POLYOLEFIN ELASTOMERS

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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 copolymerize, performed by extraction with boiling solvents, with increased 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.

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 examination of the various fractions. The ethylene–propylene copolymerizes 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 of composition is determined by only one polyolefin is present, Table I, with its behavior shown by the products obtained from the polymerization of suitable ethylene–propylene mixtures, with the aid of catalysts prepared from vanadium tetrachloride and triethylaluminum, it appears clear that the polymerization the middle products yield only ethylene–propylene copolymer.

In fact, polyethylene obtained from ethylene alone under the same polymerization conditions used for the synthesis of the copolymer, is not extractable with the above mentioned solvents. Also propylene, obtained from only propylene, under the same polymerization conditions, contains a fraction that is less as a result after n-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 copolymers 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 μ, bands can clearly observed, which can be attributed to the presence of sequences of methylene groups of different length.

More precisely, it is possible to observe bands due to (—CH₂—), groupings where n can be either higher than or equal to 2, and lower than 5, and the bar corresponding to n ≥ 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 methylene 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 μ, resulting from double bonds of the vinylidene type can be easily observed. It 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 vinylidene double bond, in analogy with what is observed in the homopolymerization of propylene.
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 Al(C,H₅)₃ and VOCl₃; mole Al(C₆H₅)₃/mole VOCl₃ = 3; T = 25°C; P = 1 at.; solvent: n-heptane, cm³/400.

<table>
<thead>
<tr>
<th>Product</th>
<th>Acetone extract</th>
<th>Ether extract</th>
<th>n-hexane extract</th>
<th>n-heptane extract</th>
<th>residue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>[η]</td>
<td>%</td>
<td>[η]</td>
<td>%</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.00</td>
<td>1.60</td>
<td>0.82</td>
<td>35</td>
<td>2.21</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>0.65</td>
<td>2.20</td>
<td>6.30</td>
<td>0.80</td>
<td>0.45</td>
</tr>
<tr>
<td>Ethylene-propylene copolymer</td>
<td>0.20</td>
<td>3.10</td>
<td>3.00</td>
<td>0.40</td>
<td>0.35</td>
</tr>
<tr>
<td>(51 mole ethylene %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene-propylene copolymer</td>
<td>0.60</td>
<td>2.74</td>
<td>7.00</td>
<td>1.30</td>
<td>0.20</td>
</tr>
<tr>
<td>(49 mole ethylene %)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethylene-propylene copolymer</td>
<td>0.20</td>
<td>2.50</td>
<td>5.50</td>
<td>1.00</td>
<td>0.10</td>
</tr>
<tr>
<td>(52 mole ethylene %)</td>
<td></td>
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</tr>
</tbody>
</table>
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.
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%.

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%². Moreover, crystallinity from polyethylene is usually absent in the n-heptane extractable fractions, Table I and Figure 4.

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 methylene groups having a length of at least about 40-50 / (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 isopropylene 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 TiCl₄ and triethylalumium) 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
III. ANALYTICAL METHODS FOR DETERMINATION OF THE COMPOSITION OF COPOYMERS

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

A. Radiochemical.—By copolymerizing propylene with C\(^4\)-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\(^4\)CO\(_4\), following the procedure proposed by Cox and Warne\(^4\), 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\(^4\). 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 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\(^4\), 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 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 sq cm for computation.

A Geiger counter equipped with a thin micro window of about 1.8 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\(^4\).

B. Analysis by infrared spectroscopy. 1. General method.—When dealing with the problem of the analysis of the ethylene-propylene copolymers by infrared spectroscopy, 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 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 μ. 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. 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 composi-
tion of the copolymer which was determined by other methods.

The band at 8.60 μ 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 μ 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 μ 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 μ is
read with respect to a base line drawn between 8 and 9 μ.

![Fig. 8. Dependence of the ratio between the optical densities at 8.60 and 2.32μ on the propylene content of an ethylene-propylene copolymer. ⊿ Propylene content determined by IR spectroscopy in solution. Δ Ethylene content determined radiochemically.](image)

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

2. Other infrared spectroscopy methods.—According to the method proposed
by Gössl, the sample when not completely soluble in the organic solvents, is ex-
named as a film, using the ratio

\[ R = \frac{E 13.9 \mu}{E 8.6 \mu} \]

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

The method proposed by Wei uses the ratio

\[ R' = \frac{E 8.7 \mu}{E 13.9 \mu} \]

between the extinction coefficients at 8.7 and 13.9 μ. 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 μ
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 pres-
ence of ethylene homopolymers and of long crystalline polyethylene 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 methylene sequences present in the copolymers. It has been exhaustively demonstrated how this band, attributed to the rocking motion of the methylene groups, can be separated into various components attributable to the various lengths of the methylene sequences.

It follows that the measurement of the optical density at 13.85–13.9 μ considers chiefly the long sequences of methylene 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 methylene sequences prevail over the short sequences, the optical density of the band at 13.9 μ is faintly proportional to the total content of ethylene 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 μ) the dependence of the optical density at 13.9 μ on the ethylene units is no longer linear. Consequently, the resulting measurement is less accurate, and is also affected by possible variations in the distribution of the methylene 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 spectroscopy of pyrolysis products.—Bua and Manaresi set up an analytical method based on the pyrolysis of ethylene-propylene copolymers and subsequent analysis of the products thus obtained by mass spectroscopy. 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 methylene 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.

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.

POLYOLEFIN ELASTOMERS

In fact, except for the case of the azeotropic-type copolymerizations, 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 had 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

<table>
<thead>
<tr>
<th>Composition of Ethylene-Propylene Copolymers Prepared with Different Polymerization Times</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst prepared from Al(C₂H₅)₃ and VOCl₂; mole Al(C₂H₅)₃/mole VOCl₂ = 3;</td>
<td>T = 25°C, P = 1 at; solvent: n-heptane, cm³ 400</td>
<td></td>
</tr>
<tr>
<td>Mole propylene/mole ethylene in the gaseous mixture</td>
<td>Polymerization time, min</td>
<td>Mole-% ethylene in the copolymer</td>
</tr>
<tr>
<td>6.02</td>
<td>5</td>
<td>40.26</td>
</tr>
<tr>
<td>6.02</td>
<td>10</td>
<td>40.93</td>
</tr>
<tr>
<td>4.55</td>
<td>5</td>
<td>45.98</td>
</tr>
<tr>
<td>4.55</td>
<td>10</td>
<td>45.98</td>
</tr>
<tr>
<td>3.74</td>
<td>5</td>
<td>48.95</td>
</tr>
<tr>
<td>3.74</td>
<td>10</td>
<td>49.25</td>
</tr>
<tr>
<td>2.85</td>
<td>2</td>
<td>57.6</td>
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<tr>
<td>2.85</td>
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<td>58.0</td>
</tr>
<tr>
<td>2.85</td>
<td>10</td>
<td>57.8</td>
</tr>
</tbody>
</table>
TABLE III

Composition of Ethylene-Propylene Copolymers Preparwed with Different Polymerization Times

<table>
<thead>
<tr>
<th>Mole of propylene/mole of ethylene in the gaseous mixture</th>
<th>Polymerization time,</th>
<th>Mole-% of ethylene in the copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1</td>
<td>35.0</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>35.0</td>
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<td>3</td>
<td>45.0</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>45.0</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>45.0</td>
</tr>
</tbody>
</table>

* The abbreviations used for triacetyleacetone are Ac 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, see Tables II and III. For a number of catalytic systems prepared from hydrocarbonsoluble vanadium compounds [e.g., Al(C₅H₅)₂Cl + VCl₄; Al(C₅H₅)₂Cl + VCl₄; Al(C₅H₅)Cl + VAc₃], the catalyst activity, and consequently the copolymerization rate, decreases with time. This activity can be kept constant if the polymerization is carried out for a certain period at a temperature higher than that of use; for instance, in the case of the catalytic system obtained from Al(C₅H₅)₃ + VCl₄, if the catalyst is aged for 30 minutes at 60°C, then at 25°C it shows a constant activity in time.

For some catalytic systems [e.g., Al(C₅H₅)₂Cl + VCl₄; Al(C₅H₅)₂Cl + VAc₃] the loss of activity with time is noticeably reduced by lowering the copolymerization temperature.

2. Aging of the catalyst.—Other factors being the same, the composition of the copolymer is independent of the time elapsed between the preparation of the catalyst and its use (time of aging of the catalyst), see, e.g., Tables IV and V.

TABLE IV

Composition of Ethylene-Propylene Copolymers Obtained with Differently Aged Catalysts

<table>
<thead>
<tr>
<th>Mole of propylene/mole of ethylene in the gaseous mixture</th>
<th>Aging time of catalyst, min</th>
<th>Mole-% of ethylene in the copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.02</td>
<td>11</td>
<td>40.93</td>
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<tr>
<td>6.02</td>
<td>15</td>
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<td>40.93</td>
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<tr>
<td>2.17</td>
<td>31</td>
<td>62.10</td>
</tr>
</tbody>
</table>

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 Al(C₅H₅)₃ + VCl₄, kept for 30 minutes at 60°C, and then aged for different times at 25°C], see Figure 10.

