

Polymerization of Propylene to Syndiotactic Polymer. II. Behavior of the Catalytic System $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$

A. ZAMBELLI, G. NATTA, I. PASQUON, and R. SIGNORINI, *Istituto di Chimica Industriale del Politecnico, Milano, Italy*

Synopsis

Some data on the kinetic behavior of the catalytic system $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, which is stereospecific (at low temperatures) for the polymerization of propylene to syndiotactic polymer, are reported here. The effect was studied of the reaction time and of the concentration of VCl_4 , of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, and of the monomer on the polymerization rate, on the molecular weight, and on the index of syndiotacticity of the polymers obtained. The data reported are discussed on the basis of the hypotheses previously put forth about the nature of the catalytic complexes and the polymerization mechanism.

In a previous paper,¹ we reported on some spectroscopic data about the valency state of the transition metal in the low-temperature polymerization of propylene to syndiotactic polymer in the presence of homogeneous catalytic systems, prepared from a trivalent or tetravalent vanadium compound (soluble in the reaction medium) and from an organometallic compound of aluminum. In these systems, the catalytically active V is present as monoalkylvanadium dichloride. The low thermal stability of the catalytic systems, which, on heating deactivate,^{1,2} yielding VCl_2 , suggests that, in this case, the addition of the olefin takes place on the vanadium-carbon bond.

However, the organometallic compound introduced in the catalytic system, under the conditions studied by us, exerts a determining influence on the polymerization, with regard to both the steric regularity of the polymers obtained and to the kinetic behavior. Therefore, we think it probable that the catalytically active alkyl vanadium dichloride yields, at least in some cases, bimetallic catalytic complexes containing both vanadium and aluminum.

To get a better understanding of the polymerization of propylene to syndiotactic polymer, we thoroughly studied the behavior of the $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ catalytic system at -78°C . in *n*-heptane. In order to point out the influence exerted by the organometallic compound, some polymerization runs were also carried out with the aid of the catalytic system $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ in the presence of $\text{Al}(\text{C}_2\text{H}_5)_3$ or of $\text{AlC}_2\text{H}_5\text{Cl}_2$. In general, the yield in polymer, the index of syndiotacticity (IS),² and

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the viscosimetric average molecular weight (MW) of the polymers obtained were determined for each polymerization.

RESULTS OBTAINED

Influence of the Reaction Time

Polymerization Rate. The amounts of polymer obtained with almost constant monomer concentrations are practically proportional to the polymerization time after a certain period (Figs. 1-5). Especially when operating with low Al/V ratios (Fig. 1), an induction period of a few hours is observed. In our opinion, the induction period does not depend, under the operating conditions adopted by us, on the presence of impurities, but is due, at least prevailing, to the kinetics of formation of active complexes.

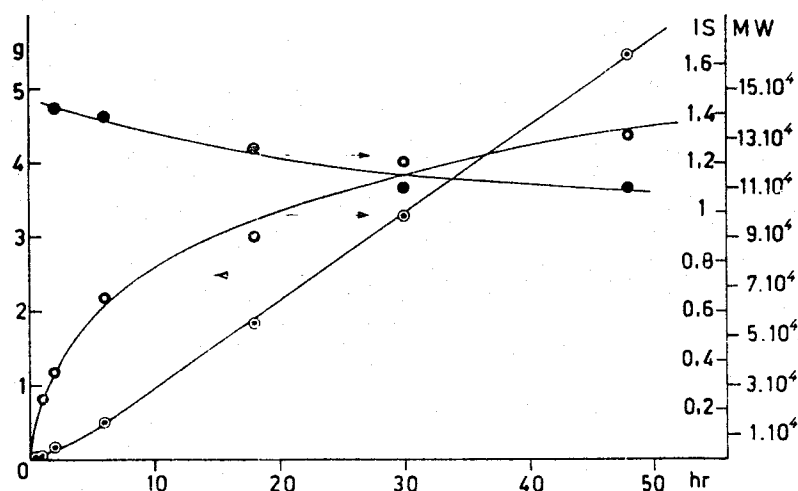


Fig. 1. Behavior of the catalytic system $VCl_4-Al(C_2H_5)_2Cl$ ($Al/V = 2$): (\odot) polymer yield, (\circ) MW , (\bullet) IS. For experimental conditions see Table I.

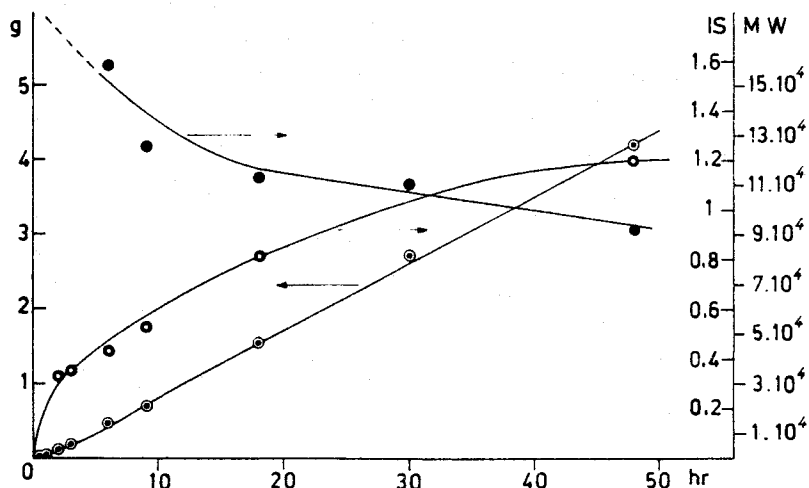


Fig. 2. Behavior of the catalytic system $VCl_4-Al(C_2H_5)_2Cl$ ($Al/V = 5$): (\odot) polymer yield, (\circ) MW , (\bullet) IS. For experimental conditions see Table I.

