Preparation of Polyether
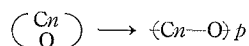
Junji FURUKAWA and Takeo SAEGUSA

(Oda Laboratory)

Polyether is prepared by the ring opening polymerization of cyclic ether which can be generalized as follows.

$$\left(\begin{array}{c} Cn \\ O \end{array} \right) \longrightarrow \left(Cn\!-\!O \right) p$$

In this article, the latest work in our laboratory on the preparation of polyether is reviewed.

In the acetaldehyde polymerization, we found that a controlled amount of water exercised a profound effect on the catalytic activity and stereoregularity of triethylaluminum catalyst.

By polymerizig acetone with aluminum alkyl-titanium chloride-salt ($CaCl_2$, Na-acetate or Mg-acetate) system under propylene atmosphere, we obtained a stable and crystalline block copolymer of acetone and propylene whose better parts consisted of acetone unit.

In the polymerization of propylene oxide, we could prepare an optically active polymer from the recemic (optically inactive) monomer by using catalytic systems of zinc alkyl and an optically active alcohol

For the ring opening polymerizations of four- and five-membered cyclic ethers, *i.e*, 3,3-bis(chloromethyl)oxacyclobutane and tetrahydrofuran, we discovered some new catalytic systems. They are Lewis acid-cocatalyst and aluminum alkyl-cocatalyst systems The behaviors of these catalytic systems are explained in terms of cationic polymerization

INTRODUCTION

Polyether can be expressed by the general formula, $(Cn\!-\!O)p$, whose main chain consists of ether linkage. Among the preparative methods of polyether, the ring opening polymerization of cyclic ether is the most familiar and suitable one, which can be generalized as follows.

$$\left(\begin{array}{c} Cn \\ O \end{array} \right) \longrightarrow \left(Cn\!-\!O \right) p$$
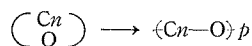
The monomer of n = 1 is carbonyl compound, whose polymerization differs from that of usual cyclic ethers in the electronic character, *i.e.*, the polymerizations of aldehyde and ketone proceed through the transformation of π-bond to σ-bond, while those of cyclic ethers are not concerned in such a change. The polymer of formaldehyde is the most important among the polymers of carbonyl compounds. Polymers of other aldehydes and of acetone are not so stable as to be used in practical application, although the possibility of their stabilization has not been completely excluded.

---

* 古川 淳二, 三枝 武夫

As the cyclic ether monomers, alkylene oxides (n=2), oxacyclobutane and its derivatives (n=3), tetrahydrofuran (n=4), and tetrahydropyran (n=5) have been employed. Among their polymers, polyalkylene oxides and 3,3-bis(chloromethyl)oxacyclobutane are being produced commercially. Studies on their polymerization catalysts and mechanisms as well as their polymers are now advancing.

In addition to the homopolymerization, the copolymerization of two different cyclic ethers is one of very interesting problems in high polymer synthesis, which may bring about new useful copolymers and may offer valuable information on the polymerization mechanism and the reactivities of these cyclic ethers.

In this article, the latest works in our laboratory on the ring-opening polymerization of cyclic ether is reviwed.

I POLYMERIZATIONS OF ACETALDEHYDE AND ACETONE

I-1. Polymerization of Acetaldehyde

The conversion of acetaldehyde into the linear polyacetal was first discovered independently by Letort[1] and by Travers[2]. They found this polymerization when they froze acetaldehyde under high vacuum at an extremely low temperature in order to degas it. This freezing polymerization is an unique type of polymerization, and its mechanism has been studied mainly by Letort and his coworkers[3~14].

The main chain of polyacetaldehyde molecule consists of psudo asymmetric carbon atoms, and hence, three types of the polymer can be assumed according to the stereoregularity of the asymmetric carbon atoms. They are isotactic, syndiotactic and atactic polymers. The polymer of the freezing polymerization was amorphous and was assumed to be of atactic structure.
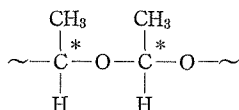
$$\sim\!\!-\!\!\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\!-\!\!O\!\!-\!\!\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}\!\!-\!\!O\!\!-\!\!\sim$$

Table 1. Polymerization of acetaldehyde

Method and catalyst	Type of polymer	Reference
Freezing method	Atactic	1—14
γ-ray irradiation	Atactic	15
Persulfate	Atactic	16
Lewis acid	Atactic	16, 17
Amine-polyphosphonic acid	Atactic	18
Trialkylphosphine	Atactic	19
Alumina	Atactic	20—22
Silica	Atactic	20
Organometallic compound	Isotactic	23—28
Metal alkoxide	Isotactic	18, 25—27
Alumina-diethylzine	Stereoblock	29
Partly hydrolyzed aluminum alkoxide	Stereoblock	30, 31

After about twenty years since the discovery of the freezing method, several procedures of the polymerization have been reported. Some of them gave the isotactic (crystalline) polymer which was quite different from the atactic (amorphous) one in physical properties. The syndiotactic polymer has not been prepared as yet. The polymerization methods of acetaldehyde are summarized in Table 1.

It is interesting that the stereoblock polymer consisting of isotactic and atactic blocks is produced by the last two catalyst systems[29,30] which may be regarded to be composed of isotactic and atactic catalysts.

Aluminum alkyl is a stereospecific catalyst giving isotactic polymer. The effect of water on its catalytic activity and stereospecificity is of interest. The reaction of triethylaluminum and a controlled amount of water is supposed as follows*.

$$Al(C_2H_5)_3 + H_2O \longrightarrow (C_2H_5)_2AlOH + C_2H_6 \uparrow$$
$$(C_2H_5)_2AlOH + Al(C_2H_5)_3 \longrightarrow (C_2H_5)_2AlOAl(C_2H_5)_2 + C_2H_6 \uparrow$$
$$(C_2H_5)_2AlOAl(C_2H_5)_2 + H_2O \longrightarrow (C_2H_5)_2AlOAl(C_2H_5)OH + C_2H_6 \uparrow$$
$$(C_2H_5)_2AlOAl(C_2H_5)OH + Al(C_2H_5)_3 \longrightarrow (C_2H_5)_2AlOAl(C_2H_5)OAl(C_2H_5)_2 + C_2H_6 \uparrow$$
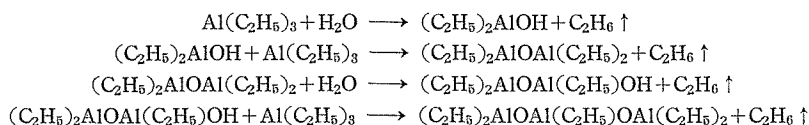
etc.