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, 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.
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, as 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, see, e.g., Tables VII 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., VCl₅, TiCl₅), on the contrary, its effect is marked when the catalysts used are obtained from hydrocarbon soluble transition metal compounds (e.g., VA₅, VCl₅, VOCl₅), see Figure 12, and in the case of the Al(C₆H₅)₃ + VCl₅ catalytic system, the catalytic activity is highest when the molar ratio of Al(C₆H₅)₃ to VCl₅ is near 2.5, see Figure 12, and in the case of the Al(C₆H₅)₃Cl + VA₅ catalytic system employed at 25°C when the ratio of Al(C₆H₅)₃Cl to VA₅ is near 3.5, see Table X. If the latter catalytic system is used.

![Graph](image-url)

**Table VI**

<table>
<thead>
<tr>
<th>Mole propylene/mole ethylene in the gaseous mixture</th>
<th>Catalyst concentration Al(C₆H₅)₃/liter</th>
<th>Mole-% ethylene in the copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.02</td>
<td>0.0045</td>
<td>40.25</td>
</tr>
<tr>
<td>6.02</td>
<td>0.0067</td>
<td>38.90</td>
</tr>
<tr>
<td>4.55</td>
<td>0.0033</td>
<td>45.98</td>
</tr>
<tr>
<td>4.55</td>
<td>0.0045</td>
<td>45.98</td>
</tr>
<tr>
<td>3.74</td>
<td>0.0045</td>
<td>49.00</td>
</tr>
<tr>
<td>3.74</td>
<td>0.0112</td>
<td>49.25</td>
</tr>
<tr>
<td>2.17</td>
<td>0.00225</td>
<td>62.10</td>
</tr>
<tr>
<td>2.17</td>
<td>0.0033</td>
<td>62.10</td>
</tr>
</tbody>
</table>

**Table VII**

<table>
<thead>
<tr>
<th>Mole propylene/mole ethylene in the gaseous mixture</th>
<th>VA₅</th>
<th>Mole-% ethylene in the copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.125</td>
<td>36.0</td>
</tr>
<tr>
<td>6</td>
<td>0.250</td>
<td>34.0</td>
</tr>
<tr>
<td>6</td>
<td>0.500</td>
<td>33.5</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>43.5</td>
</tr>
<tr>
<td>4</td>
<td>0.250</td>
<td>44.5</td>
</tr>
<tr>
<td>2</td>
<td>0.125</td>
<td>59.0</td>
</tr>
<tr>
<td>2</td>
<td>0.250</td>
<td>58.5</td>
</tr>
</tbody>
</table>

**Table VIII**

<table>
<thead>
<tr>
<th>Mole propylene/mole ethylene in the gaseous mixture</th>
<th>Mole Al(C₆H₅)₃/mole VOCl₅</th>
<th>Mole-% ethylene in the copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.93</td>
<td>8</td>
<td>43.0</td>
</tr>
<tr>
<td>4.93</td>
<td>3</td>
<td>43.6</td>
</tr>
<tr>
<td>4.93</td>
<td>2</td>
<td>42.0</td>
</tr>
<tr>
<td>5.28</td>
<td>5</td>
<td>41.5</td>
</tr>
<tr>
<td>5.28</td>
<td>3</td>
<td>41.8</td>
</tr>
</tbody>
</table>

**Table IX**

<table>
<thead>
<tr>
<th>Mole propylene/mole ethylene in the gaseous mixture</th>
<th>Mole Al(C₆H₅)₃/mole VA₅</th>
<th>Mole-% ethylene in the copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>4</td>
<td>43.5</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>44.5</td>
</tr>
<tr>
<td>4</td>
<td>6.33</td>
<td>42.5</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>43.5</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>45.5</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>42.5</td>
</tr>
</tbody>
</table>
Table X

Dependence of Copolymerization Yield on Al(C₂H₅)₃Cl/V
Triacetylacetone Molar Ratio

Catalyst prepared from 0.5 g VAc; aging time = 1 minute; T = 25°C; P = 1 atm; solvent: α-Heptane, cm³ 350; moles propylene/mole ethylene in gaseous mixture = 4; polymerization time: 18 minutes

<table>
<thead>
<tr>
<th>Mole Al(C₂H₅)₃Cl/mole VAc</th>
<th>Copolymer, g</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.1</td>
</tr>
<tr>
<td>2.5</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>3.5</td>
</tr>
<tr>
<td>3.25</td>
<td>3.5</td>
</tr>
<tr>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>2.9</td>
</tr>
<tr>
<td>5</td>
<td>1.6</td>
</tr>
<tr>
<td>6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

at −20°C, the catalytic activity increases rapidly with increase of the molar ratio of Al(C₂H₅)₃Cl/VAc 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.

![Graph](image1)

Fig. 12.—Dependence of catalyst activity on molar ratio Al(C₂H₅)₃Cl/VCl₃. Polymerization temperature = 25°C; P = 1 atm; solvent: α-Heptane, cm³ 410; mole C₃H₆/mole C₃H₄ in gaseous mixture = 2. © V: 0.0449 g; polymerization time 5 minutes; ○ V: 0.0296 g; polymerization time 10 minutes.

Fig. 13.—Dependence of catalyst activity on molar ratio Al(C₂H₅)₃Cl/VAc. Catalyst prepared and aged for 5 minutes at −20°C. Polymerization temperature: −20°C; P = 1 atm; solvent: α-Heptane, cm³ 350; mole C₃H₆/mole C₃H₄ in gaseous mixture = 4; polymerization time = 5 minutes.

Table XI

Independence of Ethylene–Propylene Copolymer Composition of Partial Pressure of Monomers

Catalyst prepared at −20°C in 30 cm³ toluene; aging time of catalyst: 5 minutes; moles Al(C₂H₅)₃Cl/mole VAc = 5; T = −20°C; P = 1 atm; solvent: α-Heptane, cm³ 350; moles C₄H₁₀/mole C₃H₄ in gaseous mixture = 4.

<table>
<thead>
<tr>
<th>Mole N₄/mole C₄H₁₀ + mole C₃H₄</th>
<th>Mole-% ethylene in copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>43.5</td>
</tr>
<tr>
<td>0.38</td>
<td>44.5</td>
</tr>
<tr>
<td>0.38</td>
<td>43.5</td>
</tr>
<tr>
<td>0.93</td>
<td>43.5</td>
</tr>
<tr>
<td>2.12</td>
<td>43.0</td>
</tr>
<tr>
<td>2.12</td>
<td>42.5</td>
</tr>
</tbody>
</table>

Table XII

Independence of Composition of Ethylene–Propylene Copolymers of Partial Pressure of Monomers

Catalyst prepared from Al(C₂H₅)₃Cl and VCl₃ aged at 60°C for 30 minutes; moles Al(C₂H₅)₃Cl/mole VCl₃ = 2.5; T = 25°C; P = 1 atm; solvent: α-Heptane, cm³ 410; moles propylene/mole ethylene in the gaseous mixture = 2.

<table>
<thead>
<tr>
<th>Mole N₂/mole (C₃H₆ + mole C₃H₄) in the gaseous mixture</th>
<th>Mole-% ethylene in the copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>50.5</td>
</tr>
<tr>
<td>0.62</td>
<td>49.8</td>
</tr>
<tr>
<td>0.98</td>
<td>51.7</td>
</tr>
<tr>
<td>1.54</td>
<td>51.0</td>
</tr>
<tr>
<td>2</td>
<td>50.8</td>
</tr>
</tbody>
</table>

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 Al(C₂H₅)₃ and VCl₃, T = 25°C; P = 1 atm; solvent: n-heptane, cm²/400; moles Al(C₂H₅)₃/mole VCl₃ = 3.

