions. It was noted that Ln(CF₃CO₂)₃ and Et₃Al could not alone initiate the polymerization of THF. This indicated that the active species of the polymerization arose from the reaction product of the two components that composed the catalyst.

Ln(CF₃CO₂)₃—R_nAlH_{3-n}—PO Catalyst System

The activity of Y(CF₃CO₂)₃—(i-Bu)₂AlH increased rapidly by adding a certain amount of PO as a promoter (Fig. 1). The conversion became highest when the PO/Y molar ratio was 7, and the activity did not change much with the ratio > 7.

The Al/Y molar ratio much affects the activity

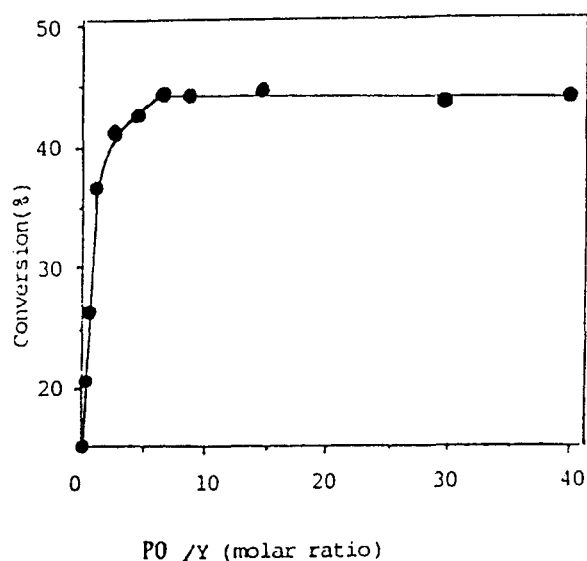


Figure 1 Effect of PO/Y on conversion. Conditions: Y = Y(CF₃CO₂)₃, [Y] = 2.2×10^{-2} mol/L, Al = (i-Bu)₂AlH, Al/Y = 4 (molar ratio), 50°C, 0.5 h, bulk polymerization. Adding order of components: Y + THF + Al + PO.

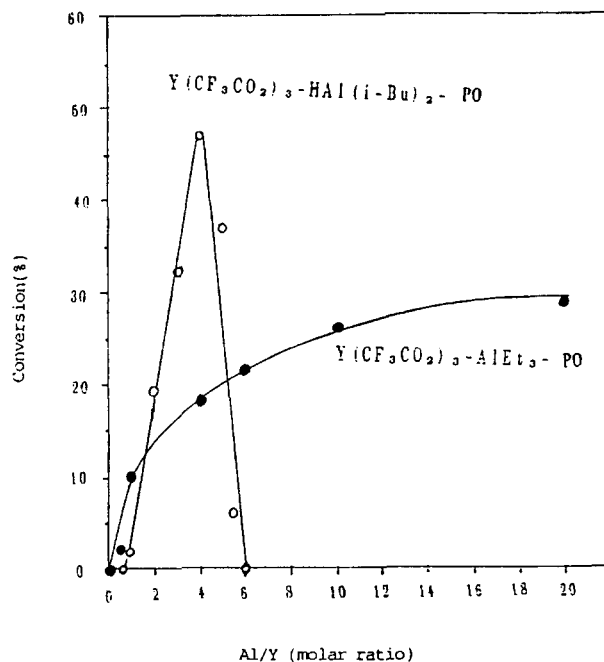


Figure 2 Effect of Al/Y on conversion. Conditions: Y(CF₃CO₂)₃—(i-Bu)₂AlH—PO, (1 h), Y(CF₃CO₂)₃—Et₃Al—PO, (2 h), PO/Y (molar ratio) = 1 (the value is the same as in Figs. 3–5 and Tables II and III); other conditions are the same as in Figure 1.

of Y(CF₃CO₂)₃—(i-Bu)₂AlH—PO (Y—Al—PO) (Fig. 2). The system was nearly inactive when Al/Y = 1. The optimum Al/Y molar ratio was 4. When Al/Y > 4, the activity decreased sharply, and it showed no activity when Al/Y = 6. The decreasing of the activity may be caused by the strong active chain termination, due to the excess of (i-Bu)₃AlH.

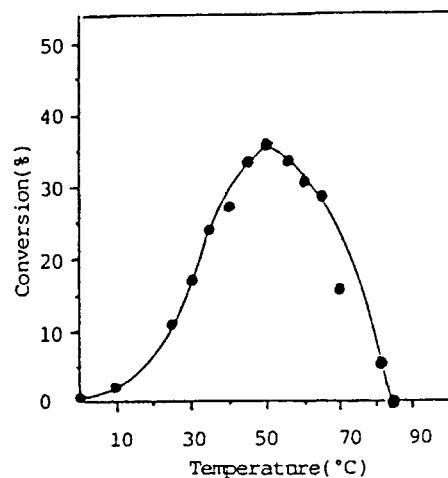


Figure 3 Effect of temperature on conversion. Conditions are the same as in Figure 1.

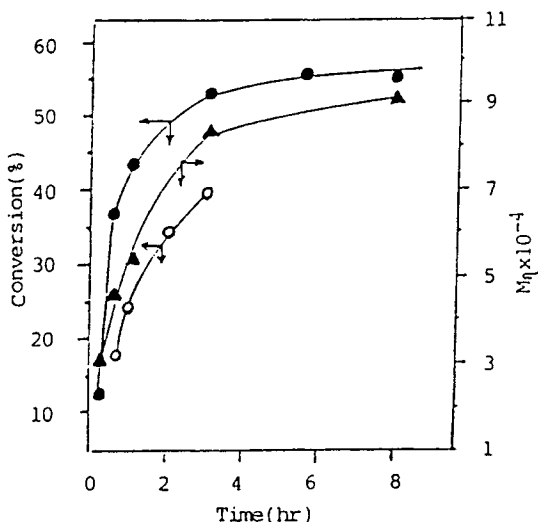


Figure 4 Effect of time on conversion and molecular weight. Conditions: (●) $[Y] = 2.2 \times 10^{-2}$ mol/L, (○) $[Y] = 1.1 \times 10^{-2}$ mol/L, (▲) corresponds to (○). Other conditions are the same as in Figure 1.

