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SUMMARY:

Polymerizations of propylene to syndiotactic polymer have been carried out in the presence of the catalyst system VCl_4-$Al(C_2H_5)_2Cl$-anisole. The data obtained have been related to those previously reported concerning the catalyst system, VCl_4-$Al(C_2H_5)_2Cl$. It was thus possible to propose a mechanism of formation of the catalytic complexes and to put forward or confirm some hypotheses on their constitution.

A polymerization mechanism is also proposed that can justify both the type of stereoregularity of the polymer and the variation of steric regularity on varying the polymerization conditions.

ZUSAMMENFASSUNG:

Propylen wurde mit dem Katalysatorsystem VCl_4-$Al(C_2H_5)_2Cl$-Anisol zu syndiotaktischem Polypropylen polymerisiert. Die Ergebnisse werden mit früheren Versuchen verglichen, bei denen das binäre System VCl_4-$Al(C_2H_5)_2Cl$ verwendet wurde. Aus den erhaltenen Daten konnten ein Bildungsmechanismus und die mutmaßliche Struktur des katalytisch wirksamen Komplexes abgeleitet werden. Ferner wird ein Polymerisationsmechanismus vorgeschlagen, der sowohl den Typ der Stereoregularität als auch deren Änderung mit wechselnden Polymerisationsbedingungen erklärt.

1. *Introduction*

At low temperature, propylene can be polymerized to syndiotactic polymer by catalyst systems obtained from vanadium salts, such as VCl_4[1–3], VA_3[1] (where A = acetylacetonic residue), $VO(OR)_3$[4] (where R = alkyl group) and organometallic compounds of aluminum, among which the halogenated ones are particularly suitable.

The kinetics of the polymerization in the presence of one of these catalyst systems was already described by us[3].

In this paper, we report some data concerning the influence of some electron donor substances, and in particular of anisole, on the behaviour of the catalyst system just considered. The comparison of these data with those previously published about the system VCl_4–$Al(C_2H_5)_2Cl$[3] in the

absence of anisole suggest some conclusions on the formation and on the constitution of the catalytic complexes, as well as on the polymerization mechanism.

2. *Performed Runs*

Systematic polymerization runs were carried out in the presence of the catalyst system VCl_4–$Al(C_2H_5)_2Cl$-anisole in *n*-heptane. The influence of the following variables was studied:

a) Polymerization time
b) Concentration of anisole
c) Concentration of $Al(C_2H_5)_2Cl$
d) Concentration of the monomer
e) Concentration of VCl_4
f) Polymerization temperature (from −78 to −37 °C)

We also carried out some polymerization runs in the presence of LEWIS bases other than anisole.

For each polymerization, we determined the polymer yield, its viscosity average molecular weight ($\overline{MW}$) and index of syndiotacticity (IS), which is an IR measure of syndiotactic crystallinity defined in a previous paper[2].

3. *Results*

3.1. *Polymerization Time*

The influence of time on the course of polymerizations carried out under very different conditions is shown in Figs. 1–12. The overall polymerization rate generally tends to increase during the runs. The $\overline{MW}$'s of the polymers increase almost linearly, while the IS's decrease. The data can be interpreted by admitting that, in the presence of anisole, no chain termination or transfer phenomena occur, or do not acquire a valuable importance. The catalytic complexes gradually form, accumulate during the polymerization and are stable under the conditions considered.

From the variations of $\overline{MW}$ during the polymerization, the "*viscosity average rate of propagation*" ($d\overline{MW}/dt$ at the beginning of the polymerization) can be determined; its value depends on the *average activity* of the catalytic complexes, on the distribution of the molecular weights and on the law of formation of the catalytic complexes with time*).

*) In the case of the particular catalyst system considered, the $\overline{MW}$'s increase linearly during the whole polymerization. An evaluation of the *viscosity average of rate propagation* can therefore be also made by simply examining the $\overline{MW}$ attained after a prefixed time t. This procedure was sometimes applied in the items that follow.

We assume here and in the following that in the presence of the same catalyst system at the same temperature, it is reasonable to extend the same relationship of equality and inequality observed among *viscosity average rates of propagation* to the *number average rates of propagation* ($d\overline{MW}_n/dt$ at the beginning of the polymerization, where $\overline{MW}_n$ is the number average molecular weight) and to the *average activity**) of the catalytic complexes. Moreover, also in the presence of different catalyst systems (in this work) it is reasonable to establish relationships of inequality among the *average activities* from the examination of the initial $d\overline{MW}/dt$, when these are very different one from another.

As previously shown[3], in the absence of anisole, the $\overline{MW}$ of the polymers initially increased much rapidly, reaching an almost steady value, which tended to further increase but very slowly; also the overall polymerization rate, after a relatively short initial time, kept constant.

We came to the conclusion that, in the absence of anisole, chain terminations existed and that the concentration of the catalytic complexes was steady.

The *viscosity average rate of propagation* though difficult to measure, appeared far higher in the absence of anisole. Therefore, we think it possible to deduce that also the *average activity* of the catalytic complexes was higher in the absence of anisole.

In our opinion, the IS's of the polymers decrease both in the presence and in the absence of anisole with increasing polymerization time, espe-

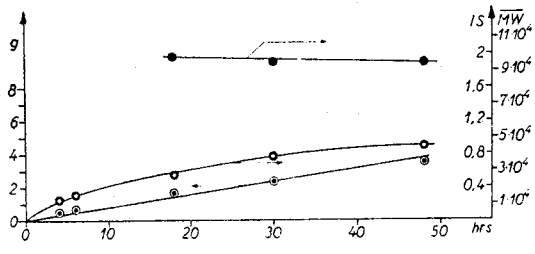


Fig. 1

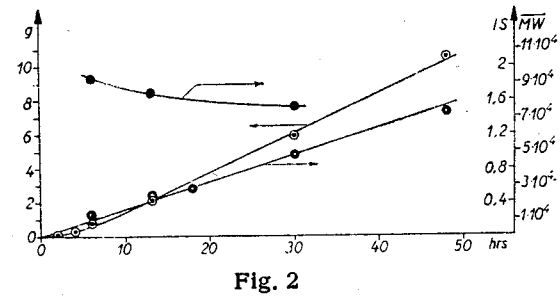


Fig. 2

Fig. 1. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 $0.5 \cdot 10^{-3}$ mole; anisole $0.5 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $2.5 \cdot 10^{-3}$ mole. Polymerization time: variable.
● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

Fig. 2. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 $0.5 \cdot 10^{-3}$ mole; anisole $0.5 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $15 \cdot 10^{-3}$ mole. Polymerization time: variable.
● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

*) For the definition of the *average activity* of the catalytic complexes, and for the relationships among *average activity* of the catalytic complexes, *viscosity average rate of propagation* and *number average rate of propagation*, *cf.* section 4.3. and Appendix.

