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SUMMARY:

Homogeneous catalytic systems for the polymerization of propylene both to syndiotactic and amorphous polymers, based on soluble vanadium compounds and organometallic compounds of aluminum, were investigated by EPR analysis at different temperatures. It was shown that the vanadium in the catalytic complex has a valence state of 3.

ZUSAMMENFASSUNG:

An homogenen Katalysatorsystemen für die Polymerisation von Propylen zu syndiotaktischen oder amorphen Polymeren, hergestellt aus löslichen Vanadium-Salzen und metallorganischen Verbindungen des Aluminiums, wurden bei verschiedenen Temperaturen EPR-Untersuchungen durchgeführt. Es wurde geschlossen, daß das Vanadium in diesen Katalysatorkomplexen im 3-wertigen Zustand vorliegt.

1. *Introduction*

Homogeneous catalytic systems for the homopolymerization of α-olefins and their copolymerization with ethylene can be obtained in a hydrocarbon medium by reaction of several vanadium compounds with a valence number of 3 or higher than 3 and suitable organometallic compounds, either halogenated or not, of the 3 first groups of the periodic system.

A necessary condition for the occurrence of catalytic activity is that at least one of the components of the catalytic system (either the vanadium compound or the organometallic compound) contains at least one halogen atom[1,2].

Among the most typical catalytic systems the following can be mentioned: $VCl_4-Al(C_2H_5)_3$, $VCl_4-Al(C_2H_5)_2Cl$, $VCl_4-Al(C_2H_5)_2Cl$-anisol, $VA_3-Al(C_2H_5)_2Cl$ (A = acetylacetonate).

All the catalytic systems quoted have a low thermal stability[3]; *e.g.*, if they are maintained at room temperature, they show, already after a few minutes, a very reduced or no catalytic activity (Tab. 1).

On the contrary, their activity is maintained for a fairly long time if they are kept at low temperature (*e.g.*, at −78 °C.). Likewise, their catalytic activity during the polymerization remains unaltered for long times only at low temperatures[2].

With regard to the homopolymerization of propylene, the above mentioned catalytic systems allow to prepare either essentially amorphous polypropylene or, in the case of the last three, by choosing suitable operating conditions, syndiotactic polypropylene having a high steric regularity[3].

The purpose of this paper is to identify the actual valence state of vanadium in the catalytic complexes from EPR examination of the various catalytic systems, taking into account polymerization and copolymerization data, which are known either from the literature[2,3] or in our possession.

The interest of this paper is due to the fact that it is stated in literature[4] and in particular in patent literature[5] that the catalytic activity is connected with the presence of vanadium in a lower valence state than 3, which is in contrast with other experimental results[6].

2. *Results*

2.1. *EPR Analysis*

2.1.1. Examination of the Single Vanadium Compounds and of Aluminum Alkyls

If examined alone, no single component of the various catalytic systems gives rise to EPR signals, either owing to the absence of paramagnetic ions, or owing to the too high examination temperature as in the case of VA_3 and in general of all the trivalent vanadium compounds[7].

VCl_4 in hydrocarbon solution does not give rise to detectable EPR signals (at least above −78 °C.), not even in the presence of the amounts of anisol usually employed in the preparation of the catalytic system VCl_4–AlR_2Cl-anisol, while its spectrum is similar to that of the VO^{++} ion[8] in the presence of other LEWIS bases, such as tetrahydrofuran.

On the other hand, V^{II} compounds can be easily detected by EPR analysis, both in the solid state such as crystalline VCl_2 (Fig. 1), and in hydrocarbon solution, such as the reaction products of VA_3 with $Al(C_2H_5)_3$ at room temperature, observed by us in toluene solution (Fig. 2) or as those already described by SCIULIDYN[9] as $VCl_2 \cdot 2\,Al(C_2H_5)_2Cl$.