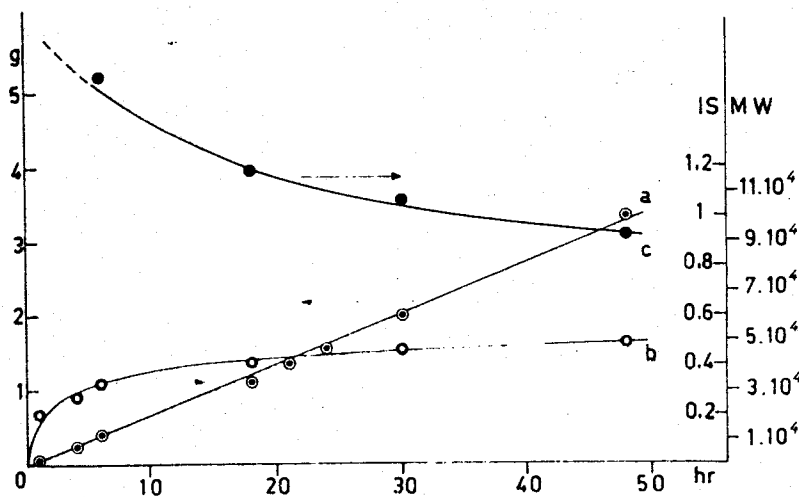


Fig. 3. Behavior of the catalytic system $VCl_4-Al(C_2H_5)_2Cl$. ($Al/V = 30$): (\odot) polymer yield, (\circ) MW , (\bullet) IS . For experimental conditions see Table I.

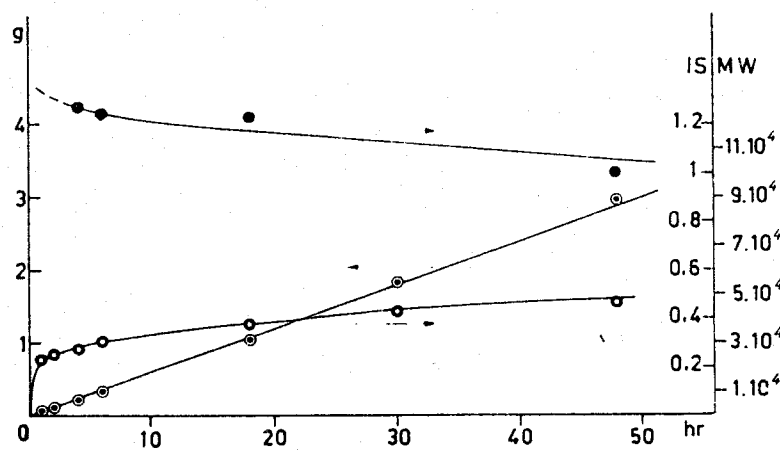


Fig. 4. Behavior of the catalytic system $VCl_4-Al(C_2H_5)_2Cl$. ($Al/V = 40$): (\odot) polymer yield, (\circ) MW , (\bullet) IS . For experimental conditions see Table I.

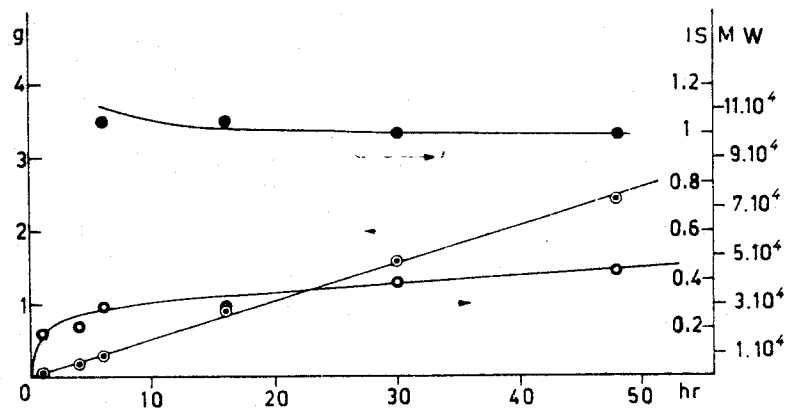


Fig. 5. Behavior of the catalytic system $VCl_4-Al(C_2H_5)_2Cl$. ($Al/V = 50$): (\odot) polymer yield, (\circ) MW , (\bullet) IS . For experimental conditions see Table I.

Molecular Weight. The molecular weight of the polymers obtained from the same series of polymerizations increases with the increase in the polymerization time for a considerable extent. This indicates that the

