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## POLYOLEFIN ELASTOMERS

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## I. FOREWORD

The new processes of anionic co-ordinated polymerization have permitted the synthesis of new polymers which are of interest as plastics, fibers, and elastomers. Among these last, the ethylene-propylene rubbers are particularly interesting for the future of the rubber industry. In fact these elastomers are prepared from low-cost raw materials (ethylene and propylene) and show good mechanical and elastic properties as well as excellent resistance to aging.

## II. THE COMPOSITION OF ETHYLENE-PROPYLENE COPOLYMERS

When tackling the problem of ethylene-propylene copolymerization, it has been necessary to have at our disposal a series of criteria which enable us to establish that the products obtained actually consist of copolymers, and not of homopolymer mixtures.

It has also been necessary to set up analytical methods which allow the quantitative determination of the monomers present in the copolymer.

The systems adopted to establish that the polymers under examination actually consist of copolymers are based primarily on an accurate fractionation of the crude

copolymerizate, performed by extraction with boiling solvents, with increasing solvent power, and then on the comparison between the results obtained both from this fractionation and from the extraction carried out on homopolymers (and the mixtures) obtained from the single olefins, under the same conditions<sup>1</sup>.

Further proof that the various fractions actually consist of copolymers is given by various physical chemical methods, such as x-ray and infrared spectrograph analyses, and by the determination of mechanical properties.

*A. Fractionation by hot solvent extraction and physical chemical examination of the various fractions.*—The ethylene-propylene copolymerizates were fractionated by hot solvent extraction in Kumagawa extractors.

The solvents used are, in order: acetone, ethyl ether, *n*-hexane, and *n*-heptane. If the behavior on extraction of a pure polyethylene is compared, Table I, with the behavior shown by the products obtained from the copolymerization of suitable ethylene-propylene mixtures, with the aid of catalysts prepared from vanadium tetrachloride and trihexylaluminum, it appears clear that the polymerization of these mixtures yielded only ethylene-propylene copolymer.

In fact, polyethylene obtained from ethylene alone under the same polymerization conditions used for the synthesis of the copolymers, is not extractable with the above mentioned solvents. Also polypropylene, obtained from only propylene, under the same polymerization conditions, contains a fraction that is left as a residue after heptane extraction. On the contrary, by extraction of the products obtained by us from the polymerization of ethylene-propylene mixtures, no residue is left after *n*-heptane extraction, in the case of crude copolymers having a content up to about 75 mole % of ethylene. This shows that ethylene and propylene copolymerize without formation of homopolymers.

Further proof that the copolymerization products actually consist of copolymer is given by the examination of the properties of the various fractions.

The infrared spectra of the fractions that can be obtained by ether extraction show easily detectable differences with respect to the spectrum of the amorphous ether-extractable polypropylene fraction and of polyethylene, Figure 1.

In particular, in the region comprised between 13 and 13.8  $\mu$ , bands can be clearly observed, which can be attributed to the presence of sequences of methylenic groups of different length.

More precisely, it is possible to observe bands due to  $(-CH_2-)_n$  grouping where *n* can be either higher than or equal to 2, and lower than 5, and the bar corresponding to  $n \geq 5$ .

Also the infrared spectra of the fractions that can be extracted from the copolymers by hexane and heptane are quite different from the spectra of the analogous fractions, obtained by extraction of the propylene homopolymer. In fact, the latter show characteristic bands, due to the presence of crystalline regions that can be attributed to chain portions of isotactic polypropylene, but the former do not show such bands, but other characteristic bands, some of which are due to the presence of methylenic groups, Figure 2.

It may be interesting to point out that in the spectra of copolymers, and in particular of the lower-molecular-weight fractions, the band at about 11.2  $\mu$ , resulting from double bonds of the vinylidenic type can be easily observed. This demonstrates that in the anionic copolymerization considered here, one of the prevailing chain rupture processes is due to the transfer of a hydride ion from the tertiary carbon atom of a terminal propylene monomeric unit, with formation of vinylidenic double bond, in analogy with what is observed in the homopolymerization of propylene<sup>2</sup>.

TABLE I

COMPARISON OF THE EXTRACTION OF POLYETHYLENE AND POLYPROPYLENE WITH THAT OF SOME ETHYLENE-PROPYLENE COPOLYMERS PREPARED UNDER THE SAME EXPERIMENTAL CONDITIONS

Catalyst prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VOCl}_3$ ; mole  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{mole VOCl}_3 = 3$ ;  $T = 25^\circ\text{C}$ ;  $P = 1$  at.; solvent: *n*-heptane,  $\text{cm}^3/400$ .

Product	Acetone extract			Ether extract			n-hexane extract			n-heptane extract			residue		
	%	$[\eta]$	Crystall. %	%	$[\eta]$	Crystall. %	%	$[\eta]$	Crystall. %	%	$[\eta]$	Crystall. %	%	$[\eta]$	Crystall. %
Polyethylene	0	—	—	0	—	—	0	—	—	0	—	—	0	—	—
Polypropylene	0.61	0.60	0	14.95	0.82	35	11.05	1.2	45	100	1.9	>70	9.52	2.5	70
Ethylene-propylene copolymer (31 mole ethylene %)	1.00	2.20	0	14.29	3.10	0	3.21	3.9	0	0	3.21	—	0	—	—
Ethylene-propylene copolymer (49 mole ethylene %)	0.60	2.74	0	25.10	4.22	0	4.00	5.65	<5	0	—	—	0	—	—
Ethylene-propylene copolymer (62 mole ethylene %)	0.20	3.10	0	59.00	4.72	0	12.20	6.20	<5	0	—	—	0	—	—

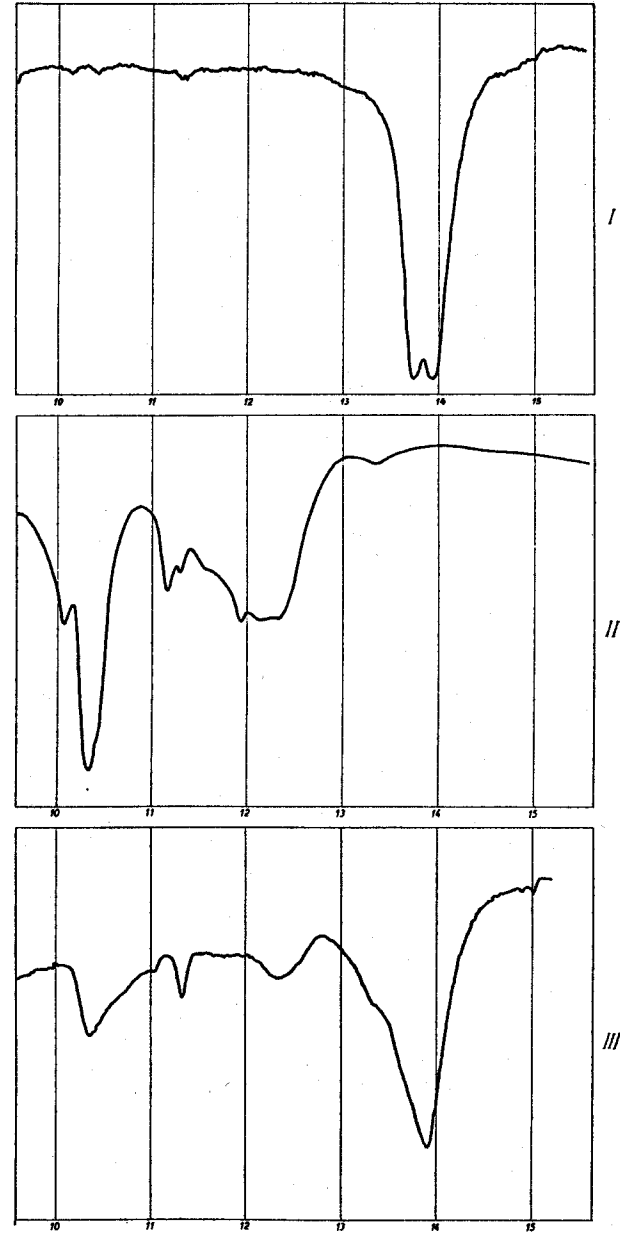


FIG. 1.—IR spectra, between  $9.5$  and  $15\mu$ , of a linear polyethylene (I), an ether extract of polypropylene (II) and an ether extract of an ethylene-propylene copolymer, containing 35 mole % ethylene (III), prepared with the catalytic system  $\text{VOCl}_3 + \text{Al}(\text{C}_6\text{H}_{13})_3$ . Thickness of laminae:  $0.1$  mm.

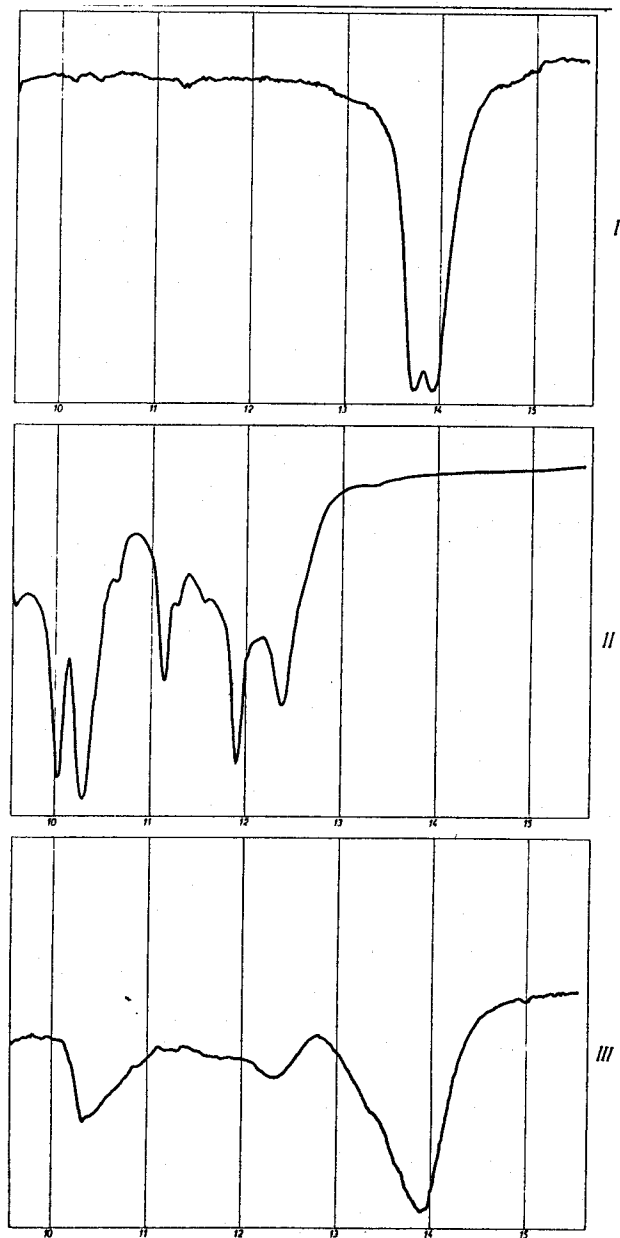


FIG. 2.—IR spectra, between 9.5 and 15 $\mu$  of a linear polyethylene (I) a fraction of polypropylene not extractable by boiling *n*-hexane but extractable by boiling *n*-heptane (II) and a corresponding fraction of an ethylene-propylene copolymer, containing 75 mole % ethylene (III), prepared with the catalytic system  $\text{VOCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_3$ . Thickness of laminae: 0.1 mm.

Also x-ray examination of the different fractions of ethylene-propylene copolymers, proves that the products under examination actually consist of copolymers.

The fractions isolated by ether extraction are completely amorphous, Table I; however, the curve of the diffraction intensity shows a maximum that corresponds to an angle, which is different both from that of pure amorphous polypropylene and from the angle that can be observed for an amorphous polyethylene, Figure 3.

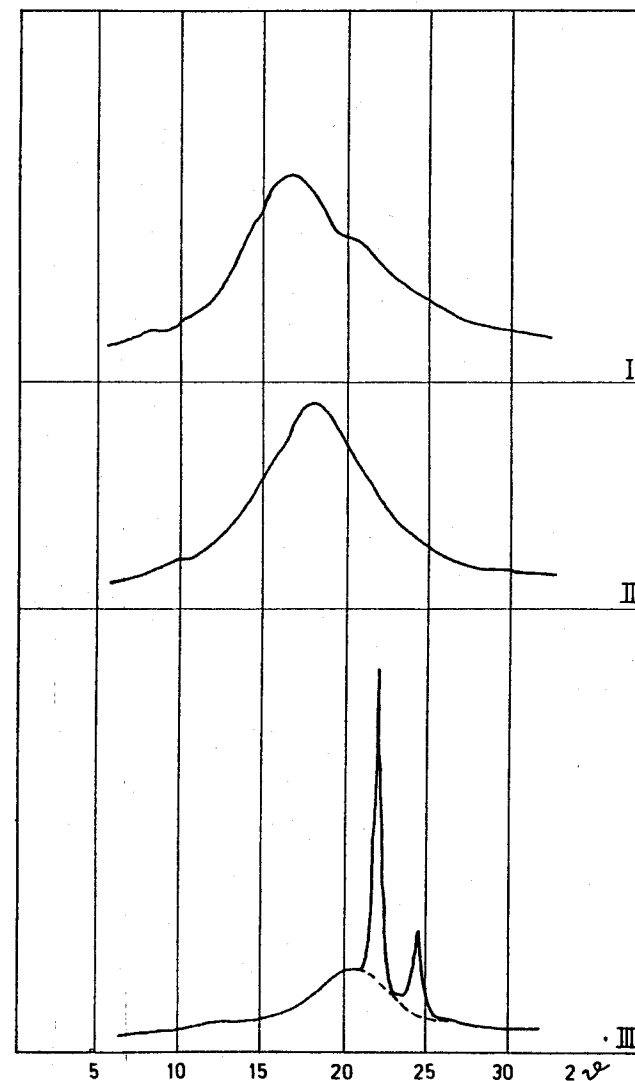


FIG. 3.—X-ray diffraction records (Cu  $K\gamma$ ) of an ether extract of polypropylene (I), an ether extract of an ethylene-propylene copolymer containing 35 mole % ethylene and extractable by boiling ether (II) and a linear polyethylene (III).

The x-ray analysis reveals also that the *n*-hexane extractable fractions are amorphous; on the contrary, the analogous fractions obtained from propylene homopolymers generally show a partial crystallinity, corresponding to about 30–40%<sup>3</sup>.

Crystallinity from polypropylene has never been observed in the *n*-heptane extractable fractions, even for very low ethylene contents; on the other hand the analogous fractions obtained from pure polypropylene show a fairly high crystallinity, corresponding to about 50%<sup>3</sup>. Moreover, crystallinity from polyethylene is usually absent in the *n*-heptane extractable fractions, Table I and Figure 4.

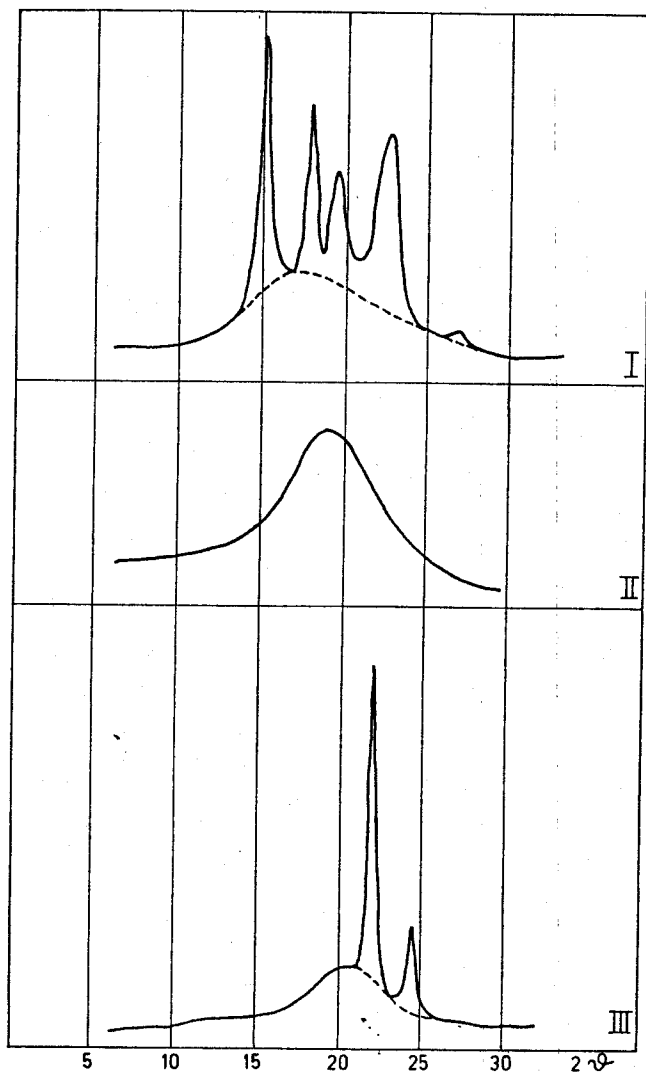


Fig. 4.—X-ray diffraction records (Cu  $K\alpha$ ) of a stereoblock polypropylene, partially crystallizable; extractable by boiling *n*-heptane (I), a fraction of an ethylene-propylene copolymer containing 70 mole % ethylene and extractable by boiling *n*-heptane (II) and a linear polyethylene (III).

A low crystallinity (usually lower than 10%) was observed only for fairly high ethylene contents: it can be observed on the evidence of diffraction maxima, which however, are slightly displaced with respect to those of pure polyethylene. This crystallinity can be attributed to the presence of a small amount of copolymer that consists of macromolecules having a high ethylene content, which allows the existence of blocks of methylenic groups having a length of at least about 40–50 Å (about 20 monomeric units).

As already stated, for our ethylene-propylene copolymers there is usually no residue after heptane extraction. However, if copolymers having an ethylene content higher than 75 mole % are fractionated, the presence of a fraction nonextractable with hot *n*-heptane is observed.

The x-ray and IR spectrographic analyses of these fractions reveal both displacements and broadenings of the polyethylene bands and the absence of the typical bands of polypropylene. This allows one to establish that such a residue consists of copolymers richer in ethylene; portions of considerable length consisting of methylenic groups are present in some of their single chains. These portions are presumed to cause the slight crystallinity and the lower solubility of the polymer.

*B. Mechanical properties of ethylene-propylene copolymers.*—The mechanical properties of the ethylene-propylene copolymers will be described in detail in another section of this review. However, it must be mentioned here that the copolymerization procedures developed by us yield products that show peculiar and interesting mechanical properties. Such properties differ markedly from those of the homopolymers, of their mixtures, as well as of the products (e.g., obtained from discontinuous runs carried out with the aid of catalysts prepared from  $TiCl_4$  and triethylaluminum) consisting of mixtures of homopolymers and of copolymers with very dispersed compositions.

This is made evident by comparing the stress-strain curves of testpieces obtained from artificial mixtures of the two homopolymers (Figure 5). These mixtures were prepared by coprecipitation and had an empirical composition comparable with that of the copolymers that gave the testpieces used to secure the curves of Figure 6.

The behavior of the mixtures obtained by coprecipitation of polyethylene with atactic polypropylene in a three-to-one and one-to-one weight ratio, shows that the two products have little compatibility. Already on molding at 150° C, the resulting

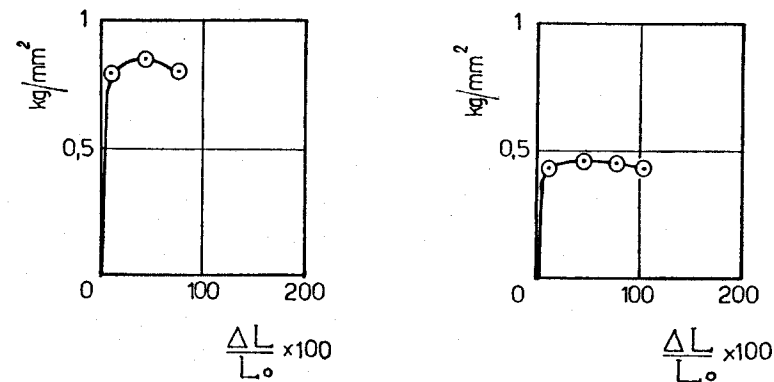


Fig. 5.—Stress-strain curves of artificial mixtures of polyethylene and polypropylene, weight ratio 1:1 (left) and 1:3 (right).

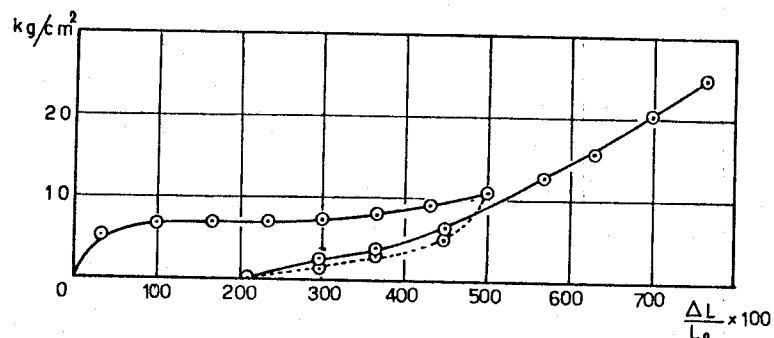


Fig. 6.—Stress-strain curve of a fraction of ethylene-propylene copolymer (residue after boiling ether extraction). Mole %  $C_2H_4$  = 65;  $[\eta]$  = 4.05.

sheet is not homogeneous. Testpieces obtained from it, give stress-strain curves, Figure 5, that are characteristic of heterogeneous mechanical mixtures. The stress-strain curves of the mixtures show a yield point, which is absent in the curves of the copolymers, a high initial elastic modulus, which differs from the low modulus of the copolymers, Figure 6, and a low breaking elongation due to the strains caused by the different deformations of the components of the heterogeneous mixtures. As will be described in more detail in another section of this review, the mechanical tests have shown that these copolymers have high elastic elongations, which are characteristic of amorphous, linear high-molecular-weight substances, having a low second-order transition temperature.

On the other hand, the behavior of products obtained by copolymerization in the presence of unsuitable catalysts and under discontinuous conditions, is shown in Figure 7; the high initial modulus and lower elastic elongation indicate that this behavior corresponds to that of mixtures of homopolymers and of copolymers.

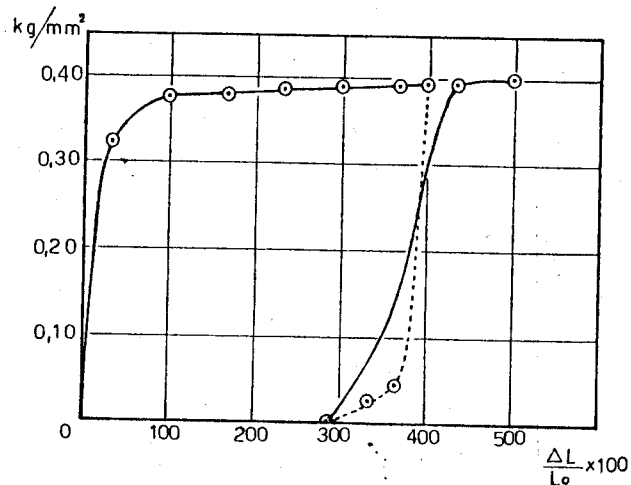


Fig. 7.—Stress-strain curve of a sample formed by a mixture of copolymers and homopolymers, obtained by batch copolymerization of ethylene and propylene (mole  $C_2H_4$ /mole  $C_3H_6$  in the gaseous mixture = 4) with a catalyst prepared from  $TiCl_4$  and  $Al(C_2H_5)_3$ .

### III. ANALYTICAL METHODS FOR DETERMINATION OF THE COMPOSITION OF COPOLYMERS

The composition of the ethylene-propylene copolymers was established by different methods.

*A. Radiochemical.*—By copolymerizing propylene with  $C^{14}$ -labelled ethylene the weight percentage of ethylene units in the copolymer is given by the ratio of the specific activity of the copolymer to that of polyethylene obtained by homopolymerization of the radioactive ethylene.

Radioactive ethylene is prepared starting from tagged  $Ba^*CO_3$ , following the procedure proposed by Cox and Warne<sup>4</sup>, based on the following reactions:

Transformation of barium carbonate into carbide  
Preparation of acetylene from the carbide  
Selective hydrogenation of acetylene to ethylene, in the presence of chromium salts.

The preparation was effected on one millimole of substance, containing  $1 \mu c$  of  $C^{14}$ . Removal of possible traces of unconverted acetylene was effected by absorption in ammonia solutions of cuprous salts, after diluting the high-specific-activity ethylene with 2-3 liters of high-purity ethylene of the type used to prepare polyethylene by high-pressure processes.

The diluted ethylene had a specific activity of  $0.8 \mu c$  per mg of substance.

Ethylene obtained from the first dilution was kept in a small gasometer of 2.5 liters capacity; at various times, 100-200 ml of the product were removed for the subsequent dilutions. Dilution was performed by sucking 100-200 ml of ethylene of the first dilution into an 800 ml stainless steel cylinder, and then condensing 350-400 g of ethylene through cooling with methanol/Dry Ice.

After homogenization, various samples, which were subsequently polymerized were obtained from the ethylene mentioned above. Polymerization was carried out, according to the procedure described<sup>5</sup>, with the aid of a catalytic system consisting of triethylaluminum and titanium tetrachloride.

The samples of polyethylene and of the copolymers whose specific activity has to be measured are prepared as follows: 40-50 mg of polymer are molded between aluminum sheets, with spacers of about 0.3 mm, in a small press at  $140^\circ-150^\circ C$  and at about  $100 \text{ kg/cm}^2$ . Thus, a small sheet is obtained; stamping gives discs having a diameter of about 14 mm. Finally, the discs are introduced into small aluminum plates and fixed by an aluminum template, so that they have a free circular surface of  $1.33 \text{ sq cm}$  for computation.

A Geiger counter equipped with a thin mica window of about  $1.8 \text{ mg/cm}^2$  is used for counting. All measurements are corrected for the background; moreover, counting is continued for a time sufficient to reduce the standard error due to statistical fluctuation to about 1%. No correction is made for self-absorption, since the samples, prepared as mentioned above, are "infinitely thick" with respect to the weak  $\beta$  emission from  $C^{14}$ .

*B. Analysis by infrared spectrography.* 1. *General method.*—When dealing with the problem of the analysis of the ethylene-propylene copolymers by infrared spectrography, it is necessary to distinguish two cases, depending on whether the copolymer under study is or is not completely soluble in solvents suitable for infrared spectroscopic examination (for instance carbon tetrachloride).

The analysis, in the former case, is fairly simple: the measurement of the optical density of the absorption band at  $7.25 \mu$ , due to methyl groups, allows the determination of the number of propylene units<sup>1,6</sup> present, incurring an error lower than

3%. The optical density is read with respect to a base line drawn between 7.10 and 7.60  $\mu$ . The value of the coefficient used is the mean obtained from the values determined by measurements performed on various solutions of atactic polypropylene.

A limitation of this method is that the ethylene-propylene copolymers often yield seemingly homogeneous solutions, which, however, contain swollen copolymer particles. In this case, the measurement is effected on the copolymer in the solid state, having the shape of laminae about 0.1 mm thick, obtained by diecasting the copolymer<sup>7</sup>. A ratio was set between two bands, one of which is proportional to the content of propylene units and the other to that of ethylene units vs. the composition of the copolymer which was determined by other methods.

The band at 8.60  $\mu$  was chosen as a band proportional to the concentration of propylene units: in fact it is hardly disturbed by the appearance of crystallinity in polypropylene. The band at 2.32  $\mu$  was chosen as a band sensitive to the number of ethylene units; however, this is effected by variations in length of the methylenic sequences and also, though very little, by the possible presence (which appears very seldom in the copolymers under examination) of small amounts of crystalline polyethylene and polypropylene sequences. It can be noticed that the band at 2.32  $\mu$  is proportional to the number of all the carbon-hydrogen bonds present in the copolymer, and therefore is essentially proportional to the thickness of the lamina under examination.