<table>
<thead>
<tr>
<th>Mole C₃H₆/mole C₃H₃ in gaseous mixture</th>
<th>C₃H₆ mole %</th>
<th>C₃H₃ mole %</th>
<th>Catalyst concentration mole Al(C₂H₅)₃/liter</th>
<th>Polymerization time, min</th>
<th>Mole-% ethylene in the copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.50</td>
<td>95.0</td>
<td>4.6</td>
<td>0.0045</td>
<td>10</td>
<td>10.5</td>
</tr>
<tr>
<td>5.10</td>
<td>83.2</td>
<td>16.3</td>
<td>0.00225</td>
<td>10</td>
<td>30.5</td>
</tr>
<tr>
<td>5.10</td>
<td>83.2</td>
<td>16.3</td>
<td>0.00225</td>
<td>10</td>
<td>32.0</td>
</tr>
<tr>
<td>4.08</td>
<td>79.9</td>
<td>19.1</td>
<td>0.00337</td>
<td>10</td>
<td>33.8</td>
</tr>
<tr>
<td>4.06</td>
<td>79.9</td>
<td>19.1</td>
<td>0.0045</td>
<td>10</td>
<td>34.5</td>
</tr>
<tr>
<td>2.12</td>
<td>67.7</td>
<td>32.0</td>
<td>0.00225</td>
<td>10</td>
<td>50.0</td>
</tr>
<tr>
<td>2.12</td>
<td>67.7</td>
<td>32.0</td>
<td>0.00112</td>
<td>10</td>
<td>50.0</td>
</tr>
<tr>
<td>2.12</td>
<td>67.7</td>
<td>32.0</td>
<td>0.000384</td>
<td>4</td>
<td>50.0</td>
</tr>
<tr>
<td>1.70</td>
<td>62.9</td>
<td>36.9</td>
<td>0.00225</td>
<td>60</td>
<td>55.0</td>
</tr>
<tr>
<td>1.27</td>
<td>55.8</td>
<td>43.9</td>
<td>0.00112</td>
<td>10</td>
<td>58.0</td>
</tr>
<tr>
<td>1.27</td>
<td>55.8</td>
<td>43.9</td>
<td>0.00225</td>
<td>5</td>
<td>60.0</td>
</tr>
<tr>
<td>1.22</td>
<td>54.7</td>
<td>44.8</td>
<td>0.00112</td>
<td>10</td>
<td>62.0</td>
</tr>
<tr>
<td>1.01</td>
<td>49.9</td>
<td>49.5</td>
<td>0.00112</td>
<td>10</td>
<td>66.0</td>
</tr>
<tr>
<td>0.98</td>
<td>49.1</td>
<td>50.3</td>
<td>0.00169</td>
<td>10</td>
<td>64.3</td>
</tr>
<tr>
<td>0.98</td>
<td>49.1</td>
<td>50.3</td>
<td>0.00112</td>
<td>10</td>
<td>67.5</td>
</tr>
<tr>
<td>0.98</td>
<td>49.1</td>
<td>50.3</td>
<td>0.00112</td>
<td>10</td>
<td>66.0</td>
</tr>
<tr>
<td>0.71</td>
<td>41.3</td>
<td>58.2</td>
<td>0.00056</td>
<td>10</td>
<td>70.0</td>
</tr>
<tr>
<td>0.71</td>
<td>41.3</td>
<td>58.2</td>
<td>0.00056</td>
<td>10</td>
<td>70.0</td>
</tr>
<tr>
<td>0.60</td>
<td>40.7</td>
<td>59.3</td>
<td>0.00056</td>
<td>10</td>
<td>72.0</td>
</tr>
<tr>
<td>0.55</td>
<td>35.3</td>
<td>64.2</td>
<td>0.00112</td>
<td>10</td>
<td>77.0</td>
</tr>
</tbody>
</table>

Other factors being the same, and with all the catalytic systems used, the copolymerisation 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 copolymerisation process.

### D. Catalytic systems.

Amorphous ethylene-propylene copolymers can be prepared either in the presence of the catalytic systems that in α-olefin homopolymerization promote the formation of amorphous polymers (e.g., Al(C₂H₅)₃ + VOCl₃, Al(C₂H₅)₃ + VCl₃, Al(C₂H₅)₃Cl + vanadium acetylacetonate, or of those promoting the formation of isotactic polymers (e.g., Al(C₂H₅)₃ + VCl₃, Al(C₂H₅)₃ + TiCl₄).

Less homogeneous products, often containing crystallizable fractions are obtained when operating in the presence of catalysts that, in the homopolymerization of α-olefins, yield mixtures formed of high proportions of macromolecules of different steric composition (e.g., Al(C₂H₅)₃ + TiCl₄).

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 VCl₄, VoCl₃), either a trialkyl aluminum compound or a halogen-containing alkyl aluminum compound can be used for the preparation of the catalyst.
On the contrary, when using a halogen-free vanadium compound (such as vanadium triacetylacetonate, vanadyl triacolohalates), the halogen must be present in the alkyl aluminum compound in order to obtain active catalysts able to promote the ethylene–propylene copolymerization11,21.

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

Fig. 14.—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 copolymers 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 two typical catalytic systems are schematically given in Figures 17 and 18.

E. Reactivity ratios.—Alfrey and Goldfinger22, Mayo and Lewis23 and W5 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:

Reactions

\[
\begin{align*}
M_1^* + M_1 & \rightarrow M_1^* \quad V_{11} = k_{11}[M_1^*][M_1] \\
M_2^* + M_2 & \rightarrow M_2^* \quad V_{12} = k_{12}[M_2^*][M_2] \\
M_1^* + M_3 & \rightarrow M_3^* \quad V_{21} = k_{21}[M_1^*][M_3] \\
M_2^* + M_4 & \rightarrow M_4^* \quad V_{22} = k_{22}[M_2^*][M_4]
\end{align*}
\]

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

\[
\begin{align*}
- \frac{d[M_1]}{dt} &= k_{11}[M_1^*][M_1] + k_{12}[M_2^*][M_1] \\
- \frac{d[M_2]}{dt} &= k_{12}[M_1^*][M_2] + k_{22}[M_2^*][M_2]
\end{align*}
\]

Solvent

- \( n \)-heptane, 400 cm³

Temperature

- 20 °C

Pressure

- 1 atm

Catalyst

- \( V \) triacetylacetonate
- \( Al(C_2H_5)_2Cl \)

Aging time of the catalyst

- 0.35 mmol
- 1.75 mmol
- 5 min
- 4:1

Monomers: propylene/ethylene molar ratio in the gaseous mixture

- 5 min
- 4.9 g

Time

- Product obtained
- Composition (determined by radiochemical methods)

43.5% ethylene in moles

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

Solvent

- \( n \)-heptane, 400 cm³

Temperature

- 25 °C

Pressure

- 1 atm

Catalyst

- \( VCl_3 \)
- \( Al(C_2H_5)_3 \)

Aging time of the catalyst

- 0.2 mmol
- 0.5 mmol
- 5 min
- 2:1

Monomers: propylene/ethylene molar ratio in the gaseous mixture

- 3 min
- 1.3 g

Time

- Product obtained
- Composition (determined by radiochemical methods)

89% ethylene in moles

Fig. 17.—Synthesis of an ethylene–propylene copolymer on a laboratory scale.
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.15,17

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

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(CH$_2$H)$_3$Cl + VAC$_2$), 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 viscosity is

Table XVI

<table>
<thead>
<tr>
<th>Catalyst prepared from triacetylacetone at −20°C; moles Al(CH$_2$H)$_3$C</th>
<th>mole VAC$_2$ = 5; T = −20°C; P = 1 atm; solvent: n-heptane, cm$^3$ 350.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole propylene/mole ethylene in the gaseous mixture</td>
<td>Polymerization time, min</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>4</td>
</tr>
<tr>
<td>6</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>

* Determined in tetrahydroxyphthalalene at 135°C.

Table XVII

| INTRINSIC VISCOSITIES OF ETHYLENE-PROPYLENE COPOLYMERS OBTAINED WITH STABILIZED CATALYSTS AT DIFFERENT POLYMERIZATION TIMES (See Sect. VAI of text) |
|-----------------------------|-----------------------------|
| Catalyst prepared from Al(CH$_2$H)$_3$Cl and VCl$_4$, and aged at 60°C for 30 minute V (g vanadium present in the catalytic system) = 0.0299 g; moles Al(CH$_2$H)$_3$Cl = 2.5; T = 25°C; P = 1 atm; solvent: n-heptane, cm$^3$ 410; moles propylene/mole ethylene in the gaseous mixture = 2. |
| Polymerization time, min | Copolymer yield, g | [η]$^*$ |
| 5 | 2.80 | 4.36 |
| 7 | 3.92 | 4.50 |
| 8 | 4.60 | 4.23 |
| 9 | 4.96 | 4.20 |
| 10 | 5.45 | 4.44 |
| 12 | 6.95 | 4.19 |

* Determined in tetrahydroxyphthalalene 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(C₆H₅)₃ + VCl₃ aged for 30 minutes at 60°C and used at 25°C), the time of copolymerization does not exert a noticeable effect on the intrinsic viscosity, Table XVIII.

3. 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

| Mole C₆H₅Cl/mole C₄H₈ in gas phase | VAc’s, g | Aging time, min | Polymerization time, min | Copolymer, g | Ethylene, mole % in copolymer | | [η] | | |
|---|---|---|---|---|---|---|---|---|
| 6 | 0.125 | 5 | 4 | 3.9 | 36.0 | 3.01 | |
| 6 | 0.250 | 5 | 5 | 5.6 | 34.0 | 2.05 | |
| 6 | 0.500 | 5 | 5 | 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 | 5 | 6.8 | 44.5 | 2.11 | |
| 4 | 0.125 | 15 | 4 | 4.1 | 45.0 | 4.70 | |
| 4 | 0.250 | 15 | 4 | 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 | |

* Determined in tetrahydroxaphthalene at 135°C.

### Table XIX

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>[η]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>VCl₃</td>
<td>0.00127</td>
<td>4</td>
</tr>
<tr>
<td>VCl₃</td>
<td>0.000844</td>
<td>6</td>
</tr>
<tr>
<td>VCl₃</td>
<td>0.000665</td>
<td>8</td>
</tr>
<tr>
<td>VCl₃</td>
<td>0.000375</td>
<td>10</td>
</tr>
</tbody>
</table>

* Determined in tetrahydroxaphthalene at 135°C.

