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ETHYLENE-PROPYLENE

COPOLYMERS

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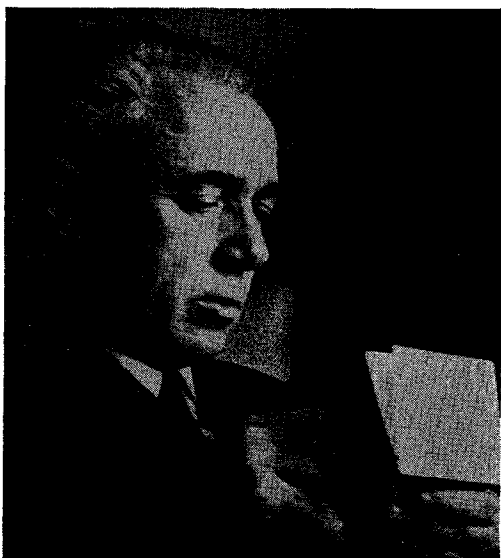*Milan, Italy*

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Whose Pioneering Research on Surface Catalysts Helped To Revolutionize Polymer Chemistry, Opening Prospects for the Detailed Control of Molecular Structure and the First Exact Synthetic Copies of Natural Materials. At present: Director of Industrial Chemistry Institute, Milan Polytechnic, Italy.

THE PROBLEM of obtaining synthetically saturated, linear hydrocarbon macromolecules, having elastomeric properties (in the absence of reinforcing additives) comparable to those of natural rubber, and better chemical resistance, has been solved in a more or less satisfactory manner only regarding the phenomenology of slow elastic elongations under small stress, but is far from resolved in respect to dynamic properties. What differentiates natural rubber from all other pure elastomers is its high synergistic response to rapid deformation and, in many cases, also its high tensile strength with high elastic modulus at high elongations.

The exceptional elastic properties of natural rubber are generally attributed to the great length and exceptional flexibility of its linear macromolecules which is related to the peculiar structure of the polyisoprene chain with cis-1,4 linkage, and especially to the little-hindered rotation of single bonds of the chain which are adjacent to a double bond. The ease of rotation of segments of the chain around such bonds makes natural rubber in the unstretched state comparable, from some points of view, to a true liquid without associative forces between the separate molecules, and one which has a very high viscosity. It has, even in its unvulcanized state, the exceptional property that viscous creep resulting from sudden and large stresses can be impeded by the orientation of the molecules, which have a high degree of regularity in their steric structure, and by resulting crystallization induced only by the application of such rapid mechanical stresses.
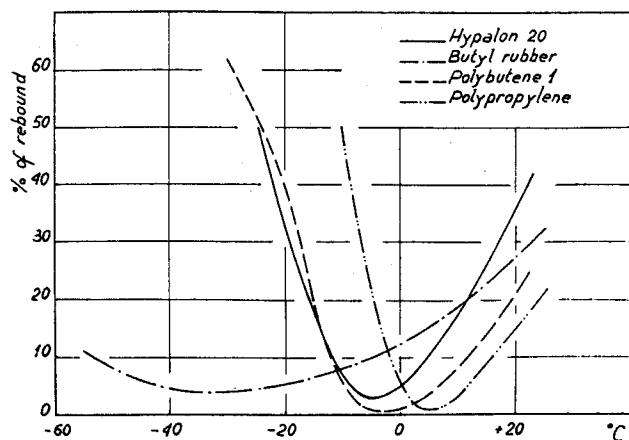
FIG. I—Rebound curves as a function of temperature for various saturated elastomers.

Graph legend:
Hypalon 20
Butyl rubber
Polybutene 1
Polypropylene

Y-axis: % of rebound (0 to 60)
X-axis: -60, -40, -20, 0, +20 °C

Properties peculiar to natural rubber

Properties peculiar to natural rubber — not fully reproduced by other types of macromolecules—are its great tendency to act like a liquid and, at the same time, its capacity to crystallize if the macromolecules become parallel by the application of mechanical stress, resulting in low elastic modulus under low stresses and high elastic modulus under high stresses. This explains why in over 50 years of research, the greatest efforts to produce synthetic rubbers having properties close to those of natural rubber have been directed toward the polymerization of diolefins in an effort to reproduce the structure of natural rubber.