The product of an ideal reaction between one mole of $Al(C_2H_5)_3$ and one and a half moles of water is considered to be alumina which is a catalyst of the
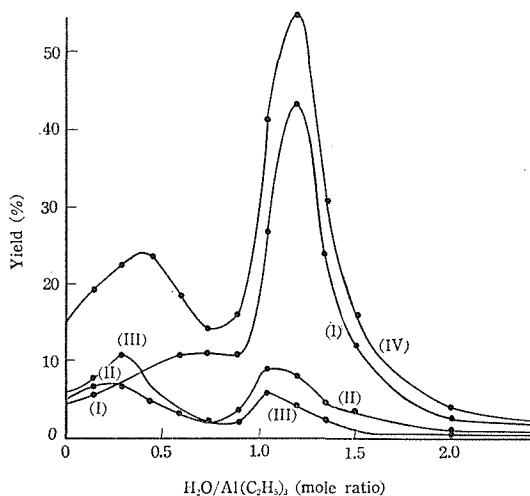

Fig. 1. Polymerization of acetaldehyde by $Al(C_2H_5)_3$-water system.
(Effect of amount of water: Acetaldehyde, 5 ml. (0.089 mole);
$Al(C_2H_5)_3$, 1 mole %; $(i\text{-}C_3H_7)_2O$, 0.0089 ml.; $(i\text{-}C_3H_7)_2O$+hexane,
8 ml.; Polymerization at −78°C. for 21.5 hrs.)
   Curve-I: Yield of methanol soluble fraction.
   Curve-II: Yield of chloroform soluble fraction.
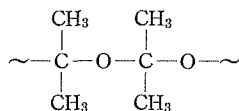   Curve-III: Yield of insoluble fraction.
   Curve-IV: Total yield.

* The reacteon between triethylaluminum and water will be too complicated to be described in such a simple expression. But the catalytic function of the product may be regarded as that of a mixture of the species given in the formulae.

atactic polymerization. We made a set of polymerizations using catalytic systems of the reaction products of $Al(C_2H_5)_3$ and varying amount of water. The total polymer was separated by solvent extraction into three fractions; the methanol-soluble fraction (atactic polymer), the chloroform-soluble but methanol-insoluble fraction (a mixture of stereoblock and isotatic polymers) and the chloroform-insoluble fraction (isotactic polymer). Figure 1 shows the effect of the amount of water upon the yields of the three fractions. The first peak of the curve IV (total yield) at $H_2O/Al(C_2H_5)_3 = 0.4$ is ascribed to the peaks of the curves II and III. At this point the average composition of the catalyst system will be near to $(C_2H_5)_2$-$AlOAl(C_2H_5)_2$*, which has been knwn to be more stereoselctive than $Al(C_2H_5)_3$ itself. As the amount of water increases, the yield of the atactic fraction (curve I) increases. This can be explained by assuming that the character of the $Al(C_2H_5)_3$-water system gradually approaches to that of alumina. The percentage of the atactic fraction exceeds 70% when the ratio of $H_2O/Al(C_2H_5)_3$ is above 1.2.

I-2. Polymerization of Acetone

The polymerization of acetone is more difficult than that of acetaldehyde. Only the molecular ray method at an extremely low temperature[33] and gamma ray irradiation[34] have been found to polymerize acetone giving rather unstable rubbery polymer. We[35] succeeded in the preparation of a crystalline polymer of acetone having comparative stablity by using a modified Ziegler catalyst in the presence of α-olefin.

The polymerization was carried out with the $Al(C_2H_5)_3$-$TiCl_3$ (or $TiCl_4$)-salt systems under α-olefin atmosphere at $-78°C$. As the third component of the catalyst system, calcium chloride, sodium acetate and magnesium acetate were employed. The presence of these salts was essential for the acetone polymerization. Without these salts, there occurred only the Ziegler type polymerization of olefin. A crystalline polymer having a melting point of $58 \sim 60°C$. was obtained by the polymerization under propylene atmosphere, which was found· to be a block copolymer of acetone and propylene. But the elementary analysis indicated that the better part of the block copolymer consisted of the acetone unit, and the resolution of the X-ray pattern gave a crystalline structure of helical chains consisting of the dimethyloxymethylene units (ketal linkages) with 7_2 symmetry.

$$\sim\!-\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CH}_3}{|}}{\text{C}}}\!-\!\text{O}\!-\!\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{CH}_3}{|}}{\text{C}}}\!-\!\text{O}\!-\!\!\sim$$

An example of the elementary analysis of the polymer was as follows: $C = 65.0\%$, $H = 10.5\%$, $O = 24.4\%$. From these values the content of the acetone unit was calculated, which was 83.7 mole % (from carbon content) or 84.7 mole % (from oxygen content). When the polymer was treated with hydrochloric acid-

---

* The species of $(C_2H_5)_2AlOAl(C_2H_5)_2$ is an ideal product at $H_2O/Al(C_2H_5)_3 = 0.5$. Because of the heterogenity of the reaction system and the inherent impurity of triethylaluminum derived from its dealkylation, oxidation and hydrolysis, the average composition of $H_2O/Al(C_2H_5)_3 = 0.4$ will be near to $(C_2H_5)_2AlOAl(C_2H_5)_2$.

2, 4-dinitrophenylhydrazin solution, it went into the solution and yellow precipitates were formed. The precipitate had a melting point of 127°C. which showed no depression with the authentic sample of acetone-2, 4-dinitrophenylhydrazone. This observation indicates that the acetone units of the polymer exist as dimethyloxymethylene (ketal) units which split into the acetone monomer by acid-hydrolysis. The ketal linkage was also indicated by the infrared spectrum which had absorptions at 1148, 1113 and 1062 cm^{-1}. of ν_{c-o-c} mode. The bands of hydroxyl and carbonyl groups were not observed.

The crystalline polymer of acetone was soluble in alcohol, chloroform and other polar solvents. A transparent film could be casted from the chloroform solution, which was oriented by cold drawing. The polymer was considerably stable, and no appreciable decomposition was observed when heated at 200°C. for a while. The X-ray fiber diagram, in which more than fifty reflections were observed, was consistent with the following unit cell;

$$a = b = 14.65A, \quad c = 10.22A, \quad N = 28, \quad \text{space group } P\bar{4}.$$

II. POLYMERIZATION OF ALKYLENE OXIDE

II-1. Coordinate Anionic Catalyst

Alkylene oxide is polymerized by anionic, cationic and the so-called coordinate anionic catalysts. High molecular weight polymer can be produced only by the coordinate anionic catalyst. Many catalysts for the coordinate anionic polymerization have been found recently, which may be classified into two great groups. The first group contains metal alkyls, metal alkoxides, metal oxides, and their modified species. The second group includes the compounds of alkaline earth metals. The behaviors of these coordinate anionic catalysts have been studied by several groups of workers but is not fully elucidated as yet.

The systems of diethylzinc and an equivalent amount of water or alcohol

Table 2. Diethylzinc-water and diethylzinc-alcohol systems.