TABLE I
Polymerization Runs Quoted in Figures 1, 2, 3, 4, and 5

Fig.	$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, moles	Time, hr.	Polymer yield, g.	MW	$IS \times 10^2$
1	1×10^{-3}	30 min.	0.016	—	—
	1×10^{-3}	1	0.03	24,000	—
	1×10^{-3}	2	0.154	35,000	142
	1×10^{-3}	6	0.500	65,000	139
	1×10^{-3}	18	1.860	90,000	128
	1×10^{-3}	30	3.270	120,000	111
	1×10^{-3}	48	5.444	131,000	110
2	2.5×10^{-3}	30 min.	0.019	—	—
	2.5×10^{-3}	1	0.053	—	—
	2.5×10^{-3}	2	0.130	33,000	—
	2.5×10^{-3}	3	0.202	35,000	—
	2.5×10^{-3}	6	0.480	42,000	158
	2.5×10^{-3}	9	0.707	52,000	125
	2.5×10^{-3}	18	1.572	81,000	113
	2.5×10^{-3}	30	2.721	—	110
3	2.5×10^{-3}	48	4.168	120,000	92
	15×10^{-3}	1	0.061	23,500	—
	15×10^{-3}	4	0.243	27,500	—
	15×10^{-3}	6	0.398	33,000	156
	15×10^{-3}	18	1.089	41,000	118
	15×10^{-3}	21	1.352	—	—
	15×10^{-3}	24	1.369	—	—
	15×10^{-3}	30	1.992	46,000	106
4	15×10^{-3}	48	3.330	48,500	93
	20×10^{-3}	1	0.066	23,000	—
	20×10^{-3}	2	0.110	25,000	—
	20×10^{-3}	4	0.210	27,000	127
	20×10^{-3}	6	0.342	30,000	124
	20×10^{-3}	18	1.029	37,000	123
	20×10^{-3}	30	1.835	42,000	—
5	20×10^{-3}	48	2.948	46,000	100
	25×10^{-3}	1	0.071	18,750	—
	25×10^{-3}	4	0.185	21,000	—
	25×10^{-3}	6	0.295	29,000	115
	25×10^{-3}	18	0.906	29,000	115
	25×10^{-3}	30	1.574	38,000	100
	25×10^{-3}	48	2.433	44,000	100

The runs reported were performed at -78°C . with VCl_4 0.5×10^{-3} moles; $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ variable amount; *n*-heptane 50 ml.; C_3H_6 40 g.

mean lifetime of the macromolecules is fairly high. However, the concentration of the catalytic complexes, and the chain propagation rate can be determined only as order of magnitude from MW measurements;

in fact, the viscosimetric-average molecular weights of the polymers do not satisfy the relationship:

$$M/W_n = \chi MW = \frac{k_p C^* m t}{C^* + \sum_i k_{t,i} C^* x_i^\alpha}$$

where MW is the viscosimetric-average molecular weight, χ is a constant of proportionality, MW_n is the number-average molecular weight, C^* is the concentration of the catalytic complexes, k_p is the chain propagation constant, m is the monomer concentration, α is a suitable exponent, $k_{t,i}$ is the constant of chain transfer or termination, t is the reaction time, and x_i is the concentration of a generic chain transfer or termination agent.

The above relationship is not even satisfied when the induction period is very short in comparison with the polymerization time (see, e.g., Fig. 5), and the concentration of the catalytic complexes can be considered as practically constant from the start.

Steric Regularity of the Polymer Obtained. The IS² (see Experimental Section) of the polymers obtained from a given series of polymerizations decreases with the increase of the time until reaching an almost constant value. Since the IS is an infrared measurement of syndiotactic-type crystallinity of the polymer and not only of its steric regularity,² the reasons for this behavior can be attributed either to an actual decrease in steric regularity or (taking into account the increase in molecular weights with the increase in the polymerization time) to the greater difficulty met by higher molecular weight polymers to crystallize.

The latter hypothesis seems more probable; in fact, as shown in Figures 1-5, when varying the reaction time, a decrease in the IS always corresponds to an increase in MW ; on the contrary when the molecular weight becomes independent of the reaction time, the IS also becomes constant.

Concentration of VCl_4

The amount of polymer obtained at a constant time of reaction from a same series of polymerizations is a linear function of the amount of VCl_4 introduced in the system (Fig. 6) when all other variables are kept constant and the Al/V ratio is fairly high. The amount of VCl_4 introduced does not influence appreciably either the molecular weights or the IS of the polymers, at least within the concentration variations experimented by us. By extrapolating the straight line polymer obtained vs. VCl_4 present in the system (Fig. 6), it is observed that the yield is practically equal to zero for VCl_4 concentrations below $1 \cdot 10^{-3}$ moles/l. This can depend on secondary reactions of VCl_4 or on impurities.

Concentration of $Al(C_2H_5)_2Cl$; Al/V Ratio

When increasing the amount of $Al(C_2H_5)_2Cl$ in the catalytic system beyond a certain limit, all other conditions being the same, a decrease is

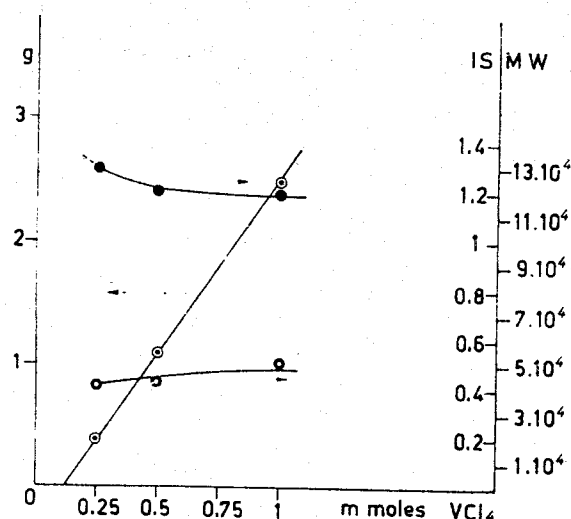


Fig. 6. Order of reaction with respect to VCl_4 . The runs reported were carried out at -78°C . with *n*-heptane (50 ml.); C_2H_6 (40 g.); VCl_4 (variable); $\text{Al}(\text{C}_2\text{H}_5)_3$ (15×10^{-3} moles); reaction time: 18 hr. (⊙) Polymer yield, (○) *MW*, (●) *IS*.

observed in the polymer yield, in the *MW*, and in the *IS* (Figs. 1–5) of the polymers obtained at constant polymerization times. The influence exerted by this variable can hardly be evaluated.

