JOURNAL OF POLYMER SCIENCE VOL. 51, PAGES 487–504 (1961)

Stereospecific Polymerization of 2-Vinylpyridine

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INTRODUCTION

The vinylpyridine polymers known up to now were obtained using free radicals as initiators, and consisted of noncrystallizable amorphous macromolecules.[1]

As we mentioned in a Communication[2] to the Editor of *Die Makromolekulare Chemie*, and in papers presented during the I.U.P.A.C. Symposium in Moscow[3] and in Paris,[4] when operating in the presence of particular stereospecific catalysts acting with an ionic mechanism, we have prepared acetone insoluble and crystallizable polymers of 2-vinylpyridine having an isotactic structure. Under the same conditions and operating with the same catalysts, 4-vinylpyridine yields only amorphous, noncrystallizable polymers. The preferred catalysts are metalloorganic compounds of magnesium or of beryllium, or metal amide compounds of magnesium, beryllium, or aluminum. In this communication we refer to some results obtained from a systematic study of the stereospecific polymerization of 2-vinylpyridine and to the evidence which allowed us to conclude that it takes place through an anionic coordinated mechanism.

We also discuss the causes of the stereospecificity of this process and of the lack of stereospecificity in the polymerization of 4-vinylpyridine.

I. PROPERTIES OF THE POLYMERS OBTAINED

The polymerization of 2-vinylpyridine has been generally carried out by us in the presence of toluene as diluting agent. At the end of polymerization the product, depending on its molecular weight, appears either dissolved in the reaction medium or as a gel. By extraction with diluted hydrochloric acid, the polymer dissolved into the aqueous phase as polyvinylpyridine hydrochloride. By subsequent precipitation with ammonia, in the presence of ammonium chloride (if the polymer has been obtained with Mg or Be compounds as catalysts), or with sodium hydroxide (if it has been operated with Al compounds as catalysts), the polymer is recovered essentially free of the components of the catalyst. The product thus obtained has a high water content, which is very likely bound as pyridinium hydrate, which may be removed by azeotropic distillation with

benzene. The polymer is rapidly precipitated by addition of *n*-heptane to the benzene solution; in these conditions it generally appears amorphous by x-ray examination.

While only a small fraction of the polymer is permanently dissolved by treatment with acetone, the remaining part precipitates as a white powder which is crystalline by x-ray examination (see Fig. 1a). In some cases, when the molecular weight of the crude polymer is very low, a certain crystallinity can be observed in the fraction of the polymer soluble in acetone.

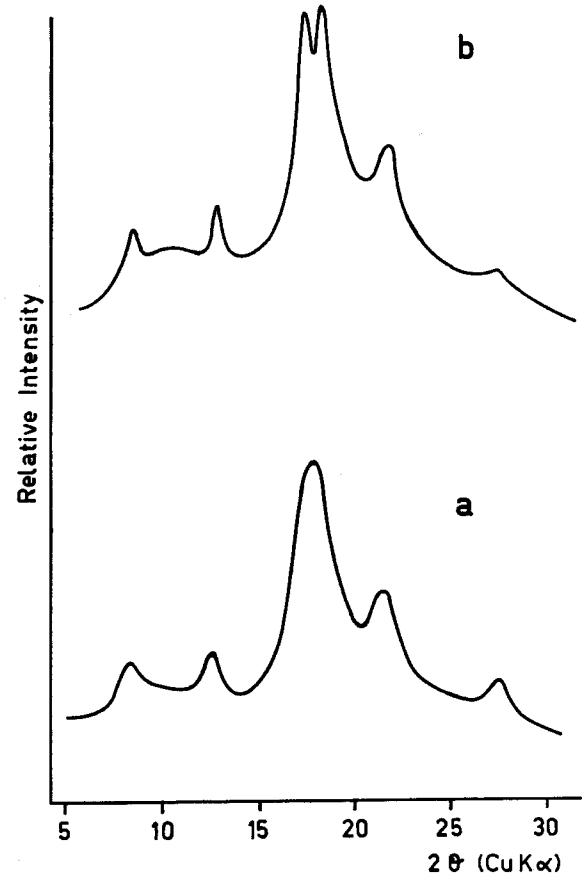


Fig. 1. Geiger counter registration of x-rays diffraction spectrum of isotactic poly-2-vinylpyridine: (*a*) crystalline modification 1, (*b*) crystalline modification 2.

The crystallization of the amorphous polymer may also be brought about by treatment with aliphatic hydrocarbons at high temperature (130–160°C.) or by simple heating in an inert atmosphere at 140–160°C. The polymers crystallized at high temperature generally show a crystal structure (Fig. 1b) characterized by an identity period of about 6.7 A., which is different from that of the polymers crystallized at low temperature.

The crystalline polymers of 2-vinylpyridine are insoluble in boiling aliphatic hydrocarbons and in diethyl ether. They are soluble in some

polar solvents, such as methyl alcohol, dimethylformamide, and chloroform, and in boiling aromatic hydrocarbons.

The determination of the melting temperatures (by polarized light microscope) of the crystalline acetone insoluble polymers, gave values generally between 190 and 212°C. The differences observed in the melting temperatures should be attributed to differences in the steric purity of the samples.

In the case of polymers having low molecular weight ([η] in dimethylformamide at 30°C. lower than 0.4 × 100 cm.^{3}/g.), we have observed that the melting temperatures of samples having about the same crystallinity decrease markedly with decreasing molecular weight.

Some attempts made to isolate fractions of different steric purity, using solvent extraction of the acetone-insoluble polymers, did not furnish satisfactory results. For instance, by extracting an acetone-insoluble polymer with boiling methyl ethyl ketone, the extracted fraction has a lower molecular weight, whereas the degree of crystallinity and the melting temperature are very close to those of the residue.

These results would indicate that the polymers of 2-vinyl pyridine, which are insoluble in boiling acetone, are formed by macromolecules having approximately the same degree of steric order.