$Zn(C_2H_5)_2$—H_2O	
C_2H_5ZnOH	$\begin{array}{c} H \\ O \\ C_2H_5-Zn\diagup^{\diagdown}_{\diagdown\ O\diagup}Zn-C_2H_5 \\ H \end{array}$
$C_2H_5ZnOZnC_2H_5$	
$C_2H_5ZnOZnOH$	
$C_2H_5ZnOZnOZnC_2H_5$, etc.	
$Zn(C_2H_5)_2$—ROH	
C_2H_5ZnOR	$\begin{array}{c} R \\ O \\ C_2H_5-Zn\diagup^{\diagdown}_{\diagdown\ O\diagup}Zn-C_2H_5 \\ R \end{array}$
$ROZnOR$	$\begin{array}{c} R \\ O \\ RO-Zn\diagup^{\diagdown}_{\diagdown\ O\diagup}Zn-OR \\ R \end{array}$

which have been found in our laboratory[36,37] are counted among the most active catalysts for the alkylene oxide polymerization, whose behaviors are discussed in the following section.

II-2. Mechanisms of Diethylzinc-Water and Diethylzinc-Alcohol Systems

When diethylzinc is treated with water or alcohol, the compounds of Table 2 are assumed to be produced.
Probably these compounds exist in the associated form. These species have zinc-oxygen-zinc linkage as a common structure which is suggested to play an important role in the propagation step. The alkylene oxide monomer coordinated to zinc in these compound and is activated for the ring opening reaction. The alkoxyl or alkyl anion attached to zinc is assumed to induce the polymerization.

$$\overset{+}{C}H_2-\overset{+}{C}H_2$$

RO ·· O

Zn Zn

RO O OR

R
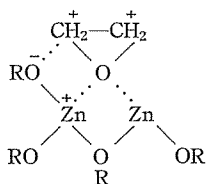
This assumption was partly comfirmed by the experiment of our laboratory, in which a particular alcohol like 9,10-dimethylolanthracene was used as the cocatalyst. The propylene oxide polymer prepared by dialkylzinc and the alcohol was shown by U. V. analysis to contain the anthracene alkoxyl fragment which was derived from the alcohol cocatalyst.

By using the catalyst system of diethylzinc and an optically active alcohol, an *optically active* polymer of propylene oxide was successfully prepared in our laboratory from the *optically inactive dl*-monomer[38] (see Table 3). It is interesting to note that the direction of the optical rotation of the obtained polymer changes according to the nature of solvent. This phenomenon has been observed by Price in the optically active polymer prepared from the *optically active* monomer.

Two possibilities may be assumed for the mechanism of stereoregulation with the diethylzinc-optically active alcohol systems. One is the indirect regula-

Table 3. Asymmetric induction in polymerization of propylene oxide.

Activator	Solvent for polymer	η_{sp}/C	$[\alpha]_D$ of polymer	
			in benzene	in chloroform
(+) Borneol	Toluene	5.63	$-5.9°$	$+7.4°$
(+) Borneol	Hexane	3.30	$-4.9°$	$+6.1°$
(+) Borneol	Benzene	3.65	$-3.7°$	$+2.5°$
(−) Menthol	Benzene	0.59	$-3.6°$	$+4.2°$

Polymerization : Propylene oxide, 0.5 mole ; solvent, 30-35 ml. ; at 80°C. ; at conversion, 17-30%.
Catalyst : Diethylzinc, 0.025 mole ; alcohol, 0.05 mole.
Polymer : Crystalline fraction, ca. 10% except for (−) menthol (2.7%).
Optical rotation : Measured in 1-3% solutions 10-15°C

tion by the alkoxyl group in the catalyst, i.e., the asymmetric center is trans-mitted successively from the asymmetric alkoxyl initiator through every propaga-tion step. Another possibility is the direct steric control by the asymmetric alkoxyl group in the catalyst, i.e., the coordination of the monomer is sterically controlled by the alkoxyl group of the catalyst.
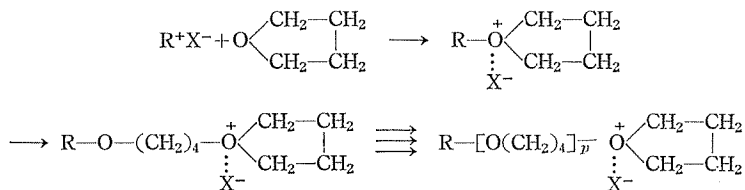
III. POLYMERIZATIONS OF FOUR AND FIVE-MEMBERED CYCLIC ETHERS

The ring-opening polymerizations of four and five-membered cyclic ethers have been known to be induced by reagents of cationic character. Among the four-membered cyclic ethers, 3,3-bis(chloromethyl)oxacyclobutane (BCMO) is the most important, especially from an industrial point of view. As the poly-merizable monomer of five-membered cyclic ethers, only tetrahydrofuran (THF) is known.

Recently we studied on the polymerizations of BCMO and THF and found some new catalytic systems for these polymerizations, which will be outlined in this section.
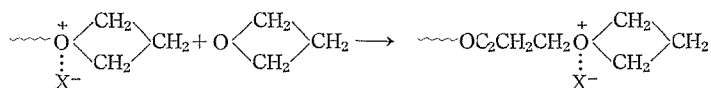
III-1. Lewis acid-Cocatalyst System

The polymerization of four-membered cyclic ethers is easily induced by sim-ple Lewis acid catalysts such as BF_3, its molecular complex compounds[39], while that of THF requires the so-called cocatalyst in addition to the Lewis acid catalyst[40]. As the cocatalyst in the THF polymerization, alkylene oxides, α-haloethers, benzotrichloride, ortho esters, acid chlorides, acid anhydrides, and hydrogen halides have been described[40]. The behaviors of these cocatalysts except hydrogen halides were considered to afford carbonium ion intermediates when they are brought into contact with the Lewis acid catalyst. The carbonium ion intermediate adds to the THF monomer giving the cyclic trialkyloxonium ion which is an initial active species of the propagation step of the cationic polymerization.

$$R^+X^- + O\!\!<^{CH_2-CH_2}_{CH_2-CH_2} \longrightarrow R-\overset{+}{\underset{\underset{X^-}{:}}{O}}\!\!<^{CH_2-CH_2}_{CH_2-CH_2}$$

$$\longrightarrow R-O-(CH_2)_4-\overset{+}{\underset{\underset{X^-}{:}}{O}}\!\!<^{CH_2-CH_2}_{CH_2-CH_2} \Longrightarrow R-[O(CH_2)_4]_{\overline{n}} \overset{+}{\underset{\underset{X^-}{:}}{O}}\!\!<^{CH_2-CH_2}_{CH_2-CH_2}$$

The propagation reaction which proceeds through the successive addition of the monomer to the oxonium end of growing polymer chain is very rapid, and the rate-determining step exists in the production of the first trialkyloxonium ion of cyclic structure.