First of all, in fact, by treating VCl_4 with $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ there is formation of $\text{AlC}_2\text{H}_5\text{Cl}_2$ in foreseen amounts. Second, the influence exerted by the $\text{AlC}_2\text{H}_5\text{Cl}_2$ formed in the system on the propagation rate and on stereospecificity is unknown. Finally, we already described the difficulties met when trying to measure the propagation rates. These facts depend on the complexity of the reaction of formation of the catalytic complexes.

Anyhow, the decrease in the *IS* is not certainly due in this case to the difficulty in crystallization of the polymers; in fact, the higher *IS* are observed in the higher molecular weight polymers.

Therefore, two non-alternative hypotheses are possible: (1) the polymers obtained in the presence of higher amounts of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, on the whole, contain a greater number of steric irregularities. (2) Steric irregularities are distributed in a more random way along the macromolecules obtained in the presence of higher concentrations of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$.

It seems reasonable to explain the behavior observed by the hypothesis that VCl_2R can yield catalytic complexes having a different stereospecificity depending on its complexation state.

The uniform steric regularity of the macromolecules contained in the crude polymers (see a next section) can indicate that the catalytic complexes can lose and regain their stereospecificity during the growth of the same macromolecule bound to them.

Additions of $\text{Al}(\text{C}_2\text{H}_5)_3$ and $\text{AlC}_2\text{H}_5\text{Cl}_2$

The influence of the organometallic compound, considered above, can become more relevant when variable amount of $\text{Al}(\text{C}_2\text{H}_5)_3$ or $\text{AlC}_2\text{H}_5\text{Cl}_2$ are added to the VCl_4 – $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ catalytic system.

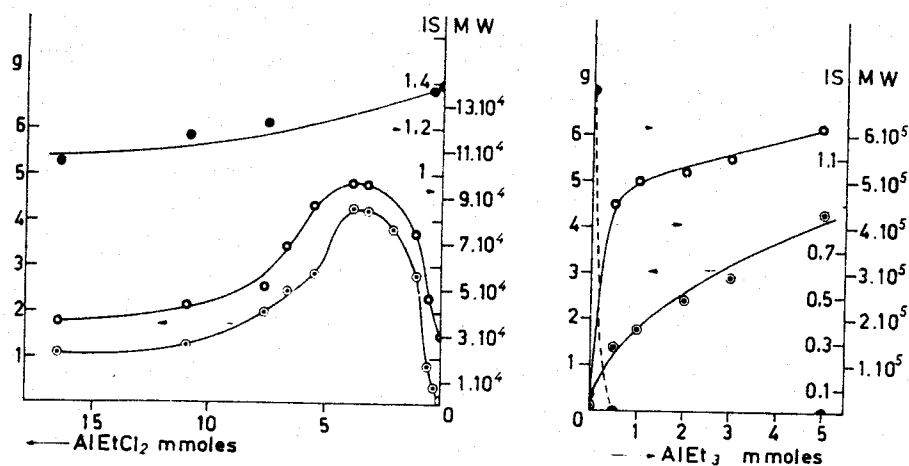


Fig. 7. Behavior of the catalytic system $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ with $\text{AlC}_2\text{H}_5\text{Cl}_2$ (a) or $\text{Al}(\text{C}_2\text{H}_5)_3$ (b): (○) polymer yield, (○) MW , (●) IS. For experimental conditions see Table II.

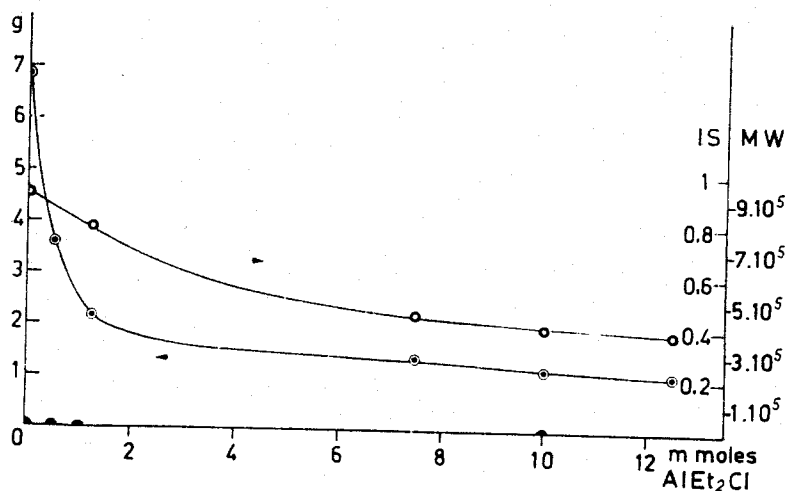


Fig. 8. Effect of addition of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ to the $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_3$ catalytic system: (○) polymer yield, (○) MW , (●) IS. The polymerization runs were performed at -78°C . with *n*-heptane (75 ml.); C_3H_6 (20 g.); VCl_4 (0.25×10^{-3} moles); $\text{Al}(\text{C}_2\text{H}_5)_3$ (0.5×10^{-3} moles); $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (variable); reaction time: 6 hr.

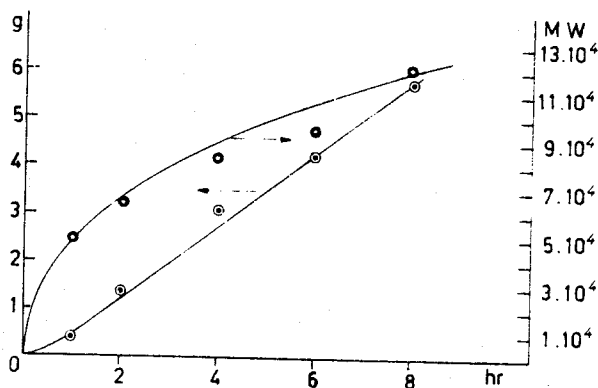


Fig. 9. Behavior of the catalytic system $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl-AlC}_2\text{H}_5\text{Cl}_2$: (○) polymer yield, (○) MW . For experimental conditions see Table II.