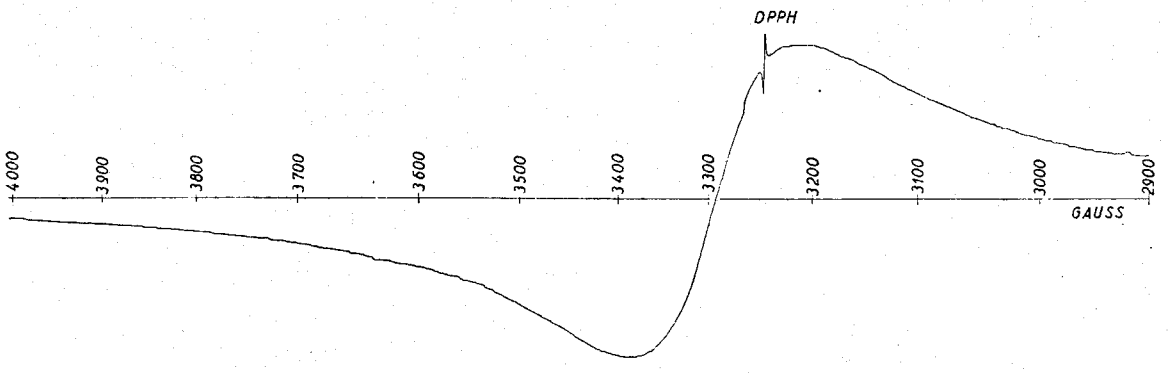

Fig. 1. EPR spectrum of solid VCl_2; DPPH = α,α-diphenyl-β-picrylhydrazyl

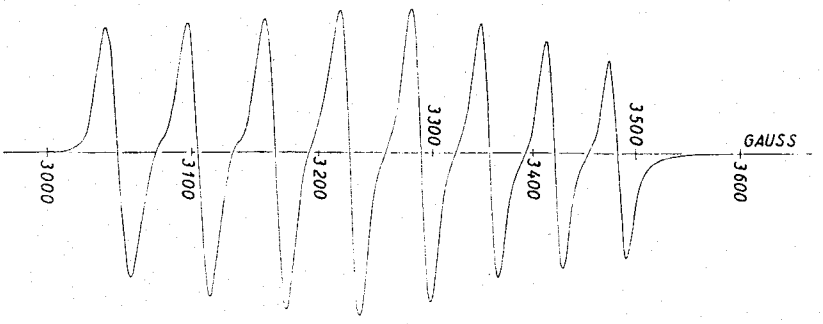

Fig. 2. EPR spectrum of VA_3–$Al(C_2H_5)_3$ in toluene solution

2.1.2. Examination of the Catalytic Systems

The various catalytic systems were prepared by us at −78 °C. and examined both at −78 °C. and subsequently at room temperature, unless otherwise stated. This method allowed us to distinguish the reaction products between vanadium compounds and organometallic compounds of aluminum that are inactive in the polymerization from those actually active.

a) VA_3–$Al(C_2H_5)_2Cl$ System

The sample examined was prepared by reacting $0.5 \cdot 10^{-3}$ moles of VA_3 with $15 \cdot 10^{-3}$ moles $Al(C_2H_5)_2Cl$ at −78 °C. in 100 ml. of anhydrous toluene. The EPR analysis was performed twice on a sample of 0.4–0.5 ml. at −78 °C., about 15 min. and 3 hrs. after its preparation and subsequently on the sample rapidly heated to room temperature.

The catalytic system does not show any characteristic EPR signal soon after its preparation nor after being maintained for 3 hrs. at −78 °C. The sample re-examined soon after heating to room temperature shows a spectrum identical with that of solid VCl_2 (Fig. 3, *cf.*, Fig. 1).

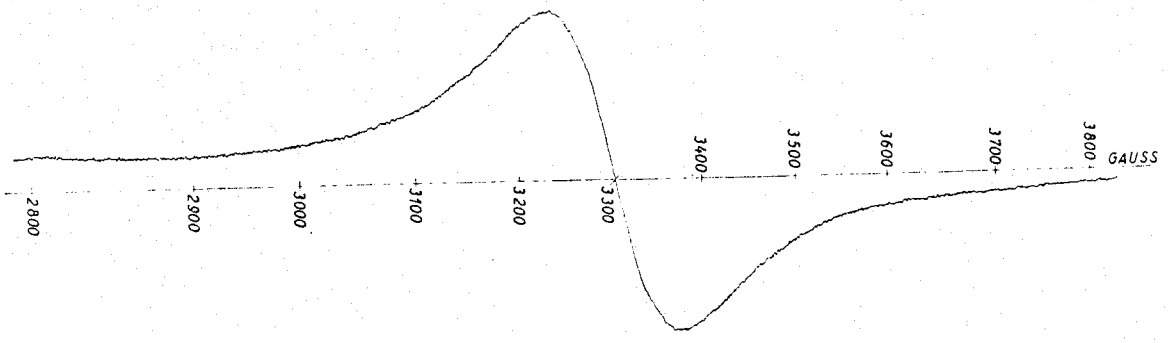

Fig. 3. EPR spectrum of thermal decomposition products of the catalytic system VA_3–$Al(C_2H_5)_2Cl$