Recent Polymerization Breakthrough

The results obtained have not, however, completely resolved the problem, and qualities of the best currently available diolefin synthetic rubbers (Buna S, styrene rubber, etc.) correspond only partially to the desired properties. Rebound properties and tensile strength, in the absence of reinforcing additives, have not been satisfactory. These deficiencies were due to irregularities, either in the type of linkage of the monomeric units which reduced the flexibility of the chain, or to steric irregularities in the units having the same linkage. Only recently, by stereospecific polymerization processes, have isoprene polymers been obtained with a cis-1,4 chain structure (1-4) which reproduces closely that of natural rubber. However, cis-1,4 butadiene polymers (5-6) have been made with elastic properties similar or even superior to natural rubber in the low-temperature field.

At the time these fundamental discoveries in the field of diolefin polymers were made, no less important results (which can be called unexpected in rubber industry circles) were obtained in the field of polyhydrocarbon rubbers, based on alpha-olefins made up completely or chiefly of saturated monomeric units. Compared to polydiolefins, these rubbers have greater stability when exposed to atmospheric agents, and greater resistance to aging. Furthermore, they are obtained from low-cost monomeric raw materials. Research carried out in order to obtain linear macro-

molecules with a high degree of flexibility, practically free from polar groups, has been successful.

Previously known elastomers, made up completely or extensively of saturated polyhydrocarbons, are polyisobutylene and its copolymers which contain a high percentage of isobutylene (butyl rubber). At room temperature, they have high elastic elongation that is slowly reversible, since the rapid deformation cycles are accompanied by large absorption of mechanical energy through hysteresis. Such rubbers, even though they have improved elastic properties at high temperatures, differ significantly from natural rubber at low temperatures. Their slight permeability to gases, significantly lower than that of natural rubber, has nevertheless permitted their wide application to certain specialized fields.

Efforts to produce rubbers from more flexible chains, such as the polyethylene chain, ran into difficulties because of the high crystallinity of linear polyethylene. Attempts were made to surmount these difficulties by creating irregularities in the chains; for example, by chlorination or by sulfo-chlorination. However, to destroy the crystallinity of polyethylene, a high chlorine content is necessary: about 28 to 30 per cent. Rubber obtained in this manner (e.g., Dupont's Hypalon), while having elastic properties for slow deformations, because of its high chlorine content, also exhibited high density, lower flexibility, and a tendency toward association between polar groups of different chains. This resulted in worsening of its dynamic properties.

New processes of coordinated anionic catalysis, using heterogeneous catalysts with microcrystalline supports, have made it possible to obtain isotactic polymers from alpha-olefins. These had a regular structure and were, therefore, crystallizable. The same processes made it possible, as well, to obtain amorphous, atactic, linear polymers, by using special amorphous catalysts. Such polymers have elastomeric properties which, at room temperature, are no better than those of polyisobutylene, in spite of the minor steric hindrance to rotation presented by the single, lateral, methyl group per monomeric unit (instead of the two methyl groups in polyisobutylene), because of higher, second-order transition temperature (Figure 1). Moreover, the dynamic properties of the elastomers obtained from such polymers were not yet entirely satisfactory, and their tensile strength was rather low without reinforcing agents.

There was then programmed at the Milan Polytechnic Institute a study of the synthesis of polyolefinic macromolecules, containing a chain chiefly made up of polyethylene (poor in side groups), to give high flexibility to the chain. Their crystallinity (at least in the unstretched state) should be hindered by the statistical substitution of hydrogen atoms with substantially non-polar groups, in order to produce associative forces between different chains. This research has now led to the synthesis of copolymers (ethylene-propylene, ethylene-butylene, etc.) which have proved to have extremely interesting elastic properties, as well as good dynamic properties (low

hysteresis). The process for the synthesis of such polymers has been described in other papers (7-14). In this article, we shall describe their elastomeric properties in more detail.

Characteristics of the Polyethylene Chain

It is known that the free molecule of linear polyethylene has a high flexibility, due to the relatively limited energy barrier which opposes rotation of its CH_2-CH_2 bond. The molecule is characterized by the ease with which different conformations can coexist because of the small energy difference between them. Research carried out by Flory on the elastomeric properties of the polyethylene chain has shown that this difference is about 450 cal/mole—significantly lower than that of other olefin chains, particularly polyisobutylene's. However, Flory's research (15) was carried out at high temperatures where the crystallinity disappears.

