

Higher Aluminum Trialkyls and Magnesium Aluminum Alkyls as Components of Ziegler–Natta Catalysts

L. V. GAPONIK, A. M. ANTIPOVA, T. K. MOROZOVA, and
V. P. MARDYKIN, *Research Institute of Physico-Chemical
Problems, Byelorussian State University, 220080, Minsk, USSR*

Synopsis

Magnesium aluminum alkyls containing higher (C_4 – C_{10}) radicals were studied as components of Ziegler–Natta catalysts in styrene polymerization. The effects of alkyl radical length and MgR_2 contents in the components mentioned on the degree of $TiCl_4$ reduction and stereospecific activity of the catalysts were investigated. The components studied exhibited high reducing (for $TiCl_4$) and catalytic activities. Molecular weight of the synthesized isotactic polystyrene was abnormally high.

INTRODUCTION

The recent publications^{1–18} show that magnesium-aluminum-containing components of Ziegler–Natta catalytic systems are among the leaders in the development of new effective organometallic polymerization catalysts. Modification of the catalytic systems by organomagnesium compounds does not only increase their activity but sometimes gives polymers with new valuable properties. The effect is mainly studied for aluminum ethyl and isobutyl derivatives—containing catalysts, whereas the higher aluminum trialkyl-based systems remain actually unstudied in this respect. Nevertheless, being more stable and markedly less dangerous than lower organoaluminum compounds (OAC), they may be of interest as components of complex catalysts for polymerizing α -olefines, dienes, and the monomers. The catalytic systems based on higher aluminum alkyls exhibit rather high polymerization activity that is due to long lifetime of the active sites (AS).^{1,18–27} In view of the above, higher magnesium aluminum alkyls (MAA) used as organometallic components (OMC) undoubtedly combine the advantages both of higher aluminum alkyls and magnesium-containing compounds in the polymerization process.

It should be noted that a convenient method for preparation of hydrocarbon solutions of higher magnesium aluminum alkyls with a controllable composition has been developed recently.²⁸ Unlike individual MgR_2 , these compounds are soluble in hydrocarbons and may be used without separation and additional purification.²⁸

In view of all the above, it seems of interest to study organometallic compounds mentioned as components of stereospecific polymerization of styrene.

EXPERIMENTAL

Organometallic compounds were synthesized following the procedure described in Ref. 28 from powdered aluminum (PA-4), magnesium chips and halide alkyl in *n*-octane at 90–110°C. Metal concentration in organometallic compound solution was 0.5 mol/L.

Titanium tetrachloride, styrene, and solvents were purified by conventional methods employed in ionic polymerization.

The reduction of TiCl_4 and styrene polymerization were performed in a thermostatic reactor in dry argon atmosphere. The time of TiCl_4 reduction process was 20 min at 20°C; the components were added in the following succession: TiCl_4 —solvent—OMC. The amount of trivalent titanium produced was determined by ammonium iron alum back titration with ammonium rhodanide.

The catalytic complex for styrene polymerization was obtained by mixing TiCl_4 (0.5 mol/L heptane solution) and a half of the required OMC amount at room temperature. After the catalyst "aging" time elapsed (20 min), the remaining OMC, solvent, and monomer were added. The polymerization was carried out at 70°C under stirring by a magnetic stirrer for 0.25–4 h. The process was stopped by addition of 10% HCl solution in methanol, and the obtained mix was poured into a large amount of methanol.

The polymer was isolated, washed with methanol, and dried up to a constant weight at 50°C/1 mm Hg.

Isotactic polystyrene (IPS) was separated from atactic polystyrene (APS) by extracting the latter with boiling methylethyl ketone. Molecular weights (\bar{M}_v) of APS and IPS ($\bar{M}_v < 10^6$) were found from the equation $[\eta] = 1.1 \times 10^{-4} \bar{M}_v^{0.725}$ (toluene, 30°C)²⁹; \bar{M}_v of IPS ($\bar{M}_v > 10^6$) was calculated from $[\eta] = 2.8 \times 10^{-4} \bar{M}_v^{0.67}$ (toluene, 25°C), which is valid for superhigh-molecular-weight polystyrene.³⁰

