

Ethylene-Propylene Copolymerization in the Presence of Catalysts Prepared from Vanadium Triacetylacetonate

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Introduction

For several years we have found that, by operating under particular conditions and using catalytic systems prepared from suitable transition metal compounds and organometallic compounds, it is possible to prepare high molecular weight, homogeneous ethylene-propylene copolymers that are amorphous under x-ray examination.¹⁻⁶ The catalytic systems that prove to be particularly convenient for promoting this copolymerization are prepared from hydrocarbon-soluble vanadium compounds and from aluminum organometallic compounds. In our previous communications we reported the results obtained in the presence of catalytic systems belonging to this class, and prepared from halides or oxyhalides (such as VCl_4 or $VOCl_3$).

Continuing our research in the field of ethylene-propylene copolymerization in the presence of catalysts obtained from hydrocarbon-soluble vanadium compounds, we have examined the properties of the catalytic systems prepared from vanadium compounds containing alkoxy or acetylacetonate groups. Their activity is much lower than that of the catalysts obtained from VCl_4 and trialkyl aluminum compounds; nevertheless, we have found some conditions for the preparation and use of these catalysts that enable us to reach copolymerization rates and copolymer yields which, though inferior to those obtainable with VCl_4 catalysts, can be of practical interest.

We have observed that active catalysts for the copolymerization can be obtained when either the aluminum organometallic compounds or the vanadium compounds (or both) contain at least one halogen atom. This is in agreement with some results recently published by Bier,⁸ and is demonstrated by the results obtained by us and reported in Table I. In this table the yields of copolymers obtained under the same copolymerization conditions and in the presence of catalysts prepared from various vanadium compounds are compared with one another and with the yields, obtained using the $VCl_4-Al(C_6H_{13})_3$ catalytic system.

As may be seen from the table, the ratio between the concentrations of

TABLE I

Comparison of Activities of Different Catalytic Systems Prepared from Vanadium Compounds in the Ethylene-Propylene Copolymerization
 Experimental conditions: catalyst prepared at 25°C. in 30 cc. toluene: aging time = 1 min.; polymerization temperature = 25°C.; pressure = 1 atm.; *n*-heptane = 350 cc.; mole C₃H₆/mole C₂H₄ in gaseous feed = 4.

Catalytic system	V compd., mmole	Al/V molar ratio	Polym. time, min.	Co-poly-mer, g.	g. co-polymer mmole V × hr.	C ₂ H ₄ , mole-% in co-polymer
VAc ₃ + Al(C ₂ H ₅) ₂ Cl	1.4	3.5	18	3.5	8.34	54.0
VOAc ₂ + Al(C ₂ H ₅) ₂ Cl	1.4	3.5	18	3.4	8.1	57.0
VO(OC ₂ H ₅) ₃ + Al(C ₂ H ₅) ₂ Cl	1.4	5	10	3.1	7.38	54.5
VO(OC ₂ H ₅) ₂ Cl + Al(C ₂ H ₅) ₂ Cl	1.4	3.5	10	4.2	18.0	52.2
VO(OC ₂ H ₅)Cl ₂ + Al(C ₂ H ₅) ₂ Cl	1.4	3.5	10	2.45	10.5	50.7
VAc ₃ + Al(C ₂ H ₅) ₃	5.6	5	20	Traces	—	—
VOAc ₂ + Al(C ₂ H ₅) ₃	5.6	5	20	Traces	—	—
VO(OC ₂ H ₅) ₂ Cl + Al(C ₂ H ₅) ₃	5.6	5	25	1.1	0.47	59.0
VO(OC ₂ H ₅)Cl ₂ + Al(C ₂ H ₅) ₃	2.8	5	12	4.0	7.15	50.5
VCl ₄ + Al(C ₂ H ₅) ₃	0.2	2.5	3	2.0	200.0	28.0