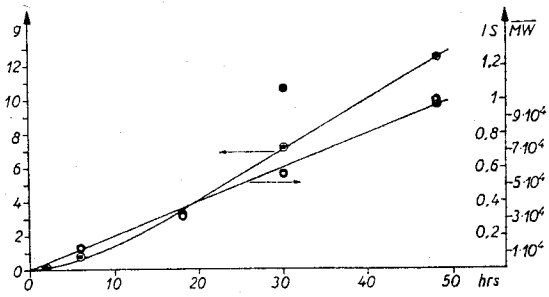


Fig. 3

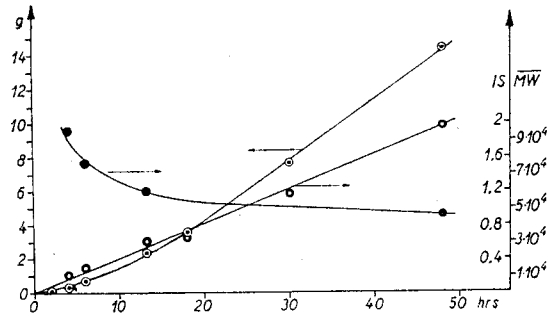


Fig. 4

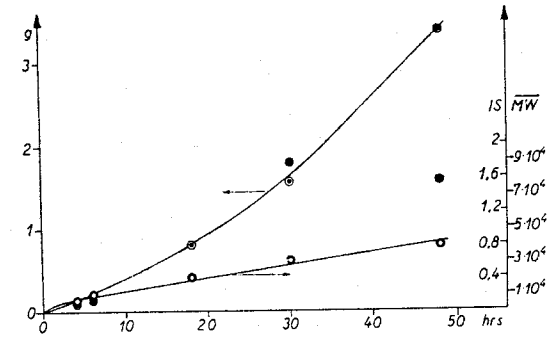


Fig. 5

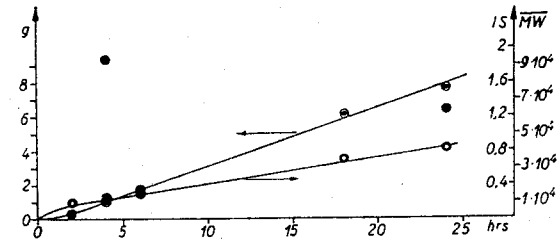


Fig. 6

Fig. 3. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 $0.5 \cdot 10^{-3}$ mole; anisole $0.5 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $20 \cdot 10^{-3}$ mole. Polymerization time: variable.
● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

Fig. 4. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 $0.5 \cdot 10^{-3}$ mole; anisole $0.5 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $25 \cdot 10^{-3}$ mole. Polymerization time: variable.
● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

Fig. 5. Polymerization conditions: T = −78 °C; C_3H_6 20 g; *n*-heptane 75 ml; VCl_4 $0.25 \cdot 10^{-3}$ mole; anisole $0.25 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $7.5 \cdot 10^{-3}$ mole. Polymerization time: variable.
● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

Fig. 6. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 $0.5 \cdot 10^{-3}$ mole; anisole $1 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $15 \cdot 10^{-3}$ mole. Polymerization time: variable.
● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

cially owing to the greater difficulty to crystallize polymers with a higher $\overline{MW}$; in some cases, however, there are also variations of steric regularity, which can be detected by NMR analysis.

3.2. *Concentration of anisole*

When passing from zero concentrations of anisole (the results of such runs were reported in [3]) to the lowest concentrations used in the runs described here (Figs. 1–5), we observe a strong decrease in the *viscosity average rate of propagation* and the disappearance of, or a considerable decrease in chain termination processes. In the presence of anisole, the overal polymerization rate is initially lower, but after some time it reaches higher

values. By comparing polymers with the same $\overline{MW}$, the IS's of the polymers obtained in the absence of anisole are not much lower; therefore the stereospecificity of the catalytic complexes is not deeply influenced.

By further increasing the concentrations of anisole, further marked variations of the *viscosity average rate of propagation* are not observed;

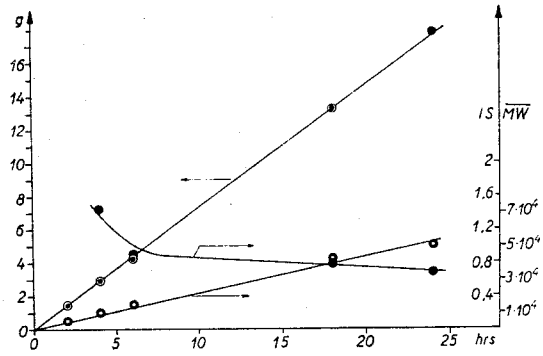


Fig. 7

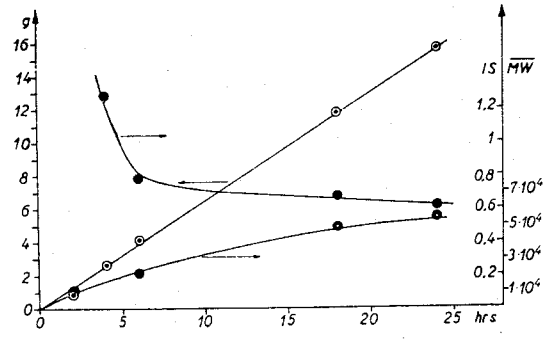


Fig. 8

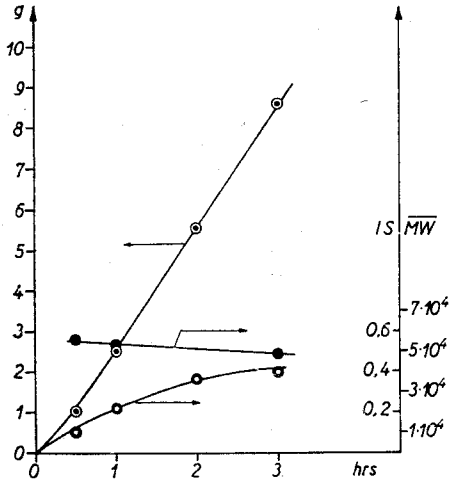


Fig. 9

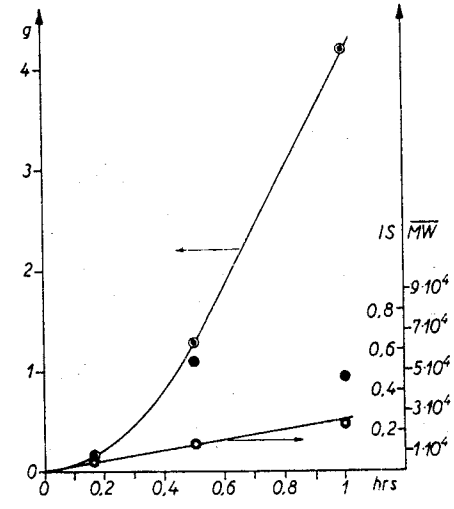


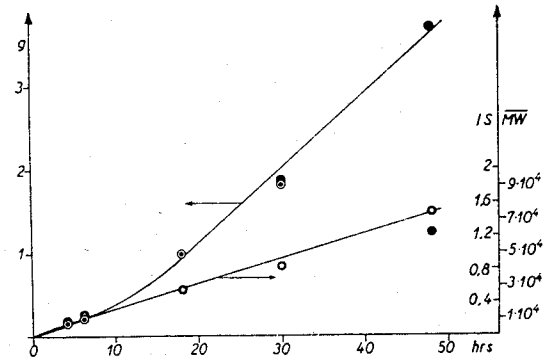
Fig. 10

Fig. 7. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 $0.5 \cdot 10^{-3}$ mole; anisole $5 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $15 \cdot 10^{-3}$ mole. Polymerization time: variable. ● = IS; ○ = $\overline{MW}$; ◉ = Polymer yield

Fig. 8. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 $0.5 \cdot 10^{-3}$ mole; anisole $7.5 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $15 \cdot 10^{-3}$ mole. Polymerization time: variable. ● = IS; ○ = $\overline{MW}$; ◉ = Polymer yield

Fig. 9. Polymerization conditions: T = −50 °C; C_3H_6 20 g; *n*-heptane 75 ml; VCl_4 $0.25 \cdot 10^{-3}$ mole; anisole $0.25 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $7.5 \cdot 10^{-3}$ mole. Polymerization time: variable. ● = IS; ○ = $\overline{MW}$; ◉ = Polymer yield

