The Role of Organometallic Compounds in Vinyl Polymerization

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CONTENTS

The outline of our experimental results on the vinyl polymerization induced by various kinds of organometallic compounds is described. Boron alkyl was an active catalyst for polymerizations of vinyl chloride, vinyl acetate, acrylic esters and acrylonitrile in the presence of oxygen compounds. Cadmium alkyl also was found to be a very reactive catalyst for methacrylate polymerization especially in the presence of phenol or quinone. A binary system of cadmium alkyl and titanium tetrachloride affords cis-1.4-polyisoprene whereas in the case of butadiene it gives trans-1.4-polybutadiene. Crystalline polystyrene and polymethyl methacrylate were produced by calcium and lithium catalyst. In connection with the Ziegler catalyst, reactivities of a large variety of binary or ternary systems of metal alkyl and metal halide were studied.

INTRODUCTION

It has long been known that butadiene undergoes an anionic polymerization by metallic sodium to form a high polymer, which was once produced industrially in Germany and Russia. However, little experimental work was available on the anionic polymerization until Ziegler discovered an excellent catalyst consisting of organoaluminum and titanium compounds for the polymerization of ethylene under ordinary pressure. Natta[1] succeeded in preparing isotactic poly-α-olefin through the use of the modified Ziegler catalyst. Four isomers of stereoregular polydiolefin such as 1.4-cis-, 1.4-trans-, 1.2-syndiotactic and 1.2- isotactic-pulybutadiene were also synthesized by Natta and his coworkers[2]. The Ziegler type catalyst has been applied to synthesize a "natural rubber" (1.4-cis-polyisoprene) in the United States[3].

It is to be noted that the stereospecific polymerizations of polar vinyl com-

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pounds such as vinyl acetate[4] and vinyl chloride[5] have been realized with the Ziegler type catalyst by using some appropriate complexing agents.

Besides the Ziegler type catalyst, metallic lithium or its organic compound was proved to be a stereospecific catalyst for the polymerizations of isoprene[6] and some acrylic esters[7~9] and amides[10].

In our laboratory, an extensive study on the vinyl polymerization by organometallic compounds is in progress.

Boron alkyl was found to be active catalyst for the polymerizations of vinyl chloride, vinyl acetate, acrylic esters and acrylonitrile[11]. In this case, oxygen compounds present in the reaction system play an influential role as cocatalyst[12,13] and the binary mixtures of boron alkyl and peroxide such as hydrogen peroxide or organic peroxide were found to be the most suitable catalysts for the vinyl polymerization. Analytical study leads to the conclusion that the active species is alkylboron peroxide[13,14]. Esters and anhydrides of borinic acid such as R_2BOR' and $R_2BOBR'_2$ exhibit also stronger catalytic activity than boron alkyl itself[13].

Alkyl derivatives of zinc and cadmium were found to be suitable active component of the Ziegler type catalyst. Complex of R_2Cd and $TiCl_4$ affords cis-1,4-polyisoprene whereas in the case of butadiene it gives trans-1,4-polybutadiene[15]. It was found[16,17] that organometallic compound of cadmium, zinc or aluminum were very reactive catalyst for vinyl polymerization in the presence of phenol, hydroquinone or quinone; especially, resorcinol and diethylcadmium induced rapid polymerization of vinyl compound to form a polymer having high degree of polymerization.

Crystalline polystyrene and polymethyl methacrylate were produced by calcium and lithium catalyst[18~20]. The catalytic reactivity of metal ketyl in the vinyl polymerization was also studied[21].

In connection with the Ziegler catalyst, reactivities of a large variety of the binary or ternary systems of metal alkyl and metal halide were systematically examined.

In this paper, the authors wish to survey the outline of our experimental results and to advance a general view on the vinyl polymerization by organometallic compounds from a standpoint of the electronegativity of metallic elements as well as the reactivity of the monomer molecules.

I. VINYL POLYMERIZATION BY ORGANOBORON COMPOUND

As we communicated before[13], there was found a remarkable cocatalytic action of oxygen and oxygen compounds in this polymerization. Independently of us, Kolesnikov and Fedorova[22] dscribed that acrylonitrile was not polymerized by tributylboron in the system where the trace of molecular oxygen was completely excluded. We have carried out a series of experiments in more detail.

1.1. Effect of Oxygen

The effect of oxygen on the polymerization of vinyl acetate and of styrene

Table 1. Effect of oxygen upon polymerizations of vinyl acetate and of styrene.

A. Vinyl Acetate[a]

No.	$O_2/B(C_2H_5)_3$ (Mole ratio $\cdot 10^2$)	Conversion (%)	Average degree of polymerization $\bar{P}_{PVAc} \cdot 10^{-2}$
1	1.6	8.3	5.1
2	3.2	10.7	5.3
3	6.4	16 6	4.2
4	9.5	22.9	4.1
5	14.3	40.4	3.3

B. Styrene[b,c]

No.	Gas phase (35 cc.)	Convesion (%)	$\bar{P}_{PSt}$
1	Air	9.4	293
2	Nitrogen	Very small	—
3	Air	20.3	276
4	Nitrogen	Very small	—

[a] Experimental conditions: Vinyl acetate, 0.107 mole (10 cc); $B(C_2H_5)_3$, $2.7 \cdot 10^{-3}$ mole; temp., 30°C.; time, 26 hrs.; under standing.

[b] Experimental conditions: Styrene, 0.0872 mole (10 cc); $B(n\text{-}C_4H_9)_3$, $1.74 \cdot 10^{-3}$ mole; temp., 60°C.; time, 3 hrs.; under standing.

[c] Experiment by S. INOUE and N. KAWABATA.

is shown in Table 1. In the vinyl acetate polymerization under various partial pressures of oxygen, it was found that the larger the partial pressure of oxygen, the larger was the rate of oxygen absorption as well as the rate of polymerization. These reactions were conducted in test tubes kept standing, and the polymerization was observed to have started on the surface in contact with the gas phase. If the experiment was carried out under vigorous shaking, no polymer was isolated. These results seem to suggest that molecular oxygen may react with the boron compound to produce an active species which induces the polymerization, but excess oxygen further oxidized the active species into inactive ones, as will be stated later. Termination of the radical chain by excess oxygen may also be taken into consideration in the same manner as in the usual radical polymerization.

1.2. Effect of Hydrogen Peroxide

The effect of hydrogen peroxide upon the polymerization of various vinyl monomers is shown in Table 2. In Table 3 the effect of the molar ratio of triethylboron to hydrogen peroxide on the conversion of vinyl acetate is shown. The conversion increases with increasing quantity of hydrogen peroxide up to 80 mole-% with respect to triethylboron, but beyond this limit, the conversion decreases rapidly. The boron compound is probably further oxidized in part to inactive species by the excess of hydrogen peroxide.

1.3. Effect of Organic Hydroperoxide

Organic peroxides[23] also have marked effects on the polymerizations induced

Tabie 2. Effect of hydrogen peroxide upon triethylboron-initated polymerization of vinyl monomers.

No.	Monomer[a]		$B(C_2H_5)_3$/monomer (mole ratio$\cdot10^2$)	$H_2O_2/B(C_2H_5)_3$ (mole ratio$\cdot10^2$)	Conversion (%)
1-1	Vinyl acetate[b]	(0.104 mole)	2.6	80	66.0
1-2	//	//	2.6	60	32.3
1-3	//	//	2.6	40	24.4
1-4	//	//	2.6	0	19.8
2-1	Styrene[c,d]	(0.044 mole)	10.8	80	15.3
2-2	//	//	10.8	60	11.2
2-3	//	//	10.8	40	8.5
2-4	//	//	10.8	0	6.7
3-1	Methyl methacrylate[d,e]	(0.047 mole)	10.0	60	47.4
3-2	//	//	10.0	40	9.2
3-3	//	//	10.0	20	7.1
3-4	//	//	10.0	0	5.6
4-1	Acrylonitrile[d,e]	(0.076 mole)	6.2	60	15.1
4-2	//	//	6.2	40	10.0
4-3	//	//	6.2	20	6.2
4-4	//	//	6.2	0	4.2

[a] These monomers are not polymerized by hydrogen peroxide alone under these conditions.
[b] Temp., 23°C.; time, 22 hrs.; under rotation in nitrogen.
[c] Temp., 60°C.; time, 6 hrs.; under rotation in nitrogen.
[d] Temp., 25°C.; time, 2 hrs.; under rotation in nitrogen.
[e] Experiments by S. INOUE and N. KAWABATA.

Table 3. Effect of hydrogen peroxide upon vinyl acetate polymerization[a].

No.	$H_2O_2/B(C_2H_5)_3$ (mole ratio$\cdot10^2$)	Conversion (%)
1	50	28.7
2	75	42.6
3	100	9.9
4	125	7.5
5	150	3.6
6	200	4.2
7	300	5.6

[a] Experimental conditions: Vinyl acetate, 0.107 mole; methanol, 1cc.; $B(C_2H_5)_3$, 2.78$\cdot$ 10^{-3}mole; temp., 0°C.; time, 72 hrs.; under standing in nitrogen.

by organoboron compounds. Table 4 summarizes the effects of some organic peroxides on vinyl chloride polymerization induced by triethylboron. Results of comparative examinations with ethyl derivatives of aluminum, cadmium and zinc as catalyst are also listed in the Table. It is seen that triethylboron exhibits the most prominent activity. The polymerization proceeded explsively when cumene hydroperoxide (13 mole-% with respect to triethylboron was added

Table 4. Yinyl chloride polymerization by the system of organometallic compound and organic peroxides.

Cocatalyst, mole-%[a]	Temp., °C	Time, hr.	Conversion, %	Degree of polymerization, P	Activation energy, kcal./mole
$B(C_2H_5)_3$, 1.79 mole-%[b]					
Cumene hydroperoxide, 13	Room temp.	A few min.	Explosion	—	
Cumene hydroperoxide, 42	−55	4	22.7	560	
Cumene hydroperoxide, 50	−65	68	61.4	400[c]	
				1780[d]	
tert-Butyl hydroperoxide, 50	−55	4	19.6	820	
$Al(C_2H_5)_3$, 1.89 mole-%[b]					
Cumene hydroperoxide, 23	30	1	15.4	450	
Cumene hydropeoxide, 50	−20	4	5.4	—	12.8
Di-terl-butyl peroxide, 24.6	30	1	4.4	510	
$Cd(C_2H_5)_2$, 2.50 mole-%[b]					
Cumene hydroperoxide, 48	32	4.8	10.0		
Cumene hydroperoxide, 48	22	19.0	10.0		16.0
Cumene hydroperoxide, 48	0	25	3.5		
$Zn(C_2H_5)_2$, 2.52 mole-%[b]					
Cumene hydroperoxide, 48.5	21	1.5	25.6		
Cumene hydroperoxide, 48.5	3	2.0	16.1		9.6
Cumene hydroperoxide, 48.5	−10	2.5	4.67		

[a] With respect to the organometallic compound.
[b] With respect to the monomer.
[c] Soluble in tetrahydrofuran.
[d] Insolble in tetrahydrofuran.

to a mixture of the monomer and triethylboron at room temperature. Thus, it was possible, by the use of these catalyst systems, to obtain polyvinyl chloride in fair yield at temperatures as low as −65°C.

