

## Kinetics of Ethylene-Propylene Copolymerization

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### INTRODUCTION

By copolymerizing ethylene with aliphatic  $\alpha$ -olefins in the presence of some particular catalysts prepared from organometallic compounds and transition metal compounds, we succeeded in obtaining linear high molecular weight copolymers, free from homopolymers.<sup>1-3</sup>

Operating under such conditions as to keep the composition of the monomer mixture in the liquid phase constant, we have prepared copolymerization products having a constant composition, independent of the time of polymerization.

Polymers having a molar content of ethylene lower than 80% are amorphous under x-ray examination, and show interesting elastomeric properties.<sup>9,10</sup> When the ethylene content in the polymerization product is higher than the above-mentioned value, the copolymers show a polyethylenic-type crystallinity, increasing with the increase in ethylene content, and possess properties very close to those of polyethylenes having the same crystallinity.

The amorphous high-molecular-weight copolymers studied by us have solubility and mechanical properties very different from those of the corresponding homopolymers, or of the copolymer mixtures having lower homogeneity in composition, and show characteristic IR spectra.<sup>3,5-8</sup>

In our previous papers<sup>3-8</sup> published in Italian journals, we have given some results obtained by our study of the copolymerization of ethylene and aliphatic  $\alpha$ -olefins in the presence of catalysts acting by an anionic coordinated mechanism.

The above-mentioned papers deal particularly with the study of the variation in the composition of the copolymers, with some factors concerning the conditions of the copolymerization and of the preparation of the catalyst itself.

We have observed that amorphous copolymers of ethylene with aliphatic  $\alpha$ -olefins can be prepared either in the presence of those catalytic systems which, in the homopolymerization of  $\alpha$ -olefins, promote the formation of amorphous polymers (such as  $\text{Al}(\text{C}_6\text{H}_{13})_3\text{-VOCl}_3$  or  $\text{Al}(\text{C}_6\text{H}_{13})_3\text{-VCl}_4$ ), or in the presence of those promoting the formation of isotactic polymers (such as  $\text{AlR}_3\text{-VCl}_3$  or  $\text{AlR}_3\text{-TiCl}_3$ ). By operating with catalysts which produced mixtures formed by high proportions of macro-

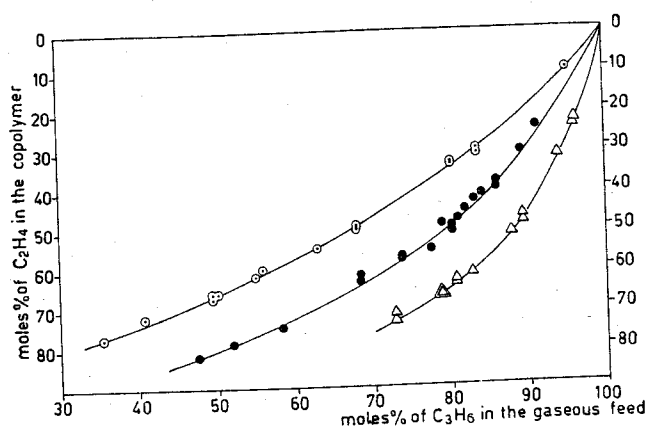


Fig. 1. Composition of ethylene-propylene copolymers plotted against the gaseous feed composition for different catalytic systems, prepared from trialkylaluminum and hydrocarbon soluble transition metal halides. Polymerization temperature, 25°C.; abs. pressure, 1 atm. Catalyst prepared from: (○)  $VCl_4 + Al(C_6H_{13})_3$ , (●)  $VOCl_3 + Al(C_6H_{13})_3$ , and (Δ)  $TiCl_4 + Al(C_6H_{13})_3$ .

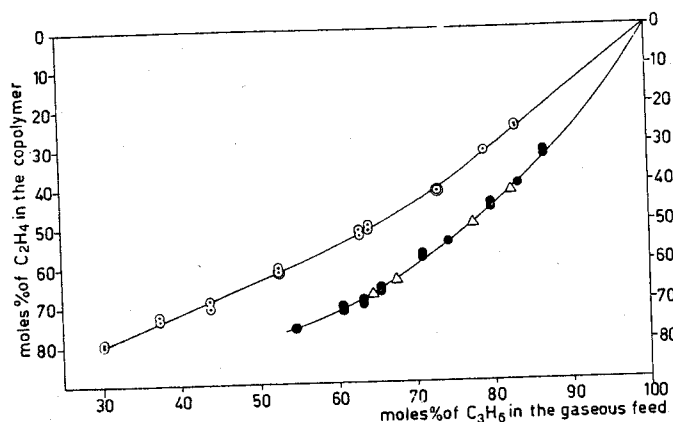


Fig. 2. Composition of ethylene-propylene copolymers plotted against the gaseous feed composition for different catalytic systems, prepared from trialkylaluminum and hydrocarbon insoluble transition metal halides. Polymerization temperature, 75°C.; abs. pressure = 1 atm. Catalyst prepared from: (○)  $VCl_3 + Al(C_6H_{13})_3$ , (●)  $TiCl_3 + Al(C_6H_{13})_3$ , and (Δ)  $TiCl_2 + Al(C_6H_{13})_3$ .

molecules with very different steric composition (such as  $TiCl_4 + Al(C_2H_5)_3$ ) in homopolymerization, we obtained less homogeneous products, very often containing crystallizable fractions.

The catalytic systems used by us have the characteristic of promoting the formation of copolymers whose composition is independent of the following factors: (1) time elapsed between the preparation of the catalyst and its use, (2) concentration of the catalyst, and (3) ratio between the moles of the alkylaluminum compound and the moles of the transition metal compound used in the preparation of the catalyst.

The composition of the copolymers thus produced is highly influenced by the feed composition and, for a certain feed, changes with the catalyst employed (see Figs. 1 and 2). In Table I, we give values for the reactivity

TABLE I  
Monomer Reactivity Ratios in the Ethylene-Propylene Copolymerization  
in the Presence of Catalysts Prepared from Trialkylaluminum and Different Transition  
Metal Halides

Catalytic system	$r_{C_2H_4}$	$r_{C_3H_6}$
$VOCl_3 + Al(C_6H_{13})_3$	17.95	0.065
$VCl_4 + Al(C_6H_{13})_3$	7.08	0.088
$VCl_3 + Al(C_6H_{13})_3$	5.61	0.145
$TiCl_4 + Al(C_6H_{13})_3$	33.36	0.032
$TiCl_3 + Al(C_6H_{13})_3$	15.72	0.110
$TiCl_2 + Al(C_6H_{13})_3$	15.72	0.110

ratios (referred to the composition of the monomer mixture present in solution) in ethylene-propylene copolymerization which was carried out in the presence of different catalytic systems. We have experimentally observed that such reactivity ratios are practically constant in the temperature range between 0 and 75°C.<sup>6</sup> Ethylene always shows a much higher reactivity than the one of propylene, in agreement with what we expected for an anionic polymerization.

TABLE II  
Monomer Reactivity Ratios in the Ethylene-1-Butene Copolymerization

Catalytic system	$r_{C_2H_4}$	$r_{C_4H_8}$
$VCl_4 + Al(C_6H_{13})_3$	29.60	0.019
$VCl_3 + Al(C_6H_{13})_3$	26.96	0.043

In Table II we report values for reactivity ratios in ethylene-butene-1 copolymerization.<sup>8</sup> The product of the reactivity ratios is always near 1, in agreement with what generally occurs for copolymerizations taking place through an ionic mechanism.

Taking this into account and starting from the values of the reactivity ratios in the ethylene-propylene and ethylene-butene-1 copolymerization, we have theoretically foreseen and experimentally verified<sup>11</sup> the reactivity ratios for the propylene-butene-1 copolymerization reported in Table III.

