

HIGH POLYMERS

A SERIES OF MONOGRAPHS ON THE CHEMISTRY, PHYSICS, AND
TECHNOLOGY OF HIGH POLYMERIC SUBSTANCES

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POLYMER CHEMISTRY OF
SYNTHETIC ELASTOMERS

Part II

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CHAPTER 7

ELASTOMERS BY
COORDINATED ANIONIC MECHANISM

B. Ethylene-Propylene Rubbers

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I. INTRODUCTION

Copolymers and terpolymers containing ethylene and α -olefins are of particular interest for many reasons. The most important of these are: (1) low cost of the lower olefins relative to diolefins as raw materials; (2) practically unlimited availability of the olefins; (3) absence of unsaturation or low content of unsaturated groups, which increases the chemical resistance and the resistance toward aging in comparison with the traditional unsaturated rubbers.

The only low unsaturation hydrocarbon rubber known for several decades is butyl rubber, a copolymer of primarily isobutylene with small amounts of isoprene. The incorporation of the latter monomer introduces a small amount of double bonds into the polymer and makes the product vulcanizable with traditional vulcanization systems based on sulfur and accelerators. The presence of two methyl side groups for each isobutylene monomer unit has a detrimental effect on the dynamic properties of the rubber thus obtained, owing to the steric hindrance caused by these groups and the resulting slowness with which a deformed product tends to regain its initial shape after the stress has ceased. As a consequence, high mechanical hysteresis will accompany every temporary deformation process of such a rubber.

This is the reason why the interest in butyl rubber is practically limited to those fields in which its high chemical resistance and in particular its very low permeability to gases are especially important (e.g., use in inner tubes for tires); however, butyl rubber is less suitable for those applications which involve frequent and rapid deformation under high stress (e.g., use as treads for tires).

As described in other chapters of this volume dealing with hydrocarbon polymers (e.g., polyalkenamers and polydiolefins), good elastic and dynamic properties can be expected only when long macromolecules exhibit high flexibility as a consequence of low hindrance to rotation of part of the macromolecule around carbon to carbon bonds in the main chain.

This is the case of the $=\text{CH}-\text{CH}_2-$ bonds in some diolefin polymers with 1,4 arrangement. Low steric hindrance, although slightly higher

than the previous case, is shown by the $-\text{CH}_2-\text{CH}_2-$ bonds of polyethylene.

The high crystallinity and high melting temperature of linear polyethylene prevent its practical use as an elastic rubber, since polyethylene behaves as an excellent rubber above its melting temperature ($\sim 130^\circ\text{C}$).

The production of synthetic rubbers from polyethylene (e.g., Hypalon by DuPont) dates far back in time. The introduction of chemical irregularities (such as the random introduction of Cl atoms or of sulfonic groups) by chlorination or sulfochlorination of linear polyethylene prevents its crystallization. However, the required introduction of Cl atoms (at least 28–30%) causes a considerable decrease in the chain flexibility. An even greater decrease in flexibility is observed when sulfonic groups are present, because of their tendency to associate.

The discovery of the coordinated ionic polymerization processes made it possible to produce long linear polymers of α -olefins, which are crystalline only when stereoregular and otherwise amorphous.

By means of nonstereospecific catalysts acting through a coordinated anionic mechanism, it was possible to produce amorphous linear polymers of α -olefins, which are of interest as elastomers from a dimensional point of view, having low elastic moduli, but which present poor dynamic properties owing to the deficient flexibility of the main chain caused by the presence of side groups. This is the reason why poly- α -olefins by themselves are not suitable for the production of elastic rubbers of good dynamic properties.

As the crystallinity of polyethylene can be prevented by the introduction of irregularities (20–30%), the authors of this article visualized already in 1955 the copolymerization of ethylene with α -olefins as a process for the production of very valuable hydrocarbon rubbers. To this end, they studied the copolymerization of ethylene with α -olefins, and in particular with propylene, so as to obtain the most suitable compositions and structures. First of all they observed that not all Ziegler-Natta type catalysts are suitable for the production of homogeneous polymers. The best known coordinated anionic catalysts obtained by reaction between Ti halides and Al alkyls present the disadvantage of being heterogeneous and of containing active centers exhibiting not only different catalytic activities, but also different reactivity ratios.*

* The reactivity ratios referred to in this chapter correspond to those defined for the butadiene-acrylonitrile system in the chapter by Hofmann on nitrile rubber in this volume (Part I, page 192). The reader further interested in the general mathematics of copolymerization may refer to one of the comprehensive treatises on this subject, e.g., *Copolymerization*, G. E. Ham, Ed., Interscience, New York, 1964.

For instance, some of the centers present on the surface of the solid phase can polymerize ethylene with a higher relative rate than the others. Different types of macromolecules are therefore formed: some contain polyethylenic chain segments that are long enough to give rise to crystallinity of the polyethylenic type and a worsening of the elastomeric properties, which can be corrected only partly by increasing the proportion of copolymerized propylene, which in turn causes a decrease in the flexibility of the chains.

The problem of obtaining amorphous homogeneous products by the use of the lowest possible amount of α -olefin was solved by the authors through the discovery of suitable catalysts, particularly of the homogeneous type.

First of all we shall describe the preparation of the most effective copolymerization catalysts; then we shall report on the variations in the properties of the copolymers resulting from variation of their composition.