The calibration curve is reported in Figure 8. The optical density at 8.60  $\mu$  is read with respect to a base line traced between 8 and 9  $\mu$ .

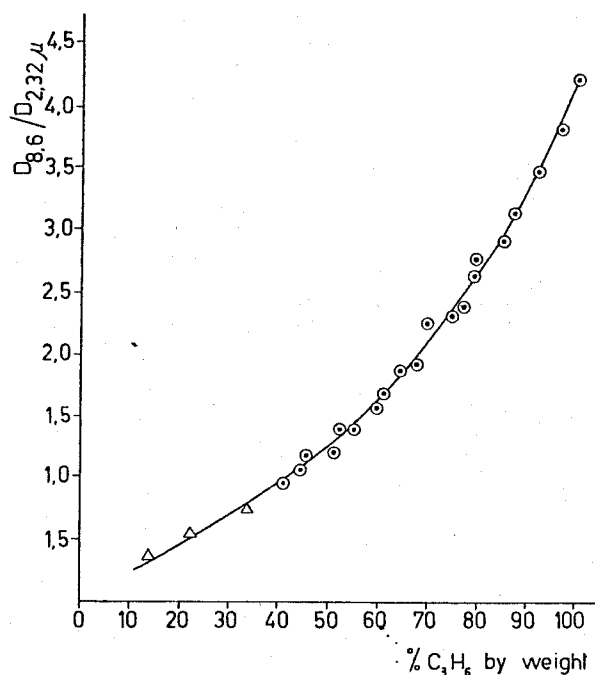


FIG. 8.—Dependence of the ratio between the optical densities at 8.60 and 2.32  $\mu$  on the propylene content of an ethylene-propylene copolymer.  $\circ$  Propylene content determined by IR spectrography in solution.  $\Delta$  Ethylene content determined radiochemically.

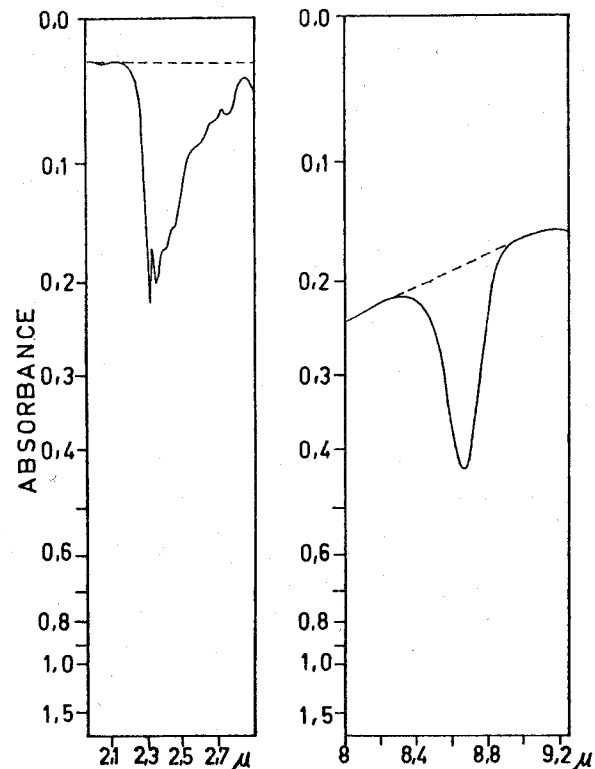


FIG. 9.—IR spectra of an ethylene-propylene copolymer; spectral regions employed for the IR analysis on laminae.

The optical density of the band at 2.32  $\mu$  is read with respect to a base line traced as in Figure 9.

2. *Other infrared spectrography methods.*—According to the method proposed by Gössl<sup>6</sup>, the sample when not completely soluble in the organic solvents, is examined as a film, using the ratio

$$R = E_{13.9 \mu} / E_{8.6 \mu}$$

between the extinction coefficients at 13.9 and 8.6  $\mu$ . The calibration curve is traced by using samples which are completely soluble in carbon tetrachloride; consequently, the band at 7.25  $\mu$  can be used for them.

The method proposed by Wei<sup>8</sup> uses the ratio

$$R' = E_{8.7 \mu} / E_{13.9 \mu}$$

between the extinction coefficients at 8.7 and 13.9  $\mu$ . The logarithm of this ratio is a linear function of the molar per cent of propylene in the copolymer.

A drawback to these methods is that the optical density of the band at 13.9  $\mu$  can only in a first approximation be considered proportional to the monomeric unit content of the copolymer; this band is strongly affected by the possible presence of ethylene homopolymers and of long crystalline polyethylenic sequences.

However, the most serious drawback is that both the intensity, and the position of the band are strongly influenced by the length of the methylenic sequences present in the copolymers. It has been exhaustively demonstrated<sup>9</sup> how this band, attributed to the rocking motion of the methylenic groups, can be separated into various components attributable to the various lengths of the methylenic sequences.

It follows that the measurement of the optical density at 13.85–13.9  $\mu$  considers chiefly the long sequences of methylenic groups while in practice it does not take into account the short sequences. Thus, it is clearly apparent that, to the extent that the long methylenic sequences prevail over the short sequences, the optical density of the band at 13.9  $\mu$  is faintly proportional to the total content of ethylenic units. But, when there are shorter sequences (they can be noticed easily due to the appearance of absorption bands at 13.3 and between 13.5 and 13.8  $\mu$ ) the dependence of the optical density at 13.9  $\mu$  on the ethylenic units is no longer linear. Consequently, the resulting measurement is less accurate, and is also affected by possible variations in the distribution of the methylenic sequences in the copolymer.

Thus the methods mentioned above give good results only if they are applied to samples having a rather narrow range of compositions and an analogous distribution of sequences.

*C. Analysis by mass spectrography of pyrolysis products.*—Bua and Manaresi<sup>10</sup> set up an analytical method based on the pyrolysis of ethylene-propylene copolymers and subsequent analysis of the products thus obtained by mass spectrography. A drawback to this method consists in the considerable length of time required for the analysis. Therefore, its possible field of application is rather narrow.

*D. Relationship between the composition of the ethylene-propylene copolymers and the minimum rebound temperature.*—The sequences of methylenic groups in ethylene-propylene copolymers constitute the most flexible part of the macromolecule; on the contrary, propylene sequences are the least flexible parts. By increasing the ethylene content in the copolymers, the flexibility of the macromolecular chains increases; thus a higher rebound is obtained at the same temperature<sup>11</sup>.

A quantitative relationship between the ethylene content of the copolymers and the rebound values at ordinary or slightly lower temperatures, cannot be easily obtained, especially with uncured testpieces; in fact, it can be affected by the viscosity of the copolymer, which is, in turn, a function of the average molecular weight.

At temperatures much lower than room temperature, the effect exerted by the molecular weight becomes negligible; therefore, the rebound values are a function only of the copolymer composition. If the minimum rebound temperature is assumed as a reference, it appears to be a linear function of the ethylene molar content.

The quantitative relationship between copolymer composition and minimum rebound temperature is dealt with later in this review.

#### IV. SYNTHESIS OF ETHYLENE-PROPYLENE COPOLYMERS IN THE LABORATORY

*A. Preliminary runs and setting up of the synthesis.*—It is well known that, to make possible the study of a copolymerization, the runs must be affected in such a way that the composition of the copolymer may be related to that of the monomer mixture; that is it is advisable to maintain, as constant as possible the concentration of the two monomers during the run.

In order to approach this condition as closely as possible, it is necessary, when operating in a discontinuous way, that the conversion of each monomer be sufficiently limited.

In fact, except for the case of the azeotropic-type copolymerizations<sup>12</sup>, one of the two monomers reacts more than the other; it follows that with elapsing time the composition of the reacting mixture varies continuously, and the concentration of the less reactive monomer grows higher and higher.

This leads to the formation of copolymers having a composition that can vary with time and, in some cases, of homopolymers of one of the two monomers.

Due to the above mentioned reasons, during the earliest copolymerizations of ethylene-propylene mixtures, the authors tried to obtain low conversions. However it was observed that, even if the reaction had been stopped a few minutes after it started, too high conversions and formation of very heterogeneous copolymers having considerable amounts of crystalline polymers were obtained. Moreover, owing to the rapid course of the run, it was practically impossible to obtain a sufficiently constant temperature. On the other hand, the increase of temperature favored the formation of low-molecular-weight oily products, thus contributing to the heterogeneity of the reaction product.

Therefore, we subsequently adopted continuous feeding and discharge of the monomers in our copolymerization runs. Using very high velocities of the circulating gases, it is possible to obtain such a limited conversion for each passage that the composition of the outlet gaseous mixture can be considered practically the same as that of the inlet mixture.

In order to maintain the concentration of the monomers in solution constantly the same as that of saturation equilibrium, it is advisable to obtain a large contact surface between the circulating gaseous stream and the solution, and an intensive stirring of the liquid mass.

*B. Effect of the operating conditions at constant ethylene-propylene ratio.*—Before engaging in the systematic study of the effect of the ratio of the relative concentrations of the two monomers on the composition of the copolymer, and therefore the calculation of the reactivity ratios, we investigated the possible effect of some parameters connected both with the preparation of the catalyst and with the copolymerization.

The catalytic system used being the same, these parameters are: 1) time of copolymerization; 2) time elapsed between the preparation of the catalyst and its use (aging of the catalyst); 3) concentration of the catalyst; 4) molar ratio between the aluminum alkyl compound and the transition metal compound; 5) total monomeric concentration.

TABLE II  
COMPOSITION OF ETHYLENE-PROPYLENE COPOLYMERS PREPARED WITH DIFFERENT POLYMERIZATION TIMES

Catalyst prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VOCl}_3$ ; mole  $\text{Al}(\text{C}_6\text{H}_{13})_3$ /mole  $\text{VOCl}_3 = 3$ ;  $T = 25^\circ\text{C}$ ,  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  400

Mole propylene/mole ethylene in the gaseous mixture	Polymerization time, min	Mole-% ethylene in the copolymer
6.02	5	40.26
6.02	10	40.93
4.55	5	45.98
4.55	10	45.98
3.74	5	48.95
3.74	10	49.25
2.85	2	57.6
2.85	5	58.0
2.85	10	57.8



TABLE III

COMPOSITION OF ETHYLENE-PROPYLENE COPOLYMERS PREPARED WITH DIFFERENT POLYMERIZATION TIMES

Catalyst prepared from  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  and V triacetylacetonate<sup>a</sup>; mole  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ /mole  $\text{VAc}_3 = 5$ ;  $T = -20^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  350

Moles propylene/mole ethylene in the gaseous mixture	Polymerization time, min.	Mole-% ethylene in the copolymer
6	1	35.0
6	3	33.5
6	4	36.0
6	6	35.5
4	1	45.0
4	3	42.5
4	4	45.0
4	6	43.5

<sup>a</sup> The abbreviations used for triacetylacetonate is  $\text{Ac}_3$  in tables and in the text.

1. *Time of copolymerization.*—If the ratio between the concentrations of the monomers in the reacting phase is kept constant, the composition of the copolymer is independent of the polymerization time<sup>1,13</sup>, see Tables II and III. For a number of catalytic systems prepared from hydrocarbon soluble vanadium compounds [e.g.,  $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_4$ ;  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} + \text{VCl}_4$ ;  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} + \text{VAc}_3$ ], the catalyst activity, and consequently the copolymerization rate, decreases with time<sup>13,14,15</sup>. This activity can be kept constant if the catalyst is maintained for a certain period at a temperature higher than that of use: for instance, in the case of the catalytic system obtained from  $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_4$ , if the catalyst is aged for 30 minutes at  $60^\circ\text{C}$ , then at  $25^\circ\text{C}$  it shows a constant activity in time<sup>14</sup>.

For some catalytic systems [e.g.,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} + \text{VCl}_4$ ;  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} + \text{VAc}_3$ ] the loss of activity with time is noticeably reduced by lowering the copolymerization temperature<sup>13</sup>.

2. *Aging of the catalyst.*—Other factors being the same, the composition of a copolymer is independent of the time elapsed between the preparation of the catalyst and its use (time of aging of the catalyst)<sup>1,13,16,17,18</sup>, see, e.g., Tables IV and V.

TABLE IV

COMPOSITION OF ETHYLENE-PROPYLENE COPOLYMERS OBTAINED WITH DIFFERENTLY AGED CATALYSTS

Catalysts prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VOCl}_3$ ; mole  $\text{Al}(\text{C}_6\text{H}_{13})_3$ /mole  $\text{VOCl}_3 = 3$ ;  $T = 25^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  400

Moles propylene/mole ethylene in the gaseous mixture	Aging time of catalyst, min	Mole-% ethylene in the copolymer
6.02	11	40.93
6.02	15	40.26
6.02	35	40.93
4.55	0	45.48
4.55	15	45.98
3.74	10	49.00
3.74	34	49.25
3.74	45	48.53
3.74	60	48.45
3.46	0	56.00
3.46	16	57.20
2.17	10	62.10
2.17	31	62.10

TABLE V

COMPOSITION OF ETHYLENE-PROPYLENE COPOLYMERS OBTAINED WITH DIFFERENTLY AGED CATALYSTS

Catalysts prepared from  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  and V triacetylacetonate; mole  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ /mole  $\text{VAc}_3 = 5$ ;  $T = -20^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  350

Moles propylene/mole ethylene in the gaseous mixture	Aging time of catalyst, min	Mole-% ethylene in the copolymer	$\text{VAc}_3$ , g <sup>a</sup>
6	5	34.0	0.25
6	15	35.0	0.25
6	30	35.0	0.25
6	5	33.5	0.50
6	15	35.0	0.50
6	30	36.0	0.50
4	1	42.0	1.25
4	5	43.5	1.25
4	15	45.0	1.25
4	30	45.0	1.25
4	60	44.1	1.25

<sup>a</sup> See footnote to Table III for meaning of  $\text{VAc}_3$ .

In the case of a number of catalytic systems, prepared from hydrocarbon soluble vanadium halides, the copolymerization rate decreases, with increase in the aging period of the catalyst. This does not occur in the case of thermally stabilized catalysts [e.g., in the case of the catalytic system obtained from  $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_4$ , kept for 30 minutes at  $60^\circ\text{C}$ , and then aged for different times at  $25^\circ\text{C}$ ]<sup>14</sup> (see Figure 10).

Also a lowering of the aging temperature of the catalyst leads to a decrease of the loss of activity, see, e.g., Figure 11.

3. *Concentration of the catalyst.*—Other factors being the same, the composition of a copolymer is independent, within certain limits, of the concentration of the catalyst<sup>1,13,16,17,18</sup>, see, e.g., Tables VI and VII. The limit of highest concentration is determined by the operating conditions (concentration of the monomers, molar ratio of ethylene to propylene in the reacting phase, catalyst used, molar ratio of the aluminum alkyl compound to the transition metal compound used in the preparation of the catalyst, aging of the catalyst, and polymerization temperature). In any case, the reaction conditions must be such as to maintain a low conversion of ethylene, which is the more reactive monomer.

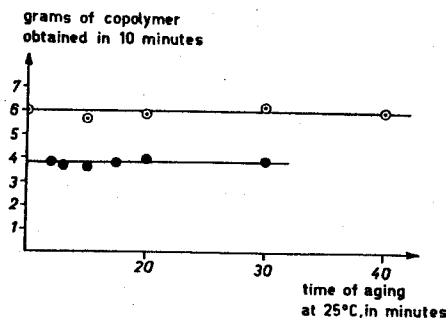


Fig. 10.—Independence of the activity of catalysts prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$  and aged at  $60^\circ\text{C}$  for 30 minutes of the aging times at  $25^\circ\text{C}$ . Polymerization temperature =  $25^\circ\text{C}$ ; pressure = 1 at; solvent: *n*-heptane,  $\text{cm}^3$  410;  $\text{V} = 0.0299$  g; mole  $\text{C}_2\text{H}_4$ /mole  $\text{C}_3\text{H}_6$  in the gaseous mixture = 2; polymerization time = 10 minutes.  $\circ$  Mole  $\text{Al}(\text{C}_6\text{H}_{13})_3$ /mole  $\text{VCl}_4 = 2.5$ ;  $\bullet$  Mole  $\text{Al}(\text{C}_6\text{H}_{13})_3$ /mole  $\text{VCl}_4 = 4$ .

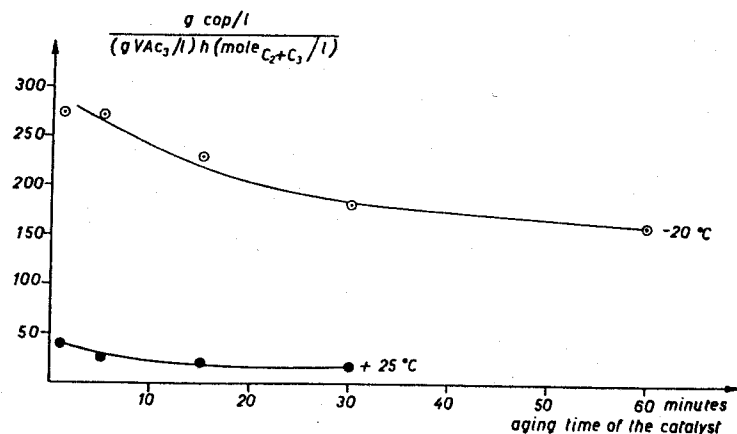


Fig. 11.—Copolymerization rate in the presence of catalysts prepared and aged for different times at  $-20^{\circ}\text{C}$  (○) and  $+25^{\circ}\text{C}$  (●).  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  350; mole  $\text{C}_2\text{H}_4$ /mole  $\text{C}_3\text{H}_6$  in the gaseous mixture = 4;  $T = -20^{\circ}\text{C}$  (○) and  $+25^{\circ}\text{C}$  (●).

TABLE VI

COMPOSITIONS OF ETHYLENE-PROPYLENE COPOLYMERS OBTAINED WITH DIFFERENT CATALYST CONCENTRATIONS

Catalyst prepared from  $\text{Al}(\text{C}_2\text{H}_5)_3$  and  $\text{VOCl}_3$ ; mole  $\text{Al}(\text{C}_2\text{H}_5)_3$ /mole  $\text{VOCl}_3 = 3$ ;  $T = 25^{\circ}\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane  $\text{cm}^3$  400

Moles propylene/mole ethylene in the gaseous mixture	Catalyst concentration mole $\text{Al}(\text{C}_2\text{H}_5)_3$ /liter	Mole-% ethylene in the copolymer
6.02	0.0045	40.26
6.02	0.0067	38.90
4.55	0.00335	45.98
4.55	0.0045	45.98
3.74	0.0045	49.00
3.74	0.0112	49.25
2.17	0.00225	62.10
2.17	0.00335	62.10

TABLE VII

COMPOSITION OF ETHYLENE-PROPYLENE COPOLYMERS OBTAINED WITH DIFFERENT CATALYST CONCENTRATIONS

Catalyst prepared from  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  and V triacetylacetonate; mole  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ /mole  $\text{VAc}_3 = 5$ ;  $T = -20^{\circ}\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  350

Moles propylene/mole ethylene in the gaseous mixture	$\text{VAc}_3$ g	Mole-% ethylene in the copolymer
6	0.125	36.0
6	0.250	34.0
6	0.500	33.5
4	0.125	43.5
4	0.250	44.5
2	0.125	59.0
2	0.250	58.5

In fact, it was observed that, by operating with catalyst concentrations above this value, the other conditions being the same, a certain variation of the copolymer composition occurs, when increasing the catalyst concentration. The reason for this is that for high catalyst concentrations, the reaction rate is such that it no longer allows the attainment of saturation equilibrium between the gaseous and liquid phases. Thus the diffusion phenomena of the reagents determine the copolymer composition. Considering that, other factors being the same, the reaction rate increases with increase of the ratio of ethylene to propylene, the concentration of the catalyst above which a certain effect is exerted by the concentration itself on the copolymer composition, varies with the above-mentioned ratio of ethylene to propylene.

On the other hand, the lowest concentration limit is determined first of all by the purity of the monomers, of the solvent, and of the reagents used in the copolymerization and also by the operating factors which determine the highest limit.

4. *Molar ratio of alkyl aluminum compound to transition metal compound used for the preparation of the catalyst.*—Other factors being the same, the copolymer composition is independent of the molar ratio of the alkyl aluminum compound to the transition metal compound used for the preparation of the catalyst<sup>1,13,16,17,18</sup>, see, e.g., Tables VIII and IX. This ratio exerts little effect on the copolymerization rate when the catalysts used are prepared from hydrocarbon insoluble transition metal compounds (e.g.,  $\text{VCl}_3$ ,  $\text{TiCl}_3$ )<sup>17,18</sup>; on the contrary, its effect is marked when the catalysts used are obtained from hydrocarbon soluble transition metal compounds (e.g.,  $\text{VAc}_3$ ,  $\text{VCl}_4$ ,  $\text{VOCl}_3$ )<sup>13,14,15,19</sup>. For instance, in the case of the  $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{VCl}_4$  catalytic system, the catalytic activity is highest when the molar ratio of  $\text{Al}(\text{C}_2\text{H}_5)_3$  to  $\text{VCl}_3$  is near 2.5<sup>14</sup>, see Figure 12, and in the case of the  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} + \text{VAc}_3$  catalytic system employed at  $25^{\circ}\text{C}$  when the ratio of  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  to  $\text{VAc}_3$  is near 3.5<sup>13</sup>, see Table X. If the latter catalytic system is used

TABLE VIII

COMPOSITIONS OF ETHYLENE-PROPYLENE COPOLYMERS OBTAINED WITH DIFFERENT  $\text{Al}(\text{C}_2\text{H}_5)_3/\text{VOCl}_3$  MOLAR RATIOS

$T = 25^{\circ}\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  400

Moles propylene/mole ethylene in the gaseous mixture	Mole $\text{Al}(\text{C}_2\text{H}_5)_3$ /mole $\text{VOCl}_3$	Mole-% ethylene in the copolymer
4.93	8	43.0
4.93	3	43.6
4.93	2	42.0
5.28	5	41.5
5.28	3	41.8

TABLE IX

COMPOSITIONS OF ETHYLENE-PROPYLENE COPOLYMERS OBTAINED WITH DIFFERENT  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{V}$  TRIACETYLACETONATE MOLAR RATIOS

Moles propylene/mole ethylene in the gaseous mixture	Mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ /mole $\text{VAc}_3$	Mole-% ethylene in the copolymer
4	4	43.5
4	5	44.5
4	6.33	42.5
4	10	43.5
4	20	45.5
4	30	42.5

TABLE X

DEPENDENCE OF COPOLYMERIZATION YIELD ON  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{V}$   
TRIACETYLACETONATE MOLAR RATIO

Catalyst prepared from 0.5 g  $\text{VAc}_3$ ; aging time = 1 minute;  $T = 25^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  350; moles propylene/mole ethylene in gaseous mixture = 4; polymerization time: 18 minutes

Mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3$	Copolymer, g
2	0.1
2.5	0.2
3	3.5
3.25	3.5
3.5	3.5
4	2.9
5	1.6
6	1.0

at  $-20^\circ\text{C}$ , the catalytic activity increases rapidly with increase of the molar ratio of  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$  from 3 to 4, and much more slowly by increasing this ratio from 4 to 20, see Figure 13.

5. Total monomeric concentration.—When using ethylene-propylene monomeric mixtures diluted differently with very pure nitrogen, it was observed that, other factors being the same, the composition of an ethylene-propylene copolymer is independent of the total monomeric concentration, Tables XI and XII.

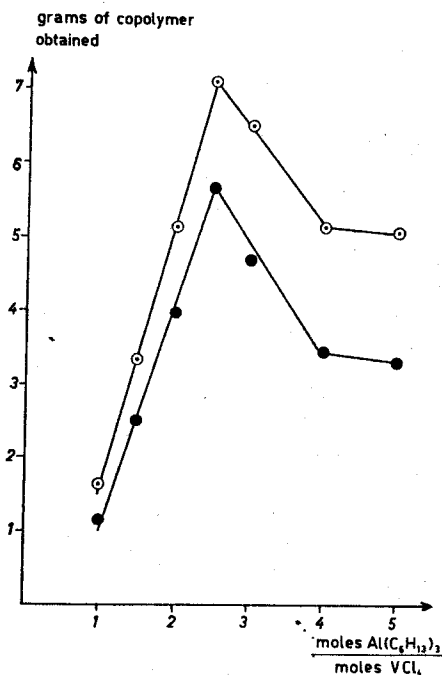


FIG. 12.—Dependence of catalyst activity on molar ratio  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VCl}_4$ . Polymerization temperature  $= 25^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  410; mole  $\text{C}_2\text{H}_4/\text{mole C}_3\text{H}_6$  in gaseous mixture = 2.  $\circ$  V: 0.0449 g; polymerization time 8 minutes;  $\bullet$  V: 0.0209 g, polymerization time 10 minutes.

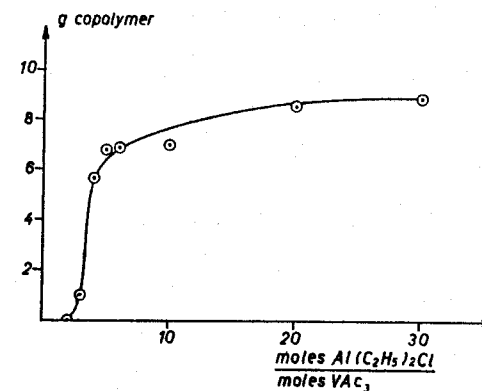


FIG. 13.—Dependence of catalyst activity on molar ratio  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ . Catalyst prepared and aged for 5 minutes at  $-20^\circ\text{C}$ . Polymerization temperature:  $-20^\circ\text{C}$ ;  $P = 1$  at; solvent = *n*-heptane,  $\text{cm}^3$  350; mole  $\text{C}_2\text{H}_4/\text{mole C}_3\text{H}_6$  in gaseous mixture = 4; polymerization time = 3 minutes.

TABLE XI

INDEPENDENCE OF ETHYLENE-PROPYLENE COPOLYMER COMPOSITION OF  
PARTIAL PRESSURE OF MONOMERS

Catalyst prepared at  $-20^\circ\text{C}$  in 30  $\text{cm}^3$  toluene; aging time of catalyst: 5 minutes; moles  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3 = 5$ ;  $T = -20^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  350; moles  $\text{C}_2\text{H}_4/\text{mole C}_3\text{H}_6$  in gaseous mixture = 4.

Mole $\text{N}_2/(\text{mole C}_2\text{H}_4 + \text{mole C}_3\text{H}_6)$	Mole-% ethylene in copolymer
0	43.5
0	44.5
0.38	44.5
0.38	43.5
0.93	43.5
0.93	44.0
2.12	43.0
2.12	42.5

TABLE XII

INDEPENDENCE OF COMPOSITION OF ETHYLENE-PROPYLENE COPOLYMERS OF  
PARTIAL PRESSURE OF MONOMERS

Catalyst prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$ , aged at  $60^\circ\text{C}$  for 30 minutes; moles  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{mole VCl}_4 = 2.5$ ;  $T = 25^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  410; moles propylene/mole ethylene in the gaseous mixture = 2.

Mole $\text{N}_2/(\text{mole C}_2\text{H}_4 + \text{mole C}_3\text{H}_6)$ in the gaseous mixture	Mole-% ethylene in the copolymer
0	50.5
0.62	49.8
0.98	51.7
1.54	51.0
2.0	50.8

C. Effect of the molar ratio of the monomers present in the feed mixture.—When using the same catalytic system, the composition of the copolymers is strongly affected by the composition of the monomer mixture, Tables XIII and XIV.

TABLE XIII

DEPENDENCE OF COMPOSITION OF ETHYLENE-PROPYLENE COPOLYMERS ON COMPOSITION OF MONOMER MIXTURE

Catalyst prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$ ,  $T = 25^\circ \text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  400; moles  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{mole VCl}_4 = 3$ .