The mechanism of the BCMO polymerization may be assumed to be similar to that of the unsubstituted oxacyclobutane (trimethylene oxide) for which a similar mechanism of the propagation reaction via cyclic trialkyloxonium ion intermediate was suggested[41].

$$\text{~}\overset{+}{O}\overset{CH_2}{\underset{CH_2}{\diagdown}}CH_2 + O\overset{CH_2}{\underset{CH_2}{\diagdown}}CH_2 \longrightarrow \text{~}OC_2H_2CH_2\overset{+}{O}\overset{CH_2}{\underset{CH_2}{\diagdown}}CH_2$$
$$\underset{X^-}{\vdots} \qquad\qquad\qquad\qquad \underset{X^-}{\vdots}$$

Recently we[42] found that the BCMO polymerization by Lewis acid catalyst was also much accelerated by the presence of alkylene oxide as the cocatalyst. As mentioned before, $BF_3 \cdot (C_2H_5)_2O$ alone can polymerize BCMO*, but propylene oxide and epichlorohydrin much enhance the catalytic reactivity of $BF_3 \cdot (C_2H_5)_2O$. Thable 4 shows the effect of alkylene oxide on the BCMO polymerization by Lewis acid catalyst.

Table 4. Polymerization of 3, 3-bis(chloromethyl)oxacyclobutane by Lewis acid-cocatalyst systems.
(Monomer, 0.025 mole ; CH_2Cl_2, 20 ml.)

Cocatalyst[a]	(mole)	Temp. (°C.)	Time (hrs.)	Conv (%)
Lewis acid : $BF_3 \cdot (C_2H_5)_2O$, 0.00125 mole				
None		−78	96	0
PO	0.00250	−78	48	95.6
ECH	0.00250	−78	24	95.8
Lewis acid : $SnCl_4$, 0.00250 mole				
None		0	96	0[b]
ECH	0.00125	0	24	91.7
Lewis acid : $AlCl_3$, 0 00250 mole				
None		0	48	0
ECH	0.00250	0	48	91.9

[a] PO=Propylene oxide, ECH=Epichlorohydrin.
[b] No polymer but an addition product of the monomer and $SnCl_4$ was produced.

The cocatalytic effects were manifested in the polymerization carried out at a lower temperature where the rate of polymerization without the cocatalyst was very small. Alkylene oxide also activates other Lewis acid catalysts such as $SnCl_4$ and $AlCl_3$ which are less active than $BF_3 \cdot (C_2H_5)_2O$ for the BCMO polymerization. Alkylene oxide as the cocatalyst may function to precede the BCMO monomer in the ring opening reaction which produces a carbonium ion intermediate*).
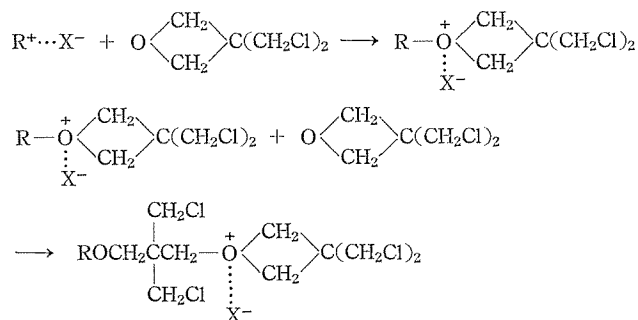
The addition of the carbonium ion thus produced to the BCMO monomer gives the trialkyloxonium ion of ring structure whose cleavage constitutes the initiation reaction of the polymerization,

$$\text{Lewis acid} + \text{Alkylene oxide} \longrightarrow R^+ \cdots X^-$$

---
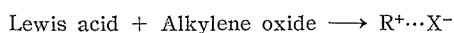
* It was reported that gaseous BF_3 did not polymerize BCMO in an exclusively dry system[45], but $BF_3 \cdot (C_2H_4)_2O$ does polymerize it in usual dry system.
*) Several possibilities may be assumed as to the production of carbonium ion intermediate in the reaction of Lewis acid and alkylene oxide. The formation of trialkyloxonium salt such as triethyloxonium borofluoride[44] which liberates ethyl cation is one of the possibilities, but simple cationic cleavage of epoxide ring by $BF_3 \cdot (C_2H_5)_2O$ or by $H^+[BF_3OH]^-$ can not be excluded.

$$R^{+}\cdots X^{-} + O\!\!\underset{CH_2}{\overset{CH_2}{<}}\!\!\!>\!\!C(CH_2Cl)_2 \longrightarrow R\!-\!\overset{+}{\underset{\vdots}{O}}\!\!\underset{CH_2}{\overset{CH_2}{<}}\!\!\!>\!\!C(CH_2Cl)_2$$
$$X^{-}$$

$$R\!-\!\overset{+}{\underset{\vdots}{O}}\!\!\underset{CH_2}{\overset{CH_2}{<}}\!\!\!>\!\!C(CH_2Cl)_2 + O\!\!\underset{CH_2}{\overset{CH_2}{<}}\!\!\!>\!\!C(CH_2Cl)_2$$
$$X^{-}$$

$$\longrightarrow ROCH_2\!\!\underset{CH_2Cl}{\overset{CH_2Cl}{C}}\!\!CH_2\!-\!\overset{+}{\underset{\vdots}{O}}\!\!\underset{CH_2}{\overset{CH_2}{<}}\!\!\!>\!\!C(CH_2Cl)_2$$
$$X^{-}$$

where $R^{+}\cdots X^{-}$ indicates a reactive oxonium salt or an unstable, highly reactive intermediate which affords a carbonium.

In the Lewis acid catalyzed polymerization of THF, we[42] found some new cocatalysts other than those described by Meerwein[40]. Our cocatalysts are BCMO, β-propiolactone, diketene, trioxane, α-methylstyrene-alkyl halide, isoprene, phenylisocyanate, and acetonitrile. The behaviors of these cocatalysts may be assumed to be of the same nature as those of Meerwein cocatalysts and as those proposed in the BCMO polymerization, i.e., they work in conjuction with Lewis acid to afford a carbonium or an active oxonium ion. Table 5 illustrates their cocatalytic activities which are compared with those of Meerwein cocatalysts.

Table 5. Polymerization of tetrahydrofuran by Lewis acid-cocatalyst systems.