This result suggests a method for producing a stereoregular polyvinyl chlo-
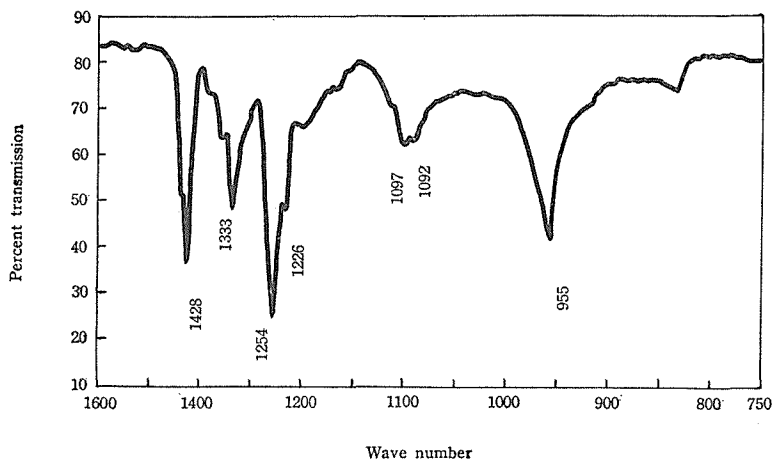

Fig. 1. Infra-red spectrum of crystalline polyvinyl chloride.

Wave number

Fig. 2. Infra-red spectrum of amorphous polyvinyl chloride.

ride. Figure 1 shows the infrared spectrum of a polymer sample which was produced with triethylboron and cumene hydroperoxide as catalyst at $-65°C$.

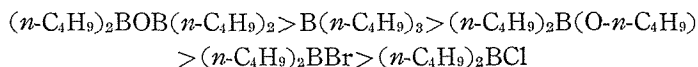For comparison, infrared spectrum of amorphous polymer is shown in Fig. 2.

1.4. Effect of Metal Oxides

Some metal oxides such as manganese dioxide or vanadium pentoxide were found to have cocalytic activity toward the vinyl polymerization catalyzed by trialkylboron under nitrogen. The effects of various metal oxides upon the vinyl polymerization are listed in Table 5.

In general it can be said that the higher order oxide of transition metals have considerable activity, in opposition to the halides* and the oxyhalides*.

1.5. Polymerizations with Alkylboron Derivatives

It has long been known that, in the reaction of trialkylboron with oxygen compounds, various oxidized compounds, such as R_2BOR, $RB(OR)_2$ and $B(OR)_3$, are obtainable according to reaction conditions[24]. We examined on the activities of these oxidized products toward the polymerization of vinyl acetate. For comparison, the behavior of di-n-butylboron halide was also examined. The results are summarized in Table 6. These oxidized compounds, except for n-$C_4H_9B(O$-n-$C_4H_9)_2$, $B(O$-n-$C_4H_9)_3$, and $(n$-$C_4H_9BO)_3$ were found to exhibit catalytic activities which decrease in the order:

$$(n\text{-}C_4H_9)_2BOB(n\text{-}C_4H_9)_2 > B(n\text{-}C_4H_9)_3 > (n\text{-}C_4H_9)_2B(O\text{-}n\text{-}C_4H_9)$$
$$> (n\text{-}C_4H_9)_2BBr > (n\text{-}C_4H_9)_2BCl$$

It is to be noted that, in these cases too, oxygen exerted a remarkable co-catalytic action, as seen in Table 6. From the results obtained above, it may be considered that a compound which combines more easily with oxygen has a greater catalytic action. Triphenylboron, which was not inflammable in air,

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* Effect of halides and oxyhalides will be discussed later in this paper (see chapter 4).

Table 5. Effect of metal oxides upon the polymerization of some vinyl monomers[a]

No.	Monomer	Metal oxide	Gas phase	Conversion (%)	$\overline{P} \cdot 10^{-2}$
1- 1	Vinyl acetate[b]	MnO_2	N_2	23.0	15.1
1- 2	//	V_2O_5	N_2	23.2	19.5
1- 3	//	CuO	N_2	13.8	6.5
1- 4	//	WO_3	N_2	13.0	—
1- 5	//	H_2WO_4	N_2	5.8	—
1- 6	//	$TiCl_3$	N_2	—	—
1- 7	//	$VOCl_3$	N_2	—	—
1- 8	//	—	N_2	4.4	13.4
1- 9	//	—	Air	15.7	10.1
2- 1	Styrene[g,c]	MnO_2	N_2	37.4	—
2- 2	Styrene[c]	V_2O_2	N_2	28.2	—
2- 3	//	WO_3	N_2	16.5	—
2- 4	//	—	N_2	7.5	—
2- 5	Styrene[d]	MnO_2	N_2	7.78	—
2- 6	//	V_2O_5	N_2	6.55	—
2- 7	//	CoO	N_2	6.13	—
2- 8	//	WO_3	N_2	6.86	—
2- 9	//	—	N_2	5.86	—
2-10	//	—	Air	13.0	—
3- 1	Methyl methacrylate[g,e]	MnO_2	N_2	34.8	—
3- 2	//	V_2O_5	N_2	13.0	—
3- 3	//	CuO	N_2	14.7	—
3- 4	//	WO_3	N_2	28.2	—
3- 5	//	—	N_2	11.5	—
3- 6	//	—	Air	65.5	—
4- 1	Acrylonitrile[g,f]	MnO_2	N_2	6.2	6.91
4- 2	//	V_2O_5	N_2	20.0	8.57
4- 3	//	CuO	N_2	18.1	8.42
4-4	//	—	N_2	1.8	—

[a] All the polymerizations were carried out under rotation.
[b] Ezperimental conditions: 1.3 mole% $B(C_2H_5)_3$ for monomer; 50 mole% metal oxide for $B(C_2H_5)_3$; temp., 25°C.; time, 72 hrs.
[c] Experimental conditions: 10.8 mole% $B(C_2H_5)_3$ for monomer; 25 mole% metal oxide for $B(C_2H_5)_3$; temp., 25°C.; time, 32 hrs.
[d] Experimental conditions: 10.8 mole% $B(C_2H_5)_3$ for monomer; 25 mole% metal oxide for $B(C_2H_5)_3$; temp., 60°C.; time, 3 hrs.
[e] Experimental conditions: 10 mole% $B(C_2H_5)_3$ for monomer; 25 mole% metal oxide for $B(C_2H_5)_3$; temp., 25°C.; time, 2 hrs.
[f] Experimental conditions: 10 mole% $B(C_2H_5)_3$ for monomer; 25 mole% metal oxide for $B(C_2H_5)_3$; temp., 25°C.; time, 19 hrs.
[g] Experiments by S. INOUE and N. KAWABATA

was found to have much smaller activity compared with the aliphatic boron derivatives. In Table 7 the catalytic activities of triphenyl-, tribenzyl- and tricyclohexylboron are compared.

Table 6. Vinyl Acetate polymerization with tri-n-butylboron derivatives[a].

No.	Tri-n-butylborn derivative	Conversion (%)	
		in air	in nitrogen
1	B(n-C$_4$H$_9$)$_3$	70.0	7.7
2	(n-C$_4$H$_9$)$_2$BOB(n-C$_4$H$_9$)[b]	92.3	20.6
3	(n-C$_4$H$_9$)$_2$B(O-n-C$_4$H$_9$)	75.2	1.5
4	(n-C$_4$H$_9$)$_2$B(O-n-C$_4$H$_9$)$_2$	0	0
5	B(O-n-C$_4$H$_9$)$_3$	0	0
6	(n-C$_4$H$_9$BO)$_3$	0	0
7	(n-C$_4$H$_9$)$_2$BBr	58.8	very small
8	(n-C$_4$H$_9$)$_2$BCl	11.9	very small

[a] Experimental conditions: Vinyl acetate, 0.107 mole; the boron compound used are 1 mole% with respect to the monomer. Temp. 20°C.; time, 20hrs.; under standing.
[b] 1/2 Mole% with respect to the monomer.

Table 7. Triphenyl-, tribenzyl- and tricyclohexylboron-initiated polymerization of vinyl monomers[a].

No.	Catalyst	Monomer	Gas phase	Convesion (%)	$\bar{P}\cdot10^{-2}$
1-1	Triphenylboron[b]	Styrene	Air	0	—
1-2	//	Styrene	N$_2$	0	—
1-3	//	Methyl methacrylate	Air	2.2	—
1-4	//	Methyl methacrylate	N$_2$	5.9	—
1-5	//	Acrylonitrile	Air	very small	—
1-6	//	Acrylonitrile	N$_2$	very small	—
1-7	//	Vinyl acetate	Air	0	—
1-8	//	Vinyl acetate	N$_2$	0	—
2-1	Tribenzylboron[c]	Styrene	Air	14	3.3
2-2	//	Styrene	N$_2$	10	4.3
2-3	//	Methyl methacrylate	Air	92	21.0
2-4	//	Methyl methacrylate	N$_2$	16	22.3
2-5	//	Acrylonitrile	Air	— [e]	—
2-6	//	Acrylonitrile	N$_2$	27	12.9
2-7	//	Vinyl acetate	Air	31	3.4
2-8	//	Vinyl acetate	N$_2$	0	—
3-1	Tricyclohexylboron[d]	Methyl methacrylate	Air	100	15.1
3-2	//	Methyl methacrylate	N$_2$	100	29.0
3-3	//	Vinyl acetate	Air	56	16.4
3-4	//	Vinyl acetate	N$_2$	55	18.1

[a] Experiment by S INOUE and N. KAWABATA
[b] Experimental conditions: Monomer, 0.1 mole; triphenylboron, 5 mole% for monomer; temp., 20°C.; time, 21 hrs.
[c] Experimental conditions: Monomer, 0.1 mole; tribenzylboron, 1mole% for monomer; temp. 10°C.; time, 19 hrs.
[d] Expermental conditions: Monomer, 0.1 mole; tricylohexylboron, 1 mole% for monmer; temp., 10°C.; time, 19 hrs.
[e] Explosive polymerization.

The prominent catalytic activity of tricyclohexylboron seems to suggest that the decrease of activity in triphenylboron can not be ascribed to the steric hindrance of the phenyl group, because cyclohexyl group is considered to have much the same bulkiness. Thus, we feel the lowering of the reactivity in triphenylboron to be better interpreted in terms of the resonace stabilization to which the $2p$- and π-orbitals of boron and phenyl groups may contribute, respectively.

Tribenzylboron, on the other hand, exhibits the significant activity, the conjugation between phenyl and boron being interrupted with the methylene group.