RESULTS AND DISCUSSION

Reduction of TiCl_4 by Higher Aluminum Trialkyls with Modifiers

Studies of the interaction between complex catalyst components may throw some light onto the nature of active sites since their formation, functioning, and deactivation are closely related with transition metal reduction.^{31,32} As to the highly active catalytic systems containing soluble magnesium aluminum alkyls as OMC, the problem has not been investigated as yet. Discussion usually concerns magnesium compound effects on the resultant polymerization process, and there is actually no information on the component interaction during prepolymerization period when titanium compound (III) active in stereospecific polymerization is produced. Earlier we studied the influence of the alkyl radical length and MgR_2 content in magnesium–aluminum organometallic compounds on TiCl_4 reduction.^{33–35} The experimental data indicate that when AlR_3 alone is used as OMC the degree of Ti(IV) reduction diminishes as the alkyl radical length increases [Fig. 1(b)], the decrease rate being more the longer is the alkyl radical. The effect may probably be ascribed to steric hindrances arising during alkylation of transition metal salt.

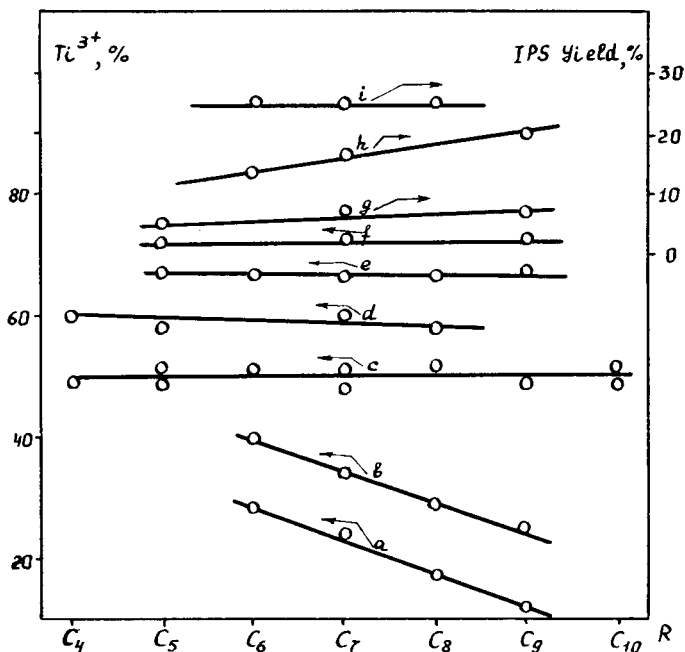


Fig. 1. The effect of alkyl radical length in organometallic component (OMC) on the degree of TiCl_4 reduction (a-f) and styrene polymerization (g-i). MgR_2 content in OMC (mol %): (a, b) 0; (c) 10 and 40; (h, i) 25; (e) 50; (f, g) 60.

Complexation of triethylaluminum with certain electron-donor compounds is known to increase its alkylating and reducing properties.^{31,36} We have, however, found that addition of some ethers (e.g., phenetole) to higher aluminum trialkyls even decreases the degree of Ti(IV) reduction as compared to the ether-free system [Fig. 1(a)]. This fact suggests that the behavior of higher organoaluminum compounds is specific and mainly controlled by steric effects in the course of their interaction with transition metal halides.

The influence of MgR_2 bound in complex with AlR_3 on the reducing activity of the system is of special interest. The experiments have revealed that the substitution of equivalent MgR_2 amount for some of AlR_3 increases the degree of Ti(IV) reduction and actually levels the difference in the activities due to the alkyl radical length [Fig. 1(c-f)]. The shape of the curve describing the degree of Ti(IV) reduction as a function of molar content of MgR_2 in $\text{AlR}_3 \cdot n \text{MgR}_2$ complex is intricate [Fig. 2(a)] and is, in fact, the same for all metal alkyls studied irrespective of the alkyl radical size. The figure shows that in this process the complexes containing ~ 15 –25% and 50–60% (mol) of MgR_2 are most active. The effect is likely to be ascribed to different abilities of magnesium aluminum alkyls of variable composition. The higher activity of those compounds as compared to an equivalent amount of individual aluminum trialkyl is caused by participation of both MgR_2 radicals in alkylation of Ti(IV) compound. This may be attributed to the fact that $\text{AlR}_3 \cdot \text{MgR}_2$ complex occurs in some specific associated state, in which radical exchange between metal atoms is effected quite easily.^{28,37} On the