II. POLYMERIZATION IN PRESENCE OF METAL AMIDE COMPOUNDS

Using some metal amides of the Ia group, such as lithium *N*-carbazyl, lithium diphenylamide, or sodium amide as polymerization catalysts, we have obtained noncrystallizable amorphous polymers of 2-vinylpyridine. When employing *N*-dialkylamides of beryllium or of aluminum, only a

TABLE I
Polymerization of 2-Vinylpyridine Using Metal Amide Compounds of Different Metals as Catalysts[a]

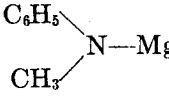
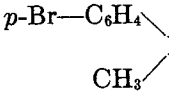
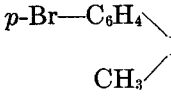
Catalyst	g. polymer/ g. monomer, %	Acetone-insoluble crystalline polymer	
		% of total polymer	[η],[b] 100 cm.^{3}/g.
$LiN(C_6H_5)_2$	65	0	—
$LiNC_{12}H_8$	25	0	—
$NaNH_2$	60	0	—
$Be[N(CH_3)_2]_2$	40	40	0.27
$Be[N(C_6H_5)_2]_2$	0	0	—
$Al[N(CH_3)_2]_3$	15	85	0.35
$Al[N(C_6H_5)_2]_3$	0	0	—

[a] Polymerization conditions: temperature, 45°C.; time, 5 hr.; monomer, 10 g. in 30 cm.^{3} toluene added during about 2 min. to suspension of catalyst in 40 cm.^{3} toluene; monomer/catalyst molar ratio, about 40.

[b] Determined in dimethyl formamide at 30°C.

small part of the polymers obtained is formed by crystalline macromolecules, insoluble in acetone. The diarylamides of the same metals do not promote polymerization at all (see Table I).

TABLE II
Polymerization of 2-Vinylpyridine Using Metal Amide Compounds of Magnesium as Catalysts[a]

Catalyst	g. polymer/ g. monomer, %	Acetone-insoluble crystalline polymer	
		% of total polymer	$[\eta]$[b], 100 cm.^{3}/g.
$(C_2H_5)_2NMgCl$	96	88	0.30
$(C_2H_5)_2NMgBr$	96	85	0.27
$(C_2H_5)_2NMgBr$[c]	60	91	0.36
$(C_2H_5)_2NMgI$	98	83	0.17
$(C_6H_5)_2NMgBr$	0	0	—
$[(C_6H_5)_2N]_2Mg$	0	0	—
	93	88	0.49
	85	93	0.58
	98	85	0.15

[a] Polymerization conditions: temperature, 45°C.; time, 5 hr.; monomer, 10 g. in 30 cm.^{3} toluene added during about 2 min. to suspension of catalyst in 40 cm.^{3} toluene; monomer/catalyst molar ratio, 80.

[b] Determined in dimethylformamide at 30°C.

[c] A clear saturated solution of the catalyst was used with the same quantity of toluene.

Among the metal amide derivatives, magnesium amides have furnished more stereospecific catalysts. As is shown from Table II, when operating under suitable conditions it is possible to obtain, in the presence of certain magnesium amides (such as amides corresponding to the general formula X—Mg—NR_1R_2 in which R_1 and R_2 are alkyl groups) high coversions in fairly short times. Furthermore, the polymer contains more than 90% of acetone-insoluble crystallizable macromolecules.

Some magnesium amides of the X—Mg—NR_1R_2 and of the $Mg(NR_1R_2)_2$ type, in which R_1 and R_2 are aromatic groups, such as diphenyl amide magnesium bromide, do not promote polymerization. This probably may be attributed to steric factors, the polymerization proceeding through an anionic mechanism. In the case in which R_1 is an alkyl and R_2 an aryl group, the catalysts are still active (Table II).

All the metal amide compounds of magnesium employed are scarcely soluble in toluene which was used as the polymerization solvent. We observed, however, that by adding the monomer all the metal amide compound is dis-

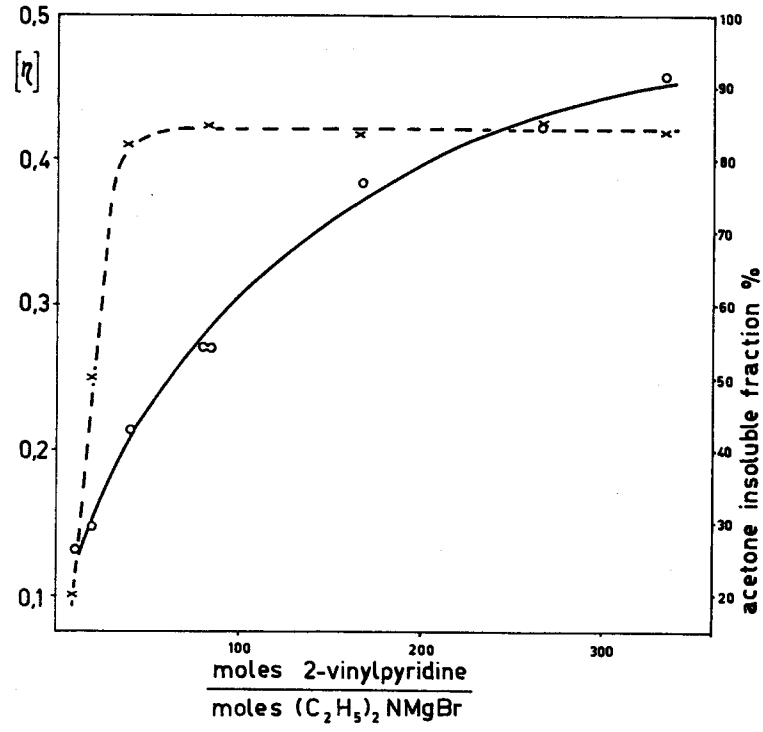


Fig. 2. Influence of 2-vinylpyridine/$(C_2H_5)_2NMgBr$ molar ratio on the intrinsic viscosity (full line) and on the percentage of acetone insoluble crystalline fraction (dashed line) of poly-2-vinylpyridine. Polymerization conditions: temperature, 45°C., time, 5 hr.; monomer, 10 g. in 30 cm.^{3} of toluene added for a period of about 2 min. to the catalyst suspension in 40 cm.^{3} of toluene.

solved. This indicates that the monomer coordinates itself to the catalyst, forming soluble complexes, in agreement with the well-known ability of the pyridinic nitrogen to react by formation of coordinate bonds with suitable lithium,[5] magnesium,[6] beryllium,[7] or aluminum[8] compounds. We have confirmed that the polymerization of 2-vinylpyridine in the presence of magnesium amides may take place in a stereospecific way, even if the system does not contain a solid heterogeneous phase before the addition of the monomer. In fact, if one separates the undissolved phase by filtering a suspension of diethylamide magnesium bromide in toluene, one obtains a very diluted, clear solution of catalyst which still promotes the stereospecific polymerization of 2-vinylpyridine. The lower activity of this solution and the high intrinsic viscosity of the polymer obtained must be attributed to the addition polymerization mechanism and to the small amount of initiator present in the system (see Table II).