Fig. 10. Polymerization conditions: T = −37 °C; C_3H_6 20 g; *n*-heptane 75 ml; VCl_4 $0.25 \cdot 10^{-3}$ mole; anisole $0.25 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $7.5 \cdot 10^{-3}$ mole. Polymerization time: variable. ● = IS; ○ = $\overline{MW}$; ◉ = Polymer yield



Fig, 11

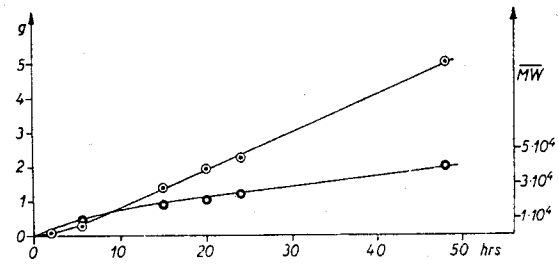


Fig. 12

Fig. 11. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 $0.25 \cdot 10^{-3}$ mole; anisole $0.25 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $7.5 \cdot 10^{-3}$ mole. Polymerization time: variable. ● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

Fig. 12. Polymerization conditions: T = −78 °C; C_3H_6 10–11 g; *n*-heptane 87 ml; VCl_4 $0.5 \cdot 10^{-3}$ mole; anisole $0.5 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $15 \cdot 10^{-3}$ mole. Polymerization time: variable. ○ = $\overline{MW}$; ⊙ = Polymer yield

on the other hand, the IS of the polymers decreases (Figs. 2, 6, 7, 8). The polymerization yield after a constant time increases with the increase in the concentration of anisole up to a maximum and then decreases (Figs. 13, 14).

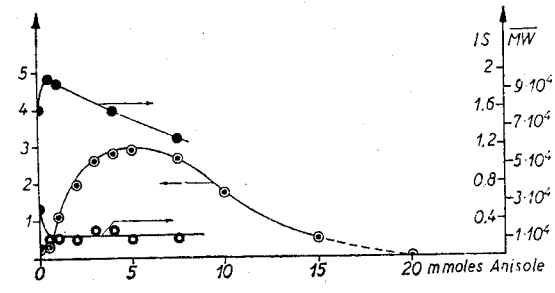


Fig. 13

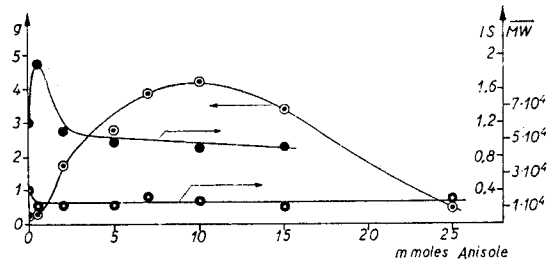


Fig. 14

Fig. 13. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 $0.5 \cdot 10^{-3}$ mole; anisole = variable amount; $Al(C_2H_5)_2Cl$ $15 \cdot 10^{-3}$ mole; Polymerization time: 4 hrs. ● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

Fig. 14. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 $0.5 \cdot 10^{-3}$ mole; anisole = variable amount; $Al(C_2H_5)_2Cl$ $25 \cdot 10^{-3}$ mole. Polymerization time: 4 hrs. ● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

The position of the maximum and the values of the polymerization rates*) depends on other reaction parameters and in particular on the concentration of $Al(C_2H_5)_2Cl$.

*) As in general the polymerization rate is not constant with time, we shall refer to the average polymerization rate observed in each run.

The data reported suggest that the variations of yield observed on varying the concentration of anisole, above a certain value, are due to corresponding variations of the rate of formation of the catalytic complexes. In general, the formation of catalytic complexes is faster in the presence of anisole.

In fact the *viscosity average propagation rate* decreases abruptly when passing from a zero concentration of anisole to the lowest values used by us, but for higher addition it does not further diminish.

3.3. *Concentration of $Al(C_2H_5)_2Cl$* (Figs. 1–4, 13, 14)

By increasing the concentration of $Al(C_2H_5)_2Cl$, the IS of the polymers decreases (if the comparison is made between polymers having the same $\overline{MW}$, or obtained after the same polymerization time). The *viscosity average rate of propagation* is little or not influenced at all. The overall polymerization rate increases. We may conclude that the higher is the concentration of $Al(C_2H_5)_2Cl$ the higher is the rate of formation of *catalytically active vanadium* *).

On the contrary, in the absence of anisole, increasing concentration of $Al(C_2H_5)_2Cl$ caused decreases in the overall polymerization rate (except for very low concentrations) [3].

However, we remind that in the absence of anisole, the *viscosity average rate of propagation* was not well evaluable and in any case, this quantity varied to a considerable extent by introduction of either $Al(C_2H_5)Cl_2$ or $Al(C_2H_5)_3$ in the systems. Thus, it is reasonable to attribute, at least in part, the changes in overall polymerization rate, when no anisole is present [3], to variations of the activity of the catalytic complexes. This point would involve considerations on the constitution of the catalytic complexes, which will be dealt with in a subsequent section.

It must be also borne in mind that, in the absence of anisole, the concentration of catalytically active vanadium was nearly constant throughout the polymerization, its value depending on the rates of formation and on the rate of termination.

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*) It has been previously shown [5] that in all the catalytic systems considered here, VCl_2R is formed. The polymerization of propylene occurs on the V–R bond. It has also been suggested [2–4] that the presence of stereospecificity in the syndiotactic sense depended on the presence of additional ligands around V. We call *catalytically active vanadium* the VCl_2R present in a catalytic system without considering the presence of these additional ligands. This topic will be discussed later.

3.4. *Initial concentration of the monomer*

The runs performed with different monomer concentrations are reported in Figs. 5, 12, 15. For the sake of simplicity, we assume that the monomer concentrations during the entire course of the runs are constant.

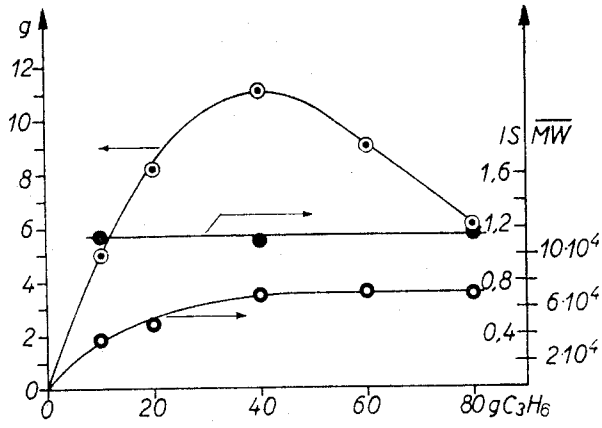


Fig. 15. Polymerization conditions: T = −78 °C; C_3H_6 = variable amount; *n*-heptane = variable amount; VCl_4 $0.5 \cdot 10^{-3}$ mole; anisole $0.5 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $15 \cdot 10^{-3}$ mole. Polymerization time: 48 hrs. ● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield. Except when C_3H_6 = 80 g, *n*-heptane was added in the runs in order to always attain a nearly constant reaction volume

By increasing the monomer concentration, we observe that:

a) the polymerization rate increases to a maximum and subsequently decreases;
b) the *viscosity average rate of propagation* increases to a constant value;
c) the IS's of the polymers are slightly lower for lower monomer concentrations (the comparison is made among polymers with the same molecular weight).

3.5. *Concentration of VCl_4*

The effect of VCl_4 on the polymerization is shown in Figs. 16 and 17.