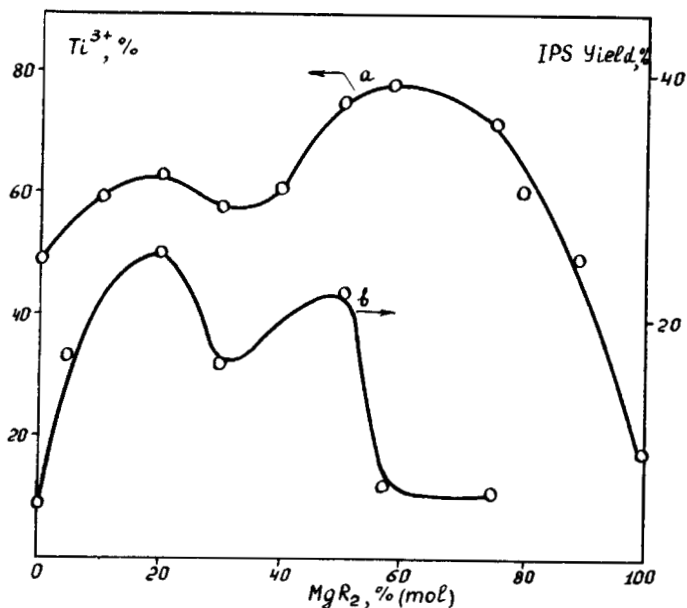


Fig. 2. The effect of MgR_2 content in organometallic component on the degree of $TiCl_4$ reduction (a) and isotactic polystyrene yield (b).

contrary, in the case of aluminum trialkyl under the present conditions only AlR_3 radical is active.³¹

It should be emphasized that in the case of equimolecular complex the degree of $Ti(IV)$ reduction predicted on the basis of the above concepts is close to the experimental data. Lowering of the degree of $Ti(IV)$ reduction at MgR_2 percentage above $\sim 65\%$ (mol) is rather due to some diffusion effects since hydrocarbonic MAA solutions with high MgR_2 content are metastable and have increased viscosity.³⁷

The studies of the influence of some ethers (phenetole, diphenyl ether, dibenzofuran) on the reducing ability of magnesium aluminium alkyl $Al(C_8H_{17})_3 \cdot 0.6 Mg(C_8H_{17})_2$ have revealed that succession of addition of the components and the ether nature are important (Table I). If ether and organometallic component are the first to begin interacting, the degree of $Ti(IV)$ reduction drops drastically, which fact may be explained by the

TABLE I
Reduction of $TiCl_4$ by $Al(C_8H_{17})_3 \cdot 0.6 Mg(C_8H_{17})_2$ Complex (OMC)
with Ether Additive (Ether/Al = 1)

Item no.	Catalytic system	Ti^{3+} (%)
1	$TiCl_4 + OMC$	42.2
2	$TiCl_4 + OMC \cdot C_6H_5OC_2H_5$	7.1
3	$TiCl_4 + OMC \cdot (C_6H_5)_2O$	18.1
4	$TiCl_4 + OMC \cdot (C_6H_4)_2O$	31.8
5	$TiCl_4 \cdot C_6H_5OC_2H_5 + OMC$	38.8
6	$TiCl_4 \cdot (C_6H_5)_2O + OMC$	22.7
7	$TiCl_4 \cdot (C_6H_4)_2O + OMC$	34.4

formation of $AlR_3 \cdot$ ether complex accompanied by destruction of soluble magnesium–aluminum complex and by participation of AlR_3 etherate alone in the reduction reaction. This effect is weakened in a $C_6H_5OC_2H_5 > (C_6H_5)_2O > (C_6H_4)_2O$ series that is consistent with a decrease of the donor strength and an increase of steric hindrances of ethers. If ethers– $TiCl_4$ complex is formed first and OMC is added subsequently, the adverse effect of ether on the reducing activity of the system appears less pronounced. The efficiency of MAA with ether additives is, however, much smaller as compared to pure MAA, which is also the case for individual higher OAC and their etherates.