To clarify the mechanism of this polymerization better, we have also examined the influence of some factors on the course of the reaction and on the properties of the polymers obtained.

(*a*) *Nature of the halogen present in the catalyst.* Table II shows that, comparing different diethylamide magnesium halides, the intrinsic viscosity of the crystalline polymer increases with decreasing atomic weight of the halogen. On the other hand, the percentage of boiling acetone-

insoluble product and the degree of crystallinity of this fraction does not change.

(*b*) *Monomer catalyst molar ratio.* When employing diethylamide magnesium bromide and operating with monomer/catalyst molar ratios ranging from 10 to 330, we have obtained, after 5 hr., at 45°C., monomer conversions higher than 95%. The intrinsic viscosity of the crystalline polymers increases with increasing monomer to catalyst ratio (Fig. 2). From Figure 2 it also appears that the percentage of the boiling acetone-insoluble fraction is practically constant (about 85%) at monomer/catalyst molar ratios higher than 40, which correspond to intrinsic viscosity values higher than 0.2. At lower monomer/catalyst molar ratios, the acetone-insoluble fraction of the polymer is smaller. However, we have observed in these cases that the acetone-soluble fraction exhibits crystallinity by x-ray examination. This proves that crystalline polymers of 2-vinylpyridine may dissolve in acetone if their molecular weight is sufficiently low.

(*c*) *Temperature.* We also carried out polymerizations in which, using diethylamide magnesium bromide as initiator and with the other conditions as before, the polymerization temperature was varied between −20 and +100°C. At polymerization temperatures lower than −20°C. no large amounts of polymer were obtained, even after a long period of polymerization. At temperatures higher than 100°C. the polymer was partially insoluble in boiling toluene, probably owing to the presence of cross-linked macromolecules. In the above-mentioned temperature range we obtained polymers which are completely soluble in boiling toluene, and the percentage of acetone-insoluble crystallizable product does not change much in the range from 0 to 75°C. (Table III).

The intrinsic viscosity of the crystalline polymers decreased remarkably with increasing temperature, as is shown in Figure 3.

TABLE III

Polymers of 2-Vinylpyridine Obtained at Various Polymerization Temperatures with $(C_2H_5)_2NMgBr$ as Catalyst[a]

Polymerization temperature, °C.	g. polymer/ g. monomer, %	Acetone-insoluble crystalline polymer, % of total polymer
−78	0	0
−18	60	71
0	90	90
15	92	88
30	95	87
45	96	85
60	96	87
75	95	86
90	96	74
97	95	78

[a] Polymerization conditions: time, 5 hr.; monomer, 10 g. in 30 cm.^{3} toluene added during about 2 min. the suspension of catalyst in 40 cm.^{3} of toluene; monomer/catalyst molar ratio, 80.

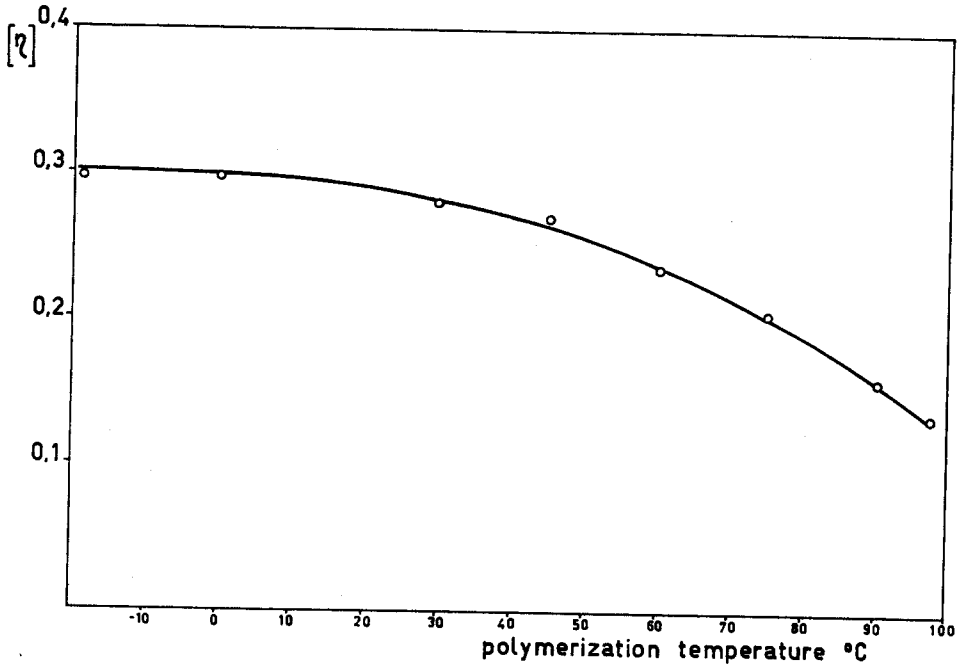


Fig. 3. Influence of polymerization temperature on intrinsic viscosity of poly-2-vinylpyridine. Polymerization conditions identical to those given in Table 3.

(*d*) *Independence of Molecular Weight on the Quantity of Polymerized Monomer.* In the polymerization of 2-vinylpyridine, using the above-described catalytic systems, "living" polymers are not present.[9] In fact, if after a period sufficient to allow a practically complete conversion of monomer into polymer (16 hr.), one adds a new equal quantity of monomer, one obtains almost double the amount of polymer without any detectable variation of intrinsic viscosity (Table IV).