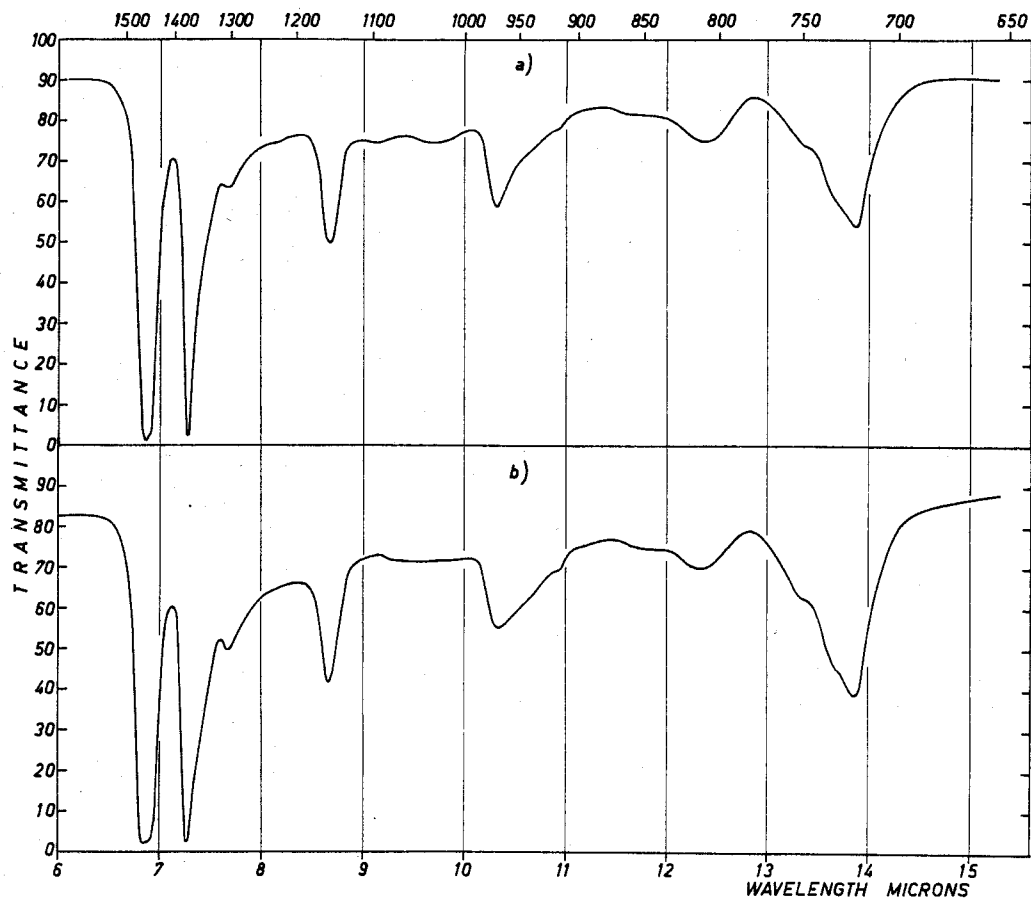


Fig. 1. IR absorption spectra between 6 and 15 μ of ethylene-propylene copolymers: (a) Catalyst used: VCl₄-AlR₃; molar content of ethylene = 40%. (b) Catalyst used: VAc₃-AlR₂Cl; molar content of ethylene = 45%.

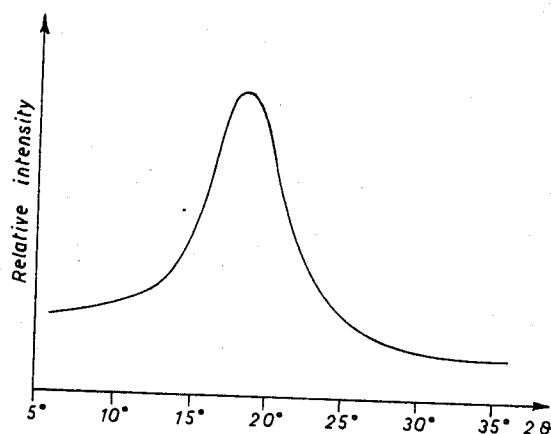


Fig. 2. X-ray diffraction spectra ($\text{CuK}\alpha$) of an ethylene-propylene copolymer prepared with the $\text{VAc}_3\text{-AlR}_2\text{Cl}$ catalytic system. Molar content of ethylene = 45%.

ethylene and propylene present in the liquid phase being equal, the composition of the copolymer can vary when varying the catalytic system used. When the composition is equal, the copolymers obtained present, however, the same x-ray diffraction and the same absorption spectra in the infrared. This is shown clearly (for instance, from Fig. 1) in the infrared spectra of two copolymers obtained in the presence of $\text{VCl}_4\text{-Al}(\text{C}_6\text{H}_{13})_3$ and vanadium triacetylacetonate- $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. In these spectra, broad absorptions between 13.3 and 13.8 μ are present. As we have previously indicated,^{1,2} these absorptions can be attributed to short sequences of methylene groups.

The total absence of crystallinity is shown either by IR spectra or by x-ray diffraction (see Fig. 2).

In this communication we report some of the results obtained in the study of ethylene-propylene copolymerization carried out in the presence of a catalytic system prepared from $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and from a halogen-free vanadium compound, vanadium triacetylacetonate (which will be indicated by VAc_3). When this catalytic system was used, and as with the $\text{VCl}_4\text{-Al}(\text{C}_6\text{H}_{13})_3$ catalyst, amorphous copolymers could be obtained which had a molar content of ethylene up to 80% and which were completely extractable with boiling *n*-heptane. A deeper examination of the characteristics of the copolymers obtained with the $\text{VAc}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ catalyst will be reported in other communications.

Influence of Aging Time, Temperature and Al/V Ratio on Catalyst Activity

Carrying out copolymerization tests with the catalytic system $\text{VAc}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, we have noted that, when preparing and using the catalysts at 25°C., the overall rate of copolymerization depends on the ratio between the moles of the two reagents employed in the preparation of the catalyst, and the highest activity is found for molar ratios $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ near 3.5 (see Table II).

From Table II we also see that the composition of the copolymers is independent of the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ ratio. We have furthermore ob-

TABLE II
Variation in Yield of Copolymerization and in Composition of
Copolymers with $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ Ratio

Experimental conditions: catalyst prepared in 30 cc. toluene from 0.5 g. VAc_3 ; aging time = 1 min.; polymerization temperature = 25°C .; abs. pressure = 1 atm.; *n*-heptane = 350 cc.; mole C_3H_6 /mole C_2H_4 in gaseous feed = 4; polymerization time = 18 min.

Mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ Mole VAc_3	Copolymer, g.	C_2H_4 , mole-% in copolymer
2	0.1	—
2.5	0.2	—
3	3.5	52.5
3.25	3.5	55.0
3.5	3.5	50.1
4	2.9	52.5
5	1.6	53.6
6	1.0	52.5

served that, under the above-mentioned conditions and though keeping the concentration of the monomers in the liquid phase constant (see experimental part), the production of copolymer increases with time to a much lower extent than should correspond to a linear dependence (see Table III).

TABLE III
Ethylene-Propylene Copolymerization Carried Out at 25°C . with
Catalysts Prepared in Presence of Monomer Mixture

Experimental conditions: g. VAc_3 = 0.25 (dissolved in 30 cc. toluene); mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ /mole VAc_3 = 3.5; polymerization temperature = 25°C .; abs. pressure = 1 atm.; *n*-heptane = 350 cc.; mole C_3H_6 /mole C_2H_4 in gaseous feed = 4.

Polymerization time, min.	Copolymer, g.	C_2H_4 , mole-% in copolymer	$[\eta]$
1	3.3	54.0	1.07
3	4.9	52.5	1.25
9	6.1	53.5	1.66

$[\eta]$ = intrinsic viscosity, measured at 135°C . in tetrahydronaphthalene, and expressed in 100 cc./g.

