New Ethylene-Propylene Elastomers

by

Giulio Natta, Guido Sartori, Alberto Valvassori,
Giorgio Mazzanti, Giovanni Crespi

New Ethylene-Propylene Elastomers

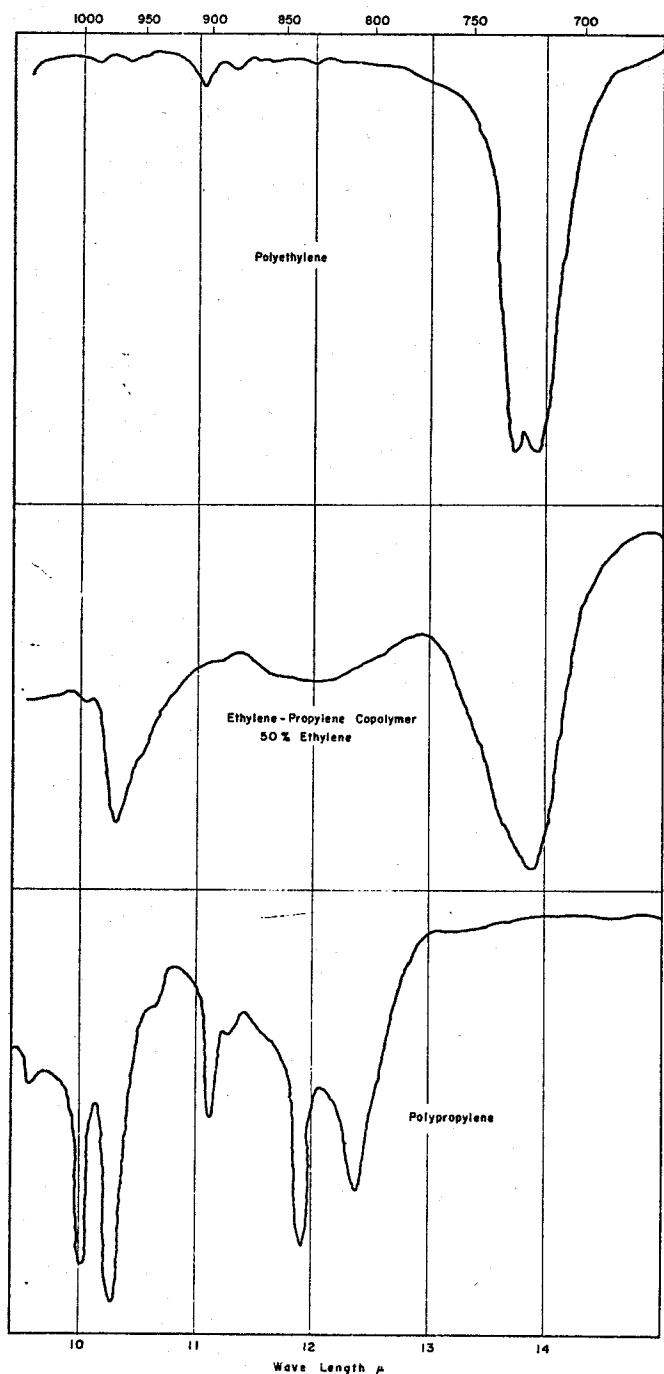FIGURE 1—Infrared spectra of polyethylene, ethylene-propylene copolymer (50 percent ethylene) and polypropylene between 9.5 and 15μ.

Part 1: Characterization, constitution, analysis and monomer distribution

Giulio Natta, Guido Sartori, Alberto Valvassori, Giorgio Mazzanti, Giovanni Crespi
Polytechnic Institute of Milan, Milan, Italy

SUCCESSFUL POLYMERIZATION of alpha olefins with ethylene has led to ethylene-propylene copolymers of high interest. Forecasts[1,2] show these copolymers to have interesting elastomeric properties. Important results obtained from ethylene-propylene copolymerization studies indicate a method of characterization, significant elastomeric properties and vulcanization methods for the products.

CHARACTERIZATION OF COPOLYMERS

When studying the copolymerization of two or more monomers, a series of criteria of analysis are necessary to establish whether the products obtained actually consist of a copolymer and not of homopolymer mixtures. Moreover, it is necessary to improve methods of analysis to determine quantitatively the monomers present in the copolymer.

Constitution Criteria. The criterion adopted to establish that the products examined actually consisted of ethylene-propylene (EP) copolymers is based on a comparison of the IR (Infrared) spectrum of the raw copolymerization product (or of the fractions obtained from it by extraction with boiling solvents), with the IR spectrum of pure polyethylene and with the IR spectrum of polypropylene (or of its corresponding fractions obtained by extraction with boiling solvents).

The IR spectrum of EP copolymers shows remarkable differences from the spectra of the two homopolymers (see Figure 1). As a matter of fact, while the last ones show absorption bands due to the presence of crystalline zones which can be ascribed to sterically ordered chains or chain segments, in the IR spectra of copolymers there are no such bands, but other characteristic bands. Particularly in the zone between 13 and 13.8 μ, bands which can be ascribed to the presence of sequences of methylene groups of different length are present.

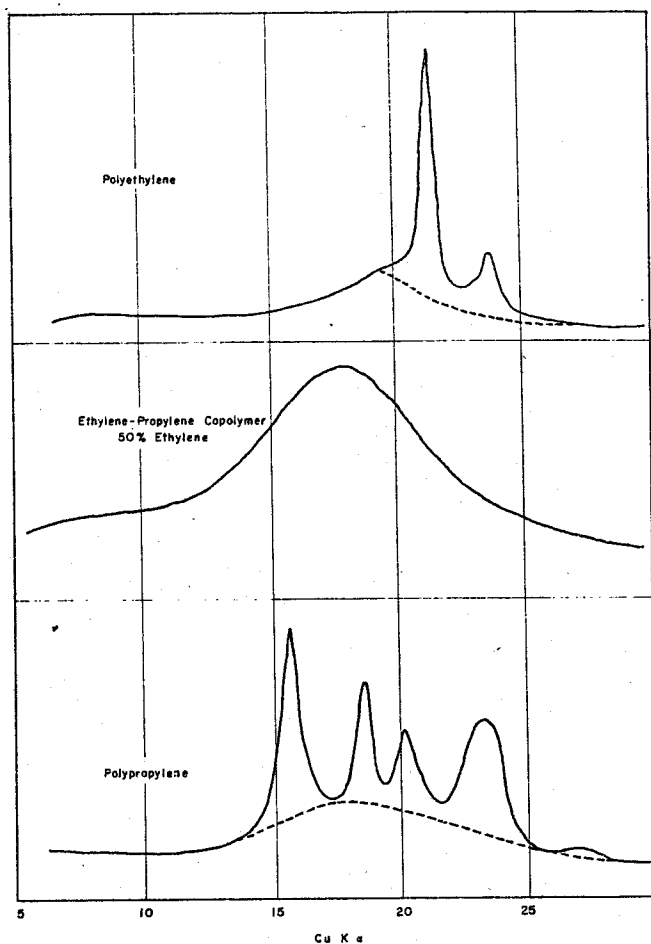More precisely, it is possible to find bands due to

FIGURE 2—X-ray diffraction spectra (Cu K α) of polyethylene, ethylene-propylene copolymer (50 percent ethylene) and polypropylene.

TABLE 1—Boiling solvent extraction of pure ethylene and propylene homopolymers and of some ethylene-propylene copolymers obtained under the same conditions

Product	WEIGHT PERCENT EXTRACTED BY			
	Ether	n-Hexane	n-Heptane	Residue
Polyethylene..................	0	0	0	100
Polypropylene................	39	30	16	15
Ethylene-propylene copolymer (mole % ethylene = 30)....	84	16	0	0
Ethylene-propylene copolymer (mole % ethylene = 50)....	65	35	0	0
Ethylene-propylene copolymer (mole % ethylene = 66)....	30	60	10	0

(—CH_2—)$_n$ sequences, where n < 5 and the band corresponding to n ⩾ 5.

The X-ray examination of the copolymerization products of EP mixtures confirms too that such products actually consist of copolymers.

The products prepared, unlike ethylene and propylene homopolymers prepared in the same conditions which show a high crystallinity, are completely amorphous (see Figure 2).

Besides, the curve of diffraction intensity for EP copolymers shows a maximum which corresponds to an angle different from that of pure amorphous polypropylene and from the one which can be foreseen for an amorphous polyethylene.

From the comparison of the fractionation of the copolymerization products with the results of the fractionation carried out on homopolymers, it was further confirmed that the products obtained consist of EP copolymers.

Table 1 shows the polyethylene obtained from pure ethylene, under the same polymerization conditions adopted for the synthesis of the copolymers, cannot be extracted with the solvents used. Polypropylene obtained from pure propylene, under the same polymerization conditions, contains a fraction which remains as a residue

after n-heptane extraction. The copolymerization products, having an ethylene content lower than 75 mole percent, are completely extractable with boiling n-hexane or boiling n-heptane.