TABLE IV
Polymerization of 2-Vinylpyridine in Presence of $(C_2H_5)_2NMgBr$[a]

First addn. of monomer		Sec. addn. of monomer		Final polymer obtained		
					Acetone-insoluble crystalline polymer	
Wt., g.	Polymerization time, hr.	Wt., g.	Polymerization time, hr.	g. polymer/ g. monomer, %	% of total polymer	$[\eta]$,[b] 100 cm.^{3}/g.
30	16	—	—	96	85	0.23
30	16	30	20	93	80	0.22

[a] Monomer is added to suspension of catalyst in one or two successive times. Polymerization conditions: temperature, 45°C.; toluene, 200 cm.^{3}; catalyst, 0.006 mole.
[b] Determined in dimethylformamide at 30°C.

III. POLYMERIZATION IN PRESENCE OF METALLOORGANIC COMPOUNDS

As is shown in Tables V and VI, some metalloorganic compounds of magnesium or of beryllium may promote the stereospecific polymerization

of 2-vinylpyridine. Using metalloorganic compounds of magnesium as catalysts, the polymer obtained is almost completely insoluble in acetone and exhibits high crystallinity by x-rays. The polymer, obtained in the presence of metalloorganic beryllium compounds, contains a smaller fraction of acetone-insoluble product and, furthermore, this fraction is only slightly crystalline.

TABLE V

Polymerization of 2-Vinylpyridine Using Metalloorganic Compounds of Different Metals[a]

Catalyst	g. polymer/ g. monomer, %	Acetone-insoluble crystalline polymer, % of total polymer
Li *n*-C_4H_9	98	0
Na *n*-C_8H_{17}	85	0
K $C(C_6H_5)_3$	80	0
$Be(C_2H_5)_2$	97	65[b]
$ZnC_2H_5 \cdot Br$	2	0
$ZnC_6H_5 \cdot Br$	Traces	0
$Zn(C_2H_5)_2$[c]	Traces	0
$Zn(C_4H_9)_2$	0	0
$LiAlH_4$	98	82[b]
$Al(C_2H_5)_2 \cdot Cl$	0	0
$Al(C_2H_5)_3$	0	0
$Pb(C_2H_5)_4$	0	0

[a] Polymerization conditions: temperature, 45°C.; time, 5 hr.; monomer, 10 g. in 40 cm.^{3} toluene added during about 30 min. to suspension or solution of catalyst in 60 cm.^{3} toluene; monomer/catalyst molar ratio, about 15.

[b] The boiling acetone-insoluble fraction exhibits only weak crystallinity by x-ray examination.

[c] When polymerizing at 70°C. in presence of $Zn(C_2H_5)_2$, a remarkable quantity of completely acetone-soluble, amorphous polymer is obtained (probably by free radicals from the $Zn(C_2H_5)_2$ decomposition at that temperature).

TABLE VI

Polymerization of 2-Vinylpyridine Using Metalloorganic Compounds of Magnesium as Catalysts[a]

Catalyst	g. polymer/ g. monomer, %	Acetone-insoluble crystalline polymer: % of total polymer	Acetone-insoluble crystalline polymer: $[\eta]$,[b] 100 cm.^{3}/g.
$Mg(C_2H_5)_2$	97	90	0.28
$Mg(C_6H_5)_2$	96	93	0.34
C_6H_5MgBr	92	98	0.49
C_6H_5MgBr[c]	90	89	Not determined

[a] Polymerization conditions: temperature, 45°C.; time, 5 hr.; monomer, 10 g. in 40 cm.^{3} toluene added during about 30 min. to solution of catalyst in 60 cm.^{3} toluene; monomer/catalyst molar ratio, about 30.

[b] Determined in dimethylformamide at 30°C.

[c] In this case a clear saturated solution of catalyst in 60 cm.^{3} toluene was used corresponding to the much higher monomer/catalyst molar ratio.

Metalloorganic compounds of lithium or of sodium, even if they are very active for the polymerization of 2-vinylpyridine, yield completely amorphous, noncrystallizable polymers. This can be attributed to the lower coordinating ability with respect to the monomer of the Ia group metal compounds in comparison with those of magnesium.

Metalloorganic compounds of metals with lower electropositivity and therefore characterized by less polar metal-carbon bonds, such as zinc or particularly lead, do not appreciably promote the polymerization of 2-vinylpyridine. In the case of metalloorganic compounds of aluminum, the lack of activity for the initiation of polymerization may probably be attributed to the high electrophilic character of aluminum and to the formation of less reactive complexes between the metalloorganic compound and the monomer. When the strong electron deficiency of the aluminum compounds is lowered by suitable coordination, catalysts can be obtained (e.g., in the lithium aluminum hydride or in the above-mentioned aluminum amides) which polymerize the 2-vinylpyridine to a polymer having rather low crystallinity.

We have examined the influence of some factors on the polymerization carried out in the presence of catalysts constituted of metalloorganic compounds of magnesium.

(*a*) *Nature of the metalloorganic magnesium compound.* As may be seen from Table VI, phenylmagnesium bromide, diphenylmagnesium and diethylmagnesium exhibit practically the same catalytic activity. It is interesting to observe that in this case the catalyst is, at least for the most part, undissolved in the polymerization medium (toluene) and is completely dissolved only after the addition of the monomer. However, it is possible to promote the stereospecific polymerization of 2-vinylpyridine using a toluene solution of phenylmagnesium bromide, even if very diluted (Table VI). Thus, it is confirmed that for the stereospecificity of this

TABLE VII

Polymerization of 2-Vinylpyridine in Presence of Phenylmagnesium Bromide Using Different Dilution Mediums[a]

Monomer/ C_6H_5MgBr molar ratio	Polymerization temperature, °C.	Diluting medium	Acetone-insoluble crystalline polymer		
			g. polymer/ g. monomer, %	% of total polymer	$[\eta]$,[b] 100 cm.^{3}/g.
15:1	45	Toluene	98	94	0.56
15:1	70	"	98	77	0.2
30:1	45	Chlorobenzene	87	97	0.44
15:1	45	*n*-Heptane	0	0	—
15:1	70	"	0	0	—

[a] Polymerization conditions: time, 5 hr.; monomer, 10 g. added during about 30 min. to catalyst suspension in 100 cm.^{3} of diluting medium.