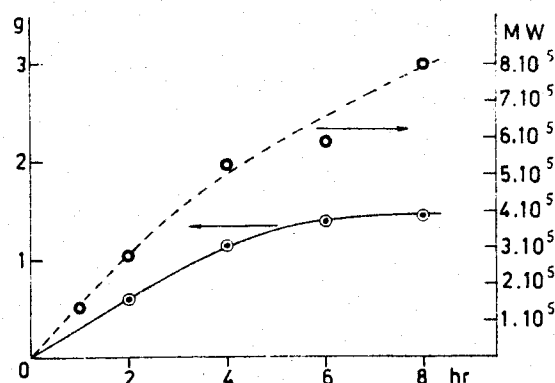


Fig. 10. Behavior of the catalytic system $\text{VCl}_4\text{-Al(C}_2\text{H}_5)_2\text{Cl-Al(C}_2\text{H}_5)_3$: (\odot) polymer yield, (\circ) MW . For experimental conditions see Table II.

Figures 7a and 7b show the polymer yields, the viscosimetric-average molecular weights, and the IS of the polymers obtained from a series of polymerizations. It can be observed that the IS is the highest when neither $\text{Al(C}_2\text{H}_5)_3$ nor $\text{Al(C}_2\text{H}_5)_2\text{Cl}$ is added to the catalytic system. By addition of $\text{Al(C}_2\text{H}_5)_3$ (Fig. 7b), the index of syndiotacticity decreases rapidly and becomes equal zero already when $\text{Al(C}_2\text{H}_5)_3/\text{VCl}_4 = 2$.

TABLE II
Experimental Conditions for the Polymerization Runs Reported in Figures 7a and 7b

	$\text{Al(C}_2\text{H}_5)_2\text{Cl}_2$, moles	$\text{Al(C}_2\text{H}_5)_3$, moles	Polymer yield, g.	MW	$\text{IS} \times 10^2$
Fig. 7a	0	0	0.15	31,000	140
	0.1×10^{-3}	0	0.40	—	—
	0.55×10^{-3}	0	0.85	45,000	137
	1.1×10^{-3}	0	2.89	75,000	—
	2.2×10^{-3}	0	3.86	—	—
	3.3×10^{-3}	0	4.20	95,000	—
	3.9×10^{-3}	0	4.23	95,000	—
	5.5×10^{-3}	0	2.82	87,000	—
	6.7×10^{-3}	0	2.45	69,000	120
	7.7×10^{-3}	0	1.76	47,000	—
	11.0×10^{-3}	0	1.28	43,000	116
Fig. 7b	16.6×10^{-3}	0	1.10	36,000	105
	0	0	0.15	31,000	140
	0	0.5×10^{-3} ^a	1.40	450,000	0
	0	1×10^{-3}	1.76	500,000	—
	0	2×10^{-3}	2.37	520,000	—
	0	3×10^{-3}	2.73	550,000	—
	0	5×10^{-3}	4.31	620,000	0

The polymerization runs were performed at -78°C . with *n*-heptane 75 ml.; VCl_4 0.25×10^{-3} mole; $\text{Al(C}_2\text{H}_5)_2\text{Cl}$ 7.5×10^{-3} moles; C_3H_6 20 g.; $\text{Al(C}_2\text{H}_5)_2\text{Cl}_2$ variable amount; $\text{Al(C}_2\text{H}_5)_3$ variable amount; polymerization time: 6 hr.

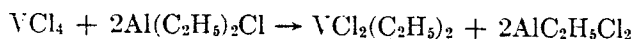
^a These runs were performed at different reaction times and correspond to the runs reported in Figures 9 and 10.

On the contrary, if $\text{AlC}_2\text{H}_5\text{Cl}_2$ is added (Fig. 7a), the IS decreases slowly; this is due both to the increase in viscosimetric-average molecular weight (for small additions of $\text{AlC}_2\text{H}_5\text{Cl}_2$) and to an actual decrease in the steric regularity (at least for high additions of $\text{AlC}_2\text{H}_5\text{Cl}_2$).

Both polymer yields and molecular weights are the lowest when neither $\text{Al}(\text{C}_2\text{H}_5)_3$ nor $\text{AlC}_2\text{H}_5\text{Cl}_2$ is introduced in the catalytic system and increase by addition of $\text{Al}(\text{C}_2\text{H}_5)_3$. When adding $\text{AlC}_2\text{H}_5\text{Cl}_2$, there is an increase in the polymer yield and MW until a maximum for an addition of 4×10^{-3} moles of $\text{AlC}_2\text{H}_5\text{Cl}_2$ for 0.25×10^{-3} moles of VCl_4 and 7.5×10^{-3} moles of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. If the addition of $\text{AlC}_2\text{H}_5\text{Cl}_2$ exceeds the above value, both the polymer yield and MW decrease gradually.

An agreeing behavior is shown by the polymerization runs carried out by keeping the amount of $\text{Al}(\text{C}_2\text{H}_5)_3$ at a constant value ($\text{Al}(\text{C}_2\text{H}_5)_3/\text{VCl}_4 = 2$), and by adding increasing amounts of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (Fig. 8). In this case, the IS is always equal to 0, both molecular weights and yields decrease.

