Now, substituting eq A4 into eq A3, the general form of the equation is obtained in terms of the experimental variables.

$$K\{(1/y)[\mathrm{EtLi}]_0 - (v/y)(2 - N)[\mathrm{RM_jLi}]_0\}(2v/y) = \frac{2(2 - N)^2[\mathrm{RM_jLi}]_0}{(N - 1)} \quad \text{(A5)}$$

Appendix C

Calculation of *K* for a Specific Case. The general equation (A5) for K in terms of the experimental variables was shown in Appendix B. Now, for $y = 6$ and $v = 3$, the left side of the equation becomes

$$K\{(1/6)[\mathrm{EtLi}]_0 - (1/2)(2 - N)[\mathrm{RM_jLi}]_0\} = K[\mathrm{RM_jLi}]_0\left\{(1/6)\frac{[\mathrm{EtLi}]_0}{[\mathrm{RM_jLi}]_0} - (1/2)(2 - N)\right\}$$

Letting $r = [\mathrm{EtLi}]_0/[\mathrm{RM_jLi}]_0$ we have

$$K[\mathrm{RM_jLi}]_0\{(r/6) - (1/2)(2 - N)\} = K\frac{[\mathrm{RM_jLi}]_0}{2}[(r/3) + N - 2]$$

Substituting this into eq A5 in Appendix B and rearranging yields

$$K = \frac{4(2 - N)^2/(N - 1)}{[(r/3) + N - 2]}$$

which is the form desired.

Stereospecific Polymerization of Methyl Methacrylate by Organomagnesium Catalysts with a Magnesium–Nitrogen Bond

Yasushi Joh and Yahide Kotake

Research Laboratories, Mitsubishi Rayon Company, Miyuki-cho, Otake, Hiroshima, 739-06, Japan. *Received December 29, 1969*

ABSTRACT: The polymerization of methyl methacrylate by organomagnesium compounds with the magnesium–nitrogen bond was carefully studied and a number of new catalysts were disclosed. The stereostructure of the resulting polymer as well as the catalytic activity is quite different depending on the amide group in the catalyst. The organomagnesium compounds with a piperidine ring such as ethylpentamethyleniminomagnesium or bis-pentamethylenimino)magnesium are found to be an effective catalyst for the syndiotactic polymerization of methyl methacrylate. The polymerization is affected by the polymerization conditions such as temperature and the solvent employed. The lower the polymerization temperature, the higher the syndiotacticity of the polymer, and toluene is a best solvent in the syndiotactic polymerization. On the other hand, organomagnesium compounds with a pyrasole ring such as ethylvinyleniminomagnesium, or bis(divinylenimino)magnesium are the novel catalyst for the isotactic polymerization of methyl methacrylate. The isotacticity of polymer is not affected by the polymerization conditions such as polymerization temperature and the solvent employed and the polymers obtained by these catalysts have all 100% isotactic units. The mechanism of the polymerization was discussed in considerable detail in view of the aggregation of the catalyst and a reasonable mode of polymerization is proposed that the propagation occurs at magnesium–nitrogen bond, and the propagation is affected by another coordinated nitrogen-bridged group in the catalyst throughout the polymerization.

Since the pioneering works by Fox, *et al.*,[1] Miller, *et al.*,[2] and Watanabe, *et al.*,[3] who independently succeeded in the preparation of the stereoregular poly(methyl methacrylate) in 1958, considerable literature on the syntheses and characterization of the stereoregular poly(methyl methacrylate) has appeared.[4–10]

The utilization of organometallic catalysts has been the most useful method in these researches and many new effective catalysts were disclosed. Natta, *et al.*,[11,12] and Nishioka, *et al.*,[13] have described nitrogen Grignard reagents, but did not study these catalysts intensively. Recently Joh, *et al.*,[14,15] disclosed several kinds of new catalysts containing the Mg–N bond which are particularly effective in the stereospecific polymerization of methacrylonitrile at moderately high temperatures. The polymerization of methyl methacrylate by the various kinds of organomagnesium catalysts containing the Mg–N bond brought us new interesting information on the polymerization of methyl methacrylate. The stereostructure of the resulting polymer depends sub-

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(1) T. G Fox, B. S. Garrett, W. E. Goode, S. Gratch, J. F. Kincaid, A. Spell, and J. D. Stroupe, *J. Amer. Chem. Soc.*, **80**, 1768 (1958).

(2) R. G. Miller, B. Mills, P. A. Small, A. Turner Jones, and D. G. M. Wood, *Chem. Ind.* (London), 1323 (1958).

(3) H. Watanabe and Y. Sono, paper presented at meeting of the Chemical Society of Japan, Nagoya, Nov 1958.

(4) U. Baumann, H. Schreiber, and K. Tessmar, *Makromol. Chem.*, **36**, 81 (1960).

(5) J. D. Stroupe and R. E. Hughes, *J. Amer. Chem. Soc.*, **80**, 2341 (1958).

(6) W. E. Goode and F. W. Owens, *J. Polym. Sci.*, **46**, 317 (1960); **47**, 75 (1961).

(7) D. L. Glusker, J. Lysloff, and E. Stiles, *ibid.*, **49**, 315 (1961).

(8) D. L. Glusker, E. Stiles, and B. Yonkoskie, *ibid.*, **49**, 297 (1961).

(9) J. D. Cram and K. R. Kopecky. *J. Amer. Chem. Soc.*, **81**, 2748 (1959).

(10) T. Tsuruta, T. Makimoto, and H. Kanai, *J. Makromol. Chem.*, **1**, 31 (1966).

(11) G. Natta, G. Mazzanti, P. Longi, G. Dall'Asta, and F. Bernardini, *J. Polym. Sci.*, **51**, 487 (1951).

(12) G. Natta, G. Mazzanti, P. Longi, and F. Bernardini, *Chim. Ind.* (Milan), **42**, 457 (1960).