Moles $\text{C}_3\text{H}_6/\text{mole C}_2\text{H}_4$ in gaseous mixture	Gaseous feed		Catalyst concentration mole $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{liter}$	Polymerization time, min	Mole-% ethylene in the copolymer
	$\text{C}_2\text{H}_4$ mole %	$\text{C}_3\text{H}_6$ mole %			
20.50	95.0	4.6	0.0045	10	10.5
5.10	83.2	16.3	0.00225	10	30.5
5.10	83.2	16.3	0.00225	10	32.0
4.06	79.9	19.7	0.00337	10	33.8
4.06	79.9	19.7	0.0045	10	34.5
2.12	67.7	32.0	0.00225	10	50.5
2.12	67.7	32.0	0.00112	10	50.0
2.12	67.7	32.0	0.00112	10	49.5
2.12	67.7	32.0	0.00084	4	50.0
1.70	62.9	36.9	0.00225	60	55.0
1.27	55.8	43.9	0.00112	10	58.5
1.27	55.8	43.9	0.00225	5	60.0
1.22	54.7	44.8	0.00112	7	62.0
1.01	49.9	49.5	0.00112	10	66.0
0.98	49.1	50.3	0.00169	10	64.3
0.98	49.1	50.3	0.00112	10	67.5
0.98	49.1	50.3	0.00112	10	66.0
0.71	41.3	58.2	0.00112	10	70.2
0.71	41.3	58.2	0.00056	10	71.0
0.69	40.7	59.0	0.00056	10	72.0
0.55	35.3	64.2	0.00112	10	77.0

Other factors being the same, and with all the catalytic systems used, the copolymerization rate increases strongly with increase in the ethylene content in the feed. This result can be attributed to the fact that, of the four fundamental propagation processes, those occurring through the attack of an ethylene unit occur with a rate higher than that of the others.

The increase of ethylene concentration will favor these more rapid propagation processes and consequently will increase the overall rate of the copolymerization process.

*D. Catalytic systems.*—Amorphous ethylene-propylene copolymers can be prepared either in the presence of the catalytic systems that in  $\alpha$ -olefin homopolymerization promote the formation of amorphous polymers (e.g.,  $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VOCl}_3^{20}$ ,  $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_4^{16}$ ,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} + \text{vanadium acetylacetonate}^{13}$ , or of those promoting the formation of isotactic polymers (e.g.,  $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_3^{17}$ ,  $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{TiCl}_3^{18}$ ).

Less homogeneous products, often containing crystallizable fractions are obtained when operating in the presence of catalysts that, in the homopolymerization of  $\alpha$ -olefins, yield mixtures formed of high proportions of macromolecules of different steric composition (e.g.,  $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{TiCl}_4^{18}$ ).

One of the most suitable types of catalysts for the preparation of homogeneous amorphous copolymers consists of highly dispersed catalysts (either amorphous and colloidal dispersed, or completely dissolved), prepared from vanadium compounds (generally soluble in hydrocarbons).

With the aid of halogen-containing vanadium compounds (such as  $\text{VCl}_4$ ,  $\text{VOCl}_3$ ), either a trialkyl aluminum compound or a halogen-containing alkyl aluminum compound can be used for the preparation of the catalyst.

TABLE XIV

DEPENDENCE OF COMPOSITION OF ETHYLENE-PROPYLENE COPOLYMERS ON COMPOSITION OF MONOMER MIXTURE

Catalyst prepared from  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  and *V* triacetylacetonate; moles  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{mole VAc}_3 = 5$ ;  $T = -20^\circ \text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  350.

Moles $\text{C}_3\text{H}_6/\text{mole C}_2\text{H}_4$ in gas phase	Gaseous feed		Catalyst VAc, g	Aging time, min	Polymerization time, min	Ethylene, mole % in copolymer
	$\text{C}_2\text{H}_4$ mole %	$\text{C}_3\text{H}_6$ mole %				
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	0.250	30	4	34.0
6	85.7	14.3	0.250	5	3	35.0
6	85.7	14.3	0.250	15	3	35.0
6	85.7	14.3	0.500	30	3	33.0
6	85.7	14.3	0.500	5	2	35.0
6	85.7	14.3	0.500	15	3	35.0
4	80.0	20.0	0.125	30	3	33.5
4	80.0	20.0	0.125	3	4	44.4
4	80.0	20.0	0.125	5	4	43.5
4	80.0	20.0	0.125	15	4	44.5
4	80.0	20.0	0.125	30	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	60	6	43.5
4	80.0	20.0	0.250	3	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
2	66.7	33.3	0.125	15	3	44.5
2	66.7	33.3	0.125	15	3	42.5
2	66.7	33.3	0.125	15	3	59.0
2	66.7	33.3	0.125	30	3	57.5
2	66.7	33.3	0.250	5	3	58.5
2	66.7	33.3	0.250	15	3	56.5
1.5	60.0	40.0	0.250	30	3	59.5
1	60.0	40.0	0.125	5	3	65.0

On the contrary, when using a halogen-free vanadium compound (such as vanadium triacetylacetonate, vanadyl triacetylacetonates), the halogen must be present in the alkyl aluminum compound in order to obtain active catalysts able to promote the ethylene-propylene copolymerization<sup>13,21</sup>.

The feed being the same, the composition of the copolymers varies when the catalytic system is varied.

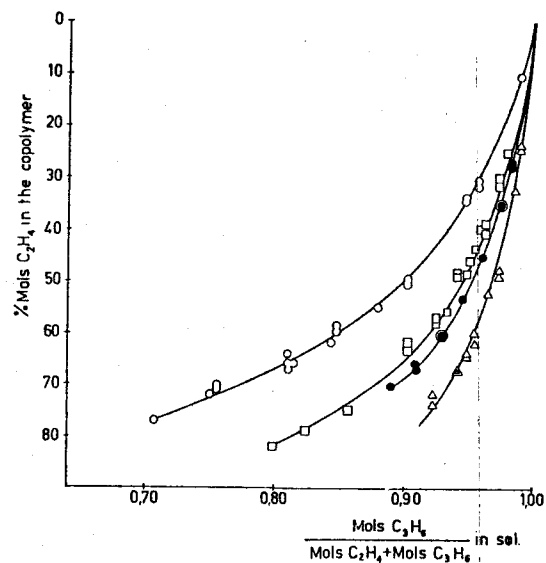


Fig. 4.—Composition of ethylene-propylene copolymers plotted against the ratio between the moles of dissolved propylene and the total moles of the two monomers in solution for different catalytic systems prepared from hydrocarbon soluble transition metal compounds.

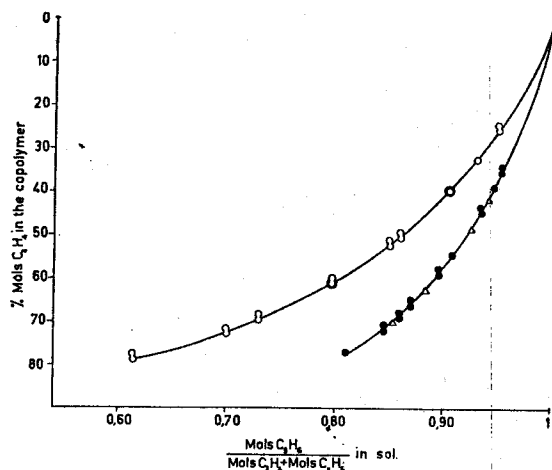
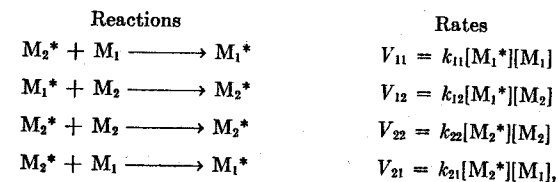


Fig. 15.—Composition of ethylene-propylene copolymers plotted against the ratio between the moles of dissolved propylene and the total moles of the two monomers in solution for different catalytic systems prepared from hydrocarbon insoluble transition metal halides.

Figures 14 and 15 show the compositions of the ethylene-propylene copolymer vs. the molar percentage of propylene with respect to the total moles of olefin present in the dissolved phase, in the presence of various catalytic systems.

The copolymerization runs, performed on a laboratory scale, in the presence of three of the most typical catalytic systems are schematically given in Figures 17 and 18.

*E. Reactivity ratios.*—Alfrey and Goldfinger<sup>22</sup>, Mayo and Lewis<sup>23</sup> and Walling<sup>24</sup> proposed an equation that connects the composition of the copolymer with that of the feed mixture, by means of two parameters called reactivity ratios. The fundamental chain growth reactions and the corresponding rates are:



where  $M_1^*$  and  $M_2^*$  represent growing chains which end, respectively, in  $M_1$  and  $M_2$ . Taking into account that:

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^*][M_1] + k_{21}[M_2^*][M_1]$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]$$

Solvent	<i>n</i> -heptane, 400 cm <sup>3</sup>
Temperature	-20° C
Pressure	1 at
Catalyst	
V triacetylacetonate	0.35 mmol
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl	1.75 mmol
Aging time of the catalyst	5 min
Monomers: propylene/ethylene molar ratio in the gaseous mixture	4:1
Time	5 min
Product obtained	4.9 g
Composition (determined by radiochemical methods)	43.5% ethylene in moles

Fig. 16.—Synthesis of an ethylene-propylene copolymer on a laboratory scale.

Solvent	<i>n</i> -heptane, 400 cm <sup>3</sup>
Temperature	25° C
Pressure	1 at
Catalyst	
VCl <sub>4</sub>	0.2 mmol
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	0.5 mmol
Aging time of the catalyst	5 min
Monomers: propylene/ethylene molar ratio in the gaseous mixture	2:1
Time	3 min
Product obtained	1.3 g
Composition (determined by radiochemical methods)	50% ethylene in moles

Fig. 17.—Synthesis of an ethylene-propylene copolymer on a laboratory scale.

Solvent	<i>n</i> -heptane, 400 cm <sup>3</sup>
Temperature	-20° C
Pressure	1 at
Catalyst	
VCl <sub>4</sub>	0.2 mmol
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl	1 mmol
Aging time of the catalyst	5 min
Monomers: propylene/ethylene molar ratio in the gaseous mixture	2:1
Time	3 min
Product obtained	12 g
Composition	49.5% ethylene in moles

Fig. 18.—Synthesis of an ethylene-propylene copolymer on a laboratory scale.

and, assuming a steady state, owing to which

$$k_{21}[M_2^*][M_1] = k_{12}[M_1^*][M_2]$$

and considering  $r_1 = k_{11}/k_{12}$  and  $r_2 = k_{22}/k_{21}$  the copolymerization equation is obtained

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left( \frac{r_1[M_1] + [M_2]}{[M_1] + r_2[M_2]} \right)$$

Thus, if one knows the compositions of copolymers corresponding to different feeds, the values of the reactivity ratios can be determined.

In order to obtain values of the reactivity ratios, independent of the conditions (temperature and pressure), which exert a determinant influence on the solubility of the monomers, it is more convenient to refer to the relative concentrations of the monomers present in the liquid reacting phase, than to the concentrations of the monomers present in the gaseous feeding mixture.

If the ethylene-propylene-solvent ternary system is known, then from the composition of the gaseous feed mixture it is possible to calculate the molar fractions ( $N_{C_2H_4}$  and  $N_{C_3H_6}$ ) of the two monomers in the liquid phase. Then the relative concentrations ( $M_{C_2H_4}$  and  $M_{C_3H_6}$ ) of the two monomers in the dissolved phase will be

$$M_{C_2H_4} = \frac{N_{C_2H_4}}{N_{C_2H_4} + N_{C_3H_6}}$$

and

$$M_{C_3H_6} = \frac{N_{C_3H_6}}{N_{C_2H_4} + N_{C_3H_6}}$$

TABLE XV  
MONOMER REACTIVITY RATIOS IN ETHYLENE-PROPYLENE COPOLYMERIZATION WITH DIFFERENT CATALYTIC SYSTEMS

Catalytic system	$r_{C_2H_4}$	$r_{C_3H_6}$	Reference
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + VOCl <sub>3</sub>	17.95	0.065	20
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + VCl <sub>4</sub>	7.08	0.088	16
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + VCl <sub>3</sub>	5.61	0.145	17
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> Cl + V triacetyl-acetate	15.0	0.04	13
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + TiCl <sub>4</sub>	33.36	0.032	18
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> + TiCl <sub>3</sub>	15.72	0.110	18
Al(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> + TiCl <sub>2</sub>	15.72	0.110	18

Table XV shows the values of the reactivity ratios (referred to the composition of the monomeric mixture present in solution) in the ethylene-propylene copolymerization, carried out in the presence of various catalytic systems.

We have experimentally observed that these reactivity ratios are practically constant within a wide temperature range<sup>13,17</sup>.

The reactivity of ethylene is always much higher than that of propylene; it agrees with what can be foreseen for an anionic copolymerization.

The valence of the transition metal being the same, the relative reactivity of ethylene is higher when using titanium compounds than with vanadium compounds.

The relative reactivity of ethylene decreases with decrease of the transition metal valence.

### V. INTRINSIC VISCOSITY OF THE ETHYLENE-PROPYLENE COPOLYMERS

A. Influence of operating conditions. 1. Time of copolymerization.—In the presence of some catalytic systems (e.g., Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl + VAc<sub>3</sub>)<sup>13</sup>, other factors being the same, the intrinsic viscosity of the ethylene-propylene copolymers increases slightly with increased time of copolymerization; Table XVI. The increase in intrinsic

TABLE XVI  
EFFECT OF POLYMERIZATION TIME ON THE INTRINSIC VISCOSITY OF ETHYLENE-PROPYLENE COPOLYMERS

Catalyst prepared from triacetylacetate at -20° C; moles Al(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Cl/mole VAc<sub>3</sub> = 5; T = -20° C; P = 1 at; solvent: *n*-heptane, cm<sup>3</sup> 350.

Mole propylene/mole ethylene in the gaseous mixture	Polymerization time, min	Aging time of catalyst, min	[η] <sup>a</sup>
6	1	5	2.55
6	3	5	2.75
6	4	5	3.01
6	6	5	3.11
4	1	30	5.30
4	3	30	5.44
4	4	30	5.70
4	6	30	5.90

<sup>a</sup> Determined in tetrahydronaphthalene at 135° C.

TABLE XVII  
INTRINSIC VISCOSITIES OF ETHYLENE-PROPYLENE COPOLYMERS OBTAINED WITH STABILIZED CATALYSTS AT DIFFERENT POLYMERIZATION TIMES

(See Sect. V A 1 of text)

Catalyst prepared from Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and VCl<sub>4</sub>, and aged at 60° C for 30 minutes. V (g vanadium present in the catalytic system) = 0.0299g; moles Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>/mole VCl<sub>4</sub> = 2.5; T = 25° C; P = 1 at; solvent: *n*-heptane, cm<sup>3</sup> 410; moles propylene/mole ethylene in the gaseous mixture = 2.

Polymerization time, min	Copolymer yield, g	[η] <sup>a</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> Determined in tetrahydronaphthalene at 135° C.

viscosity observed is rather limited, also on account of the short polymerization times adopted in order to limit the viscosity of the polymerization mass. In the presence of other catalytic systems (e.g.,  $Al(C_6H_{13})_3 + VCl_4$  aged for 30 minutes at  $60^\circ C$  and used at  $25^\circ C$ ), the time of copolymerization does not exert a noticeable effect on the intrinsic viscosity, Table XVIII.

2. *Temperature.*—Everything else being the same, the intrinsic viscosity of the ethylene-propylene copolymers increases with decrease of the polymerization temperature. This phenomenon must be attributed to the presence of one or more rupture or chain transfer processes of the growing chains: the temperature coefficients of their rates are higher than that of the propagation rate.

3. *Concentration of the catalyst.*—Other factors being the same, the intrinsic viscosity of the copolymers decreases with increase in the concentration of the catalyst. This is in agreement with the hypothesis that the termination of the growing chains occurs, partly at least, through a transfer process with the catalytic system present in solution, Tables XVIII and XIX.

4. *Concentration of the monomers.*—Other factors being the same, the intrinsic viscosity of the ethylene-propylene copolymers decreases with increase of concentration of the monomers, Table XX. This shows the existence of a transfer process with the monomers present in the reacting phase.

5. *Molar ratio of ethylene to propylene in the reacting phase.*—Other factors being the same, the intrinsic viscosity of the ethylene-propylene copolymers increases with increase of the molar ratio of ethylene to propylene in the reacting phase, Table XXI. This experimental result can lead to the conclusion that one or more chain termination or transfer processes occur, which are strongly affected by the presence of propylene as the last monomeric unit entered in the copolymer. Of these processes, mention must be made of that originated by a spontaneous chain dis-

TABLE XVIII

EFFECT OF CATALYST CONCENTRATION ON THE INTRINSIC VISCOSITY OF ETHYLENE-PROPYLENE COPOLYMERS

Catalyst prepared from  $Al(C_2H_5)_2Cl$  and  $VAc_3$ ; moles  $Al(C_2H_5)_2Cl$ /mole  $V$  triacetylacetonate = 5;  $T = -20^\circ C$ ;  $P = 1$  at; solvent: *n*-heptane  $cm^3$  350. (See Sect. VA3)

Mole $C_2H_4$ /mole $C_3H_6$ in gas phase	$VAc_3$ , g	Aging time, min	Polymerization time, min	Copolymer, g	Ethylene, mole % in copolymer	$[\eta]^a$
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

<sup>a</sup> Determined in tetrahydronaphthalene at  $135^\circ C$ .

TABLE XIX

EFFECT OF CATALYST CONCENTRATION ON INTRINSIC VISCOSITY OF ETHYLENE-PROPYLENE COPOLYMERS

Catalyst prepared from  $Al(C_6H_{13})_3 + VCl_4$  and aged at  $60^\circ C$  for 30 minute; moles  $Al(C_6H_{13})_3$ /mole  $VCl_4 = 2.5$ ;  $T = 25^\circ C$ ;  $P = 1$  at; solvent: *n*-heptane  $cm^3$  410; moles propylene/mole ethylene in gaseous mixture = 2. (See Sect. VA4)

$VCl_4$ mole	Polymerization time, min	$[\eta]^a$
0.00127	4	2.14
0.000844	6	2.83
0.000565	8	3.90
0.000375	10	4.44

<sup>a</sup> Determined in tetrahydronaphthalene at  $135^\circ C$ .

TABLE XX

EFFECT OF THE TOTAL MONOMER CONCENTRATION ON THE INTRINSIC VISCOSITY OF ETHYLENE-PROPYLENE COPOLYMERS

Catalyst prepared from  $Al(C_6H_{13})_3$  and  $VCl_4$  and aged at  $60^\circ C$  for 30 minute;  $VCl_4$  concentration: 0.0021 mole/liter; moles  $Al(C_6H_{13})_3$ /mole  $VCl_4 = 2.5$ ;  $T = 25^\circ C$ ;  $P = 1$  at; solvent: *n*-heptane  $cm^3$  410; moles propylene/mole ethylene in the gaseous mixture = 2. (See Sect. VA4)

Molar ratio $N_2/(C_2H_4 + C_3H_6)$ in the gaseous mixture	$[\eta]^a$
0	2.40
0.62	2.83
0.98	3.37
2	4.19

<sup>a</sup> Determined in tetrahydronaphthalene at  $135^\circ C$ .

TABLE XXI

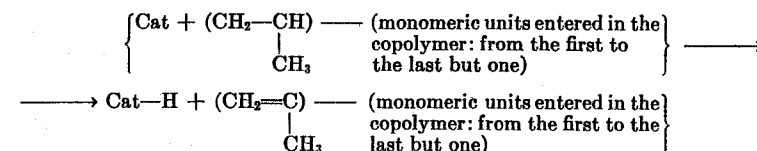
EFFECT OF PROPYLENE/ETHYLENE MOLAR RATIO ON INTRINSIC VISCOSITY OF ETHYLENE-PROPYLENE COPOLYMERS

Catalyst prepared from  $Al(C_6H_{13})_3$  and  $VOCl_3$  concentration: 0.00373 mole liter  $T = 25^\circ C$ ;  $P = 1$  at; solvent: *n*-heptane,  $cm^3$  400. Moles  $Al(C_6H_{13})_3$ /mole  $VOCl_3 = 3$ .

Mole propylene/mole ethylene in the gaseous mixture	Copolymer $[\eta]^a$	Mole-% ethylene
10.50	2.85	25.15
8.26	3.36	31.12
5.33	4.90	29.90
4.07	5.33	50.00
2.85	5.90	57.80
1.06	6.95	79.05

<sup>a</sup> Determined in tetrahydronaphthalene at  $135^\circ C$ .

sociation with transfer of a hydride ion (deriving from the hydrogen bound to the tertiary carbon atom of propylene) to the catalyst, according to the scheme:



With increase of the concentration of ethylene, the occurrence of this rupture process will be less and less probable.

6. *Molar ratio of alkyl aluminum compound to transition metal compound.*—In the presence of various catalytic systems (e.g.,  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} + \text{VAc}_3^{13}$ , or  $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_4$ , aged at  $60^\circ\text{C}$  for 30 minutes and used at  $25^\circ\text{C}^{14}$ ) the concentration of the vanadium compound and other factors being the same, the intrinsic viscosity decreases with increase in the molar ratio of the alkyl aluminum compound to the vanadium compound, Tables XXII and XXIII.

This agrees with the hypothesis mentioned above, that the termination of the growing chains occurs, at least in part, through a transfer process with the catalytic system present in solution, and in particular with the organometallic compound.

7. *Aging of the catalyst.*—Everything else being the same, in the presence of some catalytic systems (e.g.,  $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_4$ ) the aging of the catalyst does not have any effect on the intrinsic viscosity of the ethylene-propylene copolymer. On the contrary, in the presence of the  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} + \text{VAc}_3^{13}$  catalytic system, the intrinsic viscosity increases with increased aging of the catalyst, see Table XXIV. The reason for this could be that the concentration of the catalytic complexes, which are suitable to promote the copolymerization may decrease with elapsing time. Therefore, the increase in the intrinsic viscosity with increase of the aging of the catalyst should be considered on the basis of the hypothesis formulated above with regard to the lowering of the intrinsic viscosity when increasing the concentration of the catalyst.

TABLE XXII

EFFECT OF  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{VCl}_4$  MOLAR RATIO ON THE INTRINSIC VISCOSITY OF ETHYLENE-PROPYLENE COPOLYMERS

Catalyst aged at  $60^\circ\text{C}$  for 30 minutes;  $\text{VCl}_4$  concentration: 0.0022 mole/liter;  $T = 25^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  410; mole propylene/mole ethylene in the gaseous mixture = 2.

Mole $\text{Al}(\text{C}_6\text{H}_{13})_3$ /mole $\text{VCl}_4$	$[\eta]^a$
2	3.89
2.5	3.39
3	3.13
4	2.58

<sup>a</sup> Determined in tetrahydronaphthalene at  $135^\circ\text{C}$ .

TABLE XXIII

EFFECT OF  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{V}$  TRIACETYLACETONATE MOLAR RATIO ON THE INTRINSIC VISCOSITY OF ETHYLENE-PROPYLENE COPOLYMERS

Aging time: 5 minutes;  $\text{VAc}_3$ , g 0.25;  $T = -20^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  350; moles propylene/mole ethylene in the gaseous mixture = 4; polymerization time = 3 minutes.

Mole $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ /mole $\text{VAc}_3$	$[\eta]^a$
4	2.92
5	2.11
6.33	1.63
10	1.57
20	0.99
30	0.77

<sup>a</sup> Determined in tetrahydronaphthalene at  $135^\circ\text{C}$ .

TABLE XXIV

EFFECT OF AGING TIME OF CATALYST ON INTRINSIC VISCOSITY OF ETHYLENE/PROPYLENE COPOLYMERS

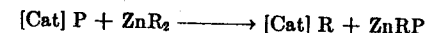
Catalyst prepared from  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$  and  $\text{VAc}_3$ ; moles  $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ /mole V triacetylacetonate = 5;  $T = -20^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  350.

Mole propylene/mole ethylene in the gaseous mixture	$\text{VAc}_3$ g	Aging time, min	$[\eta]^a$
6	0.25	5	2.05
6	0.25	15	3.38
6	0.25	30	3.44
6	0.50	5	1.35
6	0.50	15	2.18
6	0.50	30	2.57
4	0.125	1	1.65
4	0.125	5	3.00
4	0.125	15	4.70
4	0.125	30	5.70
4	0.125	60	6.70

<sup>a</sup> Determined in tetrahydronaphthalene at  $135^\circ\text{C}$ .

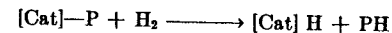
B. *Regulating agents.*—The intrinsic viscosity of the ethylene-propylene copolymers can be reduced if the copolymerization is effected in the presence of substances that react with the growing chains, in competition with the monomers. This fact can be utilized in order to regulate the molecular weight of the copolymers. Now, a distinction must be made between the chain transfer agents, which interrupt the growing chains but start new chains, and the chain interupters, which stop the chain growth, but do not start new chains (e.g., alkyl halides). The best chain transfer agents, used in practice to regulate the molecular weight of polyolefins, are zinc alkyls<sup>24</sup> and hydrogen<sup>25</sup>.

In analogy with what is observed in the case of the polymerization of propylene, the process by which zinc dialkyls should regulate the molecular weight can be a simple process of alkyl exchange between the alkyls of zinc dialkyl and the polymeric chains growing on the active centers, according to the reaction:



where Cat is the catalytic complex on which the polymeric chain P grows.

When using hydrogen, in analogy with what is observed in the case of the ethylene and propylene polymerization, the rupture process of the growing chain could be a hydrogenolysis on the complex polymeric chain-catalyst, according to the reaction:



## VI. PURIFICATION OF THE PRODUCTS AND REACTIVES USED IN THE ETHYLENE-PROPYLENE COPOLYMERIZATION

A. *Aluminum-alkyl compounds.*—Purification is generally affected by vacuum distillation. The content is determined by potentiometric means, following the method proposed by Bonitz<sup>26</sup> which has been much improved in our laboratory<sup>27</sup>.

B. *Transition metal compounds.*—In the case of liquid compounds (e.g.,  $\text{VCl}_4$ ,  $\text{VOCl}_3$ ,  $\text{TiCl}_4$ ,  $\text{VO}(\text{OC}_2\text{H}_5)_3$ ,  $\text{VO}(\text{OC}_2\text{H}_5)_2\text{Cl}$ ), purification is affected by distillation, while in the case of solid halides (e.g.,  $\text{VCl}_3$ ,  $\text{TiCl}_3$ ), they are repeatedly washed with heptane, and subsequently ground in a ball mill. Hydrocarbon-soluble solid compounds (e.g.,  $\text{VAc}_3$ ,  $\text{VOAc}_2$ ), are purified by recrystallization.



C. *Solvents*.—Solvents must be free from moisture, from dissolved air and sulfur compounds. After a possible treatment with sulfuric acid in order to eliminate the thiophene compounds, solvents are made anhydrous by means of a drying agent; then they are distilled over potassium, or aluminum alkyls, and kept over sodium under a nitrogen atmosphere.

D. *Monomers*.—Monomers must be free from moisture and from acetylenic compounds. The content has been determined by us by chromatography and mass spectrography.

### VII. SYNTHESIS OF THE ETHYLENE-PROPYLENE COPOLYMERS ON AN INDUSTRIAL SCALE

Continuous and discontinuous processes are described for obtaining ethylene-propylene copolymers on an industrial scale. Whereas the former must be affected in the presence of hydrocarbon solvents, the latter can occur both in the presence and in the absence of such solvents.

In order to avoid too high molecular weights of the copolymer, suitable agents, acting as chain transfer agents (e.g., controlled quantities of hydrogen or zinc-alkyls) must generally be added to the reaction mass.

A. *Discontinuous process in the absence of solvents*.—This process requires a continuous feed of ethylene and a constant ratio of ethylene to propylene in the liquid phase.

The reactor consists of a stainless steel autoclave, equipped with a mechanical stirrer, a thermometer, a manometer, inlet tubes for the olefins and the catalyst, and outlet tubes.

Liquid propylene is introduced in the autoclave; the temperature is kept between  $-10$  and  $-20^{\circ}\text{C}$ ; then ethylene is introduced at a certain pressure (usually a few atmospheres), which depends on the type of copolymer composition wanted, on the copolymerization temperature and on the catalyst employed.