Most of the research on the elasticity of rubbers has, in fact, been based on a description of models of free chains, whose average length can be predicted by certain statistical calculations. It can be postulated, for example, that every CH_2-CH_2 bond is free to assume any of three positions 120 degrees apart, corresponding to the positions of least potential energy. Such statistical conformations of the chains should be modified by forces causing elongation of the chains themselves, which thereby tend to assume a more linear configuration and become parallel. The low modulus observed under small deformations, even for some chains in which rotation of the C-C bonds is hindered by quite high energy barriers, could ultimately be traced to the further effect of chain flexibility.

A remarkable flexibility in the long chain of a perfectly linear polyethylene can exhibit itself with rotations of the CH_2-CH_2 bond, much smaller than that necessary to overcome the energy barrier which corresponds to a rotation of 60 degrees. Beyond this, there is a tendency to pass over from the planar trans (zig-zag) configuration to a left-handed one.

A Note on Terminology

For readers to whom Dr. Natta's work may be new, we quote the following illuminating passage from Herbert R. Simonds' "Source Book of the New Plastics" (Reinhold Publishing Corp., New York, N. Y.):

"Professor Natta found it necessary to coin a series of words that have now become widely known, if not so widely understood. These words are applicable to any polymer formed by polymerization of a monomer containing an ethylene group which has a chain or substituent on one carbon of the ethylene group. Propylene is the simplest such monomer, having a methyl group on one carbon of its ethylene group.

"Professor Natta discovered catalysts which had the property of directing the growth of the polymer from such a monomer so that the substituent would always appear in the same relative position to the chain. Such catalysts are called "stereospecific," and the polymer produced is called "isotactic." The term "syndiotactic" is used to describe other arrangements of the polymer where the substituent regularly alternates in two positions, and the term "atactic" is used where the substituent falls into its possible locations at random.

"The important configuration as it relates to polypropylene is isotactic. Isotactic polypropylene is harder, stronger, stiffer, and has greater temperature resistance than polypropylene that is atactic . . . It combines the excellent electrical properties, moisture resistance, and dimensional stability of the pure hydrocarbon plastics (polyethylene and styrene) with strength, toughness and heat resistance."
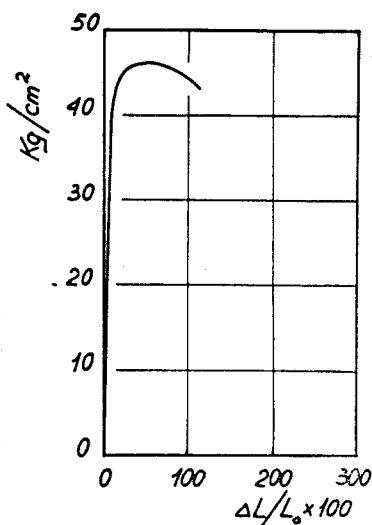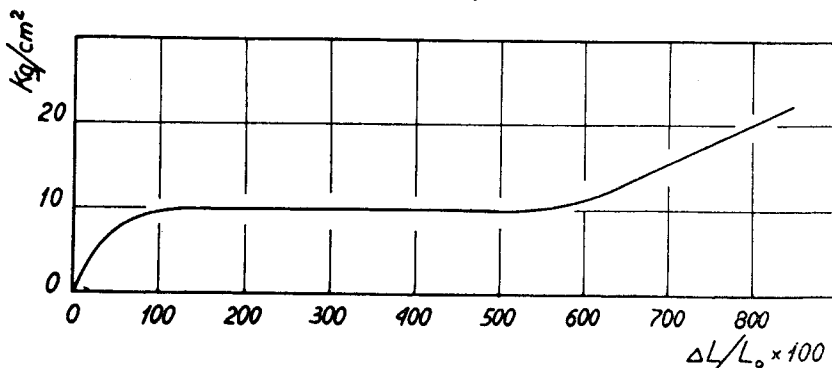

◀ FIG. 2—Stress-elongation diagram for a 50:50 mechanical mixture by weight of linear polyethylene (MW 90,000) and atactic polypropylene (MW 70,000).