(13) A. Nishioka, H. Watanabe, K. Abe, and Y. Sono, *J. Polym. Sci.*, **43**, 241 (1960).

(14) Y. Joh, T. Yoshihara, Y. Kotake, F. Ide, and K. Nakatsuka, *ibid., Part B*, **4**, 673 (1966).

(15) Y. Joh, T. Yoshihara, Y. Kotake, Y. Imai, and S. Kurihara, *ibid., Part A-1*, **5**, 2503 (1967).

stantially on the kind of the N-substituted group in the catalysts. When ethylpentamethyleniminomagnesium or bis(pentamethylenimino)magnesium were used as catalyst, highly syndiotactic polymer was formed, whereas ethyldivinyleniminomagnesium or bis(divinylenimino)magnesium were used, highly isotactic poly(methyl methacrylate) was obtained. The present paper deals with these interesting new catalysts and the polymerization behavior of methyl methacrylate by these catalysts.

Experimental Section

Methyl Methacrylate (MMA). After commercial MMA was dried over CaH_2, it was fractionally distilled under nitrogen and stored over molecular sieves at −20°.

Toluene and *n*-Heptane. Toluene and *n*-heptane were treated with concentrated H_2SO_4 followed by successive washing with aqueous NaOH and water, dried over $CaCl_2$, and then distilled over metallic sodium under nitrogen.

Ethers. Diethyl ether, anisole, and tetrahydrofuran were refluxed for 8 hr over metallic sodium, then fractionally distilled.

Diethylmagnesium (Et_2Mg). Diethylmagnesium was prepared according to the Schlenk's procedure[16] from the Grignard reagent and dioxane, special precautions being taken for exclusion of atmospheric contamination. To remove the complexed dioxane, the prepared diethylmagnesium–dioxane complex was treated at 120° under the reduced pressure at 1–2 mm for 30 hr. The white crystals of diethylmagnesium were powdered under a nitrogen atmosphere.

Amines. Amines used in this investigation were dried over CaH_2 and fractionally distilled immediately before use.

Catalyst Preparation. Magnesium amide derivatives were prepared by the reaction between diethylmagnesium and amines. The typical procedure was as follows. The reaction vessel was carefully purged with nitrogen and the diethylmagnesium and a solvent were introduced. To this suspension, a stoichiometric amount of amines was added dropwise by means of a hypodermic syringe through a self-sealing rubber cap. Instantaneously, an exothermic reaction took place with the evolution of ethane gas.

$$HNR_2 + Et_2Mg \longrightarrow EtMgNR_2 + EtH$$

$$EtMgNR_2 + HNR_2 \longrightarrow Mg(NR_2)_2 + EtH$$

Polymerization. The polymerizations were run in the Schlenk-type reactor under nitrogen. The catalysts were prepared in the polymerization vessel by the addition of amine to the stirred solution (or suspension) of diethylmagnesium in inert solvent. After being cooled to a prescribed temperature, the polymerizations were started by the addition of monomer. During the preparation of the catalyst, the addition of monomer, and the polymerization, the reactants were maintained in good agitation. The polymers were recovered by precipitating the reaction mixture with an excess of methanol acidified with a small amount of HCl. The polymers were washed with methanol and dried under vacuum.

Intrinsic Viscosity and Molecular Weight. Relative viscosity was measured at 20° in $CHCl_3$ solution at the concentration of 0.1 g/dl using an Ostwald viscometer, and the intrinsic viscosity was calculated by the equation[17]

$$[\eta] = \frac{3[\eta^{1/3}{}_{\mathrm{rel}} - 1]}{C}$$

The molecular weight was calculated using Meyerhoff and Schulz's relationship.[18]

$$[\eta] = 4.85 \times 10^{-5} M^{0.80}$$

Determination of the Stereoregularity. The stereoregularity of the resulting poly(methyl methacrylate) was determined by nmr[13] and infrared spectra.[19]

Results

The Effect of Kind of the N-Substituted Group in the Catalyst. The polymerizations were run in toluene at −78° by the organomagnesium catalyst with the Mg–N bond which was prepared from diethylmagnesium and the various kinds of amines. The results are shown in Tables I, II, and III. The stereostructures of the resulting polymers are different depending on the catalyst used. Table I shows that ethylpentamethyleniminomagnesium and bis(pentamethylenimino)magnesium, which were prepared from diethylmagnesium and piperidine, are the novel catalysts for the syndiotactic polymerization of methyl methacrylate. Both catalysts are soluble in toluene. The rate of polymerization was extremely fast and the polymerization was completed within 10 min. The nmr analysis indicates the resulting polymer is highly syndiotactic (93% syndiotactic triad). On the contrary, ethyldivinyleniminomagnesium and bis(divinylenimino)magnesium induce the isotactic polymerization of methyl methacrylate. These catalysts are insoluble in toluene, thus are heterogeneous catalysts, and the rate of polymerization was rather low compared with the syndiotactic polymerization by the catalyst with a pentamethylenimino ring. The results of polymerization by various kinds of organomagnesium catalysts containing a Mg–N bond are summarized in Table I. It is very interesting that the stereostructure of the resulting polymer depends on the N-substituted group in the catalysts. Table II shows the results of the polymerization of methyl methacrylate by the reaction products between diethylmagnesium and an equimolar amount of primary amines. The structure of the reaction products has not been clarified as yet. Since both the diethylmagnesium and the primary amine are bifunctional, the reaction products might have complex polymeric structure. The rate of the polymerization by these catalysts is very low, but the polymer with predominantly syndiotactic units was obtained by the reaction product between cyclohexylamine and diethylmagnesium. Table III shows the results of the polymerization by several kinds of Grignard reagents. Interestingly, the nitrogen Grignard reagent with pentamethylenimino ring gave a highly isotactic polymer similar to the C_6H_5MgBr catalyst.