b) VCl_4–$Al(C_2H_5)_2Cl$ and VCl_4-anisol–$Al(C_2H_5)_2Cl$ Systems

These samples have been prepared and observed under the conditions reported above. Also in this case the catalytic systems do not give rise to any detectable EPR signal, both 15 min. after their preparation, and after being maintained for 4 hrs. at −78 °C. However, when examined soon after being heated to room temperature, they originate a spectrum identical with that of solid VCl_2.

c) VCl_4–$Al(C_2H_5)_3$ System

The catalytic system VCl_4–$Al(C_2H_5)_3$ was prepared by treating $0.5 \cdot 10^{-3}$ moles of VCl_4 with $2 \cdot 10^{-3}$ moles of $Al(C_2H_5)_3$ in 100 ml. of anhydrous toluene at −78 °C. Also in this case, the catalytic system does not give rise to detectable EPR signals at −78 °C. By observing the sample again soon after heating at room temperature, a spectrum identical with that of solid VCl_2 is observed.

On the other hand, a system of 8 lines superposed on the spectrum of solid VCl_2, can be observed (Fig. 4a) with high sweep, from a sample

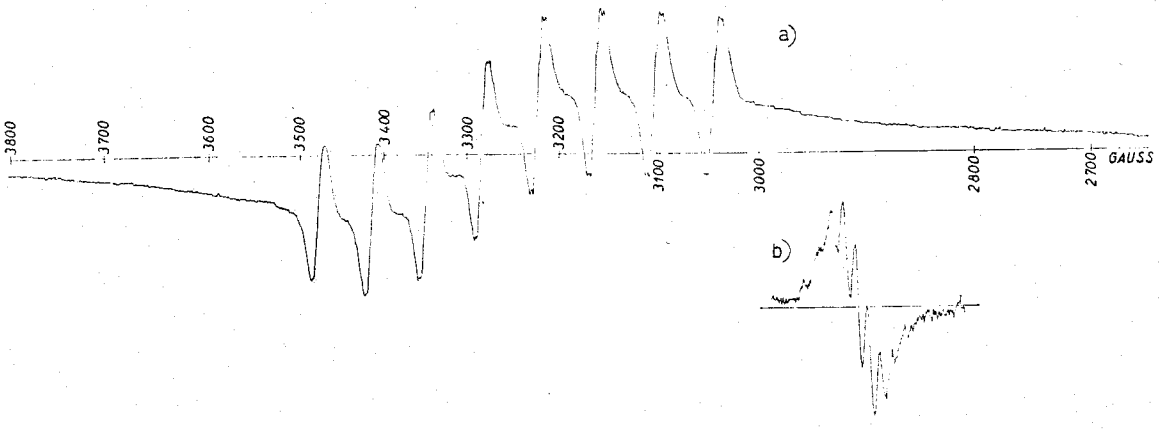

Fig. 4. EPR spectrum of thermal decomposition products of the catalytic system VCl_4–$Al(C_2H_5)_3$

obtained by treating VCl_4 with $Al(C_2H_5)_3$ directly at room temperature, or from the sample prepared in the cold, observed after a few days during which it was maintained at room temperature. The 8 bands are spaced by about 60 gauss with total length of the spectrum of about 500 gauss (Fig. 4a). With lower sweep a fine structure is observed on the 8 lines (Fig. 4b) already described by SCIULYDIN [9]; he attributed this spectrum to the presence of a $VCl_2 \cdot 2\,Al(C_2H_5)_2Cl$ complex. The spectrum of the solid VCl_2 is not observed in such conditions, being too flattened. The 8 lines do not disappear even if the sample is kept at room temperature for a few weeks.