Analysis for Copolymer Composition. The composition of the EP copolymers has been determined by means of a radiochemical method and IR spectrography.

Radiochemical Method. Carbon 14 labelled ethylene has been used in the synthesis of the copolymers. The specific activity of ethylene used (A_o) and that of the copolymers to be examined (A) has been determined by means of a counter with a 1.6 mg/cm² thin window on a polymer plate.[3, 4]

Indicating by X the mole fraction of ethylene in the copolymer:

$$\frac{A}{A_0} = \frac{2x}{3 - x}$$

IR Method. The propylene content in the copolymers has been measured from the absorption intensity of the 7.25 μ band, using carbon tetrachloride as a solvent.

Other methods of analysis for the EP copolymers by means of IR spectrography have been proposed.[5, 6]

MONOMERIC DISTRIBUTION

The characterization of copolymerizates, carried out as stated above, and the determination of composition of the copolymers obtained, are not sufficient to determine their chemical structures. It is obvious that a very great number of possible distributions of the monomeric units corresponds to a given composition of a copolymer.

For instance, in a copolymer consisting of m_1 and m_2 monomers, with 50 mole percent of m_1 monomer, and 50 mole percent of m_2 monomer, the arrangement of the monomeric units may be schematically indicated as follows, calling R the first monomer that starts the polymerization chain:

$$R - (m_1)_{x_1} - (m_2)_{y_1} - (m_1)_{x_2} - (m_2)_{y_2} - \cdots$$

where x_1 and y_1 are integers that may assume values equal or higher than unity.

If x_1 and y_1 are always equal to 1, the monomeric units alternate regularly and the polymer will show a regular chemical structure. In the case where a regularity of steric structure also occurs, the polymer is crystallizable.[7]

By adopting particular copolymerization conditions, it is also possible to obtain copolymers having high values
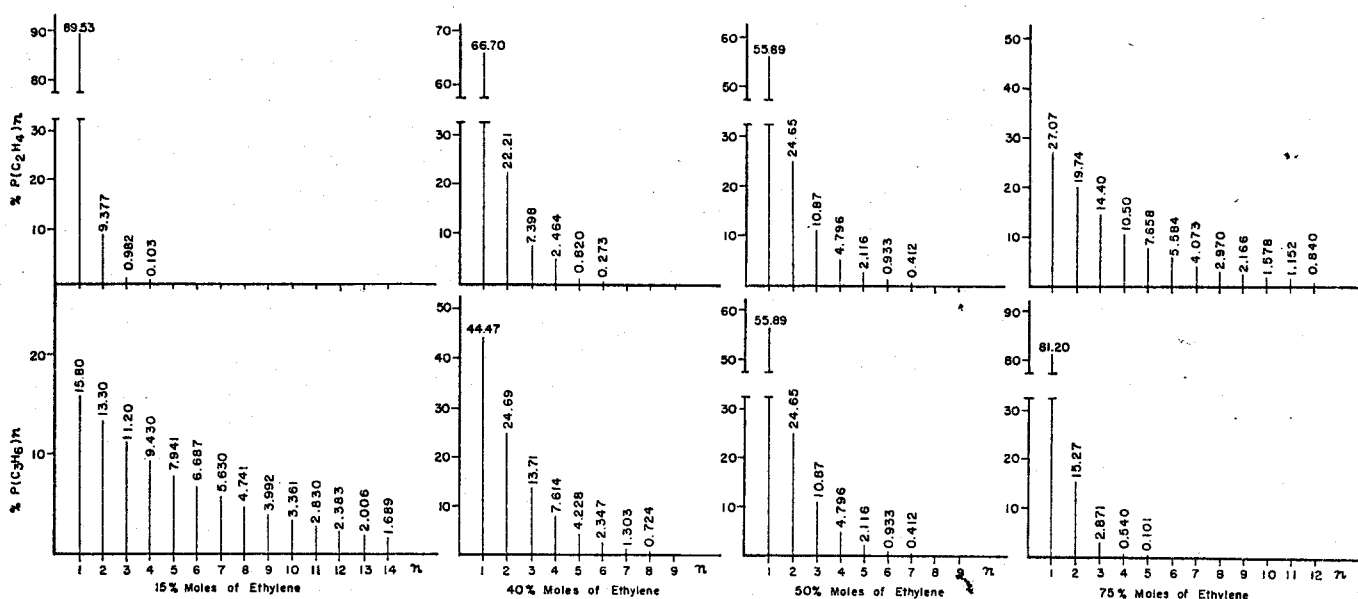
FIGURE 3—Distribution function of sequences of different lengths in ethylene-propylene copolymers, having different compositions and prepared with $Al(C_6H_{13})_3$-VCl_4 catalyst.

of x_1 and y_1 that the crystallization of the sterically ordered m_1 and m_2 sequences is possible (block copolymers).[8,9]

Therefore, depending on the average values of x_1 and y_1, the physical properties can be different, even when comparing polymers with an identical over-all composition.

The distribution of the monomeric units must be necessarily determined for a complete characterization of the copolymerizate.

The method of calculation, indicated by Alfrey and Goldfinger[10] was applied to the EP copolymerization, carried out in the presence of catalysts prepared from transition metal compounds and organic aluminum compounds.

The values thus obtained of the distribution functions for the sequences well agree with the values deduced experimentally from both IR and X-ray analyses.[11]

Distribution of Monomeric Units. By indicating with V_{11}, V_{12}, V_{21} and V_{22} the rates of the four propagation reactions that occur in the copolymerization of two m_1 and m_2 monomers, one obtains:

$$V_{11} = k_{11} [M_1^*] [M_1^*]$$
$$V_{12} = k_{12} [M_1^*] [M_2^*]$$
$$V_{21} = k_{21} [M_2^*] [M_1]$$
$$V_{22} = k_{22} [M_2^*] [M_2]$$

$[M_1^*]$ and $[M_2^*]$ indicate the concentrations of the growing polymeric chains having an m_1 or m_2 monomeric unit respectively at their end. $[M_1]$ and $[M_2]$ are the concentrations of the two monomers. The probability that a sequence of m_1 units contains n members is:

$$P(m_1)_n = P_{11}^{(n-1)} (1 - P_{11}) = \left(\frac{1}{1+\frac{1}{r_1 F}}\right)^{n-1} \frac{1}{1 + r_1 F}$$

Similarly:

$$P(m_2)_n = P_{22}^{(n-1)} (1 - P_{22}) = \left(\frac{1}{1+\frac{F}{r_2}}\right)^{n-1} \frac{1}{1 + \frac{r_2}{F}}$$

where

$$r_1 = \frac{k_{11}}{k_{12}}; \quad r_2 = \frac{k_{22}}{k_{21}} \text{ and } F = \frac{[M_1]}{[M_2]}.$$

These values represent the fraction of all the m_1 sequences (or m_2 respectively) formed by n members.

TABLE 2—Distribution function of sequences of different length in ethylene-propylene copolymers having different compositions and prepared with $Al(C_6H_{13})_3$ - VCl_4 catalyst—

Mole Percent of M_1 in the Copolymer	PERCENT P $(m_x)_n$									
	n = 1	n = 2	n = 3	n = 4	n = 5	n = 6	n = 7	n = 8	n = 9	n ≥ 15
85	15.80	13.20	11.20	9.430	7.941	6.687	5.630	4.741	3.992 for n between 10 and 14, P(mx)n = 12.271%	9.006
75	27.07	19.74	14.40	10.50	7.658	5.584	4.073	2.970	2.166 for n between 10 and 14, P(mx)n = 4.631%	1.204
60	44.47	24.69	13.71	7.614	4.228	2.347	1.303	0.724	for n between 9 and 14, P(mx)n = 0.762%	0.142
50	55.89	24.65	10.87	4.796	2.116	0.933	0.412	....	for n between 8 and 14, P(mx)n = 0.324%	0.003
40	66.70	22.21	7.398	2.464	0.820	0.273	....	....	for n between 7 and 14, P(mx)n = 0.136%	1.10⁻³
25	81.20	15.27	2.871	0.540	0.101	....	....	....	for n between 6 and 14, P(mx)n = 0.023%	1.10⁻³
15	89.53	9.377	0.982	0.103	....	....	....	....	for n between 5 and 14, P(mx)n = 0.012%	1.10⁻³

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

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

$$F = \frac{f - 1 + \sqrt{(f-1)^2 + 4r_1 r_2 f}}{2r_1}$$

(which can be obtained from the copolymerization equation of Lewis and Mayo,[12] written as proposed by Fineman and Ross[13]) new expressions of the sequence distribution functions are obtained that result in a function of only the $r_1 r_2$ product.