Cocatalyst	(mole % for monomer)	Polymeri- zation time (days)	Conv.[a] (%)	η_{sp}/C[b]
Lewis acid : BF$_3$·(C$_2$H$_5$)$_2$O				
Nococatalyst		7	3.8	0.51
3, 3–Bis(chloromethyl)oxacyclobutane	1	1	17.9	0.51
β-Propiolactone	1	7	13.6	0.48
Diketene	1	1	24.9	0.28
〃	1	2	84.5	
Trioxane	1	7	6.7	
α-Methylstyrene-ethyl bromide	1	7	5.7	
Isoprene	1	7	6.9	
Phenylisocyanate	1	7	5.9	
〃	2	7	9.7	
Acetonitrile	1	7	6.1	
Propylene oxide[e]	1	7	78.1	
Acetic anhydride[e]	1	7	8.6	
Lewis acid : FeCl$_3$				
No cocatalyst		7	0	
3, 3–Bis(chloromethyl)oxacyclobutane	1	7	5.9	

[a] All the products were resinous solids.
[b] Measured on a solution of 0.2 g. polymer in 100 ml. benzene at 30°C.
[e] Meerwein cocatalyst.

The cocatalytic activities of cyclic compounds, BCMO, β-propiolactone, diketene and trioxane, may be ascribed to their high reactivities toward Lewis acid. They

are first cloven to give carbonium ions which induce the THF polymerization.

It is interesting to note that, in the series of three-, four- and five-membered cyclic ethers, the ring-opening polymerization by Lewis acid catalyst is accelerated by the addition of a homologue of smaller ring size, i. e., the polymerization of BCMO by Lewis acid catalyst is cocatalyzed by alkylene oxide and that of THF is accelerated by alkylene oxide and by BCMO.

III-2. Alkylaluminum-Cocatalyst System

In the polymerizations of BCMO and THF, we discovered a group of new catalysts which were derived from organoaluminum compound. It was already reported that triethylaluminum was active for the BCMO polymerization at higher temperature, usually above 90°C.[45], but inactive for the THF polymerization[46]. We found that the catalytic activity of organoaluminum compound for the BCMO and THF polymerizations was much increased by the addition of a suitable co-

Table 6. Polymerization of 3, 3-bis(chloromethyl)oxacyclobutane by triethylaluminum-cocatalyst systems.

$Al(C_2H_5)_3$ (mole % for monomer)	Cocatalyst[a]	$\dfrac{Cocatalyst}{Al(C_2H_5)_3}$ (mole ratio)	Polymerization Temp. (°C.)	Time (hr.)	Conv. (%)	η_{sp}/C[b]
5	None	0	0	48	2.5	
5	ECH	0.5	0	48	95.8	
5	ECH	1.0	0	48	ca.100	
5	Chloromethyl ether	1.0	0	48	24.1	
5	None	0	30	35	3.5[c]	
5	PO	0.5	30	6	5.6	
5	PO	1.0	30	6	3.0	
2.5	H_2O	1.0	0	1	64.4[d]	1.25

[a] ECH=Epichlorohydrin, PO=Propylene oxide.
[b] In o-dichlorobenzene at 110°C.
[c] From the dato of Hatano and Kambara (J. Polymer Sci. 35 (1959) 275.
[d] From ref. (1).

Table 7. Polymerization of 3, 3-bis(chloromethyl)oxacyclobutane by diethylaluminum chloride-cocatalyst systems.
(Monomer, 0.025 mole ; $Al(C_2H_5)_2Cl$, 5 mole % for monomer ; hexane, 10 ml. ; polymerization at 30°C. for 6 hrs.)

Cocatalyst[a]	$\dfrac{Cocatalyst}{Al(C_2H_5)_2Cl}$ (mole ratio)	Conversion (%)
None	0	Trace
ECH	0.5	4.4
ECH	1.0	10.7
ECH	2.0	68.6
PO	0.5	0.7
PO	1.0	0.7
PO	2.0	0.8

[a] ECH=Epichlorohydrin, PO=Propylene oxide.

catalyst. Among the systems of $Al(C_2H_5)_3$ and cocatalysts, the most active ones polymerized BCMO even at $-78°C$. and THF at $0°C$. Some catalyst systems gave polymers of much higher molecular weight than those given by usual cationic catalysts.

Tables 6 and 7 indicate the cocatalytic effects of epichlorohydrin (ECH), propylene oxide (PO) and chloromethyl ether on the catalytic activity of $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Cl$, respectively, for the BCMO polymerization. The cocatalytic activity of ECH is larger than that of PO.

The systems consisting of $Al(C_2H_5)_3$ and cocatalysts such as PO, ECH, acetyl chloride and chloromethyl ether were found to induce also the THF polymerization at $0°C$. (See Table 8.)

Table 8. Polymerization of tetrahydrofuran by triethylaluminum-cocatalyst systems.
(Monomer, 0.25 mole ; $Al(C_2H_5)_3$, 0.0025 mole (1 mole %) ;
cocatalyst, 0.0025 mole ; bulk polymerization at $0°C$. for 1 day.)

Cocatalyst[a]	Conv. (%)	η_{sp}/C[b]
None	0	—
ECH	24.7	3.49
PO	25.8	3.49
Acetyl chloride	5.3	0.33
Chloromethyl ether	4.1	1.06

[a] ECH=Epichlorohydrin, PO=Propylene oxide.
[b] Measured on a solution of 0.2 g. of polymer in 10 ml. of benzene at 30°C.

The $Al(C_2H_5)_3$-ECH and $Al(C_2H_5)_3$-PO systems gave polymers of extremely high molecular weight.

The behaviors and natures of the cocatalysts in the polymerizations of BCMO and THF by $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Cl$ are similar to the observation in the polymerizations catalyzed by $BF_3·(C_2H_5)_2O$ and by other typical Lewis acids. These facts may be taken to suggest that organoaluminum compounds act as Lewis acid. The Lewis acid character of $Al(C_2H_5)_3$ may be pointed out also in the alkylene oxide polymerization. Trialkylaluminum is one of active initiators of the alkylene oxide polymerization[45,47~49], and this polymerization was described in terms of coordinate propagation. It is to be noted here that in the ethylene oxide polymerization by trialkylaluminum considerable amounts of the cyclic dimer (dioxane) and the cyclic tetramer are always produced besides linear polymer, the regular polymerization product[47]. The production of dioxane is one of the features of the cationic polymerization of ethylene oxide initiated by boron trifluoride, a typical Lewis acid[50]. Thus the dioxane formation seems to support the Lewis acid character of trialkylaluminum.

III–3. Alkylaluminum-Water System

The catalytic activities of $Al(C_2H_5)_3$ and $Al(C_2H_5)_2Cl$ are also increased by the addition of a proper quantity of water[54]. Table 9 indicates the BCMO polymerization by $Al(C_2H_5)_3$-water and $Al(C_2H_5)_2Cl$-water systems. The maximum

catalytic activity was attained at about 1 : mole ratio of the catalyst compontents.

Table 9. Polymerization of 3,3-bis(chloromethyl)oxacyclobutane by $Al(C_2H_5)_3$-water
system : Effect of amount of water.
(Monomer, 0.025 mole ; $Al(C_2H_5)_3$, $Al(C_2H_5)_2Cl$, 0.000625 mole
(2.5 mole %) ; hexane, 10 ml. ; polymerization at 0°C.)