This is due to a remarkable decrease in catalyst activity, one that takes place independently of the fact whether it is, or is not, employed in the polymerization. We have confirmed this by carrying out the preparation of the catalyst at 25°C . and by introducing its solution into the copolymerization apparatus after maintaining the catalyst under nitrogen atmosphere at 25°C . for varying times. In fact, as Figure 3 shows, some minutes after its preparation the catalyst already possesses a very low activity.

We have observed, however, that the composition of the copolymer does not depend on aging time of the catalyst. A rapid, though less remarkable,

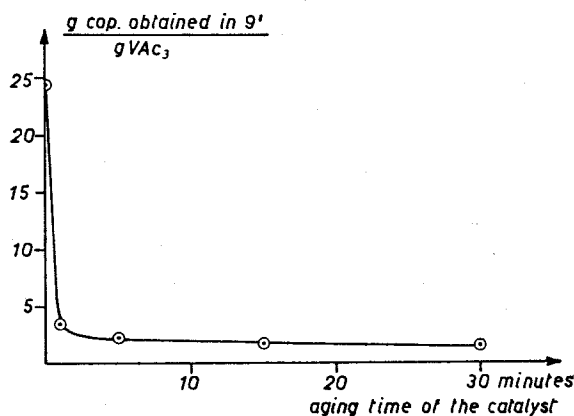


Fig. 3. Variation of copolymer yield in grams with time of aging of catalyst. Catalyst prepared in 30 cc. toluene at 25°C. and aged at 25°C; mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3 = 3.5$. Polymerization conditions: 25°C., $p = 1$ atm.; solvent = 350 cc. *n*-heptane; mole $\text{C}_3\text{H}_6/\text{mole C}_2\text{H}_4$ in gaseous feed = 4, time = 9 min.

loss of activity had already been found for many catalytic systems prepared from hydrocarbon-soluble transition metal compounds.^{7,9,10}

If we assume that catalyst activity is related to the presence of highly unstable organometallic complexes, it seems convenient to examine whether, when operating at low temperatures, their decomposition could be avoided or reduced, thus permitting higher yields and a fairly constant rate of copolymerization. As a matter of fact, when carrying out the preparation of the catalyst and the copolymerization at temperatures below 0°C., we obtained catalysts whose activity decreases to a much lower extent with time. By comparing the values of the rates reported in Figure 4 which are determined for catalysts prepared, aged, and employed at 25 and at -20°C., it clearly appears that, even referring to the same total concentration of monomers in the liquid phase, the copolymer yields that can be obtained in a specific time per weight unit of catalyst are higher by far when the preparation of the catalyst and the copolymerization are carried out at low temperature.

Evidently this result must not be attributed to a negative energy of activation for the propagation, but it must be related to the possibility of existence of highly active catalytic complexes that are sufficiently stable at low temperatures but undergo rapid decomposition at temperatures higher than 0°C.

This result is rather peculiar for the catalytic system $\text{VAc}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. In fact, with catalytic systems prepared from different vanadium compounds—such as $\text{VCl}_4\text{-AlR}_3$ or $\text{VO}(\text{OC}_2\text{H}_5)_3\text{-AlR}_2\text{Cl}$ —we have found that the rate of copolymerization (referred to an equal total concentration of monomers) decreases, though to a limited extent, when decreasing the temperature of the preparation and of use of the catalyst.

When operating at -20°C., all other conditions being equal, the composition of the copolymers obtained in the presence of the $\text{VAc}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ catalytic system is not influenced by aging time of the catalyst. The in-

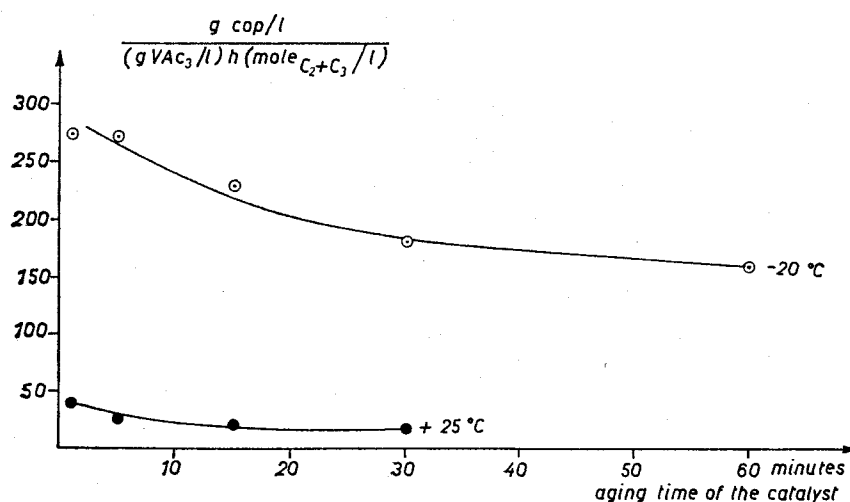


Fig. 4. Copolymerization rate in presence of catalyst prepared and aged for different times at -20°C (O) and $+25^\circ\text{C}$. (●). Catalyst prepared in 30 cc. toluene; mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3 = 5$ (O) and 3.5 (●). Polymerization conditions: $p = 1$ atm., solvent = 350 cc. *n*-heptane, mole $\text{C}_3\text{H}_6/\text{mole C}_2\text{H}_4$ in gaseous feed = 4, $t = -20^\circ\text{C}$. (O) and $+25^\circ\text{C}$. (●).

trinsic viscosities of the copolymers obtained increased when increasing the aging time (see Table IV). In agreement with what will be reported later, the above-mentioned result could originate with a decrease in concentration of the active catalytic complexes present in the system with aging time.