The Influence of Organomagnesium and Nucleophilic Compounds on $TiCl_4$ —Higher Aluminum Trialkyl System-Catalyzed Stereospecific Styrene Polymerization

This section contains the results on styrene polymerization on the above catalytic system with a varying length of alkyl group in AlR_3 and also in the presence of different amounts of organomagnesium or nucleophilic compound.^{18,38}

Diminishing of stereospecificity observed at nearly invariable activity of styrene polymerization catalysts in transition from triethylaluminum to trihexylaluminum (Table II, 1–2) should not be a surprise and is fully consistent with the known concepts on the effect of the alkyl radical length upon stereospecificity of organometallic catalyst. The decrease of the catalyst stereospecificity as the alkyl radical length in AlR_3 increases may be attributed to steric hindrances.³⁹ This is also reflected in a lower degree of Ti(IV) reduction (Fig. 1) and smaller crystallinity of the resultant catalytic precipitate.³¹ The use of trihexylaluminum phenetolate as OMC results in fully atactic polystyrene with a relatively high yield (Table II, 3). In terms of the well-known concepts on the stereoregulation mechanism in such catalysts, it should be assumed that ether occupying a definite vacant site within the coordination sphere of octahedral titanium atom changes the steric structure and electrostatic properties of AS so that it becomes completely unable to effect stereoregulation during styrene polymerization.⁴⁰

The study of styrene polymerization with organomagnesium modifier has shown that just as in the Ti(IV) reduction process, the alkyl radical length (C_5 – C_9) in MAA has a slight effect upon the isotactic polystyrene yield [Fig. 1(g–i)], but the content of MgR_2 in OMC is essential for stereospecific catalyst activity [Fig. 2(b)]. Good correlation of the polymerization and reduction activities is observed until the magnesium and aluminum contents become nearly equimolecular. As magnesium component percentage is above 50% (mol), the IPS yield decreases.

The observed increase of the stereospecific activity of the catalytic system containing MgR_2 is primarily due to a higher reducing ability of the system with respect to $TiCl_4$. On the other hand, magnesium dichloride produced in the reaction may be considered as a microcarrier which promotes, to a certain extent, the surface development and, consequently, increases the catalytic activity. Finally, magnesium compounds which enter into the active catalytic complexes influence the electron characteristics of the Ti—C bond⁴¹ and may

TABLE II
Styrene Polymerization on TiCl_4 -Organometallic Component System^a

Item no.	Organometallic component (OMC)	OMC/ TiCl_4 (M)	Conversion (%)	Crystallinity (%)	PS yield (g/g TiCl_4)			$\bar{M}_v \times 10^{-5}$		
					Total	IPS	APS	IPS	APS	IPS
1		3	4	5	6	7	8	9	10	
1	$\text{Al}(\text{C}_2\text{H}_5)_3$	3.0	13.0	52	—	—	—	5.6	0.1	
2	$\text{Al}(\text{C}_6\text{H}_{13})_3$	3.0	15.0	32	6.9	2.2	4.7	17.2	0.2	
3 ^b	$(\text{C}_6\text{H}_{13})_3\text{Al} \cdot \text{C}_6\text{H}_5\text{OC}_2\text{H}_5$	3.0	14.0	0	—	—	—	—	0.08	
4	$(\text{C}_6\text{H}_{13})_3\text{Al} \cdot 0.3 \text{Mg}(\text{C}_6\text{H}_{13})_2$	3.0	18.0	88	8.5	7.5	1.0	35.0	1.0	
5	$(\text{C}_6\text{H}_{13})_3\text{Al} \cdot 0.2 \text{Mg}(\text{C}_6\text{H}_{13})_2$	3.0	28.0	86	13.3	11.4	1.9	24.0	—	
6	$(\text{C}_6\text{H}_{13})_3\text{Al} \cdot 0.04 \text{Mg}(\text{C}_6\text{H}_{13})_2$	3.0	14.0	91	6.6	6.0	0.6	23.0	0.34	
7	$(\text{C}_7\text{H}_{15})_3\text{Al} \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$	3.0	35.0	80	16.4	13.1	3.3	18.0	—	
8	$(\text{C}_7\text{H}_{15})_3\text{Al} \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$	2.0	38.0	85	17.5	14.6	2.9	58.0	1.5	
9	$(\text{C}_7\text{H}_{15})_3\text{Al} \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$	1.0	33.0	22	15.7	3.5	12.2	18.0	0.21	
10 ^b	$(\text{C}_7\text{H}_{15})_3\text{Al} \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$	1.0	53.0	0	25.0	—	25.0	—	0.05	
11	$(\text{C}_7\text{H}_{15})_3\text{Al} \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$	1.5	34.0	60	16.2	9.7	6.5	—	—	
12 ^c	$(\text{C}_7\text{H}_{15})_3\text{Al} \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$	2.0	28.0	84	13.0	10.9	2.1	59.0	0.44	
13	$(\text{C}_7\text{H}_{15})_3\text{Al} \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$	2.5	38.0	80	17.2	13.8	3.4	—	—	
14 ^d	$(\text{C}_7\text{H}_{15})_3\text{Al} \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$	1.0	22.0	92	10.5	9.7	0.8	20.2	1.8	
15 ^e	$(\text{C}_7\text{H}_{15})_3\text{Al} \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$	1.0	38.0	70	15.3	10.7	4.6	26.3	11.2	
16 ^f	$(\text{C}_7\text{H}_{15})_3\text{Al} \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$	1.0	29.0	81	13.7	11.1	2.6	—	—	