### Table XX

| Effect of the Total Monomer Concentration on the Intrinsic Viscosity of Ethylene-Propylene Copolymers |
|---|---|---|---|---|---|---|---|---|
| Molar ratio Na/(C₆H₅ + C₄H₈) in the gas phase | 0.0001 | 0.001 | 0.01 | 0.1 | 1.0 |
| 0 | 2.40 | |
| 0.62 | 2.53 | |
| 0.98 | 3.37 | |
| 2.00 | 4.19 | |

* Determined in tetrahydroxaphthalene at 135°C.

### Table XXI

| Effect of Propylene/Ethylene Molar Ratio on Intrinsic Viscosity of Ethylene-Propylene Copolymers |
|---|---|---|---|---|---|---|---|---|
| Mole propylene/mole ethylene | 1.00 | 2.00 | 3.00 | 4.00 | 5.00 | 6.00 | 7.00 | 8.00 | 9.00 | 10.00 |
| Copolymer | 2.85 | 3.36 | 3.56 | 4.00 | 4.53 | 5.00 | 5.50 | 6.00 | 6.50 | 7.00 |
| Mole-% ethylene | 25.15 | 31.12 | 29.00 | 25.00 | 25.00 | 25.00 | 25.00 | 25.00 | 25.00 | 25.00 |

* Determined in tetrahydroxaphthalene at 135°C.
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., Al(C_{6}H_{5})_{3}Cl + VACl, or Al(C_{6}H_{5})_{3} + VCl_{4}), aged at 60° C for 30 minutes and used at 25° C, 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., Al(C_{6}H_{5})_{3} + 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 Al(C_{6}H_{5})_{3}Cl + VACl catalyst 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 Al(C_{6}H_{5})_{3}/VCl_{4} Molar Ratio on the Intrinsic Viscosity of Ethylene-Propylene Copolymers**

<table>
<thead>
<tr>
<th>Mole Al(C_{6}H_{5})<em>{3}/mole VCl</em>{4}</th>
<th>( \eta^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3.89</td>
</tr>
<tr>
<td>2.5</td>
<td>3.39</td>
</tr>
<tr>
<td>3</td>
<td>3.13</td>
</tr>
<tr>
<td>4</td>
<td>2.58</td>
</tr>
</tbody>
</table>

* Determined in tetrahydrodiphenylamine at 135° C.

### Table XXIII

**Effect of Al(C_{6}H_{5})_{3}Cl/V Acetylacetone Molar Ratio on the Intrinsic Viscosity of Ethylene-Propylene Copolymers**

<table>
<thead>
<tr>
<th>Mole Al(C_{6}H_{5})_{3}Cl/mole VAc</th>
<th>( \eta^* )</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.92</td>
</tr>
<tr>
<td>5</td>
<td>2.11</td>
</tr>
<tr>
<td>6.33</td>
<td>1.63</td>
</tr>
<tr>
<td>10</td>
<td>1.57</td>
</tr>
<tr>
<td>20</td>
<td>0.99</td>
</tr>
<tr>
<td>30</td>
<td>0.77</td>
</tr>
</tbody>
</table>

* Determined in tetrahydrodiphenylamine at 135° C.

### Table XXIV

**Effect of Aging Time of Catalyst on Intrinsic Viscosity of Ethylene-Propylene Copolymers**

<table>
<thead>
<tr>
<th>Mole propylene/mole ethylene in the gaseous mixture</th>
<th>VAc g</th>
<th>Aging time, min</th>
<th>Aging, [( \eta^* )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>0.25</td>
<td>5</td>
<td>2.05</td>
</tr>
<tr>
<td>6</td>
<td>0.25</td>
<td>15</td>
<td>3.38</td>
</tr>
<tr>
<td>6</td>
<td>0.25</td>
<td>30</td>
<td>3.44</td>
</tr>
<tr>
<td>6</td>
<td>0.50</td>
<td>5</td>
<td>1.35</td>
</tr>
<tr>
<td>6</td>
<td>0.50</td>
<td>15</td>
<td>2.18</td>
</tr>
<tr>
<td>6</td>
<td>0.50</td>
<td>30</td>
<td>2.57</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>5</td>
<td>1.65</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>5</td>
<td>3.00</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>15</td>
<td>4.70</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>30</td>
<td>5.70</td>
</tr>
<tr>
<td>4</td>
<td>0.125</td>
<td>60</td>
<td>6.70</td>
</tr>
</tbody>
</table>

* Determined in tetrahydrodiphenylamine at 135° 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 interrupters, 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 and hydrocarbons.

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

\[
\text{[Cat]} + \text{ZnR} \rightarrow \text{[Cat] R} + \text{ZnR}
\]

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:

\[
\text{[Cat]} + \text{H} \rightarrow \text{[Cat] H} + \text{PH}
\]

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 which has been much improved in our laboratory.

B. Transition metal compounds.—In the case of liquid compounds (e.g., VCl, VOCl_{3}, TiCl_{3}, VO(OCC_{8}H_{18})_{2}, VO(OCC_{8}H_{18})Cl), purification is affected by distillation, while in the case of solid halides (e.g., VCl, TiCl_{3}), they are repeatedly washed with heptane, and subsequently ground in a ball mill. Hydrocarbon-soluble solid compounds (e.g., VAc, VOAc), 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 spectrometry.

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°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 α-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 α-olefins, in particular with butene-1. 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

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$r_{CH_2}$</th>
<th>$r_{CH_3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(C,H$_5$)$_2$ + VCl$_4$</td>
<td>29.60</td>
<td>0.019</td>
</tr>
<tr>
<td>Al(C,H$_5$)$_2$ + VCl$_3$</td>
<td>26.96</td>
<td>0.043</td>
</tr>
</tbody>
</table>

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 Al(C,H$_5$)$_2$ + VCl$_4$ and Al(C,H$_5$)$_2$ + VCl$_3$ 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, so a must be expected in the case of anionic copolymerizations. The catalyst 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 $Q$–$ɛ$ scheme, proposed by Allfrey and Price; but no study has been undertaken yet in the case of ionic copolymerizations. In fact the original $Q$–$ɛ$ scheme evidently cannot be applied to the latter case, since equal values of $ɛ$ cannot be attributed both to the monomer and to the corresponding terminal monomeric unit present in the growing chain.

As observed by other authors 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 $r_2$ in the case that

$$ r_1 \cdot r_2 = 1 $$

then

$$ \frac{k_{12}}{k_{21}} = \frac{k_{13}}{k_{23}} $$

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

$$ v_1 = k_1[M_1^*][M_1] $$

(a)

$$ v_2 = k_2[M_1^*][M_2] $$

(b)

$$ v_3 = k_3[M_2^*][M_1] $$

(c)

$$ v_4 = k_4[M_2^*][M_2] $$

(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

\[
\frac{k_{11}}{k_{12}} = \frac{k_{21}}{k_{22}}
\]

can be generalized as follows:

\[
\frac{k_{1i}}{k_{1j}} = \frac{k_{2i}}{k_{2j}},
\]

where \(i\) can be any terminal monomeric unit, equal to or different from \(2^n\).

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 \(r_{31}\), and of monomer 1 with monomer 3, indicated below as \(r_{13}\) and \(r_{31}\), then:

\[
\begin{align*}
    r_{12} &= \frac{k_{11}}{k_{12}} \quad \frac{r_{12}}{k_{12}} \\
    r_{13} &= \frac{k_{11}}{k_{13}} \quad \frac{r_{13}}{k_{13}}
\end{align*}
\]

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

\[
\begin{align*}
    r_{23} &= \frac{k_{22}}{k_{23}} \quad \frac{r_{23}}{k_{23}}
\end{align*}
\]

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

\[
\frac{k_{22}}{k_{23}} = \frac{k_{12}}{k_{13}}
\]

from which

\[
\frac{r_{23}}{k_{23}} = \frac{k_{12}}{k_{13}}.
\]

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

\[
\frac{r_{23}}{k_{23}} = \frac{k_{12}}{k_{11}} \cdot \frac{k_{11}}{k_{13}}.
\]

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

\[
\frac{r_{23}}{k_{23}} = \frac{r_{13}}{k_{13}} \cdot \frac{r_{12}}{k_{12}}.
\]

Analogyously, by multiplying numerator and denominator of the ratio corresponding to \(r_{23}\) by \(k_{11}\), then:

\[
\frac{r_{23}}{k_{23}} = \frac{k_{22}}{k_{11}} \frac{k_{11}}{k_{23}}.
\]

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:

\[
\frac{r_{23}}{k_{23}} = \frac{r_{21}}{k_{21}} \frac{k_{22}}{k_{21}} = \frac{r_{21}}{k_{22}}.
\]

Moreover the reactivity ratios \(r_{23}\) and \(r_{21}\) must satisfy the equation

\[
\frac{r_{21}}{k_{21}} = \frac{1}{r_{21}}
\]

If the product of the reactivity ratios is not strictly equal to one, two other values of \(r_{21}\) and \(r_{23}\) can be calculated, by substituting the results of Equation (7)

<table>
<thead>
<tr>
<th>Table XXVI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Catalytic system</strong></td>
</tr>
<tr>
<td>Al(C(_6)H(_5))(_3) + VCL(_4)</td>
</tr>
<tr>
<td>Al(C(_6)H(_5))(_3) + VCL(_4)</td>
</tr>
</tbody>
</table>

and of Equation (6), respectively, in Equation (8). Then, by averaging the results obtained with those deduced from Equations (6) and (7), more approximate value of \(r_{23}\) and \(r_{21}\) 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\(_6\)H\(_5\))\(_3\) and VCL\(_4\) and from Al(C\(_6\)H\(_5\))\(_3\) an VCL\(_4\). 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\(^2\). 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 monomer units can be indicated as follows: (R is the first monomer starting the polymer chain)

\[
R = (m_1)_i (m_2)_i (m_1)_i (m_2)_i \ldots
\]

where \(x_i\) and \(y_i\) are integers, which can assume values equal to or higher than unity.