Polymerization by Ethylpentamethyleniminomagnesium and Bis(pentamethylenimino)magnesium. Effect of the Polymerization Temperature. The organomagnesium compounds containing the piperidine ring like ethylpentamethyleniminomagnesium and bis(penta-

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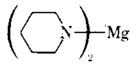
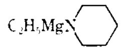
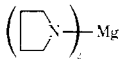
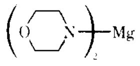
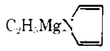
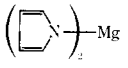
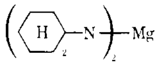
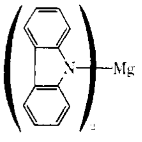
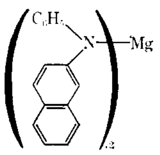
(16) W. Schlenk and W. Schlenk, Jr., *Ber.*, **62B**, 920 (1920); **64B**, 734 (1961).

(17) I. Sakurada, *Kobunshi Kagaku*, **2**, 253 (1945).

(18) G. Meyerhoff and G. V. Schulz, *Makromol. Chem.*, **7**, 294 (1951).

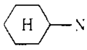
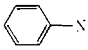
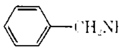
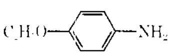
(19) H. Watanabe, *Kogyo Kagaku Zasshi*, **64**, 1851 (1961).

TABLE I
RESULTS OF POLYMERIZATION OF METHYL METHACRYLATE BY ORGANOMAGNESIUM CATALYST

Catalyst	Solubility[a] of catalyst	Polymerization time, min	Conversion, %	Tacticity triads, % s	h	i	$M_w \times 10^{-4}$
$((C_2H_5)_2N)_2Mg$	S	60	11	68	23	9[c]	118
$((n\text{-}C_3H_8)_2N-)_2Mg$	S	15	92	79[b]			40
$((i\text{-}C_3H_8)_2N-)_2Mg$	S	15	82	73[b]			10
$((n\text{-}C_4H_9)_2N)-)Mg$	S	180	88				5
	S	5	95	93	7	0[c]	12
	S	5	93	93	7	0[c]	30
	I	180	39	80[b]			46
	I	60	46	74[b]			37
	I	180	45	0	0	100[c,d]	41
	I	120	52	0	0	100[c,d]	34
	I	120	79	68[b]			4
$((C_6H_5)_2N-)_2Mg$	I	120	49	45	31	24[c]	29
$((C_6H_5CH_2)_2N-)_2Mg$	S	15	74	45[b]			9
	I	360	13	36[b]			12
	S	180	90.8	48[b]			10
$MgEt_2$	I	360	47	70[b]			3

[a] Solubility of the catalyst in toluene: I, insoluble, S, soluble. [b] Triad syndiotacticity from ir method. [c] Triad measured by nmr. [d] Triad isotacticity 100%; polymerization conditions: catalyst, 0.001 mol; toluene, 50 ml; methyl methacrylate, 5 ml; polymerization temperature, −78°.

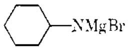
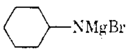
TABLE II
RESULTS OF THE POLYMERIZATION OF METHYL METHACRYLATE BY THE REACTION PRODUCTS BETWEEN $Mg(C_2H_5)_2$ AND PRIMARY AMINES

Amine	Amine/$MgEt_2$ ratio	Solubility[a] of catalyst	Time, min	Conversion, %	s content,[b] %
	1	I	240	25	72
	1	I	360	3	56
	1	I	120	18	67
	1	I	180	6.2	48

[a] Solubility of the catalyst in toluene: I, insoluble. [b] Triad syndiotacticity by infrared method; polymerization conditions: catalyst, 0.001 mol; toluene, 50 ml; methyl methacrylate, 5 ml; polymerization temperature, −78°.

methylenimino)magnesium are the interesting novel catalysts which induce the syndiotactic polymerization of methyl methacrylate. Thus the polymerization behavior was investigated in considerable detail. Figure 1 shows the effect of the polymerization temperature on the conversion and on the stereoregularity of the resulting polymer. The polymerization rate at low temperature like −78° was extremely fast. The reaction medium was solidified within a few minutes, and the polymerization was almost completed in this period. The rate of polymerization decreased with increasing temperature. The syndiotacticity of

TABLE III
RESULTS OF THE POLYMERIZATION[a] BY GRIGNARD REAGENTS

Catalyst	Polymerzn temp, °C	Polymerzn time, min	Conversion, %	Tacticity triads, % s	h	i	DP[b]
C_2H_5MgBr	−78	360	2.3	35			
C_6H_5MgBr	0	30	55.5	0	0	100	4000
	0	60	23.9	0	0	100	3700
	−78	180	38.9	0	0	100	3700

[a] Polymerization condition: catalyst, 0.001 mol in 2 ml of ether; toluene, 50 ml; methyl methacrylate, 5 ml. [b] Degree of polymerization.

TABLE IV
THE EFFECT OF SOLVENT ON THE POLYMERIZATION[a] OF METHYL METHACRYLATE BY BIS(PENTAMETHYLENIMINO)MAGNESIUM

Solvent	Solubility of catalyst	Polymerzn temp, °C	Polymerzn time, min	Conversion, %	Tacticity triads, % s	h	i
Toluene	S	−78	5	95	93	7	0^c
		0	30	34	57^b		
THF	S	−78	30	66	92	8	0^c
		0	300	28	74	18	8^c
Diethyl ether	I	−78	30	28	80	15	5^c
		0	30	25	63^b		
Hexane	I	−78	120	3	70^b		
		0	60	11			
Anisole	S	0	15	29	32	16	53^c
Toluene–$(C_2H_5)_3N^d$	S	−78	15	62.2	83^b		
Toluene–anisole[e]	S	−78	15	94.1	83^b		
$(C_2H_5)_3N$–anisole[f]	S	−78	300	11.2	72^b		
Toluene–heptane[d]	I	−78	240	24.4			

[a] Polymerization conditions: catalyst, 0.001 mol; solvent, 50 ml, monomer, 5 ml. [b] Syndiotacticity, triad measured by infrared spectra. [c] Syndiotacticity, triad measured by nmr. [d] Volume ratio 1:1. [e] Volume ratio 9:1. [f] Volume ratio 4:1.

the resulting polymer decreased also with increasing temperature, and the syndiotacticity of the polymer obtained at room temperature is approximately comparable to that obtained by a radical initiater. Figure 2 shows the results of the polymerization by ethylpentamethyleniminomagnesium. Similar to the bis(pentamethylenimino)magnesium, the polymerization proceeds very fast at temperatures lower than −40°. The syndiotacticity of the resulting polymer decreased as the polymerization temperature increased.