The catalyst components (vanadium compound and organic aluminum compound) can be introduced in the reactor as solutions in hydrocarbons, through separate, addition openings, or else after previous mixing. The total concentration of the catalyst varies, depending on the composition, from 0.05 to 0.3 g per liter of olefinic mixture. The addition of the catalyst can be either continuous or intermittent.

Pressure in the reactor is regulated, during the copolymerization, by feeding with ethylene, so that the ratio of ethylene to propylene in the liquid phase is constant. The time of copolymerization generally ranges from 10 to 40 minutes.

B. *Discontinuous process in the presence of solvents*.—This process is effected by establishing a given initial ratio of ethylene to propylene in the hydrocarbon solvent. After the copolymerization starts by addition of the catalyst, the two olefins are fed in a continuous way, at a given ratio, which is the same as that wanted in the copolymer, but is different from that established in the reacting liquid phase, at the start of polymerization.

### VIII. OTHER $\alpha$ -OLEFIN COPOLYMERS

A. *Ethylene butene-1 copolymers*.—Investigations have been accomplished not only on the ethylene-propylene copolymers, but also on the copolymers of ethylene with other  $\alpha$ -olefins, in particular with butene-1<sup>28</sup>. The characterization of these latter was obtained by methods, which are analogous to those adopted in the case of the ethylene-propylene copolymers. Within a wide range of composition, they are amorphous and completely soluble in boiling *n*-heptane. Their mechanical properties are similar to those of the ethylene-propylene copolymers.

TABLE XXV

MONOMER REACTIVITY IN ETHYLENE-BUTENE-1 COPOLYMERIZATION WITH DIFFERENT CATALYTIC SYSTEMS

Catalyst	$r_{\text{C}_2\text{H}_4}$	$r_{\text{C}_4\text{H}_6}$
$\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_4$	29.60	0.019
$\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_3$	26.96	0.043

The best catalysts are prepared from organometallic compounds of aluminum and compounds of vanadium. The values of the reactivity ratios for the ethylene-butene-1 copolymerization in the presence of the  $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_3$  and  $\text{Al}(\text{C}_6\text{H}_{13})_3 - \text{VCl}_4$  catalytic systems are reported in Table XXV.

In analogy with what happens in the case of ethylene-propylene copolymerizations, the reactivity of ethylene is always much higher than that of butene-1, a must be expected in the case of anionic copolymerizations. The catalytic system and the composition of the reaction mixture being the same, the composition of the ethylene-butene-1 copolymers is independent of the following factors:

- 1) Polymerization time
- 2) Time elapsed between the preparation of the catalyst and its use (aging of the catalyst)
- 3) Concentration of the catalyst
- 4) Molar ratio of organoaluminum compound to vanadium compound used in the preparation of the catalyst.

B. *Reactivity ratios predicted for ionic copolymerizations; propylene-butene-1 copolymers*.—The literature shows that a number of systematic studies have been carried out in order to establish the reactivity ratios of radical-type copolymerizations, using the  $Q-e$  scheme, proposed by Alfrey and Price<sup>29</sup>; but no study has been undertaken yet in the case of ionic copolymerizations. In fact the original  $Q-e$  scheme evidently cannot be applied to the latter case, since equal values of  $e$  cannot be attributed both to the monomer and to the corresponding terminal monomeric unit present in the growing chain.

As observed by other authors<sup>30</sup> for a number of ionic copolymerizations, if the product of the reactivity ratios is very near one, the ratio between the rate constants of addition of two monomers to the growing chains, which end in a certain monomeric unit, is practically independent of the terminal unit of the chains themselves.

Indicating the reactivity ratios with  $r_1$  and  $r_2$

$$r_1 = k_{11}/k_{12}, \quad r_2 = k_{22}/k_{21}$$

in the case that

$$r_1 \cdot r_2 = 1;$$

then

$$k_{11}/k_{12} = k_{21}/k_{22},$$

that is, by taking into account the rates of the four fundamental growth reactions in the  $M_1$ - $M_2$  copolymerization:

$$v_{11} = k_{11}[M_1^*][M_1] \quad (a)$$

$$v_{12} = k_{12}[M_1^*][M_2] \quad (b)$$

$$v_{22} = k_{22}[M_2^*][M_2] \quad (c)$$

$$v_{21} = k_{21}[M_2^*][M_1] \quad (d)$$

The ratio between the rate constant of reaction (a) and that of reaction (b) is equal to the ratio between the rate constant of reaction (d) and of reaction (c).

Now the hypothesis is made that the relationship

$$k_{11}/k_{12} = k_{21}/k_{22}$$

can be generalized as follows:

$$k_{11}/k_{12} = k_{i1}/k_{i2}, \quad (1)$$

where  $i$  can be any terminal monomeric unit, equal to or different from 2<sup>21</sup>.

This hypothesis permits one to obtain very simple relationships that allow the prediction of the reactivity ratios of the ionic copolymerization of two monomers, if the reactivity ratios for the copolymerization of each of them with a third monomer are known.

Now let us consider the case of three monomers, indicated with the numbers 1, 2, 3. If one knows the reactivity ratios of the copolymerizations of monomer 1 with monomer 2, indicated below as  $r_{12}$  and  $r_{21}$ , and of monomer 1 with monomer 3, indicated below as  $r_{13}$  and  $r_{31}$ , then:

$$r_{12} = k_{11}/k_{12} \quad r_{21} = k_{22}/k_{21} \quad (2)$$

$$r_{13} = k_{11}/k_{13} \quad r_{31} = k_{33}/k_{31} \quad (3)$$

The reactivity ratios in the copolymerization of monomer 2 with monomer 3 will be:

$$r_{23} = k_{22}/k_{23} \quad r_{32} = k_{33}/k_{32}$$

but, since the reactivity of monomer 2 with respect to that of monomer 3 with a certain terminal unit does not depend on the terminal unit itself, it will be

$$k_{22}/k_{23} = k_{12}/k_{13},$$

from which

$$r_{23} = k_{12}/k_{13}. \quad (4)$$

By multiplying numerator and denominator of Equation (4) by  $k_{11}$ , then:

$$r_{23} = (k_{12}/k_{11})(k_{11}/k_{13}). \quad (5)$$

By taking into account Equations (2) and (3), Equation (5) becomes:

$$r_{23} = r_{13}/r_{12}. \quad (6)$$

Analogously, by multiplying numerator and denominator of the ratio corresponding to  $r_{32}$  by  $k_{31}$ , then:

$$r_{32} = (k_{33}/k_{31})(k_{31}/k_{32}).$$

Taking into account Equations (2) and (3) and also the fact that the ratio of the addition rate constants of the two monomers to the growing chains, ending in the same monomeric unit, does not depend on the nature of the terminal unit, then:

$$r_{32} = r_{31}(k_{21}/k_{22}) = r_{31}/r_{21}. \quad (7)$$

Moreover the reactivity ratios  $r_{23}$  and  $r_{32}$  must satisfy the equation

$$r_{23} \cdot r_{32} = 1. \quad (8)$$

If the product of the reactivity ratios is not strictly equal to one, two other values of  $r_{23}$  and  $r_{32}$  can be calculated, by substituting the results of Equation (7)

TABLE XXVI  
MONOMER REACTIVITY RATIOS IN PROPYLENE-BUTENE-1 COPOLYMERIZATION

Catalytic system	$r_{C_2H_4}$	$r_{C_3H_6}$
$Al(C_6H_{13})_3 + VCl_4$	4.39	0.227
$Al(C_6H_{13})_3 + VCl_3$	4.04	0.252

and of Equation (6), respectively, in Equation (8). Then, by averaging the results obtained with those deduced from Equations (6) and (7), more approximate values of  $r_{23}$  and  $r_{32}$  will be obtained.

The formulas indicated above have been utilized in order to predict the reactivity ratios of the propylene-butene-1 copolymerization, carried out in the presence of catalysts prepared from  $Al(C_6H_{13})_3$  and  $VCl_4$ , and from  $Al(C_6H_{13})_3$  and  $VCl_3$ . The reactivity ratios of the copolymerization of each of the said monomers with ethylene, are already reported in Tables XV and XXV.

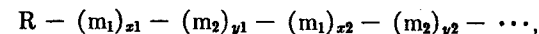
By using the formulas which we have proposed for the propylene-butene-1 copolymerization with the aid of the above mentioned catalytic systems, the value of the reactivity ratios reported in Table XXVI have been calculated.

In order to check the reliability of such values, some propylene-butene-1 copolymerization runs have been performed, using radioactive butene<sup>22</sup>. The compositions of the copolymers, determined by the radiochemical method have been in good agreement with those predicted, employing the reactivity ratios calculated and reported above.

#### IX. DETAILED STRUCTURE OF THE ETHYLENE-PROPYLENE COPOLYMER

The knowledge of the copolymer composition is not enough to establish its structure. In fact a great number of possible distributions of the monomeric unit can correspond to a given composition of a copolymer.

Thus, for instance, in a copolymer consisting of  $m_1$  and  $m_2$  monomeric units having 50 mole-% of  $m_1$  and 50 mole-% of  $m_2$ , the arrangement of the monomeric units can be indicated as follows: (R is the first monomer starting the polymer chain)



where  $x_1$  and  $y_1$  are integers, which can assume values equal to or higher than unity

If all  $x$  and  $y$  are equal to 1, the monomeric units are regularly alternated; consequently the polymer shows a regular chemical structure. When a regularity or steric structure occurs, the polymer is crystallizable<sup>23</sup>.

By adopting particular copolymerization conditions, copolymers can be obtained having so high  $x$  and  $y$  values that the crystallization of the ordered  $m_1$  and  $m_2$  segments becomes possible (block copolymers)<sup>21</sup>. Thus, depending on the average when comparing copolymers of the same over-all composition. Evidently it can be deduced that the distribution of the monomeric units must be determined in order to obtain a complete characterization of a copolymer.

The formulas proposed by Alfrey and Goldfinger<sup>22</sup> have been applied<sup>24</sup> in the case of ethylene-propylene copolymers, prepared with the aid of catalysts obtained from vanadium tetrachloride and trihexylaluminum.

The values thus obtained for the sequence distribution functions are in good agreement with those found experimentally by infrared spectrography and x-ray analysis.

A. *Distribution of sequences.*—By indicating with  $V_{11}$ ,  $V_{12}$ ,  $V_{21}$  and  $V_{22}$  the rates of the four propagation reactions occurring in the polymerization of two  $M_1$  and  $M_2$  monomers, one obtains:

$$V_{11} = k_{11}[M_1^*][M_1]$$

$$V_{12} = k_{12}[M_1^*][M_2]$$

$$V_{21} = k_{21}[M_2^*][M_1]$$

$$V_{22} = k_{22}[M_2^*][M_2],$$

where  $[M_1^*]$  and  $[M_2^*]$  are the concentrations of the growing polymeric chains, ending, respectively, in an  $m_1$  or  $m_2$  monomeric unit;  $[M_1]$  and  $[M_2]$  are the concentrations of the two monomers.

Depending on the relative values of the propagation rate constants, sequences of different length of  $m_1$  and  $m_2$  units will be found in the copolymer.

If the  $k_{11}$  and  $k_{22}$  rate constants have high values in comparison with  $k_{12}$  and  $k_{21}$ , long sequences of  $m_1$  and  $m_2$  units should be expected. On the contrary, if the values of  $k_{11}$  and  $k_{22}$  are low in comparison with those of  $k_{12}$  and  $k_{21}$ , the polymer will consist of short sequences of  $m_1$  and  $m_2$  units.

Let us define now the quantity  $P_{11}$ , as the probability that an  $m_1$  monomer molecule adds to a chain ending in  $M_1^*$ . Analogously we define the quantity  $P_{12}$  as the probability that an  $m_2$  monomer molecule adds to a chain ending in  $M_1^*$ ,  $P_{21}$  as the probability that an  $m_1$  monomer molecule adds to a chain ending in  $M_2^*$ , and  $P_{22}$  as the probability that an  $m_2$  monomer molecule adds to a chain ending in  $M_2^*$ .

The distribution of the sequences of different length of monomer  $m_1$  and of monomer  $m_2$  can be calculated in the following way.

A chain ending in  $M_1^*$  can react according to one of the following elementary processes:

- 1) It can add an  $m_1$  monomer
- 2) It can add an  $m_2$  monomer
- 3) It can undergo a chain termination or chain transfer process.

As far as high-molecular-weight polymers are concerned, the third item can be neglected with respect to the other two, with regard to its effect on the composition of the copolymer. The probability  $P_{11}$  is then given by the addition rate of  $m_1$  divided by the sum of the addition rates of  $m_1$  and  $m_2$  to the chains ending in  $M_1^*$ . The probability is not referred to all possible events, but only to those concerning the chains ending in  $M_1^*$ .

The probabilities  $P_{12}$ ,  $P_{21}$  and  $P_{22}$  can be expressed analogously.

$$P_{11} = \frac{k_{11}[M_1^*][M_1]}{k_{11}[M_1^*][M_1] + k_{12}[M_1^*][M_2]} = \frac{r_1[M_1]}{r_1[M_1] + [M_2]} = \frac{r_1F}{r_1F + 1}$$

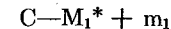
$$P_{12} = \frac{k_{12}[M_1^*][M_2]}{k_{11}[M_1^*][M_1] + k_{12}[M_1^*][M_2]} = \frac{[M_2]}{r_1[M_1] + [M_2]} = \frac{1}{r_1F + 1}$$

$$P_{21} = \frac{k_{21}[M_2^*][M_1]}{k_{21}[M_2^*][M_1] + k_{22}[M_2^*][M_2]} = \frac{[M_1]}{[M_1] + r_2[M_2]} = \frac{1}{1 + (r_2/F)}$$

$$P_{22} = \frac{k_{22}[M_2^*][M_2]}{k_{21}[M_2^*][M_1] + k_{22}[M_2^*][M_2]} = \frac{r_2[M_2]}{r_2[M_2] + [M_1]} = \frac{r_2}{r_2 + F},$$

where  $r_1$  and  $r_2$  are the reactivity ratios and  $F$  the ratio  $[M_1]/[M_2]$  between 1 concentrations of the monomer  $m_1$  and of the monomer  $m_2$  in the reacting mixture.

In determining the distribution of the sequences of different length, it must be taken into account that, in order for a sequence of  $n$  units of  $m_1$  to be formed, 1 addition reaction, on the growing chain C



(occurring on the first constituent of a sequence of  $m_1$  units), whose probability is  $P_{11}$ , must occur  $(n - 1)$  times.

The probability of these  $(n - 1)$  subsequent additions is  $P_{11}^{(n-1)}$ . Thus the sequence of reactions must be followed by the addition of an  $m_2$  unit having probability  $P_{12}$ , that is  $(1 - P_{11})$ . Therefore the probability that a sequence of units contains  $n$  members is

$$P(m_1)_n = P_{11}^{(n-1)} \cdot (1 - P_{11}).$$

Analogously:

$$P(m_2)_n = P_{22}^{(n-1)} \cdot (1 - P_{22})$$

represents the fraction of all  $m_2$  sequences formed by  $n$  members.

By substituting  $P_{11}$  and  $P_{22}$  in these two last expressions, with the values given above, we obtain:

$$P(m_1)_n = \left( \frac{1}{1 + (r_1F)^{-1}} \right)^{n-1} \frac{1}{1 + r_1F}$$

$$P(m_2)_n = \left( \frac{1}{1 + (F/r_2)} \right)^{n-1} \frac{1}{1 + (r_2/F)}$$

By introducing in these two last equations the values of  $F$  expressed as a function of the ratio ( $f$ ) between the molar concentrations of  $m_1$  and  $m_2$  in the copolymer

$$F = \frac{f - 1 + [(f - 1)^2 + 4r_1r_2f]^{\frac{1}{2}}}{2r_1}$$

new expressions are obtained for the sequence distribution functions which are function only of the  $r_1r_2$  product and not of the single  $r_1$  and  $r_2$  values.

Therefore, the distribution of the monomeric units in the ethylene-propylene copolymers, obtained with the aid of catalysts acting through an anionic coordinated mechanism is practically independent of the catalytic system used. In fact the  $r_1r_2$  product in the ethylene-propylene copolymerization carried out in the presence of various catalytic systems is always very near unity, see Table XV.

We applied<sup>34</sup> this method to the case of the ethylene-propylene copolymerizations in the presence of catalysts prepared from  $Al(C_6H_{13})_3$  and  $VCl_4$ ; for them we calculated<sup>16</sup> the following values of the reactivity ratios

$$r_{C_2H_4} = 7.08; \quad r_{C_3H_6} = 0.088$$

from which the product  $r_{C_2H_4} \cdot r_{C_3H_6} = 0.623$  was calculated.

Table XXVII shows the values of the  $P$  distribution functions of sequences of different length concerning copolymers of different composition. Figure 19 shows the probabilities of finding sequences of ethylene and of propylene of determined length, for copolymers of different composition.

TABLE XXVII

DISTRIBUTION FUNCTION OF SEQUENCES OF DIFFERENT LENGTH IN ETHYLENE-PROPYLENE COPOLYMERS HAVING DIFFERENT COMPOSITIONS PREPARED WITH  $\text{Al}(\text{C}_2\text{H}_5)_2\text{---VCl}$ , CATALYST

Mole % of $m_2$ in the copolymer	% $P(m_2)_n$															
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$	for $n$ between 10 and 14, $P(m_2)_n = 12.271\%$						$n > 15$
85	15.80	13.20	11.20	9.430	7.941	6.687	5.630	4.741	3.992							9.006
75	27.07	19.74	14.40	10.50	7.658	5.584	4.073	2.970	2.166							1.204
60	44.47	24.71	13.71	7.614	4.228	2.347	1.303	0.724	—							0.142
50	55.89	24.65	10.87	4.796	2.116	0.933	0.412	—	—							0.003
40	66.70	22.21	7.398	2.464	0.820	0.273	—	—	—							$< 1 \times 10^{-3}$
25	81.20	15.27	2.871	0.540	—	—	—	—	—							$< 1 \times 10^{-3}$
15	89.53	9.377	0.982	0.103	—	—	—	—	—							$< 1 \times 10^{-3}$

%  $P(m_2)_n$  = percentage of sequences of ethylene (or of propylene) containing  $n$  monomer units.  $n$  = number of monomer units present in each sequence.

TABLE XXVIII

DISTRIBUTION FUNCTION OF SEQUENCES OF DIFFERENT LENGTH IN COPOLYMERS HAVING DIFFERENT COMPOSITIONS, FOR  $r_1 r_2 = 1$

Mole % of $m_2$ in the copolymer	% $P(m_2)_n$									
	$n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n = 6$	$n = 7$	$n = 8$	$n = 9$	
15	85.00	12.75	1.91	0.29	0.29	—	—	—	—	—
25	75.00	18.75	4.69	1.17	0.29	—	—	—	—	—
40	60.00	24.00	9.60	3.84	1.54	0.62	—	—	—	—
50	50.00	25.00	12.50	6.25	3.13	1.56	0.78	—	—	—
60	40.00	24.00	14.40	8.64	5.18	3.11	1.87	—	—	—
75	25.00	18.75	14.06	10.55	7.91	5.93	4.45	3.34	2.51	—
85	15.00	12.75	10.84	9.21	7.83	6.66	5.66	4.81	4.09	—

%  $P(m_2)_n$  = percentage of sequences of  $m_2$  containing  $n$  monomer units.  
 $n$  = number of monomer units present in each sequence.

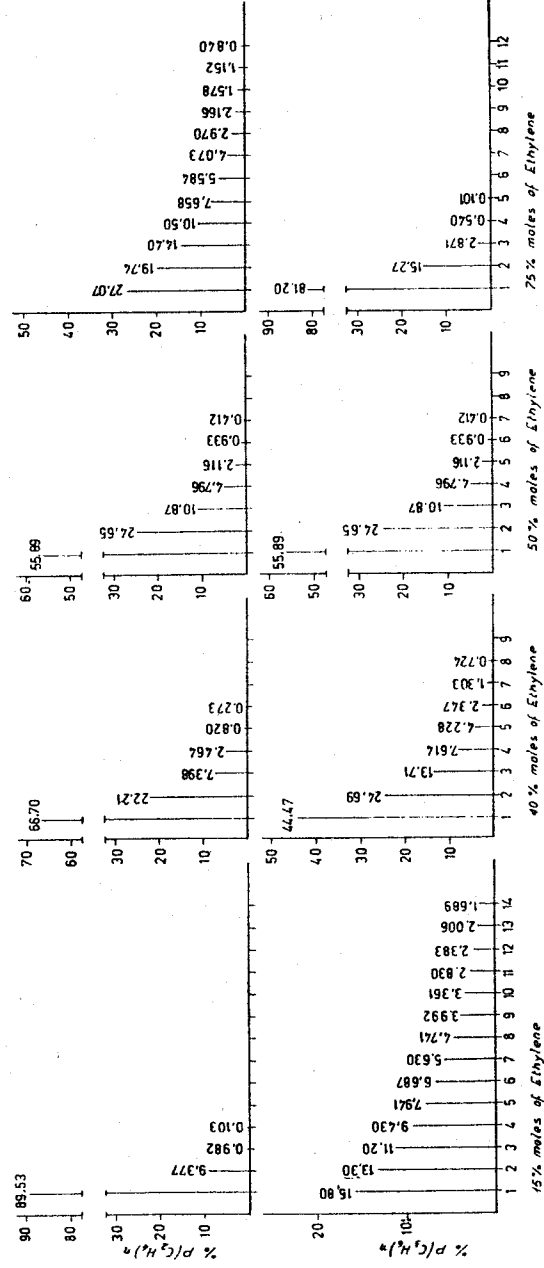


Fig. 19.—Distribution function of sequences of different length in ethylene-propylene copolymers having different compositions and prepared with the catalytic system  $\text{Al}(\text{C}_2\text{H}_5)_2 + \text{VCl}_4$ .

Obviously, see Table XXVII and Figure 19, the probability of existence of long sequences of ethylene and of propylene, respectively, increases with the increase of the monomer concentration in the copolymer. The highest dispersion in the lengths of the sequences of both monomers occurs for copolymers containing equimolecular amounts of ethylene and propylene.

Table XXVII also shows that ethylene sequences that are long enough to be crystallizable, e.g., containing at least 15 monomeric units, can exist in practice only for ethylene contents in the copolymer of the order of 85 mole %. In agreement with this supposition, we have already experimentally found<sup>16</sup> that copolymers can be prepared that contain up to 80% of ethylene, and, as revealed by x-ray analysis, do not show crystallinity due to long sequences of methylenic groups.

Tables XXVIII, XXIX, and XXX show the  $P$  distribution functions of the monomeric units, which should occur in copolymers for which the  $r_1r_2$  product is 1, 0.1, and 10, respectively. Comparison of the values of  $P(m_2)_n$  found for the copolymers obtained with the aid of catalysts prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$ , and the values reported in Tables XXVIII, XXIX, and XXX clearly shows that the distribution of the monomeric units of our most typical ethylene-propylene copolymers does not differ very much from the merely random one, which can be predicted for those copolymers having an  $r_1r_2$  product equal to one.

*B. Distribution of the monomeric units in sequences of different lengths.*—Having determined the distribution of the sequences of two monomeric units in a copolymer, it is easy to determine the distribution of the monomeric units in the sequences of different length.

The number of  $m_1$  monomeric units that is present in sequences of  $n$  units is given by the product of the total number of sequences of the  $m_1$  monomer present in the copolymer, by  $nP(m_1)_n$ .

The  $\phi(m_1, n)$  fraction of  $m_1$  units, present in sequences of  $n$  units is given by

$$\phi(m_1, n) = \frac{nP(m_1)_n}{\sum_{n=1}^{\infty} nP(m_1)_n} = \frac{nP_{11}^{n-1}P_{12}}{\sum_{n=1}^{\infty} nP_{11}^{n-1}P_{12}}$$

from which it is easy to obtain

$$\phi(m_1, n) = \frac{nP_{11}^{n-1}P_{12}}{1/P_{12}} = nP_{11}^{n-1}(P_{12})^2.$$

Analogously it has been found that the  $\phi(m_2, n)$  fraction of units of the  $m_2$  monomer, which are present in sequences of  $n$  units, is

$$\phi(m_2, n) = nP_{22}^{n-1}(P_{21})^2$$

Figure 20 shows the values of  $\phi(m_1, n)$  and  $\phi(m_2, n)$ , corresponding to various values of  $n$ , for ethylene-propylene copolymers of different composition, obtained with the aid of catalysts prepared from  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$ . It also shows that in these ethylene-propylene copolymers, if a monomer is present in a high percentage, higher than about 50%, most of its units appear in non-unitary sequences.

*C. Experimental controls.*—It has been tried experimentally to confirm the values of the sequence distribution functions deduced by the statistical theory described above.

A first proof is given by the absence of polyethylenic-type crystallinity in copolymers containing up to 80 mole-% of ethylene units<sup>16</sup>. This agrees with the

TABLE XXIX

DISTRIBUTION FUNCTION OF SEQUENCES OF DIFFERENT LENGTH IN COPOLYMERS HAVING DIFFERENT COMPOSITIONS, FOR  $r_1r_2=0.1$ 

Mole % of $m_2$ in the copolymer	% $P(m_2)_n$									
	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	$n=9$	$n=10$
15	97.95	2.01	0.04							
25	95.54	4.26	0.19							
40	87.67	10.81	1.33	0.16						
50	79.97	18.26	4.39	1.06	0.25					
60	58.45	24.29	10.09	4.19	1.74	0.72				
75	31.85	21.71	14.80	10.09	6.88	4.69	3.20	2.18	1.49	
85	17.29	14.30	11.83	9.78	8.10	6.70	5.54	4.58	3.79	

%  $P(m_2)_n$  = percentage of sequences of  $m_2$  containing  $n$  monomer units.  
 $n$  = number of monomer units present in each sequence.

TABLE XXX

DISTRIBUTION FUNCTION OF SEQUENCES OF DIFFERENT LENGTH IN COPOLYMERS HAVING DIFFERENT COMPOSITIONS, FOR  $r_1r_2 = 10$ 

Mole % of $m_2$ in the copolymer	% $P(m_2)_n$									
	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	$n=9$	$n=10$
15	50.53	25.00	12.37	6.12	3.03	1.50	0.74			
25	39.64	23.93	14.44	8.72	5.26	3.17	1.91	1.15		
40	29.23	20.69	14.64	10.37	7.33	5.19	3.67	2.60	1.84	
50	24.02	18.25	13.87	10.54	8.01	6.09	4.63	3.52	2.67	
60	19.49	15.69	12.63	10.17	8.19	6.59	5.31	4.28	3.45	
75	13.21	11.46	9.95	8.64	7.50	6.51	5.65	4.90	4.25	
85	8.92	8.12	7.40	6.74	6.14	5.59	5.09	4.64	4.23	

%  $P(m_2)_n$  = percentage of sequences of  $m_2$  containing  $n$  monomer units.  
 $n$  = number of monomer units present in each sequence.

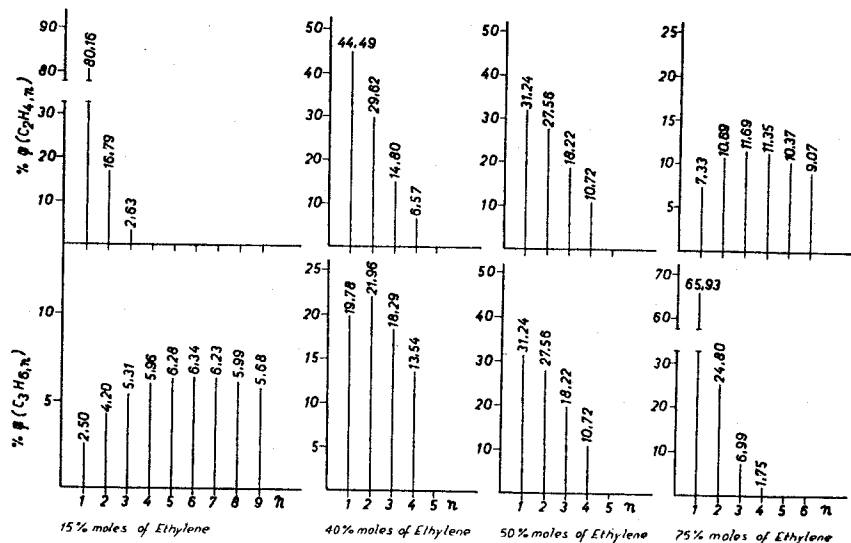


FIG. 20.—Distribution of monomer units in sequences formed by *n* monomer units for ethylene-propylene copolymers prepared with the catalytic system Al(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub> + VCl<sub>4</sub>.

values of the sequence distribution functions which are reported in Table XXVII. Actually, the value of  $P(C_2H_4)_n$  (with  $n \geq 15$ ) reaches appreciable values only for copolymers containing more than 80 mole-% of ethylene.