TABLE IV

Ethylene-Propylene Copolymers Obtained at -20°C . with Catalyst Aged for Different Times

Experimental conditions: catalyst prepared at -20°C . in 30 cc. toluene; mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3 = 5$; polymerization temperature = -20°C .; abs. pressure = 1 atm.; solvent = 350 cc. *n*-heptane.

Mole $\text{C}_3\text{H}_6/\text{mole C}_2\text{H}_4$ in gaseous feed	VAc_3 , g.	Aging time, min.	C_2H_4 , mole-% in copolymer	[η]
6	0.25	5	34.0	2.05
6	0.25	15	35.0	3.38
6	0.25	30	35.0	3.44
6	0.50	5	33.5	1.35
6	0.50	15	35.0	2.18
6	0.50	30	36.0	2.57
4	0.125	1	42.0	1.65
4	0.125	5	43.5	3.00
4	0.125	15	45.0	4.70
4	0.125	30	45.0	5.70
4	0.125	60	44.1	6.70

When operating at -20°C . and plotting the activity of the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{VAc}_3$ catalyst versus the ratio between the moles of the two reagents, a definite maximum is not noticeable. As may be seen from Figure 5, the activity of the catalyst rapidly increases when increasing the molar ratio

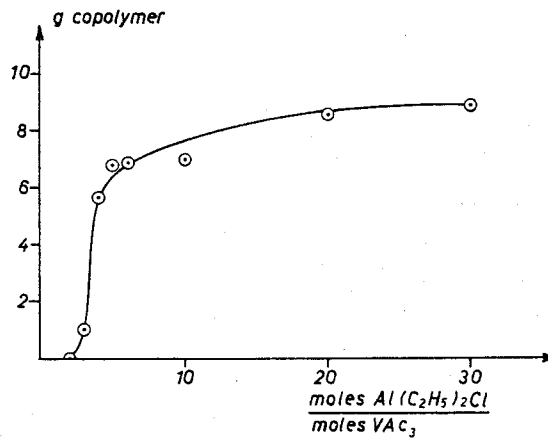


Fig. 5. Dependence of catalyst activity on the molar ratio $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$. Catalyst prepared and aged for 5 min. at -20°C . Polymerization conditions: -20°C ., $p = 1$ atm., solvent = 350 cc. *n*-heptane, mole $\text{C}_3\text{H}_6/\text{mole C}_2\text{H}_4$ in gaseous feed = 4; time = 3 min.

$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ from 3 to 4, while it increases to a less remarkable extent when the ratio varies from 4 up to 20.

The composition of the copolymers obtained at -20°C . does not vary with the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ ratio. Furthermore, all the conditions and the quantity of VAc_3 employed being equal, the intrinsic viscosity of the copolymers decreases when increasing the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ ratio (see Table V). This result can be attributed to a termination process that takes place through a transfer between the growing chains and the alkyl aluminum

TABLE V

Dependence of Composition and Intrinsic Viscosity of Ethylene-Propylene Copolymers on Molar Ratio $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ for Catalysts Prepared and Employed at -20°C .

Experimental conditions: catalyst prepared in 30 cc. toluene; aging time = 5 min.; polymerization temperature = -20°C .; abs. pressure = 1 atm.; *n*-heptane = 350 cc.; mole $\text{C}_3\text{H}_6/\text{mole C}_2\text{H}_4$ in gaseous feed = 4.

Mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$		Polym. time, min.	C_2H_4 , mole-% in copolymer	[η]	Copolymer, g.
Mole VAc_3	VAc_3 , g.				
3	0.125	4	—	—	0.6
3.5	0.125	4	—	—	0.7
3.75	0.125	4	—	—	0.8
4	0.125	4	44.0	3.16	4.9
5	0.125	4	43.5	3.00	4.9
10	0.125	4	43.5	2.15	6.5
3	0.250	3	—	—	1.05
4	0.250	3	43.5	2.92	5.70
5	0.250	3	44.5	2.11	6.80
6.33	0.250	3	42.5	1.63	6.90
10	0.250	3	43.5	1.57	7.00
20	0.250	3	45.5	0.99	8.60
30	0.250	3	42.5	0.77	8.90

compounds present in the solution, in agreement with kinetic studies already described for several anionic coordinated polymerizations.¹¹⁻¹³

Influence of Copolymerization Conditions

By a series of systematic tests, we have examined the influence of various conditions on the behavior of copolymerization and on the properties of the copolymers obtained. Unless otherwise stated, in all the tests to be reported here, the preparation of the catalyst and the copolymerization were carried out at -20°C . with $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ molar ratios equal to 5. We have always operated by feeding the mixture of the two monomers continuously at a very high space velocity in order to renew the gaseous phase rapidly and to keep the solution as close as possible to saturation conditions. The conversion of each monomer was, for each passage, lower than 5%.

(a) Time of Copolymerization

The composition of the copolymers is independent of time of copolymerization, and polymer yields are, in practice, directly proportional to time, when adopting sufficiently short reaction times (between 1 and 10 min.) (see Table VI). From Table VI one can see that the intrinsic

TABLE VI
Ethylene-Propylene Copolymers Prepared at -20°C . with Different Polymerization Times

Experimental conditions: catalyst prepared at -20°C . in 30 cc. toluene; g. $\text{VAc}_3 = 0.125$; mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3 = 5$; polymerization temperature = -20°C .; abs. pressure = 1 atm.; *n*-heptane = 350 cc.