[b] Determined in dimethylformamide at 30°C.

polymerization the presence of a catalyst acting in a heterogeneous phase is not required, which is in agreement with what we have already observed for other stereospecific polymerizations of monomers containing, besides the polymerizable double bond, another group, rich in electron (10–16) which can be coordinated with the catalyst.

(*b*) *Polymerization solvent.* In the above-referred to polymerizations of 2-vinylpyridine, it may be assumed that the catalyst or its complex with the monomer must be soluble in the polymerization medium. In fact, in employing phenylmagnesium bromide, high monomer conversions can be obtained when toluene or chlorobenzene are used as solvents. The conversion is practically zero when an aliphatic solvent such as *n*-heptane is employed (Table VII).

(*c*) *Polymerization temperature.* As is shown in Table VIII, phenylmagnesium bromide does not promote the polymerization at −78°C. At temperatures ranging from −20 to 70°C., the polymerization takes place at a fairly high rate and in 5 hr. it is possible to reach practically complete conversion of monomer. When the polymerization temperature is increased the intrinsic viscosity decreases progressively, but the percentage of crystalline, acetone-insoluble fraction of the polymer decreases only at high temperatures. The lowering of the molecular weight of the stereoordered polymers is also accompanied by a decrease of the melting temperature and, as shown by x-ray examination, by an increase of the degree of crystallinity. This latter fact may probably be attributed to the higher crystallization rate of the shorter macromolecules. At temperatures higher than 90°C. crosslinking phenomena are observed which lower both the percentage of crystallizable fraction of the polymer and its degree of crystallinity, whereas their intrinsic viscosity increases.

(*d*) *Monomer/catalyst molar ratio.* As has been observed for polymeriza-

TABLE VIII
Polymerization of 2-Vinylpyridine in Presence of Phenylmagnesium Bromide at Different Temperatures[a]

Polymerization temperature, °C.	g. polymer/ g. monomer, %	Acetone-insoluble crystalline polymer		
		% of total polymer	$[\eta]$,[b] 100 cm.³/g.	Melting temp., °C.[c]
−78	0	0	—	—
−20	76	92	1.52	212.5
0	85	95	Not determined	211
15	98	92	1.07	210
45	98	94	0.56	207
70	98	77	0.2	193.5

[a] Polymerization conditions: time = 5 hr.; monomer = 10 g. added during about 30 min. to suspension of C_6H_5MgBr in 100 cm.³ toluene; monomer/catalyst molar ratio = 15:1.

[b] Determined in dimethylformamide at 30°C.

[c] Melting temperature was determined using a polarized light microscope.

tion in the presence of metalamide compounds, when phenylmagnesium bromide is employed as catalyst the molecular weight of polyvinylpyridine increases when an increase in the monomer/catalyst ratio, the other conditions being the same (Table IX).

TABLE IX
Polymerization of 2-Vinylpyridine in Presence of Phenylmagnesium Bromide at Different Monomer/Catalyst Ratios[a]

Monomer/C_6H_5MgBr molar ratio	Polymerization temperature, °C.	g. polymer/ g. monomer, %	Acetone-insoluble crystalline polymer	
			% of total polymer	$[\eta]$,[b] 100 cm.^{3}/g.
15:1	15	98	92	1.07
50:1	15	96	98	1.69
15:1	70	98	77	0.2
100:1	70	83	99	0.51

[a] Polymerization conditions: time, 5 hr.; monomer, 10 g. added during about 30 min. to suspension of C_6H_5MgBr in 100 cm. toluene.
[b] Determined in dimethylformamide at 30°C.

(*e*) *Polymerization time.* When comparing samples produced at different times at the temperature of 45°C. and with a 30:1 monomer/catalyst ratio, it appears that the polymerization is practically complete after about 1 hr., whereas the percentage of crystalline polymer is practically constant for polymerization times higher than 15 min. (Table X).

TABLE X
2-Vinylpyridine Polymerization in Presence of Phenylmagnesium Bromide[a]

Drawing after	15 min.	30 min.	45 min.	1 hr.	3 hr.	4 hr.	5 hr.
g. polymer/ g. monomer, %	19	71	87	87	86	87	89
Acetone-insoluble cryst. polymer, % of total polymer	Not determined	99	98	99	Not determined	98	98

[a] Polymerization conditions: temperature, 45°C.; monomer, 30 g. rapidly added to suspension of catalyst in 600 cm.^{3} toluene; monomer/catalyst molar ratio, 35; for analysis 10 cm.^{3} samples are successively drawn from the stirred mixture.

IV. POLYMERIZATION MECHANISM AND CAUSES OF STEREOSPECIFICITY

The IR examination of the polymers prepared in the presence of phenylmagnesium bromide or of magnesium arylamide, allowed us to establish that at least a part of the macromolecules produced contain as terminal groups the organic groups which are initially present in the catalyst (Fig. 4). Based on the content in phenyl groups determined by IR examination,

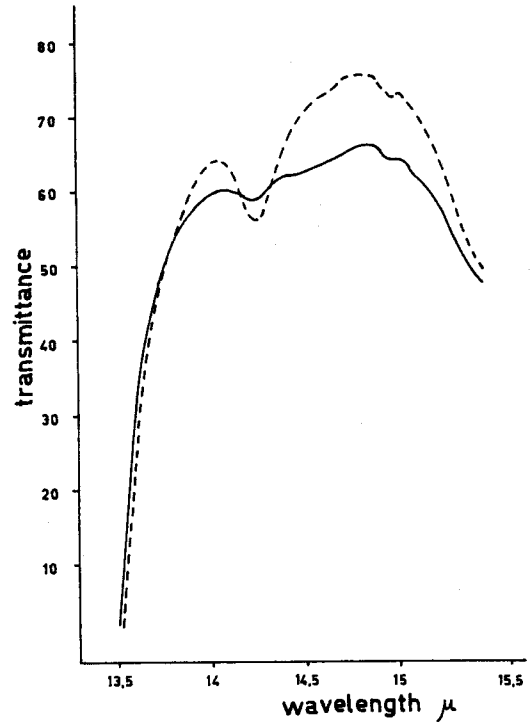


Fig. 4. Phenyl group region in IR absorption spectrum of poly-2-vinylpyridine, prepared under the following polymerization conditions: (——) mole monomer/mole C_6H_5MgBr, 30, temperature, 45°C.; (- -) mole monomer/mole C_6H_5MgBr, 15; temperature, 70°C.

and assuming the presence of one terminal phenyl group for each polymeric chain formed, we have calculated the apparent numerical molecular weights of the polymer (Table XI). These results are about proportional to the intrinsic viscosity of the same polymer determined in dimethylformamide.