The polymerization rate is approximately of first order with respect to the concentration of VCl_4 (Fig. 16) only if the effect of the other parameters connected (*e.g.* ratio between the concentrations of the reagents) is minimized by working in a suitable interval. Generally, by increasing the concentration of VCl_4, the overall polymerization rate reaches a maximum and then decreases (Fig. 17). Also these variations of the overall polymerization rate essentially depend on the variations of the rate of formation of the *catalytically active vanadium*, as indicated by the values of the $\overline{MW}$'s which are nearly independent of the VCl_4 concentration.

3.6. *Influence of polymerization temperature*

The results obtained from polymerization runs carried out at −50 and −37 °C, respectively, are reported in Figs. 9 and 10. By considering the polymer yield, $\overline{MW}$ and IS's, it clearly appears that temperature influ-

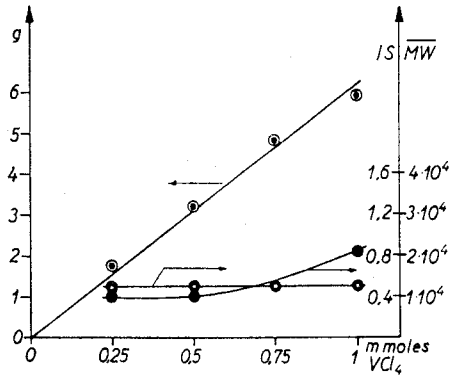


Fig. 16

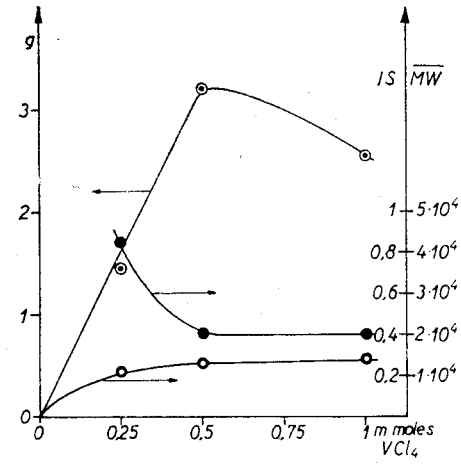


Fig. 17

Fig. 16. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 = variable amount; anisole $10 \cdot 10^{-3}$ mole; $Al(C_2H_5)_2Cl$ $25 \cdot 10^{-3}$ mole; Polymerization time: 4 hrs.
● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

Fig. 17. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 = variable amount; anisole/VCl_4 = 20; $Al(C_2H_5)_2Cl$ $25 \cdot 10^{-3}$ mole. Polymerization time: 4 hrs.
● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

ences both the rate of formation of *catalytically active vanadium* and the *average activity* of the catalytic complexes and their stereospecificity.

Apart from these considerations, we do not think it significant to deduce the activation energy of polymerization or of propagation from the data reported, since the way of formation of the *catalytically active vanadium* is not sufficiently known.

3.7. *Runs accomplished in the presence of* $Al(iC_4H_9)_2Cl$

We performed some polymerization runs in the presence of the catalyst system VCl_4-anisole-$Al(iC_4H_9)_2Cl$.

The results reported in Fig. 18 clearly show that the rate of formation of the catalytically active vanadium is lower than it would be by operating in the presence of $Al(C_2H_5)_2Cl$. On the other hand, the steric regularity of the polymers is higher, as shown from the comparison between their IS's and the IS's of the polymers with the same $\overline{MW}$ but obtained in the presence of $Al(C_2H_5)_2Cl$; moreover, with $Al(iC_4H_9)_2Cl$, polymers without appreciable amounts of isotactic IR crystallinity are obtained.

The main reason for the decreased rate of formation of the *catalytically active vanadium* must be probably looked for in the lower ease of alkylation of VCl_4 from the organometallic compounds having very bulky alkyl substituents. The differences, although modest, in the stereospecificities of these catalyst systems will be discussed later.

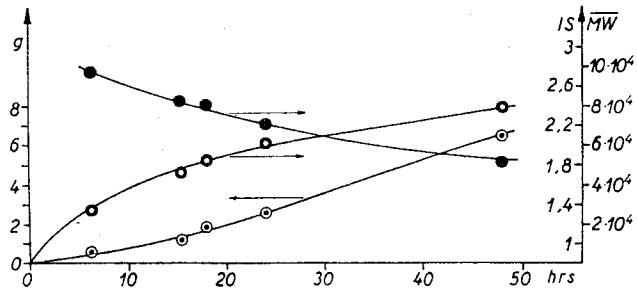


Fig. 18. Polymerization conditions: T = −78 °C; C_3H_6 120 g; *n*-heptane 150 ml; VCl_4 $4 \cdot 10^{-3}$ mole; anisole $4 \cdot 10^{-3}$ mole; $Al(iC_4H_9)_2Cl$ $20 \cdot 10^{-3}$ mole. Polymerization time: variable. ● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

3.8. *Runs performed in the presence of different* LEWIS *bases*

We also report some comparison runs carried out in the presence of LEWIS bases other than anisole (Table 1).

Every LEWIS base gives rise to considerable variations in the behaviour of the catalyst systems. The reasons for this will be apparent in the discussion hereinafter, concerning in particular the influence of anisole both on the formation of the *catalytically active vanadium* and the constitution of the stereospecific catalytic complexes.

Table 1. Polymerization runs of propylene performed in the presence of different LEWIS bases

LEWIS bases $0.5 \cdot 10^{-3}$ [mole]	Polymer yield [g]	$\overline{MW}$	IS
—	1.20	40,500	1.2
Thiophene	1.59	51,000	1.3
Anisole	3.15	31,000	1.6
Furan	4.07	57,000	n.d.
Isopropyl ether	4.17	35,000	n.d.
Ethyl ether	3.35	34,000	1.3
Tributylamine	0.22	29,000	n.d.
Pyridine	0.18	51,000	0.7;

The polymerization runs reported were performed at −78 °C by using: *n*-heptane 50 ml; C_3H_6 40 g; LEWIS bases $0.5 \cdot 10^{-3}$ mole; VCl_4 $0.5 \cdot 10^{-3}$ mole; $AlEt_2Cl$ $15 \cdot 10^{-3}$ mole; polymerization time: 18 hrs.

4. *Discussion*

4.1. *Formation of the catalytically active vanadium*

The catalyst system VCl_4-anisole-$Al(C_2H_5)_2Cl$ is particularly useful for the study of this aspect of the polymerization. In fact, in the presence of this system, and if the ratio VCl_4/anisole is lower than 1, the *viscosity average rate of propagation* depends to a first approximation only on the

concentration of the monomer and on the reaction temperature; therefore all remaining parameters influence the overall polymerization rate in that they modify the rate of formation of the *catalytically active vanadium*, while the *average activity* of the catalytic complex remains, in first approximation, unchanged.

The data reported in sections 3.1., 3.2., 3.3., and 3.5. can be easily interpreted by considering that anisole can be complexed both with VCl_4 and with the organometallic compounds of aluminum according to the following equilibria:

$$VCl_4 + An \underset{}{\overset{K_1}{\rightleftarrows}} VCl_4 \cdot An \tag{1}$$

$$[Al(C_2H_5)_2Cl]_2 + 2\,An \underset{}{\overset{K_2}{\rightleftarrows}} 2\,Al(C_2H_5)_2Cl \cdot An \tag{2}$$

The complexes $VCl_4 \cdot An$ and $Al(C_2H_5)_2Cl \cdot An$ are little soluble in *n*-heptane.