Effect of the Solvent. The effect of the solvent on the polymerization of methyl methacrylate by the bis(pentamethylenimino)magnesium is shown in Table IV. Toluene is a best solvent for high syndiotacticity and rate of polymerization. The syndiotacticity of the polymer obtained in tetrahydrofuran was comparable to that obtained in toluene, although the polymerization rate was relatively low. Other solvents used are not so effective for the syndiotactic polymerization, since the stereoregularity and the polymerization rate

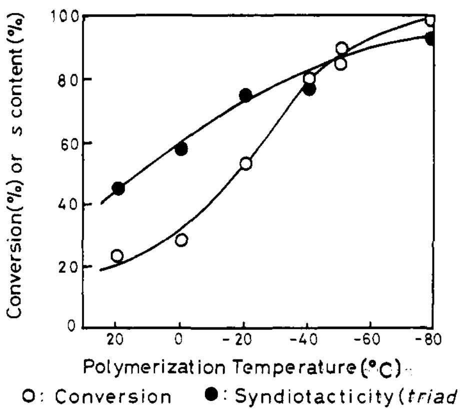


Figure 1. Effect of temperature on the polymerization of methyl methacrylate with the $Mg(NC_5H_{10})_2$ catalyst. Polymerization conditions, catalyst 0.001 mol, toluene 50 ml, monomer 5 ml, polymerization time 15 min.

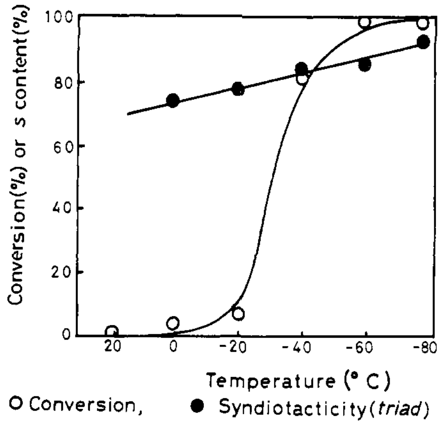


Figure 2. Effect of temperature on the polymerization of methyl methacrylate with the $EtMgN(C_5H_{10})$ catalyst. Polymerization conditions, catalyst 0.001 mol, toluene 50 ml, monomer 5 ml, polymerization time 15 min.

TABLE V
EFFECT OF THE SOLVENT ON THE POLYMERIZATION[a] OF METHYL METHACRYLATE BY BIS(DIVINYLENIMINO)MAGNESIUM

Solvent	Solubility of catalyst	Polymerzn temp, °C	Polymerzn time, min	Conversion, %	Tacticity triads, % s	h	i
Toluene	I	−30	15	99	0	0	100
		0	15	36	0	0	100
Tetrahydrofuran	I	−30	60	1			
		0	300	3	0	0	100
Diethyl ether	I	−30	60	18	0	0	100
		0	15	72	0	0	100
Hexane	I	−30	60	0			
		0	300	2	0	0	100
Anisole	I	0	15	48	0	0	100

[a] Polymerization conditions: catalyst, 0.001 mol; solvent, 50 ml, monomer, 5 ml.

relatively decreased in these solvents. In case of the ethylpentamethyleniminomagnesium, the same trend was observed and toluene is the best solvent for syndiotactic polymerization.

Polymerization by Ethyldivinyleniminomagnesium and Bis(divinylenimino)magnesium. Effect of the Polymerization Temperature. A highly isotactic poly(methyl methacrylate) can be obtained by the organomagnesium compound containing the pyrrole ring such as ethyldivinyleniminomagnesium or bis(divinylenimino)magnesium. Effect of temperature and solvent on the polymerization was carefully investigated by using the bis(divinylenimino)magnesium. Figure 3 shows that the optimum polymerization temperature in this polymerization was around −30°. Interestingly, the resulting polymer has 100% isotactic units regardless of the polymerization temperature.

Effect of Solvent. Table V gives the effects of the solvent on the polymerization at −30 and 0° by bis(divinylenimino)magnesium catalyst which is insoluble in these solvents. All the polymers obtained had 100% isotactic units. It should be notable that in the polymerization by the bis(divinylenimino)magnesium, the stereostructure of the polymers does not depend on the polymerization conditions and is completely isotactic within our range of the experiments.

Polymerization by Bis(diethylamino)magnesium. Effect of the polymerization temperature and the solvent on the polymerization by the bis(diethylamino)magnesium is shown in Figure 4 and Table VI. The catalyst was soluble in the solvents except in hexane. The conversion increased with increasing the polymerization temperature from −78 to −40°, then decreased with further rise of the temperature above −40°. Syndiotacticity of the resulting polymers increased with decreasing the polymerization temperature.

TABLE VI
EFFECT OF THE SOLVENT ON THE POLYMERIZATION[a] OF METHYL METHACRYLATE BY BIS(DIETHYLAMINO)MAGNESIUM

Solvent	Polymerzn temp, °C	Polymerzn time, min	Conversion, %	Tacticity triad, % s
Toluene	−78	15	3	63
	0	15	38	52
THF	−78	300	37	85
	0	60	35	73
Ether	−78	360	9	72
	0	15	33	56
Hexane	−78	360	3	59
	0	15	13	47
Anisole	0	15	43	55

[a] Polymerization conditions: catalyst, 0.001; solvent, 50 ml; monomer, 5 ml.