TABLE XI
Determination of Phenyl Endgroups in Crystalline Poly-2-vinylpyridine[a]

Polymerization conditions		Acetone-insoluble crystalline % of the total polymer	$[\eta]$,[b] 100 cm.^{3}/g.	Content in phenyl[c] endgroups in moles (C_6H_5/moles vinyl-pyridine)	Apparent wt.[d] av. MW
Monomer/ catalyst molar ratio	Polymerization temperature, °C.				
15	70	77	0.2	8×10^{-3}	1.2×10^4
30	45	89	0.49	1.3×10^{-3}	10×10^4
15	45	94	0.56	1×10^{-3}	10×10^4
15	15	92	1.07	0.5×10^{-3}	20×10^4

[a] The polymers were obtained using phenylmagnesium bromide as catalyst; polymerization time, 5 hr.

[b] Determined in dimethylformamide at 30°C.

[c] Calculation based on the absorption band at 14.25 μ.

[d] For apparent molecular weight, we mean the one calculated on the basis of the molar ratio vinylpyridine/phenyl groups, supposing a phenyl group for each polymeric chain.

The presence of phenyl groups in the polymer allows us to attribute an anionic mechanism to this polymerization, according to which the polymerization initiation takes place by the insertion of a monomer molecule into a polarized magnesium-carbon or magnesium-nitrogen bond. On the new magnesium-carbon bond thus formed, other monomer molecules enter successively, so that chain propagation can take place. By examining the different catalysts for the polymerization of 2-vinylpyridine it can be observed that the highest stereospecificity is exhibited by the compounds of very electropositive metals having a short ionic radius, in analogy with what has already been observed in the anionic coordinated polymerization of α-olefins.[17] The higher stereospecificity can therefore be attributed to the higher coordinating power of the metal atom present in the catalyst.

The stereospecificity of the process is probably due to the fact that both the double bond and the nitrogen atom present in the molecules of 2-vinylpyridine are coordinated to the catalytic complex at the very moment of addition of the monomer molecule, causing a constant type of presentation of the monomer with regard to the growing chain. The constant presentation of the monomer together with a constant type of opening of the double bond cause the sterically ordered growing of the macromolecules.

The fact that the stereospecificity in the polymerization of 2-vinylpyridine is connected with the formation of coordinate bonds between the nitrogen atom of the monomer entering into the polymeric chain and the metal present in the catalyst has been confirmed by us by operating in the presence of different organic bases of the Lewis type.

By adding bases of lower basicity than vinylpyridine, such as ethers, to the system, we have shown that polymerization still takes place, but with a reduced stereospecificity (Table XII). In such a case the added base

TABLE XII

Polymerization of 2-Vinylpyridine in Presence of Catalysts Previously Complexed with Lewis Bases[a]

Catalyst	Complexing agent[b]	Moles complexing agent/ moles catalyst	g. polymer/ g. monomer, %	Acetone-insoluble crystalline polymer, % of obtained polymer
$(C_2H_5)_5NMgBr$	C_5H_5N	2	48	0
C_6H_5MgBr	C_5H_5N	2.5	45	0
C_6H_5MgBr	$(C_2H_5)_2O$	4	80	38
$(CH_3)_3CMgCl$	$(C_2H_5)_2O$	2	45	40

[a] Polymerization conditions: temperature, 45°C.; monomer, 5 g. added during about 5 min. to catalyst solution in 50 cm.^{3} toluene; monomer/catalyst molar ratio, about 10; time, 5 hr.

[b] The complexing agent was added to the suspension of the catalyst in toluene, except in the case of $(CH_3)_3CMgCl$, which was already an etherate. After stirring for 4 hr. at 40°C., the solution was filtered and then added to 2-vinylpyridine.

acts in a competitive way in comparison with the coordination of the nitrogen atom of the monomer to the catalyst.

On the other hand, employing the catalyst previously complexed with compounds having a strongly basic nature, e.g., pyridine, a very low quantity of completely amorphous polymer is formed (Table XII). In this case, the base previously added to the catalyst hinders the coordination of the monomer and therefore its constant type of presentation.

It is therefore possible to conclude that the stereospecific polymerization of 2-vinylpyridine with the catalysts studied by us takes place in the homogeneous phase with a mechanism of the anionic coordinated type.

Other stereospecific polymerizations with an ionic mechanism in a homogeneous phase and with monomers containing groups rich in electrons near to the polymerizable double bond have been indicated by some of us in the cases of the cationic polymerizations of vinyl ethers,[10] of alkenyl ethers,[11] of methoxy styrenes,[12] of vinylcarbazole,[13] of vinyldiphenylamine,[14] of benzofuran,[15] and in the cases of the anionic polymerizations of the acrylates and methacrylates.[16]

It is interesting to observe that when employing catalysts for the polymerization of 4-vinylpyridine which are stereospecific for 2-vinylpyridine, only completely amorphous, noncrystallizable polymers are obtained.

This may probably be attributed to the fact that the nitrogen atom, in the case of 4-vinylpyridine, is too far from the vinyl double bond to form an addition complex with the catalyst which is able to orientate each monomer molecule in the same way with respect to the last monomeric unit of the growing polymeric chain.