TABLE III  
Monomer Reactivity Ratios in the Propylene-1-Butene Copolymerization

Catalytic system	$r_{C_3H_6}$	$r_{C_4H_8}$
$VCl_4 + Al(C_6H_{13})_3$	4.39	0.227
$VCl_3 + Al(C_6H_{13})_3$	4.04	0.252

Starting from the values of the reactivity ratios, we have finally established that the distribution of the monomer units in ethylene-propylene copolymers is very close to the one which is to be expected for a random distribution.<sup>12</sup>

TABLE IV  
Distribution Function of Sequences of Different Lengths in Ethylene-Propylene Copolymers Having  
Different Compositions and Prepared with  $\text{Al}(\text{C}_6\text{H}_{13})_3\text{-VCl}_4$  Catalyst

Mole-% of $m_x$ in the copolymer	% $P(m_x)_n^a$															
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$	$n > 15$						
85	15.80	13.20	11.20	9.430	7.941	6.687	5.630	4.741	3.992	for $n$ between 10 and 14, $P(m_x)_n = 12.271\%$						9.006
75	27.07	19.74	14.40	10.50	7.658	5.584	4.073	2.970	2.166	for $n$ between 10 and 14, $P(m_x)_n = 4.631\%$						1.204
60	44.47	24.69	13.71	7.614	4.228	2.347	1.303	0.724	...	for $n$ between 9 and 14, $P(m_x)_n = 0.762\%$						0.142
50	55.89	24.65	10.87	4.796	2.116	0.933	0.412	...	...	for $n$ between 8 and 14, $P(m_x)_n = 0.324\%$						0.003
40	66.70	22.21	7.398	2.464	0.820	0.273	...	...	...	for $n$ between 7 and 14, $P(m_x)_n = 0.136\%$						$< 1 \times 10^{-3}$
25	81.20	15.27	2.871	0.540	0.101	...	...	...	...	for $n$ between 6 and 14, $P(m_x)_n = 0.023\%$						$< 1 \times 10^{-3}$
15	89.53	9.377	0.982	0.103	...	...	...	...	...	for $n$ between 5 and 14, $P(m_x)_n = 0.012\%$						$< 1 \times 10^{-3}$

<sup>a</sup> %  $P(m_x)_n$  = percentage of sequences of ethylene (or of propylene) containing  $n$  monomer units.  $n$  = number of monomer units present in each sequence.

The values of distribution functions of sequences having different lengths for ethylene-propylene copolymers of various compositions and prepared by using the catalytic system  $\text{Al}(\text{C}_6\text{H}_{13})_3\text{-VCl}_4$  are given in Table IV. From this table we can see that, for copolymers containing equimolecular amounts of the two monomers, the major part of the sequences is formed by only one monomer unit and the probability of sequences containing more than five monomer units is extremely low. The theoretical prevision for the distribution of different length sequences was found to be in agreement with the length values of the sequences of methylene groups, determined through IR spectrography. Additional evidence is the absence of polyethylenic-type crystallinity in copolymers containing more than 20% propylene moles.<sup>12</sup>

In this paper the kinetic study of ethylene-propylene copolymerization in the presence of catalysts prepared from vanadium tetrachloride and trihexylaluminum is described. In particular, the influence on the copolymerization rate of a series of factors, such as preparation conditions of the catalyst, concentration of the catalyst and monomers, ratio between the moles of the two monomers present in the reaction medium, and temperature, is described. The kinetic interpretation of the experimental data reported here will be the subject of a following paper.

#### Conditions Chosen for the Copolymerization Experiments

All the copolymerization experiments reported in this paper were carried out in the presence of *n*-heptane as solvent. The concentration of the two monomers was kept constant during each experiment.

The solvent was saturated with the monomer mixture before introduction of the catalyst. Furthermore, to make certain that the monomer concentration did not change noticeably during polymerization, we have adopted high space velocity in order to renew the gaseous phase rapidly, to keep the solution as close as possible to a saturation condition.

The conversion of each monomer was, for each passage, lower than 5%. We also noticed that the copolymer composition was practically constant, all other conditions being equal, when we increased the feed rate of the mixture.

The experiments carried out for our kinetic study were interrupted after relatively short times in order to limit the concentration of the copolymers in the reaction medium (not beyond 5%), and to avoid the excessive viscosity which might make difficult the mass transfer process of the monomers from the gaseous phase to the liquid phase.

The copolymer formed in the absence of inert solvents was not soluble in a mixture of the two monomers, and much higher yields, referred to the used catalyst, could be reached without an increase of viscosity in the liquid phase.<sup>13</sup> However, the absence of an inert diluent caused too high reaction rates to enable an accurate kinetic study. In the conditions chosen by us, we reached<sup>3,5-3</sup> an excellent reproducibility of results, either for the composition of the copolymers or for the polymerization rate.

## Catalytic System

### (a) Transition Metal Halide

For carrying out the study of the kinetics of ethylene-propylene copolymerization, we selected, from among the different possible catalytic systems, the one prepared from trihexylaluminum and vanadium tetrachloride. This catalytic system proved to be preferable in respect to those prepared by other hydrocarbon soluble transition metal halides (such as  $\text{TiCl}_4$  or  $\text{VOCl}_3$ ) because it yields completely amorphous copolymers within a larger range of composition of the monomer mixture.<sup>5</sup> In addition, the copolymers thus obtained possess a better homogeneity of composition.

The use of catalysts prepared from low-valency halides, insoluble in hydrocarbons (as  $\text{VCl}_3$ ), has not proved to be convenient for our kinetic study because they show an induction period of remarkable length at low temperatures.

### (b) Stabilization of the Catalysts

In accordance with what generally occurs for catalysts prepared from transition metal halides which are soluble in hydrocarbons, the catalytic system  $\text{VCl}_4\text{-Al}(\text{C}_6\text{H}_{13})_3$  loses activity with time (see Fig. 3). In order to obtain catalysts having an activity constant with time, we prepared and kept the catalysts for a certain time at a temperature higher than that of

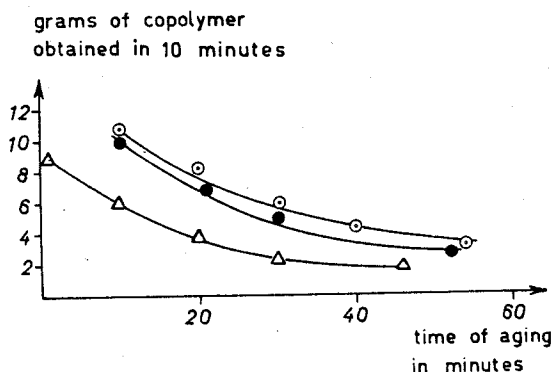


Fig. 3. Dependence of the production on the time of aging. Experimental conditions: polymerization temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles  $\text{C}_3\text{H}_6$ /moles  $\text{C}_2\text{H}_4$  in the gaseous feed, 2; polymerization times, 10 min. (○) Catalyst aged at 25°C.; moles  $\text{Al}(\text{C}_6\text{H}_{13})_3$ /moles  $\text{VCl}_4$ , 1; *V* (g. vanadium present in the catalytic system), 0.0224. (●) Catalyst aged at 25°C.; moles  $\text{Al}(\text{C}_6\text{H}_{13})_3$ /moles  $\text{VCl}_4$ , 2.5; *V*, 0.0162. (△) Catalyst aged at 60°C.; moles  $\text{Al}(\text{C}_6\text{H}_{13})_3$ /moles  $\text{VCl}_4$ , 2.5; *V*, 0.0299.

their intended use. We found that by mixing the solutions of  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$  at 60°C. and keeping the mixture at that temperature for 30 min., catalysts were obtained which, when used between 0 and 40°C., showed a lower activity which remained constant for a time longer than that generally required for the polymerization experiments mentioned in

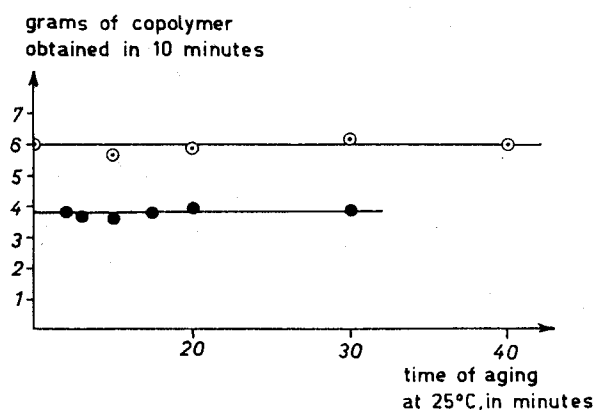


Fig. 4. Independence of the activity of catalysts prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$  and aged at  $60^\circ\text{C}$ . for 30 min. of the times of aging at  $25^\circ\text{C}$ . Experimental conditions: polymerization temperature,  $25^\circ\text{C}$ .; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; *V*, 0.0299; moles  $\text{C}_3\text{H}_6$ /moles  $\text{C}_2\text{H}_4$  in the gaseous feed, 2; polymerization times, 10 min. (○) moles  $\text{Al}(\text{C}_6\text{H}_{13})_3$ /moles  $\text{VCl}_4$ , 2.5; (●) moles  $\text{Al}(\text{C}_6\text{H}_{13})_3$ /moles  $\text{VCl}_4$ , 4.