By admitting that only uncomplexed $Al(C_2H_5)_2Cl$ can alkylate VCl_4 and $VCl_4 \cdot An$, the reaction will be ruled by the following equilibria:

$$VCl_4 + {}^1/_2[Al(C_2H_5)_2Cl]_2 \overset{K_3}{\rightleftarrows} VCl_3(C_2H_5) + {}^1/_2[Al(C_2H_5)Cl_2]_2 \tag{3}$$

$$VCl_4 \cdot An + {}^1/_2[Al(C_2H_5)_2Cl]_2 \overset{K_4}{\rightleftarrows} VCl_3(C_2H_5) \cdot An + {}^1/_2[Al(C_2H_5)Cl_2]_2 \tag{4}$$

$$VCl_3(C_2H_5) + {}^1/_2[Al(C_2H_5)_2Cl]_2 \overset{K_5}{\rightleftarrows} VCl_2(C_2H_5)_2 + {}^1/_2[Al(C_2H_5)Cl_2]_2 \tag{5}$$

$$VCl_3(C_2H_5) \cdot An + {}^1/_2[Al(C_2H_5)_2Cl]_2 \overset{K_6}{\rightleftarrows} VCl_2(C_2H_5)_2 \cdot An + {}^1/_2[Al(C_2H_5)Cl_2]_2 \tag{6}$$

If we admit that $K_4K_6 \gg K_3K_5$ and if we bear in mind the low solubility of the complex $VCl_4 \cdot An$, it is easy to demonstrate that the sum of the concentrations:

$$[VCl_2(C_2H_5)_2] + [VCl_2(C_2H_5)_2 \cdot An]$$

always increases if the concentration of $Al(C_2H_5)_2Cl$ increases whereas it reaches a maximum and then decreases with increasing both anisole and VCl_4.

The rate of formation of catalytically active vanadium is given by the sum of the rates of the two reactions:

$$\left.\begin{array}{ll} VCl_2(C_2H_5)_2 & \overset{\chi_1}{\longrightarrow} \\ VCl_2(C_2H_5)_2 \cdot An & \overset{\chi_2}{\longrightarrow} \end{array}\right| \begin{array}{l} \textit{catalytically active vanadium} \\ (VCl_2(C_2H_5) \text{ or one of its complexes}) + C_2H_5^{\bullet} \end{array} \tag{7}$$

By putting χ_1 and χ_2 slightly different one from the other, the interpretation of the polymerization data obtained is immediate. For a quantitative interpretation of the data reported, it is actually necessary to take into account the complexation of anisole with the $Al(C_2H_5)Cl_2$ formed in the systems, the possible complexation of organometallic compounds of Al with $VCl_2(C_2H_5)_2$, the consumption of V^{IV} during the polymerization, etc. However, in our opinion attempts of this kind should not essentially alter the scheme of reactions proposed.

The data reported in section 3.5. show that also the monomer can somehow interact with VCl_4 and influence the reactions of formation of the catalytic complexes.

Boor and co-workers[4] observed that also some olefins unable to polymerize, such as cyclohexene, influence the polymerization course. However, at least at −78 °C, the reaction of the monomer with VCl_4 would be far less favoured than the complexation of anisole to give $VCl_4 \cdot An$.

The mechanism proposed for the formation of *catalytically active vanadium* agrees with the experimental data obtained by us, in spite of the oversimplified assumptions made, *e.g.* that several chemical species are present under equilibrium conditions. Probably, these assumptions are not completely allowed and no wonder whether some data fall outside this picture. For example, it is difficult to explain why the system VCl_4-$Al(C_2H_5)_2Cl$-Anisole, for very short polymerization times, gives rise to polymerization rates that are the lower the higher is the concentration of $Al(C_2H_5)_2Cl$.

4.2. *Constitution of the stereospecific catalytic complexes*

4.2.1. In the presence of anisole

We defined $VCl_2(C_2H_5)$ *catalytically active vanadium* to mean that it is present in the catalytic complexes, with which however it must not be identified[5]. The stereospecific catalytic complexes have a more complicated composition.

The homogeneous catalyst systems prepared from VCl_4 and $Ga(C_2H_5)_3$ at low temperature also promote the polymerization of propylene. The polymer obtained, however, is amorphous by operating both in the presence and in the absence of anisole[3,6]. The reducing power of $Ga(C_2H_5)_3$ is intermediate between that of $Al(C_2H_5)_2Cl$ and of $Al(C_2H_5)_3$[7]; however, $Ga(C_2H_5)_3$ and $Ga(C_2H_5)_2Cl$ have a lower tendency (with respect to the organometallic compounds of Al) to form bridge bonds.

Similarly, both in the absence[3] and in the presence of anisole[6], non-stereospecific catalyst systems are obtained from VCl_4 in the presence of $Al(C_2H_5)_3$, which hinders the formation of $Al(C_2H_5)Cl_2$.

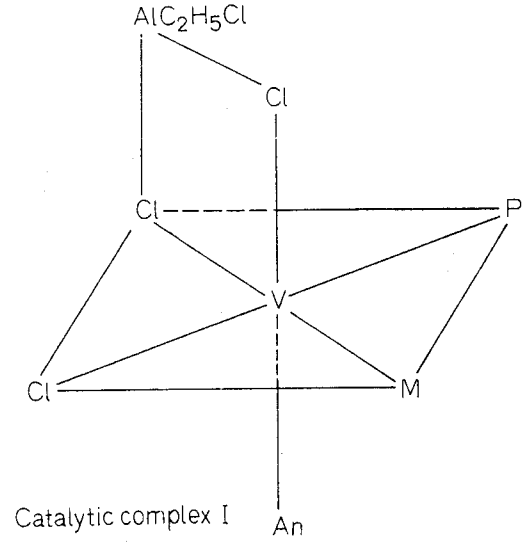
These facts suggest that the stereospecific catalytic complexes contain both $VCl_2(C_2H_5)$ and $Al(C_2H_5)Cl_2$ formed in the reaction between VCl_4 or its complexes and $Al(C_2H_5)_2Cl$.

If $AlC_2H_5Cl_2$ is absent, complexes containing $VCl_2(C_2H_5)$ and $Al(C_2H_5)_2Cl$ or $Ga(C_2H_5)_2Cl$ may perhaps form; however, they are less stereospecific or not stereospecific at all probably due to their lower stability to dissociation.

It is also clear that anisole, by itself, does not lead with $VCl_2(C_2H_5)$ to the formation of stereospecific complexes. However, in the presence of anisole, the kinetic parameters of the catalytic stereospecific complexes that form from VCl_4 and $Al(C_2H_5)_2Cl$ are very different from those of the stereospecific catalytic complexes that form in the absence of anisole. Starting from very low values of the concentration of anisole, however, the *average activity* of the catalytic complexes is nearly independent of this parameter. Therefore, it must be excluded that the low propagation rate is due to a competitive complexation between the monomer and anisole on catalytic complexes, which would thus become temporarily inactive. Therefore, the difference in the kinetic parameters related to the stereospecific catalytic complexes observed in the two cases must depend on a difference in their constitution.

Due to the previously mentioned reasons, we cannot admit that in this case the stereospecific catalytic complexes contain only complexed anisole instead of $Al(C_2H_5)Cl_2$, but they must contain both $Al(C_2H_5)Cl_2$ and anisole.

