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## **Polymerization of 1,2-Epoxydes Initiated by Tetraalkyl Aluminates.\* I. Polymerization of Ethylene Oxide in the Presence of Sodium Tetrabutyl Aluminate**

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### **ABSTRACT**

The polymerization of ethylene oxide (EO) initiated by  $\text{NaAlBu}_4$  is shown to proceed upon initial complex formation between monomer and initiator. In polymerization in toluene a high order of the kinetic equation with respect to initiator was found, indicating that chain propagation proceeds on dimers and trimers of the active center. An induction time of polymerization in THF is observed. It is necessary to reach a specific concentration of the  $\text{NaAlBu}_4$ .EO complexes which take part in the polymerization process. The wide molecular weight distribution, the high effectivity coefficient (initiation efficiency), and the polymerization rate increase with polymer yield are evidence of a polycentric polymerization mechanism.

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\*Dedicated to Prof Dr B. L. Erusalimsky on the occasion of his 70th birthday.

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"Ate" complexes with aluminum as the central atom (aluminates) are capable of initiating the polymerization of vinyl [1], diene [2], and cyclic [3] monomers. Due to their large solubility in hydrocarbons (especially  $\text{NaAlBu}_4$ ), they offer favorable possibilities for studying the specific solvation of alkali and alkaline-earth metal cations by electron donor agents. Thus, tetrahydrofuran (THF) was found to form two types of complexes with  $\text{NaAlBu}_4$ , with 1:1 and 4:1 stoichiometry, respectively [4], the ethereal oxygens being coordinated to the sodium counterion and not to the central aluminum atom [5].

The aim of the present communication is to summarize our results on the mechanism of  $\text{NaAlBu}_4$ -initiated polymerization of another cyclic monomer-ethylene oxide. In several cases, experiments were also carried out with  $\text{NaAlEt}_4$  and  $\text{Ca}(\text{AlEt}_4)_2$ . It is known that, in spite of its lower basicity, EO exceeds THF in solvation capacity with respect to alkali metal counterions, presumably due to the steric factor [6]. This favors the formation of an intermediate complex in the interaction between alkali aluminates and EO even in THF solutions. Thus, in the proposed reaction scheme for the alkylation of epoxides by alkali aluminates, the participation of an intermediate complex of the type  $\text{EO} \cdots \text{M}^+\text{AlR}_4$  was assumed [7]. The alkylation reaction actually represents the initial step, viz., the initiation of EO polymerization. Due to the high strain in the triatomic monomer ring, the formation of products of higher molecular weight can be further expected, all the more as it was already shown by Stewart [8] that calcium and magnesium aluminates of the general formula  $\text{M}^{2+}(\text{Al}(\text{OPr})_4)_2$  initiated the polymerization of EO.

## EXPERIMENTAL

All experiments were carried out in vacuo ( $10^{-5}$  torr) by using a high vacuum line technique as described elsewhere or in an atmosphere of absolutely pure and dry argon using sealed glass systems equipped with break seals. Sodium aluminates,  $\text{NaAlBu}_4$ , and  $\text{NaAlEt}_4$  were prepared following the procedure of Frey [9] by heating the respective trialkylaluminum derivative with a sodium dispersion (excess of metal) for 2 to 3 h at  $110^\circ\text{C}$  in toluene.  $\text{Ca}(\text{AlEt}_4)_2$  was prepared as described in Ref. 10. The products obtained were analyzed for aluminum and sodium by complexometric titration with EDTA and back titration of the 0.1 N HCl excess with 0.1 N NaOH.

Ethylene oxide (Fluka) was evacuated, dried over calcium hydride, and distributed in vacuo into ampules equipped with break seals. The usual purification procedure for solvents was applied, with toluene, THF, and n-hexane being refluxed over a sodium-potassium alloy, rectified, and evacuated immediately afterward.