^a $[\text{TiCl}_4] = 0.02 \text{ mol/L}$, [styrene] = 1.7 mol/L, heptane or octane as solvents; polymerization conditions: 4 h, 70°C, 20-min "aging" of catalyst at 20°C;

[OMC] = $[\text{AlR}_3] + [\text{MgR}_2]$.

^b Phenetole additive, TiCl_4 /phenetole = 2.0.

^c Polymerization in toluene.

^d Polymerization at 40°C.

^e Polymerization at 90°C.

^f Catalyst "aging" at 70°C.

thereby increase the catalytic complex reactivity, simultaneously decreasing its stability (lifetime).³²

That there is no correlation between reducing and catalytic activities of the system provided MgR_2 is excessive in MAA may be due to deficiency of OAC under such conditions. Free OAC is necessary for active sites to be formed on TiCl_3 surface. Nevertheless, AS formed are highly stereospecific and long-lived. The finding supports the current concept on the bimetallic nature of active site in Ziegler–Natta catalysts.

The above experimental data were obtained under definite conditions optimal for styrene polymerization with the classical catalytic system $\text{TiCl}_4\text{-AlEt}_3$.²⁹ It was interesting to clear up the effect of some factors (OMC/Ti molar ratio, temperature, the solvent nature, electron-donor additive) on the activity of magnesium-containing system. First of all, optimal OMC/Ti molar ratio (2) and polymerization temperature (70°C) were found (Table II). The latter did not change in the test system as compared to the conventional catalyst. Why IPS yield is lower at temperatures above the optimum value will be clear if following Ref. 42 one assumes that stereospecific AS is the chlorine vacancy in the titanium coordination sphere provided that OAC is obligatory chemisorbitized in the direct vicinity to it. At temperatures above the optimum either OAC desorption or further Ti(III) alkylation may occur. In both cases the stereospecific site disappears that results in a higher atactic polystyrene yield. The optimal molar ratio of the catalytic components in the system of study is somewhat lower than that in the classical one ($\text{AlEt}_3/\text{Ti} = 3$). In view of the high reducing activity of magnesium-containing systems, it is not improbable that excessive OMC can also facilitate deeper alkylation and reduction of TiCl_4 to produce nonstereospecific AS. As is known, under reduction of transition metal up to bivalent state the activity of even the most effective lower OAC-based magnesium-containing catalyst in ethylene polymerization becomes smaller.⁴³ Moreover, excess MAA can compete with monomer molecules for vacant sites on the catalytic precipitate during reversible adsorption.

The solvent nature and presence of electron-donor compound are essential for stereospecific activity of the catalyst considered (Table II). The polymerization system studied exhibits a higher activity (~25% conversion) in stereospecific styrene polymerization provided the medium is aliphatic hydrocarbon (*n*-octane), which is a thermodynamically "poor" polystyrene solvent, as compared to polymerization in toluene medium, a thermodynamically "good" solvent. It seems that, though toluene is a rather weak electron donor, it is, however, able to compete, to some extent, with monomer in the coordination process on electron-deficient titanium atom in the active site.

It was found earlier²⁹ that if styrene polymerization was catalyzed by the conventional Ziegler system, electron-donor additive (ether) increased the catalyst stereospecificity, the total activity of the system being lowered. Such an effect may be caused by electron donor coordination and poisoning the most accessible nonstereospecific AS, and/or by participation of electron donor in disproportionation reactions of aluminum alkyl halides resulting in more alkylated aluminum derivatives, thus increasing the stereospecific catalyst efficiency. As follows from Table II (3, 10), nothing of the kind is observed for higher aluminum trialkyls and magnesium aluminum alkyls in the pres-

ence of the same electron donors. In both cases the system fully loses its stereospecificity.