As will be shown, the polymerization is of the coordinate type; therefore, there should be at least a coordination vacancy on the vanadium present in the catalyst complex for the coordination of the monomer. It is also known that generally the chlorine bridge bonds are more stable than the alkyl ones. It follows that this type of stereospecific catalytic complexes probably will have a structure of the following type:

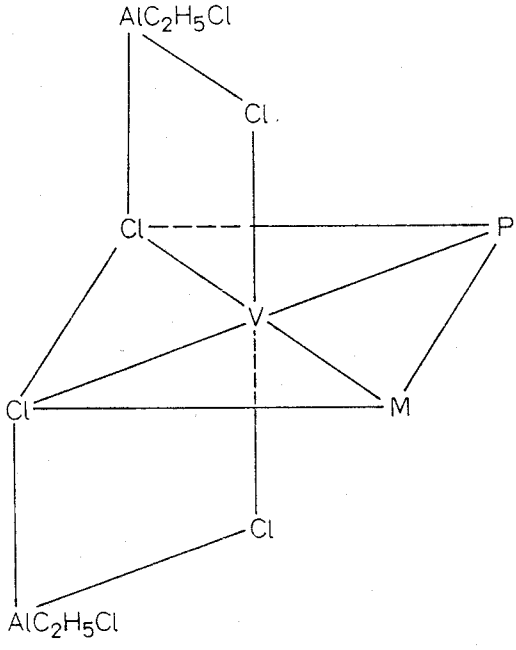


Catalytic complex I

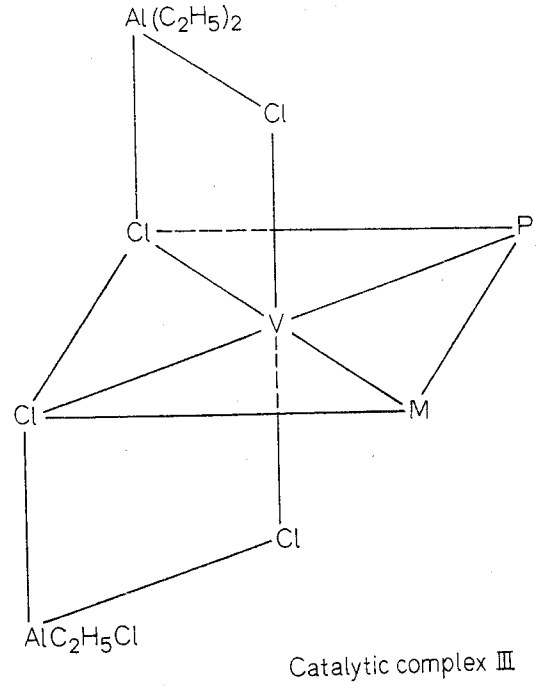
where P is the growing molecule, M the complexed monomer, An a molecule of anisole or of another suitable LEWIS base.

4.2.2. In the absence of anisole

The catalytic complexes, which form in the absence of anisole and which are stereospecific in the syndiotactic sense, must be very similar, from the steric standpoint, to the already described ones. If, as we have seen, anisole cannot completely replace the organometallic compounds of Al, this does not mean that the latter cannot completely replace the former. By imposing the condition that the stereospecific complexes reach in any case the hexacoordination of V^{III}, when the monomer is complexed, two types of catalytic complexes can be postulated:



Catalytic complex II



Catalytic complex III

In the presence of high concentrations of $Al(C_2H_5)Cl_2$, complexes of type II probably prevail, while in the presence of low concentrations, complexes of type III prevail. The *average catalytic activity* of the different complexes*), which can be evaluated from the *viscosity average rates of propagation* seems the lowest for complex I. In the presence of anisole, the catalytic complex also presents the highest stability, as shown by the absence of terminations.

The comparison between the data concerning complexes II and III is more difficult.

*) See section 4.3. and Appendix.

The data reported in [3] (Note II), which refer to runs performed by adding $Al(C_2H_5)Cl_2$ to the VCl_4–$Al(C_2H_5)_2Cl$ catalyst system, suggest that complex II give rise to a higher propagation rate.

4.3. *Polymerization mechanism*

The data reported in section 3.4. and particularly the dependence of the propagation rate on the monomer concentration can be easily explained by admitting that the polymerization is of coordinate type[2]. In other words, the polymerization takes place in two steps:
a) coordination of the monomer on the catalytic complexes:

$$C^*-P_n + M \overset{K_c}{\rightleftarrows} M-C^*-P_n \tag{8}$$

b) insertion in chain:

$$M-C^*-P_n \xrightarrow{\chi_i} C^*-P_{(n+1)} \tag{9}$$

where C^*-P_n = catalytic complex to which a polymeric radical having a polymerization degree n (P_n) is bound; M = monomer; $M-C^*-P_n$ = catalytic complex, bound to the radical P_n, on which a monomer molecule is coordinated; K_c = equilibrium constant of coordination; χ_i = constant of insertion in the chain.

By putting K_c and χ_i as independent of n and:

$$\Sigma[C^*P_n] + \Sigma[M-C^*-P_n] = C^* \tag{10}$$

the *number average rate of propagation* will be:

$$\frac{d\overline{MW}_n}{dt} = \chi_i K_c \tau \frac{[M]}{1 + K_c[M]} M_0 \text{ *)} \tag{11}$$

where M_0 is the molecular weight of the monomer unit and τ is a factor that takes into account the variation of the concentration of the catalytic complexes during the polymerization. The value of τ is generally unknown; however, we can demonstrate that $\tau = 1$ if C^* is constant,

*) By admitting that the coordination step (8) is not at equilibrium, Eq. (11) becomes:

$$\frac{d\overline{MW}_n}{dt} = \chi_i \chi_c \tau \frac{[M]}{\chi_c[M] + \chi_i} M_0$$

where χ_c is the kinetic constant relative to the reaction:

$$C^*-P_n + M \xrightarrow{\chi_c} M-C^*-P_n$$

which is not supposed at equilibrium any longer.

while $\tau = 1/2$ if C* is a linear function of the time of polymerization*). In the case considered by us C* is sometimes constant, sometimes it increases less than linearly and therefore it will always be $1 \geqslant \tau \geqslant 1/2$.

The dependence of the overall polymerization rate on the monomer concentration indicates also variation of the instantaneous concentrations of catalytic complexes, which are analogous to those resulting by the action of anisole.

An analogous behaviour was observed also in the absence of anisole[3]. However, the presence of a maximum of the viscosity average molecular weights was observed in correspondence of the higher polymerization rates. By taking into account the presence of chain terminations, we may interpret the experimental data[3] by admitting that one of them might be of the type

$$M-C-P_n + M \xrightarrow{\chi_t} iM + C + P_{(n+2-i)} \qquad (12)$$

where: C = decomposition products of the catalyst; P_n = polymeric radical with a degree of polymerization n; i is equal to 0, 1 or 2.

4.4. *Causes of stereospecificities in the syndiotactic sense of the catalytic complexes proposed*

In all the catalytic complexes proposed, the vanadium atom is dissymmetric. The stereospecificity of the syndiotactic type might be explained by admitting that the configuration of vanadium is inverted whenever a previously co-ordinated monomer molecule enters into the Vanadium-

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) $\overline{MW}_n = \dfrac{\chi_i K_c[M] \int_o^t C^* dt}{(1 + K_c[M])C^*} M_o$. If C is constant:

$$\overline{MW}_n = \frac{\chi_i K_c[M]t}{1 + K_c[M]} M_o; \quad \frac{d\overline{MW}_n}{dt} = \frac{\chi_i K_c[M]}{1 + K_c[M]} M_o$$

On the contrary, if C* increases linearly with time according to the equation:

$$C^* = At$$

(where the value of A, the temperatures being the same, depends on the concentration of the reagents which is supposed not to vary during the initial period of each run):

$$\overline{MW}_n = {}^1/_2 \frac{\chi_i K_c[M]t}{1 + K_c[M]} M_o$$

$$\frac{d\overline{MW}_n}{dt} = {}^1/_2 \frac{\chi_i K_c[M]}{1 + K_c[M]} M_o$$

In general, for the runs reported by us: $\dfrac{d\overline{MW}_n}{dt} = \tau \dfrac{\chi_i K_c[M]}{1 + K_c[M]} M_o$ with $1 \geqslant \tau \geqslant {}^1/_2$

Carbon bond. However, the dissymmetry of V in the complexes proposed does not seem enough in this case from the steric standpoint to justify a preferential presentation of the monomer. It seems more satisfactory the hypothesis of BOOR *et al.* that the asymmetric last added unit cannot freely rotate; thus the addition would be faster when a new monomer molecule approaches the growing chain end (from the direction imposed by the structure of the counterion) presenting the face having configuration opposite to that of the last unit[4].