H_2O/Al (mole ratio)	Polymerization time (hrs.)	Yield of polymer (%)	$\eta_{sp}/C^{a)}$
$Al(C_2H_5)_2Cl$–H_2O system			
0	24	$2.5^{b)}$	—
0.5	1	16.4	$^{c)}$
1.0	1	64.4	1.25
1.5	1	5.3	$^{c)}$
2.0	48	0	—
$Al(C_2H_5)_2Cl$–H_2O system			
0	96	0	—
0.5	48	7.47	—
1.0	48	10.1	—

[a)] Measured on a 0.25% solution in o-dichlorobenzene at 110°C.
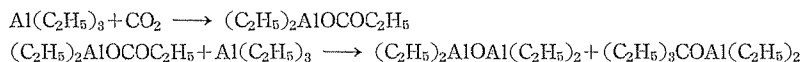[b)] $Al(C_2H_5)_3$, 0.00125 mole, twice as much as those in other experiments.
[c)] Soluble in o-dichlorobenzene at the boiling point, 180°C., but insoluble at 110°C.

The BCMO polymers produced by $Al(C_2H_4)_3$-water system were found to have much
higher molecular weight than those of polymers formed by BF_3 or $BF_3(C_2H_5)_2O$.
Most polymers were soluble in o-dichlorobenzene only at the boiling point but in-
soluble at 110°C. This solubility characteristic is quite different from that of
BF_3-catalyzed polymers which are readily soluble at 110°C.

The reaction between $Al(C_2H_5)_3$ and water was already assumed. The
product is considered to be a mixture of the species,

$$C_2H_5-\left(-Al-O-\right)_n -Al-C_2H_5 \quad (n=1, 2, 3\cdots\cdots),$$
$$\begin{array}{cc} | & | \\ C_2H_5 & C_2H_5 \end{array}$$
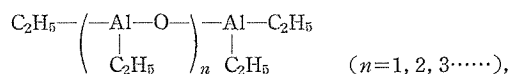
which is designated here *ethylaluminum oxide*. The solublity of the above species
in hydrocarbon solvent will be controlled by the degree of condensation, n. We
found that the reaction product of equimolar amounts of $Al(C_2H_5)_3$ and water
consisted of the hydrocarbon soluble fraction and the insoluble one, and that only
the soluble fraction was catalytically active. Tetraethylaluminum oxide $(n=1)$
and the like which are soluble in hydrocarbon may be the active species of the
$Al(C_2H_5)_3$-water system. In fact, tetraethylaluminum oxide, which was prepared
by the reaction of $Al(C_2H_5)_3$ and carbon dioxide (Ziegler's procedure)[52],

$$Al(C_2H_5)_3+CO_2 \longrightarrow (C_2H_5)_2AlOCOC_2H_5$$
$$(C_2H_5)_2AlOCOC_2H_5+Al(C_2H_5)_3 \longrightarrow (C_2H_5)_2AlOAl(C_2H_5)_2+(C_2H_5)_3COAl(C_2H_5)_2$$

was found to be active for the BCMO polymerization at 0°C.

The nature of the $Al(C_2H_5)_3$-H_2O system in the BCMO polymerization may be
cationic, and activation of $Al(C_2H_5)_3$ by water may be ascribed to the replacement
of the carbon-aluminum bonds by oxygen-aluminum bonds and hence, to the in-

crease of electron affinity (Lewis acid character) of aluminum. Therefore, the function of water is different from that of the so-called cocatalyst such as BCH, PO or acetyl chloride. The former converts triethylaluminum into a stronger Lewis acid, whereas the latter co-operates with triethylaluminum in the production of an active oxonium or carbonium ion intermediate.

The alkylaluminum-water system is known to be one of the most active catalysts for the alkylene oxide polymerization[53,54], whose behavior was explained in terms of *coordinate anionic* mechanism[53]. In this connection, other systems which are considered to be coordinate anionic catalysts in the alkylene oxide polymerization were also examined in the BCMO polymerization. They were diethylzinc-water system[36,37], alumina[55], alumina-triethylaluminum system[56,57], partly hydrolyzed aluminum isopropoxide[58], and various systems[53,59] consisting of triethylaluminum and a cocatalyst such as methanol, ethanol, acetylacetone, dimethylglyoxime, acetaldehyde, which were all *inactive* for the BCMO polymerization. Thus, the triethylaluminum-water system in the BCMO polymerization differs in nature from these coordinate anionic catalysts and may be reasonably assumed to be cationic. The cationic character of the triethylaluminum-water system was suggested also by Vandenberg in the polymerization of 2,3-epoxybutane[60]. Furthermore, the nature of cocatalysts upon the triethylaluminum-water system, which is described in the following paragraph, supports this assumption.

III-4. Alkylaluminum-Water-Cocatalyst System

It has been assumed in the preceding section that an appropriate amount of water converts trialkylaluminum into another stronger Lewis acid. Therefore, it will be reasonably assumed that the trialkylaluminum-water system is further activated by the cocatalysts which are effective for typical Lewis acids. This assumption was realized in the polymerizations of BCMO and THF.

As is shown in Table 10, triethylaluminum-water-cocatalyst systems are active for the THF polymerization at 0°C. Because the triethylaluminum-water

Table 10. Polymerization of tetrahydrofuran $Al(C_2H_5)_3$-H_2O-cocatalyst systems.
(Monomer, 0.125 mole; $Al(C_2H_5)_3$, H_2O, each 0.00315 mole; cocatalyst, 0.00630 mole; bulk polymerization at 0°C for 2 days.)

Cocatalyst[a]	Conversion (%)	η_{sp}/C[b]
None	0	—
ECH	ca. 100	1.33
PO	32.9	0.56
β-Propiolactone	99.0	0 19
Diketene	44.5	1.06
Phenylisocyanate	0.89	
Acetyl chloride	64.4	
Chloromethyl ether	ca. 100	

[a] ECH=Epichlorohydrin, PO=Propylene oxide.
[b] Measured on a solution of 0.2 g. polymer in 10 ml benzene at 30°C.

system is inactive for the THF polymerization, the effects of the cocatalysts are manifested.

The activation of the triethylaluminum-water system by the cocatalyst was observed also in the BCMO polymerization (Table 11). Even at −78°C., triethyl-aluminum-water-cocatalyst systems induced the BCMO polymerization at considerable rate.

The natures and behaviors of these cocatalysts support the view that the character of the triethylaluminum-water system is cationic. In addition, the cationic character of the triethylaluminum-water-cocatalyst systems was justified by the observation that these systems induced the polymerizations of styrene and α-methylstyrene[42].