If all \(x_i\) and \(y_i\) are equal to 1, the monomeric units are regularly alternated; consequently the polymer shows a regular chemical structure. When a regular \(\alpha\) stereic structure occurs, the polymer is crystallizable.

By adopting particular copolymerization conditions, copolymers can be obtained having so high \(x_i\) and \(y_i\) values that the crystallization of the ordered \(m_1\) and \(m_2\) segments becomes possible (block copolymers). 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 formula proposed by Alfrej and Goldfinger\(^2\) have been applied in the case of ethylene–propylene copolymers, prepared with the aid of catalysts obtained from vanadium tetrachloride and triethylaluminum.

The values thus obtained for the sequence distribution functions are in good agreement with those found experimentally by infrared spectroscopy 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:

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

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 \( k_{12} \) and \( k_{21} \) are low in comparison with those of \( k_{11} \) and \( k_{22} \), 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.

\[
\begin{align*}
P_{11} &= \frac{k_{11}[M_1]^* [M_1]}{k_{11}[M_1]^* [M_1] + k_{12}[M_1]^* [M_2]} = \frac{r_1[M_1]}{[M_1]^*} = r_1 \\
P_{12} &= \frac{k_{12}[M_1]^* [M_2]}{k_{11}[M_1]^* [M_1] + k_{12}[M_1]^* [M_2]} = \frac{[M_2]}{[M_1]^*} = \frac{1}{r_1 + F} \\
P_{21} &= \frac{k_{21}[M_2]^* [M_1]}{k_{21}[M_2]^* [M_1] + k_{22}[M_2]^* [M_2]} = \frac{[M_1]}{[M_2]^*} = 1 + (r_2/F) \\
P_{22} &= \frac{k_{22}[M_2]^* [M_2]}{k_{21}[M_2]^* [M_1] + k_{22}[M_2]^* [M_2]} = \frac{r_2[M_2]}{[M_2]^*} = r_2
\end{align*}
\]

where \( r_1 \) and \( r_2 \) are the reactivity ratios and \( F \) the ratio \( [M_1]/[M_2] \) between the 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, \( n+1 \) addition reaction, on the growing chain \( C \)

\[
C-M_1^* + m_1
\]

(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 \( m_1 \) unit having probability \( P_{11} \), that is \( (1-P_{11}) \). Therefore the probability that a sequence of units contains \( n \) members is

\[
P(m_n) = P_{11}^{n-1} (1 - P_{11})
\]

Analogously:

\[
P(m_2) = P_{11}^{n-1} (1 - P_{11})
\]

represents the fraction of all \( m_2 \) sequences formed by \( n \) members.

By substituting \( P_{11} \) and \( P_{21} \) in these two last expressions, with the values given above, we obtain:

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

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

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

\[
F = \frac{f - 1 + [(f-1)^2 + 4r_2r_3f]}{2r_1}
\]

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 this method to the case of the ethylene-propylene copolymerizations in the presence of catalysts prepared from \( Al(C_2H_5)_3 \) and \( VCl_4 \); for them we calculated the following values of the reactivity ratios:

\[
r_{C2H5} \equiv 7.08; \quad r_{VCl4} \equiv 0.088
\]

from which the product \( r_{C2H5}r_{VCl4} = 0.623 \) 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 Al(C₆H₅)₃—VCl Catalyst**

<table>
<thead>
<tr>
<th>Mole % of mₓ in the copolymer</th>
<th>n = 1</th>
<th>n = 2</th>
<th>n = 3</th>
<th>n = 4</th>
<th>n = 5</th>
<th>n = 6</th>
<th>n = 7</th>
<th>n = 8</th>
<th>n = 9</th>
<th>n &gt; 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>27.07</td>
<td>19.74</td>
<td>14.50</td>
<td>10.50</td>
<td>7.666</td>
<td>5.584</td>
<td>4.073</td>
<td>2.970</td>
<td>2.156</td>
<td>1.584</td>
</tr>
<tr>
<td>60</td>
<td>44.47</td>
<td>24.67</td>
<td>13.71</td>
<td>7.614</td>
<td>4.228</td>
<td>2.347</td>
<td>1.303</td>
<td>0.724</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>50</td>
<td>55.89</td>
<td>24.55</td>
<td>10.57</td>
<td>4.794</td>
<td>2.116</td>
<td>0.533</td>
<td>0.412</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>40</td>
<td>66.70</td>
<td>22.21</td>
<td>7.398</td>
<td>5.464</td>
<td>0.820</td>
<td>0.273</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>35</td>
<td>83.20</td>
<td>16.27</td>
<td>2.871</td>
<td>0.540</td>
<td>0.101</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>25</td>
<td>89.53</td>
<td>3.777</td>
<td>0.982</td>
<td>0.103</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

% P(mₓ)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 rₓz = 1**

<table>
<thead>
<tr>
<th>Mole % of mₓ in the copolymer</th>
<th>n = 1</th>
<th>n = 2</th>
<th>n = 3</th>
<th>n = 4</th>
<th>n = 5</th>
<th>n = 6</th>
<th>n = 7</th>
<th>n = 8</th>
<th>n = 9</th>
<th>n &gt; 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>85.00</td>
<td>12.75</td>
<td>1.91</td>
<td>0.29</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>25</td>
<td>75.00</td>
<td>18.75</td>
<td>4.69</td>
<td>1.17</td>
<td>0.29</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>40</td>
<td>60.00</td>
<td>24.00</td>
<td>9.60</td>
<td>3.84</td>
<td>1.54</td>
<td>0.62</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>50</td>
<td>60.00</td>
<td>25.00</td>
<td>12.50</td>
<td>6.25</td>
<td>3.13</td>
<td>1.56</td>
<td>0.78</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>60</td>
<td>40.00</td>
<td>24.00</td>
<td>14.40</td>
<td>8.64</td>
<td>5.18</td>
<td>3.11</td>
<td>1.87</td>
<td>1.12</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>75</td>
<td>25.00</td>
<td>18.75</td>
<td>14.06</td>
<td>10.55</td>
<td>7.91</td>
<td>5.95</td>
<td>4.45</td>
<td>3.34</td>
<td>2.51</td>
<td>—</td>
</tr>
<tr>
<td>85</td>
<td>15.00</td>
<td>12.75</td>
<td>10.84</td>
<td>9.21</td>
<td>7.83</td>
<td>6.66</td>
<td>5.66</td>
<td>4.81</td>
<td>4.09</td>
<td>—</td>
</tr>
</tbody>
</table>

% P(mₓ)ₙ = percentage of sequences of mₓ 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 Al(C₆H₅)₃ + VCl.**

---

**Polyolefin Elastomers**
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 %, and in agreement with this supposition, we have already experimentally found 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 ethylene groups.

Tables XXVIII, XXIX, and XXX show the P distribution functions of the monomeric units, which should occur in copolymers for which the \( r_{12} \) product is 1, 0.1, and 10, respectively. Comparison of the values of \( P(m_n) \) found for the copolymers obtained with the aid of catalysts prepared from \( 
mid \text{Al(C}_{\text{2}}\text{H}_{\text{5}}\text{)} \mid \text{2} \) and VCl4, 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 \( r_{12} \) 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 \( nP(m_1) \).

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

\[
\phi(m_1, n) = \frac{n P(m_1)}{\sum_{n=1}^{\infty} n P(m_1) + \sum_{n=1}^{\infty} n P(n_{12})}
\]

from which it is easy to obtain

\[
\phi(m_1, n) = \frac{n P_{12}^{-1} P_{12}}{1/P_{12}} = n P_{12}^{-1}(P_{12})^n.
\]

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

\[
\phi(m_2, n) = n P_{22}^{-1}(P_{22})^n
\]

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 \( \text{Al(C}_{\text{2}}\text{H}_{\text{5}}\text{)} \mid \text{2} \) and VCl4. 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 by the statistical theory described above.

A first proof is given by the absence of polyethylene-type crystallinity in copolymers containing up to 80 mole-% of ethylene units\(^4\). This agrees with the
values of the sequence distribution functions which are reported in Table XXVII. Actually, the value of \( P(C_5H_{11})_n \) (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\(^{34}\). The absorption band between 13.0 and 14.0 \( \mu \) can be attributed to sequences of methylenic groups of different lengths, 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\(^{36}\). 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 spectroscopy are in a very good agreement\(^{34,36}\).

**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\(^{43}\) on the kinetics of ethylene–propylene copolymerization in the presence of the thermally-stabilized catalytic system \( \text{Al}^3\text{(C}_4\text{H}_8)_2 + \text{VCl}_4 \).