Polymerization was carried out in vacuo in thick-walled glass ampules immersed in a thermostated liquid. After the reaction, solvent and unreacted monomer were removed by vacuum distillation and the polymer was dried in vacuo to constant weight. In order to eliminate catalyst inclusion, the polymer was dissolved in water, salted out with NaCl, and extracted with chloroform.

The average molecular weights were determined on a Knauer vapor pressure apparatus, and the viscometric molecular weights were calculated according to

$$[\eta] = 3.97 \times 10^{-4} M^{0.686} \quad [11]$$

using data for benzene at 25°C.

IR spectra of the reaction mixtures in NaAlBu<sub>4</sub>-EO were recorded in thermostated cells in the temperature range -60 and +20°C on a Carl Zeiss Jena Spectrometer UR-20 (NaCl cells with path lengths of 0.1 and 0.25 cm).

Conductivity measurements of NaAlBu<sub>4</sub> solutions in toluene in the presence of small amounts of EO were carried out in a thermostated cell provided with platinum electrodes (cell constant, 0.009 cm<sup>-1</sup>) with the aid of a TESLA BM 509 automatic capacitance bridge.

## RESULTS AND DISCUSSION

### 1. Complex Formation between EO and NaAlBu<sub>4</sub>

In order to get an idea about the nature of the interaction between EO and initiator, the IR spectra of equimolar EO-NaAlBu<sub>4</sub> reaction mixtures in toluene were recorded at -50°C. As a result of the interaction with NaAlBu<sub>4</sub>, the band at 866 cm<sup>-1</sup> of the C-O-C asymmetric stretching vibrations in the EO ring shifted to 873 cm<sup>-1</sup>, which is an indication of complex formation. This is most probably due to coordinative bonding of the oxygen atoms to the sodium counterions rather than to the central aluminum atoms. This assumption is supported by the results of Day on the structure of NaAlBu<sub>4</sub> complexes with THF [5], as well as by reference to IR spectra of equimolar EO-AlBu<sub>3</sub> mixtures recorded in the course of our studies. In the latter case the spectrum of EO was similarly affected by the aluminum compound but the change was appreciably smaller, the C-O-C band shifting only to 869 cm<sup>-1</sup>; i.e., as expected, the interaction of EO with group III metals was weaker than with alkali metals.

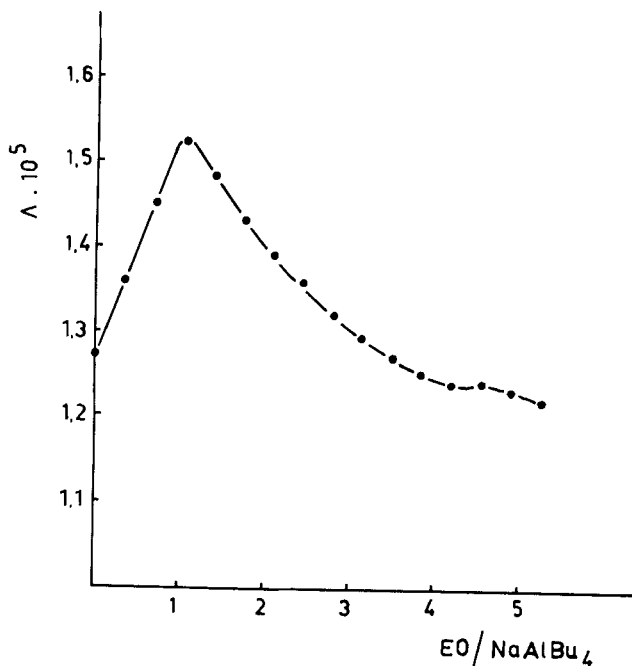


FIG. 1. Conductivity measurements at different EO/NaAlBu<sub>4</sub> ratios in toluene at 20°C. [NaAlBu<sub>4</sub>] = 0.27 mol/L.