Table 2 and Figure 3 show the values of the distribution functions P for sequences of different length for EP copolymers of different composition, obtained with the aid of the $VCl_4 - Al$ $(C_6H_{13})_3$ catalytic system.[11]

By comparing the values of the distribution functions for the monomeric units, which should be present in copolymers for which the $r_1 r_2$ product ranges from 0.1 to 10, it can be easily observed[11] that the distribution of the monomeric units of the EP copolymers, obtained with the aid of the $VCl_4 - AlR_3$ catalytic system, does not differ considerably from the random distribution that can be foreseen for copolymers in which the $r_1 r_2$ product is equal to unity.

From the data reported above, it is possible to conclude that:

1. The probability of existence of long sequences of ethylene, or of propylene respectively, increases with the increase of the content of the considered monomer in the copolymer.

2. The highest dispersion in the lengths of sequences of both monomers takes place for copolymers containing equimolecular amounts of ethylene and propylene.

3. Ethylene sequences that are long enough to be crystallizable, containing, for instance, at least 15 monomeric units, may in practice exist only for ethylene contents of 80 mole percent in the copolymer.

4. The distribution of monomeric units in the EP copolymers, obtained with the aid of catalysts acting through an anionic coordinated mechanism, is practically independent of the catalytic system adopted. In fact, the $r_1 r_2$ product of the EP copolymerization, in the presence of different catalytic systems is always very near 1,[14,15] and the distribution of the monomeric units is a function only of the $r_1 r_2$ product and not of the single values of r_1 and r_2.

Experimental Verification has been tried to confirm the values of the distribution functions for the sequences deduced from the statistical theory outlined above.

The first verification is given by the absence of crystallinity of the polyethylenic type in copolymers containing up to 80 mole percent of ethylene.[11] This agrees with
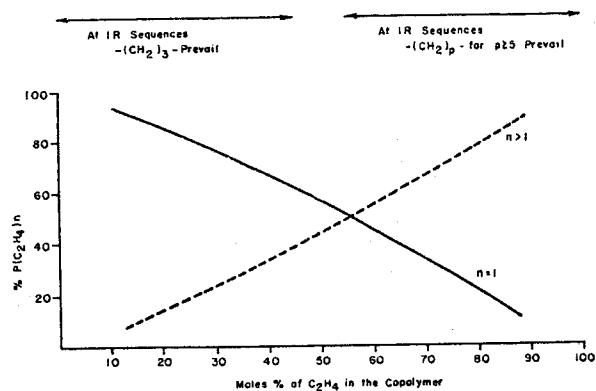
FIGURE 4—Experimental values as compared with theoretical values for sequence lengths in ethylene-propylene copolymers from Infra Red analysis.

the values of the distribution functions for sequences reported in Table 2. In fact, only for copolymers containing more than 80 mole percent of ethylene, does the $P_{(C_2H_4)_n}$ value (with $n > 15$) reach significant values.

A further experimental verification is based on the IR analysis. In fact the wide absorption between 13.4 and 13.8 μ which can be ascribed to sequences of methylenic groups of different length is originated by three bands respectively at 750, 731, 724 cm^{-1}. The one with a lower frequency can be ascribed to sequences formed by 5 or more than 5 methylenic groups, whereas the two bands with a higher frequency can be ascribed to sequences formed by less than 5 methylenic groups.[16]

From an examination of the intensity of the absorption maxima, it is possible to state that for copolymers containing less than 45 moles percent of ethylene, the sequences of less than five methylenes (band at about 731 cm^{-1}) prevail, with respect to those of 5 or more, whereas for copolymers containing more than 55 mole percent of ethylene, most of the methylenic sequences have a length equal to 5 or more units.

As was previously described, the polymerization of propylene with catalysts acting with anionic coordinated mechanism, takes place by insertion of the monomer molecules in a metallorganic bond and the subsequent monomeric units orient themselves in such a way that the tertiary carbon atom is at the side of the growing chain, whereas the methylenic group is on the side of the catalyst.[17]

By operating in such a way that this mechanism is valuable also for ethylene-propylene copolymerization, the chemical structure of the resulting copolymers corresponds to the formula:

$$- CH - CH_2 - (CH_2 - CH_2)_n - CH - CH_2$$
$$\quad | \qquad\qquad\qquad\qquad\qquad | $$
$$\quad CH_3 \qquad\qquad\qquad\qquad\quad CH_3$$
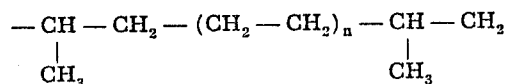
For $n = 1$ there is just one ethylene molecule, situated between two units of propylene (polymerized head-to-tail, with respect to one another), which gives rise to a sequence of 3 methylenes, and for $n = 2$ (or more than 2) there are sequences of 5 methylenes (or more than 5).

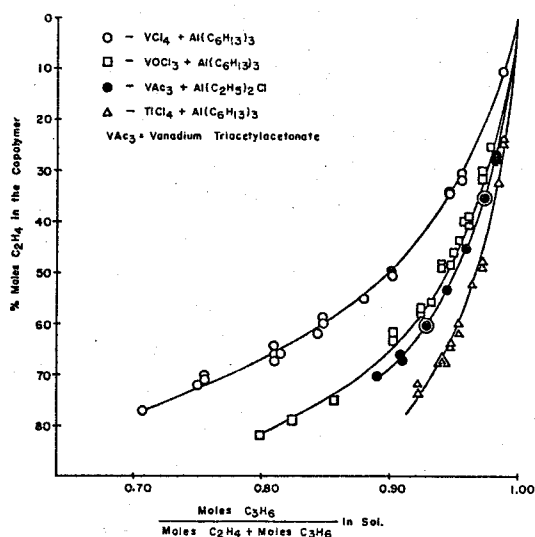Therefore the calculated probability of existence of

FIGURE 5—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.
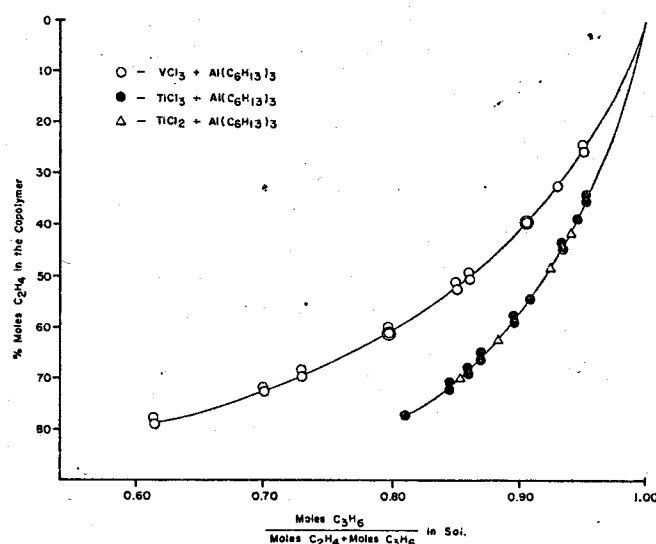

FIGURE 6—Composition of ethylene-propylene copolymers plotted against the ratio between the moles of dissolved propylene and the total moles of the two monomers in solution from different catalytic systems, prepared from hydrocarbon insoluble transition metal halides.

sequences of one ethylene monomeric unit shall be compared with the content of sequences of three methylenic groups, deduced from the IR experimental measure.

The sequences of two or more than two ethylene molecules should correspond to those of 5 (or more than 5) methylenic groups. The comparison of the calculated values with those deduced from the measurements by means of the IR spectrography show a very good agreement (see Figure 4).

MONOMER REACTIVITY RATIOS IN THE COPOLYMERIZATION

The monomer reactivity ratios has been determined by carrying out the copolymerization tests in the presence of n-heptane as a solvent, at temperatures between — 20 and + 75°C. The monomer mixture was circulated continuously through the reactor at high space velocity, so as to have a low conversion of each monomer per pass.[4]

As previously published[14, 15, 18, 19, 20] we have found that the EP copolymer composition is independent of the following factors:

1. Time elapsed between the preparation of the catalyst and its use

2. Catalyst concentration

3. Ratio between the moles of alkyl aluminum and the moles of transition metal compound used in the preparation of the catalyst.

The composition of the copolymers is, on the contrary, highly influenced by the feed composition and, for a certain feed, changes with the employed catalyst (see Figures 5 and 6).

The catalytic systems most suitable for the production of EP copolymers are those prepared from hydrocarbon-soluble vanadium compounds. By using halogen containing vanadium compounds (as $VOCl_3$, VCl_4), it is

possible to employ either trialkyl aluminum compounds or halogen containing alkyl aluminum compou.ds in the catalyst preparation.