Table 11. Polymerization of 3, 3-bis(chloromethyl)oxacyclobutane by Al$(C_2H_5)_3$-H_2O-cocatalyst systems.
(Monomer, 0.025 mole; Al$(C_2H_5)_3$, H_2O, each 0.00125 mole (5 mole %); second co-cocatalyst, 0.00125 mole; CH_2Cl_2, 20 ml.; polymerization at −78°C. for 2 days.)

Second concatalyst	Conversion (%)
None	0
ECH	ca 100
PO	60.7
β-Propiolactdne	42.7
Acetyl chloride	4.6
Chloromethyl ether	small

IV. COPOLYMERIZATIONS OF 3, 3-BIS(CHLOROMETHYL)OXACYCLOBUTANE WITH SOME CYCLIC ETHERS

In the ring-opening polymerization of cyclic ether, many studies on polymerization catalyst, polymerization mechanism and the polymer produced have been made, but comparatively less studies on the copolymerization have been given. We made the copolymerizations of BCMO with some cyclic ethers.

IV-1. Copolymerization of BCMO and THF[61]

Several Lewis acids were examined upon their catalytic behaviors in the copolymerization of BCMO and THF, and some complex compounds of BF$_3$(BF$_3$·$(C_2H_5)_2O$, BF$_3$·$2C_6H_5OH$, BF$_3$·$2CH_3COOH$) and SnCl$_4$ were found to give rubbery polymeric product from 1 : 1 molar mixtures of BCMO and THF at 0°C. The polymeric products obtained here were insoluble in methanol but soluble in chloroform. Because the homopolymer of THF is soluble in both methanol and chloroform and that of BCMO is insoluble in both solvents, the polymeric product from 1 : 1 mixture of BCMO and THF may be regarded as a true *copolymer*, but not a mixture of homopoly-BCMO and homopoly-THF. Random copolymerization was also supported by the infrared spectrum analysis. The spectrum of the polymeric product lacked in the absorption band at 1000 cm.$^{-1}$ although the other region of the spectrum corresponded to the composite of the spectra of the two separate

homopolymers. The band at 1000 cm.$^{-1}$ was shown by us[62] to be one of crystalline bands of solid homopolymer of THF. The absence of the crystalline band of poly-THF indicates that the polymeric product is essentially amorphous and, hence, is a random copolymer but not a mixture of the two separate homopolymers.

The copolymers from the monomers mixtures containing more than 80 mole % of BCMO were resinous solids while those from mixtures less than 80 mole % of BCMO were rubbery materials.

From a set of copolymerizations of varying monomer compositions by BF$_3$·(C$_2$H$_5$)$_2$O in toluene at 0°C., the monomer reactivities ratios of BCMO and THF were determined, which were,

$$r_1(BCMO) = 0.82 \pm 0.05$$
$$r_2(THF) = 1.00 \pm 0.05.$$

According to the mechanism of propagation via trialkyloxonium ion intermediates which was proposed for the homopolymerizations of oxacyclobutane[41] and of THF[40], the following four steps can be formulated for the propagation reactions of the copolymerization.
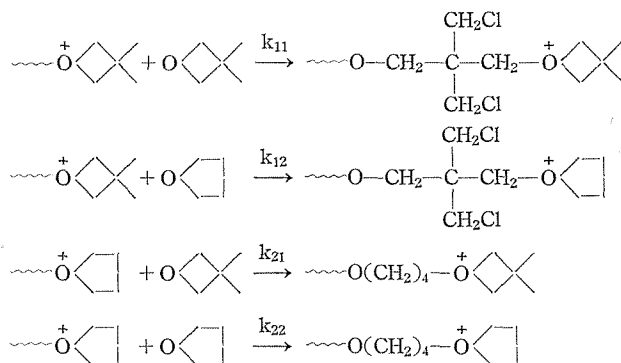
where $O\langle\rangle\times$ = BCMO and $O\langle\_]$ = THF.

The values of monomer reactivity ratio indicate that, $k_{11}/k_{12} = 0.8$ and $k_{22}/k_{21} = 1.0$. The rate of homo-polymerization of BCMO is known to be much higher than that of THF.

$$k_{11} \gg k_{22}$$

Therefore, $k_{22} = k_{21} \gg k_{11} = 0.8\ k_{12}$. From the above consideration it may be implied that the rate of each propagation step in the copolymerization of BCMO and THF depends mainly upon the reactivity of the cyclic oxonium ion at the growing chain end.

IV-2. Copolymerizations of BCMO with Tetrahydropyran and with 1,4-Dioxane

Tetrahydropyran (THP) and 1,4-dioxane are cyclic ethers of six members, which are rather stable and are reluctant to polymerize. The Lewis acid catalyzed homopolymerizations of tetrahydropyran and of 1,4-dioxane have not been re-

ported.   We[63] found that THP and 1, 4-dioxane were copolymerized with BCMO by $BF_3 \cdot (C_2H_5)_2O$ catalyst.

When an equimolar mixture of BCMO and THP was treated with 5 mole % of $BF_3 \cdot (C_2H_5)_2O$ in CH_2Cl_2 solvent at 0°C. for 7 days, a chloroform-soluble waxy product was produced at a conversion of 81.7%.   Because the homopolymer of BCMO is insoluble in chloroform, the waxy product may be assumed to be a co-polymer.   From the chlorine content, the composition of the waxy product was determined, which was

<div align="center">

BCMO unit   6.:.: mole %

THP   unit   33.5 mole %.

</div>

The polymerization of an equimolar mixture of BCMO and dioxane with 5 mole % of $BF_3 \cdot (C_2H_5)_2O$ was carried out at 20°C. for 3 days.   A chloroform-insoluble resinous product was obtained at a yield of 68.1%.   The elemental analysis of the product manifested that 19.5 mole % of dioxane unit was incorporated in the product.   From the solubility, the resinous product may be regarded as the copolymer of BCMO and dioxane or a mixture of the copolymer and the BCMO homopolymer.

<div align="center">

REFERENCES

</div>

(1)   M. Letort, *Compt. rend.*, 202, 767 (1936).

(2)   M. S. Travers, *Trans. Farad. Soc.*, 32, 246 (1936).

(3)   M. Letort, X. Duval, Y. Rollin, *Compt. rend.*, 224, 50 (1947).

(4)   M. Letort, A. J. Richard, *Comp. rend.*, 240, 86 (1955).

(5)   M. Letort, X. Duval, *Compt. rend.*, 216, 58 (1943).

(6)   M. Letort, X. Duval, *Compt. rend.*, 216, 608 (1943).

(7)   M. Letort, J. Petry, *Compt. rend.*, 231, 519 (1950).

(8)   M. Letort, P. Mathis, *Compt. rend.*, 241, 951 (1955).

(9)   M. Letort, P. Mathis, *Compt. rend.*, 241, 1765 (1955).

(10)   M Letort, P. Mathis, *Compt. rend.*, 242, 371 (1956).

(11)   M. Letort, J. Petry, *J. chim. phys.*, 48, 594 (1951).