EPR spectra of these catalytic systems have been observed also in the presence of monomer, by preparation of the samples in a medium consisting of a mixture of liquified propylene (40 g.) and of toluene (50 ml.); their behaviour was analogous to that of the corresponding samples prepared in the absence of monomer. Likewise, the results do not change qualitatively using an aliphatic hydrocarbon (*n*-heptane) instead of toluene as reaction medium.

2.2. *Kinetic Behaviour of the Catalytic Systems in the Polymerization of Propylene*

The kinetic behaviour of homogeneous catalytic systems based on V in the polymerization of propylene will be reported in subsequent papers. Therefore, only a few data are considered here.

Table 1 gives a comparison of the activity of the various catalytic systems in the polymerization of propylene. In particular it can be observed that all the catalytic systems considered are stable only at low

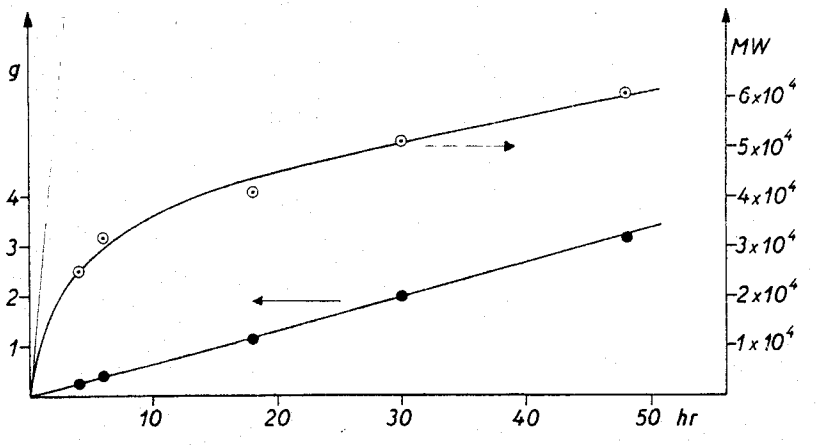

Fig. 5. Behaviour of the catalytic system VCl_4–$Al(C_2H_5)_2Cl$ in the polymerization of propylene. Polymerization conditions: C_3H_6: 40 g.; VCl_4: $0.5 \cdot 10^{-3}$ moles; $Al(C_2H_5)_2Cl$: $15 \cdot 10^{-3}$ moles; *n*-heptane: 50 ml.; −78 °C.

Table 1. Activity of various homogeneous catalytic systems based on vanadium compounds (prepared at −78 and +20 °C.) in the homopolymerization of propylene[a)]

No.	Vanadium compound	Organometallic compound of Al	Anisol (moles $\cdot 10^3$)	Al/V (moles)	Solvent	Prepar. temp. of catalyst (°C.)	Polymeriz. time (hrs.)	Polymer obtained (g.)	Crystallinity of polymers IS[b)]
1	VCl_4	$Al(C_2H_5)_2Cl$	0	30	*n*-heptane	−78	8	0.5	1.1
2[c)]	VCl_4	$Al(C_2H_5)_2Cl$	0	30	*n*-heptane	−78	8	0.6	1.1
3	VCl_4	$Al(C_2H_5)_2Cl$	0	30	*n*-heptane	+20	8	traces	—
4	VCl_4	$Al(C_2H_5)_2Cl$	0.5	30	*n*-heptane	−78	4	0.6	2.4
5	VCl_4	$Al(C_2H_5)_2Cl$	0.5	30	*n*-heptane	+20	8	traces	—
6	VCl_4	$Al(C_2H_5)_3$	0	8	toluene	−78	1/3	8	0
7	VCl_4	$Al(C_2H_5)_3$	0	8	toluene	+20	8	0.08	0
8	VA_3	$Al(C_2H_5)_2Cl$	0	30	toluene	−78	8	2.2	n.d.
9	VA_3	$Al(C_2H_5)_2Cl$	0	30	toluene	+20	8	traces	—

a) Polymerization runs were performed at −78 °C., with $0.5 \cdot 10^{-3}$ moles VCl_4 in 50 ml. solvent, 40 g. propylene, without stirring. The catalytic systems prepared at +20 °C. were cooled as rapidly as possible to −78 °C. before introducing monomer. The catalytic systems prepared at −78 °C. (with exception of run 2) were obtained by mixing the reagents in the presence of monomer.

b) The polymers observed do not show the crystallinity of the isotactic type. The IR index of syndiotacticity, (IS), defined in previous paper[3)]is a relative measure of the crystallinity of the polymer. An absolute evaluation of the high steric regularity of some syndiotactic polypropylenes obtained, can be deduced from the NMR spectrum of sample 4, reported in Fig. 6.

c) The catalytic system was prepared in the absence of monomer and maintained for 4 hrs. at −78° C. before use.

temperature (*e.g.*, at −78 °C.). Under the same operating conditions there is practically no activity of the catalytic systems prepared at room temperature.