The interaction between NaAlBu<sub>4</sub> and EO was confirmed by equivalent conductivity measurements of NaAlBu<sub>4</sub> solutions in toluene taken at gradual increases of the EO/NaAlBu<sub>4</sub> ratio (Fig. 1). Two extremes in the curve at different EO/Na ratio values, the maximum at EO/Na = 1 and the inflection at EO/Na = 4, proved the formation of two types of complexes with the corresponding stoichiometry.

It should be noted that the complexes formed were relatively stable, since the band at 873 cm<sup>-1</sup> can also be registered even at 20°C without a tendency to shift in direction to the band at 866 cm<sup>-1</sup> which is characteristic of free EO.

Mixtures of approximately equimolar amounts of NaAlBu<sub>4</sub>, THF, and EO showed in the IR spectrum the formation of mixed complexes. Thus, the addition of EO to a previously formed NaAlBu<sub>4</sub>.THF complex resulted in an increase of the ratio between free and bound THF (Fig. 2).

A certain part of the THF molecules was obviously expelled from the coordination shell of the sodium counterions by EO molecules, in

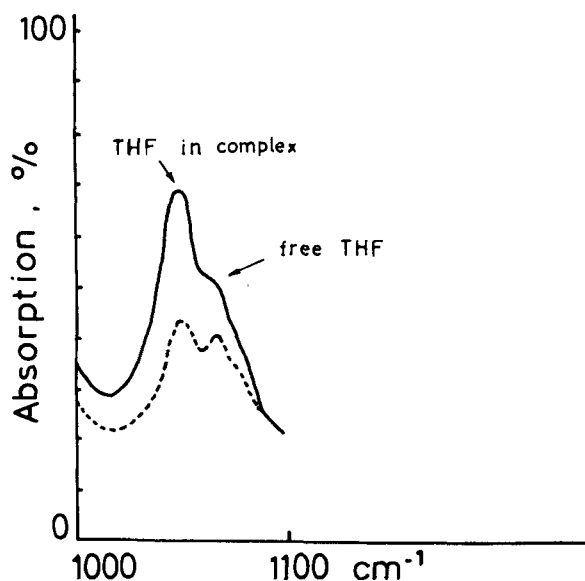


FIG. 2. IR spectra of  $\text{NaAlBu}_4$ -THF-toluene solutions at  $20^\circ\text{C}$ : (—)  $\text{THF}/\text{NaAlBu}_4 = 1$ ,  $[\text{NaAlBu}_4] = 0.27 \text{ mol/L}$ ; (---) after adding equimolar amount of EO,  $[\text{NaAlBu}_4] = 0.15 \text{ mol/L}$ .

agreement with the greater solvation power of EO in comparison with THF, as reported by Hogen-Esch [6].

## 2. EO Polymerization in Toluene

Yield vs time plots made under equal conditions for different initiator and monomer concentrations are presented in Figs. 3 and 4. Kinetic data computed according to the differential method produced the following equation for the apparent polymerization rate in toluene:

$$R_p = k[\text{In}]^{2.8}[\text{M}]$$

The high order of the kinetic equation with respect to the initiator can be explained by assuming that the polymer chain growth proceeds on associates (predominantly trimers of the "ate" complex). This assumption is confirmed by the aggregation of  $\text{NaAlBu}_4$  in cyclohexane (from dimers to pentamers, depending on concentration) as previously