On the contrary, by using halogen free vanadium compounds (as vanadium triacetylacetonate, vanadyl trialcoxide), the presence of a halogen in the alkyl aluminum compound is necessary to obtain catalysts capable of promoting the EP copolymerization.[9, 20]

TABLE 3—Monomer reactivity ratios in the ethylene-propylene copolymerization, in the presence of different catalytic systems

Catalytic System	$r_{C_2H_4}$	$r_{C_3H_6}$	References
VOCl₃ + Al(C₆H₁₃)₃	17.95	0.065	(18)
VCl₄ + Al(C₆H₁₃)₃	7.08	0.088	(19)
VCl₃ + Al(C₆H₁₃)₃	5.61	0.145	(14)
VAc*₃ + Al(C₂H₅)₂Cl	15.0	0.04	(20)
TiCl₄ + Al(C₆H₁₃)₃	33.36	0.032	(15)
TiCl₃ + Al(C₆H₁₃)₃	15.72	0.110	(15)
TiCl₂ + Al(C₆H₁₃)₃	15.72	0.110	(15)

* VAc₃ = Vanadium triacetylacetonate.

In Table 3, the values of the reactivity ratios in EP copolymerization carried out in the presence of different catalytic systems are reported. The reactivity ratio of ethylene is always much higher than that of propylene and the product of the reactivity ratios is always very near 1. This is in agreement with what generally happens in ionic polymerization.[21, 22, 23]

The values of the reactivity ratios have been calculated by the methods of Fineman and Ross[13] and Lewis and Mayo.[12] These methods derive from the copolymerization equation proposed by Alfrey and Goldfinger,[10] Mayo and Lewis[12] and Wall.[24] When applying this equation, the reactivity of a monomer with respect to a growing chain is supposed to depend only on the last chain unit. The good results obtained confirm that also for EP copolymerization this assumption is valid. Some authors[25] have proposed copolymerization equations which take into account

a possible contribution of the penultimate unit (or of still preceding units) but up to now, such a contribution has never been demonstrated as experimentally noticeable.[22] In the particular case of ionic copolymerizations the reactivity of a monomer with respect to a growing chain is independent also of the last chain unit and depends only on the nature of the monomer.[21,26,27] In other words, the ratio between the reactivities of two monomers with respect to a growing chain should be constant, independently of the last chain unit.

Besides the reactivity ratios for EP copolymerization, also those concerning the ethylene-butene-1 copolymerization, in the presence of different catalytic systems, have been determined.[28] Their values are reported in Table 4.

TABLE 4—Monomer reactivity ratios in the ethylene-butene-1 copolymerization.

Catalytic System	$r_{C_2H_4}$	$r_{C_4H_8}$
VCl₄ + Al(C₆H₁₃)₃	29.60	0.019
VCl₃ + Al(C₆H₁₃)₃	26.96	0.043

LITERATURE CITED

[1] G. Natta, Rubber and Plastics Age, 38, 6 (1957).
[2] G. Natta, Experientia, Suppl. VII, 21 (1957).
[3] F. Danusso, and G. Pajaro, J. Polymer Science, 22, 179 (1956).
[4] G. Natta, G. Mazzanti, A. Valvassori and G. Pajaro, Chimica e Industria (Milan), 39, 733 (1957).
[5] P. E. Wei, Anal. Chem., 33, 215 (1961).
[6] T. Gössel, Makromol. Chemie, 42, 1 (1960).
[7] G. Natta, G. Dall'Asta, G. Mazzanti, I. Pasquon, A. Valvassori and A. Zambelli, J. Am. Chem. Soc,. in press.

[8] G Natta, J. Polymer Science, 34, 531 (1959).
[9] G. Bier, Angewandte Chemie, 73, 186 (1961); G. Bier, G. Lehman, J. Lengering, Makromol. Chemie, 44, 347 (1961).
[10] T. Alfrey and G. Goldfinger, J. Chem. Phy., 12, 205 (1944).
[11] G. Natta, G. Mazzanti, A. Valvassori, G. Sartori and D. Morero, Chimica e Industria (Milan), 42, 125 (1960).
[12] F. M. Lewis and F. R. Mayo, J. Am. Chem. Soc., 66, 1594 (1944).
[13] N. Fineman and S. D. Ross, J. Polymer Science, 5, 269 (1950).
[14] G. Natta, G. Mazzanti, A. Valvassori and G. Sartori, Chimica e Industria (Milan), 40, 717 (1958).
[15] G. Natta, A. Valvassori, G. Mazzanti and G. Sartori, Chimica e Industria (Milan), 40, 896 (1958).
[16] H. L. McMurry and V. Thornton, Anal. Chem., 24, 318 (1952).
[17] G. Natta, P. Pino, E. Mantica, F. Danusso, G. Mazzanti, M. Peraldo, Chimica e Industria (Milan), 38, 124 (1956).
[18] G. Mazzanti, A. Valvassori and G. Pajaro, Chimica e Industria (Milan), 39, 743 (1957).
[19] G. Mazzanti, A. Valvassori and G. Pajaro, Chimica e Industria (Mlian), 39, 825 (1957).
[20] G. Natta, G. Mazzanti, A. Valvassori, G. Sartori and D. Fiumani, J. Polymer Science, in press.
[21] P. J. Flory, "Principles of Polymer Chemistry" Cornell University Press, p. 227 (1953).
[22] F. R. Mayo and C. Walling, Chem. Rev., 46, 19 (1950).
[23] D. C. Pepper, Quart. Reviews, 8, 117 (1954).
[24] F. T. Wall, J. Am. Chem. Soc., 66, 2050 (1944).
[25] E. Merz, T. Alfrey and G. Goldfinger, J. Polymer Science, 1, 75 (1946).
[26] Y. Landler, J. Polymer Science, 8, 63 (1952).
[27] G. Mazzanti, A. Valvassori, G. Sartori and G. Pajaro, Chimica e Industria (Milan), 42, 468 (1960).
[28] G. Natta, G. Mazzanti, A. Valvassori and G. Pajaro, Chimica e Industria (Milan), 41, 764 (1959).
[29] G. Moraglio, Chimica e Industria (Milan), 41, 984 (1959).
[30] G. Natta, G. Crespi, Chimica e Industria (Milan), 41, 123 (1959).
[31] G. Natta, G. Crespi, Rubber Age, 87, 459 (1960).
[32] G. Natta, G. Crespi, Rev. Gen. du Caoutchouc, 37, 1003 (1960).
[33] G. Crespi, unpublished data.
[34] G. Natta, G. Crespi, M. Bruzzone, Kautchuk und Gummi, 14, 3, 54 (1961).
[35] G. Natta, G. Crespi, M. Bruzzone, Chimica e Industria (Milan), 42, 463 (1960).
[36] G. Crespi, M. Bruzzone, Chimica e Industria (Milan), 41, 741 (1959).
[37] G. Crespi, M. Bruzzone, Chimica e Industria (Milan), 43, 137 (1961).
[38] E. Di Giulio, G. Ballini, Deutsche Kautschuk Gesellschaft Congress, Berlin 4-7 October 1960.
[39] G. Natta, G. Crespi, G. Mazzanti, A. Valvassori, G. Sartori, and P. Scaglione, Rubber Age, 45, 636 (1961).