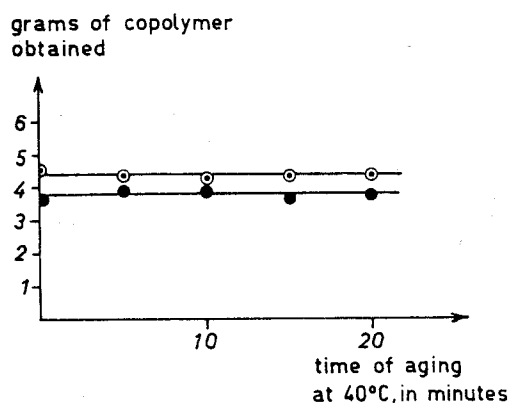


Fig. 5. Independence of the activity of catalysts prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$  and aged at  $60^\circ\text{C}$ . for 30 min. of the times of aging at  $40^\circ\text{C}$ . Experimental conditions: polymerization temperature,  $40^\circ\text{C}$ .; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles  $\text{Al}(\text{C}_6\text{H}_{13})_3$ /moles  $\text{VCl}_4$ , 2.5; moles  $\text{C}_3\text{H}_6$ /moles  $\text{C}_2\text{H}_4$  in the gaseous feed, 2.15. (○) *V*, 0.0299; polymerization time, 10 min. (●) *V*, 0.0449; polymerization time, 6 min.

this paper (see Figs. 4 and 5). In every experiment reported in this paper, the catalysts have been thermally stabilized in the above-mentioned conditions (30 min. at  $60^\circ\text{C}$ .). The activity of the catalyst is higher when the aging times are lower, but it is not constant.

### (c) Influence of the $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{VCl}_4$ Ratio

In our previous papers, we have seen that the copolymer composition does not vary when the ratio between the moles of  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and of  $\text{VCl}_4$  used in the preparation of the catalysts is varied, at least for an  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{VCl}_4$  ratio between 1 and 8. This result is also valid in the case in which the stabilized catalysts are used.

The catalyst activity also changes, being the highest for  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{VCl}_4$  molar ratios of about 2.5 (see Fig. 6). This is in agreement with what has

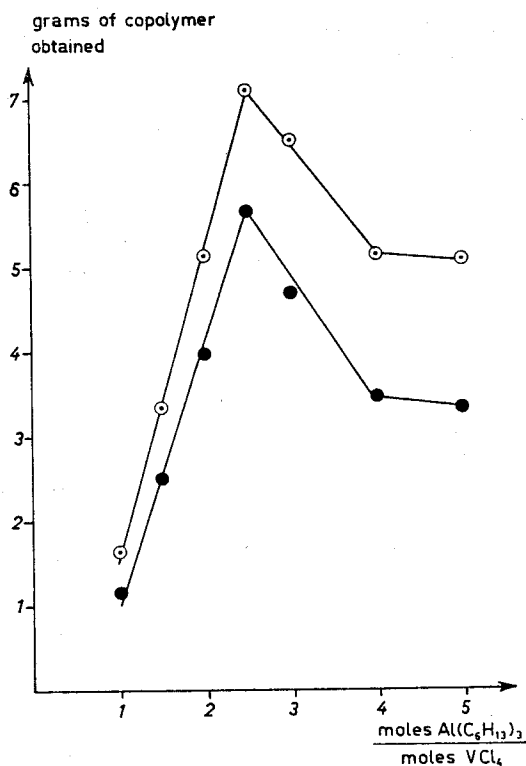


Fig. 6. Dependence of the catalyst activity on the molar ratio  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{VCl}_4$ . Experimental conditions: polymerization temperature,  $25^\circ\text{C}$ .; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles  $\text{C}_3\text{H}_6$ /moles  $\text{C}_2\text{H}_4$  in the gaseous feed, 2. (○)  $V = 0.0449$ ; polymerization time, 8 min. (●)  $V = 0.0299$ ; polymerization time, 10 min.

been found in propylene<sup>14-18</sup> and ethylene<sup>19-23</sup> homopolymerizations carried out in the presence of catalysts prepared from soluble halides of transition metals. An  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{VCl}_4$  molar ratio of 2.5 has been used in every copolymerization experiment mentioned in this paper unless otherwise stated.

### Influence of the Operative Conditions on the Copolymerization Rate

#### (a) Time

We have noticed that, other conditions being equal, the quantity of copolymer is directly proportional to the time of polymerization (see Fig. 7). This has been proved in a large composition range of the monomer mixture and, for each composition, in a large concentration range of the catalyst. For example, in Figures 8 and 9, the copolymer yields are plotted against polymerization time for different catalyst concentrations and for copolymers containing 50.6 and 41.7 mole-% ethylene, respectively. The results show that catalysts thermally stabilized in the way mentioned above present an activity constant with time, independent of whether the catalyst is, in the meantime, used or not used for the copolymerization.



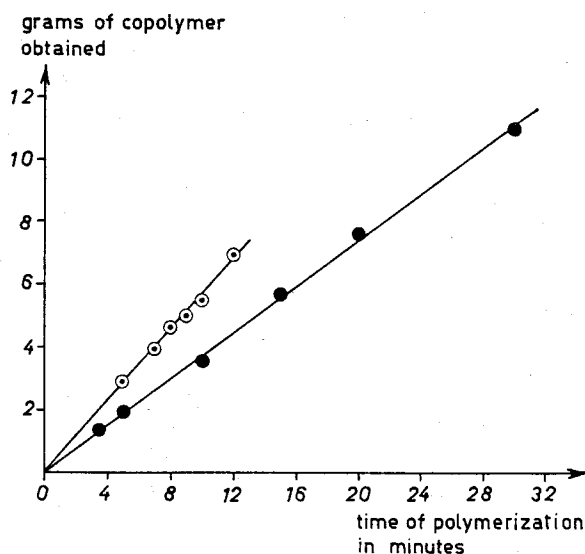


Fig. 7. Dependence of the copolymer yield (in grams) on the polymerization time. Experimental conditions: polymerization temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; *V*, 0.0299; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 2. (○) moles Al(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>/moles VCl<sub>4</sub> = 2.5; (●) moles Al(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>/moles VCl<sub>4</sub> = 4.

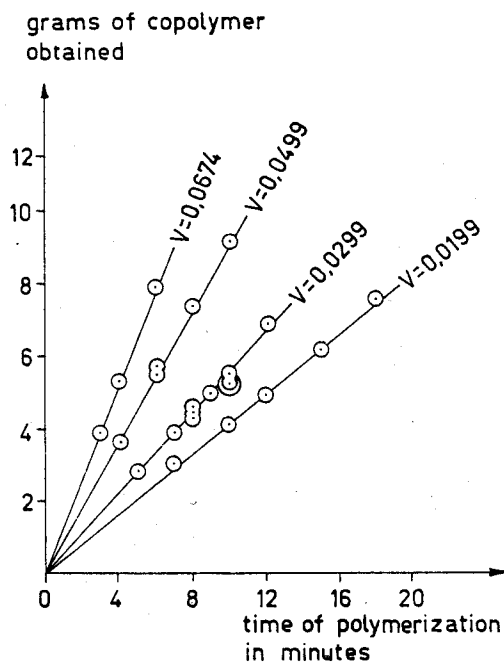


Fig. 8. Dependence of the copolymer yield (in grams) on the polymerization time for different catalyst concentrations. Experimental conditions: polymerization temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 2; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 50.6.