In particular, the effect on the copolymerization rate was studied at 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 9-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 decrease 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 at 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 triethylalumininum 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\(_4\) or VOCl\(_3\); in fact it yielded completely amorphous copolymers within a broader range of composition of the monomer mixture\(^{43}\). 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\(_4\), 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\(_4\) + Al(C\(_4\)H\(_8\))\(_2\) loses activity with time, see Figure 21.

---

**Fig. 20.**—Distribution of monomer units in sequences formed by a monomer units for ethylene–propylene copolymers prepared with the catalytic system \( \text{Al}^3\text{(C}_4\text{H}_8)_2 + \text{VCl}_4 \).

---

**Fig. 21.**—Dependence of copolymer yield on aging time. Polymerization temperature = 25\(^\circ\)C; \( P = 1 \) atm; solvent: 9-heptane cm\(^3\) 410; mole Al(C\(_4\)H\(_8\))/mole C\(_4\)H\(_8\)); in gaseous mixture = 2; polymerization time = 10 minutes. \( \bigodot \) Catalyst aged at 25\(^\circ\)C; mole Al(C\(_4\)H\(_8\))/mole VCl\(_4\) = 2.5; V: 0.0224 g. \( \bigodot \) Catalyst aged at 25\(^\circ\)C; mole Al(C\(_4\)H\(_8\))/mole VCl\(_4\) = 2.5; V: 0.0162 g. \( \Delta \) Catalyst aged at 60\(^\circ\)C; mole Al(C\(_4\)H\(_8\))/mole VCl\(_4\) = 3.5; V: 0.0389 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 Al(C$_6$H$_5$)$_3$ and VCl$_4$ at 60° C and then keeping the mixture at this temperature for 30 minutes, catalysts were obtained which, when used at temperatures between 0 and 40° 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° 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 Al(C$_6$H$_5$)$_3$ to VCl$_4$.—The copolymer composition does not vary when varying the ratio of the Al(C$_6$H$_5$)$_3$ moles to the VCl$_4$ moles used in the preparation of the catalysts, at least for an Al(C$_6$H$_5$)$_3$/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 Al(C$_6$H$_5$)$_3$/VCl$_4$ molar ratios of about 2.5 (see Figure 12). This is in agreement with what was observed in propylene-ethylene homopolymerization, carried out in the presence of catalysts prepared from soluble halides of transition metals.

An Al(C$_6$H$_5$)$_3$/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 concentrations. 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.

![Figure 23](image_url)  
**Figure 23.**—Dependence of copolymer yield (in grams) on polymerization time for different catalyst concentrations. Polymerization temperature = 25° C; P = 1 atm; solvent: n-heptane, cm$^3$ 410; mole CaH$_4$/mole CaH$_4$ 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 VCl$_4$ + AlR$_3$ catalyst at 25° C, the average molecular weight of the copolymer, determined on the basis of its intrinsic viscosity, is practically constant with time and with the amount of copolymer produced (see 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 catalystic 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.

![Figure 24](image_url)  
**Figure 24.**—Dependence of G (g copolymer obtained) referred to V (g of vanadium) on polymerization time. Polymerization temperature = 25° C; P = 1 atm; solvent: n-heptane, cm$^3$ 410; mole CaH$_4$/mole CaH$_4$ in the gaseous feed = 2; mole % CaH$_4$ in the copolymer = 50.6.
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.
### Table XXXII

**Rate of Ethylene-Propylene Copolymerization for Copolymer Containing 50.6 Mole-% Ethylene**

Catalyst prepared from Al(C₅H₅)₃ and VCl₅ aged for 30 min at 60°C; moles Al(C₅H₅)₃ to mole VCl₅ = 2.5; T = 25°C; P = 1 atm; solvent - n-heptane, cm³ 410; moles C₅H₅/mole C₃H₆ in gaseous mixture = 2; P₀(CH₄) + P₀(CH₅) = 715 mm Hg.

<table>
<thead>
<tr>
<th>V₁, g vanadium</th>
<th>Polymerization time, min</th>
<th>G₁, g copolymer</th>
<th>R₁ = (G₁/V₁)(1615/(P₀(CH₄) + P₀(CH₅)))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0674</td>
<td>3</td>
<td>3.89</td>
<td>1154</td>
</tr>
<tr>
<td>0.0674</td>
<td>4</td>
<td>5.31</td>
<td>1182</td>
</tr>
<tr>
<td>0.0674</td>
<td>6</td>
<td>7.95</td>
<td>1180</td>
</tr>
<tr>
<td>0.0449</td>
<td>4</td>
<td>3.05</td>
<td>1219</td>
</tr>
<tr>
<td>0.0449</td>
<td>6</td>
<td>5.50</td>
<td>1203</td>
</tr>
<tr>
<td>0.0449</td>
<td>6</td>
<td>5.55</td>
<td>1330</td>
</tr>
<tr>
<td>0.0449</td>
<td>8</td>
<td>7.41</td>
<td>1238</td>
</tr>
<tr>
<td>0.0449</td>
<td>10</td>
<td>9.15</td>
<td>1223</td>
</tr>
<tr>
<td>0.0499</td>
<td>5</td>
<td>2.80</td>
<td>1124</td>
</tr>
<tr>
<td>0.0499</td>
<td>7</td>
<td>3.92</td>
<td>1124</td>
</tr>
<tr>
<td>0.0499</td>
<td>9</td>
<td>4.00</td>
<td>1154</td>
</tr>
<tr>
<td>0.0499</td>
<td>8</td>
<td>4.57</td>
<td>1145</td>
</tr>
<tr>
<td>0.0499</td>
<td>8</td>
<td>4.48</td>
<td>1124</td>
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<td>0.0499</td>
<td>9</td>
<td>4.06</td>
<td>1106</td>
</tr>
<tr>
<td>0.0499</td>
<td>10</td>
<td>5.55</td>
<td>1114</td>
</tr>
<tr>
<td>0.0499</td>
<td>10</td>
<td>5.53</td>
<td>1110</td>
</tr>
<tr>
<td>0.0299</td>
<td>10</td>
<td>5.45</td>
<td>1094</td>
</tr>
<tr>
<td>0.0299</td>
<td>12</td>
<td>6.95</td>
<td>1181</td>
</tr>
<tr>
<td>0.0199</td>
<td>7</td>
<td>2.89</td>
<td>1245</td>
</tr>
<tr>
<td>0.0199</td>
<td>10</td>
<td>4.10</td>
<td>1236</td>
</tr>
<tr>
<td>0.0199</td>
<td>12</td>
<td>4.95</td>
<td>1241</td>
</tr>
<tr>
<td>0.0199</td>
<td>15</td>
<td>6.22</td>
<td>1250</td>
</tr>
<tr>
<td>0.0199</td>
<td>18</td>
<td>7.30</td>
<td>1221</td>
</tr>
</tbody>
</table>

* R₁ = (G₁/V₁)(1615/(P₀(CH₄) + P₀(CH₅)).

Because of the different solubility coefficients of ethylene and propylene, it may be interesting to express these 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 production in moles of polymerized monomer, rather than in grams, the comparative rate values were calculated, see Table XXXIII, expressed as follows:

$$\left(\frac{M}{I}\right) = \left(\frac{V}{I}\right)\overline{h(m/l)}$$

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 abscissas 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.
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 \( \text{C}_4\text{H}_8 \) 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\(^\circ\) C, 25\(^\circ\) C and 40\(^\circ\) 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: \( E = 6650 \text{ cal/mole} \)
- polymerization of propylene: \( E = 6600 \text{ cal/mole} \)

![Figure 27](image)

**Table XXXIV**

**Rate of Ethylene Homopolymerization**

Catalyst prepared as for Table XXXIII. Moles \( \text{Al(C}_2\text{H}_5)_3/mole V\text{Cl}_4 = 2.5; T = 25^\circ \text{C}; P = 1 \text{ at}; \) solvent: n-heptane, cm\(^4\) 410.

| Mole \( N_0 \)/mole \( \text{C}_4\text{H}_8 \) in the gas phase | \( V, g \) vanadium | Polymerization, min. | \( G, g \) polymer | \( G/V, g \times 10^7 \text{ mole} \) \( \text{cm}^4 \text{ mole}^{-1} \) \( \text{C}_4\text{H}_8 \) | \( M/l \) \( (V/0.1\text{m}^3) \) |
|---|---|---|---|---|---|---|
| 3.30 | 0.0299 | 6 | 2.70 | 3832 | 886 |
| 3.30 | 0.0299 | 8 | 3.55 | 3825 | 773 |
| 3.05 | 0.0299 | 8 | 3.93 | 3903 | 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 | 3962 | 862 |
| 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 |

![Figure 28](image)

**Table XXXV**

**Rate of Propylene Homopolymerization**

Catalyst prepared as for Table XXXIII. Moles \( \text{Al(C}_2\text{H}_5)_3/mole V\text{Cl}_4 = 2.5; T = 25^\circ \text{C}; P = 1 \text{ at}; \) solvent: n-heptane, cm\(^4\) 410.

| \( V, g \) vanadium | Polymerization, min. | \( G, g \) polymer | \( G/V, g \times 10^7 \text{ mole} \) \( \text{cm}^4 \text{ mole}^{-1} \) \( \text{C}_4\text{H}_8 \) | \( M/l \) \( (V/0.1\text{m}^3) \) |
|---|---|---|---|---|---|
| 0.2731 | 40 | 2.62 | 14.30 | 0.4012 |
| 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 | 0.4965 |

![Figure 29](image)
where \( Z \) is the collision number and \( \beta \) is the steric factor. As is well known, the \( i \) factor is essentially independent of temperature and the \( Z \) factor is affected only slightly. Therefore the ratios:

\[
P_{12}Z_{12}/P_{12}Z_{12} \quad \text{and} \quad P_{22}Z_{22}/P_{22}Z_{22}
\]

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 catalysts prepared from vanadium halides and aluminum trialkyls, the reactivity ratios of practice do not vary with temperature, at least for temperatures between \( 0^\circ \) and \( 75^\circ \) C.\[18,17]\n
Given

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

and

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

then

\[E_{12} = E_{11}\]

and

\[E_{21} = E_{22}\].