About the Authors

Natta   Sartori

Valvassori   Mazzanti   Crespi

Giulio Natta is director of the Institute of Industrial Chemistry, Polytechnic Institute of Milan, Italy. Dr. Natta joined the Institute in 1938 coming from the University of Rome where he had been professor of physical chemistry. Prior to that he had been professor of general chemistry at the University of Pavia. Dr. Natta is well known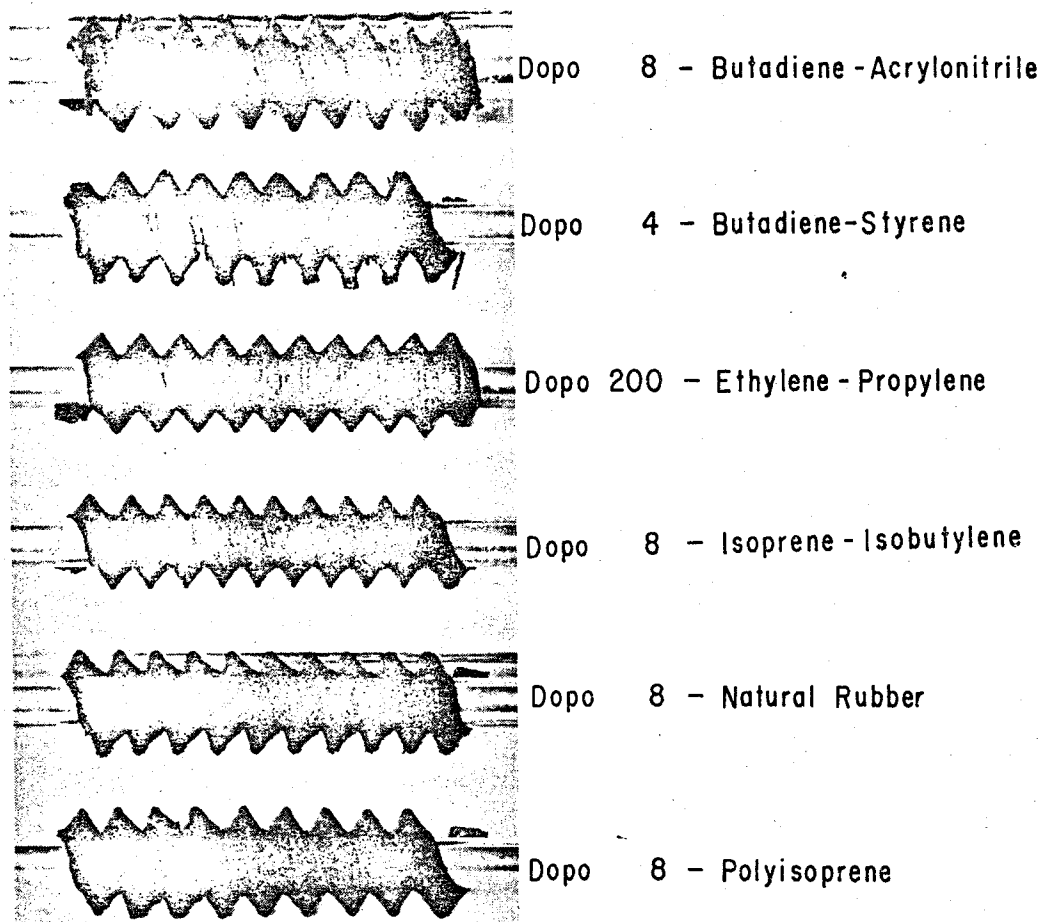 for his work in determination of crystal structures of inorganic and organic compounds, particularly of high polymers. It was Dr. Natta who coined the terms "isotactic," "syndiotactic" and "atactic" to define the special structures obtained by means of his stereospecific catalysts.

Guido Sartori is with Montecatini S.p.A., Milano, Italy, and does research in the field of olefin polymerization, particularly of ethylene-alpha-olefin copolymerization. Since 1957 he has been in the hydrocarbon department of the research division specializing in the field of macromolecular chemistry. He received his degree in chemistry from the University of Pavia.

Alberto Valvassori is with Montecatini S.p.A., Milano, Italy, and does research in the field of olefin polymerization. Since 1955 when he joined the research division of the hydrocarbon department he has specialized in the field of macromolecular chemistry research. He received his degree in chemistry from the University of Pavia.

Giorgio Mazzanti is with Montecatini in Milano. In addition to his position in the hydrocarbons division research department with Montecatini he is also assistant professor at the Institute of Industrial Chemistry of Milan's Polytechnic. He has always been engaged in the field of stereospecific polymerizations. Dr. Mazzanti holds a doctor's in chemistry and a professor in industrial chemistry.

Giovanni Crespi is with Montecatini S.p.A., Milano, and is engaged in the evaluation of the physical properties of new polymers and research on the vulcanization of new types of rubbers. Dr. Crespi received his Ph.D. in chemical engineering from the Polytechnic Institute of Milan.

Dopo	8	Butadiene-Acrylonitrile
Dopo	4	Butadiene-Styrene
Dopo	200	Ethylene-Propylene
Dopo	8	Isoprene-Isobutylene
Dopo	8	Natural Rubber
Dopo	8	Polyisoprene

Notice the stability of ethylene-propylene and isoprene-isobutylene in 150 ppm ozone as compared to four other common elastomers.

New Ethylene-Propylene Elastomers

Part 1: Characterization, constitution, analysis, and monomer distribution
Part 2: Viscoelastic behavior and Vulcanization

Giulio Natta, Guido Sartori, Alberto Valvassori, Giorgio Mazzanti, Giovanni Crespi
Polytechnic Institute of Milan, Milan, Italy

PART 1 DISCUSSED methods of proving the structure and characterization of ethylene-propylene copolymers. Also methods of analysis and proof of monomer distribution were shown. Catalysts systems and copolymers resulting from different monomer compositions were shown. Part 2 will show the elastomer properties of EP copolymers and discuss methods of vulcanization.

Viscoelastic Behavior of Copolymers. High molecular weight ethylene-propylene EP copolymers are typical rubber-like substances having a behavior similar to that of the best known synthetic elastomers. Their elastic-viscous properties are connected with the intrinsic properties of the macromolecular chains of the copolymer itself. The main parameters influencing these properties are:

1. Average molecular weight of the copolymer

2. Distribution of molecular weights

3. Average chemical composition

4. Homogeneity of such composition.

The molecular weight of a copolymer can be determined by measuring the intrinsic viscosity in various solvents. From measurements in tetralin at 135°C. and knowing the chemical composition of the copolymer,[29] it is possible to determine the average molecular weight.

The viscosity of a copolymer and, therefore, its processability depend on its average molecular weight and on the distribution of molecular weights. High molecular weight copolymers are difficult to process, owing also to the fact that they do not undergo the usual degradation during the processing operations. It is therefore necessary to produce, directly in the polymerization step, copolymers having a molecular weight suitable for a good processability and having good mechanical and elastic properties after vulcanization.

Processability is also influenced by the distribution of molecular weights; the average molecular weight being equal, copolymers containing high molecular weight fractions are difficult to process.

Furthermore the crude copolymers containing fractions with high ethylene content (higher than 75 mole percent)
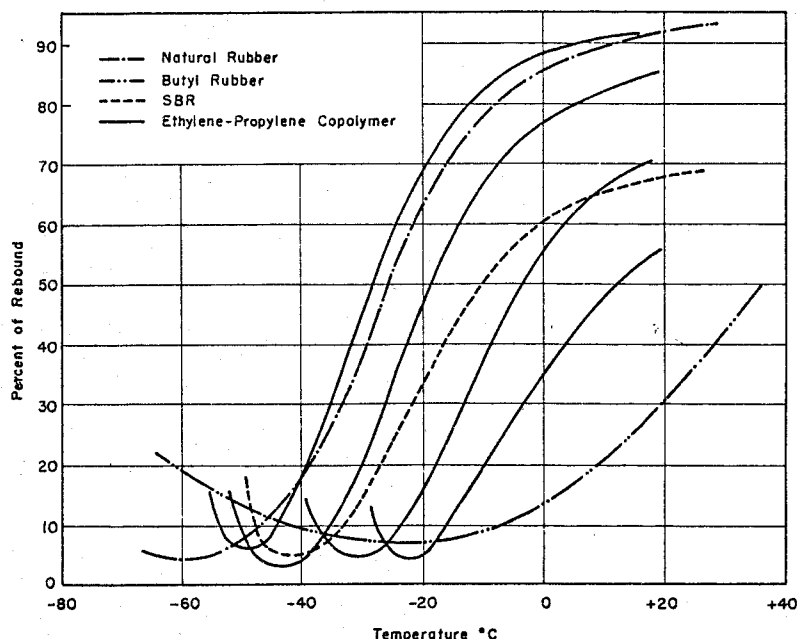
FIGURE 7—Rebound versus temperature curves for different types of rubbers with ethylene-propylene copolymers shaded.

FIGURE 8—High ethylene content in the EP copolymer results in these rebound versus temperature curves.

can be hardly processed even if their average molecular weight is low enough; this is due to the fact that the high ethylene content fractions do not behave as an elastomeric material.

As already reported,[30,31] the average chemical composition of the copolymer exerts its influence mainly on the dynamic properties of the elastomer and on its 2nd order transition temperature.

By increasing the total ethylene content in the copolymers, within the limits allowed to avoid crystallization, the number of the chain sections formed by methylene groups increases; thus an increase of the overall flexibility of the macromolecules and an improvement of the dynamic properties of the elastomer derive from it.

Figure 7 shows the rebound vs. temperature curves for different types of rubbers, compared with the field covered (shaded region) by the EP copolymers, having an ethylene content ranging from 30 to 70 mole percent. As may be seen, it is possible to obtain copolymers showing a dynamic behavior similar to that of natural rubber, whereas copolymers having a lower ethylene content, have a resilience lower than that of butadiene-styrene rubber (SBR).

TABLE 5—Fractionation of ethylene-propylene copolymer.
Data of raw copolymer: $[\eta]* = 1.65$ dl/g; C_2H_4
Mole Content $= 57\%$

Fraction N	Weight	Percent Ethylene In Moles	$[\eta]*$ dl/g	$\overline{M}_v$
I	0.175	61	1.90	132.000
II	0.115	59	....	......
III	0.120	59	1.43	91.000
IV	0.131	58	....	......
V	0.123	57	1.04	58.000
VI	0.097	57	....	......
VII	0.074	55	0.74	39.000
VIII	0.118	55	....	......
	$\Sigma W_i = 0,953$			

$[\eta]*$ = Intrinsic viscosity in tetralin at 135° C.