This fact allows us to conclude that kinetic chain termination processes do not take place during the copolymerization; that is, each possible interruption of the propagation reactions of each single macromolecule takes place through transfer mechanism, leaving the number of growing

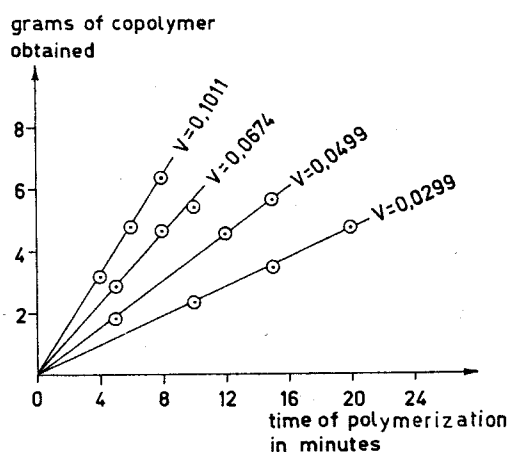


Fig. 9. Dependence of the copolymer yield (in grams) on the polymerization time for different catalyst concentrations. Experimental conditions: polymerization temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 3; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 41.7.

chains practically unchanged. This last hypothesis is confirmed by the fact that when using a stabilized VCl<sub>4</sub>—AlR<sub>3</sub> catalyst at 25°C., the average molecular weight of the copolymer, determined on the basis of its intrinsic viscosity, is practically constant with time and with the amount of copolymer produced (see Tables V and VI).

(b) *Catalyst Concentration*

If the copolymer yields shown in Figures 8 and 9, and which were obtained at different times and at different catalyst concentrations, are related to the weight unity of vanadium present in the catalytic system, values directly proportional to the polymerization time are obtained (see

TABLE V  
Intrinsic Viscosities of Ethylene-Propylene Copolymers Obtained with Stabilized Catalysts at Different Times of Polymerization<sup>a</sup>

Polymerization time, min.	Copolymer yield, g.	[ $\eta$ ] <sup>b</sup>
5	2.80	4.36
7	3.92	4.50
8	4.60	4.21
9	4.96	4.20
10	5.45	4.44
12	6.95	4.19

<sup>a</sup> Experimental conditions: temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 2; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 50.6; *V* (grams of vanadium present in the catalytic system), 0.0299; moles Al(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>/moles VCl<sub>4</sub>, 2.5.

<sup>b</sup> [ $\eta$ ] = intrinsic viscosity, measured at 135°C. in tetrahydronaphthalene, and expressed in 100 cm.<sup>3</sup>/g.

TABLE VI  
Intrinsic Viscosities of Ethylene-Propylene Copolymers, Obtained with Stabilized Catalysts at Different Times of Polymerization<sup>a</sup>

Polymerization time, min.	Copolymer yield, g.	$[\eta]^b$
5	2.85	2.61
8	4.65	2.89
10	5.41	2.57

<sup>a</sup> Experimental conditions: temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 3; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 41.7; *V* (grams of vanadium present in the catalytic system), 0.0674; moles Al(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>/moles VCl<sub>4</sub>, 2.5.

<sup>b</sup>  $[\eta]$  = intrinsic viscosity, measured at 135°C. in tetrahydronaphthalene, and expressed in 100 cm.<sup>3</sup>/g.

Figs. 10 and 11). We can therefore conclude that the copolymerization occurs at a first-order rate with respect to the catalyst concentration.

The plots shown in Figure 12 confirm that the copolymerization rates expressed as:

$$G/Vh \quad (1)$$

where *G* is the grams of copolymer produced in time *h* expressed in hours, and *V* is the grams of vanadium present in the catalytic system, all other conditions being equal, are constant with time.

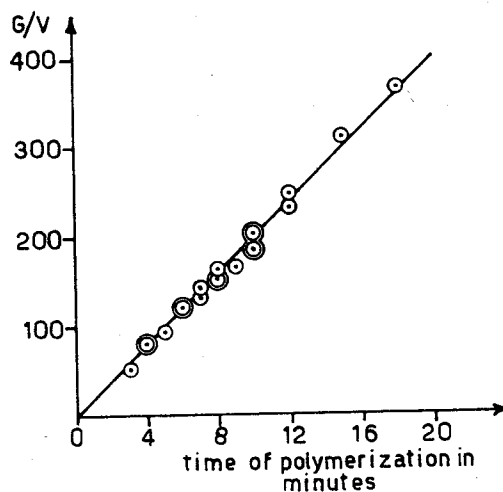


Fig. 10. Variation of *G* (g. copolymer obtained) referred to *V* with the polymerization time. Experimental conditions: polymerization temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 2; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 50.6.

### (c) Monomer Concentration

To study the dependence of the copolymerization rate on the concentration of the dissolved monomers, we carried out a series of experiments in

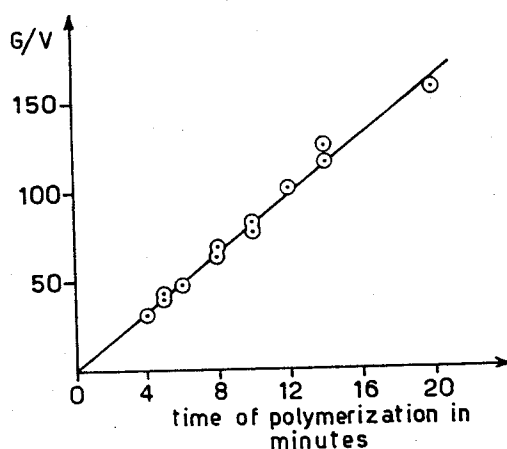


Fig. 11. Variation of  $G$  referred to  $V$  with the polymerization time. Experimental conditions: polymerization temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 3; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 41.7.

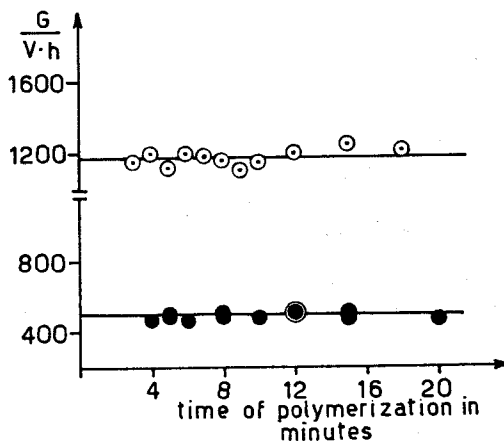


Fig. 12. Copolymerization rate vs. polymerization time. (○) moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 2; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 50.6. (●) moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 3; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 41.7.

which, while the ratio between the concentrations of the two monomers remained constant, their total concentration was changed. These experiments were carried out at a total absolute pressure of 1 atm., while the monomer partial pressure was varied by diluting the gaseous monomer mixture, having a certain composition, with known amounts of highly pure nitrogen (see Tables VII, VIII, and IX). We preferred to work with pressures no larger than 1 atm. because otherwise the copolymerization rate would have been too high, thus making the thermostabilization of the system more difficult.

In the three series of experiments we used mixtures of monomers corresponding, respectively, to molar ratios of propylene/ethylene of 2, 0.95 and 0.56.

As can be seen from the last column of Tables VII, VIII, and IX, when

TABLE VII  
Dependence of the Rate of Copolymerization on the Total Monomer Concentration<sup>a</sup>

<u>moles N<sub>2</sub></u> moles C <sub>2</sub> H <sub>4</sub> + moles C <sub>3</sub> H <sub>6</sub> in the gaseous feed	Poly- meriza- tion time, min.	G, g. copoly- mer	V, g. vana- dium	G/Vh	R <sup>b</sup>
0	3	3.89	0.0674	1154	1154
0	4	5.31	0.0674	1182	1182
0	6	7.95	0.0674	1180	1180
0	4	3.65	0.0449	1219	1219
0	6	5.40	0.0449	1203	1203
0	8	7.41	0.0449	1238	1238
0.62	5	2.80	0.0449	748	1212
0.62	10	5.21	0.0449	696	1127
0.98	6	3.91	0.0674	580	1149
0.98	8	5.14	0.0674	572	1133
0.98	12	7.85	0.0674	582	1152
0.98	8	3.61	0.0449	603	1194
0.98	10	4.46	0.0449	596	1180
0.98	12	5.40	0.0449	601	1190
1.54	3	1.55	0.0674	460	1168
1.54	8	4.25	0.0674	473	1201
1.54	6	2.10	0.0449	468	1189
1.54	10	3.50	0.0449	468	1189
2	8	3.45	0.0674	384	1152
2	10	4.35	0.0674	387	1161
2	10	3.05	0.0449	408	1224
2	12	3.68	0.0449	410	1230

<sup>a</sup> Experimental conditions: temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane = 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 2; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 50.6.