A further proof is based on infrared analysis<sup>34</sup>. The absorption band between 13.0 and 14.0  $\mu$  can be attributed to sequences of methylenic groups of different length, even if it is difficult to establish a mutual unequivocal relationship between the length of the methylenic sequences and the position of the corresponding bands in the infrared spectrum<sup>9,35</sup>. From the examination of the intensities of the absorption maxima, it can be established that, in the case of copolymers containing less than 45 mole-% of ethylene, sequences of less than 5 methylenes prevail over those of 5 or more methylenes, whereas in the case of copolymers containing more than 55 mole-% of ethylene, sequences of 5 or more methylenes prevail.

The calculated probability of existence of sequences of one or more monomeric units can be compared with the content of sequences of methylenic groups of different length, revealed by infrared analysis.

The calculated values and those obtained from infrared spectrography are in a very good agreement<sup>34,35</sup>.

X. KINETICS OF THE ETHYLENE-PROPYLENE COPOLYMERIZATION

After determining the reactivity ratios of the ethylene-propylene copolymerization in the presence of various catalytic systems, a systematic study was made<sup>14</sup> on the kinetics of ethylene-propylene copolymerization in the presence of the thermally-stabilized catalytic system Al(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub> + VCl<sub>4</sub>.

In particular, the effect on the copolymerization rate was studied of a series of factors, such as the preparation conditions of the catalyst, the concentration of both catalyst and monomers, the ratio between the moles of the two monomers present in the reacting liquid phase, and the temperature.

A. Conditions chosen for the copolymerization runs.—All the copolymerization runs were carried out in the presence of *n*-heptane as solvent, keeping the concentration of the two monomers constant during each run.

The solvent was saturated with the monomer mixture, before the introduction of the catalyst. Furthermore, to be sure that the monomer concentration did not change noticeably during the polymerization, high velocities were used in order to renew the gaseous phase rapidly, and keep the solution as close as possible to saturation.

Owing to the high velocities chosen, the conversion of each monomer was, for each passage, less than 5%. In practice, the copolymer composition did not change all other conditions being equal, when further increasing the feeding rate of the mixture.

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

Under these conditions, there was excellent reproducibility both for the composition of the copolymers and the polymerization rate.

B. Catalytic system. 1. Transition metal halide.—In order to carry out the study of the kinetics of the ethylene-propylene copolymerization, the catalytic system prepared from trihexylaluminum and vanadium tetrachloride was selected from among the various possible ones. This catalytic system proved to be preferable over those prepared by other hydrocarbon soluble transition metal halides, (such as TiCl<sub>4</sub> or VOCl<sub>3</sub>); in fact it yielded completely amorphous copolymers within a broader range of composition of the monomer mixture<sup>16</sup>. Moreover, the copolymers thus obtained possessed a better homogeneity of composition.

The use of catalysts prepared from low-valency hydrocarbon insoluble halides, (such as VCl<sub>3</sub>), has proved to be unsuitable for the kinetic studies on copolymerization; in fact, at low temperatures, these catalysts show an induction period of remarkable length.

2. Stabilization of the catalysts.—In accordance with what generally occurs for catalysts prepared from hydrocarbon soluble transition metal halides, the catalytic system VCl<sub>4</sub> + Al(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub> loses activity with time, see Figure 21.

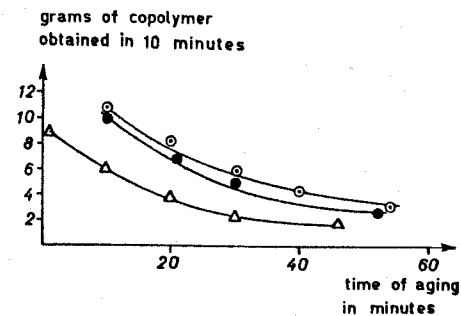


FIG. 21.—Dependence of copolymer yield on aging time. Polymerization temperature = 25° C;  $P = 1$  at; solvent: *n*-heptane cm<sup>3</sup> 410; mole C<sub>3</sub>H<sub>6</sub>/mole C<sub>2</sub>H<sub>4</sub> in gaseous mixture = 2; polymerization time = 10 minutes. ○ Catalyst aged at 25° C; mole Al(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>/mole VCl<sub>4</sub> = 1; V: 0.0224 g; ● Catalyst aged at 25° C; mole Al(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>/mole VCl<sub>4</sub> = 2.5; V: 0.0162 g; Δ Catalyst aged at 60° C; mole Al(C<sub>6</sub>H<sub>13</sub>)<sub>3</sub>/mole VCl<sub>4</sub> = 2.5; V: 0.0299 g.

In order to obtain catalysts with a constant activity, the authors prepared and kept the catalysts at a temperature above the operating one for a certain time. They found that by mixing the solutions of  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{VCl}_4$  at  $60^\circ\text{C}$  and then keeping the mixture at this temperature for 30 minutes, catalysts were obtained which, when used at temperatures between  $0$  and  $40^\circ\text{C}$ , show a lower activity, which remains constant for a time longer than that generally required for the polymerization runs, see Figure 10.

In every experiment, the catalysts were thermally stabilized under the above mentioned conditions (at  $60^\circ\text{C}$  for 30 minutes). The catalyst activity is higher when the aging times are shorter, but changes with time.

3. *Effect of the ratio of  $\text{Al}(\text{C}_6\text{H}_{13})_3$  to  $\text{VCl}_4$ .*—The copolymer composition does not vary when varying the ratio of the  $\text{Al}(\text{C}_6\text{H}_{13})_3$  moles to the  $\text{VCl}_4$  moles used in the preparation of the catalysts<sup>16</sup>, at least for an  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{VCl}_4$  ratio between 1 and 8. This result is valid also when stabilized catalysts are used.

The catalyst activity changes along with change of this ratio, and is highest for  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{VCl}_4$  molar ratios of about 2.5 (see Figure 12). This is in agreement with what was observed in propylene<sup>36-40</sup> and ethylene<sup>41-46</sup> homopolymerization, 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 was used, unless otherwise stated, in every copolymerization run of this kinetic study.

C. *Effect of the reaction conditions on the copolymerization rate. 1. Time.*—We noticed that, other conditions being the same, the quantity of copolymer is directly proportioned to the polymerization time, Figure 22. This has been proved for a large composition range of the monomer mixture and, for each composition, for a broad range of catalyst concentration. For example, in Figure 23 the copolymer yields are plotted against the polymerization time for different catalyst concentrations (for copolymers containing 50.6 mole % of ethylene). The result obtained shows that catalysts which are thermally stabilized by the above-mentioned method, show a constant activity with time, independently of whether the catalyst is or is not used in the meantime for the copolymerization.

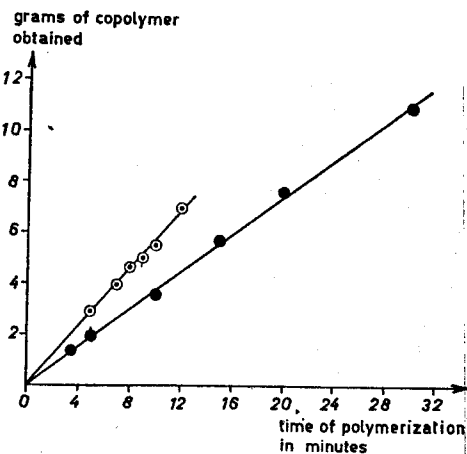


FIG. 22.—Dependence of copolymer yield (in grams) on polymerization time. Copolymerization temperature =  $25^\circ\text{C}$ ;  $P = 1$  at; solvent  $n$ -heptane,  $\text{cm}^3$  410;  $V: 0.0299$  g; mole  $\text{C}_2\text{H}_4/\text{mole}$   $\text{C}_6\text{H}_6$  in the gaseous mixture = 2;  $\text{O}$  mole  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{mole}$   $\text{VCl}_4 = 2.5$ ;  $\bullet$  mole  $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{mole}$   $\text{VCl}_4 = 4$ .

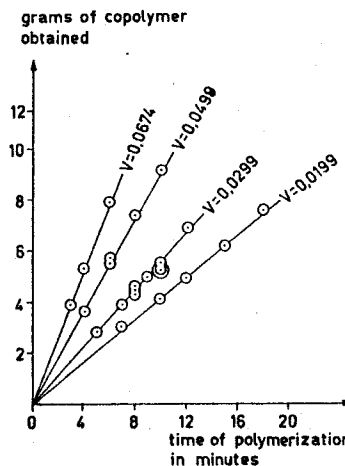


FIG. 23.—Dependence of copolymer yield (in grams) on polymerization time for different catalyst concentrations. Polymerization temperature =  $25^\circ\text{C}$ ;  $P = 1$  at; solvent:  $n$ -heptane,  $\text{cm}^3$  410; mole  $\text{C}_2\text{H}_4/\text{mole}$   $\text{C}_6\text{H}_6$  in the gaseous mixture = 2; mole-% ethylene in the copolymer = 50.6.

This fact allowed 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 macromolecule takes place through a transfer mechanism, which leaves the number of the growing chains practically unchanged. This last hypothesis is confirmed by the fact that using a stabilized  $\text{VCl}_4 + \text{AlR}_3$  catalyst at  $25^\circ\text{C}$ , 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 Table XVII).

2. *Catalyst concentration.*—Referring the copolymer yields (shown in Figure 23), obtained at different times and at different catalyst concentrations, to the unit weight of vanadium present in the catalytic system, values are obtained, see Figure 24, which are directly proportional to the polymerization time.

Therefore, it can be concluded that the copolymerization occurs with a first-order rate, with respect to the catalyst concentration.

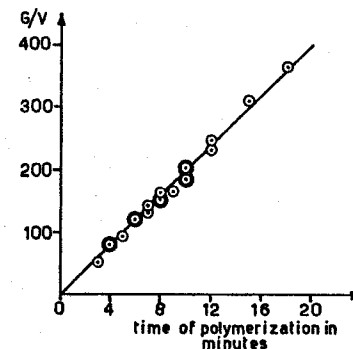


FIG. 24.—Dependence of  $G$  (g copolymer obtained) referred to  $V$  (g of vanadium) on polymerization time. Polymerization temperature =  $25^\circ\text{C}$ ;  $P = 1$  at; solvent:  $n$ -heptane,  $\text{cm}^3$  410; mole  $\text{C}_2\text{H}_4/\text{mole}$   $\text{C}_6\text{H}_6$  in the gaseous feed = 2; mole-%  $\text{C}_2\text{H}_4$  in the copolymer = 50.6.

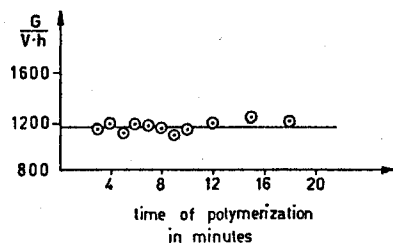


FIG. 25.—Copolymerization rate vs. polymerization time. Mole  $C_2H_4$ /mole  $C_3H_6$  in the gaseous mixture = 2; mole-%  $C_2H_4$  in the copolymer = 50.6.

The plot shown in Figure 25 confirms that the copolymerization rate, expressed as:

$$G/(V \cdot h), \quad (9)$$

(where  $G$  = grams of copolymer produced in  $h$  hours and  $V$  = grams of vanadium present in the catalytic system), all other conditions being the same, is constant with time.

**3. Monomer concentration.**—In order to investigate the dependence of the copolymerization rate on the concentration of the dissolved monomers, we carried out a series of experiments, in which, holding the ratio of the concentrations of the two monomers constant, their total concentration was changed. The total pressure for these runs was 1 at, while the monomer partial pressure was varied by diluting the gaseous monomer mixture, having a certain composition, with known amounts of very pure nitrogen, see Table XXXI.

TABLE XXXI

DEPENDENCE OF COPOLYMERIZATION RATE ON TOTAL MONOMER CONCENTRATION

Catalyst prepared from  $Al(C_2H_5)_2$  and  $VCl_4$ ; aged for 30 min. at  $60^\circ C$ ; moles  $Al(C_2H_5)_2$ /mole  $VCl_4$  = 2.5.  $T = 25^\circ C$ ;  $P = 1$  at; solvent: *n*-heptane,  $cm^3$  410; mole propylene/mole ethylene in gaseous mixture = 2.

Mole $N_2$ /(mole $C_2H_4$ + mole $C_3H_6$ ) in the gas phase	Polymerization time, min.	$G$ , g copolymer	$V$ , g vanadium	$G/Vh$	$R^*$
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

\*  $R = (G/Vh) [715/(P_{C_2H_4} + P_{C_3H_6})]$ .

Pressures up to atmospheric were preferred, for, otherwise, the copolymerization rate would have been too high, and consequently the temperature control of the system would have been more difficult.

As shown by the last column of Table XXXI, the copolymerization rates reduced to a pressure of 715 mm Hg (sum of the partial pressures of the two monomers, when operating at 1 at, without addition of an inert component to the gaseous feed), are constant for a given ratio  $P_{C_2H_4}/P_{C_3H_6}$ .

Thus for each value of this ratio, the copolymerization rate was directly proportional to the sum of the partial pressures, and consequently to the sum of the molar concentration in the dissolved phase, as shown in Figure 26.

The copolymerization rate varies strongly with variation in the ratio between the concentrations of the two monomers. In order to effect some comparable copolymerization runs using different feed compositions, we adopted certain catalyst and monomer concentrations for each composition that would always allow easily measurable rates, avoiding too high copolymerization rates. In particular, in the case of copolymerizations carried out with high-ethylene-content mixtures (molar ratio of ethylene to propylene in the gaseous feed  $> 2$ ) even with relatively low catalyst concentrations, we found it convenient to dilute the feed mixture with nitrogen.

Using the results previously reported (dependence of first-order rate on the catalyst concentration and holding the ratio between the monomer concentrations equal on their total concentration solution) it was possible to compare experiments carried out under different conditions.

For each feed composition, a number of runs (generally 10 or 12) were carried out, by adopting different catalyst concentrations and different polymerization times.

Table XXXII shows as an example, the values obtained for the copolymerization rates in the case of the production of copolymers having 50.6 mole % of ethylene. The rate (reduced to 715 mm Hg pressure) expressed as in Equation (9) has been calculated for each experiment and the average value of the rate for every series of experiments corresponding to the same feed mixture, has been reported in Table XXXIII.

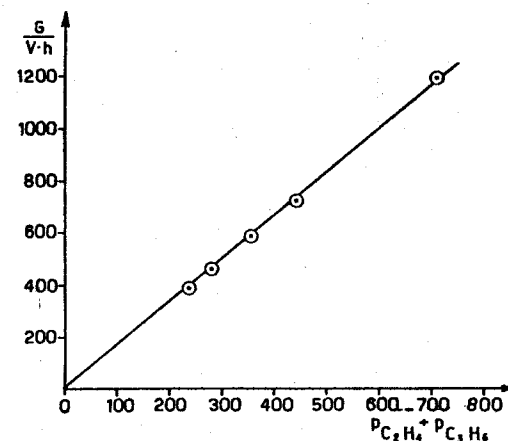


FIG. 26.—Dependence of copolymerization rate on the sum of the partial pressures of the monomers in the gaseous mixture. Polymerization temperature =  $25^\circ C$ .  $P = 1$  at; solvent: *n*-heptane  $cm^3$  410; mole  $C_2H_4$ /mole  $C_3H_6$  in the gaseous mixture = 2; mole-%  $C_2H_4$  in the copolymer = 50.6.



TABLE XXXII

RATE OF ETHYLENE-PROPYLENE COPOLYMERIZATION FOR COPOLYMER CONTAINING 50.6 MOLE-% ETHYLENE

Catalyst prepared from  $Al(C_2H_5)_3$  and  $VCl_4$ ; aged for 30 min at 60° C; moles  $Al(C_2H_5)_3$  to mole  $VCl_4 = 2.5$ ;  $T = 25^\circ C$ ;  $P = 1$  at; solvent- *n*-heptane,  $cm^3$  410; moles  $C_2H_4$ /mole  $C_3H_6$  in gaseous mixture = 2;  $P_{C_2H_4} + P_{C_3H_6} = 715$  mm Hg.

V, g vanadium	Polymerization time, min	G, g copolymer	R <sup>a</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>  $R = (G/VA) [715/(P_{C_2H_4} + P_{C_3H_6})]$ .

Because of the different solubility coefficients of ethylene and propylene, it may be interesting to express the rates corresponding to different feed compositions, with respect to the same total concentration of the olefins in the dissolved phase. The concentration corresponding to one mole of total olefins dissolved per liter of solution was chosen as the reference concentration. The volume of the solution was calculated neglecting the variation in volume due to the produced copolymer.

Finally, by indicating the copolymer productions in moles of polymerized monomer, rather than in grams, the comparable rate values were calculated, see Table XXXIII, expressed as follows:

$$\frac{(M/l)}{(V/l)h(m/l)}, \tag{10}$$

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

The rate vs. the mole percentage of dissolved ethylene referred to the total moles of the two monomers are plotted in Figure 27. In order to indicate in the plot of Figure 27, the values of the ordinates corresponding to the abscisses 0 and 1, we had to carry out some homopolymerization runs of ethylene and propylene, under the same experimental conditions as those adopted in the copolymerization runs.

The results obtained from these homopolymerization runs and the rates expressed according to a formula similar to Equation (10) are reported in Tables XXXIV and XXXV.

TABLE XXXIII  
DEPENDENCE OF ETHYLENE-PROPYLENE COPOLYMERIZATION RATE ON FEED COMPOSITION

Catalyst prepared from  $Al(C_2H_5)_3$  and  $VCl_4$  and aged at 60° C for 30 min. Moles  $Al(C_2H_5)_3$ /mole  $VCl_4 = 2.5$ ;  $T = 25^\circ C$ ;  $P = 1$  at; solvent: *n*-heptane,  $cm^3$  410.

(Mole $C_2H_4$ /mole $C_3H_6$ ) in the gas phase	Mole % $C_2H_4$ in the copolymer	$N_{C_2H_4}^a$	$N_{C_3H_6}^b$	$M_{C_2H_4}^c$	$R^d$	$M/l$ ( $V/l$ ) $h$ ( $m/l$ )
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>  $N_{C_2H_4}$  = molar fraction of ethylene in the liquid phase.

<sup>b</sup>  $N_{C_3H_6}$  = molar fraction of propylene in the liquid phase.

<sup>c</sup>  $M_{C_2H_4} = N_{C_2H_4}/(N_{C_2H_4} + N_{C_3H_6})$ .

<sup>d</sup>  $R = (G/VA) 715/(P_{C_2H_4} + P_{C_3H_6})$ .

*M* = sum of ethylene and propylene moles polymerized in *h* hours; *m* = sum of ethylene and propylene moles in the liquid phase.

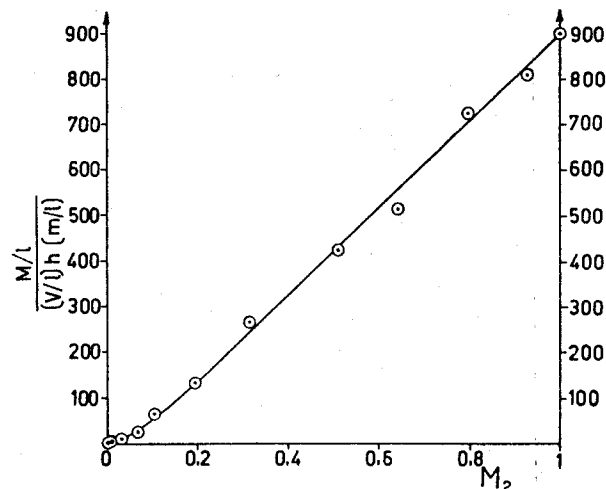


Fig. 27.—Dependence of copolymerization rate on percentage of dissolved ethylene moles, referred to the total moles of the two monomers. Mole  $\text{Al}(\text{C}_2\text{H}_5)_2/\text{mole VCl}_4 = 2.5$ ; polymerization temperature =  $25^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  410.

TABLE XXXIV

## RATE OF ETHYLENE HOMOPOLYMERIZATION

Catalyst prepared as for Table XXXIII. Moles  $\text{Al}(\text{C}_2\text{H}_5)_2/\text{mole VCl}_4 = 2.5$ ;  $T = 25^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  410.

Mole $\text{N}_2/\text{mole C}_2\text{H}_4$ in the gas phase	V, g vanadium	Polymerization time, min.	G, g polymer	$G/Vh \times \frac{715}{P_{\text{C}_2\text{H}_4}}$	M/l $(V/l)h(m/l)$
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	0.0449	4	2.85	4089	934
3.30	0.0449	6	4.25	4069	929

TABLE XXXV

## RATE OF PROPYLENE HOMOPOLYMERIZATION

Catalyst prepared as for Table XXXIII. Moles  $\text{Al}(\text{C}_2\text{H}_5)_2/\text{mole VCl}_4 = 2.5$ ;  $T = 25^\circ\text{C}$ ;  $P = 1$  at; solvent: *n*-heptane,  $\text{cm}^3$  410.

V, g vanadium	Polymerization time, min	G, g polymer	$G/Vh \times \frac{715}{P_{\text{C}_3\text{H}_6}}$	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

As shown in Figure 27, the copolymerization rate increases remarkably with increase of the ethylene content in the monomer mixture.

The copolymerization rate is approximately a linear function of the molar composition of the monomer mixture present in the liquid phase only for monomer mixture rich in ethylene. For monomer mixtures rich in propylene (beyond 80% of  $\text{C}_3\text{H}_6$  with respect to the total moles of dissolved olefins), the rate values diverge from the rectilinear behavior.

4. Temperature.—Runs were carried out at different temperatures 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. On the basis of several ethylene and propylene homopolymerization runs at  $0^\circ\text{C}$ ,  $25^\circ\text{C}$  and  $40^\circ\text{C}$ , respectively, an average value of the homopolymerization rate expressed according to Equation (10) was calculated for each temperature.

As is apparent from Figures 28 and 29, the logarithms of these rates vary linearly with the reciprocal of the absolute polymerization temperature. From the slope of the straight lines, it is possible to calculate the following values for the activation energy, referred to the monomer concentration in the dissolved phase:

polymerization of ethylene:  $E = 6650$  cal/mole

polymerization of propylene:  $E = 6600$  cal/mole

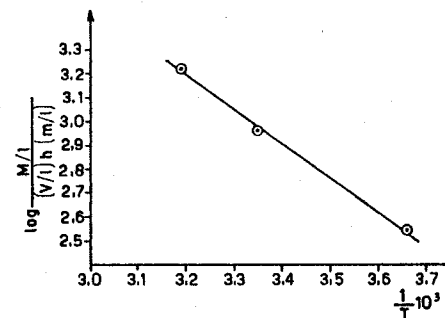


Fig. 28.—Logarithm of rate of ethylene polymerization with catalysts, prepared from  $\text{Al}(\text{C}_2\text{H}_5)_2$  and  $\text{VCl}_4$  and aged at  $60^\circ\text{C}$  for 30 minutes, vs. the reciprocal of the absolute polymerization temperature.

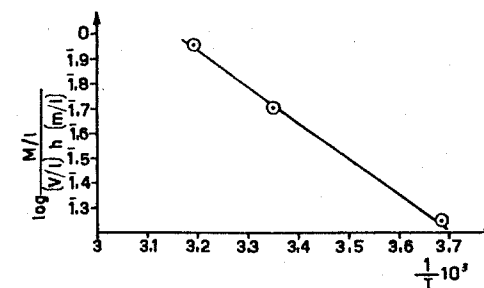


Fig. 29.—Logarithm of rate of propylene polymerization with catalysts, prepared from  $\text{Al}(\text{C}_2\text{H}_5)_2$  and  $\text{VCl}_4$ , and aged at  $60^\circ\text{C}$  for 30 minutes, vs. the reciprocal of the absolute polymerization temperature.

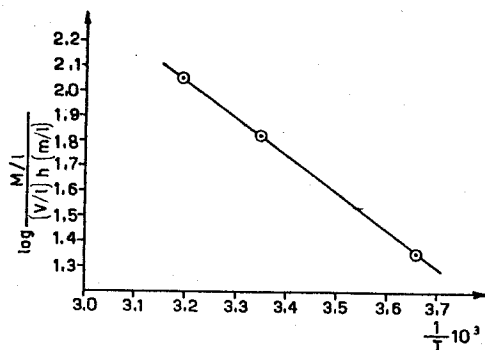


Fig. 30.—Logarithm of the rate of ethylene-propylene copolymerization (for copolymers containing 50.6 mole-% C<sub>3</sub>H<sub>6</sub>) with catalyst prepared from Al(C<sub>2</sub>H<sub>5</sub>)<sub>3</sub> and VCl<sub>4</sub>, and aged at 60°C for 30 minutes, vs. the reciprocal of the absolute polymerization temperature.

The resulting values in practice do not differ from one another and are of the same order of magnitude as the activation energy already found for propylene<sup>46,47,48</sup> and ethylene<sup>49,50</sup> homopolymerization in the presence of different catalytic systems. Therefore, the remarkable differences in the homopolymerization rates of the two monomers should be attributed, at least in part, to steric factors.

Figure 30 shows the average values of the copolymerization rate logarithms, expressed according to Equation (10) (for copolymers containing 50.6 mole-% of ethylene units) at temperatures of 0°, 25°, and 40° C. Also in this case the logarithm of the rate varies linearly, with the reciprocal of the absolute temperature and the slope corresponds to the one observed for both homopolymerizations. This equality of apparent activation energies is significant because, in the case of the copolymerization, we are not allowed to consider an activation energy of the overall process, since its overall rate depends, as is well known, upon the rates of the four elementary processes to which may correspond different activation energies<sup>51</sup>.

In fact, in the copolymerization of the two monomers M<sub>1</sub> and M<sub>2</sub>, if the instantaneous concentrations of the monomer units present at the end of the growing polymeric chains are indicated by [M<sub>1</sub>\*] and [M<sub>2</sub>\*], the rates of the four elementary processes can be indicated as follows:

$$V_{11} = k_{11}[M_1^*][M_1]$$

$$V_{12} = k_{12}[M_1^*][M_2]$$

$$V_{21} = k_{21}[M_2^*][M_1]$$

$$V_{22} = k_{22}[M_2^*][M_2]$$

The overall copolymerization rate will be:

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

The rate constant for each process is given by:

$$k_{11} = P_{11}Z_{11} \exp \left\{ -\frac{E_{11}}{RT} \right\}$$

$$k_{12} = P_{12}Z_{12} \exp \left\{ -\frac{E_{12}}{RT} \right\}$$

$$k_{22} = P_{22}Z_{22} \exp \left\{ -\frac{E_{22}}{RT} \right\}$$

$$k_{21} = P_{21}Z_{21} \exp \left\{ -\frac{E_{21}}{RT} \right\}$$

where  $Z$  is the collision number and  $P$  is the steric factor. As is well known, the  $Z$  factor is essentially independent of temperature and the  $Z$  factor is affected only slightly. Therefore the ratios:

$$\frac{P_{11}Z_{11}}{P_{12}Z_{12}} \quad \text{and} \quad \frac{P_{22}Z_{22}}{P_{21}Z_{21}}$$

can be considered as practically constant, at least in the relatively narrow range of temperatures examined.

In the ethylene-propylene copolymerization carried out with the aid of catalyst prepared from vanadium halides and aluminum trialkyls, the reactivity ratios in practice do not vary with temperature, at least for temperatures between 0° and 75° C<sup>13,17</sup>.