Mole $\text{C}_3\text{H}_6/\text{mole C}_2\text{H}_4$ in gaseous feed	Polym. time, min.	Aging time, min.	Copolymer, g.	C_2H_4 , mole-% in copolymer	$[\eta]$
6	1	5	1	35.0	2.55
6	3	5	3	33.5	2.75
6	4	5	3.9	36.0	3.01
6	6	5	5.8	35.5	3.11
4	1	30	0.70	45.0	5.30
4	3	30	2.20	42.5	5.44
4	4	30	3.20	45.0	5.70
4	6	30	4.45	43.5	5.90

viscosities of the ethylene-propylene copolymers increased with increasing time of copolymerization, all other conditions being equal. The increase in intrinsic viscosities is rather limited, also owing to the very short times adopted, in order not to reach too high viscosities of the solution in which copolymerization takes place. Variation of the average degree of polymerization with time could be in agreement with the hypothesis that, under the adopted conditions, the growing chains remain active for relatively long periods.

(b) Concentration of the Catalyst

All other conditions being equal, the composition of the copolymers does not vary when varying the concentration of the catalyst (see Table VII). The copolymer yields obtained in a specific time and using catalysts aged under the same conditions are directly proportional to the concentration of the catalyst (see Table VII). We can therefore conclude that the rate of copolymerization is first order with respect to the concentration of the catalyst.

TABLE VII

Ethylene-Propylene Copolymers Obtained at -20°C . with Different Catalyst Concentrations

Experimental conditions: catalyst prepared at -20°C . in 30 cc. toluene; mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3 = 5$; polymerization temperature = -20°C .; abs. pressure = 1 atm.; *n*-heptane = 350 cc.

Mole $\text{C}_3\text{H}_6/\text{mole C}_2\text{H}_4$ in gaseous feed	VAc_3 , g.	Aging time, min.	Polym. time, min.	Copolymer, g.	C_2H_4 , mole-% in copolymer	$[\eta]$
6	0.125	5	4	3.9	36.0	3.01
6	0.250	5	3	5.6	34.0	2.05
6	0.500	5	2	7.2	33.5	1.35
6	0.250	15	3	4.2	35.0	3.38
6	0.500	15	3	7.6	35.0	2.18
6	0.125	30	4	2.3	34.0	3.94
6	0.250	30	3	3.3	35.0	3.44
6	0.500	30	3	6.1	36.0	2.57
4	0.125	5	4	4.9	43.5	3.00
4	0.250	5	3	6.8	44.5	2.11
4	0.125	15	4	4.1	45.0	4.70
4	0.250	15	3	6.4	42.5	4.10
2	0.125	5	3	5.5	59.0	3.77
2	0.250	5	3	9.2	58.5	2.78
2	0.125	15	3	4.6	57.5	5.14
2	0.250	15	3	8.6	56.5	4.01
2	0.125	30	3	3.6	60.0	5.50
2	0.250	30	3	6.5	59.5	4.90

From Table VII it also appears that the intrinsic viscosities of the copolymers decrease when increasing the catalyst concentration. This confirms the hypothesis that the terminations of the growing chains take place, at least in part, through a transfer with the organometallic compounds present in the solution. This is also in agreement with the dependence of molecular weight on the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ ratio as already described.

(c) Concentration of the Monomers

By operating at a total pressure of 1 atm., keeping the $\text{C}_3\text{H}_6/\text{C}_2\text{H}_4$ ratio constant in the feed, and changing the partial pressure of the monomers by diluting the gaseous feed mixture with highly purified nitrogen, we

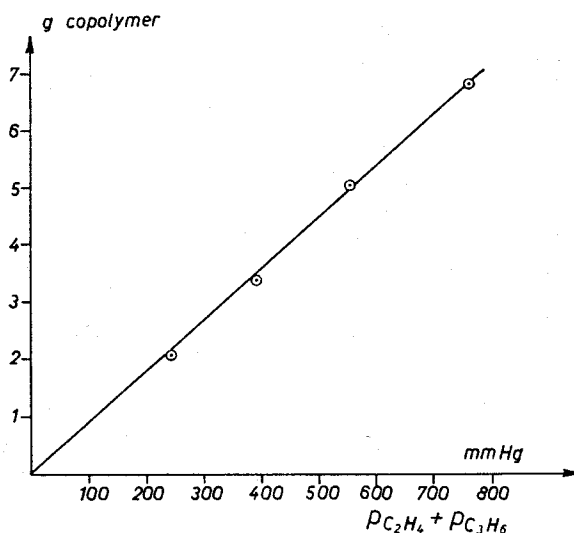


Fig. 6. Dependence of copolymerization yield in grams on partial pressure of monomers in the gaseous feed. Catalyst prepared at -20°C . in 30 cc. toluene and aged for 5 min. at -20°C .; mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3 = 5$; $\text{VAc}_3 = 0.25$ g. Polymerization conditions: -20°C ., $p = 1$ atm., solvent = 350 cc. *n*-heptane, mole $\text{C}_3\text{H}_6/\text{mole C}_2\text{H}_4$ in gaseous feed = 4; time = 3 min.

have found that: (1) The compositions of the copolymers are independent of the total concentration of the monomers present in the liquid phase (see Table VIII). (2) The copolymerization rate is first order with respect to the total concentration of the two monomers in solution (see Fig. 6).

TABLE VIII

Dependence of Composition of Ethylene-Propylene Copolymers Prepared at -20°C . on Partial Pressure of Monomers Present in Gaseous Feed

Experimental conditions: catalyst prepared at -20°C . in 30 cc. toluene; g. $\text{VAc}_3 = 0.25$; aging time = 5 min.; mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3 = 5$; polymerization temperature = -20°C .; abs. pressure = 1 atm.; *n*-heptane = 350 cc.; mole $\text{C}_3\text{H}_6/\text{mole C}_2\text{H}_4$ in gaseous feed = 4; polymerization time = 3 min.