4.5. *Syndiotactic stereoblocks, amorphous and atactic polymers. Non stereospecific catalytic complexes*

Depending on the reaction conditions, the catalyst systems obtained from VCl_4 and $Al(C_2H_5)_2Cl$ give rise to polymers with different degrees of crystallinity, which, in some cases must certainly be attributed to variations in steric regularity. The introduction in the chain of few randomly distributed irregularities may be responsible for considerable decreases in crystallinity. That is why, at least with regard to non deuterated polypropylenes, the IS is a more accurate (although ambiguous) parameter than the NMR analysis.

By developing the hypotheses put forward by BOOR and co-workers[4] on the causes of stereospecificity, the described catalytic complexes can easily justify the formation of syndiotactic stereoblock macromolecules separated by randomly distributed permanences. Actually, the stereospecific complexes can probably exchange their ligands with the reaction medium.

During the growth of a macromolecule, the substitution of a ligand might occur now and then through a hexacoordinated intermediate, in which a new ligand has the position generally assumed by the complexed monomer. On separation from this inactive complex of a ligand in a *cis* position with respect to the growing chain, the stereospecific complex is re-activated; by this process, however, the position of the co-ordination vacancy with respect to the growing chain can change. In this case it seems possible that the subsequent monomeric unit may enter into the chain giving a permanence instead of an alternance.

This hypothesis well justifies the negative influence exerted by the high concentrations of either anisole or $Al(C_2H_5)_2Cl$ or $AlC_2H_5Cl_2$ on the crystallinity of the polymers. Actually the process described will by favoured by the high concentrations of electron-donor substances in the reaction medium. Along with the exchange of the ligands with the reac-

tion medium, the catalytic complexes may dissociate, *e.g.* by the loss of a ligand. Under these conditions, the co-ordination vacancies, the monomer can be complexes on, become two, and no driving force exists any longer for the presence of stereospecificity.

This situation already occurs by removing the $Al(C_2H_5)Cl_2$ present in the system, and even better, by replacing the organometallic compounds of Aluminum by organometallic compounds of Gallium having a lower tendency to complexation. In these cases, the polymers obtained are head-to-tail, but sterically disordered[6].

The catalytic systems obtained by us from VA_3, which are stereospecific in the syndiotactic sense also in the absence of $Al(C_2H_5)Cl_2$, will be discussed later[6].

The different crystallinities of the polymers obtained by the catalyst systems that contain different aluminum alkyl monochlorides can be easily explained; in fact, each aluminum alkyl chloride can alkylate VCl_4 to a different extent and give rise to an exchange of ligands with the stereospecific complexes to a different rate depending on the alkyl group.

Another possibility of formation of randomly distributed steric irregularities, which may occur along with the previous ones, may be simply due to the not absolute stereospecificity of the complexes. The number of irregularities introduced by this mechanism should depend for each catalyst system only on temperature.

4.6. *Isotactic portions*

Under the reaction conditions employed by us, the catalyst systems containing $Al(C_2H_5)_2Cl$ give polymers showing a very low IR crystallinity of the isotactic type, which can be detected by the absorption at 11.88 μ of the polymer in the solid state. These isotactic portions could be derived from the presence of heterogeneous components in the catalytic systems.

The amount of these components obviously depends on the extent of competitive reactions with those of alkylation and of reduction that lead to the formation of VCl_2R; in the presence of organometallic compounds of Aluminum bearing bulky alkyl substituents[2] ($Al(iC_4H_9)_2Cl$, $Al(neoC_5H_{11})_2Cl$) these secondary reactions probably do not occur.

We also observe that polypropylenes obtained by the homogeneous catalyst systems, obtained from vanadium salts, always contain a few percent units in head-to-head arrangement, which may be evidenced by

IR analysis at 13.35 μ; this fact also agrees with the polymerization mechanism proposed[4].

5. *Conclusion*

By low-temperature reaction of VCl_4 with organometallic compounds, alkyl vanadium dichloride forms, which can promote the polymerization of propylene.

In the presence of aluminum alkyl dihalides, *e.g.* obtained by reaction of $Al(C_2H_5)_2Cl$ with VCl_4, complexes may form, in which V^{III} has co-ordination 5, the co-ordination vacancy representing the point where propylene complexes before entering into the chain. The polymerization takes place by co-ordination of the monomer and subsequent insertion at the V–C bond. Stereospecificity seems due to steric interactions between the methyl of the last entered monomeric unit and that of the monomer molecule to be added.

In the absence of suitable electron donor substances, VCl_2R does not attain the number of co-ordination 5, or gives rise to complexes that can be easily dissociated; under these conditions, stereospecificity cannot occur any longer.

When exchange of the ligands of the V^{III} present in the stereospecific complexes occure, the introduction into the chain of isolated isotactic diads is possible; when dissociation of the stereospecific complexes occurs, atactic macromolecules or blocks may form. The presence of different types of syndiotactic stereospecific catalytic complexes, each being characterized by particular kinetic parameters, is inferred.

6. *Experimental Part*

Purification of reagents, polymerization runs and measurements of $\overline{MW}$ and of IS were carried out as previously described[2,3]. We think it convenient to insist on the great importance of $Al(C_2H_5)_2Cl$ used for the reproducibility of the runs. Even by accurately controlling the ratio Cl/Al[3], different stocks of $Al(C_2H_5)_2Cl$ may give different results. This is why we exclusively compared the results obtained from polymerizations carried out with the same stock of $Al(C_2H_5)_2Cl$.

In our opinion, the presence of alcoholates and above all of aluminum hydrides are responsible for these inconveniences.

Fig. 19 shows, as an example, the results obtained in some polymerization runs using mixtures of $Al(C_2H_5)O(C_2H_5)Cl$ and $Al(C_2H_5)_2Cl$.

The reactions conditions adopted for the different runs are reported in the figures and in Table 1.

All runs reported were carried out by preparing the catalyst in the presence of the monomer and, in general, were stopped at low conversion.

Table 2. Results of the runs reported in Figs. 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 18