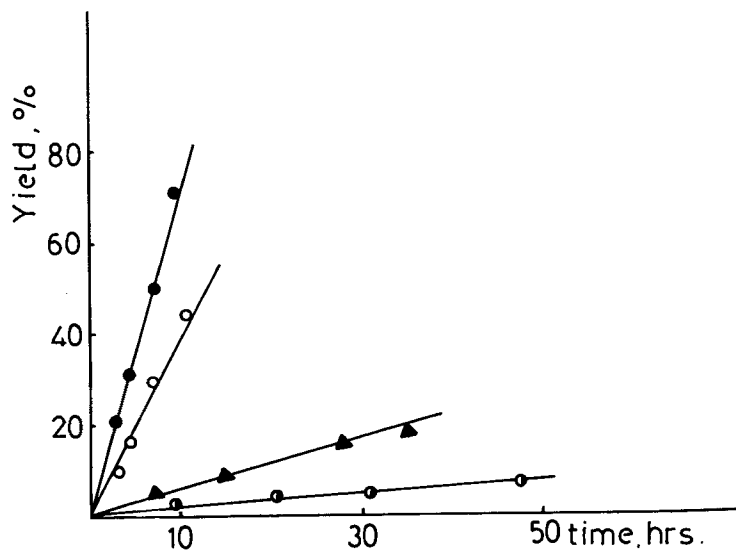


FIG. 3. Polymerization of EO in toluene at different initiator ( $\text{NaAlBu}_4$ ) concentrations: ( $\bullet$ ) 0.075 mol/L, ( $\circ$ ) 0.06 mol/L, ( $\blacktriangle$ ) 0.031 mol/L, ( $\circ$ ) 0.018 mol/L.  $[\text{EO}] = 7.7$  mol/L;  $T = 15^\circ\text{C}$ .

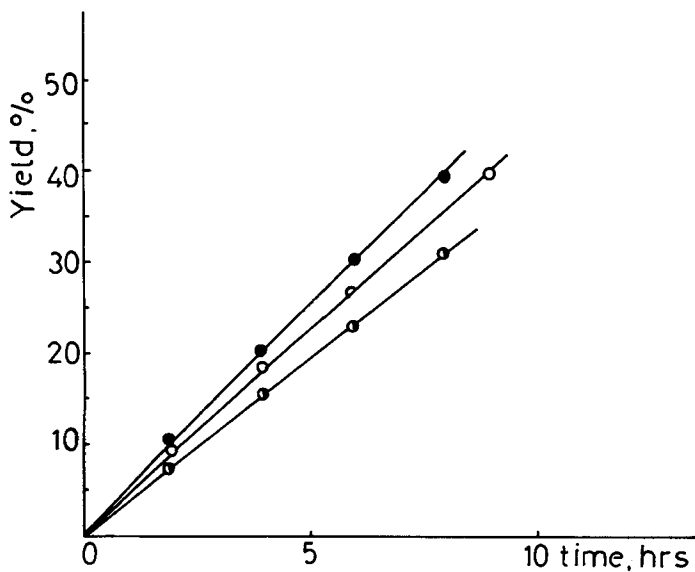


FIG. 4. Polymerization of EO in toluene at different monomer concentrations: ( $\bullet$ ) 4.8 mol/L, ( $\circ$ ) 6.45 mol/L, ( $\bullet$ ) 3.2 mol/L.  $[\text{NaAlBu}_4] = 0.052$  mol/L;  $T = 15^\circ\text{C}$ .