FIG. 3—Stress-elongation diagram for an ethylene-propylene copolymer having a molecular weight of 460,000 and containing 50 mole percent ethylene (test velocity 50 mm/minute). ▼
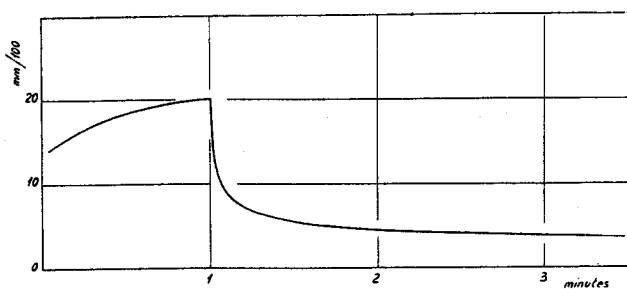
FIG. 4—Depth of indentation of the sphere of the durometer as a function of load application time (1 minute) and recovery from the deformation when the load is removed (diameter of the ball: 0.4 mm load applied: 15.7 g).

Independently of this, it should be remembered that, in the free polyethylene chain, all the C-C bonds have an equal if not greater flexibility, while in the poly-isoprene cis-1,4 molecule only the $=CH-CH_2$ bond has greater flexibility.

What has been said above, refers to the free linear polyethylene molecule without long branches. At temperatures lower than 137° C. however, linear polyethylene shows a great tendency to crystallize. If the chain is not subjected to special modifications which hinder its crystallization, this tendency precludes the appearance of elastomeric properties. Corresponding to the great variation in specific volume during crystallization, a high lattice energy forces the chains to become parallel and rigid in spite of their intrinsic flexibility.

Keeping Transition Temperature Low

Leaving aside the difficulty of high crystallinity which, as we shall see, can be eliminated by proper statistical introduction of substituents, there is another extremely important property of the polyethylene chain—its exceptionally low, second-order transition temperature. Modifications of the chain should, therefore, be made with substituents which bring about a large reduction in crystallization temperature (up to its complete disappearance), but which raise the second-order transition temperature minimally.

The statistical replacement of hydrogen atoms by various substituents can be compared to the copolymerization of ethylene with ethylenic monomers containing such substituents. A statistical copolymerization of non-isomorphous, monomeric units leads to a lowering of the melting temperature which can be calculated by Flory's expression (16), while the transition temperature generally assumes values intermediate between those for the single homopolymers.

Following these results, we compared the second-order transition temperatures of homopolymers:

	Transition Temperature (°C.)	
	Dilatometric	Dynamic
Polyvinyl chloride	77	110
Polypropylene	—33	+4
Polybutylene	—43	—5

Our research was carried out with the aim of destroying the crystallinity of the polyethylene chain, at the same time trying to raise the second-order transition temperature as little as possible. We did this by copolymerizing ethylene with other linear alpha-olefins, for example propylene or butylene.

Viscosity of Marketable Polymers

The ethylene-propylene copolymer, as it is now being made by the Montecatini Company, is normally in the form of rubbery flakes which agglomerate easily. On a roll mixer, the copolymer forms a very strong, rough band which is not noticeably plasticized even after long periods of mixing. By compression molding, sheets which have a low surface hardness and excellent flexibility, down to very low temperatures, can be easily obtained.

At normal temperatures, the behavior of ethylene-propylene copolymers, under the action of external forces (relaxation of the stress at constant elongation, creep under the action of a constant load), is completely analogous to that of the other elastomers, such as polyisobutylene, unvulcanized natural rubber, etc. This is distinctly different from the visco-elastic behavior of mechanical mixtures of the two homopolymers. In fact, these mixtures generally exhibit great intermolecular cohesion, essentially due to the presence of crystalline parts. The initial elastic modulus of such mixtures is fairly high, as can be easily seen by subjecting a sample of this material to tensile tests (see Figure 2).