Figures 5 and 6 show the time-conversion curves by

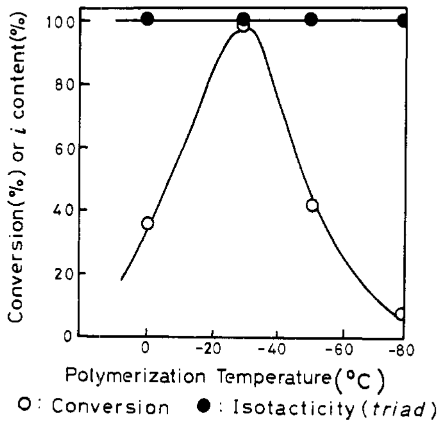


Figure 3. Effect of temperature on the polymerization of methyl methacrylate with the $Mg(NC_4H_4)_2$ catalyst. Polymerization conditions, catalyst 0.001 mol, toluene 50 ml, monomer 5 ml, polymerization time 15 min.

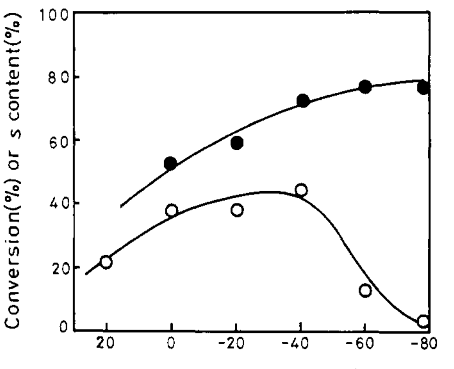


Figure 4. Effect of temperature on the polymerization of methyl methacrylate with the $Mg(NEt_2)_2$ catalyst. Polymerization conditions, catalyst 0.001 mol, toluene 50 ml, monomer 5 ml, polymerization time 15 min.

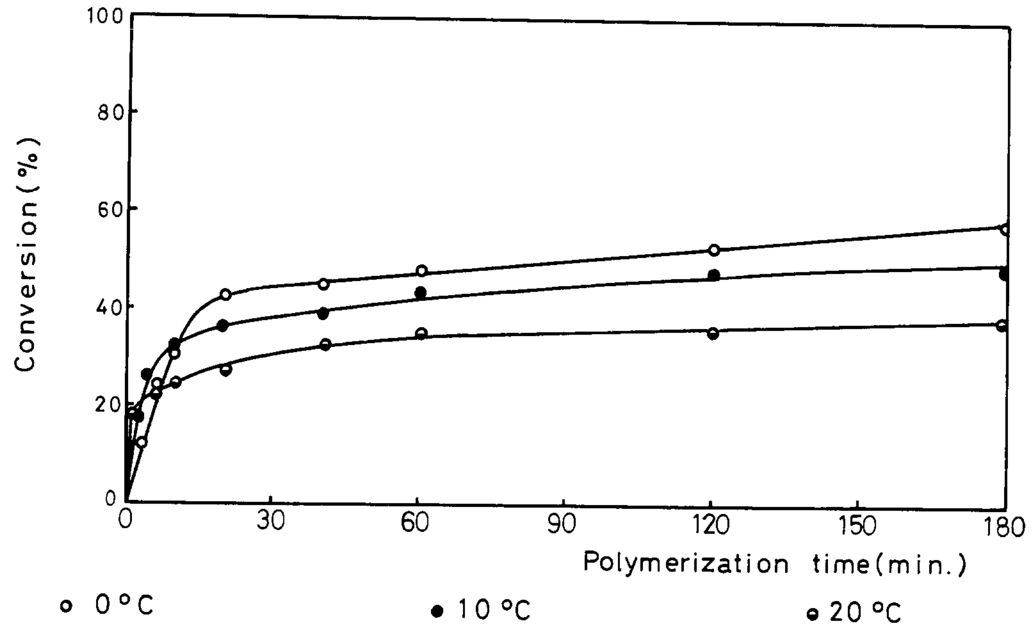


Figure 5. Time-conversion curves of the polymerization of methyl methacrylate with $Mg(NEt_2)_2$. Polymerization conditions, catalyst 0.001 mol, toluene 50 ml, monomer 5 ml.

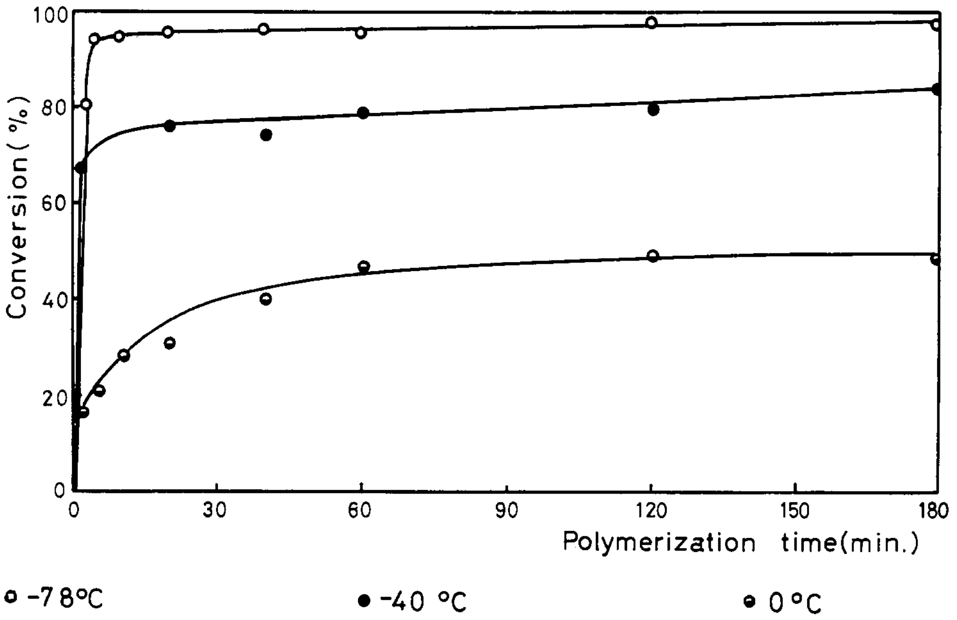


Figure 6. Time-conversion curves of the polymerization of methyl methacrylate with $Mg(NC_5H_{10})_2$. Polymerization conditions, catalyst 0.001 mol, toluene 50 ml, monomer 5 ml.

the bis(diethylamino)magnesium and the bis(pentamethylenimino)magnesium. The initial rate of polymerization increased with increasing the polymerization temperature. However, the final conversion decreased as the polymerization temperature increased.