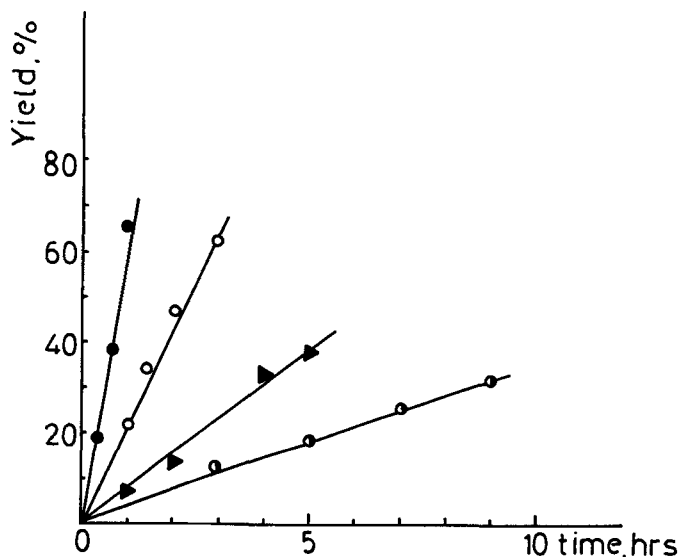


FIG. 5. Polymerization of EO in toluene at different reaction temperatures: (●) 69°C, (○) 49.3°C, (▲) 36°C, (○) 20°C.  $[\text{NaAlBu}_4] = 0.045 \text{ mol/L}$ ;  $[\text{EO}] = 7.7 \text{ mol/L}$ .

demonstrated [12], and by our studies on  $\text{NaAlBu}_4$  association in benzene carried out by the aid of the vapor pressure method.

In the concentration range from 0.07 to 0.33 mol/L the aluminate was found to form trimeric species exclusively. Acceleration of the polymerization process was observed on raising the temperature (Fig. 5). A value of  $12 \pm 1 \text{ kcal/mol}$  was derived for the effective activation energy in the range between 15 and 70°C.

Table 1 presents molecular weight and catalyst efficiency data for the polymerization in toluene.

The effectivity coefficient  $F = (x_p[M_o]) / ([\text{In}]\bar{P}_n)$  can be used as a measure of the degree to which the coordination bonds of aluminum are involved in the process of monomer incorporation. An alternative explanation for the high values of  $F$  is to take into account a chain transfer process; the probability for this, however, is very small.

At polymerization temperature of 15°C, as well as at higher temperatures in experiments of lower conversion, the effectivity coefficients were less than unity, the molecular weight distribution being relatively narrow, which is indicative of chain growth on a single coordination of aluminum. At elevated temperatures,  $F$  reached values up to 2-3 for sodium and up to 5-6 for calcium, but did not exceed the total number of coordination bonds in the initiator molecule. Presumably, propaga-



TABLE 1. Molecular Weights and Initiator Efficiencies in the Polymerization in Toluene

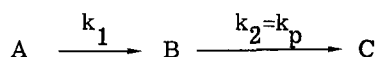
[In], mol/L	[EO], mol/L	T, °C	Reaction time, h	Conversion, %	$\bar{M}_v$	$\bar{M}_n$	$\bar{M}_v/\bar{M}_n$	F
0.019	7.7	15	24	100	9,000	8,450	1.1	0.34
0.086	7.7	15	24	100	-	11,200	-	0.35
0.047	7.0	15	240	91	-	12,200	-	0.54
0.029	5.5	15	240	72	-	11,250	-	0.75
0.07	7.7	22	24	65	2,300	1,800	1.28	1.64
0.0036 <sup>a</sup>	7.8	22	24	12.7	-	2,050	-	5.9
0.0036 <sup>a</sup>	2.2	22	24	21	-	2,500	-	2.3
0.045	7.7	36	2	13.4	-	2,400	-	0.41
0.045	7.7	36	7	52	-	3,300	-	1.60
0.041	7.7	50	1 h 20 min	18	-	1,800	-	0.84
0.041	7.7	50	2 h 10 min	27	-	1,800	-	1.28
0.041	7.7	50	3 h 20 min	79	-	2,900	-	2.34
0.041	7.7	50	4 h 20 min	93	-	3,000	-	2.62
0.041	7.7	50	6	97	11,300	3,900	2.9	2.09
0.12 <sup>b</sup>	8.9	50	7	38.4	8,000	-	-	-

<sup>a</sup>Initiator  $\text{Ca}(\text{AlEt}_4)_2$ <sup>b</sup>Initiator  $\text{NaAlEt}_4$

tion on the different coordination bonds of aluminum did not proceed simultaneously. This explanation is in agreement with the observed broadening of molecular weight distribution which follows an increase of F.