V. EXPERIMENTAL

(1) Products

2-Vinyl- and *4-vinylpyridine* are technically pure (about 90%), stabilized Fluka AG. or Reilly Tar & Chemical Co. products. The commercial product, under a pressure of 14 Torr, was dropped on KOH maintained at 120°C., and then rapidly distilled. After addition of hydroquinone as stabilizer, the monomer was distilled again at 14 Torr pressure. 2-Vinylpyridine thus purified had b.p. 53°C./14 Torr, $n_D^{20} = 1.5497$; 4-vinylpyridine had b.p. 63°C./14 Torr, $n_D^{20} = 1.5499$. The monomers thus purified remain unchanged for some weeks, even without adding stabilizer, if kept under a nitrogen atmosphere at −5°C.

Diethylamide magnesium bromide and other amide-magnesium halides were obtained from methyl or ethyl magnesium halides and the corresponding secondary amine.[18] Thus, for instance, diethylamide magnesium bromide was prepared as follows: a solution of 161 g. (2.2 moles) of anhydrous diethylamine in 250 cm.^{3} of ethyl ether was slowly added to a well-stirred solution of 1.5 moles of C_2H_5MgBr in 700 cm.^{3} of ethyl ether, kept at boiling temperature. The gas evolved, after passing through a trap cooled,

to −78°C., in order to condense the ether vapors, was collected in a gasometer; 32.6 liters of gas (18°C.) containing 96% of ethane were collected. When the gas evolution was finished, all the ether was removed by distillation, at first at ordinary and then at a reduced pressure. The solid mass, which remained in the flask, was finally maintained for 10 hr. at 140°C. and at a reduced pressure of 0.1 Torr to remove the excess of diethylamine which otherwise would remain complexed with the metal-amide.

An almost white powder which contains 8.18% of nitrogen (calculated for $(C_2H_5)_2NMgBr$, 7.94%) was obtained.

Phenyl magnesium bromide was obtained from an ether solution of C_6H_5MgBr by removing the ether and drying at 150°C. at the reduced pressure of 0.1 Torr for 12–15 hr.

Magnesium diethyl and magnesiumdiphenyl were obtained from the corresponding Grignard compounds by treatment with dioxane.[19]

Toluene employed as solvent in the polymerization was obtained from the commercial product by treatment with concentrated H_2SO_4 and subsequent distillation under nitrogen atmosphere on metallic potassium.

(2) Polymerization Process

As an example we give a detailed description of the polymerizations of 2-vinylpyridine in the presence of $(C_2H_5)_2NMgBr$ and of C_6H_5MgBr, respectively, at 45°C. When employing *magnesium diethylamide bromide* as catalyst, the procedure was as follows: in a three-necked flask of 250 cm.^{3} capacity, equipped with stirrer, dropping funnel, and nitrogen inlet tube, 0.33 g. of $(C_2H_5)_2NMgBr$ and 40 cm.^{3} of toluene were introduced under nitrogen atmosphere at 45°C. A solution of 10 g. of 2-vinylpyridine in 30 cm.^{3} of toluene was then added over a period of about 2 min. from the dropping funnel. The mass turned orange and after a while it became dark green. After 5 hr. of stirring at 45°C., the polymerization was stopped by adding 50 cm.^{3} of 10% HCl, followed by 10–15 min. of additional stirring.

For polymerization in the presence of *phenyl magnesium bromide,* we generally followed this method: in the apparatus previously described, 100 cm.^{3} of anhydrous toluene and 575 mg. (3.2 mmoles) of phenyl magnesium bromide were introduced. The well stirred mixture was heated to 45°C., and during 30 min., 10 g. (95 mmoles) of purified vinylpyridine were dropped. The monomer/catalyst molar ratio corresponds to 30. The color of the solution becomes orange, and the viscosity increased progressively. The mixture was kept well stirred for a total of 5 hr. (When effecting the polymerization at a lower temperature, a considerable part of the polymer precipitates during this period.) After these 5 hr., 150 cm.^{3} of a 5% hydrochloric acid solution were added, and stirring was continued until the whole polymer was dissolved in the aqueous phase.

(3) Recovery and Crystallization of the Polymer

Following the method described in section *2* above, polyvinylpyridine hydrochloride remains in the aqueous acid phase. This is separated from the toluene phase, then further diluted with water to a volume of about 200 cm.^{3} and then dropped to 1 l. of well stirred aqueous solution of NH_3 (2–5%) containing 20 g. NH_4Cl. Thus the polymer precipitates in white flocks which after a while convert into a semisolid compact product. By treatment with boiling benzene and azeotropic distillation of all the water contained in the polymer, a limpid and colorless solution is obtained, from which, by addition of *n*-heptane, polyvinylpyridine precipitates as a white, finely divided powder. After drying, depending on the catalyst employed: either $(C_2H_5)_2NMgBr$, or C_6H_5MgBr, 9.6 or 9.2 g. of polymer are obtained which, in this state, are amorphous by x-ray examination.

In order to crystallize the poly-2-vinylpyridine, it is treated with 30–50 times its weight of hot acetone until the solid product is transformed into a viscous mass (in some cases, especially when the polymer has a low molecular weight, it dissolves completely: then it is convenient to add *n*-heptane until the separation of the viscous mass). After some time (generally 1–2 hr.), it becomes a white powder, completely insoluble in boiling acetone. After filtering and drying, the products obtained (8.3 g. and 9.0 g., respectively, depending on the catalyst employed ($(C_2H_5)_2$-NMgBr, or C_6H_5MgBr), are crystalline by x-ray examination.

The crystallization of poly-2-vinylpyridine may also be obtained by maintaining the amorphous polymer for some hours at 150–160°C., either in a suspension of *n*-decane or decalin, or more simply, under a nitrogen atmosphere. The intrinsic viscosity, measured in dimethylformamide at 30°C., is 0.22 and 0.49, respectively; the melting temperature, as determined by a polarized light microscope, is 202 and 211.5°C., respectively.

(4) Measurements

The determinations of the intrinsic viscosity have been carried out using a Desreux-Bischoff viscometer and employing dimethylformamide as solvent at 30°C. Thin molded sheets of poly-2-vinylpyridine, kept at 160°C. for 4–6 hr. in order to speed the crystallization, has been employed for the melting point determination. The apparatus was a polarized light microscope of the Zeiss type, equipped with a small heating plate. The heating rate was of about 2°C./min.

