

Anionic Polymerization of Vinyl Monomers with Organometallic Compound—Phosphoramidate Systems

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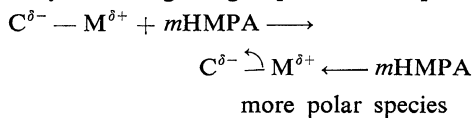
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ABSTRACT: The polymerization of vinyl monomers with organometallic compounds was carried out in the presence of monodentate or bidentate phosphoryl compounds with $-\text{N}(\text{CH}_3)_2$ substituents. The polymerization of styrene or α -methylstyrene (α -MeSt) with organomagnesium compounds was more facilitated in the presence of the bidentate donors than in the presence of the monodentate type. In the polymerization of acrylonitrile (AN) with diethylzinc or organoaluminium compounds, the bidentate phosphoramidates were less effective donors than the monodentate ones. The latter polymerization was considered to be caused by the coordination of both the phosphoramidates and AN with the organometallic compounds, and to be reduced by the undesirable coordination of the bidentate phosphoramidates to the sites required for the coordination of AN. The equilibrium monomer concentration ($[\text{M}]_e$) in the polymerization of α -MeSt was dependent on the solvents used for the polymerization; the values of $[\text{M}]_e$ was smaller in toluene than in tetrahydrofuran.

KEY WORDS Anionic Polymerization / Vinyl Monomer / Organometallic Compound / Phosphoramidates / Coordination / Initiator Efficiency / Equilibrium Monomer Concentration / Branched Polymer / Molecular Weight Distribution /

Organometallic compounds, which by themselves have no ability to initiate the polymerization of vinyl monomers, were found to cause polymerization in the presence of hexamethylphosphoramide (HMPA), *e.g.*, in the case of organomagnesium compounds—styrene or α -methylstyrene,^{1,2} alkali metal alkoxides—methyl methacrylate,³ and organoaluminium compounds—acrylonitrile^{4,5} or methyl methacrylate.⁵ Such a change in the reactivity of the organometallic compounds has been considered to be caused by the coordination of HMPA with the metal atoms of the compounds.¹⁻⁵ That is to say, such a coordination results in increases in the polarity of carbon (or oxygen)—metal bonds of the compounds and thereby in the nucleophilicity of the organic groups in the compounds:



The reactivity of the compounds has been also reported to increase in the presence of Lewis

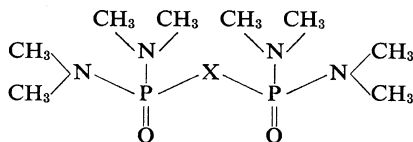
bases such as dipyridyl,⁶ triphenylphosphine,⁶ and dimethylsulfoxide^{3,7} or alkoxides such as 2-alkoxyethoxides.⁸

In this paper, the polymerization of some vinyl monomers with organometallic compounds was carried out in the presence of bidentate phosphoryl compounds with $-\text{N}(\text{CH}_3)_2$ substituents in order to investigate the effect of phosphoramidates on the reactivity of the organometallic compounds.

EXPERIMENTAL

Reagents

Nonamethylimidodiphosphoramidate (NIPA) and octamethylpyrophosphoramidate (OMPA) were



X = NCH₃, NIPA; X = O, OMPA.

place *via* the oxygen atoms of phosphoryl groups of the ligand as well as in the case of HMPA.²³ The X-ray structure analysis of the tris-OMPA complex of magnesium perchlorate showed the presence of three planar chelate rings in the complex.²² Such a chelate ring was also found to exist in the complexes of many metal ions with NIPA by measuring their IR and ligand-field spectra.²¹ Therefore, the interaction of one molecule of NIPA or OMPA with organometallic compounds must be stronger than that of two HMPA molecules with the compounds since a six-membered chelate ring can be formed in the former case.

Figure 1 shows the effect of the structure of phosphoramidate donors on the polymerization of St with benzylmagnesium bromide. Since the ratio of phosphoryl group to magnesium atom, $[P=O]/[Mg]$, is an important factor for the polymerization,^{1,2} the polymerization behavior at a constant $[P=O]/[Mg]$ ratio was examined. The polymerization proceeded very rapidly in the presence of OMPA at 0°C, but rather slowly in the presence of HMPA. This fact indicates that OMPA is much more effective in promoting the polymerization than is HMPA.