Figures 9 and 10 show the results obtained from polymerizations carried out for variable lengths of time, in the presence of such catalytic systems, which we shall call "mixed." It can be observed that, also in these cases, the polymerization yield is almost linear with respect to time and the mean lifetime of the macromolecules is still high. It is interesting to notice that when operating in *n*-heptane, by adding $\text{AlC}_2\text{H}_5\text{Cl}_2$, the polymer crystallinity does not disappear. On the contrary, crystallinity disappears ($\text{IS} = 0$) when $\text{Al}(\text{C}_2\text{H}_5)_3$ is added in the ratio $\text{Al}(\text{C}_2\text{H}_5)_3/\text{VCl}_4 = 2$. This value suggests that stereospecificity disappears or greatly decrease when $\text{AlC}_2\text{H}_5\text{Cl}_2$ does not form in the system by the reaction:



The behavior of the molecular weights vs. the reaction time in the quoted runs shows that with respect to the systems prepared from only $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, the chain propagation and the transfer or termination constants are varied, although exact numerical data can hardly be obtained.

These data also support our opinion that the particular organometallic compound of aluminum, present in the system, influences the complexation state of VCl_2R , thus determining the steric course of the polymerization.

Alkyl Radical

Figure 11 shows the data obtained by us when preparing the catalytic system with $\text{Al}(i\text{-C}_4\text{H}_9)_2\text{Cl}$, instead of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. The considerable differences observed in the polymer yield, MW , and IS indicate that the catalytic complexes can be hardly monometallic.

Concentration of the Monomer

Figures 12 and 13 show the data obtained from a series of polymerizations done with variable monomer concentrations. It can be observed

* In fact, in this case only a decrease in steric regularity can explain the decrease in IS when MW decreases.

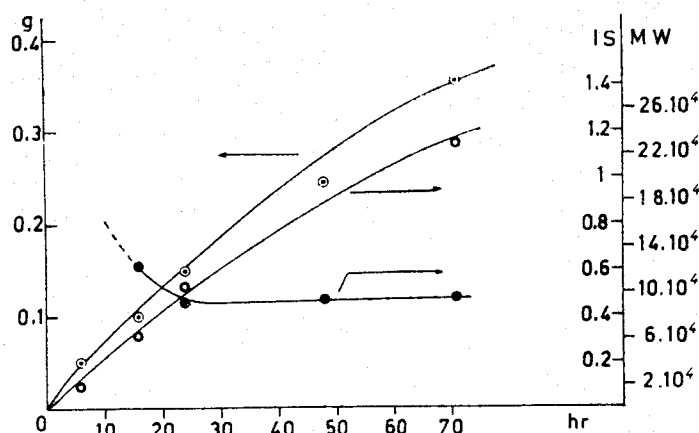


Fig. 11. Behavior of the catalytic system $\text{VCl}_4\text{--Al}(\text{iC}_4\text{H}_9)_2\text{Cl}$: (\odot) polymer yield, (\circ) MW, (\bullet) IS. The polymerization runs were performed at -78°C . with *n*-heptane (50 ml.); C_3H_6 (40 g.); VCl_4 (0.5×10^{-3} moles); $\text{Al}(\text{i-C}_4\text{H}_9)_2\text{Cl}$ (2.5×10^{-3} moles); polymerization time: variable.

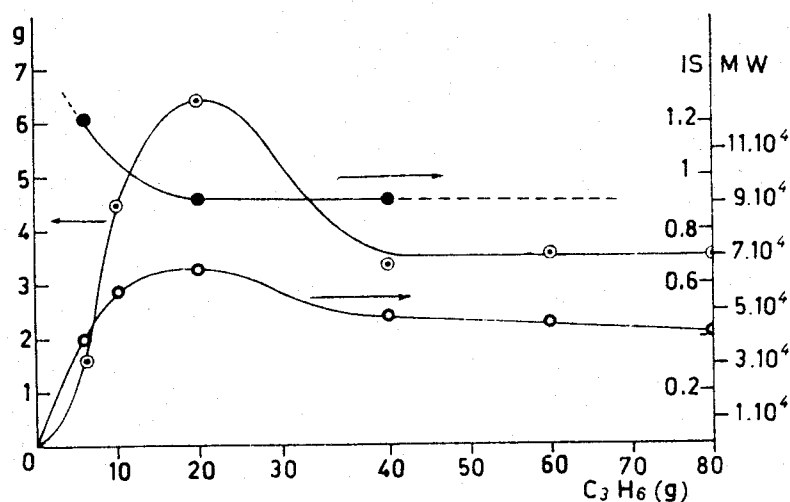


Fig. 12. Behavior of the catalytic system $\text{VCl}_4\text{--Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ at different monomer concentrations: (\odot) polymer yield, (\circ) MW, (\bullet) IS. For experimental conditions see Table III.

that the polymerization yield depends on the monomer concentration for sufficiently long times (the concentration of the reagents being nearly constant during the polymerization), in a quite complex manner. The presence of a maximum of polymer yield and of molecular weight probably indicates that the monomer exert a considerable influence on the catalyst formation or decomposition reactions. However, Figure 13 shows that molecular weights during the polymerization increase more slowly when the monomer concentration is lower, although in this case, higher final values are attained.

Influence of the Solvent

A comparison is made in Figure 14 between two series of polymerization runs carried out in the presence of *n*-heptane and of toluene, respectively.

TABLE III
Experimental Conditions of Polymerization Runs Reported in
Figures 12 and 13

	C ₃ H ₆ , g.	<i>n</i> -Heptane, ml.	Polymer yield, g.	<i>MW</i>	IS × 10 ²
Fig. 12	6.5	93	1.60	40,000	122
	10	87	4.50	58,000	—
	20 ^a	75	6.40	64,000	93
	40 ^a	50	3.35	48,000	91
	60	25	3.50	45,000	—
	80 ^a	—	3.50	42,000	—

The polymerization runs were performed at -78°C . with different amounts of *n*-heptane and C₃H₆ (almost constant volume); VCl₄ 0.5×10^{-3} moles; Al(C₂H₅)₂Cl 15×10^{-3} moles; time of polymerization: 48 hr.