$$^b R = (G/Vh)[715/(P_{C_2H_4} + P_{C_3H_6})]$$

TABLE VIII  
Dependence of the Rate of Copolymerization on the Total Monomer Concentration<sup>a</sup>

<u>moles N<sub>2</sub></u> moles C <sub>2</sub> H <sub>4</sub> + moles C <sub>3</sub> H <sub>6</sub> in the gaseous feed	Poly- meriza- tion time, min.	G, g. copoly- mer	V, g. vana- dium	G/Vh	R <sup>b</sup>
0	4	3.56	0.0299	1786	1786
0	6	5.50	0.0299	1839	1839
1.09	10	4.28	0.0299	859	1795
1.09	15	6.61	0.0299	884	1848
1.09	4	3.84	0.0674	855	1787
1.09	7	6.58	0.0674	837	1749

<sup>a</sup> Experimental conditions: temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 0.95; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 66.

$$^b R = (G/Vh) [715/(P_{C_2H_4} + P_{C_3H_6})]$$

TABLE IX  
Dependence of the Rate of Copolymerization on the Total Monomer Concentration<sup>a</sup>

moles N <sub>2</sub> moles C <sub>2</sub> H <sub>4</sub> + moles C <sub>3</sub> H <sub>6</sub> in the gaseous feed	Polymeri- zation time, min.	G, g. copolymer	$\frac{G}{Vh}$	R <sup>b</sup>
0	4	5.72	2869	2869
0	5	7.10	2850	2850
1	4	2.78	1395	2790
1	8	5.65	1417	2834

<sup>a</sup> Experimental conditions: temperature, 25°C.; abs. pressure 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 0.50; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 78; *V* (grams of vanadium present in the catalytic system), 0.0299.

<sup>b</sup>  $R = (G/Vh)[715/(P_{C_2H_4} + P_{C_3H_6})]$

the copolymerization rates are reduced to a pressure of 715 mm. Hg (sum of the partial pressures of the two monomers, when operating at 1 atm. pressure, without addition of inert components to the gaseous feed), they are constant for a given ratio  $P_{C_2H_4}/P_{C_3H_6}$ .

For each value of this ratio the copolymerization rate is directly proportional to the sum of the partial pressures and therefore to the sum of the molar concentration in the dissolved phase, as is shown in Figure 13.

The copolymerization rate varies remarkably when the ratio between the concentrations of the two monomers is changed. In order to carry out some comparable copolymerization experiments using different feed compositions, we have adopted certain concentrations of the catalyst and of the monomers for each composition, which will avoid too high copoly-

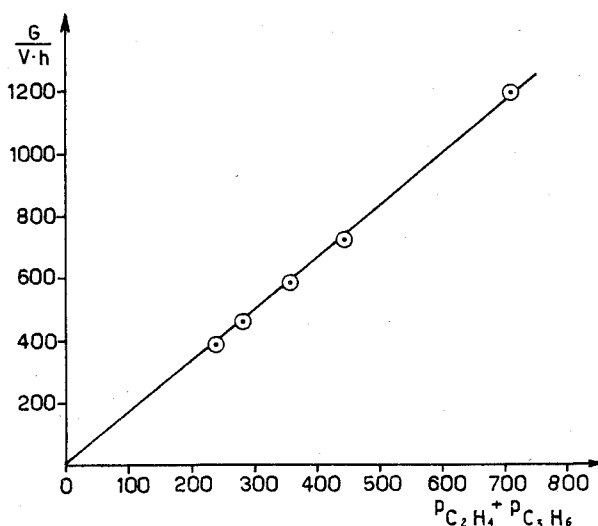


Fig. 13. Dependence of copolymerization rate on the sum of the partial pressure of the monomers (mm. Hg) in the gaseous feed. Experimental conditions: polymerization temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub>, in the gaseous feed, 2; mole-% C<sub>2</sub>H<sub>4</sub> in the copolymer, 50.6.

merization rates. In particular, in the case of copolymerizations carried out with mixtures rich in ethylene (molar ratio ethylene/propylene in the gaseous feed  $> 2$ ), we found it convenient to dilute the feeding mixture with nitrogen, even when working with relatively low catalyst concentrations.

By using the previously reported results (dependence of the first-order rate on the catalyst concentration and, since the ratio between the monomer concentrations remains equal, on their total concentration in solution), it was possible to compare experiments which were carried out under different conditions. For each feed composition we have carried out a number of experiments (generally 10 or 12) in which both different catalyst concentrations and polymerization times were used.

TABLE X  
Rate of Ethylene-Propylene Copolymerization for Copolymers Containing 41.7 Mole-% Ethylene<sup>a</sup>

V, g. vanadium	Polymeri- zation time, min.	G, g. copolymer	R <sup>b</sup>
0.1011	4	3.18	472
0.1011	6	4.82	477
0.1011	8	6.41	481
0.0674	5	2.85	507
0.0674	8	4.65	518
0.0674	10	5.41	482
0.0449	5	1.82	486
0.0449	12	4.59	510
0.0449	15	5.65	503
0.0299	10	2.32	466
0.0299	15	3.47	464
0.0299	20	4.73	475

<sup>a</sup> Experimental conditions: temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 3; *p*<sub>C<sub>2</sub>H<sub>4</sub></sub> + *p*<sub>C<sub>3</sub>H<sub>6</sub></sub>, 715.

<sup>b</sup>  $R = (G/Vh)[715/(P_{C_2H_4} + P_{C_3H_6})]$

In Tables X, XI, and XII we report the values obtained for copolymerization rates for copolymers having 41.7, 50.6, and 78 mole-% ethylene. For each experiment the rate (reduced to 715 mm. Hg pressure) expressed as in eq. (1) has been calculated, and for every series of experiments which corresponding to the same feeding mixture the average rate value is reported in Table XIII.

Because of the different solubility coefficients of ethylene and propylene, it is interesting to express the rates corresponding to different feed compositions by referring to the same total concentration of olefins in the dissolved phase. As the reference concentration we have chosen the one which corresponding to one mole of total olefins dissolved per liter of solu-

TABLE XI  
Rate of Ethylene-Propylene Copolymerization for Copolymers Containing 50.6 mole-% of Ethylene<sup>a</sup>

V, g. vanadium	Polymeri- zation time, min.	G, g. copolymer	R <sup>b</sup>
0.0674	3	3.89	1154
0.0674	4	5.31	1182
0.0674	6	7.95	1180
0.0449	4	3.65	1219
0.0449	6	5.40	1203
0.0449	6	5.55	1236
0.0449	8	7.41	1238
0.0449	10	9.15	1223
0.0299	5	2.80	1124
0.0299	7	3.92	1124
0.0299	8	4.60	1154
0.0299	8	4.57	1146
0.0299	8	4.48	1124
0.0299	9	4.96	1106
0.0299	10	5.55	1114
0.0299	10	5.53	1110
0.0299	10	5.45	1094
0.0299	12	6.95	1161
0.0199	7	2.89	1245
0.0199	10	4.10	1236
0.0199	12	4.95	1241
0.0199	15	6.22	1250
0.0199	18	7.30	1221

<sup>a</sup> Experimental conditions: temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 2;  $p_{C_2H_4} + p_{C_3H_6}$ , 715.

<sup>b</sup>  $R = (G/Vh)[715/(P_{C_2H_4} + P_{C_3H_6})]$

tion.\* The molar fractions of olefins and *n*-heptane in the dissolved phase were calculated according to the method used in a previous paper.<sup>4</sup>

Finally, by expressing the copolymer productions in moles of polymerized monomers instead of grams, we calculated the comparable rate values (see Table XIII) as follows:

$$(M/l)/[(V/l)h(m/l)] \quad (2)$$

where *M* indicates the sum of the ethylene and propylene moles polymerized in *h* time, expressed in hours, and *m* is the sum of the moles of dissolved olefins.

In Figure 14 we report the rate values versus the percentage of dissolved ethylene moles referred to the total moles of the two monomers. In

\* The volume of the solution has been calculated neglecting the variation of volume due to the copolymer produced.