Table II shows the effect of the $[P=O]/[Mg]$ ratio on the polymerization of St. The polymerization in the presence of HMPA proceeded only at $[P=O]/[Mg] > 2$, but in the presence of

OMPA proceeded appreciably even at $[P=O]/[Mg]=1.5$. An increase in the $[P=O]/[Mg]$ ratio resulted in an increase in initiator efficiency, especially in the presence of OMPA. These results also suggest that OMPA is a more efficient donor than HMPA. The large rate of polymerization in the presence of OMPA (Figure 1) is considered to be, at least in part, due to an increase in f , *i.e.*, an increase in the concentration of active species formed from the initiator system.

The ratio of the rate constant of propagation

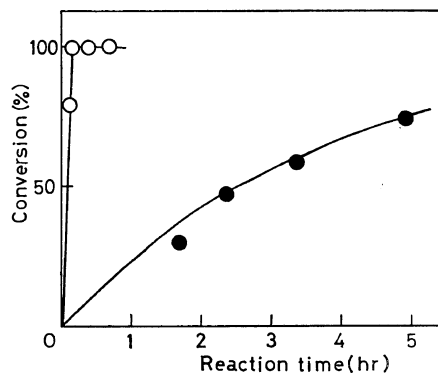


Figure 1. Effect of donors on the polymerization of St with benzylmagnesium bromide: $[M]$, 1.41M; $[C_6H_5CH_2MgBr]$, $7.77 \times 10^{-3}M$; $[P=O]/[Mg]=4.0$; (●), HMPA; (○), OMPA; solvent, toluene; temp, 0°C.

Table II. Polymerization of St by benzylmagnesium bromide with phosphoramidate donors^a

Donor	$\frac{[P=O]^b}{[Mg]}$	Yield, %	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	$\frac{M_w}{M_n}$	f^c	$\frac{k_p^d}{k_i}$
HMPA	2.0	0	—	—	—	—	—
HMPA	2.5	10.6	1.94	3.94	2.03	0.05	7400
HMPA	3.0	75.9	6.79	14.4 ₅	2.13	0.10 ₅	11700
HMPA	4.0	94.2	7.42	13.2	1.78	0.12	11000
HMPA	5.0	99.8	7.06	10.7	1.51	0.13	9700
OMPA	1.0	0	—	—	—	—	—
OMPA	1.5	26.7	4.66	12.7	2.72	0.05	18600
OMPA	2.0	100	3.32	5.27	1.58	0.28	1860
OMPA	3.0	100	2.09	3.23	1.54 ₅	0.45	610
OMPA	4.0	100	1.56 ₅	2.73	1.74 ₅	0.60	285
OMPA	5.0	100	1.50	2.70	1.80	0.63	247

^a Polymerization conditions: $[M]$, 1.41M; $[C_6H_5CH_2MgBr]$, $1.56 \times 10^{-3}M$; solvent, toluene; temp, 0°C; time, 19 hr.

^b Ratio of phosphoryl group to initiator.

^c Initiator efficiency.

^d Ratio of propagation to initiation rate constant.

(k_p) to that of initiation (k_i) was determined by use of the equation derived by Levy and Szwarc.²⁴ The values of the k_p/k_i ratio show that the initiation step of the polymerization in the presence of HMPA was much slower than the propagation, and in the presence of OMPA the initiation was facilitated more significantly than the propagation with increasing donor concentration. The molecular weight distributions of the polymers obtained were rather broad compared with those of the polymers obtained by a typical living polymerization.²⁵ It is well-known that in a living polymerization the molecular weight distribution becomes narrow with a decrease in the k_p/k_i ratio.²⁶ Such a relation, however, was not observed in this case: a decrease in the k_p/k_i ratio did not always result in a decrease in the value of M_w/M_n , the ratio of the weight-average to number-average molecular weight, which is commonly used as a measure of the polydispersity of a polymer. Other factors, such as the presence of traces of impurities or the inefficient mixing of reagents, might lead to a broadening of the distribution,²⁷ because the polymerization was initiated by introducing an initiator solution with a syringe.