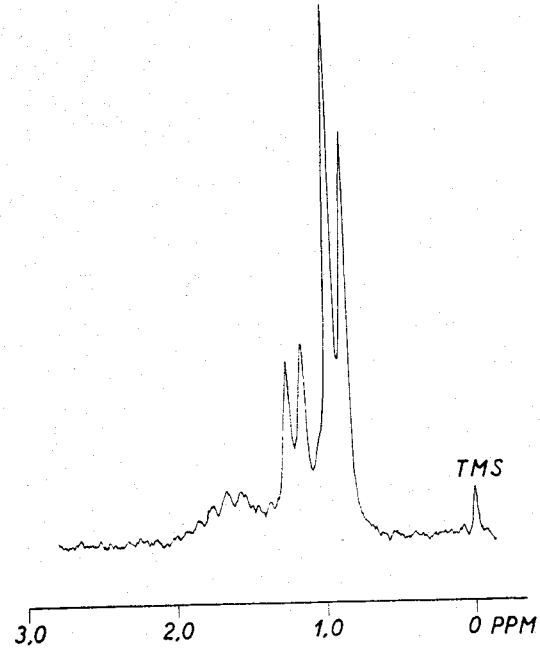

Fig. 6. NMR spectrum of syndiotactic polypropylene (sample 4 of Table 1) obtained on a VARIAN A 60 spectrometer in a 5% solution of *o*-dichlorobenzene with TMS (tetramethylsilane) as internal standard, at 140 °C.

Fig. 5 shows the amounts of polypropylene obtained *vs.* polymerization time and the relating viscosimetric average molecular weights for a series of polymerizations; the catalytic system VCl_4–$Al(C_2H_5)_2Cl$ was used under the same conditions as for examination by EPR.

From the ratio of polymerization rate to propagation rate which can be deduced from Fig. 5 it is possible to obtain the concentration of the active catalytic complexes in the system, at least as order of magnitude. It can be observed that active V constitutes at least *) 0.1–0.5 % of total V present in the system and therefore the concentration of catalytic complexes present in the samples is most probably sufficient to be detectable by EPR examination taking into account sensitivity of the apparatus used (see Exp. part).

*) Neglecting the polydispersity of the molecular weights, but taking into account that the viscosimetric molecular weight is always equal to or larger than the average number M.W., the propagation rate deduced from Fig. 5 (tangent at the origin of the molecular weight-time curve) will be equal or higher than the true rate, and therefore the number of active centres calculated will be equal to or lower than the actual number.

We have other data[10] that allow us to state that also in the remaining catalytic systems of this paper the concentration of the catalytic complexes is not very different.

The data reported in Fig. 5 also show that for such conditions the polymerization rate practically has a constant value, at least for several hours.

2.3. *Colours of the Different Catalytic Systems*

Table 2 reports the colours of the different catalytic systems, as they appear in hydrocarbon solutions of the concentrations indicated. Observations were made on samples of 1–2 cm. thickness, against light at −78 °C. Table 2 also reports, for comparison, the colours of VCl_4 and VA_3 solution.

The purple colour of VCl_4–$Al(C_2H_5)_2Cl$ suggests trivalent V. On the other hand, some complexes of VCl_4 (*e.g.*, VCl_4 in the presence of tetrahydrofuran) show a purple colour. Moreover, the only V^{III} compound which can be thought present in high amounts should be VCl_3, which is insoluble in hydrocarbons. Note that $TiCl_3 \cdot CH_3$, too, in the solid state, shows a very similar colour as $TiCl_3$. This is why we consider the intensities of colours rather than their chromatic coordinates of greater importance.