TABLE XII  
Rate of Ethylene-Propylene Copolymerization for Copolymers Containing 78 mole-% Ethylene<sup>a</sup>

moles N <sub>2</sub> moles C <sub>2</sub> H <sub>4</sub> + moles C <sub>3</sub> H <sub>6</sub> in the gaseous feed	V, g. vanadium	Polymeri- zation time, min.	G, g. copolymer	R <sup>b</sup>
0	0.0299	4	5.72	2869
0	0.0299	4.5	6.36	2836
0	0.0299	5	7.10	2850
1	0.0299	3.5	2.46	2822
1	0.0299	4	2.78	2790
1	0.0299	8	5.65	2834
1	0.0299	8	5.45	2734
1	0.0449	1	1.08	2886
1	0.0449	5	5.10	2726

<sup>a</sup> Experimental conditions: temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>; moles C<sub>3</sub>H<sub>6</sub>/moles C<sub>2</sub>H<sub>4</sub> in the gaseous feed, 0.50.

$$^b R = (G/Vh)[715/(P_{C_2H_4} + P_{C_3H_6})]$$

TABLE XIII  
Dependence of Rate of Ethylene-Propylene Copolymerization on Composition of the Feed<sup>a</sup>

moles C <sub>3</sub> H <sub>6</sub> moles C <sub>2</sub> H <sub>4</sub> in the gaseous feed	Moles-% C <sub>2</sub> H <sub>4</sub> in the copolymer	N <sub>C<sub>2</sub>H<sub>4</sub></sub> <sup>b</sup>	N <sub>C<sub>3</sub>H<sub>6</sub></sub> <sup>c</sup>	M <sub>C<sub>2</sub>H<sub>4</sub></sub> <sup>d</sup>	R <sup>e</sup>	M/l <sup>f</sup> (V/l)h(m/l)-
0.018	98.9	0.0219	0.00173	0.927	3791	811
0.059	94.8	0.0211	0.00543	0.795	3848	724
0.130	93.0	0.0198	0.01121	0.638	3263	515
0.219	88.6	0.0183	0.01752	0.511	3202	426
0.500	78.0	0.0149	0.03250	0.314	2816	266
0.950	66.0	0.0115	0.04750	0.194	1801	132
2.000	50.6	0.0075	0.06498	0.103	1178	66
3.000	41.7	0.0056	0.07312	0.071	487	24
6.250	27.0	0.0031	0.08405	0.036	219	9.2
12.500	16.3	0.0017	0.09027	0.018	55	2.1

<sup>a</sup> Experimental conditions: catalyst prepared and aged for 30 min. at 60°C. from Al(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub> and VCl<sub>4</sub>; moles Al<sub>3</sub>(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>/moles VCl<sub>4</sub>, 2.5; polymerization temperature, 25°C.; pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>.

<sup>b</sup> N<sub>C<sub>2</sub>H<sub>4</sub></sub> = molar fraction of ethylene in the liquid phase.

<sup>c</sup> N<sub>C<sub>3</sub>H<sub>6</sub></sub> = molar fraction of propylene in the liquid phase.

<sup>d</sup> M<sub>C<sub>2</sub>H<sub>4</sub></sub> = N<sub>C<sub>2</sub>H<sub>4</sub></sub>/(N<sub>C<sub>2</sub>H<sub>4</sub></sub> + N<sub>C<sub>3</sub>H<sub>6</sub></sub>).

<sup>e</sup> R = (G/Vh)[715/(P<sub>C<sub>2</sub>H<sub>4</sub></sub> + P<sub>C<sub>3</sub>H<sub>6</sub></sub>)]

<sup>f</sup> M = sum of the ethylene and propylene moles polymerized in *h* hours; *m* = sum of the ethylene and propylene moles in the liquid phase.

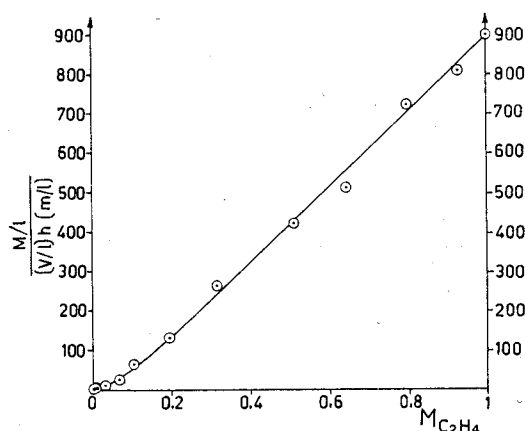


Fig. 14. Dependence of the copolymerization rate on the percentage of dissolved ethylene moles, referred to the total moles of the two monomers. Experimental conditions: catalyst prepared and aged for 30 min. at 60°C.; moles  $Al(C_6H_{13})_3$ /moles  $VCl_4$ , 2.5; polymerization temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>.

order to indicate in the plot of Figure 14, the values of the ordinates corresponding to the abscissas 0 and 1, we had to carry out some homopolymerization experiments of ethylene and propylene, under the same experimental conditions adopted in the copolymerization experiments.

The results obtained in these homopolymerization experiments and the rates expressed according to a formula similar to eq. (2) are given in Tables XIV and XV. As shown in Figure 14, the copolymerization rate increases remarkably with an increase of ethylene content in the monomer mixture. It is only for monomer mixtures rich in ethylene that the copolymerization rate is approximately a linear function of the molar composition of the monomer mixture present in the liquid phase. For monomer mixtures

TABLE XIV  
Rate of Ethylene Homopolymerization<sup>a</sup>

moles $N_2$	Moles $C_2H_4$ in the gaseous feed	<i>V</i> , g. vanadium	Polymeri- zation time, min.	<i>G</i> , g. polymer	$\frac{G}{Vh}$	$\frac{M/l}{(V/l)h(m/l)}$
					$\times \frac{715}{pc_{2H_4}}$	
3.30		0.0299	6	2.70	3882	886
3.30		0.0299	8	3.55	3825	873
3.05		0.0299	8	3.93	3993	912
3.32		0.0299	7.5	3.52	4068	929
3.00		0.0299	2	1.00	4013	916
2.85		0.0299	6	3.00	3862	882
3.30		0.0449	2	1.38	3962	905
3.30		0.0499	4	2.85	4089	934
3.30		0.0449	6	4.25	4069	929

<sup>a</sup> Experimental conditions: catalyst prepared and aged for 30 min. at 60°C. from  $Al(C_6H_{13})_3$  and  $VCl_4$ ; moles  $Al(C_6H_{13})_3$ /moles  $VCl_4$ , 2.5; polymerization temperature, 25°C.; pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>.

TABLE XV  
 Rate of Propylene Homopolymerization<sup>a</sup>

$V$ , g. vanadium	Polymeri- zation time, min.	$G$ , g. polymer	$\frac{G}{Vh} \times \frac{715}{p_{C_3H_6}}$	$\frac{M/l}{(V/l)h(m/l)}$
0.2731	40	2.62	14.39	0.4912
0.2731	40	2.75	15.10	0.5154
0.2731	33	2.28	15.18	0.5182
0.1820	40	1.83	15.08	0.5147
0.1820	40	1.86	15.33	0.5233
0.1820	40	1.68	13.85	0.4728
0.1820	25	1.09	14.37	0.4905

<sup>a</sup> Experimental conditions: catalyst prepared and aged for 30 min. at 60°C. from  $Al(C_6H_{13})_3$  and  $VCl_4$ ; moles  $Al(C_6H_{13})_3$ /moles  $VCl_4$ , 2.5; polymerization temperature, 25°C.; abs. pressure, 1 atm.; *n*-heptane, 410 cm.<sup>3</sup>.

rich in propylene (beyond 80% of  $C_3H_6$  with respect to the total moles of dissolved olefins), the rate values diverge from the rectilinear behavior.

In a later paper a kinetic interpretation will be given to explain the rate variation with the variation in the composition of the monomer mixture.

(d) *Temperature*

In order to determine whether different activation energies for the two monomers correspond to the remarkable differences found between the homopolymerization rates of ethylene and propylene, we performed some experiments at different temperatures. On the basis of numerous ethylene and propylene homopolymerization runs at temperatures of 0, 25, and 40°C., we have calculated, for each temperature, an average value of homopolymerization rate expressed according to eq. (2).