^a These runs were also performed at different reaction times (Fig. 13).

The polymerization time being the same, higher yields are obtained with toluene rather than with *n*-heptane.

MW are initially higher when using toluene, but for high polymerization times, they tend to the same value. The polymers, even if with the same molecular weight, show lower IS in comparison with those obtained when operating in *n*-heptane.

This behavior indicates that the propagation constant and the chain transfer or termination constants practically increase in a proportional manner when passing to the aromatic solvent. With the increase in the propagation constant, a decrease in stereospecificity is simultaneously observed. These facts suggest that the catalytic complexes are more dissociated in the aromatic solvent and that the most dissociated complex yields, with a higher average propagation constant, polymers with a less regular structure.

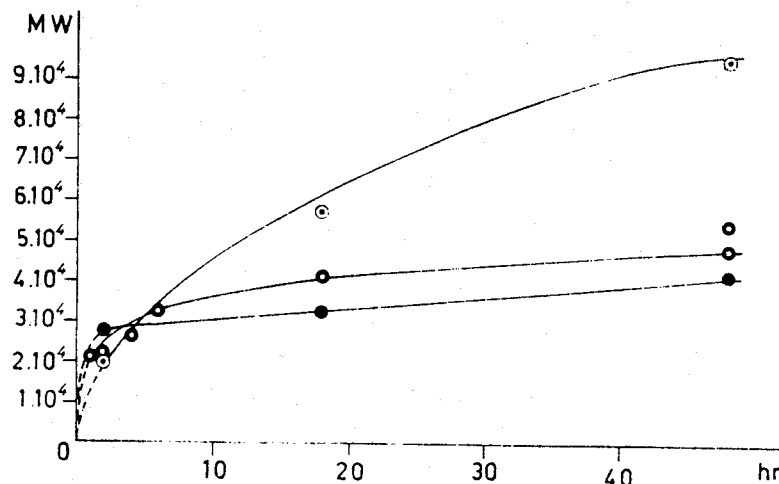


Fig. 13. Variations in *MW* vs. the polymerization time for different monomer concentrations: (○) C₃H₆ = 20 g.; *n*-heptane 75 ml. (○) C₃H₆ = 40 g.; *n*-heptane 50 ml. (●) C₃H₆ = 80 g.; *n*-heptane 0 ml.

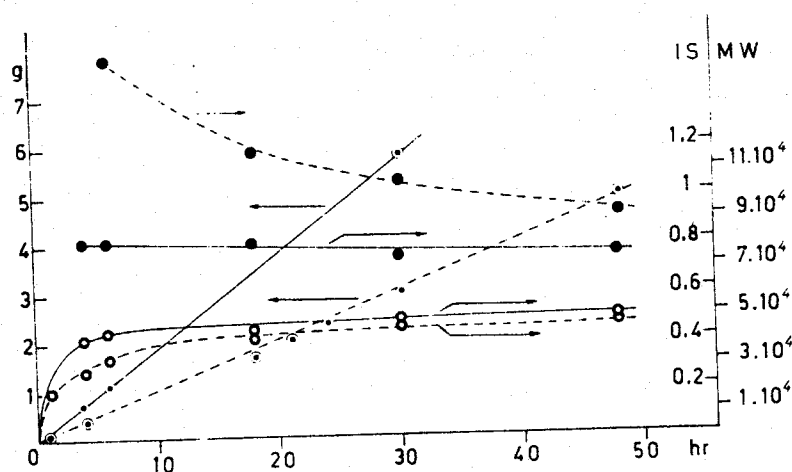


Fig. 14. Comparison between the catalytic systems prepared in toluene (full lines) and in *n*-heptane (dashed lines): (○) polymer yield, (○) *MW*, (●) *IS*. The polymerization runs were performed with *n*-heptane or toluene (50 ml.); C_3H_6 (40 g.); VCl_4 (0.5×10^{-3} moles); $Al(C_2H_5)_2Cl$ (15×10^{-3} moles); polymerization time: variable.

Composition of Polymers

The polymers obtained with the aid of homogeneous catalytic systems based on tri- and tetravalent vanadium, in general, can be scarcely fractionated according to the steric regularity.²

As previously hypothesized, this fact also suggests that the different types of catalytic complexes present can be easily transformed one into the other during the growth of the macromolecules.

With regard to the absolute value of steric purity the NMR analysis done at 100 Mc./sec.³ revealed (contrary to what we previously thought²) that the polymers with a higher index of syndiotacticity are fairly stereoregular. This involves that in these cases the stereospecific catalytic complexes predominate considerably. Sometimes a very low isotactic crystallinity can also be observed by IR analysis of the polymers in the solid state.

TABLE IV
Effect of Addition of $Al(C_2H_5)_2Cl$ to $VCl_4-Al(C_2H_5)_3$ Catalytic System

	$Al(C_2H_5)_2Cl$, moles	Polymer yield, g.	<i>MW</i>	<i>IS</i> $\times 10^2$
Fig. 8	—	6.85	910,000	0
	0.5×10^{-3}	3.60	—	0
	1.25×10^{-3}	2.15	780,000	0
	7.5×10^{-3}	1.40	450,000	—
	10.0×10^{-3}	1.20	400,000	0
	12.5×10^{-3}	1.10	380,000	—

The polymerization runs were performed at $-78^\circ C$. with *n*-heptane 75 ml.; C_3H_6 20 g.; VCl_4 0.25×10^{-3} moles; $Al(C_2H_5)_3$ 0.5×10^{-3} moles; $Al(C_2H_5)_2Cl$ variable; polymerization time: 6 hr.