### 3. EO Polymerization in THF

An induction period was observed in the polymerization in THF which was longer for low initial initiator concentration. The form of the yield vs time curves (Fig. 6) suggests a succession of reactions of the following type:



Most probably a complex between  $\text{NaAlBu}_4$  and EO was initially formed (B), the monomer expelling some of the THF molecules from the solvation shell of the sodium ion:

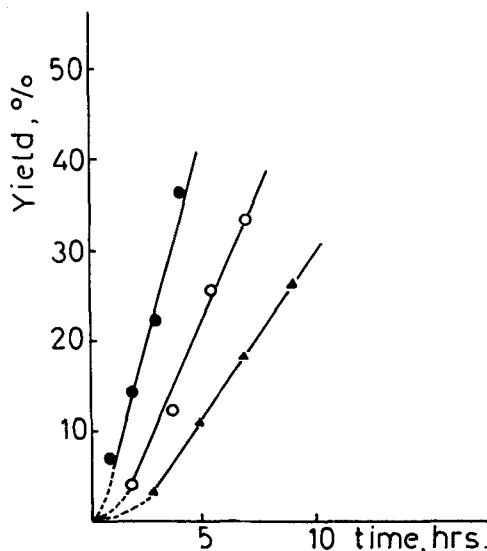
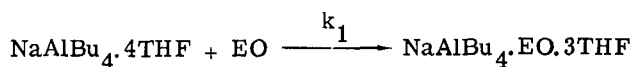


FIG. 6. Polymerization of EO in THF at different initiator concentrations: (●) 0.054 mol/L, (○) 0.036 mol/L, (▲) 0.028 mol/L.  $[\text{EO}] = 7.7 \text{ mol/L}$ ;  $T = 31^\circ\text{C}$ .

TABLE 2. Experimental Conditions and Results for EO Polymerization in THF using NaAlBu<sub>4</sub> as the Initiator

[In], mol/L	[EO], mol/L	T, °C	Conversion, %	t, s	k <sub>p</sub> × 10 <sup>4</sup>
0.036	7.7	20	0.0337	6,800	1.4
0.036	7.7	20	0.085	17,600	1.4
0.036	7.7	20	0.188	32,000	1.8
0.028	7.7	31	0.038	3,800	3.64
0.028	7.7	31	0.106	11,000	3.64
0.054	7.7	31	0.072	3,600	3.83
0.054	7.7	31	0.139	7,200	3.85
0.054	7.7	31	0.219	10,800	4.24
0.054	7.7	31	0.360	14,400	5.74
0.036	7.7	46	0.041	1,000	11.6
0.036	7.7	46	0.104	2,000	15.2
0.036	7.7	46	0.235	4,600	16.1
0.036	7.7	46	0.392	8,200	16.9
0.036	7.7	46	0.571	11,800	19.9

$$a_t = \tau - \tau_{\text{ind}}$$

Table 2 shows that the first-order equation with respect to both monomer and initiator,  $\ln M_0/M_\tau = k_p [c^*] \tau$ , as indicated by the kinetic curves when using the integral method, holds only for relatively low yields ( $k_p = \text{constant}$ ). On raising the yield, the polymerization rate increased, which is presumably due to an increase in the number of active centers.

Kinetic curves taken at different polymerization temperatures are given in Fig. 7. Reduced induction times were observed at elevated temperature, proving that the reaction of the initial complex formation between  $\text{NaAlBu}_4$  and EO ( $A \rightarrow B$ ) was intensified. The polymerization rate increased uniformly up to about  $46^\circ\text{C}$  but dropped down at higher temperatures as seen from the experiments carried out at  $60^\circ\text{C}$ . This is probably due to certain changes in the polymerization mechanism, e.g., changes related to the formation and decomposition of the activated complex B. A value of  $16.5 \pm 1$  kcal/mol for the effective activation energy was determined from the linear plot of  $\ln k$  vs  $1/T$  in the region below  $46^\circ\text{C}$ . Results from the initiator effectivity and molecular weight determinations of samples prepared under different polymerization conditions in THF are presented in Table 3.