Table III shows the results of the polymerization of St with dibenzylmagnesium. This initiator could initiate the polymerization in the presence of HMPA even at $[P=O]/[Mg] < 2$ in contrast to the benzylmagnesium halides, which could not initiate the polymerization under similar conditions.¹ This fact suggests that dibenzylmagnesium is more easily activated by coordination with HMPA than are the benzylmagnesium halides. That is to say, the former could be changed by coordination with one or two HMPA molecules to an active species with ability to initiate the polymerization of St, while the latter could only be changed to such an active species by coordination with four HMPA molecules.²

The initiator efficiency increased with increasing $[P=O]/[Mg]$ ratio, especially in the $[P=O]/[Mg]$ range of 0—ca. 2. The bidentate donors were more effective additives also in this polymerization system. The value of the k_p/k_i ratio was significantly larger than that in the case of the polymerization with benzylmagnesium bromide (see Table II). This finding also indicates that the reactivity behavior of dialkylmagnesium compounds is not always in agreement with that

Table III. Polymerization of St by dibenzylmagnesium with phosphoramidate donors^a

Donor	$\frac{[P=O]}{[Mg]}$ ^b	Yield, %	M_n $\times 10^{-4}$	M_w $\times 10^{-4}$	$\frac{M_w}{M_n}$	f^c	$\frac{k_p}{k_i}$ ^d
HMPA	0.5	94.2	27.1	45.4	1.68	0.04	54500
HMPA	1.0	100	16.9	24.3	1.44	0.06 ₅	47300
HMPA	2.0	100	13.5	20.8	1.54	0.08	30600
HMPA	4.0	99.2	12.2	18.9	1.55	0.09	25200
HMPA	10.9	99.1	13.1 ₅	22.5	1.71	0.08	28700
OMPA	0.5	98.9	11.6	19.7	1.69	0.09	22900
OMPA	1.0	100	8.22	13.4	1.63	0.13	10800
OMPA	2.0	100	7.00	12.7 ₅	1.82	0.15 ₅	7800
OMPA	6.0	100	5.65	9.38	1.66	0.19	4900
OMPA	10.0	100	5.05	8.34	1.65	0.21 ₅	3850
NIPA	0.5	97.7	13.6	29.9	2.21	0.08	32000
NIPA	1.0	94.2	6.84	20.4	2.98	0.15	7900
NIPA	2.0	95.5	5.47	12.9	2.35	0.19	4850
NIPA	6.0	98.9	4.16	9.17	2.20	0.26	2550
NIPA	10.0	98.5	3.52	7.92	2.25	0.31	1730

^a Polymerization conditions: $[M]$, 1.41M; $[(C_6H_5CH_2)_2Mg]$, $1.35 \times 10^{-2}M$; solvent, toluene; temp, 0°C; time, 19 hr.

^b Ratio of phosphoryl group to magnesium of initiator.

^c Initiator efficiency estimated by assuming that dibenzylmagnesium acts as a monofunctional initiator.

^d Ratio of propagation to initiation rate constant.

of the corresponding Grignard's reagents. A similar disagreement is also observed in the polymerization of methyl methacrylate with organo-magnesium compounds: Grignard's reagents derived from alkyl bromides exerted a more pronounced stereoregulating effect than did the dialkylmagnesium compounds.²⁸

An increase in the k_p/k_i ratio had little or no effect on the molecular weight distribution of the polymer. The polymer formed in the presence of NIPA, however, had a broader distribution than that obtained in the presence of HMPA or OMPA. In the presence of NIPA, both benzyl groups of a part of the initiator may take part in the initiation with distinct rates because of the stronger coordinating power of the donor, and hence the distribution may broaden. The slightly lower yields of the polymers in the presence of NIPA are considered to come from the cut-off of lower molecular weight polymers at the stage of polymer separation.