Mole N_2 Mole $\text{C}_2\text{H}_4 + \text{mole C}_3\text{H}_6$	C_2H_4 , mole-% in copolymer	Mole N_2 Mole $\text{C}_2\text{H}_4 + \text{mole C}_3\text{H}_6$	C_2H_4 , mole-% in copolymer
0	43.5	0.93	43.5
0	44.5	0.93	44.0
0.38	44.5	2.12	43.0
0.38	43.5	2.12	42.5

(d) Composition of the Monomer Mixture

All other conditions being equal, the composition of the copolymer changes in a remarkable way when changing the composition of the monomer mixture (see Table IX and Fig. 7). The average molecular weight of the copolymers and the overall copolymerization rate rapidly increase with increasing ethylene content (Table X).

TABLE IX

Dependence of Composition of Ethylene-Propylene Copolymers Prepared at -20°C .
on Composition of Monomer Mixture

Experimental conditions: catalyst prepared at -20°C . in 30 cc. toluene; mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3 = 5$; abs. pressure = 1 atm.; *n*-heptane = 350 cc.

Gaseous feed			Catalyst		Polym. time, min.	C_2H_4 , mole-% in copolymer
Mole C_3H_6 Mole C_2H_4	C_3H_6 , mole-%	C_2H_4 , mole-%	VAc ₃ , g.	Aging time, min.		
9.65	90.5	9.5	0.250	5	3	26.0
9.65	90.5	9.5	0.250	15	3	27.2
9.65	90.5	9.5	0.250	30	3	26.5
6	85.7	14.3	0.125	5	1	35.0
6	85.7	14.3	0.125	5	3	33.5
6	85.7	14.3	0.125	5	4	36.0
6	85.7	14.3	0.125	5	6	35.5
6	85.7	14.3	0.125	30	4	34.0
6	85.7	14.3	0.250	5	3	34.0
6	85.7	14.3	0.250	15	3	35.0
6	85.7	14.3	0.250	30	3	35.0
6	85.7	14.3	0.500	5	2	33.0
6	85.7	14.3	0.500	15	3	35.0
6	85.7	14.3	0.500	30	3	33.5
4	80.0	20.0	0.125	3	4	35.0
4	80.0	20.0	0.125	5	4	36.0
4	80.0	20.0	0.125	5	4	44.5
4	80.0	20.0	0.125	15	4	45.0
4	80.0	20.0	0.125	30	1	45.0
4	80.0	20.0	0.125	30	3	42.5
4	80.0	20.0	0.125	30	4	45.0
4	80.0	20.0	0.125	30	6	43.5
4	80.0	20.0	0.125	60	4	44.1
4	80.0	20.0	0.250	5	3	44.5
4	80.0	20.0	0.250	5	3	43.0
4	80.0	20.0	0.250	5	3	44.5
4	80.0	20.0	0.250	15	3	42.5
2	66.7	33.3	0.125	5	3	59.0
2	66.7	33.3	0.125	15	3	57.5
2	66.7	33.3	0.125	30	3	60.0
2	66.7	33.3	0.250	5	3	58.5
2	66.7	33.3	0.250	15	3	56.5
2	66.7	33.3	0.250	30	3	59.5
1.5	60.0	40.0	0.125	5	2	65.0
1.5	60.0	40.0	0.125	15	2	64.1
1.5	60.0	40.0	0.125	15	2	66.0
1.5	60.0	40.0	0.125	30	2	65.5

Monomer Reactivity Ratios

On the basis of the results reported in Table IX, we have calculated the following values for the ethylene and propylene reactivity ratios (referred to the molar fractions of the two monomers present in the solution²) in the

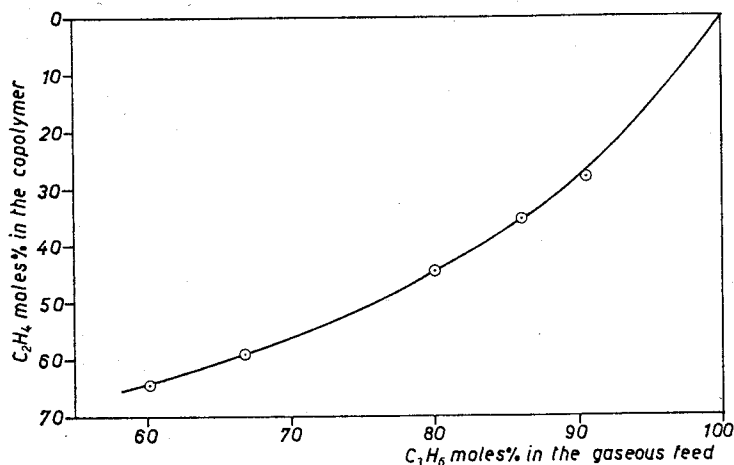


Fig. 7. Composition of ethylene-propylene copolymers vs. gaseous feed composition. Catalyst prepared from $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and VAc_3 at -20°C . Polymerization conditions: -20°C . pressure = 1 atm. The reported values are the average of numerous tests carried out for each feed.

TABLE X

Dependence of Copolymerization Rate on Composition of Gaseous Feed
 Experimental conditions: catalyst prepared at -20°C . in 30 cc. toluene; mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3 = 5$; polymerization temperature = -20°C .; abs. pressure = 1 atm.; *n*-heptane = 350 cc.

Mole $\text{C}_3\text{H}_6/\text{Mole C}_2\text{H}_4$ in gaseous feed	Aging time of catalyst	g. cop./l.
		(g. $\text{VAc}_3/\text{l.}$)hr.(mole $\text{C}_2 + \text{C}_3/\text{l.}$)
9.65	5	106
6	5	174
4	5	266
2	5	404
1.5	5	464
9.65	15	85
6	15	150
4	15	236
2	15	356
1.5	15	410
9.65	30	60
6	30	103
4	30	180
2	30	274
1.5	30	298

copolymerization carried out at -20°C : $r(\text{C}_2\text{H}_4) = 15.0$, $r(\text{C}_3\text{H}_6) = 0.04$. These are the mean values between those determined by the methods of Lewis and Mayo¹⁴ and of Fineman and Ross.¹⁵ The reactivity ratios found for the $\text{VAc}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ catalyst are very near those found for the ethylene-propylene copolymerization in the presence of the $\text{VOCl}_3\text{-AlR}_3$ catalytic system. We can also note that the difference in the reactivity ratios is larger than the one found for the $\text{VCl}_4\text{-AlR}_3$ catalyst.