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Synopsis

Some metalloorganic or metal amide compounds of very electropositive metals, such as lithium, sodium, beryllium, magnesium, and aluminum, cause the polymerization of 2-vinylpyridine. Whereas the compounds of beryllium and of aluminum furnish slightly crystalline 2-vinylpyridine polymers, by using magnesium derivatives it is possible to obtain polymers which are highly crystalline by x-rays. The results obtained from the systematic study of the polymerization in the presence of amides or of metalloorganic compounds of magnesium are reported. In particular, it has been examined the influence of the monomer/catalyst molar ratio, of the temperature, of the polymerization time, and of the nature of the substituents bound to magnesium, on the course of the polymerization and on the properties of the obtained polymers. Examination by IR spectrography allowed us to conclude that at least a part of the macromolecules contain, as endgroup, the organic groups which were initially bound to the metal in the compounds used as catalyst. The stereospecificity of the process must be ascribed to the possibility of coordination of the catalyst to the monomer molecules entering the growing chain. In fact, the addition of organic Lewis bases to the system, causes the reduction or the disappearence of stereospecificity. The obtained results allowed us to conclude that the stereospecific polymerization of 2-vinylpyridine takes place by an anionic coordinated mechanism. 4-Vinylpyridine, in the presence of catalysts which are stereospecific for the polymerization of 2-vinylpyridine, gives amorphous non-crystallizable polymers. That was ascribed by us to the fact that the nitrogen atom, in the case of 4-vinylpyridine is too far from the vinyl double bond to form, with the catalyst, an addition complex able to give the same orientation to all the monomer molecules, at the very moment of the polymerization.

Résumé

Quelques composés organométalliques ou métalloamidiques de métaux très électropositifs, comme lithium, sodium, béryllium, magnésium et aluminium, provoquent la polymérisation de la 2-vinylpyridine. Tandis que les composés de béryllium et d'aluminium fournissent des polymères de la 2-vinyl pyridine, qui sont guère cristallins, en employant des dérivés du magnésium il est possible d'obtenir des polymères nettement cristallins à l'examen aux rayons X. On reporte les résultats obtenus par l'étude systématique de la polymérisation en présence d'amides et de composé organométalliques de magnésium. En particulier, on a examiné l'influence du rapport monomère/catalyseur, de la température, de la durée de la polymérisation et de la nature des substituants liés au magnésium, sur le cours de la polymérisation et sur les caracteristiques des polymères obtenus. L'examen par spectrographie IR a permis d'arriver à la conclusion que, au moins une partie des macromolécules contient comme groupe terminal, les groupes organiques qui étaient initialement liés au métal dans le composé employé comme catalyseur. La stéréospécificité du processus doit être attribuée à la possibilité de coordination du catalyseur aux molécules de monomère qui rentrent dans la chaîne en croissance. En effet, en ajoutant des bases organiques de Lewis, au système, on provoque une réduction ou bien la stéréospécificité disparait. Les résultats que nous avons obtenus nous ont permis de conclure que la polymérisation stéréospécifique de la 2-vinylpyridine a lieu à travers un mécanisme anionique coordiné. La 4-vinylpyridine, en présence de catalyseurs qui résultent stéréospécifiques pour la polymérisation de la 2-vinylpyridine, fournit des polymères amorphes qui ne sont pas cristallisables. Cela a été attribué par nous-mêmes au fait que l'atome d'azote, dans le cas de la 4-vinylpyridine, est trop loin de la double liaison vinylique, pour former, ainsi que le catalyseur, un complexe d'addition capable d'orienter de la même façon toutes les molécules à l'instant de la polymérisation.

Zusammenfassung

Einige metallorganische und metallamidische Verbindungen von sehr elektropositiven Metallen, wie Lithium, Natrium, Beryllium, Magnesium und Aluminium, lösen die Polymerisation des 2-Vinylpyridins aus. Während die Beryllium- und die Aluminium-Verbindungen dabei nur schwach kristalline Poly-2-vinyl-pyridine liefern, kann man bei Verwendung von Magnesium-Verbindungen Polymere erhalten, deren Röntgenspektren einen hohen Kristallinitätsgrad anzeigen. Die beim systematischen Studium der Polymerisation in Gegenwart von Amiden oder von metallorganischen Verbidungen des Magnesiums erhaltenen Ergebnisse werden beschrieben. Insbesondere wird dabei der Einfluss des Verhältnisses Monomeres/Katalysator, der Temperatur, der Polymerisationsdauer und der Natur der an das Magnesium gebundenen Substituenten, auf den Polymerisationsablauf und auf die Eigenschaften der erhaltenen Polymeren untersucht. Aufgrund von Infrarotuntersuchungen konnte geschlossen werden, dass zumindest ein Teil der Makromolekeln jene organischen Gruppen als Endgruppen gebunden enthält, die ursprünglich an das Metall der als Katalysator verwendeten metallorganischen Verbindung gebunden waren. Die Stereospezifizität des Prozesses muss der Möglichkeit der Koordinierung des Katalysators an die in die wachsende Kette eintretenden Molekeln des Monomeren zugeschrieben werden. Setzt man nämlich dem Katalysatorsystem organische Lewis-Basen zu, so erfolgt eine Abnahme oder sogar ein völliges Verschwinden der Stereospezifizität. Die experimentellen Ergebnisse haben die Schlussfolgerung gestattet, dass die stereospezifische Polymerisation des 2-Vinylpyridins über einen anionisch-koordinativen Mechanismus abläuft. In Gegenwart der Katalysatoren, die Stereospezifizität für die Polymerisation des 2-Vinylpyridins zeigen, liefert das 4-Vinylpyridin lediglich amorphe, nicht kristallisierbare Polymere. Wir schreiben dies der Tatsache zu, dass das Stickstoffatom im Fall des 4-Vinylpyridins allzu weit von der Vinyl-Doppelbindung entfernt ist, um mit dem Katalysator einen Additions-Komplex zu bilden, der in der Lage ist, alle Monomeren-Molekeln bei ihrem Eintritt in die wachsende Kette gleichartig zu orientieren.

Received March 1, 1961