The polymerization of St with dibenzylmagnesium was also carried out in the presence of HMTP (Table IV). The polymerization occurred only in the presence of fairly large amounts of HMTP, in contrast to the polymerization in the presence of HMPA. This fact must be due to the weak interaction of HMTP with the organo-magnesium compound. Bases in which a donor atom is S or O have been classified as "soft" or "hard" bases, respectively, by Pearson.²⁹ HMTP has been reported to behave as a soft base and to form stable coordination compounds

with soft metal ions such as Hg(II), Ag(I), and Pd(II) *via* the sulfur atom of the ligand.³⁰ On the other hand, magnesium ion has been classified as a hard acid. The magnesium atoms of organometallic compounds also could be classified as hard acids, though the magnesium-carbon bond of the compounds is not a perfectly ionic bond but a polarized one.³¹ Therefore, it is concluded on the basis of "The Principle of Hard and Soft Acids and Bases" (HSAB)²⁹ that organomagnesium compounds interact with HMPA more strongly than with HMTP. Actually, the chemical shift of methylene protons for diethylmagnesium moved upfield only slightly in the presence of HMTP, *i.e.*, $\Delta\delta = -0.03$ at $[\text{HMTP}]/[\text{Mg}] = 6$, but moved noticeably in the presence of HMPA, *i.e.*, $\Delta\delta = -0.23$ at $[\text{HMPA}]/[\text{Mg}] = \text{ca. } 6$.³²

Figure 2 shows the effect of the donors on the polymerization of α -MeSt with dibenzylmagnesium. The value of f increased with an increase in the $[\text{P}=\text{O}]/[\text{Mg}]$ ratio. The value changed markedly in the range of $[\text{P}=\text{O}]/[\text{Mg}]$ 1–2, when the polymerization was carried out in the presence of the bidentate donors at 0°C. This finding suggests that the complex of dibenzylmagnesium with one molecule of NIPA or OMPA can initiate the polymerization of α -MeSt. The value of f obtained in the presence of the bidentate donor became greater than unity at higher $[\text{P}=\text{O}]/[\text{Mg}]$ ratios. This fact shows that dibenzylmagnesium may act as a bifunctional initiator under these conditions. The large value

Table IV. Polymerization of St with dibenzylmagnesium in the presence of HMTP^a

Solvent	$[\text{HMTP}]^b$ [Mg]	Temp, °C	Yield, %	M_n $\times 10^{-5}$	M_w $\times 10^{-5}$	$\frac{M_w}{M_n}$	f^c	$\frac{k_p^d}{k_i}$ $\times 10^{-4}$
Toluene	52.7	0	0	—	—	—	—	—
Toluene	52.7	Room temp	0	—	—	—	—	—
Toluene	105	0	93.5	4.21	8.33	1.98	0.04	19.7
Toluene	105	Room temp	96.0	2.62	6.42	2.45	0.06 ₅	7.36
THF	26.4	0	0	—	—	—	—	—
THF	52.7	0	43.0	1.24	3.15	2.54	0.06	3.82
THF	105	0	95.7	2.09	3.56	1.70	0.08	4.75

^a Polymerization conditions: $[\text{M}]$, 2.43M; $[(\text{C}_6\text{H}_5\text{CH}_2)_2\text{Mg}]$, $1.44 \times 10^{-2}\text{M}$; time, 18 hr.

^b Molar ratio of HMTP to initiator.

^c Initiator efficiency estimated by assuming that dibenzylmagnesium acts as a monofunctional initiator.

^d Ratio of propagation to initiation rate constant.

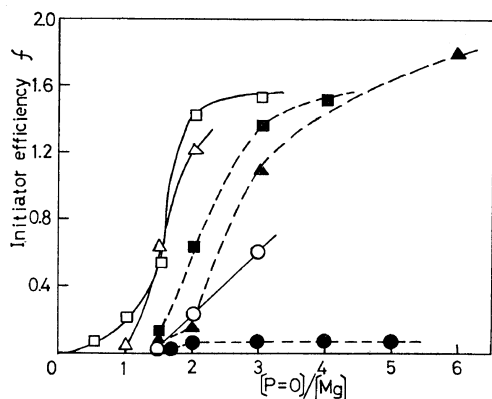


Figure 2. Effect of $[P=O]/[Mg]$ ratio on initiator efficiency in the polymerization of α -MeSt with dibenzylmagnesium: $[M]$, $2.12M$; $[(C_6H_5CH_2)_2Mg]$, $1.89 \times 10^{-2}M$; (○), HMPA, $0^\circ C$; (●), HMPA, $-20^\circ C$; (△), OMPA, $0^\circ C$; (▲), OMPA, $-20^\circ C$; (□), NIPA, $0^\circ C$; (■), NIPA, $-20^\circ C$; solvent, toluene; time 18 hr.

of f in this case compared with that in the polymerization of St (see Table III) must be due to the fact that α -MeSt has a smaller value of k_p than St in the case of an anionic polymerization.³³ The value of f decreased with decreasing polymerization temperature. The activation energy of initiation, therefore, is considered to be larger than that of propagation.