The difference in visco-elastic behavior between the mechanical mixtures and the copolymer is very evident, if Figure 2 is compared with the stress-elongation diagram for copolymers containing about 50 mole per cent ethylene (Figure 3) and having a high molecular weight ($[\eta] > 4 \div 5$). From this diagram, it can be seen that low values apply to the initial elastic modulus, but high ones to deformation at rupture. The deformation is generally reversible, according to the mechanism of delayed configurational elasticity.
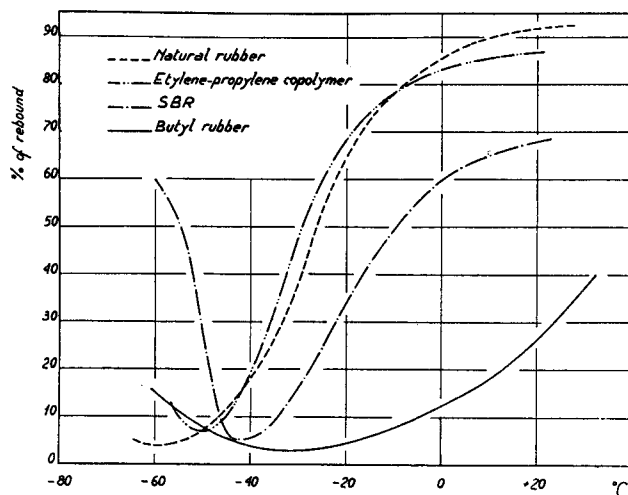

FIG. 5—Rebound curves as a function of temperature of various elastomers, compared with an ethylene-propylene copolymer containing about 70 mole percent ethylene (MW 360,000).
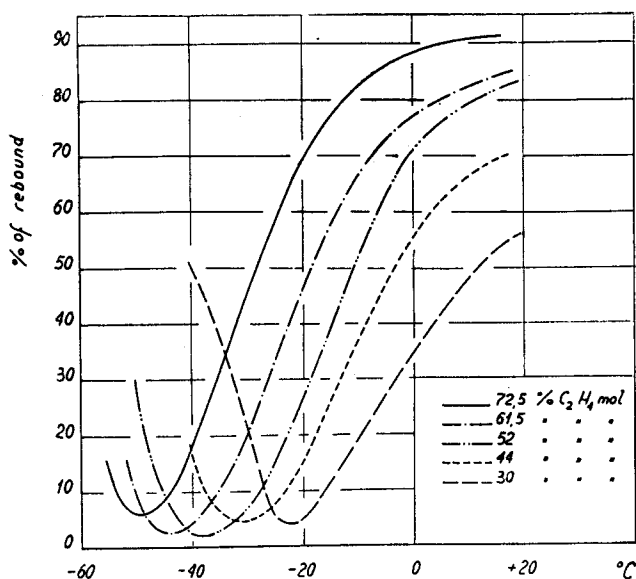
FIG. 6—Rebound curves as a function of temperature for ethylene-propylene copolymers having various ethylene contents, with molecular weights between 200,000 and 450,000.

The elastic modulus can also be measured by recording the depth of indentation of the sphere of a durometer, under a known weight, following the usual methods for the measurement of hardness. This depth of indentation, in the case of an ethylene-propylene copolymer, is a continuous function, increasing with the time of application of the load. Therefore, elastic modulus, calculated by Scott's formula (17) becomes equal to

$$G = \frac{P}{0.00051.R^{0.65} \quad H^{1.35}}$$

(where G is the modulus in kg/cm², P the load applied to the sphere in kg, R the radius of the sphere in cm, H the depth of indentation by the sphere in hundredths of mm)

and should be referred to a constant-load, application time. Making a measurement after 3 seconds of load application, the ethylene-propylene copolymers have, on the average, a modulus between 8 and 14 kg/cm², thus confirming the low values of intermolecular cohesion forces. Curves for indentation depth and deformation recovery are shown in Figure 4.

Obtaining Maximum Elasticity

A property of elastomers which is very important from a practical point of view is their ability to absorb and to give up their deformation energy in a short period of time. In fact, a rubber which exhibits low hysteresis during a slow deformation is not necessarily a good elastomer if subjected to rapid deformation. In practice one of the most widely used methods for measuring the energy given up by an elastomer after a rapid deformation, is the measurement of

impact resilience, usually defined as the percentage of rebound height of a pendulum which falls from a predetermined height. The numerical value of the resilience for the same elastomer may vary from one type of instrument to another, according to the characteristics of the instrument itself.