The product of the reactivity ratios, for copolymerization in the presence of the catalytic system $\text{VAc}_3\text{-Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, is slightly inferior to 1 and it is practically equal to the value found for the catalytic system $\text{VCl}_4\text{-AlR}_3$. In both cases, the alternating tendency is a little greater than for a perfectly random copolymerization, to which a product of reactivity ratios equal to unity corresponds.

We see from Table XI that the compositions of the ethylene-propylene copolymers prepared at 25°C . in the presence of the catalytic system $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl-VAc}_3$ are very near those calculated from the reactivity ratios determined while carrying out copolymerization and catalyst preparation at -20°C . Therefore, in the range of temperature examined by us, there is no remarkable variation of the reactivity ratios, in agreement with what is generally found.^{4,16}

TABLE XI

Comparison of Molar Compositions of Ethylene-Propylene Copolymers Obtained with $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl-VAc}_3$ Catalyst Prepared and Employed at 25°C . with Molar Compositions Calculated from Reactivity Ratios Determined with Same Catalytic System but at -20°C .

Mole C_2H_6 /mole C_2H_4 in gaseous feed	C_2H_4 , mole-% in copolymer	
	Found, at 25°C .	Calcd. from $r(\text{C}_2\text{H}_4)$ and $r(\text{C}_3\text{H}_6)$ dtd. at -20°C .
4	52.5	
4	55.0	52.5
4	53.5	
2	66.0	66.8
2	65.0	
1	78.0	79.0
1	78.0	

Conclusions

Whereas in previous communications we described the behavior of ethylene-propylene copolymerization in the presence of catalysts prepared from halogenated vanadium compounds (such as VCl_4 or VOCl_3), we report here some results obtained in the study of this copolymerization in the presence of catalysts prepared from vanadium compounds containing alkoxy or acetylacetic groups.

Should halogen-free vanadium compounds be used, in order to obtain catalysts capable of promoting ethylene-propylene copolymerization, it is necessary that the aluminum organometallic compounds contain at least one halogen atom. All other conditions being equal, the overall copolymerization rate, in the presence of these catalysts, remains lower than the one observed for the catalytic system $\text{VCl}_4\text{-AlR}_3$ or $\text{VOCl}_3\text{-AlR}_3$.

Particularly in this communication we are reporting some results obtained in a systematic study of copolymerization using the catalytic system $\text{VAc}_3\text{-}$

$\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$. At 25°C ., the activity of this catalyst decreases very rapidly with time and becomes practically unnoticeable some minutes after its preparation. But when carrying out the preparation of the catalyst and copolymerization at temperatures below 0°C . (for instance at -20°C .), the catalyst activity decreases only to a very limited extent with time. Therefore, when operating at low temperatures it is possible to obtain yields that are higher by far than those obtained under the same conditions at temperatures higher than 0°C .

When the catalyst is prepared and employed at -20°C ., the composition of the copolymers is independent of time of copolymerization, catalyst concentration and total concentration of the two monomers. The overall copolymerization rate is first order with respect to catalyst concentration and to the total monomer concentration. Therefore, the kinetic behavior of ethylene-propylene copolymerization in the presence of the catalytic system $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{VAc}_3$ is analogous to the one already studied by us for the $\text{VCl}_4-\text{Al}(\text{C}_6\text{H}_{13})_3$ system.

The average molecular weight of the copolymers increases with time of copolymerization and with a decrease in catalyst concentration and in the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ ratio. This would indicate that the propagation of the chains occurs during a relatively long time and that their termination takes place, at least in part, through a transfer with the alkyl aluminum compounds present in the solution.

For the copolymerization carried out at -20°C . with the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{VAc}_3$ catalyst, we have calculated the following monomer reactivity ratios (referred to the molar concentrations of the monomers in solution): $r(\text{C}_2\text{H}_4) = 15.0$, $r(\text{C}_3\text{H}_6) = 0.04$. These values are valid also for copolymerization carried out at $+25^\circ\text{C}$. This would indicate that the different activity of the catalysts prepared and maintained at $+25$ or at -20°C . is to be attributed not to the presence of catalytic complexes having a different chemical nature, but rather to a different concentration of these complexes.

Experimental Part

(a) Materials

Ethylene, propylene, *n*-heptane, and nitrogen were purified as described in previous papers (1-5) and in a paper published in the same issue of this journal.⁷

Toluene was purified by treatment with concentrated sulfuric acid and water. After treatment with calcium chloride it was refluxed in the presence of metallic sodium and finally fractionally distilled in the presence of triisobutylaluminum.

Diethylaluminum chloride was prepared by reaction of triethylaluminum and anhydrous aluminum chloride in stoichiometric amounts at $80-90^\circ\text{C}$.,¹⁷ and purified by successive distillations under vacuum. Its purity, as determined by potentiometric method^{18,19} was 97-98%. A very high purity of this reagent is necessary in order to obtain reproducible results.

Vanadium triacetylacetonate was prepared as described by Rosenheim and coworkers,²⁰ and purified by repeated recrystallization from a toluene-*n*-heptane mixture.

(b) *Apparatus and Procedure*

Copolymerization experiments were carried out while continuously feeding and discharging the monomer mixture. The apparatus and the procedure were the same as described earlier¹⁻⁵ and in a paper published in the same issue of this journal.⁷

Analysis of the copolymer was carried out as described in other communications.^{1-5,7} The molar content of ethylene in the copolymer was determined by a radiochemical method, using ¹⁴C-labeled ethylene.