1.6. Copolymerization

In order to examine the mechanism of the present polymerization, the copolymerizations of styrene-methyl methacrylate and of styrene vinyl acetate were studied with triethylboron as catalyst. Taking styrene as monomer (1), monomer reactivity ratios $(r_1 = 0.49; r_2 = 0.41)$ were calculated from the data according to the Mayo-Lewis equation[25]. These values are in good accord with those $(r_1 = 0.52 \pm 0.026; r_2 = 0.46 \pm 0.026)$[25] from the copolymerization induced by benzoyl peroxide. Figure 3 shows that a plot for the triethylboron-catalyzed copolymerization falls on the curved line for the typical radical copolymerization. From the above results, the propagation stage of the trialkylboron catalyzed polymerization is considered to proceed according to a radical mechanism. The data of copolymerization between styrene and vinyl acetate also support the above conclusion. Results obtained from similar runs of copolymeri-

cationic (SnCl$_4$)[25]

radical (BPO)[26]

anionic (NaNH$_2$)[26]

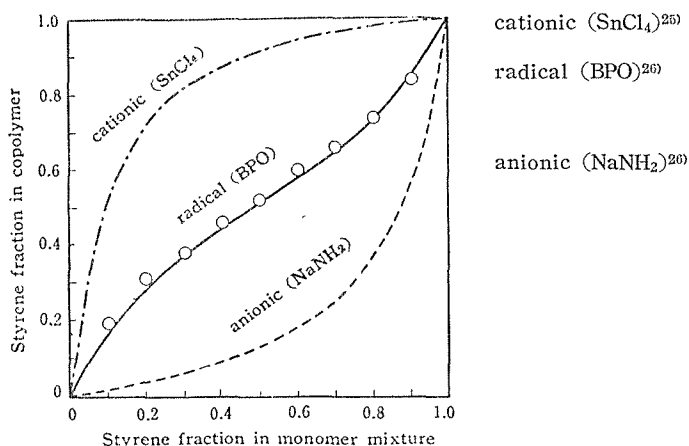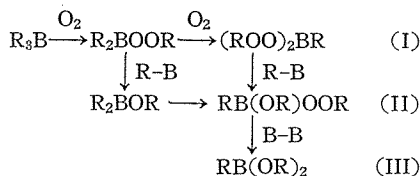Fig. 3. Copolymer composition curves for styrene-methyl methacrylate system.
○ : Triethylboron-catalyzed copolymerization

zation using other organometallics such as diethylzinc, diethylcadmium, triethylaluminum, and triethylstibine have led us to the same conclusion that propagation step in the vinyl polymerization by these organometallics proceeded through a radical mechanism.

1.7. Reaction Mechanism[14]

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Formation of boron peroxide by oxidation of trialkylboron was reported by Parsons and Petry[26], but details were not given. Abraham and Davies[27] recently demonstrated that oxidation of R_3B gave initially R_2BOOR which could be reduced by an R-B group giving R_2BOR, or could be further oxidized by oxygen to $RB(OOR)_2$ and the final products might therefore be (I), (II) or (III), depending on the conditions. From oxidation products of tri-*tert*-butylboron, boron oxide corresponding to (I) was isolated and identified by them.

$$R_3B \xrightarrow{O_2} R_2BOOR \xrightarrow{O_2} (ROO)_2BR \quad \text{(I)}$$
$$\downarrow R\text{-}B \qquad \downarrow R\text{-}B$$
$$R_2BOR \longrightarrow RB(OR)OOR \quad \text{(II)}$$
$$\downarrow B\text{-}B$$
$$RB(OR)_2 \quad \text{(III)}$$

We examined the catalytic reactivity of the oxidation products of tri-*n*-butylboron. In Table 8 the results are listed.

Table 8. Vinyl acetate polymerization by boron salt of *n*-butylhydroperoxide[a].

Vinyl Acetate (mole)	Peroxide[b]/Monomer (mole ratio $\times 10^2$)	Reaction time (hr.)	Conversion (%)
0.05	1.5	2.0	66.0
0.05	1.5	17.0	90.0

[a] Experimental condition: in a sealed tube under nitrogen at room temperature.
[b] Boron peroxide in 5 ml. etheral solution.

It is seen from the Table that boron peroxide prepared by the inverse oxidation* at low temperature exhibited a remarkable catalytic reactivity on the polymerization of vinyl acetate at room temperature. On the other hand, it was surprising that boron peroxide prepared by the oxidation at room temperature showed only a very weak catalytic reactivity on the polymerization of vinyl acetate at room temperature, although it showed the same titration value for peroxide content. There seem to exist two types of peroxide in the oxidation products. In the case of inverse oxidation at low temperature, an active peroxide (perhaps, (I)) may be initially formed in the reaction system.

When molecular oxygen is present in excess against trialkylboron, the active peroxide will survive without transformation into the inactive peroxide or alkoxide at low temperature. On the other hand, in the case of the oxidation at room temperature, an unstable active peroxide formed initially may be reduced immediately by an R-B group giving inactive peroxide or alkoxide. In the foregoing sections, we considered that the active species for the polymerization is of a very short life-time which is formed transiently in the reaction between

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* Inverse oxidation of tri-*n*-butylboron at low temperature: Tri-*n*-butylboron (4.3 g) in 45 ml. of anhydrous ether was introduced under the surface of 50 ml. of anhydrous ether at $-70°C$ in the course of 50 minutes. Vigorous stirring and introduction of a steady stream of oxygen were maintained over this period.

trialkylboron and oxygen or oxygen compounds. Since most of the polymerizations stated above conducted at room temperature in the presence of excess trialkylboron compared with oxygen, the active peroxide initially formed might have been rapidly converted into the inactive substances if the monomer had not been preliminarily added to the reaction system.

Similar results were obtained in the case of oxidation products of diethylzinc. Alkyllithium was also found to act as a radical initiator when it was oxidized by molecular oxygen prior to use. This result is in a sharp contrast to the "ionic behavior" of the usual lithium compounds in the vinyl polymerization.

II. VINYL POLYMERIZATION BY ALKYL DERIVATIVES OF CADMIUM AND SOME RELATED METALS

2.1. Cocatalytic Action of Phenol and Quinone[17]

As was stated above, oxygen and some oxygen compounds were effective cocatalysts for the trialkylboron-catalyzed polymerization. A similar phenomenon has also been found in the case of diethylcadmium as catalyst. On the other hand, diethylcadmium exhibited a unique cocatalytic activity in cooperation with phenol and quinone. With organoboron compounds as catalyst, phenol and quinone behaved only as retarder and inhibitor, respectively.

When diethylcadmium was added to the menomer involving p-benzoquinone, there was formed a large amount of precipitates colored in green. Hydroquinone, on the other hand, reacted with diethylcadmium to result in white precipitates under the evolution of a gaseous substance. In order to examine the role of p-benzoquinone in more detail, two series of comparative runs were carried out which are shown in Table 9.

The polymerization yields were found larger in series A. These results indicate that the major condition for the induction of polymerization is to bring p-benzoquinone (or hydroquinone) to the reaction with diethylcadmium in the

Table 9. Effects of p-benzoquinone and hydroquinone in diethylcadmium catalyzed polymerization of methyl methacrylate[a].

Co-catalyst	Yield %	$[\eta]$ 20°C. chloroform 100 ml./g	Molecular weight$\cdot 10^{-4}$	Series[b]
—	9.89	0.753	12.6	
p-Benzoquinone	68.9	0.338	4.5	A
p-Benzoquinone	11.5	0.120	1.2	B
Hydroquinone	86.4	1.744	35.0	A
Hydroquinone	24.3	1.534	30.0	B

[a] Methyl methacrylate, 10.7 ml. (0.10mole); diethylcadmium, 0.0025 mole; co-catalyst, 0.0025 mole; n-hexane, 10.0 ml.; polymerization time, 3.5 hrs.; temperature, room temperature.

[b] Series A: Diethylcadmium in n-hexane was added to a mixture of methyl methacrylate and p-benzoquinone (or hydroquinone). Series B: methyl methacrylate was added to a diethylcadmium-p-benzoquinone (or hydroquinone). mixture in hexane.

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Table 10. Effect of various amounts of p-benzoquinone upon the polymerization of methyl methacrylate by diethylcadmium[a].

p-Benzoquinone/diethylc- admium mole%	Yield %	$[\eta]$ 20°C. chloroform 100 ml./g.	Molecular weight·10⁻⁴
0	2.57	0.834	15.8
25	32.4	0.660	12.1
50	51.5	0.708	13.0
75	29.3	0.400	6.6
100	13.4	0.150	1.3
150	1.49	0.138	1.0
200	0	—	—
300	0	—	—
500	0	—	—

[a] Methyl methacrylate, 10.0 ml. (0.094 mole); diethylcadmium, 0.0024 mole; n-hexane, 9.75 ml.; polymerization time, 3 hrs.; temperature, 30°C.

Table 11. Comparison of the co-catalytic effects of various quinones and phenols upon methyl methacrylate polymerization by diethylcadmium[a].

Co-catalyst	Yield %	$[\eta]$ 20°C chloroform 100 ml./g.	Moleccular weight·10⁻⁴
None	2.79	0.775	14.5
p-Benzoquinone	62.6	0.730	13.6
1.4-Naphthoquinone	61.1	0.537	9.5
9.10-Anthraquinone	9.49	0.619	11.2
Chloranil	14.4	0.940	18.1
Phenol	11.5	1.442	28.8
α-Naphthol	10.0	1.430	28.5
β-Naphthol	14.1	1.356	26.9
Catechol	30.8	5.149	109
Hydroquinone	36.4	4.778	99.1
Resorcinol	100	5.772	121
Pyrogallol	7.40	4.312	89.8
1.4-Naphthohydrquinone	10.9	0.940	18.1

[a] Methyl methacrylate, 10.7 ml. (0.10 mole); diethycadmium, 0.0025 mole; co-catalyst, 0.00125 mole; n-hexane, 9.04 ml.; polimerization time, 3 hrs.; temerature, 30°C.

presence of the vinyl monomer. Table 10 shows the results of polymerization of methyl methacrylate in the presence of various amounts of p-benzoquinone. The yield of polymethyl methacrylate increased with increasing amount of p-benzoquinone up to 50 mole% with respect to diethylcadmium while beyond this limiting amount it gradually decreased.

Similar effects of various quinones and phenols were compared using each of these co-catalysts in amount of 50 mole% with respect to diethylcadmium. The polymerization results are listed in Table 11. It is to be noted that resorcinol gave the highest values both in the conversion and in the molecular weight.

The effects of quinones and phenols were found rather smaller in the cases

of other monomers such as acrylonitrile, styrene and vinyl acetate.

Co-catalytic effects of p-benzoquinone and hydroquinone were examined with respect to diethylzinc-, triethylaluminum- and triethylstibine-catalyzed polymerization. Results obtained are summarized in Tables 12, 13 and 14, from which it is obvious that p-benzoquinone and hydroquinone have more or less positive effects on the polymerization catalyzed by the zinc and aluminum compounds. The activity seems to decrease in the order: $(C_2H_5)_2Cd > (C_2H_5)_2Zn > (C_2H_5)_3Al$. To the triethylstibine-catalyzed polymerization, ether of quinone and hydroquinone exhibits only an inhibiting action.

A possible mechanism for the co-catalytic actions of quinones or phenols

Table 12. Co-catalytic effects of p-bezoquinone and hydroquinone upon methyl methacrylate polymerization by diethylzinc[a].

Co-catalyst	Yield %	$[\eta]$ 20°C chloroform 100 ml./g.	Molecular weight·10^{-4}
—	4.35	0.225	2.9
p-Benzoquinone	15.1	0.580	10.4
Hydroquinone	7.43	1.626	32.7

[a] Methyl metacrylate, 10.7 ml. (0.10 mole); diethylzinc, 0.0025 mole; co-catalyst, 0.00125 mole; n-hexane, 3 ml.; polymerization time, 3 hrs.; temperature, 30°C.