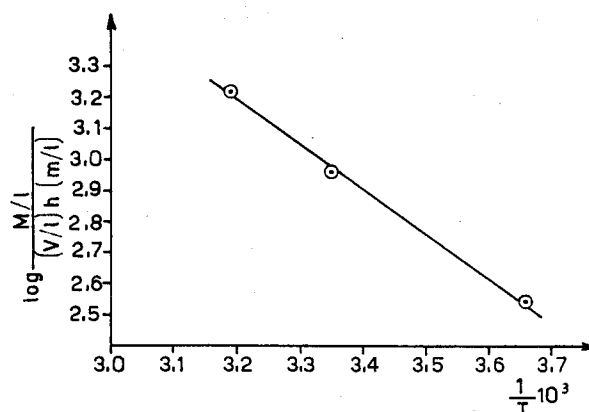


Fig. 15. Logarithm of the rate of ethylene polymerization with stabilized catalysts, prepared from  $Al(C_6H_{13})_3$  and  $VCl_4$ , vs. the reciprocal of the absolute polymerization temperature. (The reported values are the average of numerous values determined for each temperature.)

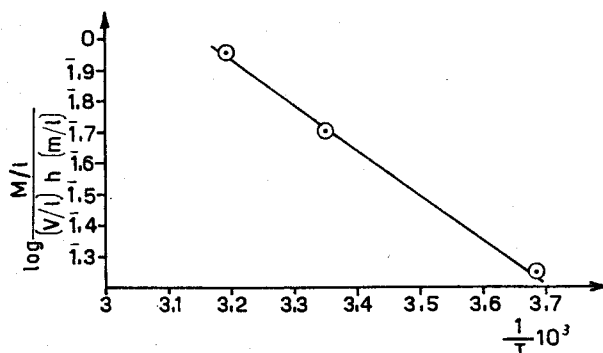


Fig. 16. Logarithm of the rate of propylene polymerization with stabilized catalysts, prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$ , vs. the reciprocal of the absolute polymerization temperature. (The reported values are the average of numerous values determined for each temperature).

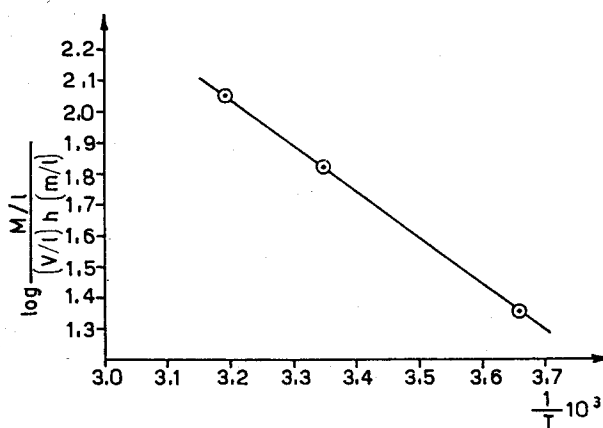


Fig. 17. Logarithm of the rate of ethylene-propylene copolymerization, for copolymers containing 50.6 mole-%  $\text{C}_2\text{H}_4$  with stabilized catalysts prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$ , vs. the reciprocal of the absolute polymerization temperature. (The reported values are the average of numerous values determined for each temperature.)

As shown in Figures 15 and 16, the logarithms of these rates vary linearly with the reciprocal of the absolute temperature of polymerization. From the slope of the straight lines we can calculate the following values for the activation energy, referred to the monomer concentration in the dissolved phase:

$$\begin{array}{ll} \text{polymerization of ethylene:} & E = 6650 \text{ cal./mole} \\ \text{polymerization of propylene:} & E = 6600 \text{ cal./mole} \end{array}$$

These resulting values do not practically differ from one another and are of the same order of magnitude as the activation energies previously found for propylene<sup>24-26</sup> and ethylene<sup>27,28</sup> homopolymerization in the presence of different catalytic systems. The remarkable differences between the homopolymerization rates of the two monomers should therefore be ascribed, at least in part, to steric factors.

In Figure 17 the average values of the copolymerization rate logarithms, expressed according to eq. (2) (for copolymers containing 50.6 mole-% ethylene) at 0, 25, and 40°C. are reported. The logarithm of the rates varies, also in this case as a straight line, with the reciprocal of the absolute temperature, with the slope corresponding to the one observed for both homopolymerizations. This equality of apparent activation energies is significant because, in the case of copolymerization, we are not allowed to consider an activation energy of the overall process, since its overall rate depends upon the rates of the four elementary processes to which different activation energies may correspond.<sup>29</sup>

In fact, in the case of the copolymerization of the two monomers  $M_1$  and  $M_2$ , when  $M_1^*$  and  $M_2^*$  are the instantaneous concentrations of the monomer units present at the end of the growing polymeric chains, the rates of the four elementary processes can be indicated as:

$$\begin{aligned} V_{11} &= k_{11}[M_1^*][M_1] \\ V_{12} &= k_{12}[M_1^*][M_2] \\ V_{21} &= k_{21}[M_2^*][M_1] \\ V_{22} &= k_{22}[M_2^*][M_2] \end{aligned}$$

The overall copolymerization rate will be:

$$V = V_{11} + V_{12} + V_{21} + V_{22}$$

The rate constant for each process is given by:

$$\begin{aligned} k_{11} &= P_{11}Z_{11} \exp \left\{ -E_{11}/RT \right\} \\ k_{12} &= P_{12}Z_{12} \exp \left\{ -E_{12}/RT \right\} \\ k_{22} &= P_{22}Z_{22} \exp \left\{ -E_{22}/RT \right\} \\ k_{21} &= P_{21}Z_{21} \exp \left\{ -E_{21}/RT \right\} \end{aligned}$$

where  $Z$  is the collision number and  $P$  is the steric factor. As it is well known, the  $P$  factor is essentially independent of temperature and the  $Z$  factor is only slightly affected. Therefore the ratios  $P_{11}Z_{11}/P_{12}Z_{12}$  and  $P_{22}Z_{22}/P_{21}Z_{21}$  can be practically considered as constant, at least in the relatively narrow range of temperature examined by us.

In our previous papers we have shown that in the ethylene-propylene copolymerization, in the presence of catalysts prepared from vanadium halides and aluminum trialkyls, the reactivity ratios do not vary practically with temperature, at least for temperatures between 0 and 75°C.

Given:

$$r_{11} = k_{11}/k_{12} = (P_{11}Z_{11}/P_{12}Z_{12}) \exp \left\{ (E_{12} - E_{11})/RT \right\}$$

and

$$r_{22} = k_{22}/k_{21} = (P_{22}Z_{22}/P_{21}Z_{21}) \exp \left\{ (E_{21} - E_{22})/RT \right\}$$

we have

$$E_{12} = E_{11}$$

and

$$E_{21} = E_{22}$$

On the other hand, from what we have shown above for the ethylene and propylene homopolymerizations, we have  $E_{22}$  practically equal to  $E_{11}$ . Therefore, by comparing the previous equations, we deduce that the energies of activation of the four elementary processes of ethylene-propylene copolymerization have to be practically the same.

### Conclusions

A systematic study of the ethylene-propylene copolymerization with catalysts prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$  has been carried out. When using low concentrations of monomers and catalyst, so that the effect of mass transfer and heat transfer phenomena can be neglected, we obtained the following results:

(1) The catalyst activity decreases with time. However if the catalyst is kept for a certain time (30 min.) at  $60^\circ\text{C}$ ., the stabilized catalyst shows an activity constant in time in the range between 0 and  $40^\circ\text{C}$ .

(2) The activity of the stabilized catalysts depends on the ratio between the moles of the two reactants used for its preparation. The highest activity is obtained for a  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{VCl}_4$  molar ratio near 2.5.

(3) The copolymerization rate varies linearly with the amount of catalyst introduced in the system when stabilized catalysts are used.

(4) When the ratio between the concentrations of the two monomers is equal, the copolymerization rate is first order with respect to the total concentration of the monomers present in the liquid phase.

(5) For a given value of the total concentration of the two monomers, the copolymerization rate increases very rapidly with the increase in ethylene concentration, deflecting remarkably from the linearity for low ethylene concentrations.

(6) The activation energies of the four elementary processes of copolymerization, referred to equal monomer concentrations in the dissolved phase, are practically the same (6600 cal./mole).

### Experimental

#### (a) Materials

Ethylene (purity higher than 99.5%) was supplied by Montecatini Co. The radioactive ethylene was prepared according to the method described by us in a previous communication.<sup>3</sup>

The propylene used was prepared by dehydration of isopropanol on activated alumina at  $360\text{--}380^\circ\text{C}$ . Propylene, after fractionated condensation, was distilled and collected in bottles containing sodium. Then propylene was distilled again and collected in bottles containing sodium tetraethyl aluminate. The product thus obtained appeared, when analyzed by mass spectrography, to have a purity higher than 99%, the remainder being mostly propane.