However, for the $Y(CF_3CO_2)_3 - Et_3Al - PO$ catalyst system, the activity increased with increased ratio of Al/Y.

The influence of temperature on the polymerization rate can be seen from Figure 3. The polymerization rate increased with increasing temperature before $50^\circ C$, and at $50^\circ C$ Y—Al—PO had the highest polymerization rate. The polymerization rate was zero at $85^\circ C$. This temperature was in agreement with the ceiling temperature of THF polymerization, reported by Dreyfuss and Dreyfuss.⁵

The rate of THF polymerization with Y—Al—PO at different times can be seen from Figure 4. The polymerization rate was high in the first two hours, and decreased with time. The declination of the polymerization rate may be caused by the increasing viscosity of the polymerization solvent. The molecular weight of PTHF increased with increasing of conversion (Fig. 4). The conversion at 8 h

Table II Effect of Adding Order of Catalytic Components on Conversion

No.	Orders	Conversion (%)
I	Y + THF + Al + PO	36.6
II	Y + THF + PO + Al	36.1
III	Y + THF + Al (Aging 16 h at Room Temperature) + PO	39.1

Conditions are the same as in Figure 1.

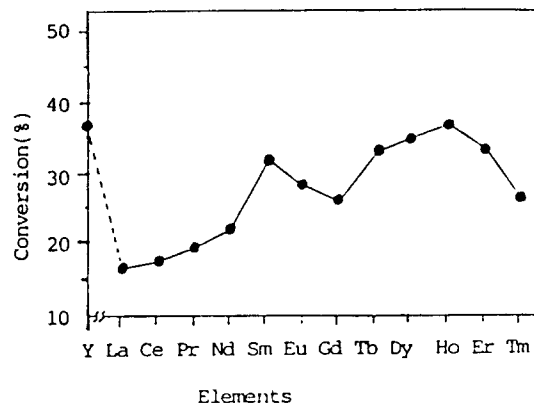


Figure 5 Effect of rare earth elements on conversion. Conditions are the same as in Figure 1.

(55.3%) was in agreement with the equilibrium conversion (56%), at the same temperature, reported by Dreyfuss and Dreyfuss.⁵

Table II shows the effects of methods of polymerization components added on the activity of Y—Al—PO. Method I and II were not different. Method III was preferable. After aging for a certain time, the catalyst was more active than the unaged one. This result revealed that the reaction of $Y(CF_3CO_2)_3$ and $(i-Bu)_2AlH$, forming the active species, took a long time.

The effects of different rare earth elements on the activity of $Ln(CF_3CO_2)_3 - (i-Bu)_2Al - PO$ is shown in Figure 5. In general, heavy rare earths were more active than light ones. Samarium was most

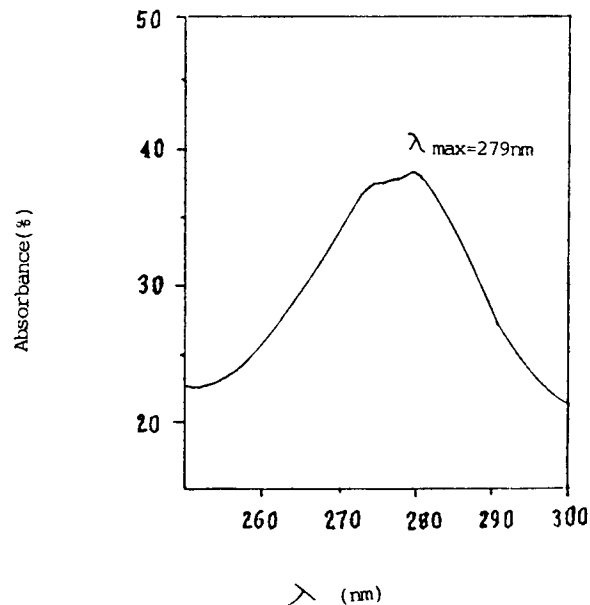


Figure 6 The UV spectrum of PTHF.

Table III Effect of R_nAlH_{3-n} on Conversion (%)

Catalysts	Me ₃ Al	Et ₃ Al	(i-Bu) ₃ Al	Oct ₃ Al	(i-Bu) ₂ AlH	Et ₂ AlH
Y + Al + PO	2.3	28.7	18.3	25.2	53.1	45.9
Al + PO ^a	1.1	6.9	1.1	4.0	0	0

^a No Y(CF₃CO₂)₃.

Conditions: 3 h; others are the same as in Figure 1.

active among the light, and Yttrium and Holium were most active among the heavy.

The (i-Bu)₂AlH system had the highest activity among the R_nAlH_{3-n} examined (Table III). It was more important that (i-Bu)₂AlH and Et₂AlH were both inactive without the addition of Y(CF₃CO₂)₃. This result produces evidence for the fact that Y(CF₃CO₂)₃ took part in the forming of active species.

Character of the Y—Al—PO Catalyst System

The UV spectrum of PTHF, prepared by the reaction of the polymerization system with C₆H₅ONa—THF, is shown in Figure 6. The characteristic absorbance of Pho- appeared at $\lambda_{max} = 279$ nm, and this indicated that the Y—Al—PO system had the cationic feature.

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