Discussion

The reaction between diethylmagnesium and primary or secondary amines to magnesium amide derivatives was carefully examined by Coates, *et al.*[20] In the present investigation, it was observed that an exothermic reaction took place upon addition of the amines to the suspension of diethylmagnesium with the evolution of a stoichiometric amount of ethane.

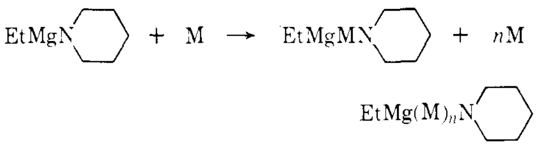
For example, when the reaction between diethylmagnesium and piperidine was carried out in diethyl ether, reaction easily occurred with the evolution of ethane at room temperature. The reaction mixture was homogeneous until an equimolar amount of piperidine was added to the diethylmagnesium. Further addition of piperidine to this homogeneous solution gave a white bulky precipitate. Isolation and analysis of the white precipitate indicates this to be bis(pentamethylenimino)magnesium which is insoluble in diethyl ether. This observation indicates that an equimolar addition of piperidine to diethylmagnesium gave only monosubstituted ethylpentamethyleniminomagnesium, and bis(pentamethylenimino)magnesium, which is insoluble in diethyl ether, could not

(20) G. E. Coates and D. Ridley, *J. Chem. Soc.*, *A*, 56 (1957).

be formed before more than an equimolar amount of piperidine was added to the diethylmagnesium.

Natta, *et al.*,[11,12] and Murahashi, *et al.*,[21] reported the polymerization of methyl methacrylate by $Al(NPh_2)_3$ and $AlEt_2(NPh_2)$, respectively. They showed that the propagation reaction took place at the Al–N bond in their catalyst.

It is of great interest to know the reaction mechanism of the polymerization by our catalyst which has the Mg–N bond instead of the Al–N bond in Natta or Murahashi's catalyst. The comparison of the polymerization behavior between Et_2Mg, $EtMgNC_5H_{10}$, $Mg(NC_5H_{10})_2$, and $C_5H_{10}NMgBr$ seems very useful. $C_5H_{10}NMgBr$ produced the isotactic polymer while Et_2Mg, $EtMgNC_5H_{10}$, and $Mg(NC_5H_{10})_2$ gave the syndiotactic polymer, the latter two giving highly syndiotactic ones. Assuming that the propagation reaction would occur at the Mg–N bond in $EtMgNC_5H_{10}$ catalyst, then we have

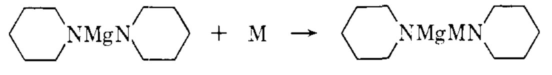


(1)

Diethylmagnesium also induces the syndiotactic polymerization and we can simply visualize as

$$EtMgEt + M \longrightarrow EtMgMEt + nM \longrightarrow EtMg(M)_nEt \quad (2)$$

By comparing (1) and (2), we can easily know that when n is larger than a few, (1) and (2) are essentially equal. The difference between Et_2Mg and $EtMgNC_5H_{10}$ is that the former is insoluble in toluene, namely is a heterogeneous catalyst, while the latter is a homogeneous catalyst. Higher rate of polymerization by the latter catalyst might be reasonably explained by the fact that the soluble catalyst has more active species than the heterogeneous catalyst. However, the syndiotacticity of the resulting polymer is extremely higher in the case of $EtMgNC_5H_{10}$ than in the case of Et_2Mg. This difference in stereostructure cannot be fully explained by the above consideration. When $Mg(NC_5H_{10})_2$ was used as the catalyst, the initiation must take place at the Mg–N bond, since there is no Mg–C bond in the catalyst. When the polymerization reaction once started, the conditions of the active site might be similar to those in case of $EtMgNC_5H_{10}$ catalyst simply visualized as follows; that is, the magnesium atom has both a Mg–N and Mg–C bond.



Both $EtMgNC_5H_{10}$ and $Mg(NC_5H_{10})_2$ are soluble catalysts and the polymerization behavior by these catalysts was quite similar except for the slight low polymerization activity at higher temperatures by the former catalyst (see Figures 1 and 2). A similarity of the polymerization behavior can be well understood by the above consideration.

The high syndiotactic polymerization activity of the $Mg(NC_5H_{10})_2$ catalyst indicates that the Mg–N bond is obviously capable of initiating the polymerization.

On the other hand, the initiation at the Mg–C bond cannot be ruled out, since the Et_2Mg also induces the syndiotactic polymerization with reduced steric controllability than the $EtMgNC_5H_{10}$ or the $Mg(NC_5H_{10})_2$ catalyst.

Assuming that the initiation would occur at the Mg–C bond in the $EtMgNC_5H_{10}$ catalyst we can also explain the experimental results as follows. The vicinal Mg–N bond would influence the ionic character of the Mg–C bond in the catalyst so that the coordinated monomer might be able to insert into it. The extreme high syndiotacticity of the resulting polymer might be the result of the effect of the piperidine ring in relation to the aggregation state of the catalyst. A more convincing experimental evidence is necessary before the above interpretations can be accepted without reservation.