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Synopsis

Ethylene-propylene copolymerization in the presence of catalysts prepared from vanadium halides was described in our previous papers. Linear, high molecular weight, completely amorphous copolymers, having an ethylene molar content up to 80%, can also be

obtained by catalysts prepared from halogen-free vanadium compounds and alkyl aluminum halides, keeping constant the ratio between the concentrations of the two monomers. The catalyst obtained from $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and vanadium triacetylacetonate, when prepared and used at temperatures below 0°C ., gives much higher copolymer yields than those observed operating at room temperature. The higher overall polymerization rate at low temperatures is rather peculiar for this catalytic system and does not occur with catalysts prepared from vanadium chlorides and AlR_3 . At -20°C . the composition of the copolymers does not depend on polymerization time, the molar ratio $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$, the catalyst concentration, or the total concentration of the monomers. The average molecular weight of the copolymers decreases with increase in $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ ratio and in the concentration of the catalyst, in agreement with the existence of a transfer process between the growing chains and the organometallic compounds present in the system. With the ratio between monomer concentrations and the ratio between catalyst components constant, the overall rate of polymerization is first order with respect to the concentration of catalysts and of monomers. The monomer reactivity ratios $r(\text{C}_2\text{H}_4) = 15.0$, $r(\text{C}_3\text{H}_6) = 0.04$ are independent of temperature between -20 and $+25^\circ\text{C}$. The value of their product (0.6) indicates that an alternating distribution of the monomeric units in the chains is more favored than random distribution, corresponding to the case in which the product of these ratios is equal to 1.

Résumé

On a décrit dans des articles précédents la copolymérisation de l'éthylène et du propylène en présence de catalyseurs préparés au départ d'halogénures de vanadium. On peut également obtenir des copolymères linéaires entièrement amorphes de poids moléculaire élevé contenant 80% molaire d'éthylène au moyen de catalyseurs préparés au départ de dérivés de vanadium sans halogène et d'halogénure d'alcoylaluminium, tout en gardant constant le rapport des concentrations des deux monomères. Le catalyseur obtenu au départ de AlEt_2Cl et le triacétylacétonate de vanadium, préparé et utilisé à des températures inférieures à 0°C fournit des rendements beaucoup plus élevés en copolymères que ceux obtenus à température de chambre. La vitesse globale de polymérisation plus élevée à basse température est plutôt spéciale pour ce système catalytique et ne se présente pas pour les catalyseurs préparés aux dépens de chlorures de vanadium. A -20°C la composition des copolymères ne dépend pas de la durée de polymérisation, ni du rapport molaire $\text{AlEt}_2\text{Cl}/\text{VAc}_3$, ni de la concentration totale en monomères. Le poids moléculaire moyen des copolymères décroît avec une augmentation du rapport $\text{AlEt}_2\text{Cl}/\text{VAc}_3$ et de la concentration du catalyseur, en accord avec l'occurrence d'un processus de transfert entre les chaînes en croissance et les composés organométalliques présents dans le système. A rapport constant des concentrations de monomères et à rapport constant des composants du catalyseur, la vitesse globale de polymérisation est du premier ordre par rapport à la concentration en catalyseur et en monomère. Les rapports de réactivité des monomères $r(\text{C}_2\text{H}_4) = 15.0$, $r(\text{C}_3\text{H}_6) = 0.04$ sont indépendants de la température entre -20 et $+25^\circ\text{C}$. La valeur de leur produit (0.6) indique qu'une alternance des unités monomériques dans les chaînes est plus fortement favorisée qu'une distribution purement statistique, en accord avec le cas auquel ce produit des deux rapports serait égal à l'unité.

Zusammenfassung

In früheren Arbeiten wurde die Athylen-Propylen-Copolymerisation in Gegenwart von Katalysatoren aus Vanadinhaliden beschrieben. Mit Katalysatoren, die aus halogenfreien Vanadinverbindungen und Alkylaluminiumhaliden dargestellt wurden, können bei Konstanthaltung des Verhältnisses der beiden Monomerkonzentrationen ebenfalls lineare, hochmolekulare, vollständig amorphe Copolymere mit einem Athylengehalt bis zu 80% erhalten werden. Der aus $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ und Vanadintriäcetylacetonat dargestellte Katalysator ergibt bei Darstellung und Verwendung unterhalb einer Temperatur

von 0°C weitaus höhere Copolymerausbeuten als bei Raumtemperatur. Die höhere Bruttopolymerisationsgeschwindigkeit bei tiefen Temperaturen ist spezifisch für dieses besonder katalytische System und tritt bei Katalysatoren, die aus Vanadinchloriden dargestellt wurden, nicht auf. Bei -20°C ist die Zusammensetzung der Copolymeren von der Polymerisationsdauer, dem Molverhältnis $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$, der Katalysatorkonzentration oder der Gesamtkonzentration der Monomeren unabhängig. Das mittlere Molekulargewicht der Copolymeren nimmt mit steigendem $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ -Verhältnis und steigender Katalysatorkonzentration ab, was für das Auftreten eines Übertragungsprozesses zwischen den wachsenden Ketten und den im System vorhandenen organometallischen Verbindungen spricht. Bei konstantem Verhältnis zwischen den Monomerkonzentrationen und zwischen den Katalysatorkomponenten ist die Bruttopolymerisationsgeschwindigkeit in bezug auf die Katalysator- und Monomerkonzentrationen von erster Ordnung. Die Reaktivitätsverhältnisse der Monomeren, $r(\text{C}_2\text{H}_4) = 15.0$, $r(\text{C}_3\text{H}_6) = 0.04$, sind zwischen -20°C und +25°C von der Temperatur unabhängig. Das Produkt der beiden Werte (0,6) weist darauf hin, dass eine Abwechslung der Monomereinheiten in den Ketten wahrscheinlicher ist als eine statistische Verteilung, bei der das Produkt dieser Verhältnisse gleich 1 ist.

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