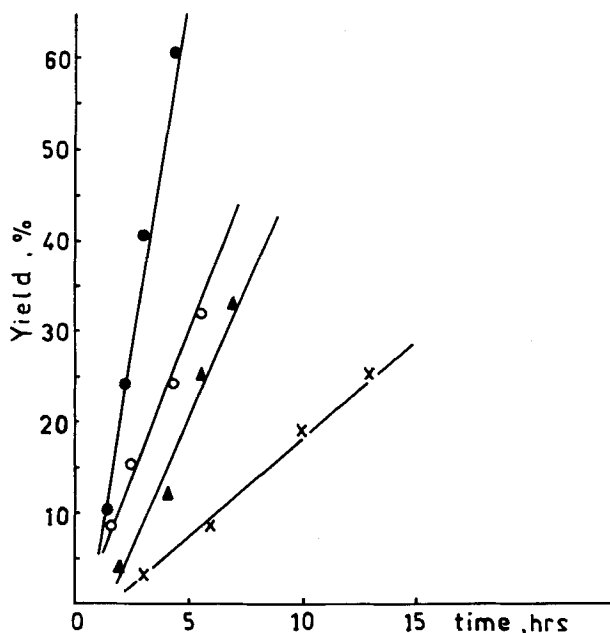


FIG. 7. Polymerization of EO in THF at different temperatures: (○)  $60^\circ\text{C}$ , (●)  $46^\circ\text{C}$ , (▲)  $31^\circ\text{C}$ , (×)  $21^\circ\text{C}$ .  $[\text{NaAlBu}_4] = 0.036$  mol/L;  $[\text{EO}] = 7.7$  mol/L.

TABLE 3. Molecular Weights and Initiator Efficiencies in the Polymerization in THF

[In], mol/L	[EO], mol/L	T, °C	Reaction time, h	Conversion, %	$\bar{M}_v$	$\bar{M}_n$	$\bar{M}_v/\bar{M}_n$	F
0.06	5.8	20	144	94	6,300	2,600	2.4	1.54
0.075	7.2	20	24	78.4	5,200	2,000	2.6	1.7
0.0046 <sup>a</sup>	5.8	20	24	27.4	-	3,200	-	4.7
0.028	7.7	31	24	100	14,400	4,450	3.2	2.72
0.036	7.7	31	7	33.4	3,000	3,000	1	1.05
0.054	7.7	31	4	37	-	1,800	-	1.29
0.036	7.7	46	5.5	73.4	5,500	4,020	1.37	1.72
0.04	7.7	50	8	65	7,700	-	-	-
0.036	7.7	60	4.5	24	9,000	2,400	3.75	0.94

<sup>a</sup>Initiator Ca(AIEt<sub>4</sub>)<sub>2</sub>.

The number-average molecular weights of the polymers obtained are in a relatively narrow range from 2000 to 4500. By raising the initial EO/In ratio, the degree of conversion, and the polymerization temperature, a slight increase in the molecular weight was observed. In most cases the molecular weight distribution was relatively broad, which was ascribed to the high effectivity coefficients.

#### 4. EO Polymerization in n-Heptane

The polymerization of EO in n-heptane proceeds at a reduced rate in comparison with the processes in toluene or THF (Fig. 8). The reason for this is probably the separation of the polymer in solid-phase precipitation polymerization. No induction period was observed as in the polymerization in toluene. Table 4 shows the molecular weight and the initiator efficiency dependence on the reaction conditions.

In contrast to polymerization in solution (in toluene or THF), the polymers prepared by precipitation polymerization in n-heptane had a broader molecular weight distribution. The polymerization rate increased uniformly with temperature.