*n*-Heptane (Esso Pure Grade) was anhydriated and rectified in the presence of potassium and kept under a nitrogen atmosphere.

Trihexylaluminum has been prepared according to a method analogous to that described by Ziegler<sup>30</sup> and according to the improvements used by Fulton.<sup>31</sup> The trihexylaluminum was free from chlorine and from alkyl aluminum hydrides; its purity, evaluated by a potentiometric method,<sup>32,33</sup> was 94–95%.

Pure nitrogen, 99.99%, proved insufficiently pure to be used in copolymerization experiments (when added to the feed mixture). It was therefore placed in a bomb containing triethylaluminum, and the bomb was shaken for many days.

Vanadium tetrachloride was supplied by the Donegani Institute of Novara and purified by distillation.

#### (b) Apparatus

The apparatus employed was as follows:

(a) A stainless steel oscillating autoclave, 3 liters capacity and equipped with a thermoregulator, acted as a tank for the mixture of the two monomers. This autoclave was provided with a valve connected with a Griesheim pressure reducing valve heated with a resistance in order to avoid condensations caused by cooling of the gases due to expansion.

(b) A flowmeter, calibrated at room pressure for gaseous mixtures of ethylene and propylene of different compositions, used to measure the flow of the gaseous feed.

(c) A reaction apparatus, formed by a glass cylindrical vessel, 700 cm.<sup>3</sup> capacity, having an internal diameter of 5.5 cm. and equipped with a mechanical stirrer, with tubes for the addition and discharge of gases, and a thermometric sheath. The gas addition tube reached the bottom of the vessel. It ended with a porous disc, having a diameter of 3.5 cm. Different porous discs have been employed; however, it has been observed that the results did not change when discs of the G<sub>1</sub>, G<sub>2</sub>, or G<sub>2</sub> types were used. All the subsequent runs were performed using a porous G<sub>3</sub> disc. The reaction apparatus was placed in a thermostatic bath at the polymerization temperature,  $\pm 0.1^\circ\text{C}$ .

(d) A water counter fit for measuring the flow of the gases.

#### (c) Procedure

As an example, we will report a detailed description of a copolymerization experiment.

A mixture of monomers which could be employed in different copolymerization runs was prepared in the tank autoclave. In the closed and deaerated autoclave, 206 g. of propylene and 69 g. of radioactive ethylene were introduced. The autoclave was heated and shaken to a temperature at which the two monomers are completely gaseous (160–170°C.); then gas samples were drawn out and analyzed. Ethylene and propylene contents were calculated on the basis of the amounts of gas introduced in the tank. Analyses by mass spectrography and gas chromatography, were in good agreement.

370 cm.<sup>3</sup> of *n*-heptane was introduced into the reaction apparatus, in which air had been replaced by nitrogen. We then started the circulation of the gaseous mixture of the two monomers at a flow rate of 150 Nl./hr. until equilibrium between the two dissolved monomers and the gaseous feed phase was reached. In the meantime, in a 50-cm.<sup>3</sup> flask kept under a nitrogen atmosphere and equipped with a magnetic stirrer and kept at 60°C., a solution of 1.47 mmoles of trihexylaluminum was introduced into 20 cm.<sup>3</sup> of *n*-heptane. Then, very rapidly under agitation, a solution of 0.59 mmoles of VCl<sub>4</sub> in 20 cm.<sup>3</sup> of *n*-heptane was introduced. It has been observed that the most suitable conditions leading to reproducible results in the copolymerization runs are obtained when the solutions of the two reagents forming the catalyst are mixed in 5–10 sec.

The catalyst thus prepared is maintained under agitation for 30 min. at 60°C. The stabilized catalyst is introduced into the reaction apparatus in a time period (5–10 sec.) which is negligible in comparison with the time of the copolymerization run.

We continued feeding and discharging the mixture of the two monomers at a feed flow of 200 Nl./hr. During this period it was possible to observe that the solution became more and more viscous. The reaction is interrupted after 10 min. by introducing about 10 cm.<sup>3</sup> of methanol. This kept the viscosity of the solution from becoming too high.

The heptane solution was repeatedly treated with diluted HCl and water in order to remove the inorganic products produced by the decomposition of the catalyst. The copolymer was completely coagulated by pouring the heptane solution into a large excess of a methanol–acetone mixture. A solid, white ethylene–propylene copolymer (5.45 g.) was isolated. It looked like a nonvulcanized rubber and was amorphous by x-rays. Low molecular weight oily polymers were not detectable by evaporation of the solvents employed.

The molar content of 50.6% ethylene in the copolymer has been determined by the radiochemical method using <sup>14</sup>C-labelled ethylene.

By indicating the specific activity of ethylene by  $A_0$  (in counts/min.) and by  $A$ , the activity of a copolymer in which the molar fraction of ethylene is  $X$ , we obtain

$$A/A_0 = 2X/(3 - X)$$

from which it is possible to calculate  $X$ .

The activities of ethylene and the copolymers have been calculated on a lamina of pressed polymer by a G.M. counter equipped with a thin window of 1.6 mg./cm.<sup>2</sup>, according to the method described earlier.<sup>3</sup> The intrinsic viscosity, corresponding to 4.4 100 cm.<sup>3</sup>/g., has been measured in tetrahydronaphthalene at 135°C. according to a procedure described in a previous paper.<sup>3</sup>



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## Synopsis

The values of the reactivity ratios for ethylene-propylene and ethylene-1-butene copolymerization, described in previous papers, and the distribution of monomer units in different length sequences are discussed. In this paper the kinetics of ethylene-propylene copolymerization in the presence of catalysts prepared from trialkylaluminum and vanadium tetrachloride is studied. Having adopted the conditions leading to the

formation of catalysts having an activity independent of time, we were able to determine that the copolymerization rate is first order with respect to the catalyst concentration and to the sum of the concentrations of the two monomers. With the total concentration of the monomers constant, the copolymerization rate increases very rapidly as the ethylene concentration increases. The activation energies of the four chain growth reactions of the copolymerization proved to be practically equal.

### Résumé

On discute d'abord les valeurs, déjà reportées dans nos travaux précédents, des rapports de réactivité pour les copolymérisations éthylène-propylène et éthylène-butène-1 et les prévisions sur la distribution des séquences des unités monomériques. Dans cette note, on étudie la cinétique de copolymérisation éthylène-propylène en présence de catalyseurs préparés à partir de trialkyle-aluminium et de tétrachlorure de vanadium. Après avoir décrit les conditions qui permettent la formation de catalyseurs à activité constante au cours du temps, on montre que la vitesse de copolymérisation est du premier ordre par rapport à la concentration en catalyseur et à la somme des concentrations des deux monomères. En supposant une concentration totale des deux monomères toujours identique, la vitesse augmente très rapidement au fur et à mesure que la concentration de l'éthylène augmente. Les énergies d'activation des quatre processus de la copolymérisation sont pratiquement équivalentes.

### Zusammenfassung

Zuerst werden die von uns in früheren Arbeiten angegebenen Werte der Reaktivitätsverhältnisse für die Äthylen-Propylen- und Äthylen-Buten-1-Copolymerisation und die Schlüsse auf die Verteilung der Monomereinheiten in verschiedenen Längensequenzen diskutiert. In der vorliegenden Arbeit wird die Kinetik der Äthylen-Propylen-Copolymerisation in Gegenwart von Katalysatoren aus Aluminiumtrialkylen und Vanadintetrachlorid untersucht. Nachdem die Bedingungen zur Bildung eines Katalysators mit zeitlich konstanter Aktivität gefunden waren, konnten wir feststellen, dass die Copolymerisationsgeschwindigkeit erster Ordnung in bezug auf die Katalysatorkonzentration und auf die Summe der Konzentrationen der beiden Monomeren ist. Bei konstanter Gesamtkonzentration der Monomeren steigt die Copolymerisationsgeschwindigkeit sehr rasch mit steigender Äthylenkonzentration an. Die Aktivierungsenergien der vier Kettenwachstumsreaktionen der Copolymerisation erwiesen sich als praktisch gleich.

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