Synthesis of Highly Branched Polystyrene. The synthesis of highly branched polystyrene was tried using vinylbenzylmagnesium chloride as an initiator. The attack of a propagating polystyryl end on the residual vinyl group of the initiator bonded to another polymer was expected to give branched polystyrene. Figure 3 shows the gel-permeation chromatogram of the polymer ob-

tained in the presence of HMPA. This polystyrene exhibited an extremely broad molecular weight distribution: the value of M_w/M_n was ca. 12, while its value was 1.5–2 in the case of the polymer formed by using benzylmagnesium halides under similar conditions (see Table II). Kurata, *et al.*, have reported that branched polystyrenes prepared by copolymerization of St and 1,4-divinyl-2,3,5,6-tetrachlorobenzene have broad molecular weight distributions; the value of M_w/M_n increased with an increase in the extent of branching reaction.³⁴ The branched polymer, therefore, must have been formed in the polymerization system St–vinylbenzylmagnesium chloride.

Polymerization of AN with Organozinc or Organoaluminum Compounds

Table V shows the results of the polymerization of AN with diethylzinc in the presence of phosphoramides. The polymerization did not occur with diethylzinc alone in toluene at $0^\circ C$. The addition of small amounts of the phosphoramides did not promote the polymerization so much, in contrast to the polymerization with organomagnesium compounds. The yield of poly(AN) increased with an increase in the concentration of the phosphoramides. The bidentate donors, however, were less effective than the monodentate donor, HMPA. This behavior also is in disagreement with that observed in the polymerization of St or α -MeSt with organomagnesium compound–phosphoramide systems.

When diethylzinc and NIPA were mixed in toluene, a toluene-insoluble product was obtained. The precipitate, which was separated by filtration, washed with toluene, and dried under vacuum, was found by complexometric titration³⁵

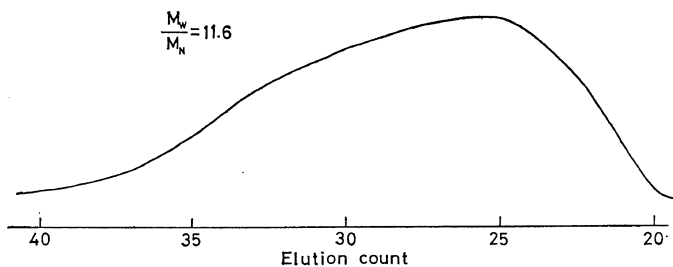


Figure 3. GPC of branched polystyrene: polymerization conditions; $[St]$, $2.46M$; $[CH_2=CHC_6H_4CH_2MgCl]$ (*m, p*-mixture), $1.63 \times 10^{-2}M$; HMPA, $6.52 \times 10^{-2}M$; solvent, toluene; temp, $0^\circ C$; time 16 hr.

Table V. Polymerization of AN by diethylzinc with phosphoramidate donors^a

Donor	$\frac{[P=O]}{[Zn]}$ ^b	Yield, %	$\frac{\eta_{sp}^c}{c}$, dl/g
HMPA	1.0	0	—
HMPA	2.0	trace	—
HMPA	5.0	15.5	0.98
HMPA	10	52.5	1.30
HMPA	20	77.7	1.23
HMPA	50	91.4	0.97
NIPA	1.0	5.0	0.25
NIPA	2.0	8.5 (25.8) ^d	0.38 (0.46) ^d
NIPA	4.0	21.3	0.61
NIPA	10	40.6	0.90
NIPA	27	61.8	1.34
OMPA	4.0	0	—
OMPA	10	trace	—
OMPA	20	10.4	0.43
OMPA	60	28.3	0.59

^a Polymerization conditions: [M], 4.22M; [Zn (C₂H₅)₂], 2.55 × 10⁻²M; solvent, toluene; temp, 0°C; time, 19 hr.

^b Ratio of phosphoryl group to initiator.