Given

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

and

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

then

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

and

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

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

*D. Variation of the total number of growing chains.*—The considerable increase in the copolymerization rate observed by increasing the ethylene/propylene ratio in the reacting phase, cannot be explained on the basis of the values of the propagation constants alone, but it is also necessary to admit a variation of the total number of growing chains, when varying the ratio of ethylene to propylene. This variation of growing chains can be explained by the existence of active centers capable of starting ethylene polymerization, but not propylene polymerization.

This phenomenon was also confirmed by direct measurement of the number of active centers (capable of originating growing chains) present in the homopolymerization of ethylene and of propylene with the catalytic systems VCl<sub>3</sub>-AlR<sub>3</sub> and TiCl<sub>4</sub>-AlR<sub>3</sub>. A further proof is given by the possibility of preparing ethylene-propylene copolymers with the aid of catalysts that cannot start the homopolymerization of propylene and are active only in the homopolymerization of ethylene.

By admitting the variation of the number of growing chains indicated above, all the polymerization rates are related to the same concentration of growing chains the ratio between the homopolymerization rates of ethylene and propylene is of the same order of magnitude as the reactivity ratio of ethylene<sup>52</sup>.

## XI. VISCOELASTIC PROPERTIES

The ethylene-propylene copolymers form a class of new elastomers rather than a new type of elastomer; some of their physical and chemical properties differ as

the various parameters are varied. The viscoelastic properties of these new rubbers are affected by the following parameters, connected with the structural characteristics of the macromolecular chains:

- Chemical composition of the copolymer
- Distribution of such composition
- Average molecular weight
- Distribution of the molecular weights.

*A. Chemical composition of the copolymer.*—The average composition of the ethylene-propylene copolymer mainly affects the dynamic properties of the elastomer and the 2nd order transition temperature. In fact, fairly flexible chain segments are present in these copolymers, due to sequences of methylene groups. The flexibility of the segments is fairly high, even at temperatures much lower than room temperature. Therefore the ethylene-propylene copolymers show fairly good dynamic properties. A comparison between the rebound vs. temperature curves of the best known elastomers with an ethylene-propylene copolymer, having a content of 65 mole-% of ethylene is shown in Figure 31.

The flexibility of the chain essentially depends on the sequences of methylene groups, as can be demonstrated by varying the copolymer composition. By increasing the total content of ethylene units in the copolymer within the limits that avoid even a partial crystallization, the chain segments consisting of methylenic sequences increase; this is a contribution to the increase of the total flexibility of the chain, which leads to an improvement in the dynamic properties of the elastomer; the resilience at room temperature is better, the other conditions being the same, for copolymers having a higher ethylene content, Figure 32<sup>53</sup>.

A property that is exclusively connected with the average composition of the copolymer is its second-order transition temperature. It was measured by dilatometric means and can be determined by measuring the minimum rebound temperature. The relationship connecting the minimum rebound temperature with the

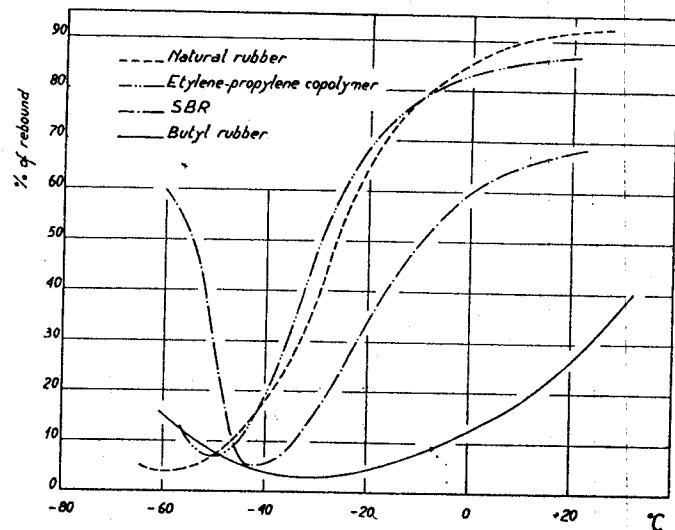


Fig. 31.—Rebound vs. temperature curves of various elastomers in comparison with ethylene-propylene copolymer (65% mole content of ethylene).

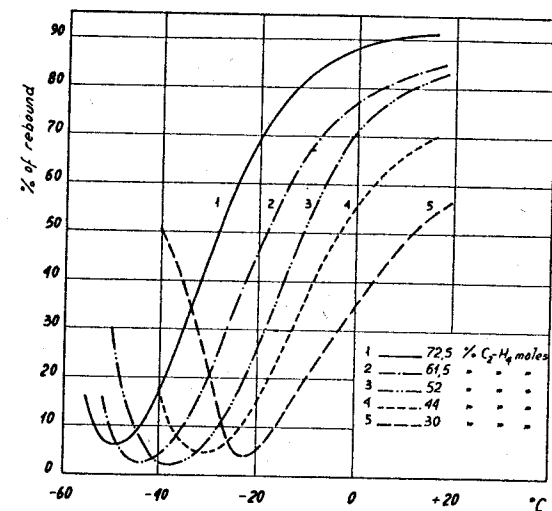


Fig. 32.—Rebound vs. temperature curves of ethylene-propylene copolymers, having various contents of ethylene.

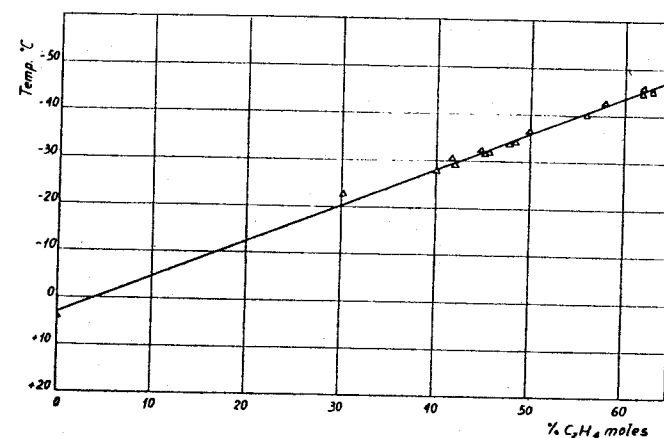


Fig. 33.—Minimum rebound temperature as a function of ethylene content in various ethylene-propylene copolymers.

molar concentration of ethylene in the ethylene-propylene copolymer is of the linear type and is reported in Figure 33. An analogous relationship is valid in the case of the ethylene-butene-1 copolymers<sup>11</sup>, Figure 34.

By increasing the ethylene content in the copolymer beyond 75–80 mole-%, products are obtained that do not show a good elastomeric behavior. For instance, in examining the rebound vs. temperature curves of these copolymers, curves are obtained like that shown in Figure 35. This figure shows that the minimum rebound value is very high with respect to the values usually occurring both in the ethylene-propylene copolymers and in other rubbers. Furthermore, the minimum rebound temperature is much higher than what could be foreseen from the copolymer composition on the basis of the relationship of Figure 33.

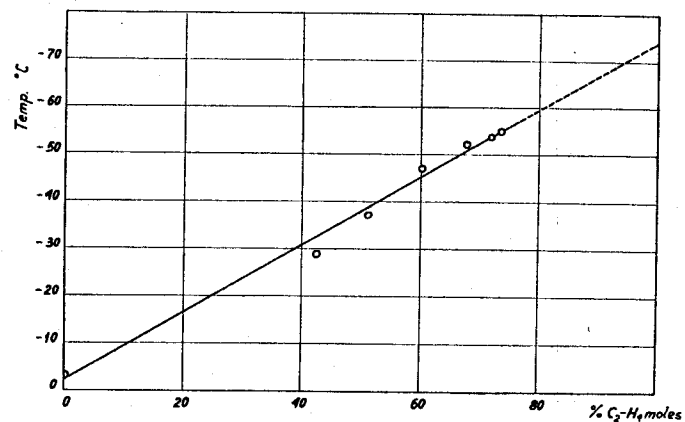


FIG. 34.—Minimum rebound temperature as a function of ethylene content in various ethylene-butene-1 copolymers.

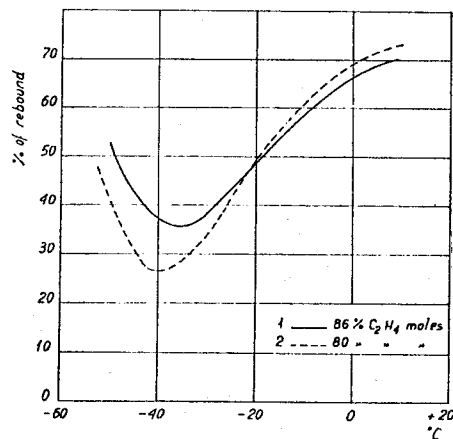


FIG. 35.—Rebound vs. temperature curves of ethylene-propylene copolymers, having a high ethylene content.

*B. Distribution of the composition.*—The regularity of distribution of the composition can be checked in the crude copolymers by extraction with solvents. By operating under suitable polymerization conditions, and using catalysts containing only one type of active center, copolymers can be obtained that show only a limited dispersion in chemical composition.

Figure 36 shows the distribution curves of the composition in the various fractions of ethylene-propylene copolymers, whose average composition is 45 mole-% of ethylene units; it can be observed that the distribution of the composition is rather narrow<sup>55</sup>.

The regularity or the irregularity of the composition distribution of the ethylene-propylene copolymers does not exert much influence on the viscoelastic properties; this is true when the distribution does not involve the presence of an appreciable fraction of high-ethylene-content-copolymer, that is of a crystallizable or easily crystallizable product. The mixing of two or more ethylene-propylene copolymers

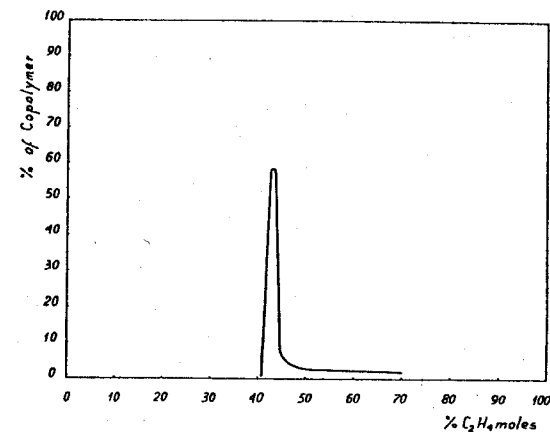


FIG. 36.—Composition distribution curve for an ethylene-propylene copolymer containing 45 mole-% ethylene.

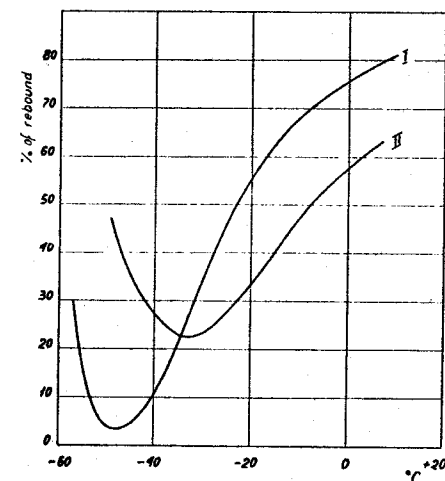


FIG. 37.—Rebound vs. temperature curves for a homogeneous and a non-homogeneous copolymer each containing 67 mole-% of ethylene.

of different homogeneous compositions, but without crystallizable portions lead to a mixed copolymer showing properties practically equivalent to those shown by a homogeneous copolymer having the same average composition. The rebound vs. temperature curve of such a mixed copolymer shows an intermediate behavior with respect to the analogous curves of the copolymers forming the blend itself. In particular, the value of the minimum rebound temperature corresponds to the average composition of the compound, according to the relationship of Figure 33.

Rather different results are obtained when the crude polymer contains crystalline fractions; the rebound vs. temperature curve shows a minimum rebound, which is markedly higher than the usual values. Furthermore this minimum value is obtained at a temperature that does not correspond to that of the copolymer average composition<sup>11</sup>. Figure 37 shows the comparison between the rebound curves of

homogeneous copolymer having an average composition of 67 mole-% of ethylene, and of a copolymer of the same composition, but consisting of at least two fractions, containing 86 mole-%, and 49 mole-% of ethylene, respectively. It can be noticed that the two types of copolymers can be clearly distinguished one from another on the basis of these curves. The high-ethylene-content fraction can be easily obtained by solvent extraction from the product consisting of the nonhomogeneous copolymer of Figure 37; the rebound vs. temperature curve of this fraction has already been shown in Figure 35; the analogy of this with Figure 37 referring to the mixture can be observed.

*C. Average molecular weight and distribution of molecular weights.*—The molecular weight of the ethylene-propylene copolymers can be varied within a wide range, depending on the synthesis conditions. Molecular weights can be determined by the usual viscosity, osmometric and light-diffraction methods. When the composition of the copolymer under examination is known, the values of the viscosity-average molecular weight can be obtained from the intrinsic viscosity values measured in tetralin at 135° C<sup>56</sup>.

The viscosity of the copolymer and consequently its processability are strictly connected with the average molecular weight. The viscosity of the copolymers can be measured by means of viscometers of various types; for practical purposes, it is preferable to measure the Mooney viscosity at 100° C, under the conditions usually adopted for the most common elastomers. In order to obtain good processability, the value of Mooney viscosity (ML 1 + 4 at 100° C) for the ethylene-propylene copolymers must range between 20 and 80. Obviously also the copolymers showing a Mooney viscosity lower than 20 can be well processed, but, after vulcanization, they show poor physical properties.

Due to the fact that the ethylene-propylene copolymer does not undergo any degradation during the usual rubber processing, in order to obtain good processability, copolymers must be produced directly in synthesis, having an average molecular weight suitable for good processability, and yielding, after vulcanization, products with good mechanical and dynamic properties<sup>57</sup>.

In this sense, the processability of the ethylene-propylene copolymers is connected not only with the average molecular weight, but also with the distribution of molecular weight. In fact, in the distribution of molecular weight of each elastomer, high molecular weights favor the final properties of the vulcanizate, but damage processability, whereas low molecular weights favor good processability, but exert a negative influence on the mechanical and dynamic properties of the vulcanized elastomer.

Under the usual conditions of industrial synthesis, by operating in the absence of a regulating agent for the molecular weight, copolymers are obtained which show high average molecular weight; the distribution of molecular weight in these products is of the type shown in Figure 38 which results rather narrow. These copolymers, due to their high viscosity, can be hardly processed, but after vulcanization they yield products with excellent mechanical and dynamic properties; these latter in particular (heat build up) attain values very near to those of natural rubber.

By degradation of the high-average-molecular-weight copolymers, it is possible to obtain products that can be well processed and show excellent vulcanizate properties. For instance, if the copolymer of Figure 38 is subjected to thermal degradation (at a temperature of 270°–280° C, for some hours in a nitrogen atmosphere), a lower molecular weight product is obtained having the distribution of molecular weight shown in Figure 39. It can be noticed that the copolymer has a narrower

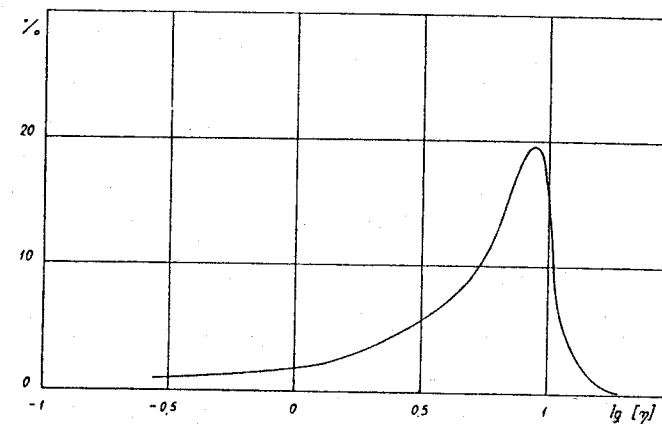


Fig. 38.—Distribution of molecular weight of a high-molecular-weight ethylene-propylene copolymer. Intrinsic viscosity  $[\eta]$  in toluene at 30° C.

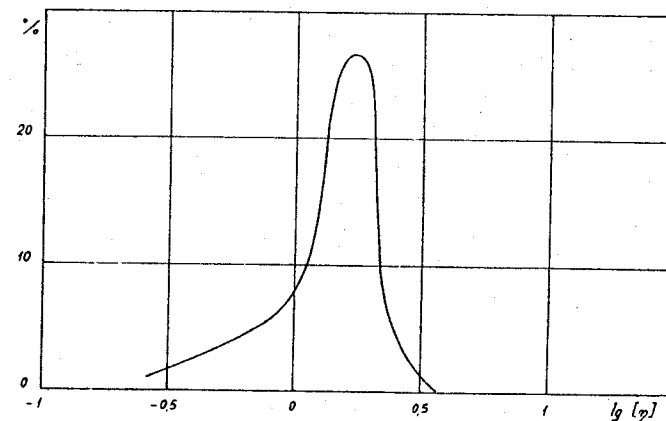


Fig. 39.—Distribution of molecular weight of an ethylene-propylene copolymer obtained by degradation of the copolymer given in Figure 38. Intrinsic viscosity  $[\eta]$  in toluene at 30° C.

distribution and that very high molecular weights are absent. The processability of such a copolymer is excellent and the vulcanizates show good properties.

The regulation of the average molecular weight of the copolymer, by using in the synthesis substances acting as chain terminators, so as to obtain a copolymer with good processability generally leads to a remarkable broadening in the distribution curve of the molecular weights. However, in this case appreciable high-molecular-weight fractions are present simultaneously with low-molecular-weight ones.

By effecting the copolymerization with the aid of particular catalytic systems, operating also in the industrial synthesis, copolymers can be obtained directly, having an average molecular weight regulated within a wide range and a narrow distribution of molecular weights. The distribution curve referred to a copolymer obtained directly under these conditions of synthesis is shown in Figure 40. It can be noticed that this last curve is very similar to that shown in Figure 39, which

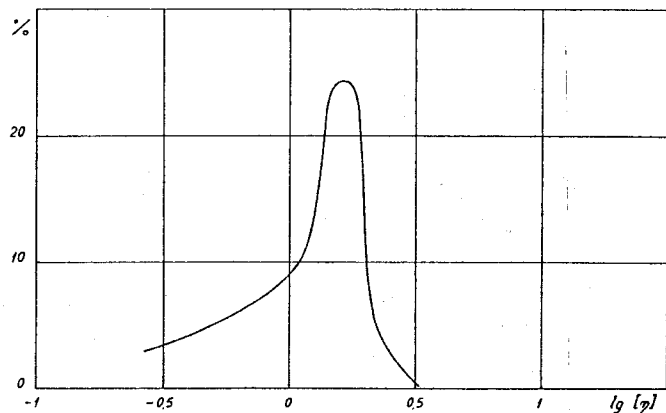


Fig. 40.—Distribution of molecular weight of an ethylene-propylene copolymer with a narrow distribution obtained directly in synthesis. Intrinsic viscosity  $[\eta]$  in toluene at 30° C.

was for a copolymer obtained from a high-average-molecular-weight product by thermal degradation. In both cases, the high-molecular-weight fraction, which makes processability worse, is absent, whereas low molecular weights are present only in a limited amount. This copolymer shows good processability: it easily forms a smooth, homogeneous band on the mill mixer, incorporates fillers easily with good dispersion, is easily extruded yielding smooth surface shapes, with well controlled dimensions and moreover it shows sufficient tack for the formation of number of composite technical articles.

## XII. EXTENSION WITH OIL

In analogy with what is usually done for other types of synthetic rubbers, the ethylene-propylene copolymers also can be extended with considerable amounts of common petroleum oils. In general copolymers and terpolymers with a high average molecular weight (Mooney viscosity at 100° C, ML 1 + 4 in the range of 80-140) are used for the extension with oil. After extension with oil a rubber with Mooney viscosity of about 30-40 is obtained, having good processability.

The type of oil, its viscosity and its amount, must be chosen in such a way as to obtain not only good processability, but also satisfactory properties of the vulcanizate for several uses. In the case in which ethylene-propylene copolymers are vulcanized with organic peroxides, it is better to use an oil of the paraffinic type; thus a considerable increase in the amount of peroxide necessary to obtain vulcanized products of good mechanical properties is avoided. In the case of terpolymers vulcanizable with recipes based on sulfur and accelerators, oils of different types can be used; the properties of the vulcanizate are particularly good using oils of the naphthenic or paraffinic types; oils of the aromatic type yield vulcanizates of lower properties<sup>58</sup>.

Petroleum oils are generally excellent plasticizers for ethylene-propylene co- and terpolymers; they are highly compatible and can be added in large quantities with only a moderate loss in physical properties.

The advantage of oils in these rubbers is given not only by the improved processability (e.g., smooth extrusion), but also by the possibility of obtaining good-quality articles at lower prices.

## XIII. STRESS RELAXATION

The viscoelastic properties of the amorphous polymers can be suitably measured by studying some simple phenomena, such as stress-relaxation, creep, etc. within a determined range of temperature; thus the range of the transition temperature, the vitreous and the elastic behavior can be determined. Figure 41 shows the values of the stress-relaxation modulus for an ethylene-propylene copolymer, having a mole % content of ethylene, measured at temperatures ranging from -60° C to +45° C. This figure shows a stress-relaxation modulus of the copolymer at -60° C of about  $10^9$  dyne/cm<sup>2</sup>, which is practically independent of time; this value is far from the value usually assumed by the modulus in the vitreous state. This explains why the brittle point of the ethylene-propylene copolymers assumes very low values (about -100° C) in comparison with those of the best known rubbers. For a number of amorphous polymers, the curves reported above can be superimposed in a single curve that represents the stress-relaxation modulus vs. time for a determined reference temperature, when the superposition principle is valid. This principle is generally applied only to amorphous polymers; to enable its application also to the ethylene-propylene copolymers, these must behave as amorphous materials within the whole range of temperatures considered.

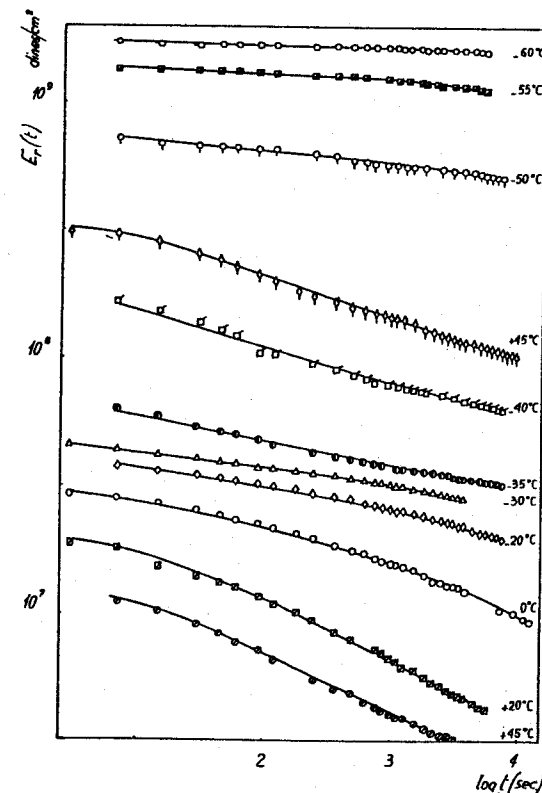


Fig. 41.—Stress-relaxation modulus of an ethylene-propylene copolymer (40% mole ethylene) vs. time, at various temperatures.

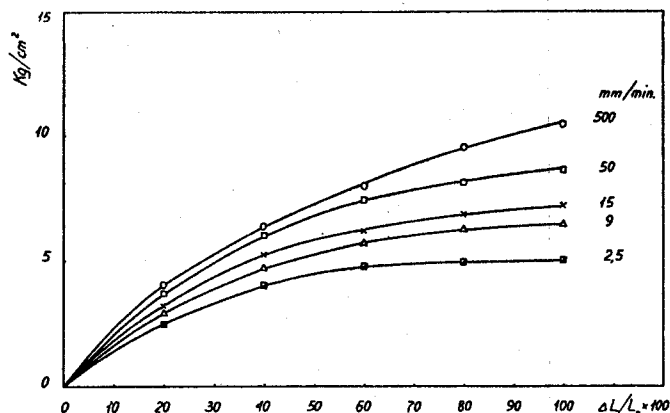


Fig. 42.—Initial part of stress-strain curves at different elongation rates at 0° C.

As an investigation of the viscoelastic properties of the copolymers, it may be interesting to examine the initial part of their stress-strain curves at different elongation rates and at different temperatures. Figure 42 shows the curves obtained at different rates, at a temperature of 0° C. The stress-relaxation modulus values at the corresponding temperatures can be obtained from these curves by applying known formulas. The values calculated by this method agree well with the data measured directly and reported in Figure 41.

The stress-strain curves, obtained at different temperatures show a progressive raising of the initial elastic modulus with decrease of temperature, as the result of a continuous increase of the cohesion forces in the material. The elongation at break, however, stays fairly high, even for very low temperatures (−60° C); this shows how this temperature is very far from the brittle temperature of the ethylene-propylene copolymers.

Obviously the values of the stress-relaxation modulus and the shape of the stress-strain curves can vary when the average composition of the copolymer is varied or, the average molecular weight, and the distribution of composition; for instance, the presence of small amounts of crystallinity leads to a noticeable increase of the initial elastic modulus, which can be observed by an accurate measurement of the first part of the stress-strain curves.

#### XIV. PHYSICAL PROPERTIES

A number of typical properties for ethylene-propylene copolymers are listed in Table XXXVI.

One of the outstanding features is their low specific gravity, which not only represents an advantage with regard to particular application possibilities, but also adds to the economics in the use, reducing the volume unit cost of the end products<sup>60</sup>.

The thermal properties are satisfactory and are of the same order as those of other rubbers.

The brittle temperature is clearly below the values shown both by natural rubber and by the most common synthetic rubbers.

Since the ethylene-propylene copolymer is essentially a polyhydrocarbon, its solubility in solvents is practically identical with that of the most common hydrocarbon rubbers.

TABLE XXXVI

#### PROPERTIES OF CRUDE ETHYLENE-PROPYLENE COPOLYMERS

Specific gravity, g/cm <sup>3</sup>	0.86–0.87
X-ray crystallinity	none
Ash content	less than 0.5%
Appearance	colorless
Mooney viscosity	varied
Heat capacity, cal/g °C	0.52
Thermal conductivity, cal/cm sec. °C	$8.5 \times 10^{-4}$
Thermal diffusivity, cm/sec.	$1.9 \times 10^{-3}$
Thermal coefficient of linear expansion/°C	$1.8 \times 10^{-4}$
Brittle point (ASTM D746)/°C	−95
Solubility:	
	soluble in aliphatic, cycloaliphatic and aromatic hydrocarbons, in chlorinated hydrocarbons
	insoluble in methanol, butanol, acetone.

TABLE XXXVII

#### ELECTRICAL PROPERTIES OF ETHYLENE-PROPYLENE COPOLYMERS

	units	ASTM test method
Volume resistivity	ohm. cm	D257 $5 \times 10^6$
Dielectric strength	kV/mm	D149 28–30
Dielectric constant at 1000 cycles		D150 2.2
Loss factor at 1000 cycles		D150 0.001–0.002

Its permeability to gases (and to vapors) is practically identical with that of natural rubber; therefore it is much higher than that shown by butyl rubber.

Its electric properties are excellent, Table XXXVII, and are equal to those of the best insulating materials. Taking into account the excellent resistance of these copolymers to aging, to ozone, and to ionization effects, the ethylene-propylene copolymers can be considered as an excellent insulating material for the production of cables.

#### XV. VULCANIZATION

The transformation of the ethylene-propylene copolymers into vulcanizates can be performed by adopting various systems able to cause crosslinking. The lower reactivity of the hydrogen atoms bound to the tertiary carbon in comparison with the reactivity of allyl hydrogen, does not allow crosslinking under the standard vulcanization conditions, using those ingredients that are generally employed for high-unsaturation-content elastomers.