An experimental series with different process durations was carried out to estimate the optimal time of the test complex system-catalyzed styrene polymerization. The major part of isotactic polymer is produced for 2 h, polystyrene isotacticity being very high and actually independent of the process duration and the yield amounting to 11 g/g TiCl_4 . It seems useful to compare these figures with the optimal polymerization times and IPS yields for the classical TiCl_4 - AlEt_3 system under similar conditions which are 4–6 h and 3 g/g TiCl_4 , respectively.²⁹ Thus, IPS yield is four-fold higher, polymerization time being at least twice as short for the system of study.

Effective activation energy (E_{eff}) determined from the starting sections of the kinetic curves over the temperature range 293–343 K is 31 kJ/mol. The comparison of this value with E_{eff} obtained by different authors for styrene and other monomers polymerization¹⁸ shows that E_{eff} of the process falls fairly well within the range of the known estimates and its value is rather low (for most of Ziegler–Natta systems-catalyzed polymerization reactions, E_{eff} varies over the range 12.6–62.9 kJ/mol). Such an agreement suggests the same chain propagation mechanism for different polymerization systems of this type.

At present, many authors have proved in every detail the two-stage chain propagation mechanism including the monomer coordination stage, which results in octahedral structure of AS, and penetration of the monomer into the growing macrochain.⁴⁰ The reaction order with respect to monomer (n) may be an indirect estimation criterion of the chain propagation mechanism. It is shown that if the monomer penetration from the bulk mixture into the Ti–C bond is the controlling stage (a single-stage mechanism), $n = 0$. Whenever the monomer adsorption rate in AS is a limiting factor (a two-stage mechanism), $n = 1$.⁴⁴ Higher reaction orders with respect to monomer are usually attributed to diffusion hindrances on the way of the monomer to AS.^{22,45} In particular, Sangalov et al.²² think that it is these factors which are the reasons of $n > 1$ they observed in TiCl_4 -higher aluminum alkyls-catalyzed ethylene polymerization. For styrene polymerization catalyzed by the TiCl_3 - AlEt_3 system it is shown⁴⁵ that at relatively low monomer concentrations (< 3.6 mol/L) the reaction was second order. For the TiCl_4 - $\text{Al}(\text{C}_7\text{H}_{15})_3 \cdot \text{Mg}(\text{C}_7\text{H}_{15})_2$ -styrene polymerization system studied here, $n = 1.9$ under the adopted conditions (at styrene concentrations also less than 3.6 mol/L). Such a result implies, first of all, the two-stage chain propagation mechanism since $n > 0$. On the other hand, as $n > 1$, it may be suggested that there is a large number of diffusion hindrances on the way of monomer to AS. This very fact is likely to be the reason of inhibition of the reaction since the early stage of the process. The ultrahigh-molecular-weight polymer produced, which is insoluble in the reaction medium, settles down on the catalyst particles and wraps them around, hindering diffusion of the monomer towards those “immured” AS that affects the polymerization kinetics. Allen and Gill⁴⁶ have come to the same conclusion as regards TiCl_4 - RMgBr -catalyzed styrene polymerization, in which case polystyrene was produced with molecular weight even of an order of magnitude lower than that for the studied TiCl_4 -MAA system. Thus, the comparison of available results has demonstrated that higher magnesium

aluminum alkyls used as OMC do not alter the basic relationships governing styrene polymerization catalyzed by complex organometallic systems. The present data are also fairly consistent with the known concepts of the two-stage chain propagation mechanism, however, with prevailing diffusion effect on the kinetics even at the very beginning of the process.

In all experiments, in which higher aluminum magnesium alkyl complex catalytic systems were used, polystyrene produced was of unusually high molecular weight (2×10^6 – 6×10^6) and included boiling toluene-insoluble fraction ($\sim 10\%$).¹⁸ IR spectra of the fractions soluble and insoluble in boiling toluene were identical and differed from that of atactic polymer preextracted by boiling methylethyl ketone. The diffraction patterns of the first two fractions from the above-mentioned (nonannealed samples) showed equal crystallinities ($\sim 20\%$) which are an indirect indication of their microstructural identity. The results suggest that some of polystyrene, insoluble in boiling toluene, is an isotactic and, probably, linear polymer, but having ultrahigh molecular weight, which hinders dissolution.