On the other hand, from the description above for the ethylene and propylene homo polymerizations, \( E_{22} \) is practically equal to \( E_{11} \). Therefore, by comparing 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 measurements of the number of active centers (capable of originating growing chains) present in the homopolymerization of ethylene and of propylene with the catalytic systems \( \text{VCl}_{4}-\text{AIR}_{3} \) and \( \text{TiCl}_{4}-\text{AIR}_{3} \). 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, it all the polymerization rates are related to the same concentration of growing chains, the ratio between the homopolymerizations rates of ethylene and propylene is of the same order of magnitude as the reactivity ratio of ethylene.\[22\]

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:

a) Chemical composition of the copolymer
b) Distribution of such composition
c) Average molecular weight
d) 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 methylene 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.

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 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, 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.

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 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 36.

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. 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 viscometry, osmometric, and light-scattering 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 tetrahydrofuran at 135°C.234.

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 cannot 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.27

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 vulcanize, 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 vulcanize properties. For instance, if the copolymer of Figure 38 is subjected to thermal degradation (at a temperature of 270°C-280°C, for some hours in a nitrogen atmosphere), a lower molecular weight product is obtained having a distribution of molecular weight shown in Figure 39. It can be noticed that the copolymer has a narrower 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
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 dimension, 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 vulcanize are particularly good using oils of the napthenic or paraffinic types; oils of the aromatic type yield vulcanizates of lower properties.

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 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 the stress-relaxation modulus for an ethylene–propylene copolymer, having a mole % content of ethylene, measured at temperatures ranging from $-60^\circ C$ to $+45^\circ C$. This figure shows a stress-relaxation modulus of the copolymer at $-60^\circ C$ of about $10^6$ dyne/cm$^2$, which is practically independent of time; this value is 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 little values (about $-100^\circ C$) in comparison with those of the best known rubbers. For a number of amorphous polymers, the curves reported above can be super imposed 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 amorphous materials within the whole range of temperatures considered.

![Fig. 41.—Stress-relaxation modulus of an ethylene–propylene copolymer (45% mole ethylene) vs. time, at various temperatures.](image-url)
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.\(^8\)

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 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**

<table>
<thead>
<tr>
<th>Properties of Crude Ethylene-Propylene Copolymers</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity, g/cm³</td>
<td>0.86—0.87</td>
</tr>
<tr>
<td>X-ray crystallinity</td>
<td>none</td>
</tr>
<tr>
<td>Ash content</td>
<td>less than 0.5%</td>
</tr>
<tr>
<td>Appearance</td>
<td>colorless</td>
</tr>
<tr>
<td>Mooney viscosity</td>
<td>varied</td>
</tr>
<tr>
<td>Heat capacity, cal/g °C</td>
<td>0.52</td>
</tr>
<tr>
<td>Thermal conductivity, cal/cm sec. °C</td>
<td>(8.5 \times 10^{-4})</td>
</tr>
<tr>
<td>Thermal diffusivity, cm/sec.</td>
<td>(1.9 \times 10^{-3})</td>
</tr>
<tr>
<td>Thermal coefficient of linear expansion/°C</td>
<td>(1.8 \times 10^{-4})</td>
</tr>
<tr>
<td>Brittle point (ASTM D746)/°C</td>
<td>—95</td>
</tr>
<tr>
<td>Solubility:</td>
<td>soluble in aliphatic, cycloaliphatic and aromatic hydrocarbons, in chlorinated hydrocarbons, insoluble in methanol, butanol, acetone.</td>
</tr>
</tbody>
</table>

**Table XXXVII**

<table>
<thead>
<tr>
<th>Electrical Properties of Ethylene-Propylene Copolymers</th>
<th>ASTM test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume resistivity, ohm cm</td>
<td>D257 5 × 10³</td>
</tr>
<tr>
<td>Dielectric strength, kV/mm</td>
<td>D149 28–30</td>
</tr>
<tr>
<td>Dielectric constant at 1000 cycles</td>
<td>D150 2.2</td>
</tr>
<tr>
<td>Loss factor at 1000 cycles</td>
<td>D150 0.001–0.002</td>
</tr>
</tbody>
</table>

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 the vulcanizates 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 essentially be solved by two different methods:\(^3, 14, 20, 25, 26, 27, 29, 30\):

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 by the synthesis of the elastomer (synthesis of terpolymers).

**A. Vulcanization by organic peroxides.**—The mechanism of crosslinking 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.

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

\[
\begin{align*}
ROOR & \rightarrow 2 RO' \\
RO' + P - H & \rightarrow ROH + P' \\
2 P & \rightarrow P - P
\end{align*}
\]

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 30 mole-% content of propylene, and less than 10% for a 90 mole-% content of propylene.

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 Sulfan R, Sulfadex, etc.), maleic anhydride and its derivatives, quinonodioxime and its derivatives, dinitrobenzene, divinylbenzene, triallylcyanurate, divinyladipate, diallylphthalate, triallylacromite, diallylmenthine, itaconic acid, etc.

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:**
\[
ROOR \rightarrow 2 RO'
\]

**Propagation:**
\[
\begin{align*}
RO' + PH & \rightarrow RO + P' \\
P' + S & \rightarrow PS' \\
P' + PS, P & \rightarrow PS, P + PS' \\
PS, P & \rightarrow PS + P'
\end{align*}
\]

**Termination:**
\[
\begin{align*}
2 P' & \rightarrow P - P \\
PH + P' & \rightarrow PS, P \\
PS, P & \rightarrow PS + P' \\
PS, P & \rightarrow PS + P'
\end{align*}
\]

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.
The characteristics of vulcanizates obtained in the presence and in the absence of sulfur, with different concentrations of peroxide, are described in Table XXXVIII. It can be observed that the increase of the peroxide concentration is not sufficient to furnish mechanical properties comparable with those obtained in the presence of sulfur. This leads one to believe that, probably, in the absence of sulfur, side reactions which can also cause copolymer breakdown, take place.

**Peroxides.**—The various peroxides differ one from another in structure, in reactivity of the radicals originated by them, and in the rate of their thermal decomposition at various temperatures. The efficiency of a peroxide as a vulcanization agent is connected with the reactivity of the peroxide radicals, whereas the vulcanization rate is connected with the decomposition rate.

A great number of peroxides were proposed for the vulcanization of the ethylene-propylene copolymers; among them, the alkyl or alkaryl compounds are the most promising for this particular use. Of these latter mention must be made of dicumyl-peroxide (Di-cumyl, Di-cumyl 40C), di-4-butyl-peroxide, cumyl-4-butyl-peroxide and their derivatives. Biperoxides, such as 2,5-dimethyl-2,5-di(t-butyl peroxo) hexane (Varox), 2,5 dimethyl-2,5-di(t-butyl peroxo) hexyne-3 (Luperco 130-XL), PX-60, are also available. They yield vulcanizates of good properties. Generally 0.01 mole of peroxide per 100 g of copolymer is enough to yield a degree of crosslinking that is satisfactory for most uses of the ethylene-propylene copolymers.

**Characteristics of the vulcanization with peroxides.**—It must be pointed out that the crosslinking efficiency with mixes of sulfur and peroxides, and with mixes of sulfur and other agents able to yield free radicals, strictly depends on the reactivity of the radicals and more precisely on the capacity of the radicals to extract hydrogen atoms from the aliphatic compounds. This may explain why the vulcanization properties of the ethylene-propylene copolymers depend on the peroxide used.
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 vulcanizes, 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.

The vulcanization curves reported above show also that the properties of the vulcanize 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. The polymer-solvent interaction coefficient could be deduced from these measurements; μ = 0.48 + 0.29 η was obtained for the copolymer-benzene system at 25°C. η is the volume fraction of polymer. This value of μ is still valid, when other crosslinking systems are used, which, however, do not have much effect on the interaction in the polymer-solvent system.
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 sulfuric 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 possible⁴⁷.

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 rubbers³⁷.

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.
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.