The problem of the transformation of copolymers into vulcanizates can be essentially solved by two different methods<sup>61, 62, 63</sup>:

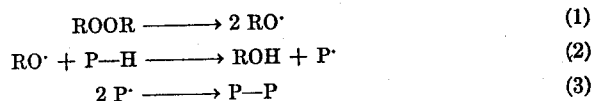
- 1) With the use of highly reactive crosslinking agents, able to react with paraffinic hydrocarbons (crosslinking with organic peroxides).
- 2) By introducing a limited number of highly reactive functions along the copolymer chain. The introduction of these reactive functions can be obtained either by reaction on the ethylene-propylene copolymer already synthesized (thus a chemically modified copolymer is produced) or during the synthesis of the elastomer (synthesis of terpolymers).

*A. Vulcanization by organic peroxides.*—The mechanism of crosslinking of saturated polymers by means of organic peroxides is already known in its fundamental outlines. An organic peroxide, when heated at a certain temperature,



decomposed into two free radicals. These radicals react in the presence of saturated polyhydrocarbons, abstracting a hydrogen atom from the polymer chain, and forming an induced radical on the chain. Two induced radicals of this type on different chains may join together, giving a crosslinking bond<sup>62</sup>.

The reactions, which are useful for crosslinking, can be briefly indicated as follows:



Together with these reactions, which are useful for crosslinking the polymer, other parasitic reactions may obviously take place, which cause a decrease in the crosslinking efficiency of the peroxide. The reasons of this decrease in crosslinking yield can be different: in general, they are connected with the reactivity both of the radicals originated by peroxide decomposition and of those induced on the polymer chain. The radicals originated by the peroxide decomposition can cause both dismutation and scission reactions with consequent lowering of the useful dehydrogenation reaction of the polymer. Also the radicals induced on the polymer chains can originate parasitic reactions: combination with radicals that do not derive from the polymer, dismutation reactions and scission of the chain, with degradation of the polymer. All these reactions and in particular that of scission contribute to lower the crosslinking yield, intervening more or less depending on the polymer structure. For instance, it is known that by heating polyisobutylene in the presence of organic peroxide, a complete degradation of the polymer occurs until an oily liquid is obtained. Under the same conditions, polypropylene and polybutene undergo a certain degree of crosslinking, but the yield is very low, whereas polyethylene and silicone rubbers are essentially crosslinked. For the ethylene-propylene copolymer, in the usual range of chemical composition, crosslinking prevails over the other reactions.

The efficiency of crosslinking obtained by the use of peroxides in the ethylene-propylene copolymers, varies depending on the composition of the copolymer (measurements were made by the swelling method): it is about 70% for a 25 mole-% content of propylene units, about 65% for a 33 mole-% content of propylene, and less than 10% for a 90 mole-% content of propylene<sup>63</sup>.

The decrease in the efficiency can be mostly attributed to chain scission reactions. In partly cured amorphous polypropylene vulcanizates, the examination of the molecular weight of the soluble part clearly shows that scission of the macromolecules took place.

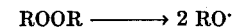
The crosslinking efficiency in the ethylene-propylene copolymers can be considerably improved by the use of vulcanization co-agents. Consequently, a remarkable improvement of the physical properties of the vulcanizates is obtained.

Different chemical compounds have been proposed as co-agents in the vulcanization of the ethylene-propylene copolymers; of them, mention must be made of: sulfur and sulfur donor agents (such as Sulfasan R, Sulfads, etc.), maleic anhydride and its derivatives, quinondioxime and its derivatives, dinitrosobenzene, divinylbenzene, triallylcyanurate, divinyladipate, diallylphthalate, triallylaconitate, diallylmelamine, itaconic acid, etc.<sup>62, 63, 69</sup>

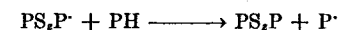
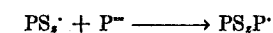
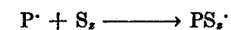
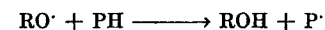
The reaction mechanism proposed for these co-agents is more or less the same. It is suggested that they react with the radicals formed on the chains of the elastomer, by a rapid addition, thus forming radicals of intermediate stability; in this way the scission reaction is lowered considerably, whereas the crosslinking is practically unaltered.

The vulcanization scheme of the saturated hydrocarbon elastomers with the use of sulfur as co-agent, can be represented as follows:

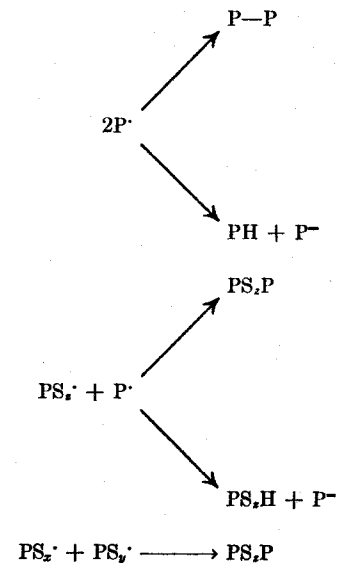
Initiation:



Propagation:



Termination:



In the above reported mechanism, sulfur improves the utilization of the radicals for crosslinking, and moreover, provides polysulfide crosslinks in addition to the carbon-carbon crosslinks. These facts can explain why the vulcanizates obtained by vulcanization of the ethylene-propylene copolymers with peroxides and sulfur show better properties than those obtained with the use of other co-agents.

Research performed on low-molecular-weight hydrocarbons, whose chemical structure is similar to that of the copolymers, also demonstrated that the main products formed during this reaction are polysulfides, containing from 2 to 4 sulfur atoms. The major single product is the disulfide.

The concentration of sulfur employed is important for the crosslink yield; the effect exerted by the concentration of sulfur on the main properties of the vulcanizate is shown in Figure 43.

By assuming the 300% modulus as an index of the degree of crosslinking, at first a small increase of sulfur up to a 1:1 ratio in *g* of sulfur atoms per mole of peroxide, causes a remarkable increase in the degree of crosslinking; beyond this limit, an increase in the sulfur concentration, causes a decrease of the crosslinking degree<sup>62</sup>.



almost exclusively. The vulcanization rate is affected only by the decomposition rate of peroxides; in order to increase the latter, it is not convenient to add substances that affect the decomposition rate, since a simultaneous decrease in the crosslinking yield would occur. Temperature affects the homolytic monomolecular decomposition of peroxide, enhancing it without altering its mechanism. Figure 44 shows the vulcanization curves (300% modulus) vs. time for various curing temperatures. Sulfur apparently shows an accelerating effect; in reality it allows better utilization of the radicals for crosslinking. This effect is shown in Figure 45; it can be noticed that the vulcanizates, obtained with a sulfur-containing mix attain a higher modulus, but the time necessary to reach the maximum modulus is equal in the two cases<sup>62</sup>.

The vulcanization curves reported above show also that the properties of the vulcanizate are practically unaltered for very long curing times, and that the same result can be obtained at very different temperatures. This is due to the absence of reversion reactions and to the thermal stability of the copolymer; thus, at a temperature of 200° C, it is possible to obtain very short vulcanization cycles (of the order of one minute).

Vulcanization based on organic peroxides is inflexible and without the extraordinary flexibility of the conventional vulcanization based on sulfur and accelerating agents. In fact, if the paraffinic nature of the ethylene-propylene elastomers compels the use of crosslinking agents as powerful as peroxides, the vulcanization reaction loses any specificity. In practice, the peroxide reacts with any substance present in the compound (apart from fillers). Therefore, the addition of plasticizers, antioxidants, tackifiers, fillers, etc., must be regulated cautiously, to avoid bad curing results.

When adding plasticizers and extenders, it must be taken into account that some types of aromatic oils react with peroxides more rapidly than the polymer; also the paraffinic-type oils consume peroxide and their introduction in the compound involves an increase of the amount of peroxide necessary to obtain a good cure.

Particular caution is necessary also when adding silica fillers and clay, which show a residual superficial acidity. They interact with the peroxide during the vulcanization, that is they adsorb it on their surface, and catalyze its heterolytic scission, with consequent lowering of the crosslink yield. In these cases, in order to obtain good curing results, it is necessary to add to the compound a small amount of substances, which can be adsorbed on the fillers and neutralize acidity, like the alcohols, the amines, the metal oxides, etc.

With regard to carbon black, it can be said that the most common furnace-types (having a basic pH) exert a very limited inhibitory action on the vulcanizing activity; this action becomes detectable only when increasing the specific surface of carbon black. The use of the usual amounts of carbon black leads to vulcanizates with high tensile strength, good tear resistance, and excellent abrasion resistance.

**B. Determination of the degree of crosslinking.**—The determination of the degree of crosslinking of the ethylene-propylene copolymers, as for other rubbers, can be made by swelling in solvents. Figure 46 shows the equilibrium swelling in benzene at 25° C vs. the crosslink density. Crosslink density was determined on specimens crosslinked with dicumyl peroxide alone, and swollen in benzene<sup>66</sup>. The polymer-solvent interaction coefficient could be deduced from these measurements;  $\mu = 0.48 + 0.29 v_r$  was obtained for the copolymer-benzene system at 25° C.  $v_r$  is the volume fraction of polymer. This value of  $\mu$  is still valid, when other crosslinking systems are used, which, however, do not have much effect on the interaction in the polymer-solvent system.

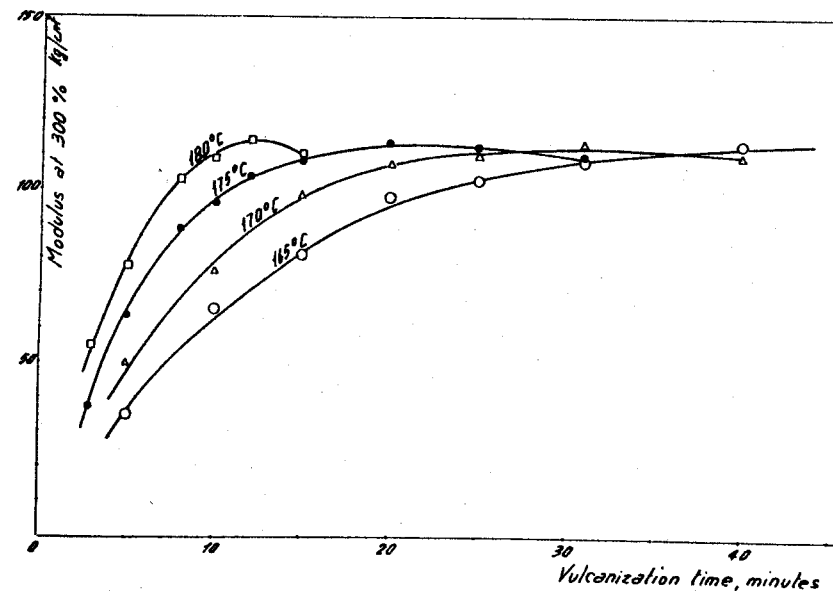


Fig. 44.—Effect of curing temperature on crosslinking degree (300% modulus) for different times (Recipe EPR 100 parts, HAF black 50 parts, *tert.* butyl-cumylperoxide 1.54 parts, sulfur 0.2 parts).

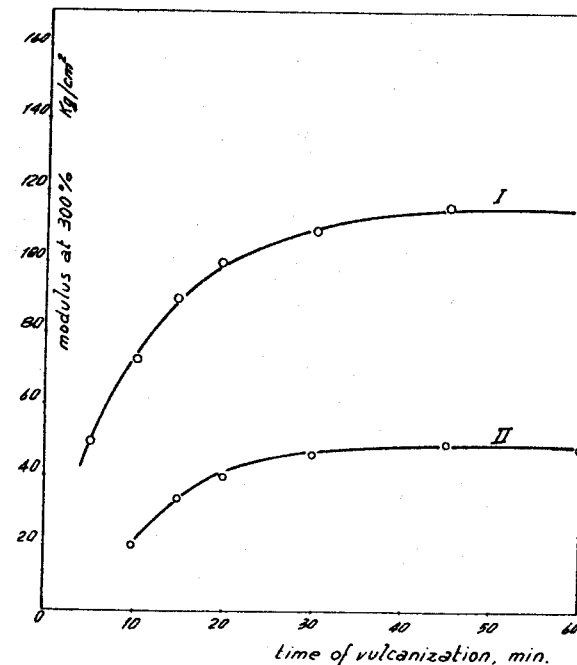


Fig. 45.—Comparison between vulcanization rate of EPR in the absence (II) and in the presence of sulfur (I). 300% modulus vs. vulcanization time at 165° C.

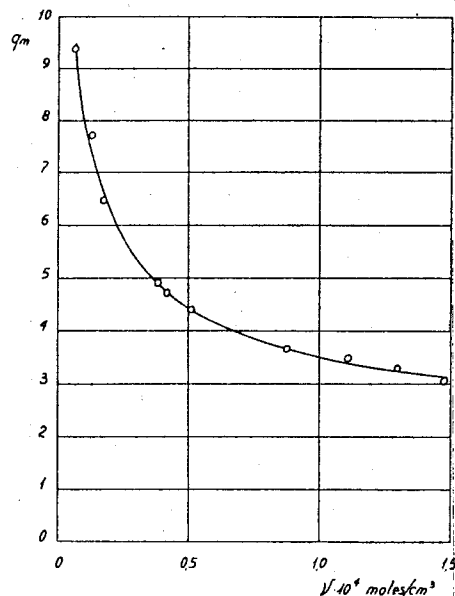


Fig. 46.—Swelling ratio at equilibrium (in benzene at 25° C) of EPR vulcanizates vs. crosslink density.

**C. Crosslinking of the chlorosulfonated ethylene-propylene copolymers.**—Since the beginning of the synthesis of poly- $\alpha$ -olefins, methods have been studied to transform them into vulcanizates. The amorphous polymers of  $\alpha$ -olefins and the amorphous high-molecular-weight ethylene- $\alpha$ -olefin copolymers have been preferably used. Contrary to polyethylene, in order to transform them to vulcanizable rubbers, it was enough to introduce a very limited number of chlorine atoms and of chlorosulfonic groups along the chains; thus a marked worsening of the elastic properties of the hydrocarbon macromolecules of the starting polymer was avoided.

Chlorosulfonation of polymers and copolymers of  $\alpha$ -olefins can be carried out on a polymer either in solution or in the swollen state, either with chlorine and sulfurous anhydride or sulfuryl chloride in the presence of suitable initiators. The most important parameters affecting the properties are represented by the chlorine and sulfur contents and by the molecular weight of the chlorosulfonated products. Therefore the best yield in chlorosulfonation must be obtained while limiting the concurrent chlorination reaction as much as possible<sup>67</sup>.

Vulcanization of the chlorosulfonated ethylene-propylene copolymers occurs by the salt-forming reaction of the sulfonic groups of the chain, by polyvalent metal oxides or by organic compounds containing more than one function able to form salts. It must be observed that vulcanizates with high tensile strength can be obtained also in the absence of the usual reinforcing fillers.

The chlorosulfonated copolymers can also be vulcanized, in analogy with chlorosulfonated polyethylene, by organic radicals acting as biradicals (e.g. quinoid compounds) in the presence of the typical radical initiators.

Table XXXIX shows the main mechanical properties of copolymers with different chlorine and sulfur contents, vulcanized both with metal oxides and with thiourea. It can be observed that the increase in the chlorine and sulfur content

causes a decrease in rebound, a progressive raising of the 200% modulus (which can be attributed to an increase in polar interactions besides a higher number of crosslinks of chemical nature) and a decrease in the elongation at break. The vulcanizates obtained with the use of thiourea have poorer mechanical properties; in this case it is better to use reinforcing fillers.

**D. Crosslinking of copolymers with radical initiators and unsaturated compounds of acid nature.**—The results that can be obtained in the crosslinking of the ethylene-propylene copolymers with the use of peroxides alone are not quite satisfactory, probably owing to the parasitic reactions that provoke a decrease in the crosslinking.

Among the several co-agents used together with peroxides, some unsaturated compounds containing one or more functional groups of acid nature are suitable. These compounds probably regulate the crosslinking action of the radical initiator, thus favoring the crosslinking homogeneity and increasing its yield. Maleic anhydride, maleic acid, fumaric acid and their derivatives are particularly effective from this point of view; it can be recalled that maleic anhydride had already been used to modify and vulcanize high unsaturated rubbers<sup>68</sup>.

The addition of small amounts of maleic anhydride to a copolymer mix already containing peroxide, causes a considerable increase in the crosslinking degree; this is clearly demonstrated by the increase in modulus and by the decrease in swelling. Figure 47 shows the behavior of the 200% modulus and of the residual deformations (after prestretching 200%) vs. the amount of maleic anhydride added to an ethylene-propylene copolymer containing 2 phr of benzoyl peroxide. This figure also shows how the best results are obtained with a definite ratio of maleic anhydride to peroxide, beyond which, in analogy with what happens for other types of co-agents, the crosslinking yield decreases again.

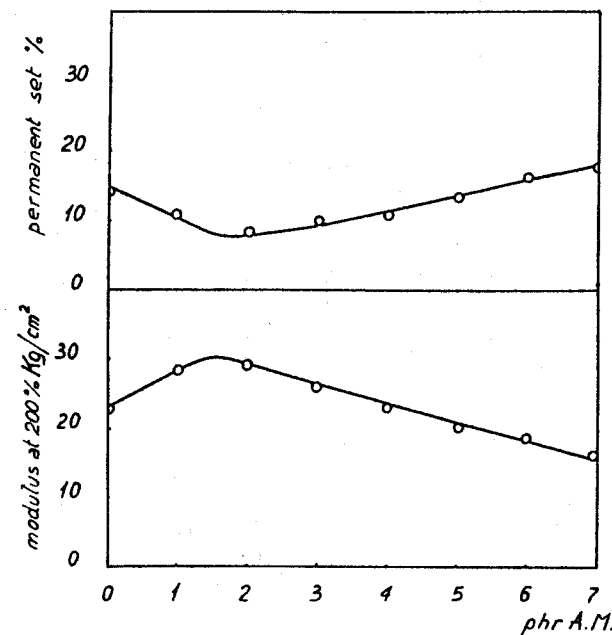


Fig. 47.—Effect of maleic anhydride on the properties of ethylene-propylene vulcanizate.

The mechanical properties of the vulcanized copolymers further improve if small amounts of polyvalent metal oxides are added to the mix in addition to peroxide and to the unsaturated compound of acid nature. This improvement must be probably attributed to salt-forming reactions of the acid compounds grafted on different copolymer chains. Table XL reports the main properties of vulcanizates containing different amounts of zinc oxide. As can be seen, the introduction of small amounts of zinc oxide markedly improves the properties of the vulcanizate; in particular the 300% modulus increases considerably, resilience improves and the swelling degree decreases markedly. Zinc oxide, when added in considerable amounts to the mix (25–50 phr), acts as an active filler.

Maleic acid and the other unsaturated compounds containing acid groups show an essentially analogous behavior to maleic anhydride. The properties of vulcanizates obtained from an ethylene-propylene copolymer compounded with benzoyl peroxide, zinc oxide and different unsaturated compounds in almost equimolecular proportions are reported in Table XLI; the results obtained are practically equivalent<sup>59</sup>.

TABLE XL  
CHARACTERISTICS OF VULCANIZATES WITH PEROXIDE AND MALEIC ANHYDRIDE,  
WITH VARIABLE AMOUNTS OF ZINC OXIDE

ZnO, phr	Tensile strength, kg/cm <sup>2</sup>	Elongation at break, %	300% modulus, kg/cm <sup>2</sup>	Hardness Shore A	Resilience		q <sub>m</sub> <sup>a</sup>
					at 20° C %	at 90° C %	
0	38	465	22	49	64	70	4.5 <sup>a</sup>
5	100	520	38	53	—	—	3.1
10	115	515	49	55	69	81	3.1
25	142	475	60	56	69	82	4.9
50	160	460	76	—	66	80	2.7

Recipe	
Copolymer	100
Dibenzoyl peroxide	2
Maleic anhydride	7
ZnO	variable
Vulcanization	45 min/160° C

<sup>a</sup> q<sub>m</sub>—swelling ratio at equilibrium in benzene at 30° C.

TABLE XLI  
CHARACTERISTICS OF VULCANIZATES WITH PEROXIDE AND DIFFERENT  
UNSATURATED ACID SUBSTANCES

Substance	Quantity, phr	Tensile strength, kg/cm <sup>2</sup>	Elongation at break, %	300% modulus, kg/cm <sup>2</sup>	Hardness, Shore A	Resilience at 20° C, %
—	—	75	660	32	51	72
Maleic acid	9	150	550	56	55	73
Fumaric acid	9	95	620	47	52	72
Itaconic acid	10	103	510	67	54	71
Cinnamic acid	11.5	90	580	54	—	73
Crotonic acid	6.7	75	510	56	—	72
Acrylic acid	11	95	450	65	52	71

Recipe	
Copolymer	100
Dibenzoyl peroxide	2
Zinc oxide	20
Acid substance	as indicated
Vulcanization	30 min/160° C

To obtain good results in a vulcanization of this type, it is necessary to use acid compounds containing at least one double bond; the use of analogous saturated compounds (succinic acid, adipic acid, etc.) does not cause any considerable improvement in comparison with crosslinking done with peroxide alone.

Instead of zinc oxide, different oxides or polyvalent hydroxides can be used. The properties of vulcanizates obtained using different basic substances are different. In particular it can be noticed how magnesium oxide and hydroxide yield vulcanizates of very high modulus in comparison to those obtained by zinc oxide, while Al<sub>2</sub>O<sub>3</sub> yields vulcanizates with low modulus values.

*E. Crosslinking of ethylene-propylene copolymers grafted with unsaturated acid compounds.*—As pointed out in the previous section, the addition of zinc oxide markedly improves the properties of the crosslinked product. This is due to salt-forming reactions among the groups grafted on different chains by the action of zinc oxide.

If the grafting reaction of the acid groups on the copolymer chains is obtained without crosslinking of the elastomer, the grafted copolymer can be subsequently vulcanized by the action of only basic substances. The grafted copolymer can be prepared by compounding the radical initiator and the unsaturated acid compound (e.g. maleic acid) to the copolymer, and subsequently heating the mix to high temperature. By operating with suitable amounts of the ingredients and under suitable temperature conditions for the thermal treatment, products are obtained that show only a limited degree of crosslinking. Some solubility data for grafted copolymers obtained by the same thermal treatment with different recipes, as well as the properties of vulcanizates obtained from a grafted copolymer by vulcanization by zinc oxide are reported in Table XLII. These data also show that it is possible to obtain good vulcanizates using in the grafting operation amounts of peroxide that are rather limited (0.6 phr per 100 parts of copolymer) in comparison with those usually employed for the crosslinking with peroxides either alone or with co-agents<sup>59</sup>.

A beneficial effect on the decrease of crosslinking during grafting can be exerted by some substances that usually interact with the radical initiators (e.g., phenyl-β-naphthylamine, aromatic oils, etc.); this effect is not accompanied by an appreciable decrease in the degree of grafting.

TABLE XLII  
PROPERTIES OF A GRAFTED COPOLYMER

Heat treatment 200° C × 30 min.	Solubility after heat treatment in CHCl <sub>3</sub> , %	Characteristics of vulcanized copolymer			
		Maleic acid phr	DTBP <sup>a</sup> phr	Tensile strength, kg/cm <sup>2</sup>	Elongation at break, %
2	0.3	89	93	565	31
2	0.6	69	89	470	45
2	1	44	62	350	49
3	0.3	93	81	490	33
3	0.6	80	76	390	49
3	1	65	76	305	73
5	0.3	97	102	760	18
5	0.6	97	123	650	23
5	1	97	117	470	53

Recipe: Grafted copolymer	
PBNA	1
Stearic acid	2
Zinc oxide	5

Vulcanization, 30 min/160° C

<sup>a</sup> DTBP = di-*tert*-butyl peroxide.

It is not easy to determine the maleic acid grafted on the copolymer; a series of analyses suggested that this value is about 1–1.5% by weight; this corresponds to a yield of 30–50% in respect to the maleic acid introduced in the mix. The vulcanization of the grafted copolymer can take place by means of polyvalent basic substances, such as metal oxides, diamines, etc.; in practice the use of zinc oxide, even if in limited amounts, yields vulcanizates of good properties. However, it must be borne in mind that crosslinking occurs by salt forming reaction of the carboxylic groups grafted on the chains; therefore it is a fairly rapid reaction. Consequently the possibility exists of a prevulcanization. In order to obtain a greater regularity of vulcanization, not only zinc oxide, but also small amounts of organic acid (e.g., stearic acid) should be added to the recipe, thus obtaining vulcanizates of better properties. Table XLIII shows the main properties of some vulcanizates obtained in the presence and in the absence of reinforcing fillers, starting from the same grafted copolymer of Table XLII (grafting on an ethylene-propylene copolymer compounded with 0.6 phr of di-*tert.* butyl peroxide and 3 phr of maleic acid). The high tensile strengths can be observed from these data, and they are essentially due to the high molecular weight of the starting copolymer and to the type of crosslink.

*F. Crosslinking of ethylene-propylene copolymers with the use of polymerizable monomers.*—Good vulcanization results are obtained if small amounts of polymerizable monomers are added, together with organic peroxide<sup>69</sup>. These moderate the action of peroxide, but, contrary to other coagents, chains of a certain length of these monomers are formed; if such chains end on two different macromolecules of an ethylene-propylene copolymer, there is formation of crosslinks. If monomers having more than one polymerizable double bond are used, the possibility of formation of crosslinks is greater, and the crosslinking yield increases.

Among the monomers that can be easily polymerized with radical initiators, mention can be made of styrene, of divinylbenzene, of the derivatives of acrylic and methacrylic acid. In the case of a hydrocarbon monomer, a vulcanizate is obtained with good mechanical and excellent electric properties.

*G. Crosslinking of the chlorinated ethylene-propylene copolymers.*—Crosslinking of the ethylene-propylene copolymers can be easily carried out on the previously chlorinated copolymer. Chlorination of the ethylene-propylene copolymers can be carried out in carbon tetrachloride solutions or on a polymer in the swollen state by direct action of chlorine. Thus starting from the same copolymer, products with different chlorine contents can be prepared<sup>69</sup>.

The properties of the ethylene-propylene copolymers are markedly modified by the introduction of chlorine in the chains. By increasing the chlorine content the initial polymer, which is prevalingly elastic is transformed into a plastic product; with high chlorine contents, it is possible to obtain hard and brittle products at room temperature. In examining the rebound vs. temperature curves of differently chlorinated copolymers, it is observed that the effect of chlorine is to provoke a shift of the curves towards high temperatures, Figure 48; the increase of the temperature of minimum rebound is practically proportional to the chlorine content of the copolymer<sup>70</sup>.

These data show that, in order to avoid any worsening of the dynamic properties of the vulcanizates, more than 15–20% of chlorine by weight should not be introduced in the copolymer. The vulcanization can be performed on the chlorinated copolymer with the use of recipes based on sulfur and accelerators taking advantage of a partial dehydrochlorination (with formation of double bonds) occurring

TABLE XLIII  
CHARACTERISTICS OF VULCANIZATES OBTAINED FROM COPOLYMERS GRAFTED WITH MALEIC ACID

Stearic acid, phr	Recipe				Properties of vulcanizates			
	Zinc oxide, phr	Oil (Dutrex R55), phr	Carbon black, EPC, phr	Tensile strength, kg/cm <sup>2</sup>	Elongation at break, %	300% modulus, kg/cm <sup>2</sup>	Resilience at 20° C, %	Hardness, IHRD
4	2.5	—	—	130	520	45	83	57
4	2.5	5	45	415	520	150	71	73
4	2.5	10	45	390	650	85	70	73
2	2.5	5	45	395	550	130	74	72
2	2.5	10	45	395	650	93	73	70

Vulcanization, 30 min./160° C.