In order to substantiate in detail the mechanism of chain propagation within the catalytic system studied, further research is necessary, namely, studies of kinetics, polymer MWD, determination of the number of AS, etc. Nevertheless, the results concerning styrene polymerization with magnesium aluminum alkyl complexes presented here are suggestive of special propagation conditions and of the existence of a stable complex structure, which is capable of ensuring quite rigid orientation of the coordinated monomer and growing chains and hinders the chain transfer and termination reactions. By using a new integrated approach to polymerization sites, Minsker et al.⁴⁰ concluded that such active sites with a peculiar "grotto"-like structure made it possible to coordinate monomer only by the vinyl end and in a single steric position, thus ensuring high stereospecificity of the catalyst.

High molecular weight of the polymer obtained unambiguously indicates that the constant of transfer to organometallic compounds is rather low. In the conventional Ziegler systems it is this type of reaction which is the main factor restricting the chain propagation. Specificity of the catalytic system studied is the use of organometallic compounds containing higher alkyl radicals, which are known to give more time-stable catalysts, and the chain transfer to higher aluminum alkyls bound in complex with MgR_2 is probably hindered or infeasible.

Thus, the present results allow a conclusion to be made that higher aluminum magnesium alkyls are quite efficient components of the complex catalyst of styrene polymerization giving superhigh-molecular-weight polymer of stereospecific structure.

References

1. R. N. Haward, A. N. Roper, and K. L. Fletcher, *Polymer*, **14**, 365 (1973).
2. D. G. Boucher, I. W. Parsons, and R. N. Haward, *Makromol. Chem.*, **175**, 3461 (1974).
3. Ph. Radenkov, T. Petrova, L. Petkov, and D. Jelazkova, *Eur. Polym. J.*, **11**, 313 (1975).
4. L. Petkov, Ph. Radenkov, and R. Kyrtecheva, *Polymer*, **19**, 570 (1978).
5. A. A. Baulin and S. S. Ivanchev, in *Homo- and Copolymerization of α -Olefines Catalyzed by Complex Systems*, Moscow, 1983, p. 134 (in Russian).