3. *Discussion*

3.1. *Valence of V in the Catalytic Complexes Active in the Polymerization*

From the data obtained by EPR analysis reported above, it can be observed that bivalent vanadium was not detected in the catalytic systems prepared and investigated at low temperature. On the contrary, after heating, large amounts of bivalent V are detected in the different catalytic systems as solid VCl_2 or as soluble complex $VCl_2 \cdot 2\,Al(C_2H_5)_2Cl$[9]. Accordingly, the activity of the catalytic systems changes from relatively very high values to practically zero. This permits us to exclude bivalent active vanadium in the different catalytic systems.

It is also possible to exclude the presence of tetravalent vanadium in the catalytic complexes, considering that VA_3, in the presence of $Al(C_2H_5)_2Cl$, gives catalytic complexes that must be assumed as identical with those originated from VCl_4: in both cases and under quite similar conditions, syndiotactic polypropylene is obtained[3].

The same conclusions about the identity of the catalytic V-complexes can be drawn from the fact that the thermal decomposition of all these catalytic systems leads to the formation of VCl_2; this can be seen in the

EPR analyses and was already known from literature[6]. Therefore, it can be stated that active vanadium contained in the different catalytic systems is trivalent.

3.2. *Composition of the Catalytic Complexes*

The data reported also lead to conclusions about the substituents bound to vanadium in the catalytic complexes. In fact, it is clear that VCl_2R is the only trivalent hydrocarbon-soluble vanadium compound that can be formed either by alkylation and reduction of VCl_4 or by halogenation and alkylation of VA_3 with suitable organometallic compounds of aluminum (which, in the case of VA_3, must contain halogen), and that can yield VCl_2 by heating.

In the different cases amorphous or syndiotactic polypropylene is obtained operating at the same temperature and varying only the stoichiometric ratios of the reagents[3]; this can be explained by admitting that the catalytic complexes consist, at least in the case of the polymerization of propylene to syndiotactic polymer, of association compounds between VCl_2R and an organometallic compound of aluminum. In any case, alkyl vanadium dichloride is the basic component of the different catalytic systems.

3.3. *Steady-state Conditions and Concentration of the Catalytic Complexes*

It was previously observed that the active vanadium in the polymerization in any case constitutes a small fraction of the total vanadium present in the different catalytic systems. It was also observed that the polymerization rate (at least in many cases) is almost constant during the polymerization.

With regard to the catalytic systems based on VA_3 these facts do not lead to particular conclusions; in fact it can be easily assumed that catalytically active vanadium is at equilibrium with the starting reagents, and this guarantees a constant concentration of the catalytic complexes.

The formation of VCl_2R starting from VCl_4 and $Al(C_2H_5)_2Cl$, however, requires an intermediate irreversible reduction reaction, according to the scheme:

$$VCl_2R_2 \longrightarrow VCl_2\,R + R^{\bullet}$$

Therefore, all VCl_4 present at $-78\,^{\circ}C$. in a more or less long time must create catalytically active VCl_2R *).

*) The homogeneity of the catalytic system allows to exclude formation of VCl_3 at $-78\,^{\circ}C$. in appreciable amount.

However, also in this case the polymerization rate is constant during the polymerization; this involves the coexistence of the two reactions of formation and decomposition of VCl_2R, according to the fundamental scheme (which is merely formal):

$$VCl_2R_2 \rightarrow VCl_2R + R^{\bullet} \quad (1)$$

$$VCl_2R + nC_3H_6 \rightarrow VCl_2P \quad (2)$$

$$VCl_2P \rightarrow VCl_2 + P^* \quad (3)$$

with P = polymer chain, P* = polymer radical.

Independently of the mechanism of the single reactions considered, of the state of complexation of the vanadium compounds considered and of possible further reactions, the steady-state conditions in the concentration of active centers in the catalytic system VCl_4–$Al(C_2H_5)_2Cl$ can be ensured only by the maintainance of practically constant amounts of tetravalent V during the polymerization.

The reaction scheme agrees with the fact that (as can be observed in Fig. 5 from the non-linear behaviour of molecular weight *vs.* time) during the polymerization chain rupture processes actually occur, which might depend, at least in part, on reaction 3.