The rebound vs. temperature curves, beside furnishing data on the dynamic properties, also give useful information on the nature of the copolymers. In fact, as mentioned before,[11] when increasing the ethylene content beyond certain limits (75-80 mole percent), it is possible to obtain long sequences of methylene groups that cause an anomalous behavior of the copolymer, at least within certain ranges of temperature.[32]

Figure 8 shows the rebound-temperature curves for two copolymers containing 86 and 80 mole percent of ethylene respectively.

It is possible to observe that the minimum rebound value is higher than that usually found (3-7 percent) in the copolymers having a good elastomeric behavior. Furthermore the minimum rebound temperature for copolymers of high ethylene content does not correspond to that foreseeable on the basis of the ethylene molar content.[32]

An analogous phenomenon is also observed in chlorinated linear polyethylene having chlorine contents lower than 30 percent by weight. In fact, in these cases, the chlorine introduced is not sufficient to completely destroy the crystallinity of polyethylene, since long sequences of methylene groups remain along the chain.[33] With regard to copolymers having an homogeneous chemical composition and ethylene molar contents lower than 75 percent, the rebound-temperature curve is similar to that of the most known elastomers, since crystallinity does not appear even at very low temperatures.

An anomalous behavior of the rebound vs. temperature curves is also observed when the copolymer contains only one fraction having a high ethylene content. Figure 9 shows the rebound vs. temperature curves for two copolymers having the same average chemical composition (67 mole percent of ethylene); however curve I refers to a homogeneous copolymer, whereas curve II refers to a non-homogeneous copolymer. By fractionating the latter, two fractions are obtained that show the rebound
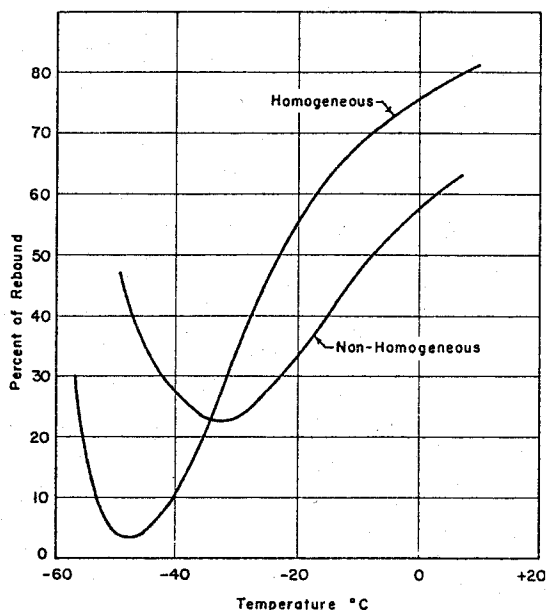
FIGURE 9—Rebound versus temperature curves for a homogeneous and a non-homogeneous copolymer each containing 67 mole percent ethylene.
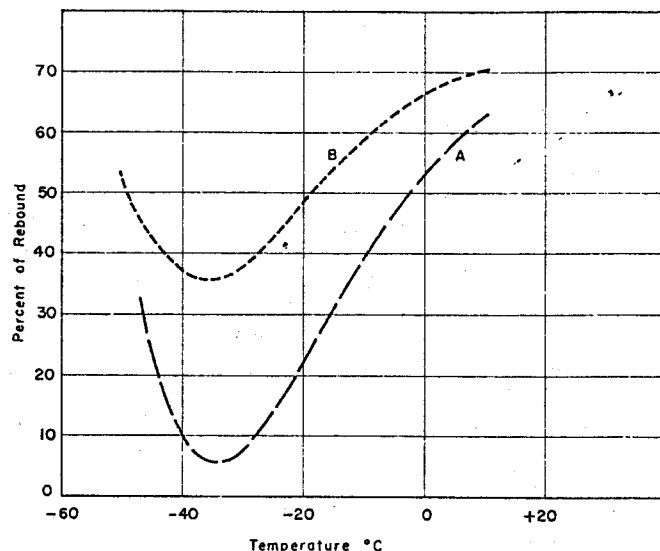

FIGURE 10—These rebound versus temperature curves are for two fractions obtained from a non-homogeneous copolymer containing 67 mole percent ethylene. Curve A is for a fraction containing 49 mole percent ethylene and Curve B for a fraction containing 86 mole percent ethylene.
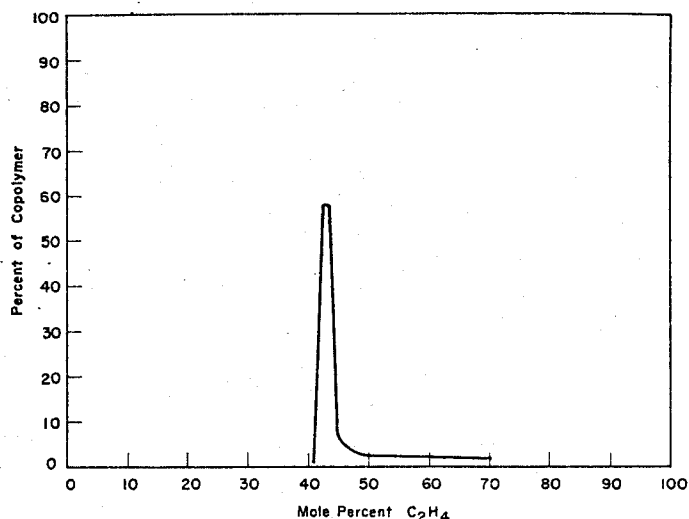

FIGURE 11—Distribution curve for an ethylene-propylene copolymer containing 45 mole percent ethylene.

curves reported in Figure 10; curve A is due to the fraction containing 49 mole percent of ethylene, curve B is due to the fraction containing 86 mole percent of ethylene.

The regularity of distribution of chemical composition for a copolymer can be determined by extraction with solvents or by fractionated precipitation. When operating under suitable polymerization conditions and using proper catalysts, it is possible to obtain copolymers that show only a limited dispersion in their chemical composition (Table 5). Figure 11 shows the distribution curve of the composition for a copolymer containing 45 mole percent of ethylene in the crude copolymer. As may be seen from this curve, the distribution of compositions is rather narrow.

The influence exerted by the dispersion of the composition upon the viscoelastic properties appears to be
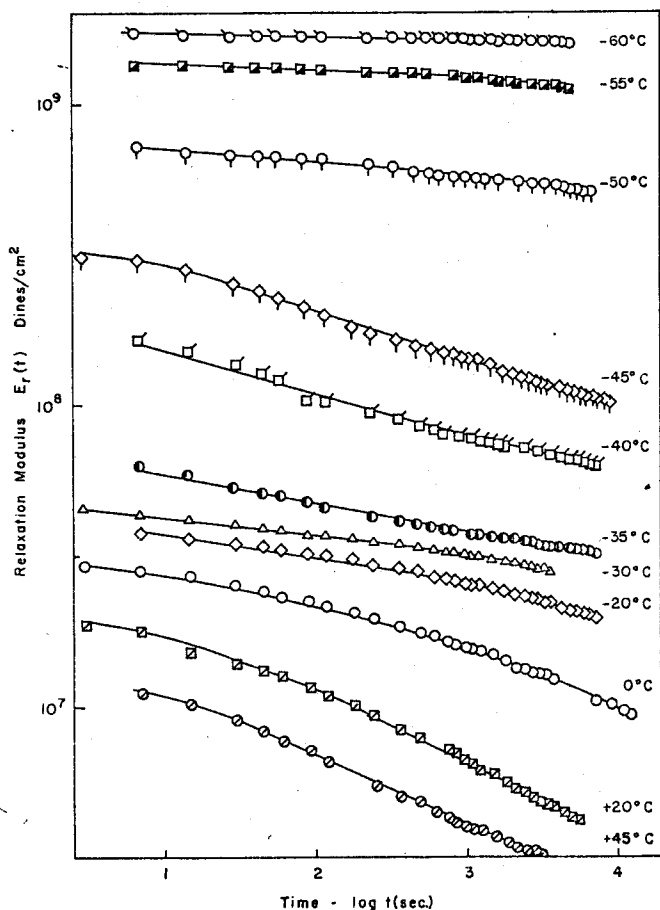

FIGURE 12—Relaxation modulus of an ethylene-propylene copolymer (40 mole percent ethylene) versus time.

important only in the case that crystallizable chain segments are present. In fact, our experiments prove that the properties of non-crystallizable copolymers consisting of different macromolecules, differing from each other in chemical composition by about 10-15 percent, do not

Chlorine Content Percent by Weight	Sulfur Content Percent by Weight	Intrinsic Viscosity dl/g	PROPERTIES OF VULCANIZATES				
			Tensile Strength kg/cm²	Elongation At Break Percent	Modulus At 200 Percent kg/cm²	Hardness Shore A	Resilience At 20°C Percent
10.8	2.1	0.70	200	530	55	..	50
4.4	1.0	1.54	200	620	39	64	58
2.3	0.6	2.25	205	775	31	57	61

```
Recipe
Chlorosulfonated copolymer.....................100
PbO.............................................40
Colophony .......................................5
Vulcafor MBT....................................2
Vulcanization 150° C x 30 min.
```

differ in practice from the properties of more homogeneous copolymers.