We measured the elastic response of the copolymer with a Pirelli instrument which consists essentially of a pendulum-type "rebound" apparatus, with a mass of 80 grams and an impact velocity of 5 cm/sec. The measurements were made at controlled temperature (18). The rebound properties depend on the ability of the elastomer to reach equilibrium rapidly under given deformation conditions; thus, on the flexibility of the polymer chain in question. Above the second-order transition temperature, as temperature increases, flexibility of the macromolecules and, consequently, the percentage of rebound also increases.

In ethylene-propylene copolymers, sections consisting of macromolecules which are quite flexible (due to sequences of methylenic groups) are present. The flexibility of these chain sections remains quite high, even at much lower than room temperatures. It follows that the ethylene-propylene copolymers have good flexibility and, therefore, very good elastic properties. Figure 5 shows the rebound curve, as a function of temperature, of an ethylene-propylene copolymer compared with various elastomers. The behavior of the copolymer is better than that of butadiene-styrene rubber, and very close to that of natural rubber. The minimum rebound temperature is found for copolymers containing more than 45 per cent ethylene, at temperatures lower than —40° C., which permits the use of the copolymer as an elastic rubber, even at temperatures considerably lower than 0° C.

The flexibility of the chains depends essentially on the sequences of methylenic groups, as can be demonstrated by varying the composition of the copolymer. An increase of the ethylene content in the copolymer increases the length of such sequences as well as their number. Rebound curves, as a function of temperature, for various ethylene contents (Figure 6) show that the flexibility of the chain is better in the case of high ethylene content. The temperature at
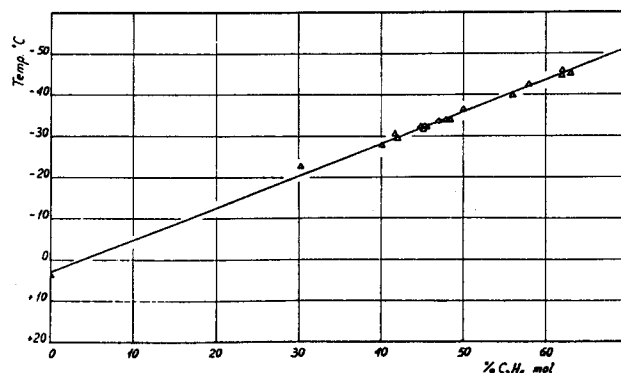

FIG. 7—Minimum rebound temperature of ethylene-propylene copolymers as a function of ethylene content.
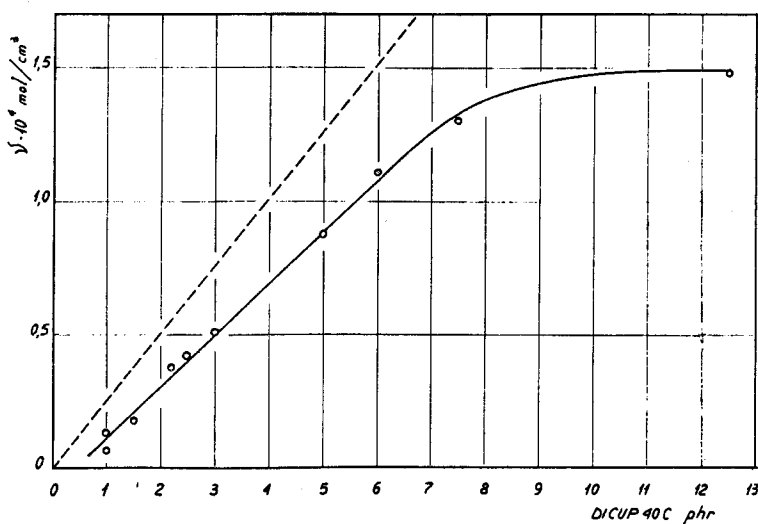
which the resilience is at a minimum (for a frequency on the order of 100 Hz) is shown in Figure 7. This temperature depends on the transition temperature that is greater for copolymers in which higher proportions of the component with a higher transition temperature are present. The position and the absolute value of the minimum confirm what had been predicted: that is, that the polyethylene chain is, theoretically, well suitable for production of good elastomers.