CONCLUSION

The reported data seem to prove, from a qualitative point of view, the hypothesis that the catalytic complexes are, at least in part, bimetallic. More proving and detailed quantitative deductions will be possible only after completing the study of the different homogeneous catalytic systems; it will be thus possible to distinguish what actually depends on the polymerization from what depends on the catalyst formation reaction and on the presence, in the catalytic system, of components that are extraneous to the catalytic complexes, but can influence their behavior.

EXPERIMENTAL

Reagents Used. VCl_4 was supplied by Montecatini S.p.A. Before being used, it was distilled *in vacuo* and maintained under nitrogen atmosphere.

Organometallic Compounds. Prepared according to literature.^{4,5} Purity of $\text{Al}(\text{C}_2\text{H}_5)_3$, used as such or as intermediate for the preparation of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and of $\text{AlC}_2\text{H}_5\text{Cl}_2$, was controlled by potentiometric analysis.⁶ The $\text{Al}(\text{C}_2\text{H}_5)_3$ used had a minimum content of 95%. Since the polymerization was very sensitive to small additions of $\text{Al}(\text{C}_2\text{H}_5)_3$ or of $\text{AlC}_2\text{H}_5\text{Cl}_2$, the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, prepared by reaction between $\text{Al}(\text{C}_2\text{H}_5)_3$ and AlCl_3 in almost stoichiometric ratios, was corrected by subsequent small additions of $\text{Al}(\text{C}_2\text{H}_5)_3$ or $\text{AlC}_2\text{H}_5\text{Cl}_2$. After every addition, the product was analyzed and a polymerization run was performed.

The product was considered satisfactory when analysis gave a ratio $\text{Al}/\text{Cl} = 1$ (with the usual approximation), and the polymerization rate reached the minimum value and the IS of the polymer obtained was the maximum (Fig. 7).

This conventional choice of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, on the basis of its behavior in the polymerization, was made in order to avoid sharp variations in the catalytic behavior for variations in the Cl/Al ratio at the limit of the analytical accuracy.

On the other hand, as to the unavoidable presence of aluminum alcoholate, attempts were made to minimize it as much as possible; however, its influence on the catalytic system was not still extensively studied.

Solvents. Commercial *n*-heptane and toluene were used after purification by usual treatment with concentrated sulfuric acid. The solvents were subsequently anhydriified by prolonged boiling on Na and then distilled. Further distillation was carried out under nitrogen atmosphere in the presence of small amounts of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (~ 0.3 cc./l.). Solvents were then stored under nitrogen. The behavior of these treated solvents in the polymerization appeared independent of subsequent purifications.

Monomer. Propylene was supplied by Montecatini S.p.A. Before being used, it was purified by stocking it for 48 hr. at least, contacted with NaAlEt_4 . The so-treated monomer behaved in the polymerization as

propylene prepared by dehydration of isopropyl alcohol. The propylene used was over 99% pure (gas chromatographic analysis).

Polymerization Procedure. A description of a polymerization run follows: *n*-heptane (50 cc.) was introduced in a graduated Pyrex glass container, which was put in a Dewar vessel containing methanol and dry ice. It was left to thermostat at -78°C . Propylene (40 g.) was subsequently condensed. After thermostating the vessel again at -78°C ., VCl_4 (0.5×10^{-3} moles) and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (15×10^{-3} moles) were pipetted into it under nitrogen. The reagents were well mixed by stirring with the pipet. The reaction mixture was left to stand at -78°C . for 18 hr. Then the polymerization was stopped by adding HCl acidulated methanol (200 cc.), thermostated at -78°C . The polymer was subsequently coagulated, repeatedly washed with methanol, dried *in vacuo* at 50°C ., and weighed. Thus 1.1 g. were obtained, having $MW = 41,000$ and an $IS = 1.2$.

In the case of mixed catalytic systems, $\text{Al}(\text{C}_2\text{H}_5)_3$ or $\text{AlC}_2\text{H}_5\text{Cl}_2$ were premixed with $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, before being added to the other reagents.

Viscosimetric Molecular Weight. The viscosimetric-average molecular weights of the polymers were performed in tetralin at 135°C .⁷

IS Determination. The IS were determined by IR analysis on polymer laminae and annealed at 100°C . for 12 hr.² See also reference 2 for a definition of IS.

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Résumé

Certain résultats sur le comportement cinétique du système catalytique $\text{VCl}_4\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (stéréospécifique aux basses températures) dans la polymérisation du polypropylène en polymère syndiotactique sont rapportés. L'effet de la durée de réaction a été étudié de même que celui de la concentration en VCl_4 , en $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ et de la concentration en monomère sur la vitesse de polymérisation, sur le poids moléculaire et sur le taux de syndiotacticité des polymères obtenus. Les résultats rapportés sont discutés sur la base d'hypothèses précédemment présentées concernant la nature des complexes catalytiques et le mécanisme de polymérisation.

Zusammenfassung

Einige Ergebnisse für das kinetische Verhalten des bei tiefen Temperaturen für die Polymerisation von Propylen zu einem syndiotaktischen Polymeren stereospezifischen Katalysatorsystems $VCl_4-Al(C_2H_5)_2Cl$ werden mitgeteilt. Der Einfluss der Reaktionsdauer und der Konzentration von VCl_4 , $Al(C_2H_5)_2Cl$ und Monomerem auf Polymerisationsgeschwindigkeit, Molekulargewicht und Syndiotaktizitätsindex des erhaltenen Polymeren wurde untersucht. Die Ergebnisse werden auf Grundlage der früher über die Natur des katalytischen Komplexes und des Polymerisationsmechanismus entwickelten Hypothesen diskutiert.