If the polymerization was initiated at the Mg–N bond in the $EtMgNC_5H_{10}$ catalyst, the end group of the polymer molecule should be $-NC_5H_{10}$. Thus, the detection of end group must present useful information for this discussion. The isolation of the extremely low molecular weight polymer which might be formed in the initial stage of the polymerization was attempted. However, the attempt was unsuccessful since the reaction products between excess of the catalyst and the monomer (approximately equimolar amount of the catalyst) had still high molecular weight which did not permit the detection of the end group by infrared spectra, and that low molecular weight materials besides the polymer could not be isolated. We have now no convincing evidence for the true active centers in the catalysts and this seems to be a problem of future intensive studies.

The data by $BrmgNC_5H_{10}$ present interesting additional information. From the nature of this Grignard compound it is acceptable that the initiation occurs by the insertion of the monomer between the Mg–N bond which has rather ionic character. All the polymers obtained by this typical Grignard catalyst have the isotactic structure as shown in Table III.

Cause of the different stereoregular control in the propagation by the difference of the substitution between the $EtMgNC_5H_{10}$ and the $BrMgNC_5H_{10}$ cannot be explained clearly at present.

The organomagnesium compounds with pyrrole ring such as ethyldivinyleniminomagnesium or bis(divinylenimino)magnesium are the novel catalysts for the isotactic polymerization of methyl methacrylate. These are insoluble in toluene and hence are the heterogeneous catalysts. The same discussion can be applied for these catalysts, that is, which of the Mg–C and Mg–N bonds is a real initiating site in this catalyst. If the polymerization was started at the Mg–N bond in the $EtMgNC_4H_4$ catalyst, a situation of the catalyst becomes similar to that of the Et_2Mg catalyst as discussed above. This consideration seems to be inconsistent with the experimental results which clearly indicate that the polymers formed by the $EtMgNC_4H_4$ are completely isotactic.

One of the characteristics of the syndiotactic polymerization by the ethylpentamethyleniminomagnesium

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(21) S. Murahashi, T. Niki, T. Obotaka, H. Yuki, and K. Hatada, *Kobunshi Kagaku*, **24**, 198, 309 (1967).

and by the bis(pentamethylenimino)magnesium is that the polymerization conditions such as polymerization temperature and the solvent employed greatly affect the syndiotacticity of the polymer.

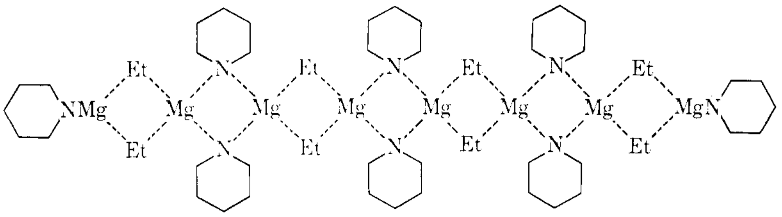
On the other hand, in the case of the isotactic polymerization by the BrMgNC$_5$H$_{10}$ and the organomagnesium compounds with pyrrole ring, the isotacticity of the polymer is independent of the polymerization conditions. All the polymers obtained by these catalysts has 100% isotactic units.

The true mechanism of the steric control to the syndiotactic or to the isotactic structure remains obscure at present.

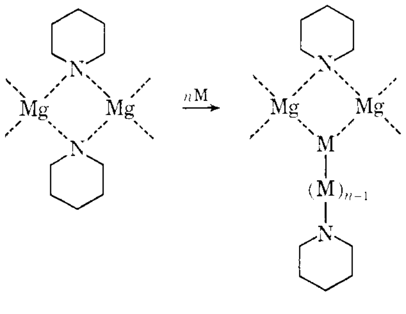
Weiss[22,23] studied the crystal structure of dimethylmagnesium and diethylmagnesium and found these crystals exist in a polymeric form through bridged structure with an almost tetrahedral arrangement of four methyl (in case of (CH$_3$)$_2$Mg) or methylene (in case of (C$_2$H$_5$)$_2$Mg) groups around each Mg atom. On the other hand, an organoaluminium compound of the type of Me$_2$AlNPh$_2$ was studied by Kawai, *et al.*,[24] using the ultraviolet absorption and proton magnetic resonance method. The structure in cyclohexane was concluded to be dimeric through two nitrogen bridges.

In case of the magnesium amide derivatives Coates, *et al.*,[20] showed that the structures are mostly bridged polymeric form through nitrogen and carbon atoms. In the case of our catalysts it is reasonably considered that the catalysts have similar polymeric forms, since the apparent molecular weight of the ethylpentamethyleniminomagnesium and of the bis(pentamethylenimino)magnesium by the cryoscopic method indicated some association of these materials in benzene solution. The apparent degree of the association of the former was estimated at 7.8, and 1.5 for the latter.

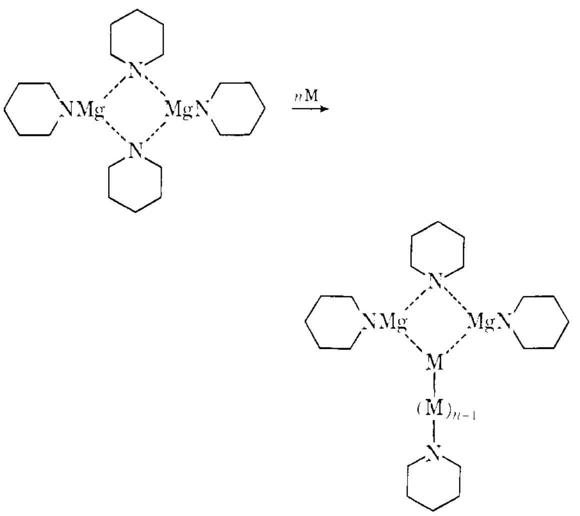
Thus, the structure of the ethylpentamethyleniminomagnesium in the polymerization medium may be simply visualized as



although we have no experimental evidence for this structure.[25] If the initiation and the propagation occurred at the Mg–N bond, the mode of the propagation may be expressed simply as



If the polymerization occurred in such a manner, the propagating chain end would have anionic and steric influences from another coordinated nitrogen bridged group throughout the polymerization. From the degree of association of the bis(pentamethylenimino)magnesium estimated in benzene solution, the structure in toluene might be a dimeric form. The difference of the degree of association between EtMgNC$_5$H$_{10}$ and Mg(NC$_5$H$_{10}$)$_2$ might be related to the steric effect of piperidine ring. Thus, the propagation and initiation might be visualized as



The above consideration enables us to understand the similar polymerization behavior between the ethylpentamethyleniminomagnesium and the bis(pentamethylenimino)magnesium, and also the difference behavior from diethylmagnesium, even if the polymerization were initiated at the Mg–N bond.