Fig.	Time [hrs]	Polym. yield [g]	$\overline{MW}$	IS	Fig.	Time [hrs]	Polym. yield [g]	$\overline{MW}$	IS
1	4	0.4	12,000	n.d.	7	2	1.5	<10,000	n.d.
	6	0.6	15,000	n.d.		4	2.9	<10,000	1.5
	18	1.6	28,000	2.0		6	4.3	13,000	0.9
	30	2.3	39,000	1.9		18	13.3	39,000	0.8
	48	3.5	45,000	1.9		24	17.9	50,000	0.7
2	2	0.05	n.d.	n.d.	8	2	0.9	<10,000	n.d.
	4	0.4	<10,000	n.d.		4	2.7	n.d.	1.3
	6	0.9	13,000	1.9		6	4.2	22,000	0.8
	13	2.3	25,000	1.7		18	11.8	49,000	0.7
	18	3.1	31,000	n.d.		24	15.7	55,000	0.6
	30	5.9	48,000	1.5					
	48	11.0	73,000	n.d.	9	0.5	1.1	<10,000	0.6
						1	2.5	22,000	0.5
3	2	0.07	n.d.	n.d.		2	5.6	36,000	n.d.
	6	0.8	13,000	n.d.		3	8.6	39,000	0.5
	18	3.2	32,000	n.d.					
	30	7.2	56,000	1.0	10	0.16	0.15	<10,000	n.d.
	48	12.5	100,000	0.9		0.5	1.3	14,000	0.6
						1	4,2	24,000	0.5
4	2	0.07	n.d.	n.d.					
	4	0.3	<10,000	1.9	11	4	0.2	<10,000	n.d.
	6	0.8	15,000	1.5		6	0.3	13,000	n.d.
	13	2.4	32,000	1.2		18	1.0	28,000	n.d.
	18	3.6	33,000	n.d.		30	1.8	42,000	1.8
	30	7.7	59,000	n.d.		48	3.7	74,000	1.2
	48	14.5	100,000	0.9					
					12	2	0.03	n.d.	n.d.
5	4	0.1	<10,000	n.d.		5.5	0.3	<10,000	n.d.
	6	0,2	11,000	n.d.		15	1.4	17,000	n.d.
	18	0.8	20,000	n.d.		20	2.0	20,000	n.d.
	30	1.5	31,000	1.8		24	2.2	24,000	n.d.
	48	3.4	40,000	1.6		48	5.0	40,000	n.d.
6	2	0.3	<10,000	n.d.	18	6	0.6	27,000	2.8
	4	1.1	<10,000	1.9		15.5	1.3	46,000	2.5
	6	1.7	15,000	n.d.		18	1.9	53,000	2.4
	18	6.1	35,000	n.d.		24	2.6	62,000	2.2
	24	7.7	41,000	1.3		48	6.5	80,000	1.8

The polymerization conditions that have not been reported in the Tables are listed in the captions to the figures.

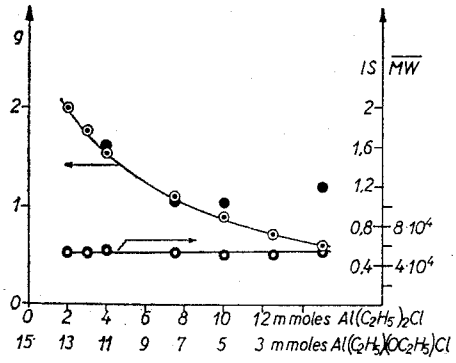

Fig. 19. Polymerization conditions: T = −78 °C; C_3H_6 40 g; *n*-heptane 50 ml; VCl_4 $0.5 \cdot 10^{-3}$ mole; $Al(C_2H_5)O(C_2H_5)Cl$ = variable amount; $Al(C_2H_5)_2Cl$ = variable amount. Polymerization time: 5 hrs. ● = IS; ○ = $\overline{MW}$; ⊙ = Polymer yield

For greater convenience, Tables 2, 3, and 4 report the numerical data concerning the diagrams shown in the figures.

Table 3. Results of the runs reported in Figs. 13, 14, 15, 16, 17

Fig.	Anisole [moles $\cdot 10^3$]	Polym. yield [g]	$\overline{MW}$	IS	Fig.	Anisole [moles $\cdot 10^3$]	Polym. yield [g]	$\overline{MW}$	IS
13	0	0.2	27,000	1.6		C_3H_6 [g]			
	0.5	0.4	<10,000	n.d.					
	1	1.1	<10,000	1.9	15	10	5.0	37,000	1.1
	2	2.0	<10,000	n.d.		20	8.3	53,000	n.d.
	3	2.6	15,000	n.d.		40	11.0	73,000	1.1
	4	2.8	15,000	1.6		60	9.1	72,000	n.d.
	5	2.9	<10,000	1.5		80	6.2	71,000	1.2
	7.5	2.7	16,000	1.3					
	10	1.8	n.d.	n.d.					
	15	0.5	n.d.	n.d.		VCl_4 [moles $\cdot 10^3$]			
	20	0	n.d.	n.d.					
14	0	0.18	21,000	1.1	16	0.25	1.7	13,000	0.4
	0.5	0.3	<10,000	1.9		0.5	3.2	13,000	0.4
	2	1.8	12,000	1.1		0.75	4.8	14,000	n.d.
	5	2.8	12,000	1.0		1	5.9	12,000	0.8
	7	3.9	16,000	n.d.					
	10	4.2	14,000	0.9	17	0.25	1.5	11,000	0.8
	15	3.4	<10,000	0.9		0.5	3.2	13,000	0.4
	25	0.5	15,000	n.d.		1	2.6	14,000	0.4

The polymerization conditions that have not been reported in the Tables are listed in the captions to the figures.

Table 4. Results of the runs reported in Fig. 19

$Al(C_2H_5)_2Cl$ [moles·10^3]	$AlC_2H_5(OC_2H_5)Cl$ [moles·10^3]	Polymer yield [g]	$\overline{MW}$	IS
15	0	0.6	56,000	1.2
12.5	2.5	0.7	41,000	n.d.
10	5	0.9	46,000	1.0
7.5	7.5	1.1	55,000	1.0
4	11	1.6	60,000	1.6
3	12	1.8	58,000	n.d.
2	13	2.0	56,000	n.d.
0	15	0	n.d.	n.d.

The polymerization conditions that have not been reported in the Table are listed in the caption to the figure.

Appendix

The polymerization runs described in this paper and in Note [3] were generally stopped at a very low conversion.

The data concerning catalyst systems containing anisole, allow one to easily measure the *average viscosity propagation rate* (VP) under different conditions, because, as may be seen from the diagrams, a nearly linear relationship exists between $\overline{MW}$ and t.

By supposing that the ratio:

$$E = \overline{MW}/\overline{MW}_n$$

is constant, by the definition of VP (see section 3.1.) and by taking into account Eq. (11), we have:

$$VP = \frac{d\,\overline{MW}}{dt} = \tau E \frac{\chi_i K_c[M]}{1 + K_c[M]} M_0 \qquad (13)$$

Since χ_i and K_c cannot be drawn from Eq. (13) VP and [M] being known, we put:

$$AC = \frac{\chi_i K_c[M]}{1 + K_c M} \qquad (14)$$

where AC = *average activity* of the catalytic complexes.

To make a comparison among the various catalyst systems under different conditions, we carried out polymerization runs, keeping the parameter [M] constant, and we assumed that for runs I and II carried out by the systems containing VCl_4-$Al(C_2H_5)_2Cl$-anisole were:

$$(VP)_I/(VP)_{II} = (AC)_I/(AC)_{II} \tag{15}$$

or

$$\tau_I E_I = \tau_{II} E_{II}$$

independently of the concentrations of the three components of the catalyst system and provided that the ratio of anisole to VCl_4 were >1.

The data of Note II, concerning the runs performed in the absence of anisole, did not allow us to accurately measure VP, although it is clear that, [M] being the same, VP reached far higher values.

To make it possible a comparison of the data of Note II[3] with those of this work, we assumed that, when passing from a type of runs to the other, the variations of τE were always contained within such limits that if

$$(VP)_{III} \gg (VP)_{IV}$$

also

$$(AC)_{III} > (AC)_{IV}.$$

Finally, [M] being the same and according to the criteria just described, when

$$(AC)_x = (AC)_y$$

it is:

$$K_{cx} = K_{cy}; \quad \chi_{ix} = \chi_{iy}$$

In this case, we assumed that the catalytic complexes present in system x and those present in system y had identical structures.

On the contrary, [M] being the same, when

$$(AC)_x \neq (AC)_y$$

it is:

$$K_{cx} \neq K_{cy} \text{ and/or } \chi_{ix} \neq \chi_{iy}.$$

In this case, we assumed that the catalytic complexes present in system x and those present in system y had different structures.

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