The relaxation modulus vs. time measured at different temperatures is reported in Figure 12.[34] As may be seen in this figure, the modulus at —60°C. assumes values of the order of 10^9 dine/cm,² which are considerably lower than those of a polymer in the vitreous state $(10^{10}—10^{10.5}$ dine/cm²$)$; the brittle temperature is, in fact, —100°C. for a copolymer containing 50 mole percent ethylene.

VULCANIZATION

Owing to the absence of unsaturation and to the lower reactivity of the hydrogen atoms bound to tertiary carbons in comparison with that of allylic hydrogen, vulcanization of chemically non-modified ethylene-alpha-olefin copolymers, and in particular of EP copolymers, cannot be carried out with the aid of ingredients usually employed for unsaturated rubbers.

The problem of transforming copolymers in cured rubbers was at first faced using methods similar to those already employed in the case of polyethylene.

Here we want to point out briefly some crosslinking methods studied for EP copolymers and the main properties of the vulcanizates obtained.

We will finally indicate the possibility of preparing terpolymers having a low unsaturation content. Following this way, sulfur-vulcanizable elastomers have been obtained which still substantially possess the elastomeric properties of EP copolymers.

Crosslinking of chlorosulphonated copolymers.
Crosslinking after chlorosulphonation has been applied to the EP copolymers by modifying the chlorosulphonation process substantially with respect to what is already known in the case of polyethylene. The chlorine content introduced in the copolymer amounts to only 2-3 percent by weight with the simultaneous introduction of chlorosulphonic groups in a number sufficient for a good vulcanization.[35] This restriction in the introduction of chlorine and of chlorosulphonic groups is made possible by the following factors:

TABLE 8—Aging properties of vulcanized ethylene-propylene copolymers

	Properties Before Ageing	Properties After Ageing	
		70h at 150° C	288h at 150° C
Tensile strength kg/cm²......	310	270	175
Elongation at break %......	600	530	469
Modulus at 300% kg/cm²....	80	100	98
Hardness Shore A..........	69	64	71
Resilience at 20° C %.......	73	72	72

RECIPE				PROPERTIES OF VULCANIZATES				
Stearic Acid phr	Zinc Oxide phr	Dutrex R 55 phr	EPC Carbon Black phr	Tensile Strength kg/cm²	Elongation At Break Percent	Modulus At 300 Percent kg/cm²	Hardness Shore A	Resilience At 20° C Percent
4	2.5	..	..	130	520	45	57	83
4	2.5	5	45	415	520	150	73	71
4	2.5	10	45	390	650	85	73	70
2	2.5	5	45	305	550	130	72	74
2	2.5	10	45	395	650	93	70	73

Vulcanization 160° C x 30 min.

(a) the copolymer is completely amorphous and (b) its molecular weight is high enough to require just a limited number of reactive groups for vulcanization.

Table 6 shows the main properties of the copolymers having a decreasing chlorine and sulfur content, after vulcanization with metal oxides. It can be observed that an increase in the chlorine and sulfur content causes a progressive increase of the modulus at 200 percent, a decrease of the elongation at break and of resilience.

Vulcanization of the Copolymers Grafted With Acid Monomers.
The mechanical properties of EP copolymers are improved if small amounts of unsaturated substances containing acid functions and of polyvalent metal oxides are added to the compound.

Also studied was the possibility of grafting small amounts of acid monomers (maleic anhydride, maleic acid) on the copolymer chain, by reacting the acid monomer on the copolymer in the presence of radicalic initiators.[34]

The grafted copolymer may be easily cured with the aid of only zinc oxide and yields vulcanizates showing good mechanical and elastic properties (Table 7). In this type of vulcanization scorching phenomena can be observed. These last can be limited or eliminated by adding small amounts of acid compounds to the recipe. Resistance to aging and to high temperatures of these vulcanizates is very high, as may be seen from the data of Table 8.

Vulcanization of Chlorinated Copolymers.
The copolymers chlorinated up to a chlorine content of 16-20 percent by weight, may be cured with the aid of the recipes usually employed for elastomers having a low degree of unsaturation, taking advantage of the partial dehydrochlorination occurring during vulcanization.[36] The

TABLE 9—Influence of reinforcing fillers (MPC carbon black)

Cl Percent By Weight	MPC Carbon Black	Tensile Strength (kg/cm²)	Elongation At Break Percent	Modulus at 300 Percent (kg/cm²)	Modulus at 500 Percent (kg/cm²)
5.24	0	72	845	11.5	17.0
5.24	30	297	820	37.0	97.0
8.40	0	72	625	14.5	26.0
8.40	30	305	695	55.0	152.0
16.98	0	203	700	16.0	36.5
16.98	30	292	490	116.0	....

```
Recipe:  chlorinated copolymer............100
         Stearic acid........................2
         ZnO................................15
         S...................................2
         Vulcafor-TMT........................2
         Vulcafor-MBT........................1
         Carbon black.............. As Indicated
Vulcanization 160° C x 30 minutes
```
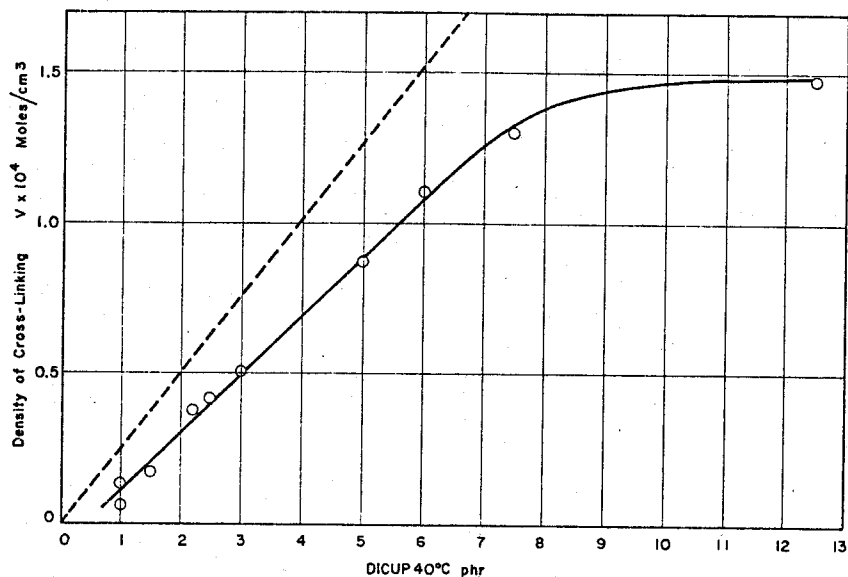
FIGURE 13—When various quantities of DICUP 40° C are used to vulcanize an ethylene-propylene copolymer these cross-linking densities result.
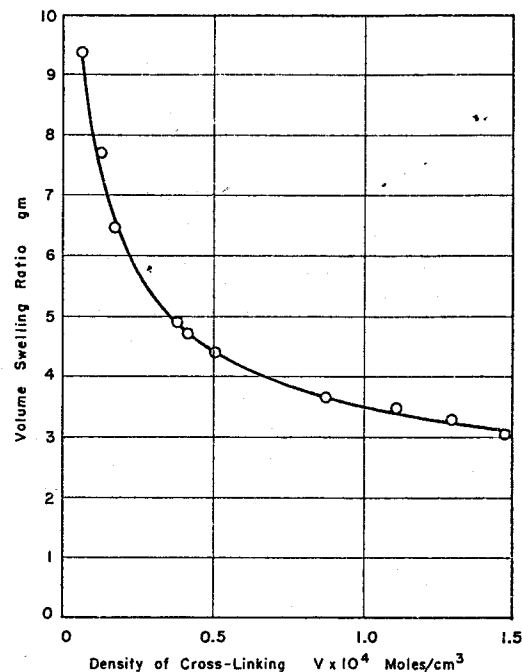

FIGURE 14—Volume swelling ratio in benzene at 25°C for an ethylene-propylene copolymer cross-linked by DICUP 40° C as a function of density of cross-linking.
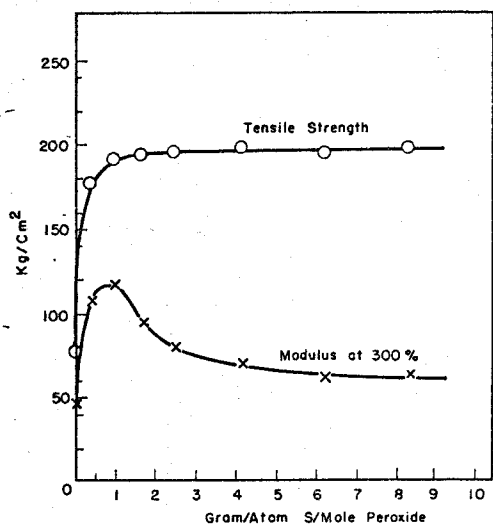