Similarly, the polymerization behavior between the bis(divinylenimino)magnesium and the ethyldivinyleniminomagnesium which gave highly isotactic polymer can be analogously explained.

The mechanism of the steric control to the isotactic or to the syndiotactic polymer which substantially depends on the divinylenimino ring or the pentamethylenimino ring, respectively, remains equivocal. The steric structure and the association state of the catalyst along with the mode of the coordination of the monomer might be very important.

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[22] E. Weiss, *J. Organometal. Chem.*, **2**, 314 (1964).

[23] E. Weiss, *ibid.*, **4**, 101 (1965).

[24] M. Kawai, T. Ogawa, and K. Hirota, *Bull. Chem. Soc. Jap.*, **37**, 1302 (1964).

[25] This structure is simply visualized in plane for convenience sake, the actual structure might be more complex in steric structure.

For the both isotactic and the syndiotactic polymerization, the coordinated anionic mechanism might be most probable. In the isotactic polymerization by the ethyldivinyleniminomagnesium, bis(divinylenimino)magnesium, and bromopentamethyleniminomagnesium, the polymers formed were 100% isotactic independent of the polymerization conditions. This indicates that steric control in the propagating chain is extremely intense, which suggests the coordination of the monomer to the catalyst. On the other hand, in the syndiotactic polymerization, the syndiotacticity increased as the polymerization temperature decreased. This phenomenon can be explained by the theory of the free anion propagating chain end. However, the experimental results that the polymer obtained in toluene has comparable or higher syndiotactic units compared with that obtained in tetrahydrofuran or diethyl ether are not fully consistent with the theory of free anion propagating species. Accordingly, the steric control in the syndiotactic polymerization is probably ascribed to the special mode of the coordination of the monomer to the catalyst, which permits the explanation for the extremely high rate of the polymerization with high syndiotacticity.

As shown in Figures 5 and 6, in the polymerization of methyl methacrylate the final conversion decreased as the polymerization temperature increased in spite of the higher initial rate of polymerization. This can be reasonably explained as the result of the deactivation of the catalysts by the reaction between the carbonyl in the monomer and the catalyst.

The Chemical Synthesis and Properties of Stereoregular Poly-α-(1→6′)-anhydro-D-galactopyranose

T. Uryu, H. Libert, J. Zachoval, and C. Schuerch

Chemistry Department, State University College of Forestry at Syracuse University, Syracuse, New York 13210. *Received December 23, 1969*

ABSTRACT: A third highly stereoregular α-(1→6′)-linked polysaccharide has been prepared by phosphorus pentafluoride-catalyzed polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose. For optimum results a higher temperature (−60°) and higher concentration of monomer is necessary than has been used to polymerize the corresponding glucose and mannose derivatives. The resulting polymer, $[\alpha]^{25}\text{D}$ 103–105° (*c* 1, chloroform) has been debenzylated to give a parent polysaccharide $[\alpha]^{25}\text{D}$ 219° (corrected to theoretical carbon content: *c* 1, 10% LiOH–0.5% borate). The polysaccharide is insoluble in all solvents tested except aqueous lithium hydroxide and borate mixtures and dimethylformamide–N_2O_4 solutions. Periodate oxidation demonstrates that this polymer is as stereoregular as the previously synthesized glucan and mannan and is, therefore, of essentially pure α configuration.

Until recently linear polysaccharides of high anomeric purity have only been available from a few natural sources. It has not been possible to synthesize regular polysaccharides of controlled structure or to relate physical properties to structure in any systematic way. With the discovery that cationic polymerization of 1,6-anhydro sugar derivatives could be controlled to produce poly-α-(1→6′)-anhydro-D-gluco- and -mannopyranose,[1–6] it has become possible to study systematically the chemical synthesis and physical properties of diastereomeric α-(1→6)-linked polysaccharides and also to investigate the immunological and other physiological properties of the individual polymers. We wish now to report the synthesis of poly-α-(1→6)-anhydro-D-galactopyranose, a proof of its structure and stereoregularity and some striking differences in its solubility from that of the two previously synthesized linear polymers.[4–6]

1,6-Anhydro-2,3,4-tri-*O*-benzyl-β-D-galactopyranose can be prepared by modified conventional methods.[2,7,8] However, yields are generally poorer in most steps and somewhat more pains must be taken than with the corresponding anhydromannose and -glucose.

The polymerization of this monomer occurs with phosphorus pentafluoride at −78° in methylene chloride as was the case with the mannose and glucose derivatives. Typical experiments are listed in Table I.

The yield of poly-α-(1→6′)-anhydro-2,3,4-tri-*O*-benzyl-D-galactopyranose was 8–59% after 100 hr with 2.5–20.0 mol % PF_5 as catalyst at −78°. In contrast with the glucose and mannose derivatives which gave yields of polymer over 90%, the galactose derivative gave relatively high conversions only at high catalyst concentration. However, stereoregularity improved and molecular weight increased with decrease in catalyst concentration in the same manner as with the glucose and mannose derivatives.

Many attempts were made to improve the conversion at −78° with only limited success. Recently, studies

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