Table 13. Co-catalytic effects of p-benzoquinone and Hydroquinone upon methyl methacrylate polymerization by triethylaluminum[a].

| Co-catalyst	Yield %	$[\eta]$ 20°C. chloroform 100 ml./g.	Molecular weight·10^{-4}
n-Hexane, 5 ml			
—	0.78	0.207	2.5
p-Benzoquinone	9.40	0.821	15.5
Hydroquinone	0.95	3.091	64.0
n-Hexane, 3 ml			
—	3.36	0.110	0.5
p-Benzoquinone	9.79	1.067	20.8
Hydroquinone	3.92	1.956	39.3

[a] Methyl methacrylate, 10.7 ml. (0.10 mole); triethylalminum, 0 0025 mole: co-catalyst, 0.00125 mole; polymerization time, 3 hrs.; temperature, 30°C.

Table 14. Effects of p-benzoquinone and hydroquinone upon methyl methacrylate polymerization by triethystibine[a].

Added compound	Yield %	$[\eta]$ 20°C. chloroform 100 ml./g.	Molecular weight·10^{-4}
—	9.71	1.596	32.1
p-benzoquinone	0	—	—
Hydroquinone	7.15	0.175	1.9

[a] Methyl methacrylate, 10.7 ml. (0.10 mole); triethylstibine, 0.0025 mole; p-benzoquinone or hydroquinone, 0.0025 mole; n-hexane, 9 ml.; reaction time, 3 hrs.; temperature, 30°C.

upon the polymerization may be, for example, assumed as follows:
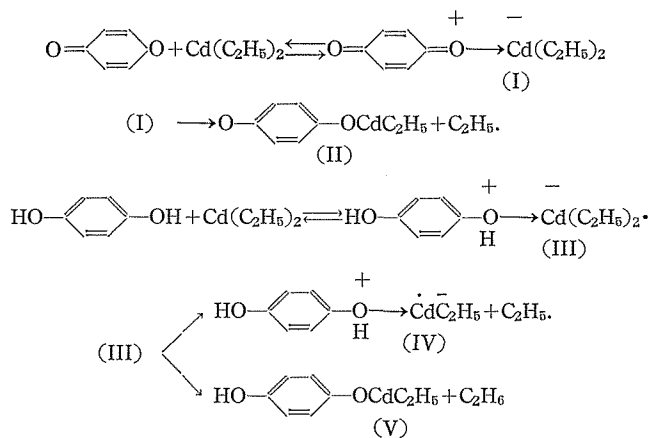
In this mechanism we assume an unstable addition compound (I) or (III) which is formed by one electron transfer from oxygen to cadmium. These adducts may rapidly decompose to give ethyl radical which induces the polymerization of methyl methacrylate.

2.2. Olefin Polymerization by Diethylcadmium-Titanium Tetrachloride Mixture Catalyst[15,17]

It was found that the binary system of diethylcadmium and titanium tetrachloride was a stereospecific catalyst for some olefins and diolefins. Thus, all-cis-1.4-polyisoprene and all-trans-1.4-polybutadiene have been prepared by use of this catalyst. Details of experiments are listed in Tables 15 and 16. Infrared spectra of these stereospecific polymers are shown in Figs. 4 and 5.

Binary systems of titanium tetrachloride and diethylzinc or diethylmagnesium were also examined, but these systems were found to have inferior characteristic for the diolefin polymerization compared with the cadmium compound. The result suggests an important role of the metal alkyl component of the Ziegler type catalyst in the stereospecific polymerization.

Table 15. Isoprene polymerization by CdEt₂—TiCl₄ mixture catalyst.
Isoprene 50 ml. (0.5 mole) CdEt₂ 29 mole % hexane 38 ml., for 2 hrs.

TiCl₄ CdEt₂ (mole%)	Polymn. temp. (°C)	Conv. (%)	Polymer	
			D 868 / D 884	$\bar{P}$
47	0	4	1 —	
47	40	25	100/291	634
47	70	43	100/182	136
39	40	10	100/182	
29	40	7	100/104	
47	40	8	100/198	
47	40	12	100/126	

Table 16. Polymerization of butadiene by diethylcadmium and titanium tetrachloride.

| Experiment No.	Catalyst		Polymerization			Configuration of polymer, %		
	$TiCl_4/CdEt_2$ molar ratio	$CdEt_2/BD$ mole %	Temp., °C.	Time, hrs.	Conversion, %	cis-1.4	trans-1.4	1.2
S-27-3	20/100	8	Room temp.	19	78	0	98	2
S-27-4	60/100	8	Room temp.	19	74	24	70	6
S-28-3	60/100	5	0-1	5	9	0	97	3
S-28-4	60/100	10	0-1	5	15	14	83	3
S-28-8	60/100	5	40	5	50	49	47	4
S-28-9	60/100	1	40	5	6	23	59	18
S-29-1	60/100	1	55	2	5	40	50	10
S-29-2	60/100	6.4	55	2	61	38	54	8
S-29-3	60/100	10	55	2	74	47	50	3
S-31-1	20/100	5	55	2	23	30	62	8
S-32-1	80/100	5	66	2	50	38	57	5
S-32-3	125/100	5	66	2	46	25	72	3
S-32-5	80/100	5	66	2	31	34	62	4

Wave length
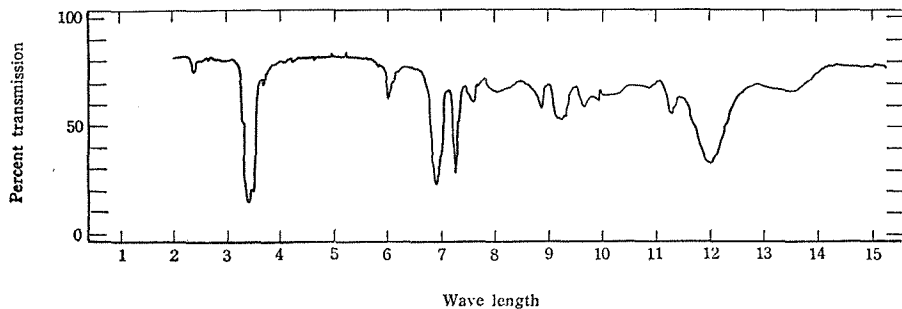
Fig. 4. Infra-red spectrum of cis-1.4 polyisoprene.

Wave length
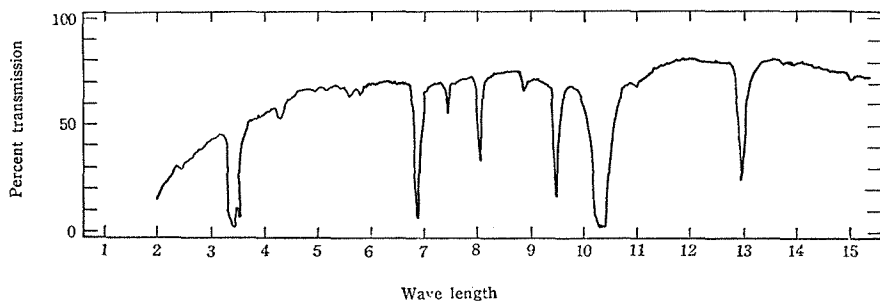
Fig. 5. Infra-red spectrum of trans-1.4 polybutadiene.

III. A POSSIBLE MECHANISM OF THE ZIEGLER TYPE POLYMERIZATION

Some interpretations[1,29,30] of the reaction mechanism of the Ziegler type polymerization have been advanced, but few of them seem to account satisfactorily for the characteristics of the polymerization.

The polymerization is considered to proceed along a crystal surface of the complex catalyst. We assign an imaginary structural unit (Fig. 6) to the com-

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Fig. 6. An imaginary structural unit of AlR$_3$-TiCl$_3$ system.
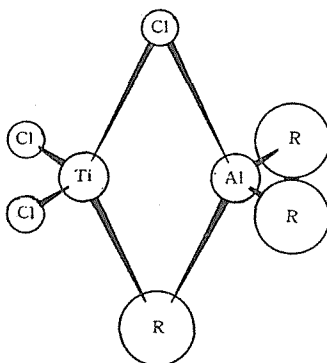
A. initiation :

B propagation (1) :
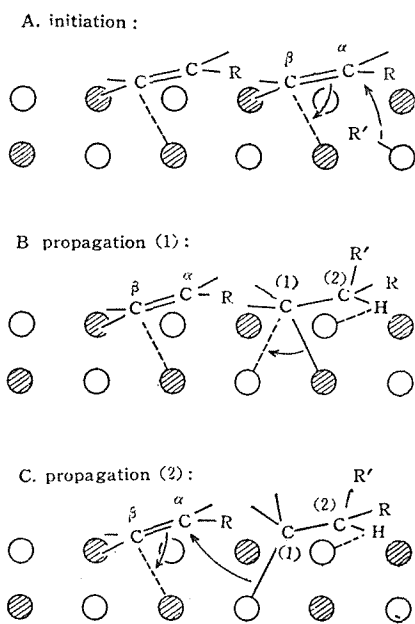

C. propagation (2) :

Fig. 7. An imaginary course for
stereospecific polymerization.
Open circles : Al.
Lined circles : Ti.

ELEVATION

PLAN
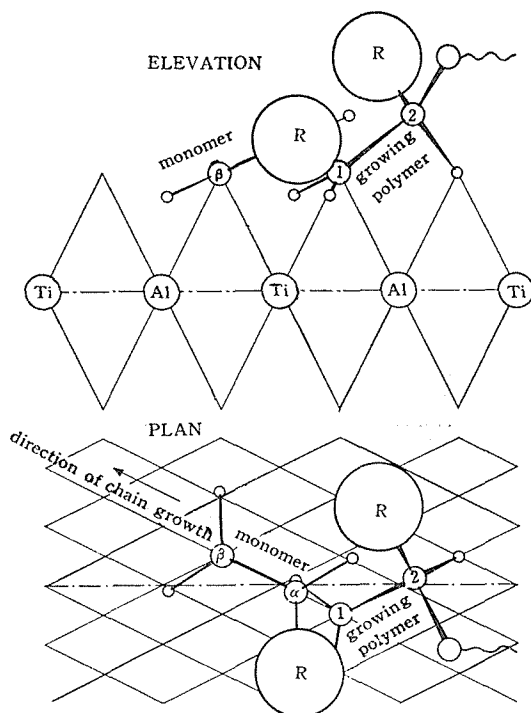
Fig. 8. Steric course of the polymerization.

plex between trialkyl aluminum and titanium trichloride. One possible structure
of the crystal lattice seems to be the one shown in Figs. 7 and 8. In such a
crystal lattice, residual valences of the metal atoms are supposed to be directed
in zigzag directions from the surface of the checkered pattern of aluminum
and titanium. Since titanium chloride has an ability to form a complex with
olefin, the latter molecules are probably adsorbed to the sites of titanium in the
checkered pattern. The stage of initiation consists in the addition of an alkyl
(or aryl) group, which had been bound to an aluminum atom, to the α-carbon
atom of the olefin molecule with the cooperation of the titanium component
(Fig. 7A). The stereochemistry of the propagation step is illustrated in Fig. 8.

We feel that the formation of stereospecific polymer requires inhibition of the rotation around the $\overset{(1)(2)}{C-C}$ axis and a specific orientation of the monomer molecule against the attacking site in the growing polymer. In view of the ease of hydrogen tranfer from a $\overset{(2)}{C}$-atom to a metal atom or to a monomer, it is plausible to consider that the hydrogen atom may exist in the proximity of the metal atom on the catalyst surface. Thus, we assume that the $\overset{(2)}{C}$-atom is fixed to a metal atom through a hydride bonding. Since the $\overset{(1)}{C}$-atom is probably bound to another atom of the metal by an ionic force, it may be considered that the rotation around the $\overset{(1)(2)}{C-C}$ axis is hindered as shown in Figs. 7 and 8.