It is not easy to determine the maleic acid grafted on the copolymer; a series of analyses suggested that this value is about 1-1.5% by weight; this corresponds to a yield of 30-50% in respect to the maleic acid introduced in the mix. The vulcanization of the grafted copolymer can take place by means of polyvalent basic substances, such as metal oxides, diamines, etc.; in practice the use of zinc oxide, even if in limited amounts, yields vulcanizates of good properties. However, it must be borne in mind that crosslinking occurs by salt forming reaction of the carboxylic groups grafted on the chains; therefore it is a fairly rapid reaction. Consequently the possibility exists of a prevulcanization. In order to obtain a greater regularity of vulcanization, not only zinc oxide, but also small amounts of organic acid (e.g., stearic acid) should be added to the recipe, thus obtaining vulcanizates of better properties. Table XLIII shows the main properties of some vulcanizates obtained in the presence and in the absence of reinforcing fillers, starting from the same grafted copolymer of Table XLII (grafting on an ethylene-propylene copolymer compounded with 0.6 phr of di-*tert.* butyl peroxide and 3 phr of maleic acid). The high tensile strengths can be observed from these data, and they are essentially due to the high molecular weight of the starting copolymer and to the type of crosslink.

*F. Crosslinking of ethylene-propylene copolymers with the use of polymerizable monomers.*—Good vulcanization results are obtained if small amounts of polymerizable monomers are added, together with organic peroxide<sup>69</sup>. These moderate the action of peroxide, but, contrary to other coagents, chains of a certain length of these monomers are formed; if such chains end on two different macromolecules of an ethylene-propylene copolymer, there is formation of crosslinks. If monomers having more than one polymerizable double bond are used, the possibility of formation of crosslinks is greater, and the crosslinking yield increases.

Among the monomers that can be easily polymerized with radical initiators, mention can be made of styrene, of divinylbenzene, of the derivatives of acrylic and methacrylic acid. In the case of a hydrocarbon monomer, a vulcanizate is obtained with good mechanical and excellent electric properties.

*G. Crosslinking of the chlorinated ethylene-propylene copolymers.*—Crosslinking of the ethylene-propylene copolymers can be easily carried out on the previously chlorinated copolymer. Chlorination of the ethylene-propylene copolymers can be carried out in carbon tetrachloride solutions or on a polymer in the swollen state by direct action of chlorine. Thus starting from the same copolymer, products with different chlorine contents can be prepared<sup>69</sup>.

The properties of the ethylene-propylene copolymers are markedly modified by the introduction of chlorine in the chains. By increasing the chlorine content the initial polymer, which is prevalingly elastic is transformed into a plastic product; with high chlorine contents, it is possible to obtain hard and brittle products at room temperature. In examining the rebound vs. temperature curves of differently chlorinated copolymers, it is observed that the effect of chlorine is to provoke a shift of the curves towards high temperatures, Figure 48; the increase of the temperature of minimum rebound is practically proportional to the chlorine content of the copolymer<sup>70</sup>.

These data show that, in order to avoid any worsening of the dynamic properties of the vulcanizates, more than 15-20% of chlorine by weight should not be introduced in the copolymer. The vulcanization can be performed on the chlorinated copolymer with the use of recipes based on sulfur and accelerators taking advantage of a partial dehydrochlorination (with formation of double bonds) occurring

TABLE XLIII  
CHARACTERISTICS OF VULCANIZATES OBTAINED FROM COPOLYMERS GRAFTED WITH MALEIC ACID

Stearic acid, phr	Recipe			Properties of vulcanizates				Hardness, IRHD
	Zinc oxide, phr	Oil (Dutrex R56), phr	Carbon black, EPC, phr	Tensile strength, kg/cm <sup>2</sup>	Elongation at break, %	300% modulus, kg/cm <sup>2</sup>	Resilience at 20° C, %	
4	2.5	—	—	130	520	45	83	57
4	2.5	5	45	415	520	150	71	73
4	2.5	10	45	390	650	85	70	73
2	2.5	5	45	395	550	130	74	72
2	2.5	10	45	395	650	93	73	70

Vulcanization, 30 min./180° C.

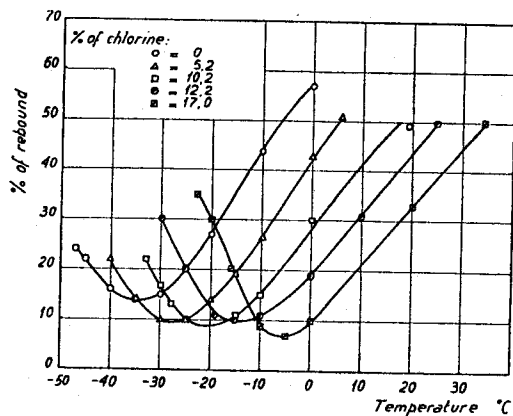


Fig. 48.—Rebound vs. temperature curves of a chlorinated ethylene-propylene copolymer with different chlorine contents.

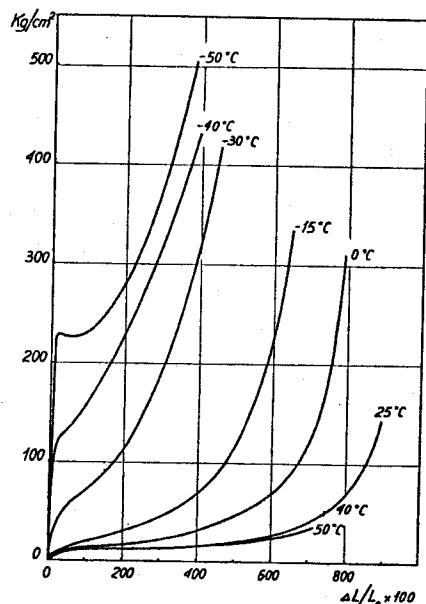


Fig. 49.—Stress-strain curves of a chlorinated (8.5 chlorine by weight) and vulcanized ethylene-propylene copolymer.

during the thermal cycle of vulcanization. Since dehydrochlorination is only partial, in order to obtain a complete state of cure, it is necessary to start from copolymers containing more than 5–8% of chlorine by weight.

Considering the mechanical properties of the chlorinated copolymers, vulcanized in the absence of reinforcing fillers, it can be noted how in some cases, it is possible to obtain high tensile strengths with low initial elastic moduli. Figure 49 shows the stress-strain curves at different temperatures of a chlorinated (8.5% by weight)

and vulcanized ethylene-propylene copolymer; as may be observed, properties are greatly affected by temperature.

In general these chlorinated copolymers vulcanize well with recipes based on sulfur and accelerators of the rapid type; the presence of zinc oxide is strictly necessary for the vulcanization. The reinforcing fillers (carbon blacks, etc.) act as with other elastomers. In order to obtain a vulcanizate with good resistance to aging, magnesium oxide and epoxidic resins should be added. Analogous results can be obtained in the case of brominated ethylene-propylene copolymers. It is interesting to point out that copolymers containing a low mole percentage of bromine, can still give good vulcanizates, contrary to what happens for chlorinated copolymers.

Moreover, brominated copolymers tend to vulcanize also in the presence of only zinc oxide and in the presence of diamines<sup>70</sup>.

When using chlorinated copolymers with low chlorine content (below 3% by weight) it is necessary to subject the product to a previous dehydrochlorination, which can be affected at high temperature<sup>71</sup>. Thus an almost completely dehydrochlorinated copolymer can be obtained, which can be considered as an ethylene-propylene copolymer containing unsaturation. Table XLIV shows the properties of the vulcanizates obtained from a chlorinated ethylene-propylene copolymer (having about 2% chlorine by weight) vs. the dehydrochlorination time at 200° C. As shown from these data, with the increase of the dehydrochlorination time, the degree of crosslinking increases progressively (increase of the 300% modulus and decrease of swelling) as a function of the increase of the degree of unsaturation of the copolymer.

*H. Crosslinking of ethylene-propylene copolymers with the use of chlorinated compounds.*—A vulcanization method that shows some analogies with that of the chlorinated copolymers is based on the use of low-molecular-weight substances with high chlorine content<sup>64</sup>.

These compounds are mixed with the copolymer, together with zinc oxide, sulfur and other ingredients (apart from fillers), and after curing they yield vulcanizates having fairly good properties. Among the chlorinated compounds used, we mention trichloromethanesulfonylchloride, trichloromelamine, quinone-N-

TABLE XLIV  
PHYSICAL PROPERTIES OF VULCANIZATES OBTAINED FROM A COPOLYMER  
HAVING 2% BY WEIGHT OF CHLORINE, WITH DIFFERENT  
DEHYDROCHLORINATION TIMES

Dehydrochlorination time at 180° C, hours	Tensile strength, kg/cm <sup>2</sup>	Elongation at break, %	300% modulus, kg/cm <sup>2</sup>	Swelling ratio, benzene, 30° C
1	128	975	14	4.40
5	135	900	15	4.10
9	54	720	17	4.00
15	102	810	16	3.96
24	78	750	17	3.86
48	89	715	21	3.72
72	93	725	20	3.70
96	78	670	19	3.67

Recipe:	Amount	Notes
Chlorinated polymer	100	} dehydrochlorination mixture
Zinc oxide	10	
Magnesium oxide	10	
Stearic acid	2	
Sulfur	2	
Tetramethylthiuramdisulfide	2	
2-Mercaptobenzothiazole	1	
Vulcanization	30 min/160° C	



chlorimide, octachloropropane, octachlorocyclopentene, etc. The presence of metal oxide is strictly necessary for the vulcanization; moreover some oils, such as tall oil, affect the final properties of the vulcanizates favorably. Vulcanization can be carried out at temperatures generally ranging from 140° to 170° C; the effect of temperature on the properties of the vulcanizate varies depending on the type of chlorinated compound used. By this type of vulcanization, considerable amounts of oils can be added, without much worsening of tensile strength; moreover this type of crosslinking is applied with analogous results to the vulcanization of polypropylene and of polyisobutene.

*I. Crosslinking of ethylene-propylene copolymers containing unsaturation.*—The introduction of a limited amount of unsaturation along the chain of the ethylene-propylene copolymers makes these elastomers vulcanizable by the traditional systems used in the rubber industry.

As previously described, a limited amount of unsaturation can be obtained along the chain of the ethylene-propylene copolymer by means of a limited chlorination, followed by an almost complete dehydrochlorination. Thus an elastomer is obtained that can be vulcanized by the traditional systems based on sulfur and accelerators.

However, the most interesting case of elastomers that prevalingly consist of ethylene and propylene and contain unsaturation, is undoubtedly that of terpolymers; these, beside ethylene and propylene, also contain a limited number of other monomeric units, having one or more reactive functions, able to give crosslinking reactions with sulfur and accelerators under the usual vulcanization conditions<sup>72,73</sup>.

Even though the number of double bonds present along the polymeric chains can be regulated over a wide range, according to the various synthesis conditions, it is usually preferred, for their use as elastomers, to limit this content to a maximum of 3-4 double bonds per 100 monomeric units of the chain. As in the production of ethylene-propylene copolymers, the ratio between ethylene and propylene and the average molecular weight, can be regulated during the production by proper selection of synthesis conditions<sup>74</sup>.

Since the macromolecules contain a limited number of units of a third monomer, beside ethylene and propylene, these elastomers generally have the same properties as the ethylene-propylene copolymers; in particular, density, permeability to gases and vapors, and the elastic properties are practically unchanged. Their viscoelastic properties are very similar to those of the ethylene-propylene copolymer when the ratio of ethylene to propylene and the average molecular weight are the same, and when the distribution of the molecular weight is analogous.

Different compounds have been proposed as the third monomer to be used in copolymerization with ethylene and propylene; it is important that such compounds must be able to copolymerize homogeneously with the two other monomers, so as not to damage the elastomeric properties of the ethylene-propylene copolymers and to guarantee a homogeneous, random distribution along the macromolecules<sup>77</sup>.

Among the various hydrocarbon monomers containing more than one double bond suitable to be copolymerized with ethylene and propylene, different types can be mentioned: aliphatic or straight chain conjugated and unconjugated dienes, dienes belonging to the class of endomethylenic compounds, and cyclic polyenes<sup>73,75</sup>. In Table XLV are summarized some monomers suitable for this terpolymerization. The synthesis conditions of the various terpolymers do not differ markedly from those of the simple copolymers; both choice and control of such conditions depend on the type of third monomer chosen, so that a statistically homogeneous distribution in all macromolecules is secured. Only in this case, it is possible to obtain good mechanical and dynamic properties in the vulcanized product.

TABLE XLV

## MONOMERS SUITABLE FOR TERPOLYMERIZATION WITH ETHYLENE AND PROPYLENE

Aliphatic dienes		Endomethylenic	Cyclic polyenes
Conjugated	Unconjugated		
butadiene	pentadiene 1-4	dicyclopentadiene	cyclo-octadiene 1-5
isoprene	2-methylpentadiene 1-4	norbornadiene	
	hexadiene 1-5	methylenenorbornene	
	hexadiene 1-4		
	2-methylhexadiene 1-5 etc.		

Vulcanization of these elastomers may be conveniently carried out by taking advantage of the reactivity of the double bonds present along the chains. Crosslinking is generally affected by means of mixes based on sulfur and accelerators, in the presence of zinc oxide as activator. The accelerators usually employed are of the "ultrapid" type, alone or possibly in combination with secondary accelerators.

With the ethylene-propylene terpolymers the presence in the mixes of zinc oxide proves very convenient to obtain a good vulcanization; in general at least three parts of zinc oxide per 100 parts of rubber is required in order to obtain good mechanical properties in the vulcanizates and to prevent a rapid reversion reaction<sup>73,74</sup>. The presence of stearic acid, on the contrary, is not essential to a good vulcanization; however, addition to the mix of small amounts of this ingredient improves processability and dispersion of the fillers especially when high loadings of oil and carbon black are used.

Other vulcanizing systems can be applied with terpolymers or at least with some types. Among these last, mention can be made of the quinoid system (use of *p-p'* dibenzoylquinone dioxime with red lead (Pb<sub>2</sub>O<sub>4</sub>) with and without sulfur), the resin cure system (use of a halo-methyl-methylolphenol with a metal-chloride catalyst). Also vulcanization with organic peroxides (normally used for the saturated ethylene-propylene copolymers) can be successfully applied to terpolymers, thus obtaining vulcanizates with low compression set and good resistance to aging and heat.

Vulcanization conditions (temperature and time) chiefly depend on the type of mix used. The final properties of the vulcanized product not only depend on the recipe used, but also on the properties of the starting terpolymer (double bond content, Mooney viscosity).

The vulcanization rate, considered as time necessary to reach the highest degree of crosslinking (expressed as the highest value of the 300% modulus and the lowest value of the elongation at break) depends not only on the type of mix but also on the type of unsaturation present along the chains of the elastomer. On comparing, for instance, the rate of vulcanization of terpolymers containing dicyclopentadiene, with the curing rates of terpolymers containing cyclo-octadiene, of butyl rubber, of ethylene-propylene copolymers vulcanized with organic peroxides (dicumyl peroxide), one obtains the curves of Figures 50 and 51. The time required to reach a plateau in the 300% modulus curves, is different for different kinds of unsaturation, for this type of compound. This behavior is quite independent, at least within certain limits, of the double bond content and of the Mooney viscosity of the starting terpolymer<sup>75</sup>.

At higher temperatures (160°-170° C) for long vulcanization times using the compounds reported in the figures, a slight reversion is noticed for cyclo-octadiene terpolymers, whereas no reversion takes place for the dicyclopentadiene terpolymer.

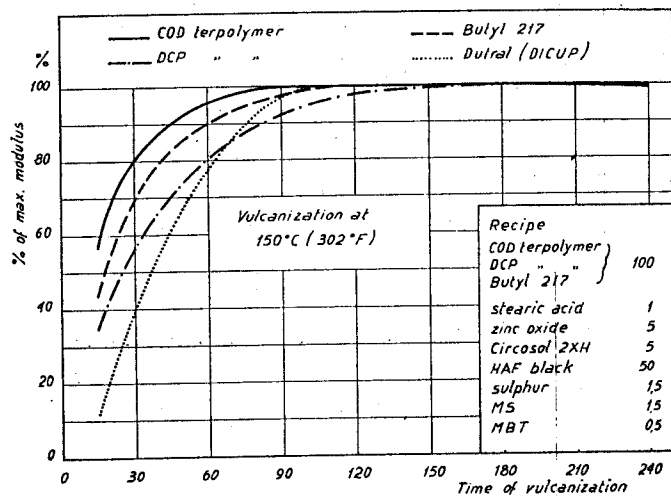


Fig. 50.—Vulcanization rate (at 150° C) of different rubbers.

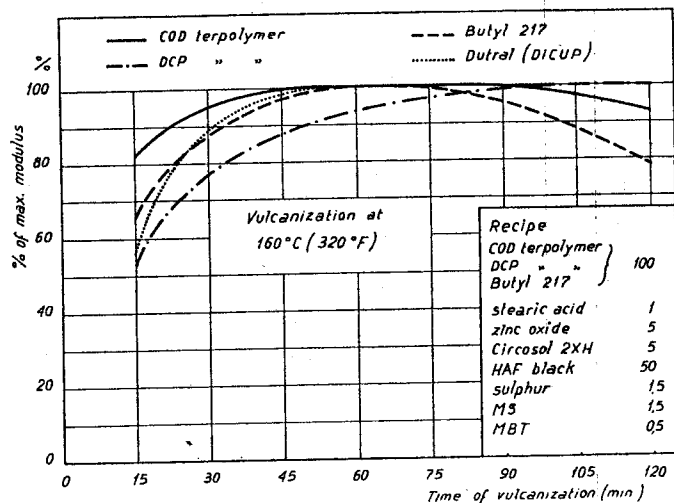


Fig. 51.—Vulcanization rate (at 160° C) of different rubbers.

Of course with terpolymers, type and amount of ingredients in the recipe may be varied within wide limits so that vulcanizates meeting the different requirements desired in the finished product are obtained.

Mechanical and elastic properties of the vulcanizates are affected by the characteristics of the starting terpolymers, the principal parameters being ethylene to propylene ratio, unsaturation content and average molecular weight.

The ethylene content does not appear to affect appreciably the mechanical properties of the vulcanizates; however, by increasing the ethylene content, the low temperature properties may be considerably improved as in the case of ethylene-propylene copolymers.

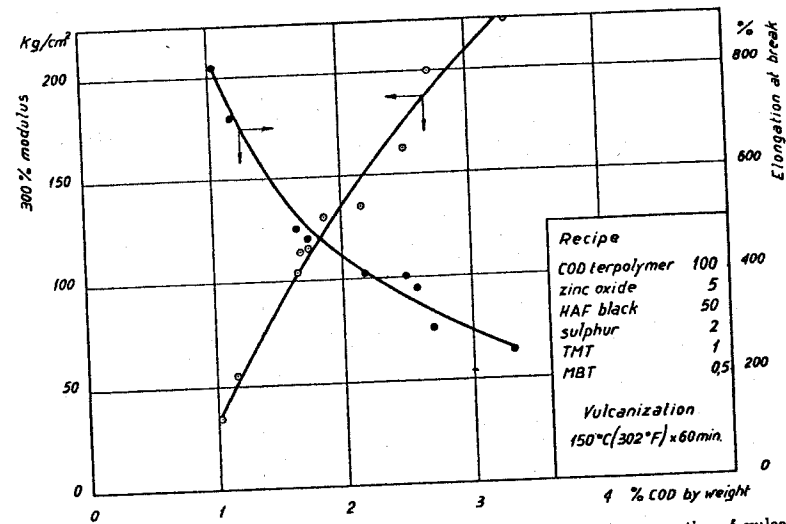


Fig. 52.—Effect of amount of unsaturation (cyclo-octadiene by weight) on the properties of vulcanizates.

The percentage of unsaturation in the crude terpolymer has a very marked effect on the properties of the vulcanizates; in Figure 52 the values relating to 300% modulus and elongation at break are reported as a function of unsaturation content in the case of cyclo-octadiene terpolymers. In Table XLVI the main mechanical characteristics of vulcanized terpolymers containing various amounts of non-conjugated aliphatic dienes are given. It can be seen that with relatively high double bond content, vulcanizates having a high degree of crosslinking (values of 300% modulus) are obtained; this permits the use of these elastomers with a lower level of curatives or the addition of considerable amounts of plasticizing oils.

The properties of the vulcanizates are also affected by the average molecular weight of the crude terpolymer; such parameters can be evaluated from the Mooney viscosity measurements. An increase in the Mooney viscosity exerts initially a strong effect on the properties of the vulcanizate, whereas above a certain value, the effect becomes weaker. High molecular weight terpolymers (Mooney viscosity at 100° C, ML 1 + 4 above 80) having a sufficiently high unsaturation, are usually extended with considerable amounts of common petroleum oils (e.g., Necton 60, Circosol 2XH, Circo-light, etc.).

The vulcanizates obtained from these terpolymers in the absence of reinforcing fillers, show low tensile strength. Therefore, in order to use them in practice, it is advantageous to add reinforcing fillers such as carbon black of various types, finely dispersed silica, etc. Table XLVII shows the main mechanical properties of terpolymers containing cyclo-octadiene, vulcanized in the presence of various types of carbon black.

It is also possible to add other types of fillers (clay, whiting, etc.) to the compound, to obtain effects comparable with those occurring for the other hydrocarbon elastomers. Improvement in processing and vulcanizate properties (modulus, resilience, electrical properties) results for these mineral fillers from high temperature treatment, especially in the presence of promoters.

The possibility of extending the various terpolymers with oils is very interesting from the commercial point of view. These elastomers are in general compatible

TABLE XLVI  
PROPERTIES OF TERPOLYMERS VULCANIZED IN THE PRESENCE OF REINFORCING FILLERS

Properties of raw polymers		Properties of vulcanizates				
Double bond content, %	Intrinsic viscosity	Mooney viscosity ML 1 + 4	Tensile strength, kg/cm <sup>2</sup>	Elongation at break, %	Modulus at 300%, kg/cm <sup>2</sup>	Resilience
						at 20° C
0.65	2.06	70	175	590	47	55
1.25	1.96	66	240	620	71	53
1.45	1.63	—	224	530	89	45
1.8	1.74	51	230	430	120	54
2.2	1.55	22	196	440	121	60
2.2	1.62	35	227	400	154	43
2.8	1.80	54	191	280	—	54
						at 90° C
						56
						56
						54
						60
						53
						60
						64

Recipe:	2 phr
Zinc oxide	Sulfur
Steric acid	TMT
Antioxidant (PBNA)	MBT
	HAF black
	50

Vulcanization, 30 min/150° C

TABLE XLVII  
EFFECT OF VARIOUS TYPES OF CARBON BLACK

Carbon black type	quantity	Tensile strength, kg/cm <sup>2</sup>	Elongation at break, %	Modulus at 300% kg/cm <sup>2</sup>	Hardness, I.H.R.D.	Resilience, %
HAF	50	197	440	132	75	54
ISAF	50	236	460	136	75	52
MPC	50	240	640	80	73	53
SRF	80	117	320	112	78	57
FEF	70	180	300	180	82	48
MT	100	69	360	62	75	63

Recipe:  
 Terpolymer 100 (ML 1 + 4 at 100° C = 52, COD 3, 1% by weight)  
 Black as shown  
 Circosol 2XH 5  
 Sulfur 2  
 MBT 0.5  
 TMTD 1  
 ZnO 5

with oils of different types; oils can be added in large amounts, without damaging to any considerable extent their end-use properties. It is possible to obtain rather high tensile strength with 70-80 parts of oil for 100 parts of terpolymer; the characteristics of vulcanizates are more satisfactory with paraffinic and naphthenic oils<sup>73,75</sup>.

In Figure 53 are shown the mechanical characteristics of vulcanizates obtained from a terpolymer containing cyclo-octadiene extended with an oil of naphthenic type; the ingredients and the filler are calculated on the sum, terpolymer + oil. Also with terpolymer to oil ratio of 1:1, tensile strengths of about 160 kg/cm<sup>2</sup> can be obtained with sufficiently high moduli and hardness and with good values for the elongation at break.

The properties of vulcanized terpolymers are quite similar to those of the saturated copolymer; this is also valid for the aging resistance of these rubbers. In fact the unsaturation that permits the vulcanization with sulfur and accelerators, are

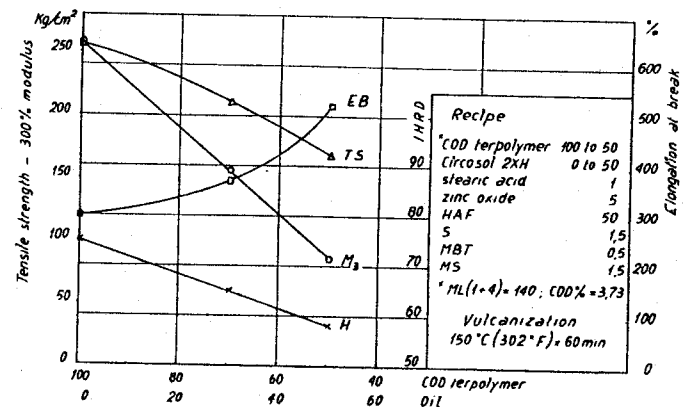


FIG. 53.—Properties of vulcanizates obtained from terpolymer with various amounts of oil.

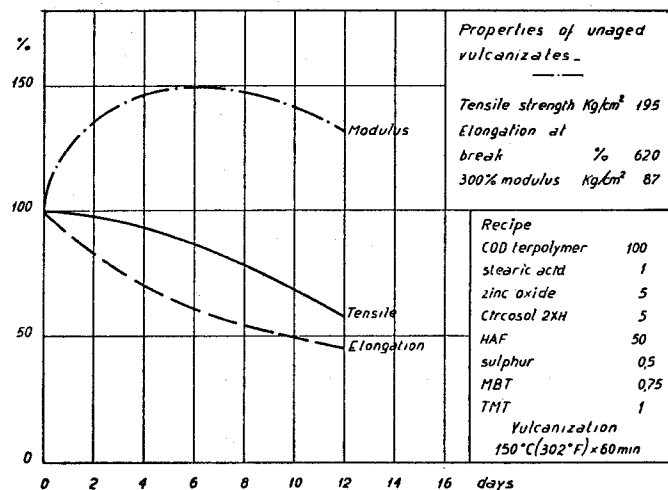


Fig. 54.—Aging properties (air circulating oven at  $150^\circ\text{C}$ ) for terpolymers.

not normally contained in the main chains. Therefore their resistance to degradation agents (oxygen, ozone, chemicals) is practically the same as that of ethylene-propylene copolymers<sup>73,75</sup>.

In Figure 54 the percentage variation of the main mechanical characteristics of vulcanized terpolymers containing cyclo-octadiene are given vs. the time of aging carried out in an air oven at  $150^\circ\text{C}$ . It can be seen that after a long period of aging, the vulcanizates still show satisfactory properties.

In conclusion it can be said that the terpolymers based on ethylene and propylene are elastomers which present an excellent balance of good mechanical and dynamic properties coupled with a high resistance to degrading agents.

The use of terpolymers in the rubber industry is very advantageous, if one keeps in mind the following factors:

- 1) Low specific gravity (about  $0.86\text{ kg/cm}^3$ ).
- 2) Possibility of extension with considerable amount of oil.
- 3) Excellent resistance to degradation.

## XVI. PROPERTIES OF VULCANIZATES AND THEIR APPLICATIONS

The elastomers, essentially consisting of ethylene and propylene, either in the form of copolymer or in the form of terpolymer, constitute a new class of general purpose rubbers. The final properties of the vulcanizates are in general practically independent of the vulcanization system, but are essentially related to the nature of the macromolecules of these elastomers.

In summarizing the special features of these rubbers, one must remember:

- Low specific gravity ( $0.86\text{--}0.87\text{ g/cm}^3$ )
- Excellent resistance to oxidation, heat, and chemicals
- Good electrical properties
- Exceptionally low brittle point
- Good resistance to polar liquids
- Low permeability to water vapor

The ethylene-propylene rubbers can be applied in a variety of ways for the production of many technical items. The projected uses include mechanical and automotive molded and extruded goods, shoe soles and heels, flooring, conveyor belts, hose, gaskets, special coatings and coverings, wire insulation and jacketing, foams, etc. The good electrical properties and resistance to ozone make them an ideal material for the insulation of high and low tension electric cables<sup>76,77</sup>.

The mechanical and dynamic properties of EPR are sufficiently good for their application in the field of tires; also the abrasion resistance is excellent. It is quite certain that in a few years these rubbers will also be used for tires.

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