### Table XL

**Characteristics of Vulcanizates with Peroxide and Maleic Anhydride, with Variable Amounts of Zinc Oxide**

<table>
<thead>
<tr>
<th>ZnO, phr</th>
<th>Tensile strength, kg/cm²</th>
<th>Elongation at break, %</th>
<th>300% modulus, kg/cm²</th>
<th>Hardness, Shore A</th>
<th>Resilience at 20°C</th>
<th>Resilience at 90°C</th>
<th>Swelling ratio*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>38</td>
<td>465</td>
<td>22</td>
<td>49</td>
<td>64</td>
<td>70</td>
<td>4.5*</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td>520</td>
<td>38</td>
<td>53</td>
<td>69</td>
<td>81</td>
<td>3.1</td>
</tr>
<tr>
<td>10</td>
<td>115</td>
<td>515</td>
<td>49</td>
<td>55</td>
<td>69</td>
<td>82</td>
<td>3.1</td>
</tr>
<tr>
<td>25</td>
<td>142</td>
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<td>60</td>
<td>56</td>
<td>69</td>
<td>82</td>
<td>4.9</td>
</tr>
<tr>
<td>50</td>
<td>100</td>
<td>460</td>
<td>76</td>
<td>79</td>
<td>66</td>
<td>80</td>
<td>2.7</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Recipe</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzoyl peroxide</td>
<td>2</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>7</td>
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<td></td>
<td></td>
<td></td>
</tr>
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<td>ZnO</td>
<td>variable</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vulcanization</td>
<td>45 min/160°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* *—swelling ratio at equilibrium in benzene at 30°C.

### Table XLI

**Characteristics of Vulcanizates with Peroxide and Different Unsaturated Acid Substances**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Quantity, phr</th>
<th>Tensile strength, kg/cm²</th>
<th>Elongation at break, %</th>
<th>300% modulus, kg/cm²</th>
<th>Hardness, Shore A</th>
<th>Resilience at 20°C, %</th>
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</thead>
<tbody>
<tr>
<td>Maleic acid</td>
<td>9</td>
<td>150</td>
<td>550</td>
<td>55</td>
<td>55</td>
<td>73</td>
</tr>
<tr>
<td>Fumaric acid</td>
<td>9</td>
<td>95</td>
<td>630</td>
<td>47</td>
<td>52</td>
<td>72</td>
</tr>
<tr>
<td>Isocnic acid</td>
<td>10</td>
<td>103</td>
<td>610</td>
<td>67</td>
<td>54</td>
<td>71</td>
</tr>
<tr>
<td>Cinnamic acid</td>
<td>11.5</td>
<td>90</td>
<td>580</td>
<td>54</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>Crotonic acid</td>
<td>6.7</td>
<td>75</td>
<td>510</td>
<td>56</td>
<td>72</td>
<td></td>
</tr>
<tr>
<td>Acrylic acid</td>
<td>11</td>
<td>95</td>
<td>450</td>
<td>65</td>
<td>52</td>
<td>71</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Recipe</th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Copolymer</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dibenzoyl peroxide</td>
<td>2</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO</td>
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<td></td>
<td></td>
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</tbody>
</table>

### Table XLII

**Properties of a Grafted Copolymer**

<table>
<thead>
<tr>
<th>Heat treatment 300°C X 30 min.</th>
<th>Solubility after heat treatment in CHCl₃, %</th>
<th>Characteristics of vulcanized copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maleic acid phr</td>
<td>DTBP* phr</td>
<td>300% modulus, kg/cm²</td>
</tr>
<tr>
<td>2</td>
<td>0.3</td>
<td>89</td>
</tr>
<tr>
<td>2</td>
<td>0.6</td>
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</tr>
<tr>
<td>3</td>
<td>0.3</td>
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</tr>
<tr>
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<td>0.6</td>
<td>80</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>65</td>
</tr>
<tr>
<td>5</td>
<td>0.3</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>0.6</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>1</td>
<td>97</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Recipe: Grafted copolymer</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td>PBNB</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>5</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vulcanization, 30 min/160°C</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
</table>

* 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 vul-
canization 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
due essentially 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 poly-
merizable monomers are added, together with organic peroxide. 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 forma-
tion 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 vulcanize is ob-
tained 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 swelled state
by direct action of chlorine. Thus starting from the same copolymer, products with
different chlorine contents can be prepared.

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 prod-
sets 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.

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 intro-
duced 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
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. These moderate the action of peroxide, but, contrary to other cogenents, 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 acryl and methaeretic acid. In the case of a hydrocarbon monomer, a vulcanize 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.

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 prevalently 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.

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**

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Carbon black, phr</th>
<th>Oil, ppi</th>
<th>Zinc oxide, ppi</th>
<th>Vulcanization, 30 min., 150°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>44</td>
</tr>
</tbody>
</table>

---

**Note:**
- Table XLIII shows the properties of vulcanizates obtained from copolymers grafted with maleic acid.
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 vulcanize with good resistance to aging, magnesium oxide and epoxide 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 diaminos.

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. 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.

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

---

**Table XLIV**

**Physical Properties of Vulcanizates Obtained from a Copolymer Having 2% by Weight of Chlorine, with Different Dehydrochlorination Times**

<table>
<thead>
<tr>
<th>Dehydrochlorination time at 180° C, hours</th>
<th>Tensile strength, kg/cm²</th>
<th>Elongation at break, %</th>
<th>300% modulus, kg/cm²</th>
<th>Swelling ratio, benzene, 30° C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>128</td>
<td>975</td>
<td>14</td>
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</tr>
<tr>
<td>5</td>
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<td>9</td>
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<td>89</td>
<td>715</td>
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<td>3.72</td>
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<td>96</td>
<td>78</td>
<td>670</td>
<td>19</td>
<td>3.67</td>
</tr>
</tbody>
</table>

Recipe: Chlorinated polymer 100%
Zinc oxide 10%
dehydrochlorination mixture
Magnesium oxide 10%
Stearic acid 2
Sulfur 2
Tetramethylthiuramdisulfide 2
2-Mercaptobenzothiazole 1
Vulcanization 30 min/190° C

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)
chloride, octachloropropene, octachlorocyclopentene, etc. The presence of metal oxide is strictly necessary for the vulcanisation; moreover some oils, such as tall oil, affect the final properties of the vulcanizates favorably. Vulcanisation can be carried out at temperatures generally ranging from 140° to 170° C; the effect of temperature on the properties of the vulcanise varies depending on the type of chlorinated compound used. By this type of vulcanisation, 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 vulcanisation of polypropylene and of polyisobutene.

1. 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.

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.

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.

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 endomethylene compounds, and cyclic polyenes.

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 single 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>
<thead>
<tr>
<th>TABLE XLV</th>
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<tbody>
<tr>
<td><strong>Monomers Suitable for Terpolymerization with Ethylene and Propylene</strong></td>
</tr>
<tr>
<td><strong>Aliphatic dienes</strong></td>
</tr>
<tr>
<td>butadiene</td>
</tr>
<tr>
<td>isoprene</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
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</table>

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 mixtures based on sulfur and accelerators, in the presence of zinc oxide as activator. The accelerators usually employed are of the "ultrarapid" type, alone or possibly in combination with secondary accelerators.

With the ethylene–propylene terpolymers the presence in the mixtures 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.

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 (PbO₄) 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 curve, 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.
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 a strong effect on the properties of the vulcanize, whereas above a certain value, the effect becomes weaker. High molecular weight terpolymers (Mooney viscosity at 100°C, ML 1+4 above 50) having a sufficiently high unsaturation, are usually extended with considerable amounts of common petroleum oils (e.g., Necton 60, Circosol 2XH, Circro-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 silicas, 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 XLVII

**Effect of Various Types of Carbon Black**

<table>
<thead>
<tr>
<th>Carbon black</th>
<th>Type</th>
<th>Quantity</th>
<th>Tensile strength, kg/cm²</th>
<th>Elongation at break, %</th>
<th>Modulus at 300% elongation, kg/cm²</th>
<th>Hardness, %</th>
<th>Resilience, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAF</td>
<td>50</td>
<td>197</td>
<td>440</td>
<td>122</td>
<td>75</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>ISAF</td>
<td>50</td>
<td>236</td>
<td>460</td>
<td>136</td>
<td>75</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>MPC</td>
<td>50</td>
<td>240</td>
<td>640</td>
<td>80</td>
<td>73</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>SRF</td>
<td>20</td>
<td>117</td>
<td>320</td>
<td>112</td>
<td>78</td>
<td>57</td>
<td></td>
</tr>
<tr>
<td>FEF</td>
<td>50</td>
<td>180</td>
<td>300</td>
<td>180</td>
<td>82</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>MT</td>
<td>100</td>
<td>69</td>
<td>360</td>
<td>62</td>
<td>75</td>
<td>63</td>
<td></td>
</tr>
</tbody>
</table>

Recipe:
- Terpolymer: 100 (ML 1 + 4 at 100°C = 52, COD 3, 1% by weight)
- Black: as shown
- Circoxol 2XH: 3
- Sulfur: 2
- MBT: 0.5
- TMQ: 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.

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/cm² 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
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.

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 °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, one keeps in mind the following factors:

1. Low specific gravity (about 0.86 kg/cm³).
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.

Independently of the special features of these rubbers, one must remember:

Low specific gravity (0.80-0.87 g/cm³)
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.

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.

XVII. REFERENCES