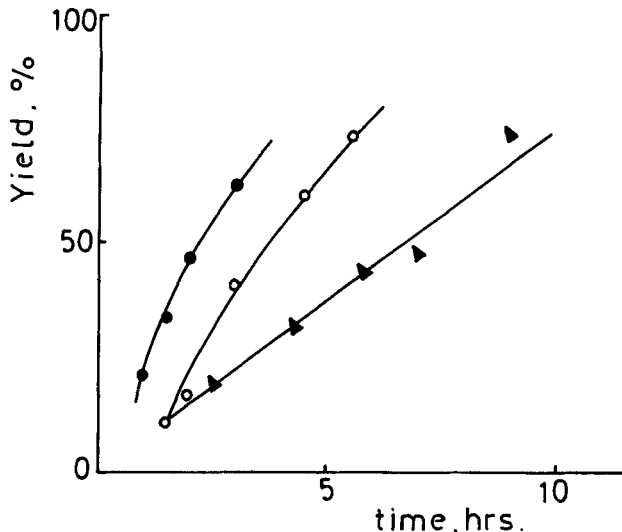


FIG. 8. Comparison between yield vs time plots in the polymerization of EO initiated by  $\text{NaAlBu}_4$  in different solvents: (○) THF, (●) toluene, (▲) n-heptane.  $[\text{NaAlBu}_4] = 0.04 \text{ mol/L}$ ;  $[\text{EO}] = 7.7 \text{ mol/L}$ ;  $T = 50^\circ\text{C}$ .

TABLE 4. Molecular Weights and Initiator Efficiencies in the Polymerization in n-Heptane

[In], mol/L	[EO], mol/L	T, °C	Reaction time, h	Conversion, %	$\bar{M}_v$	$\bar{M}_n$	$\bar{M}_v/\bar{M}_n$	F
0.04	7.7	50	4 h 20 min	32	-	3,000	-	0.93
0.04	7.7	50	5 h 50 min	44	-	3,250	-	1.15
0.04	7.7	50	7	48	-	2,800	-	1.45
0.04	7.7	50	9	75	14,500	4,000	3.62	1.59
0.09	8.9	20	24	80	5,200	2,300	2.26	1.5
0.12	6.4	20	24	71	4,700	2,100	2.24	0.79
0.05	9.7	20	48	87	6,600	1,800	3.66	4
0.09	8.3	20	24	95	-	1,400	-	2.75
0.07	8.9	20	24	87	5,100	2,500	2.36	1.95

## CONCLUSIONS

The polymerization of EO initiated by  $\text{NaAlBu}_4$  in certain aspects differs from conventional EO polymerization. Some of its typical features are:

1. The molecular weight dependence on polymer yield is not clearly defined.
2. High values of effectivity coefficients, usually higher than unity but not exceeding the coordination number of aluminum in the "ate" complex.
3. Different kinetic behavior in different solvents. An induction period is observed in THF, while in toluene the kinetic equation is of a higher order with respect to initiator.

The anomalies listed for the polymerization process suggest a relatively complicated mechanism including an initial complex formation between monomer and initiator which is characteristic of ionic-coordination polymerization. EO forms a complex in the solvation shell of the sodium ion while incorporation most probably proceeds in the coordination sphere of aluminum. This can adequately explain the high effectivity coefficients as well as the tendency of the chain growth to be limited within a fixed molecular weight. Complex formation with EO is hindered in THF because of association with the solvent molecules. The polymerization process does not start immediately after the monomer and the initiator come into contact. It appears necessary that a certain stationary concentration of complexes in which EO molecules take part must first occur in order to induce polymerization progress to an appreciable extent, and this explains the induction period for polymerization in THF. The high order with respect to initiator in the kinetic equation of polymerization in toluene can be explained by the aggregation of  $\text{NaAlBu}_4$  in nonpolar solvents as demonstrated in the present work and previously by Day et al. The addition of EO does not cause decomposition of the associates, but results only in complex formation. Hence, polymer-chain growth proceeds on "ate" complex associates and not on ion pairs as is the case with polymerization in THF.

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