6. A. A. Baulin, M. A. Budanova, S. S. Ivanchev, V. N. Sokolov, and B. V. Erofeev, *Dokl. Akad. Nauk SSSR*, **247**, 1170 (1979).
7. B. V. Erofeev, A. Ya. Valendo, L. P. Kostyan, and O. I. Utrobina, *Izv. Akad. Nauk BSSR, Ser. Khim. Nauk*, **4**, 117 (1981).
8. J. A. Licchelli, R. N. Haward, and I. W. Parsons, *Polymer*, **22**, 667 (1981).
9. A. A. Baulin and I. P. Sidorova, *Vysokomol. Soedin. B*, **24**, 781 (1982).
10. S. A. Zakharov and V. A. Sergeev, *Vysokomol. Soedin. B*, **25**, 512 (1983).
11. B. V. Erofeev, A. Ya. Valendo, and O. A. Utrobina, *Izv. Akad. Nauk BSSR, Ser. Khim. Nauk*, **3**, 71 (1983).
12. F. Karol, *Am. Chem. Soc. Polym. Prepr.*, **24**, 107 (1983).
13. V. A. Zakharov, G. D. Bukatov, and Yu. I. Ermakov, *Usp. Khim.*, **49**, 2213 (1980).
14. A. D. Caunt, J. A. Licchelli, I. W. Parsons, R. N. Haward, and R. I. Al-Hillo Malik, *Polymer*, **24**, 21 (1983).
15. I. Petkov and M. Mikhailova, *Khim. Ind. (Bulg.)*, **5**, 224 (1982).
16. L. S. Bresler, K. V. Kisin, A. V. Lubinin, and N. N. Marasanova, *Vysokomol. Soedin. A*, **25**, 2103 (1983).
17. A. Ya. Valendo and N. N. Gurinovich, *Dokl. Akad. Nauk BSSR*, **31**, 336 (1987).
18. A. M. Antipova, T. K. Morozova, L. V. Gaponik, and V. P. Mardykin, *Vysokomol. Soedin. B*, **28**, 182 (1986).
19. N. F. Lanskova, A. I. Iliasova, A. I. Baisheva, Yu. A. Sangalov, and K. S. Minsker, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **3**, 648 (1974).
20. A. A. Panasenko, O. G. Senchenko, V. S. Sultanova, L. I. Arbuzova, and K. S. Minsker, *Vysokomol. Soedin. B*, **16**, 645 (1974).
21. Yu. A. Sangalov, A. U. Baisheva, and K. S. Minsker, *Plast. Massy*, **17**, 27 (1976).
22. Yu. A. Sangalov, A. U. Baisheva, and K. S. Minsker, in *Carbon-Chain Polymers*, Nauka, Moscow, 1977 (in Russian).
23. A. I. Baisheva, A. I. Iliasova, Yu. A. Sangalov, and K. S. Minsker, *Plast. Massy*, **5**, 22 (1974).
24. Yu. B. Monakov, S. R. Rafikov, A. M. Ivanova, N. Kh. Minchenkova, and I. G. Savelieva, *Dokl. Akad. Nauk SSSR*, **229**, 667 (1976).
25. A. A. Berg, V. G. Kozlov, V. P. Budtov, Yu. V. Monakov, and S. R. Rafikov, *Vysokomol. Soedin. A*, **22**, 532 (1980).
26. N. G. Marina, Yu. B. Monakov, S. R. Rafikov, and V. L. Ponomorenko, *Usp. Khim.*, **52**, 733 (1983).
27. N. G. Marina, Kh. K. Gadeleva, Yu. B. Monakov, and S. R. Rafikov, *Dokl. Akad. Nauk SSSR*, **274**, 641 (1984).
28. L. V. Gaponik, and V. P. Mardykin, *Zh. Obshchei Khim.*, **55**, 1341 (1985).
29. V. P. Mardykin and A. M. Antipova, *Vysokomol. Soedin. A*, **11**, 1600 (1969).
30. V. Chrastova, D. Mikulasova, P. Citovsky, and J. Lacok, *Zb. Pr. Chemickotechnol. Fak. SVST*, 1977-1978, Bratislava, 1981, p. 177.
31. N. M. Chirkov, P. E. Matkovskii, and F. S. Diyachkovskii, *Organometallic Systems-Catalyzed Polymerization*, Khimiya, Moscow, 1976 (in Russian).
32. A. A. Baulin, E. I. Novikova, G. Ya. Malkova, V. I. Maksimov, I. Vyshynskaya, and S. S. Ivanchev, *Vysokomol. Soedin. A*, **22**, 181 (1980).
33. V. P. Mardykin, A. M. Antipova, L. V. Gaponik, and G. V. Listratova, *Vestnik Belorussk. Univ., Ser. II*, **2**, 14 (1978).
34. V. P. Mardykin, A. M. Antipova, and L. V. Gaponik, *Vysokomol. Soedin. B*, **23**, 52 (1981).
35. A. M. Antipova, L. V. Gaponik, S. V. Sviridov, and V. P. Mardykin, *Vysokomol. Soedin. B*, **25**, 170 (1983).
36. V. P. Mardykin, A. M. Antipova, and P. N. Gaponik, *Usp. Khim.*, **40**, 24 (1971).
37. D. B. Mallpass and L. W. Fannin, *J. Organometal. Chem.*, **93**, 1 (1975).
38. A. M. Antipova, T. K. Morozova, L. V. Gaponik, V. P. Mardykin, and N. B. Krakhina, *Vestnik Belorussk. Univ., Ser. II*, **2**, 14 (1984).
39. N. G. Gaylord and H. F. Mark, *Linear and Stereoregular Addition Polymers: Polymerization with Controlled Propagation*, Wiley-Interscience, New York, 1959 (cited from the Russian translation edited by A. A. Korotkov, Inostrannaya Literatura, Moscow, 1962).
40. K. S. Minsker, M. M. Karpasas, and G. E. Zaikov, *J. Macromol. Sci. C*, **27**, 1 (1987).

41. A. A. Baulin, M. A. Budanova, S. S. Ivanchev, V. N. Sokolov, and B. V. Erofejev, *Vysokomol. Soedin. A*, **22**, 1654 (1980).
42. L. A. M. Rodrigues and H. M. Van Looy, *J. Polym. Sci. A-1*, **4**, 1971 (1966).
43. A. A. Baulin, *Vysokomol. Soedin. B*, **23**, 723 (1981).
44. D. R. Burfield, *J. Polym.*, **25**, 1645 (1984).
45. C. H. Burneff and P. J. Tait, *Polymer*, **1**, 151 (1960).
46. P. E. M. Allen and D. Gill, *Makromol. Chem. A*, **71**, 33 (1964).

Received August 2, 1988

Accepted September 23, 1988