^c DMF solution at 25°C, c=0.25 g/dl.

^d Polymerization with Zn(C₂H₅)₂NIPA complex: [M], 3.95M; [Complex], 8.88 × 10⁻²M; solvent, toluene; temp, room temperature; time, 14 hr.

to be the complex with the formula Zn(C₂H₅)₂·NIPA. This complex alone showed a catalytic activity for the polymerization of AN. This fact indicates that the complex must be at least an active species which has the ability to initiate the polymerization.

Table VI shows the results of the polymerization of AN with organoaluminium compounds. The bidentate donors were less effective in promoting the polymerization than HMPA in this case as well as in the case of the polymerization with diethylzinc—phosphoramidate systems. In the presence of NIPA, the yield of the polymer increased with increasing NIPA concentration in the range of [P=O]/[Al] ≤ 2, but a further increase in the concentration, on the contrary, reduced the polymerization. Such a reduction did not take place in the presence of HMPA.

It was confirmed by a copolymerization with St that the polymerization of AN with diethylzinc or organoaluminium compounds—phosphoramidate

Table VI. Polymerization of AN by organoaluminium compound with phosphoramidate donors

Donor	$\frac{[P=O]}{[Al]}$ ^b	Yield, %	$\frac{\eta_{sp}^c}{c}$, dl/g
(A) Polymerization with triethylaluminium ^a			
HMPA	0.5	trace	—
HMPA	1.0	52.0	4.99
HMPA	2.0	63.0	5.38
HMPA	5.0	70.2	5.28
NIPA	1.0	9.4	0.75
NIPA	2.0	19.7	1.97
NIPA	4.0	8.5	0.73
NIPA	6.0	trace	—
OMPA	1.0	trace	—
OMPA	2.0	12.2	2.48
OMPA	4.0	15.4	2.45
OMPA	10	21.7	2.41
(C) Polymerization with triisobutylaluminium ^a			
HMPA ^e	0.5	8.7	2.12
HMPA ^e	1.0	78.4	3.48
HMPA ^e	2.0	79.2	3.18
HMPA ^e	5.0	79.0	3.04
NIPA ^f	1.0	66.0	5.35
NIPA ^f	2.0	80.0	2.92
NIPA ^f	4.0	65.1	2.52
NIPA ^f	6.0	trace	—
OMPA ^f	2.0	trace	—
OMPA ^f	4.0	13.3	1.78
OMPA ^f	6.0	22.4	2.65

^a Polymerization conditions: [M], 4.05M; [Al (C₂H₅)₃]=8.76 × 10⁻²M; solvent, toluene; temp, room temperature; time, 19 hr.

^b Ratio of phosphoryl group to initiator.

^c DMF solution at 25°C, c=0.25 g/dl.

^d Polymerization conditions: [M], 3.80M; [Al (i-C₄H₉)₃]=9.46 × 10⁻²M; solvent, toluene; temp, room temperature.

^e Reaction time, 2 hr.

^f Reaction time, 19 hr.

systems has essentially an anionic character: the copolymer formed in the equimolar-feed copolymerization had a copolymer composition (ca. 95-% AN and ca. 5-% St) similar to that of the copolymer obtained by typical anionic copolymerizations.³⁶ This conclusion is in disagreement with the radical mechanism proposed by Akimoto and Okada.⁵ It was observed in our study that these initiator systems could not polymerize methyl methacrylate or St under

conditions similar to those for the polymerization of AN. This result also cannot be explained in terms of the radical mechanism.

A Consideration Concerning the Interaction of Organometallic Compounds with Phosphoramidate Donors

The reactivities of organometallic compound—phosphoramidate systems as initiators for the polymerization of vinyl monomers could be classified into the following two categories: (1) the reactivity increases with an increase in the coordinating power of phosphoramidates; (2) the reactivity, on the contrary, decreases with increasing coordinating power of the donors. The polymerization of St or α -MeSt with organomagnesium compound—phosphoramidate systems belongs to the former class, while the polymerization of AN with organoaluminium compound or diethylzinc—phosphoramidate systems is in the latter class.