Relating Physical Properties to Cross-Linking

The physical properties of cross-linked ethylene-propylene copolymers have been determined by use of various cross-linking agents. In studying the dependence of such properties on the density of reticulation, it was found particularly useful to employ as vulcanizers some organic peroxides, such as, for example, Dicup 40C *(19)*. The density of reticulation was determined by measuring modulus, at equilibrium, of samples treated with solvents *(20-22)*, based on known relations predicted by the statistical theory of rubber elasticity.
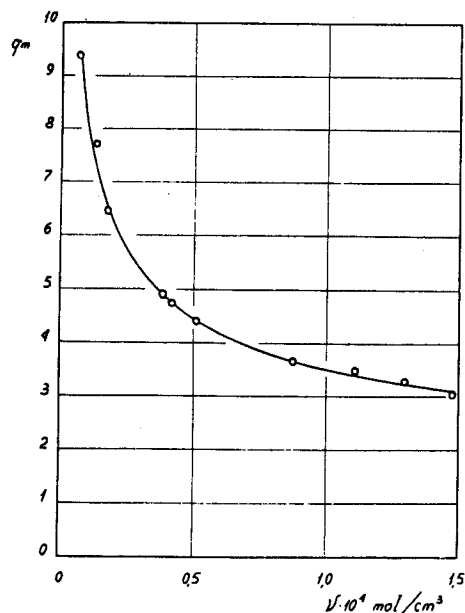
The diagram in Figure 8 shows the density of reticulation (expressed as the number of effective chains of cross-linked polymer per cm³) as a function of the quantity of peroxide employed. The curve traced in this diagram represents the number of effective chains per cm³ of cross-linked polymer which would have been formed if every molecule of peroxide had given rise to a transverse bond (corresponding to two effective chains). This curve was drawn without taking into account the possible degradation of the polymer which might be brought about by vulcanization.

A moderately good agreement can be noted between the experimental curves and the straight line drawn on the basis of peroxide content. At high peroxide levels, the experimental curve tends to decrease in slope. The reason for this greater consumption of peroxide, per transverse bond formed, is not yet completely clear. However, this is a phenomenon frequently noted in processes involving chemical radicals. The volume swelling ratio, at equilibrium, of such vulcanized polymers ($Q_m = \dfrac{1}{v_r}$), determined in benzene at 25° C. as a function of cross-linking, is shown in Figure 9. In this diagram, the density of cross-linking can be determined directly from the swelling data. Such a diagram has been shown valid also for copolymers cross-linked by different systems, where vulcanization has no noticeable influence on the constant characteristics of the polymer-solvent system. The interaction constants for ethylene-propylene copolymers in benzene at 25° C. were found to be $\mu = 0.48$ and $\beta = 0.29$.

Conclusions and Prospects

The synthesis of almost completely saturated, linear polyhydrocarbons, having good elastomeric properties, is made possible by the copolymerization of ethylene with aliphatic alpha-olefins. In particular, research on ethylene-propylene copolymers shows that many elastomers have dynamic properties which improve as the percentage of ethylene in the copolymer is increased. The minimum rebound temperature is very close to that of natural rubber and less than that of styrene rubber, if no sequences of monomeric ethylene units are present which are too long and, therefore, capable of crystallizing in a manner that can be determined by X-ray tests.

Ethylene-propylene copolymers cross-linked with organic peroxides are seen to follow faithfully the predictions of the statistical theory of rubber elasticity. The number of transverse bonds per small

FIG. 8—Density of cross-linking of the ethylene-propylene copolymer, vulcanized with various quantities of Dicup 40C.

FIG. 9—Volume swelling ratio in benzene at 25° C. for cross-linked ethylene-propylene copolymer, as a function of density of cross-linking.

quantity of peroxide used for the cross-linking, calculated on the basis of this theory, corresponds well enough to that predicted by chemical theory. The properties of the polymers open up a vast field for their use as raw materials in the production of vulcanized rubbers, if proper methods of vulcanization are employed. These predictions have been confirmed by experimentally determined properties of the vulcanized copolymers, both in the presence and in the absence of reinforcing agents.

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