In diene polymerization, there are possible two modes of addition–12-(or 34-) and 1, 4-addition–which are known to be very susceptible to the nature of metal component in the catalyst. In the butadiene polymerization catalyzed by sodium and potassium or their organic derivatives, 1.2-addition is predominant. In the case of these catalysts, the ionic nature of the $\overset{(1)}{C}$-Na or $\overset{(1)}{C}$-K bond is so large that the $\overset{(2)}{C}$-atom is sufficiently polarized to react with organic residue R. On the other hand, in cases of organic derivatives of less electropositive metals, such as aluminum, cadmium, and lithium, the polarization at the $\overset{(2)}{C}$-atom will be insufficient for the addition reaction. In the following, our discussion will be confined to the case of 1,4-addition. There may be many conceivable conformations for the type of adsorption of diene molecules on the catalyst surface. Among these conformations, we feel the following (Fig. 9) to be most probable.

Since 2.4-adsorption is more favored energetically than 1.4-adsorption, the polymerization will proceed through a preliminary adsorption of monomer in
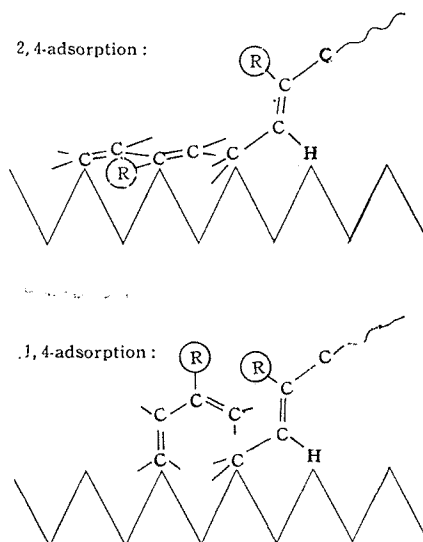
Fig. 9. Stereospecific polymerization of dienes.

the former fashion, provided that no steric requirements are present as in the polymerization of butadiene. In case of isoprene, however, steric interactions between the substituent, $R(=CH_3)$, and the catalyst surface may make 2.4-adsorption somewhat difficult. Thus, it may be concluded that 1.4-cis-polyisoprene can be more easily prepared than 1.4-cis-polybutadiene, and that the reverse is true of the trans-polymerization of the two dienes.

Recently, some investigators advaced the opinions that the nature of active site in the Ziegler type catalyst depends primarily on the transition metal component, but not on the kind of the reducing agent. For example, Carrick et al.[31] reported that the relative reactivity of propylene in the copolymerization with ethylene increased in the order of electronegativity of the transition metal elements in the catalyst, but difference in the kind of the reducing agent affected little change in the relative reactivity. From these results, Carrick et al. suggested the bimolecular complex, such as shown in Fig. 6, may not necessarily be taken into consideration. We feel, however, Carrick's conclusion stated above had not been advanced, if homopolymerizations of propylene were also conducted by the use of their catalysts; for, the relative rate of formation of the crystalline polypropylene will be no doubt affected not only by the nature of transition elements but also by the kind of reducing agent. Furthermore, they did not refer to whether the rates of copolymerization were affected by varying the kind of catalyst. This is regarded as an important point in considering the role of the reducing agent.

Considering various experimental results on the stereospecific polymerization of propylene and dienes, we had better to conclude that the reducing agent also plays an important role in the initiation and propagation stages in the Ziegler type polymerizations.

IV. CATALYTIC ACTIVITY OF THE BINARY SYSTEM OF ORGAONMETALLIC COMPOUND AND METAL HALIDE

In connection with the Ziegler catalyst, we have examined catalytic activities of a number of binary systems of metal alkyl and metal halide. Most of the examinations were conducted in sealed tubes under nitrogen at room temperature or lower. Methyl methacrylate, vinyl acetate and vinyl chloride were used as monomer. In some cases, methyl acrylate and styrene were also examined. Hexane, benzene, toluene, ether, tetrahydrofuran and dioxane were used as solvent.

The outline of results obtained is listed in Table 17. It is very difficult to draw some conclusions on the catalytic reactivities of various metal salts, but it may be meaningless to point out some significant characteristics of these metal salts which were made clear from our experiments. Alkali and alkaline earth metal salts seem to be rather indifferent toward the vinyl polymerization in combination with any of the metal alkyls examined. The electronegativity of these metals is so small that the crystals of the metal halide consist of almost pure ion lattices which are too stable to undergo any chemical changes with or-

Table 17—1. Catalytic activity of the binary system of organometallic compound and metal halide.[a)b)c)].

	LiBu	CdEt$_2$	ZnEt$_2$	AlEt$_3$	PbEt$_4$	SnEt$_4$	SbEt$_3$	HgBu$_2$	BBu$_3$
LiCl	—	—	○	—	—	—			
NaCl		—		—	—	—			
KCl		—		—	—				
CuCl		—		○	—			—	—
CuI	×	—	○	○		—	—		○
CuOAc		—				—			—
AgCl		○	○	○	—	—		—	
AgNO$_3$		—	○	◎	◎				○
BeCl$_2$		—	○	—	—	—		—	
MgCl$_2$	—	—	○	—	—	—		—	
MgBr$_2$		◎		○		—			○
CaCl$_2$		—	○	—	—				
SrCl$_2$	—	○	○	○	—				○
BaCl$_2$		—	○	—	—		—		
ZnCl$_2$	—	—	○	○	◎	—		◎	○
ZnBr$_2$		○						◎	
ZnI$_2$		—	—			—	—		
Zn(OAc)$_2$				—				—	—
CdCl$_2$	—	○	○	—	—			—	
CdBr$_2$	—	○	○	○		—	—		○
CdI$_2$	—	—	○			—			
Cd(OAc)$_2$		—		○		—			—
Hg$_2$Cl$_2$	×	○	○	○	—	—	—	—	—
HgCl$_2$		◎	◎	○	—	—	—	—	—
Hg(OAc)$_2$		—		—		—			—
BF$_3$		○	○	◎	◎	—	—	—	◎
AlCl$_3$	×	—	○	○	◎	—	—	—	—
InCl$_3$		○	○	○	◎	—	—	—	—
TlCl		○	○	○	—	—	—	—	—
CeCl$_3$		—	○	○	○	—	—	—	—
ThCl$_4$		—	○	○				—	
monomers examined	MMA	MMA	MMA	VAc VCl	MMA	VAc VCl	VAc VCl	MMA VAc	VAc VCl

[a)] Standard conditions for polymerization: under nitrogen at room temp. for 20 hours.

[g)] Extent of Polymerization: ◎ >80%; ◎ 50—80 %; ○20—50%; ○<20%

[c)] ×; Catalytic power of LiBu was destroyed with these halides.

ganometallic compounds. In the case of methacrylate polymerization with butyllithium as catalyst, however, the addition of lithium bromide or strontium chloride causes a significant variation in the spatial structure of polymers to be formed. Halides of magnesium cadmium and lead were found to behave similary. The results are shown in Table 18.

The role of these halides in the stereochemistry of the methacrylate polymerization may be interpreted in terms of a steric requirement which arises

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Table 17—2. Catalytic activity binary system of organometallic compound and metal halide[a)b)c)].

	LiBu	CdEt₂	ZnEt₂	AlEt₃	PbEt₄	SnEt₄	SbEt₃	HgBu₂	BBu₃
SnCl₄	×	—	○	—	—	—	—	○	○
PbCl₂	—	—	○		—	—	○	—	
TiCl₃		—	○	○	○	—	—	○	—
TiCl₄	×	—	—	—	—	—	—	—	—
TiI₄		○	—	○	—	—	—	—	
ZrCl₄	×	—	○	◎	◎	—	—	○	—
PCl₃		○	○	—	—	—	—	○	—
PCl₅	×	—	◎	—	—	—	—	○	—
AsCl₃		—	○		—	—		—	
SbCl₃		—	—	—	○	—		◎	—
SbCl₅		—	—	—	—	—	○	◎	—
BiCl₃		—	○	○	◎	○	—	◎	—
VCl₃	×	○	○	○	○	—	—	○	—
VCl₄		—	◎	◎	◎	○	—	—	
VOCl₂	×	—	○	○	◎	○	—		—
VOCl₃		◎	◎	○	◎	—	—		—
NbCl₅		—		○		—		—	—
TaCl₅		○	○		○	—		—	
TeCl₄		—	○	—	—	—			—
CrCl₃	×	—	○	—	—	—	○	○	—
MnCl₂	×	○	—		—	—		—	○
FeCl₃	×	◎	○	○	—	—	—	—	—
Fe(OAc)₃		—							—
Fe(OAc)₂OH				○					
CoCl₂	×	—	○		—	—	—	○	—
Co(OAc)₂		—		—		—			
NiCl₂	×	◎	○		—	—	—	—	—
Ni(OAc)₂		—				—			○
PdCl₂		—	—	○	○	—		—	—
PtCl₂		◎			◎				
monomers examined	MMA	MMA	MMA	VAc VCl	MMA	VAc VCl	VAc VCl	MMA VAc	VAc VCl

[a)] Standard conditions for polymerization: under nitrogen at room temp. for 20 hours.

[b)] Extent of Polymerization: ◎>80%; ◉50—80%; ○ 20—50%; ○<20%

[c)] ×; Catalytic power of LiBu was destroyed with these halides.

from the complex formation between the monomer and the metal halide.

In connection to this, the behavior of potassium chromate in the methacrylate polymerization was also noticeable as shown in Table 19.

It is seen from Table 19 that the crystallinity of the polymer to be formed is continuously varied to type II with the increase in quantity of potassium chromate added.

Among the metal salts examined, vanadium compounds exhibit the most prominent catalytic activity in the vinyl polymerization, whereas titanium tet-

Table 18. Effects of metal halides on the polymerization of methyl methacrylate by butyllithium[a].

Metal halide added	Extent of polymerization (%)	Type of the polymer
—	95	III
LiCl	95	III
LiBr	90	II[b]
MgCl$_2$	93	III
MgBr$_2$	96	II[b]
ZnCl$_2$	4	—
ZnI$_2$	0	—
SrCl$_2$	90	II[b]
CdBr$_2$	98	II[b]
CdCl$_2$	86	II[b]
CdI$_2$	98	II[b]
PbCl$_2$	75	II[b]

[a] Experimental conditions: methyl methacrylate, 5 ml.; BuLi 1 mmole; toluene 10 ml.; under nitrogen; temperature, −70°C.

[b] contaminated with a small quantity of Type III.

Table 19. Effect of potassium cromate on the polymerization of methyl methacrylate by butyllithium[a,b].

K$_2$CrO$_4$ (mmole)	K$_2$CrO$_4$/BuLi (mole ratio)	Crystallinity
0	0	III
0.5	0.5	
1.0	1.0	
1.5	1.5	
2.0	2.0	↓
4.0	4.0	II

[a] Reaction conditions: methyl methacrylate, 5 ml.; BuLi. 1 mmole; toluene, 10 ml.; reaction time, 1 hr.; reaction temperature, −50°C.

[b] Extent of polymerization, about 95%.

rachloride, a most conventional component in the Ziegler catalyst, was found not effective at all as shown in Table 17.