Table 2. Colours of VCl_4, VA_3, and of the different homogeneous catalytic systems in toluene and *n*-heptane

Vanadium compound	Solvent	Colours *)
Single compounds		
VCl_4	*n*-heptane	light yellow
VCl_4	toluene	very dark, tending to brown with greenish reflections
VA_3	toluene	fairly light yellow
Catalytic systems		
VCl_4–$Al(C_2H_5)_2Cl$.	*n*-heptane	very dark with purple reflections
VCl_4–$Al(C_2H_5)_2Cl$.	toluene	very dark with purple reflections
VA_3–$Al(C_2H_5)_2Cl$.	toluene	fairly light yellow

*) Controls have been made on solutions containing V ($0.5 \cdot 10^{-3}$ moles) in 100 ml. of solvent, prepared at –78 °C. An Al/V ratio = 30 was used to prepare the various catalytic systems.

Besides that, the colour of the various catalytic systems reported in Table 2 agree with the facts reported above. In fact, the colour of the catalytic systems based on VA_3 is fairly light, while that of the systems based on VCl_4 is intense, as it is characteristic of the VCl_4 complexes.

A further remark can be made by comparing the colour of VCl_4 in different solvents. The dark colour of VCl_4 in aromatic solvents, in fact, is not so much due to VCl_4 as to the presence of complexes of VCl_4 [11]. The VCl_4 solutions in aliphatic solvents have a lighter colour (light yellow), which turns dark as soon as substances able to be complexed with VCl_4 are introduced. Also the introduction of $Al(C_2H_5)_2Cl$ in a heptane solution of VCl_4 previously cooled to $-78\,^{\circ}C$. gives rise to a strong darkening of the colour, which becomes similar to that of the same catalytic system in aromatic solution. This fact seems to give a further indication that tetravalent V is present in the catalytic systems as a complex with the organometallic compounds of Al.

The addition, *e.g.*, of $Al(C_2H_5)_2Cl$ to VCl_4 in aromatic solution should cause an alkylation reaction of VCl_4, which gives rise to a slight clearing of the solution, and displacement of toluene from coloured complexes toluene-VCl_4 to form less intensely coloured complexes between the organometallic compound of tetravalent V and $Al(C_2H_5)_2Cl$; on the contrary, the addition of $Al(C_2H_5)_2Cl$, under the same conditions, to a heptane solution of VCl_4 (light colour), gives rise to simultaneous alkylation of VCl_4, which is relatively little coloured, and formation of intensely coloured complexes between organometallic compound of tetravalent V and $Al(C_2H_5)_2Cl$.

4. *Conclusion*

The results obtained prove earlier results [3] on the valence and type of V compound, active in the polymerization of propylene with homogeneous catalytic systems.

Active vanadium is present in the trivalent state and is bound to the same substituents both in the catalytic systems that promote the polymerization of propylene to syndiotactic polymer, and in those promoting the polymerization of propylene to atactic polymer.

This fact allows us to confirm that, at least in the homogeneous catalytic systems that are stereospecific in the polymerization of propylene to syndiotactic polymer, the active catalytic complexes are bimetallic and they contain an organometallic compound of Al along with VCl_2R.

5. *Experimental Part*

EPR Measurements

EPR measurements were performed with a VARIAN V 4502 spectrometer containing a VARIAN V 4012-3B magnet. The working frequency was maintained at about 9100 MHz., the frequency of modulation was 100 KHz. For checking the temperature of the sample the

VARIAN V-4557 variable temperature accessory was used. The absorption signal derived curve was registered by a potentiometric recorder; sheets were set in gauss, using a VARIAN F-8 fluxmeter. The accuracy of marking of the magnetic field was ± 0.2%.

Caution was taken to avoid saturation of the sample by a suitable attenuation of the radio frequency energy supplied by a klystron. Moreover, also the peak-to-peak amplitude of the modulation field was chosen everytime, depending on the width of the line, in order to avoid modulation broadening.

The EPR analysis of single vanadium compounds or of the catalytic systems examined were performed on samples of about 0.5 ml. of hydrocarbon solutions containing $5 \cdot 10^{-3}$ moles/l. of V.

Sensitivity of Measurements

With regard to the sensitivity of the analyses accomplished, we have, for instance, checked that it is possible to determine the presence of VOA_2 in hydrocarbon solutions, also in samples containing no more than 10^{-8}–10^{-9} moles of V. A slightly lower sensitivity was observed in the case of solid VCl_2 in hydrocarbon suspension.

Polymerization Runs

Polymerizations were carried out according to the procedures described in a previous paper[3]; see also that paper for the reagents employed.

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