(12)   M. Letort, A. J. Richard, *J. chim. phys.*, 57, 752 (1960).

(13)   H. A. Rigby, C. J. Danby, C. N. Hinshelwood, *J. Chem. Soc.*, 1948, 234.

(14)   J. G. Bevington, R. G. W. Norrish, *Proc. Roy. Soc.*, A 196, 363 (1949).

(15)   C. Chachaty, *Compt. rend.*, 251, 385 (1960).

(16)   M. Letort, P. Mathis, *Compt. rend.*, 249, 274 (1959)

(17)   O. Vogl, *J. Polymer Sci.*, 46, 261 (1960).

(18)   T. Miyagawa, T. Yamamoto, Paper presented at 10th Annual Meeting of Soc. High Polymer, Tokyo, (May, 1961).

(19)   J. N. Koral, B. W. Song, *J. Polymer Sci.*, 54, S 34 (1961).

(20)   Ger. Pat. 1,106,075 (1961).

(21)   J. Furukawa, T. Saegusa, T. Tsuruta, H. Fujii, A. Kawasaki, T. Tatano, *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 62, 1925 (1959).

(22)   J. Furukawa, T. Saegusa, T. Tsuruta, H. Fujii, A. Kawasaki, T. Tatano, *Makromol Chem.*, 33, 32 (1959); *J. Polymer Sci.*, 36, 546 (1959).

(23)   G. Natta, G. Mazzanti, Corradini, P. Chini, I. W. Bassi, *Atti, acad. nazl. Lincei. Rend. Classe sci. fig. mat. e. nat.*, [8], 28, 8 (1960).

(24)   G. Natta, G. Mazzanti, P. Corradini, I. W. Bassi, *Makromol. Chem.*, 37, 156 (1960).

(25)   J. Furukawa, T. Saegusa, T. Tsuruta, H. Fujii, Paper presented at Discussion Meeting of Sci High Polymer Japan, Tokyo (Oct., 1959).

(26) J. Furukawa, T. Saegusa, H. Fujii, A. Kawasaki, H. Imai, Y. Fujii, *Makromol. Chem.*, 37, 149 (1960).

(27) J. Furukawa, T. Saegusa, H. Fujii, *Makromol. Chem.*, 44/46, 398 (1960).

(28) S. Ishida, *Chem. High Polymer, Japan*, 18, 187 (1961).

(29) H. Fujii, J. Furukawa, T. Saegusa, *Makromol. Chem.*, 40, 226 (1960).

(30) H. Fujii, T. Saegusa, J. Furukawa, *J. Chem. Soc. Japan, Ind. Chem. Sect., in press.*

(31) J. Furukawa, T. Saegusa, Paper presented at International Symposium on Macromol. Chem., Montreal, 1961.

(32) T. Saegusa, Y. Fujii, H. Fujii, J. Furukawa, to be published.

(33) V. A. Kargin, V. A. Kabnov, V. P. Zubov, I. M. Rapisov, *Doklady Akad. Nauk S. S. S. R.* 134, 1098 (1960).

(34) S. Okamura, K. Hayashi, K. Mori, Y. Nakamura, Paper presented at 10th Annual Meeting of Soc. High Polymer, Japan (May, 1961).

(35) J. Furukawa, T. Saegusa, T. Tsuruta, S. Ohta, G. Wasai, *Makromol. Chem.*, 52, 230 (1962).

(36) J. Furukawa, T. Tsuruta, R. Sakata, T Saegusa, A. Kawasaki *Makromol. Chem.*, 32, 90 (1959).

(37) R. Sakata, T. Tsuruta, T. Saegusa, J. Furukawa, *Makromol Chem.*, 40, 64 (1960).

(38) S. Inoue, T. Tsuruta, J. Furukawa, to be published in *Makromol Chem.*

(39) A. C. Farting, Brit. Pat. 723, 777 (1955).

(40) H. Meerwein, D. Delfs, H. Morshel, *Augew. Chem.*, 72, 927 (1960).

(41) J. B. Rose, *J. Chem., Soc.*, 1956, 542, 546.

(42) T. Saegusa, H. Imai, J. Furukawa, Presented at 15th Annual Meeting of Japan Chem. Soc., Kyoto, April, 1962 and to be published in *Makromol. Chem.*

(43) A. C. Farthing, J. *Polymer Sci.*, 12, 503 (1954).

(44) H. Meerwein, H. Hinz, P. Hofmann, E. Kroning, E. Pfeil, *J. prakt. Chem.*, 147 (1937) 257 ; H. Meerwin, E. Battenberg, H. Gold, E. Pfeil, G. Willfang, *J. prakt. Chem.*, 154, 83 (1939).

(45) M. Hatano, S. Kambara, *J. Polymer Sci.*, 35, 275 (1959).

(46) S. Kambara, M. Hatano, *J. Polymer Sci*, 27 584 (1958).

(47) D. G. Stewart, D. Y. Wadden, E. T. Boriows, Brit. Pat. 785, 220 (Oct. 23, 1957).

(48) P. E. Ebert, C. C. Price, *J. Polymer Sci.*, 34, 157 (1959).

(49) R. A. Miller, C. C. Price. *J. Polymer Sci.*, 34, 161 (1959).

(50) D. J. Worsfold, A. M. Eastham, *J. Am. Chem. Soc.*, 79, 900 (1957).

(51) T. Saegusa, H. Imai, S. Hirai, J. Furukawa, to be published in *Makromol. Chem.*

(52) K. Ziegler, *Ann.*, 629, 251 (1960).

(53) E. J. Vandenberg, *J. Polymer Sci.*, 47, 486 (1960).

(54) R. O. Colclough, G. Gee, A. U. Jagger, *J. Polymer Sci.*, 48, 273 (1960).

(55) Badische Anilin-und Soda Fabrik Akt.-Ges., Ger. Pat. 821, 349 (Nov. 11, 1951).

(56) J. Furukawa, T. Saegusa, G. Kakogawa, *J. Polymer Sci.*, 36, 541 (1959).

(57) J. Furukawa, T. Saegusa, T. Tsuruta, G. Kakogawa, *Makromol. Chem.*, 31, 25 (1959)

(58) J. Furukawa, T. Saegusa, Y. Kato, Presented at 15th Annual Meeing of Japan Chem Soc., Kyoto, (April, 1962).

(59) E. J. Vandenberg, Japan. Pat. Appl. Pub. 15797 (1960).

(60) E. J. Vandenberg, *J. Am. Chem. Soc.*, 83, 3538 (1960).

(61) T. Saegusa, H. Imai, J. Furukawa, to be published in *Makromol. Chem.*

(62) G. Wasai, J. Furukawa, T. Saegusa, unpublished.

(63) T. Saegusa, H. Imai, J. Furukawa, Paper presented at 11th Annual Meeting of Soc. High Polymer, Japan, (May, 1962).