Such a difference must be due to a difference in structure between the organometallic compounds, especially in the polarity of carbon—metal bonds of the compounds. The electronegativity of magnesium in diethylmagnesium was estimated to be 0.94 from NMR data,³² and Pauling's value for the magnesium atom is 1.2.³⁷ The magnesium atom in the organometallic compounds, therefore, is considered to behave as a more hard acid, and, on the basis of the principle of HSAB,²⁹ to interact strongly with the phosphoramidates. Actually the electronegativity of magnesium in diethylmagnesium decreased in the presence of HMPA (*ca.* 0.79 at $[\text{HMPA}]/[\text{Mg}] > \text{ca. } 2$).³² This result supports the above concept. Such a strong coordination of magnesium with the phosphoramidates could easily make the carbon—magnesium bonds of the organomagnesium compounds polar enough to react with St or α -MeSt.^{1,2} An increase in the coordinating power of the phosphoramidates must result in a further increase in the reactivity of the compounds.

On the other hand, the carbon—metal bonds of organozinc or organoaluminium compounds must be less polar than the bonds of organomagnesium compounds, because the electronegativities of zinc and aluminium atoms are larger than the electronegativity of the magnesium atom: the electronegativities of zinc in diethylzinc

and of aluminium in triethylaluminium are reported to be 1.45⁶ and 1.59⁶ (1.57)⁵, respectively, and Pauling's values for the zinc and aluminium atoms are 1.6 and 1.5, respectively.³⁷ The electronegativity of aluminium in triethylaluminium decreased in the presence of HMPA (1.29 at $[\text{HMPA}]/[\text{Al}] > \text{ca. } 1$),⁵ while that of zinc in diethylzinc decreased gradually with increasing $[\text{HMPA}]/[\text{Zn}]$ ratio (1.37, 1.34, and 1.32 at $[\text{HMPA}]/[\text{Zn}] = 1.2, 2.7, \text{ and } 7.3$, respectively).⁴³ The extent of decrease in the electronegativities of the aluminium and zinc atoms is smaller than that in the electronegativity of the magnesium atom. This result indicates that the aluminium and zinc atoms in the organometallic compounds behave as less hard acids and do not interact strongly with the phosphoramidates. The phosphoramidates, therefore, could not make the organoaluminium or organozinc compounds active enough to react with AN. This result also suggests that the interaction of the phosphoramidates with the zinc atom is weaker than that with the aluminium atom.

However, if AN is activated, the reaction of the AN with the organometallic compounds must take place. The double bond of AN should be activated by the coordination of the nitrile group of AN with the zinc or aluminium of the organometallic compounds. Actually, it is reported that nitriles interact strongly with Lewis acids such as AlR_3 ,³⁸ $\text{AlR}_n\text{Cl}_{3-n}$,³⁸ and $\text{Zn}(\text{C}_2\text{H}_5)_2$.³⁹ The polymerization of AN, therefore, is considered to be caused by the coordination of both the phosphoramidates and AN to the organometallic compounds. The fact that NIPA was a less efficient donor than HMPA in the polymerization with organoaluminium compounds could be explained by assuming that the bidentate NIPA blocks the coordination site required for the coordination of AN. Such an undesirable coordination of phosphoramidates has been already observed in both isomerization of epoxides with LiBr—HMPA system⁴⁰ and reactions of epoxides or aldehydes with alkylaluminiums in HMPA.⁴¹ In the case of the polymerization with diethylzinc, the undesirable coordination of the bidentate phosphoramidates may be reduced more than in the polymerization with alkylaluminiums, because of the weak interaction between diethylzinc and the phosphoramidates.

Several complexes of trialkylaluminiums with bidentate donors have been thought to contain 5-coordinated aluminium atoms.⁴² However, it could not be determined whether or not the bidentate phosphoramides used in this study could form such a complex.

The structure of organic moieties of the organometallic compounds is considered to affect the reactivity of the compounds. When the compounds are composed of organic moieties in which there is resonance stabilization, the polarization of the carbon—metal bonds of the compounds must take place more easily. Actually Grignard's reagents derived from benzyl or allyl halides were activated by coordination with HMPA more easily than the reagents derived from alkyl halides.² Moreover, benzylzinc bromide could polymerize not only AN but also methyl methacrylate in the presence of HMPA.⁴³ The polymerization with benzyl derivatives such as dibenzylzinc and tribenzylaluminium is now under investigation.

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