Zirconium tetrachloride has an excellent activity in combination with tetraethyllead, triethylaluminum or dibutylmercury. Zinc chloride is an effective cocatalyst for dibutylmercury, while mercuric chloride is for diethylzinc.

Thus, it is to be noted that there seems to exist "a selective rule" for an organometallic compound to establish an active combination with a metal salt partner.

As was mentioned above, the vinyl polymerizations by the alkyl derivatives of metal with electronegativity larger than 12 proceed according to a radical mechanism in the presence of oxygen compounds. On the other hand, it is widely blieved that the olefin polymerization by the Ziegler catalyst is anionic in nature.
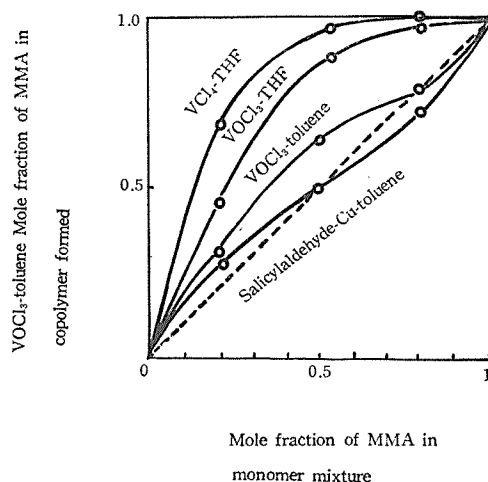
Fig. 10. Styrene-methyl methacrylate copolymerization induced by
CdEt$_2$ with various cocatalysts.

Results of styrene-methyl methacrylate copolymerization with diethylcadium (XCd=1.4) and vanadium halide as catalyst are shown in Fig. 10. It is clearly seen from the Figure that the anionic nature of the copolymerization increases in parallel to the polarity of the solvent used. The duality in the catalytic nature has also been found in the binary system of triethylaluminum and vanadium oxychloride.

Based on the electron magnetic resonance absorption measurement, Shilov[32] suggested a free radical mechanism for the Ziegler type polymerization. Shilov's report seems to present an evidence for the radical characteristic of the Ziegler catalyst, even if his interpretation is not necessarily valid.

These facts indicate that the alkyl derivatives of metal having moderate magnitude (X=1.4−1.6) of electronegativity can manifest their catalytic activities

Table 20. Vinyl acetate polymerization catalyzed by dibutylmercury and
some metal salts[a].

Metal salt	Solvent (ml)	Conversion (%)	Degree of porimerization
—	Dioxane (5)	0	—
ZnCl$_2$	do.	72.8	—
BiCl$_3$	do	80.8	150
SbCl$_3$	do.	38.9	260
ZnBr$_2$	Dioxane (1) Hexane (1)	100	380
ZnO	do.	0	—
Zn(OAc)$_2$	Dioxane (1.5)	0	—
ZnCl$_2$	Ethyl acetate (3)	83.7	860
do.	Ether (5)	16.0	—
do.	Benzene (5)	trace	—
BiCl$_3$	Heptane (5)	18.2	270

[a] Monomer, 5 ml.; HgBu$_2$, metal halide, 1 mole % for monomer; reaction temperature, 15°C.; reaction time, 50 hrs.

in two fashions in response to the reaction conditions. The chemical structures of cocatalyst, monomer and solvent as well as reaction temperature are probably the most important factors determining the nature of the polymerization.

Thus, it may be too early to conclude that the polymerizations of vinyl acetate[4] and of vinyl chloride[5] induced by the Ziegler type catalyst do proceed according to an anionic mechanism even if the mechanism of copolymerization between styrene and methyl methacrylate was proved to be anionic in nature. Table 20 is a partial list for results of vinyl acetate polymerization catalyzed by dibutylmercury ($X_{Hg}=1.9$). The C$-$Hg bond is known very weak, but dibutylmercury alone has no ability to induce the polymerization. The effects of zinc
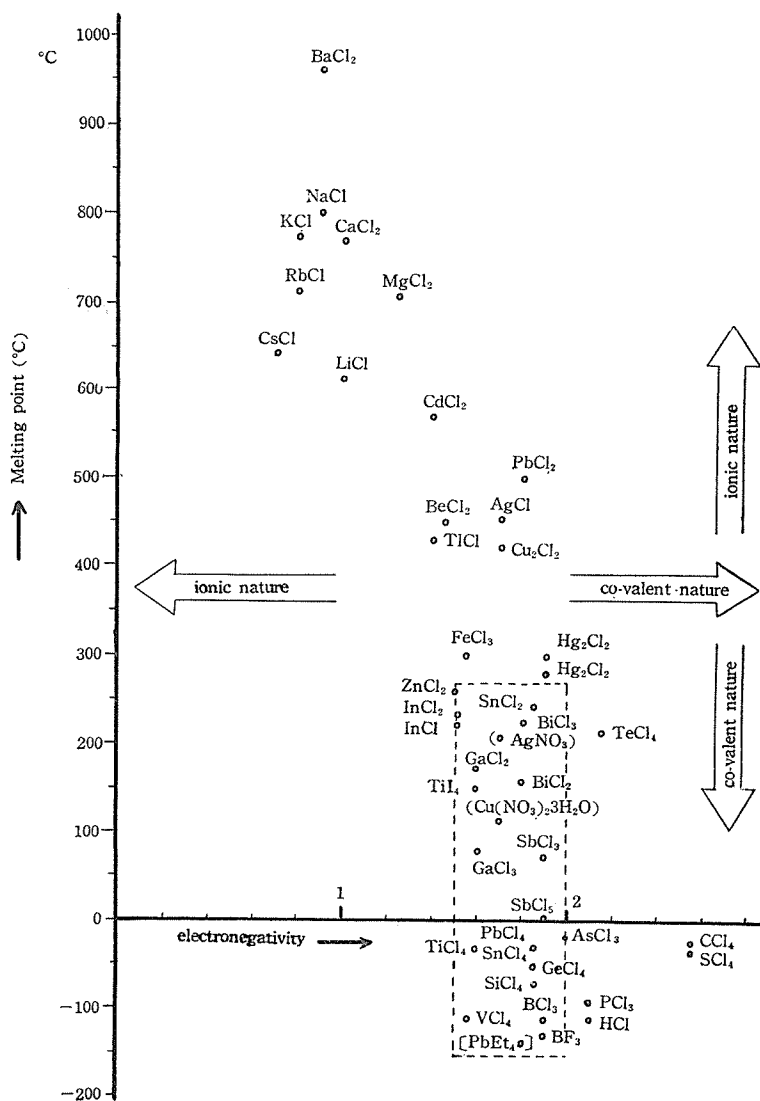

Fig. 11. Cocatalytic activities and nature of chemical bonds in various metal chloride. (catalyst : tetraethyllead)

halide and bismuth chloride are noticeable.

The copolymerization between styrene and methyl methacrylate by the binary systems of dibutylmercury and metal halide such as zinc chloride, antimony chloride, bismuth chloride and so on suggested a radical mechamism.

It has long been known that mercury alkyl reacts with some metal halides in the following way :

$$HgR_2+MXn \longrightarrow RHgX+RMXn_{-1}$$

For example :

$$HgBu_2+ZnCl_2 \longrightarrow RHgCl+RZnCl$$
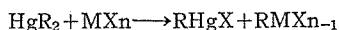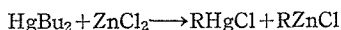
Since these reaction products have been found not to induce the polymerization, it is probable that the effective radicals may be generated from unstable intermediates which are formed in the course of reation between $HgBu_2$ and $ZnCl_2$. As a possible structure of the intermediate we assume a complex (I) similar to that stated in the foregoing section (Fig. 6).

$$HgBu_2+ZnCl \longrightarrow Bu-Hg \overset{R\cdot}{\underset{\cdot Cl}{\diagdown}} ZnCl \longrightarrow R-Hg\cdot +R\cdot +ZnCl_2$$

(I)
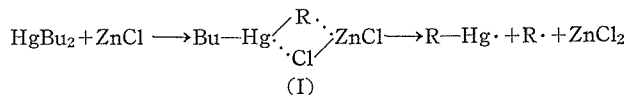
The mechanism may be true of the case of tetraethyllead ($X_{Pb}=1.8$) catalyst.

Y. Takeda, a member of our laboratory, arranged a large variety of metal salts as cocatalyst in order of the scales of electronegativity, ion radius, melting
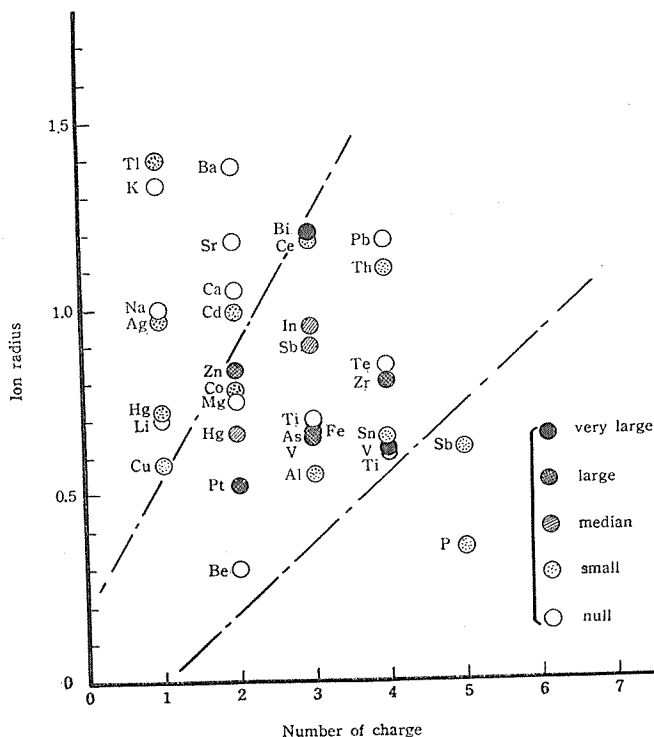
Fig. 12. An illustration of catalytic activity of metal chloride with respect of the ion potential.

point and other physical properties of the metals. One of his works is quoted in Fig. 11.

Fig. 12 is a similar illustration of the activities of metal chloride with respect to the ion potential.

These Figures show that an appropriate covalent nature is necessary for a metal salt to be active in inducing the polymerization.

The covalent nature, which arises from the proper magnitude ($X = 1.5$ to 2.0) of electronegativity of the relevant metal, will probably favor the formation and decomposition of a three-centered bonding as is stated above.

The selective property observed in the combinations of catalyst components is also interpreted in terms of energetic and steric accesibility of the three-centered complex formation from the catalyst components.

V. ANIONIC POLYMERIZATIONS BY CALCIUM ATE COMPLEX AND ALKALI METAL KETYL

5.1. Organocalcium Compound

Alkyl compounds of alkaline earth metals, *i.e.*, calcium, strontium or barium, have not been isolated as yet, and the nature of organoalkaline earth metal compounds as polymerization catalyst seems to remain obscure. We prepared an organocalcium compound, calcium zinctetraethyl, by the reaction of calcium metal with diethylzinc and studied the reactivity of this compound on various

Table 21. Vinyl polymerization by calcium zinctetraethyl complex.