FIGURE 15—Effect of sulfur on tensile strength and modulus of an ethylene-propylene copolymer vulcanized with peroxides and sulfur.
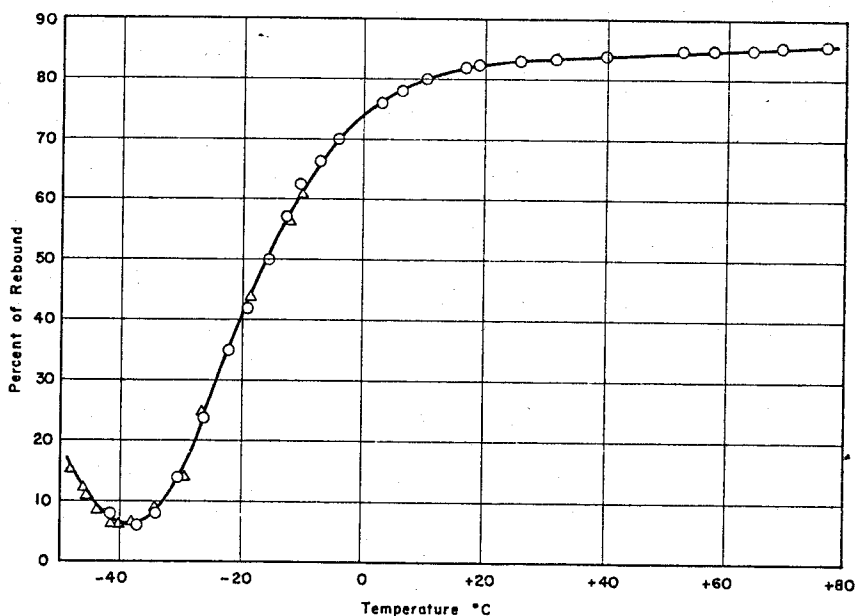

FIGURE 16—Typical rebound curve versus temperature of a vulcanized ethylene-propylene copolymer containing double bonds.

chlorine content in the copolymer must be high enough in order to obtain a complete vulcanization, but it must not be too high, otherwise it would exert a negative influence on the dynamic properties of the elastomer.

Table 9 shows the main characteristics of these vulcanizates obtained both in the presence and in the absence of reinforcing fillers (carbon black) ; it can be observed that for chlorine contents of about 15-20 percent by weight, high tensile strengths are obtained also in the absence of reinforcing fillers.

Crosslinking of Copolymers by Organic Peroxides. Crosslinking with the aid of organic peroxides alone has been effected mainly in order to study the crosslinking yield as a function of the amount of vul-

canizing agent employed, the mechanical properties of the chain of the copolymer, and in order to determine the parameters of interaction between copolymer and solvent.[37]

The mechanical properties of these vulcanizates can reach good values if vulcanization is effected in the presence of suitable reinforcing fillers.

Figure 13 shows the crosslinking density of an EP copolymer vs. the amount of peroxide (DICUP 40° C) employed for vulcanization, whereas Figure 14 shows the swelling degree at equilibrium in benzene at 25° C vs. the crosslinking density.

Vulcanization of Copolymers With Peroxides and Sulfur. If the copolymer is cured with an organic per-

TABLE 10—Properties of the copolymers vulcanized in the absence of reinforcing fillers—vulcanization 150° C x 30 min.

| Sample N | PROPERTIES OF RAW POLYMERS | | | PROPERTIES OF VULCANIZATES | | | | | | |
	Double Bonds Content Percent	Intrinsic Viscosity	Mooney Viscosity ML 1 + 4	Tensile Strength kg/cm²	Elongation At Break Percent	Modulus At 300 Percent kg/cm²	Hardness Shore A	RESILIENCE At 20° C Percent	RESILIENCE At 90° C Percent	Q_m
1	0.65	2.06	70	60	750	10.5	65	76	76	3.68
3	1.25	1.96	66	21	550	10.0	62	75	74	3.46
4	1.45	1.63	..	24	510	11.8	56	66	72	3.43
5	1.8	1.74	51	33	465	14.5	64	76	78	3.01
6	2.2	1.55	22	22	460	12.0	58	69	71	3.57
7	2.2	1.62	35	34	460	15.2	65	80	82	3.00
8	2.8	1.80	54	25	325	21.5	68	80	86	2.78

RECIPE: zinc oxide ... 5 phr   sulphur ... 2 phr
stearic acid ... 2 phr   TMTDS ... 1 phr
antioxidant (FβNA) ... 1 phr   MBT ... 0.5 phr

TABLE 11—Properties of the copolymers vulcanized in the presence of reinforcing fillers—vulcanization 150° C x 30 min.

| Sample N | PROPERTIES OF RAW POLYMERS | | | PROPERTIES OF VULCANIZATES | | | | | |
	Double Bonds Content Percent	Intrinsic Viscosity	Mooney Viscosity ML 1 + 4	Tensile Strength kg/cm²	Elongation At Break Percent	Modulus At 300 Percent kg/cm²	Hardness Shore A	RESILIENCE At 20° C Percent	RESILIENCE At 90° C Percent
1	0.65	2.06	70	175	590	47	82	55	56
3	1.25	1.96	66	240	620	71	86	53	56
4	1.45	1.63	..	224	530	89	80	45	54
5	1.8	1.74	51	230	430	120	85	54	60
6	2.2	1.55	22	196	440	121	85	43	53
7	2.2	1.62	35	227	400	154	84	54	60.
8	2.8	1.80	54	191	280	...	90	54	64

RECIPE: zinc oxide ... 5 phr   sulfur ... 2 phr
stearic acid ... 2 phr   TMTDS ... 1.25 phr
antioxidant (FβNA) ... 1 phr   MBT ... 0.75 phr
HAF black ... 50 phr

oxide, in the presence of small amounts of sulfur, a high crosslinking yield and a remarkable improvement of the physical properties of the vulcanizates are obtained.[38]

Figure 15 shows the effect of sulfur on the main physical properties of the vulcanizate (165°C × 45 min.)[38] One can observe that the modulus at 300 percent increases rapidly up to a concentration of 0.2 percent of sulfur; beyond this limit, an increase of sulfur concentration causes a marked decrease in the crosslinking degree.

The vulcanizates obtained with peroxide cure have good characteristics, even for long vulcanization times or by performing the vulcanization at very high temperature. This is due to the fact that during this cure, reversion or breakdown reactions do not take place.

Resistance to aging is a characteristic of these vulcanizates; also the resistance to ozone is excellent. If we consider the excellent electric properties of the copolymer and its resistance to degradation agents, we can foresee that these vulcanizates will acquire a particular importance in the field of cables.

It is also interesting to mention here the very high resistance of the copolymers vulcanized in this way to chemical reagents such as concentrated sulfuric acid and nitric acid.

Sulfur Vulcanization of EP Copolymers Containing Unsaturations.

In order to obtain, through vulcanization with the aid of compounds normally used for synthetic rubber of low unsaturation vulcanized products having good mechanical properties, we have studied the preparation of copolymers containing double bonds in their macromolecules. These unsaturations should be present in such a limited number so as not to reduce the

very good properties of resistance to aging and to oxidation; on the other hand, it is necessary that these double bonds are present in all the macromolecules and, furthermore, that they are distributed in a suitable way in each macromolecule.

By choosing particular catalytic systems and particular types of monomers, we succeeded in preparing unsaturated sulfur-vulcanizable copolymers of homogeneous composition.[39] These copolymerization products are made of macromolecules essentially consisting of ethylene and propylene monomeric units and containing small amounts of double bonds. Therefore, the physical properties of these terpolymers are very similar to those of the pure EP copolymers. The rebound vs. temperature curve of a vulcanized terpolymer is reported in Figure 16; one can observe the very high resilience at room temperature and the rather low minimum rebound temperature (about —40° C).

The vulcanization, when using recipes based on sulfur and accelerating agents, leads to vulcanized products having good mechanical properties. Table 10 reports some characteristics of pure gum vulcanizate obtained from terpolymers having a different content of double bonds.

Table 11 gives the properties of carbon black reinforced vulcanizates obtained from the same terpolymers.

As may be seen from the data reported in the two tables, these products show mechanical and dynamic properties that are similar to, or even better than those of SBR rubber, whereas their resistance to aging can be compared with that of butyl rubber.

The high content of ethylene and propylene indicates economic production of these copolymers; this should make possible large scale commercial application. ##