Monomer	Conversion %	D.P.
Acrylonitrile	48.2	410
Methyl methacrylate	64.3	5300
Styrene	9.6	5490

[a] Monomer, 0.05 mole; catalyst, 5% for monomer; 20 hrs. reaction at 10°C.: under nitrogen.
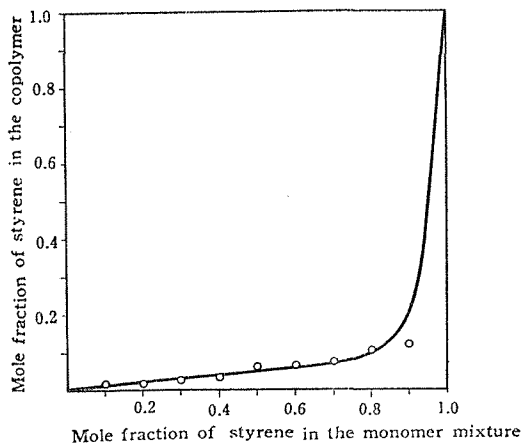

Fig. 13. Copolymerization between styrene and methyl methacrylate.

vinyl monomers. Results are shown in Table 21.

Vinyl acetate, vinyl chloride and methyl acrylate were not polymerized by the calcium complex.

The results of copolymerization betweem styrene and methyl methacrylate are shown in Fig. 13. Monomer reactivity ratios calculated from the results are $r_1 = 0.31$ and $r_2 = 17.1$ with styrene as monomer 1. Considering the reactivity ratios, the polymerization induced by calcium zinctetraethyl complex seems to be a typical anionic polymerization.

The overall activation energy is 5.7 kcal/mole for the methacrylate polymerization in benzene. This value is rather small and of the same order of magnitude as those found for the ionic polymerizations in literature[33].

The rate of polymerization is proportional to the concentrations of monomer and catalyst, and the degree of polymerization proportional to the monomer concentration but independent of the catalyst concentration.

These kinetic results may make it possible to consider the mechanism of the polymerization to be anionic.

A sample of polystyrene prepared by calcium zinctetraethyl complex as catalyst was found to involve 13% fraction insoluble in hot methyl ethyl ketone; infrared spectrum of the insoluble part distinctly showed the crystalline band (Fig. 14).

An X-ray diffraction pattern of this polymer has shown discrete rings.

From the above results together with the large value of density ($d_4^{25} = 1.064$), the polystyrene by this catalyst is considered an isotactic polymer.
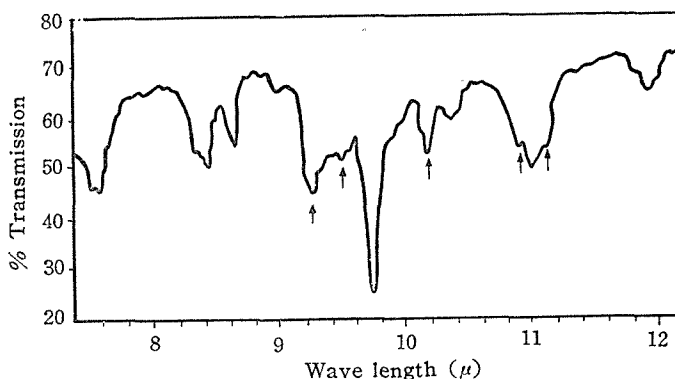
Fig. 14. Infrared spectrum of polystyrene. Arrows indicate crystalline bands.

Table 22. Fractionation of F-polymer.

Original Sample	Solubility	Content of the fraction based on the original sample (%)	Sample No.
ICM-1	Soluble in cold acetone	15	ICM-3
	Insoluble in cold acetone	85	ICM-2'
ICM-2'	Soluble in cold chloroform	64	ICM-2
	Insoluble in cold chloroform	36	ICM-4[a]

[a] Soluble in boiling methy ethyl ketone.

Polymethyl methacrylate obtained by calcium zinctetraethyl complex as catalyst was found to have a fraction insoluble acetone or chloroform, being quite different from the usual polymethyl methacrylate.

A typical example of the fractionation of the polymer is shown in Table 22.

The polymer samples were treated with 3-heptanone and were subjected to the infrared and X-ray analysis. The infrared spectra are illustrated in Fig. 15.

We called this crystalline polymer F-polymer. F-polymer has also been found to be producible with *n*-butyllithium[19] as catalyst at low temperature.

If the monomer is polymerized at low temperature with lithium aluminum-tetraalkyl complex[19] or diethylcadium[17] as catalyst, another type of crystalliza-

Wave number

Fig. 15. Infra-red spectrum of crystalline polymethyl methacrylate (Type III).

Wave number

Fig. 16. Infra-red spectrum of crystalline polymethyl methacrylate (Type 1).

ble polymer is produced; we called it G-polymer. G-polymer is soluble in acetone (Fig. 16). As seen in the Figures, the X-ray diffraction patterns of the two polymers are obviously different from each other. The infrared absorption spectra of F- and G-polymer differ each other in the crystalline and amorphous states.
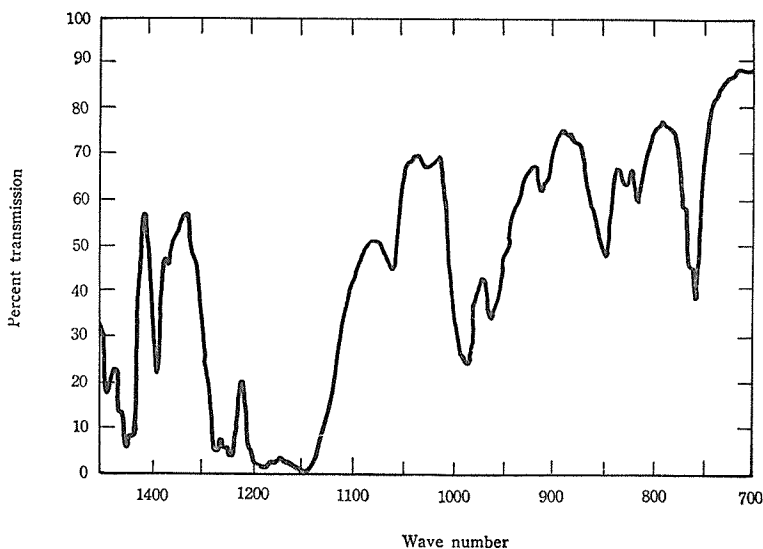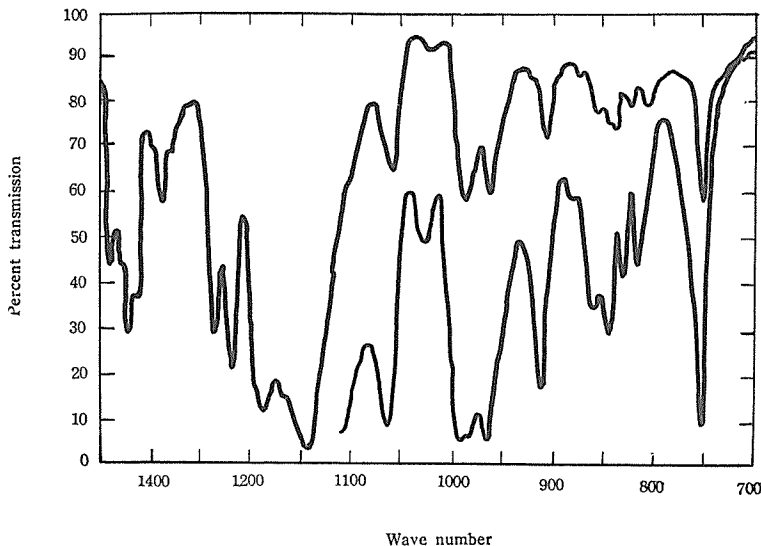
Comparison with the results reported by Fox et al. has led us to the conclusion that F- and G-polymer correspond to Type 3 and Type 1 polymers, respectively. According to Fox et. al., Type 1 polymer is syndiotactic while Type 3 is a stereoblock polymer consisting of syndiotactic and isotactic portions.

5.2. Metal Ketyl

Metal ketyl (momo-alkali mital complex of unenolizable ketone), [I], the magnetic property of which was intensively investigated by E. Müller[34], can be prepared by the reaction of alkali metal

with the excess of an unenolizable ketone in a polar solvent such as dioxane and tetrahydrofuran[35]. The dialkali metal complex of the ketone, [II], is prepared by the reaction of one mole of ketone with two moles of alkali metal in a polar solvent. The monoalkali complex [I] induces the polymerization of vinyl compounds such as acrylonitrile and methyl methacrylate. Styrene was not polymerized by [I]. On the other hand, the di-alkali metal complex, [II], had greater activity than [I]. By complex [II] styrene also was polymerized rapidly to a quantitative yield even at low temperature. Details are shown in Table 23.

Table 23. Vinyl polymerization by mono- and di-potassium complex of benzophenone[a].

Calyst (mole %)	Monomer (ml.)	Solvent (ml.)	Time (hr.)	Conversion (%)	Degree of Polymerization
K–benzophenone (3)	Acrylonitrile (10)	Dioxane (5)	20	31.5	—
K–benzophenone (6)	Methyl Methacrylate (2)	Ether (5)	do.	59.2	120
do.	do.	Hexane (5)	do.	99.8	220
do.	Styrene (10)	Ether (5)	do	0	—
do.	do.	Hexane (5)	do.	0	—
do	Vinyl Acetate (10)	do.	do	0	—
K₂–benzophenone (2)	Acrylonitrile (5)	Dioxane (1)	7	Explosive	—
do.	Methyl Methacrylate (5)	do	do.	78.3	170
do.	Styrene (5)	do.	do.	100	2500
do.	Vinyl Acetate (5)	do.	do.	0	—

[a] Polymerization at room temperature.

Table 24. Polymerization of acrylonitrile by alkali benzophenone-ketyl[*].

Exp. No.	Acrylonitrile (ml.)	Dioxane (ml.)	Catalyst (mole %)	Reaction time (hrs.)	Extent of polymerization (%)
BL-2-1	10	7	Li-benzophenone (6)	50	trace
BN-2-1	2	5	Na-benzophnone (7)	70	21.4
BK-1-1	10	5	K-benzophenono (3)	50	31.5

[*] Reaction at 25°C.

Table 25 Polymerization of methyl methacrylate by various ketyls[*].

Exp. No.	Methyl methacrylate (ml.)	solvent (ml.)	Catalyst (mole %)	Reaction time (hrs.)	Extent of polymerization (%)	Degree of polymerization
BL-2-5	10	Dioxane (7)	Li-benzophenone (6)	50	18.2	320
BN-2-5	2	Dioxane (5)	Na-benzophenone[a] (7)	70	0	—
BN-3-2	5	Tetrahydro-furan (2)	Na-benzophenone[b] (1)	50	63.2	360
BK-2-21	2	Dioxane (3)	K-benzopenone (9)	50	90.7	100
MN-0-5	5	Dioxane (5)	Na-MICHEL's ketone (0.8)	50	2.9	4100
MK-0-5	5	Dioxane (5)	K-MICHEL's ketone (0.6)	120	1.5	15000

[*] Reaction at 25°C.
[a] Dioxane solution.
[b] Tetrahyrofran solution.

Table 26. Polymerization of methacrylate by some ketyls in Various solvents[*]

Exp. No.	Methyl methacrylate (ml.)	Solvent (ml.)	Catalyst (mole %)	Extent of polymerization (%)	Degree of polymerization
BL-2-5	10	Dioxane (7)	Li-benzo-phenone (6)	18.2	320
BL-2-6	10	Ether (7)	do.	0	—
BL-2-7	10	Benzene (7)	do.	29.2	820
BL-2-8	10	Hexane (7)	do.	32.8	830
MN-0-5	5	Dioxane (5)	Na-MICHLER's ketone (0.8)	2.9	4100
MN-0-6	5	Ether (5)	do.	4.0	4400
MN-0-7	5	Benzene (5)	do.	11.3	3900
MN-0-8	5	Hexane (5)	do.	35.0	2900

[*] Reaction time, 50 hr.; reaction temperature, 25°C.

The character of the polymerization seemed to be affected by the variation in the kind of ketone, metal and solvent. For example, lithium benzophenone-ketyl, in contrast to sodium or potassium benzophenone-ketyl, did not induce the polymerization of acrylonitrile, as shown in Table 24.

Table 25, shows similar results in the polymerization of methyl methacrylate. Prominent effects of solvents on the polymerization of methye methacrylate are shown in Table 26.

The initiation and propagation reactions of the methacrylate polymerization by ketyl [I] is considered to take place according to the 1.4-addition mechanism

of metal compounds onto the conjugated carbonyl system of the monomer molecule.

initiation :

$$\text{ketyl}^- \text{ Na}^+ + \text{C}=\text{C}-\text{C}=\text{O} \longrightarrow \text{ketyl}-\text{C} \boxed{-\text{C}=\text{C}=\text{O}}^- \text{ Na}^+$$

$$\text{(4)(3)(2)(1)} \qquad\qquad \text{[III]}$$

propagation :

$$\text{ketyl}-\text{C} \boxed{-\text{C}=\text{C}=\text{O}}^- \text{ Na}^+ \longrightarrow \text{ketyl}-\text{C}-\text{C}-\text{C}=\text{O}$$

$$\underset{\text{C}=\text{C}-\text{C}=\text{O}}{} \qquad\qquad \underset{\text{C}\boxed{-\text{C}=\text{C}=\text{O}}^- \text{ Na}^+}{}$$

$$\text{[IV]}$$
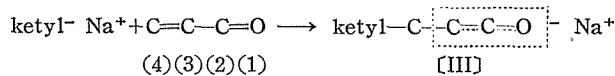
(Dotted lines show conjugated systems.)

The conjugated system within the dotted line is the structure of an enolate ion. The ability to form such an enolate ion may be a unique characteristic of alkali metal.

The enolate ion will be formed in a similar way in the polymerizations by the usual alkyl alkali (or alkaline earth) catalyst.

In cases of organic compounds of metals with larger electronegativity such as cadmium (X=1.4) or aluminum (X=1.5) as catalyst, the corresponding conjugated system becomes a structure of undissociated metallic salt of the enol, —C=C—O—M, which can not cause a further addition reaction.
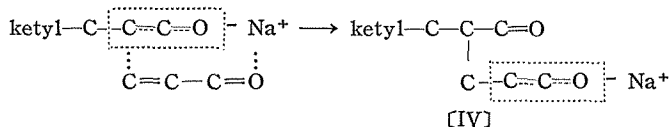
In the polymerization of styrene by di-alkali complex [II] the formation of living polymer was observed. To a solution of 5 ml. of styrene in 10 ml. of tetrahydrofuran, dipotassium benzophenone (6 mole % with regard to the monomer) was added at −70°C. After one hour standing, 10 ml. of methyl methacrylate was added. Extent of polymerization was 63.4% after 1.5 hours.

Polymers formed were fractionated as shown in Table 27.

Fraction 3 (insoluble in either cold cyclohexane or hot acetonitrile) was proved to be a block copolymer.

Table 27. Fractionation of block copolymer.

Fraction	Solubility	Amount of extraction (%)	Content of methyl methacrylate (mole %)
1	Soluble in cold acetonitrile	31.2	99.7
2	Soluble in cold cyclohexane	2.5	7.9
3	Insoluble in either acetonitrile or cold cyclohexane; soluble in hot cyclohexane	25.0	33.6
4	Insoluble in either cyclohexane or cold acetonitrile; soluble in hot acetonitrile	30.1	89.9
5	Insoluble in either cyclohexane or acetonitrile; soluble in benzene	Small amount	—

The reaction mechanism for the formation of block copolymer may be as follows :

$$K^{+-}\overset{|}{\underset{|}{C}}-O^-K^+ + C{=}C \xrightarrow[\text{transfer}]{\overset{\text{one}}{\text{electron}}} \left[\overset{|}{\underset{|}{C}}{=}O \right]^- K^+ + \cdot\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}K^+$$

reddish violet   deep blue

$$\xrightarrow{} \cdots\cdots \xrightarrow{\text{styrene}} \cdot\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}\cdots\cdots\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}K^+$$

$$\xrightarrow{}\cdots\cdots\xrightarrow[\text{methacrylate}]{\text{methyl}} \cdot C{-}C{-}C{-}C{-}\cdots\cdots C{-}C{-}C{-}\overset{|}{\underset{CO_2CH_3}{\overset{C}{\underset{|}{C}}}}{-}\overset{|}{\underset{CO_2CH_3}{\overset{C}{\underset{|}{C}}}}{-}\cdots\cdots\overset{|}{\underset{\overset{C{=}O}{\underset{OCH_3}{|}}}{\overset{C}{\underset{|}{C}}}} K^{\oplus}$$
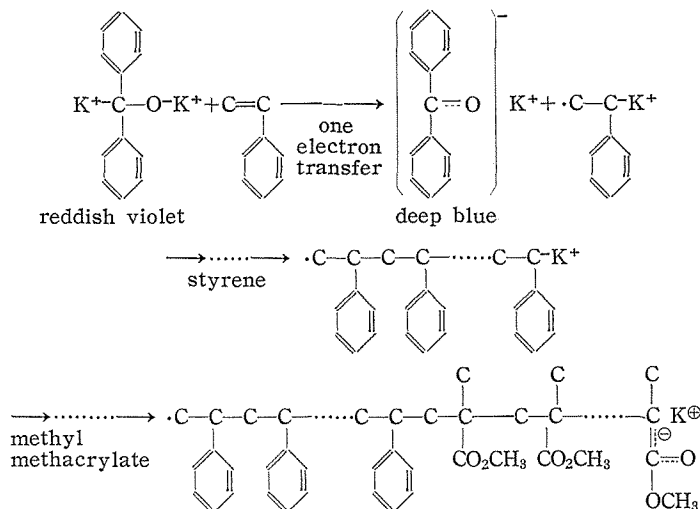
Some samples of polymethyl methacrylate obtained by ketyl (I) or di-metal complex (II) were proved to have the same infrared absorption spectrum as that of F-polymer (type III),
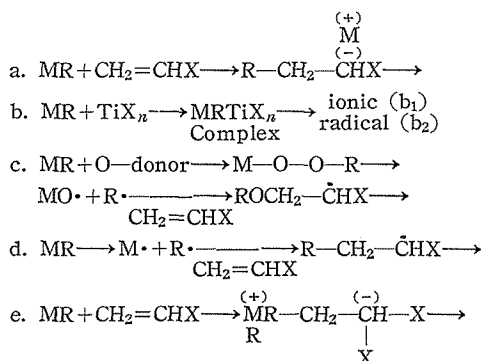
VI. CLASSIFICATION OF ORGANOMETALLIC COMPOUNDS AS POLYMERIZATION CATALYSTS

It will be reasonable from the foregoing discussion to consider that organometallic compounds are classified into six groups according to their catalytic nature, as shown in Table 28.

Type 1 (K, Na, Ba, Ca, Sr), X<1.0

The ionic property of C-M bond of these organometallics is so large that the reaction of type (a) takes place very easily, but peroxide formation such as reaction type (c) seems very difficult in these organometallic compounds. The Ziegler type reaction (type (b₁)) also is possible with the organometallics, but

Table 28. Classification of organometallic compounds as polymerization catalysts.

$$\text{a. } MR + CH_2{=}CHX \longrightarrow R{-}CH_2{-}\overset{(+)}{\underset{(-)}{\overset{M}{CHX}}} \longrightarrow$$

$$\text{b. } MR + TiX_n \longrightarrow \underset{\text{Complex}}{MRTiX_n} \xrightarrow{\overset{\text{ionic } (b_1)}{\text{radical } (b_2)}}$$

$$\text{c. } MR + O{-}donor \longrightarrow M{-}O{-}O{-}R \longrightarrow$$
$$MO\cdot + R\cdot \underset{CH_2{=}CHX}{\xrightarrow{}} ROCH_2{-}\overset{\cdot}{CHX} \longrightarrow$$

$$\text{d. } MR \longrightarrow M\cdot + R\cdot \underset{CH_2{=}CHX}{\xrightarrow{}} R{-}CH_2{-}\overset{-}{CHX} \longrightarrow$$

$$\text{e. } MR + CH_2{=}CHX \longrightarrow \overset{(+)}{\underset{R}{MR}}{-}CH_2{-}\overset{(-)}{\underset{X}{\overset{|}{CH}}}{-}X \longrightarrow$$

Electronegativity	Family number					Reaction type					Cat. type
	I	II	III	IV	V	a	b	c	d	e	
0.8 – 1.0	K 0.8 Na 0.9	Ba 0.9 Ca 1.0				⊘	⊘	○			1
1.0 – 1.2	Li 1.0	Mg 1.25				⊘	⊘	○			2
1.2 – 1.4		Zn 1.5 Cd 1.4	Al 1.5				⊘ ○	○			3
1.4 – 1.6			B 1.9					○			4
1.6 – 1.8	Hg 1.9		Pb 1.8	Sb 1.9 Bi 0.8				○	○		5
1.8 – 2.0				P 2.1						⊘	6

⊘ ionic polymerization

○ radical polymerization

excellent stereospecificity of polymers formed may not be expected because these metals are incapable of forming the three centered bonding and their ion radii are too large.

Type 2 (Li, Mg) $X = 1.0 - 1.25$

The covalent nature of the bond increases at the expense of the ionic one, but reaction (a) is still possible with these organometallics. The alkyl derivative of lithium, which has a small ion radius and co-ordination power, reacts with some metal halides (type (b_1)) to afford and excellent stereospecific catalyst. Reaction (c) is also possible.

Type 3 (Be, Al, Zn, Cd) $X = 1.4 - 1.5$

On account of the larger covalent nature, reaction (a) does not take place. Beryllium and aluminum alkyls become splendid stereospecific catalyst by reaction (b). These metals also are small in ion radii and large in co-ordination power. Reaction (c) is possible with these organometallic compounds.

Type 4 (B) $X = 1.8 - 2.0$

Organoboron compound occupies a special position in the classification, because the atomic radius of boron is very small despite of its larger electronegativity. Type (c) and (b_2) reactions are possible with the boron compound.

Type 5 (Hg, Pb, Sb, Bi) $X = 1.8 - 1.9$

Small disociation energy of C–M bond is a characteristic of these organometallic compounds. Type (d) reaction takes place easily, especially with the aid of light. In some cases, the radical decomposition is effected under the co-operation with metal halide (type (b_2)).

Type 6 (P) $X = 2.1$

The vinyl polymerization induced by trialkylphosphin is considered anionic in nature, where the initiation is caused by putting the lone pair electrons of phosphor atom into the double bond of the vinyl monomer (type e).

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