II. ETHYLENE-PROPYLENE COPOLYMERS

A. Synthesis

The best anionic coordinated catalysts for the synthesis of ethylene-propylene copolymers are those obtained by reaction of alkyl aluminum compounds (e.g., $\text{Al}(i\text{-C}_4\text{H}_9)_3$, $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$, $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$, $\text{Al}(\text{C}_6\text{H}_{13})_3$) with hydrocarbon soluble vanadium compounds (e.g., VOCl_3 , VCl_4 , $\text{V} = \text{trisacetylacetonate} (\text{VAc}_3)$, alkyl esters of vanadic or chlorovanadic acid). Other transition metals, such as niobium, titanium, and chromium, can be substituted for vanadium; beryllium, zinc, and alkali metals can be used instead of aluminum. However, the copolymers obtained in the presence of aluminum- and vanadium-based catalysts are by far the best as regards elastomeric properties, amorphousness and absence of homopolymer fractions.

As in the case of propylene homopolymerization, it has been established also for ethylene-propylene copolymerization (1,2) that at least one of the reagents employed in the catalyst preparation must contain a halogen, something that is not required for ethylene homopolymerization. The reaction is usually carried out in the presence of a solvent. Aliphatic, cycloaliphatic, and aromatic hydrocarbons, as well as some of their halogenated derivatives (e.g., methylene chloride, chlorobenzene, tetrachloroethylene) have been claimed useful.

In order to control the copolymer composition, the ethylene/propylene

ratio in the liquid phase must be kept as constant as possible throughout the polymerization.

To this end, a gaseous ethylene-propylene mixture, whose composition can be calculated from the desired ethylene to propylene ratio in the reacting liquid phase and the partition coefficients of the two olefins, is continuously fed through the polymerization system at such a high rate that the conversion of ethylene, which is the more reactive monomer, is kept at a low value (e.g., under 5%) (3).

According to another procedure, an ethylene-propylene mixture, the composition of which is calculated as described above, is fed through the diluent before the copolymerization (i.e., before the catalyst is added) until saturation is reached. After the copolymerization has started, an ethylene-propylene mixture having the same composition as the copolymer being formed is fed without any exit gas being discharged (4). A combination of the two systems has also been suggested (5).

In order to control the monomer composition (and also the average molecular weight of the copolymer, as explained below) during the copolymerization the temperature must be very carefully controlled. As the copolymerization is exothermic, cooling must be provided (5). To avoid a large, uncontrollable increase in temperature, the addition of large amounts of catalyst should be avoided.

To maintain equilibrium between the gaseous and the liquid phases and to keep a constant temperature throughout the reaction mass, sufficient agitation must be provided. As the reaction progresses, the mass becomes more and more viscous and it becomes more and more difficult to maintain saturation. Mass and heat transfer phenomena can exert a certain influence on the composition and properties of the product and on the course of the polymerization.

Particularly high copolymer yields can be obtained if the copolymerization is carried out without an inert solvent, i.e., with liquid propylene acting as solvent (6). Since the copolymer being formed is insoluble in the reaction mixture, there is no appreciable increase in viscosity during the reaction and high copolymer yields per unit volume can be attained without any particular stirring problems.

If the copolymerization is carried out batchwise or with an insufficient supply of olefins, copolymers whose composition varies with time are formed (diagonal copolymers (1,7)). Since ethylene is more reactive than propylene, the copolymer formed at the beginning of the copolymerization has the highest content of ethylene, whereupon its propylene content increases with time.

B. Influence of Operating Conditions on Copolymer Composition

In order to determine the influence of the ethylene/propylene ratio in the reacting phase on the copolymer composition, one has to be able to eliminate the influence of some parameters connected with the preparation of the catalyst and the polymerization procedure.

It has been established (3,8) that if the catalyst is the same, the copolymer composition is independent of the following factors: (1) polymerization time; (2) catalyst aging time (time elapsed between catalyst preparation and use); (3) catalyst concentration; and (4) alkyl aluminum to transition metal compound molar ratio. The last factor has little or no influence on the copolymer composition when aliphatic hydrocarbons are used as solvents; if benzene or tetrachloroethylene is used, the Al/V ratio influences the copolymer composition within a certain range (8). Experiments carried out in cyclohexane have also shown a certain dependence of monomer reactivities on Al/V ratio (9). If the catalyst system $\text{HCl}_2\text{Al}\cdot\text{O}(\text{C}_2\text{H}_5)_2 + \text{VCl}_4$ is used in benzene, an increase in Al/V ratio favors the relative reactivity of ethylene (10).

The nature of the organometallic compound plays only a minor role as regards the relative reactivities of the monomers in the presence of a certain transition metal compound. In experiments with VCl_4 it has been shown (11) that the relative reactivities do not change significantly if $\text{Zn}(\text{C}_2\text{H}_5)_2$, $\text{Zn}(n\text{-C}_4\text{H}_9)_2$ or CH_3TiCl_3 are substituted for $\text{Al}(i\text{-C}_4\text{H}_9)_3$.

If $\text{Al}(i\text{-C}_4\text{H}_9)_3$ is used as the alkyl aluminum and the transition metal compound is varied, the relative reactivity of propylene increases in the order $\text{HfCl}_4 < \text{ZrCl}_4 < \text{TiCl}_4 < \text{VOCl}_3 < \text{VCl}_4$, that is with increasing electronegativity of the transition metal (11).

In the presence of certain vanadium compounds, e.g., VCl_4 and VOCl_3 , a certain decrease in the relative reactivity of ethylene is noticed if $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$ or $\text{Al}(\text{C}_2\text{H}_5)_3\text{Cl}_2$ are substituted for $\text{Al}(\text{C}_2\text{H}_5)_3$ or $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (7).

These results disagree in part with those obtained by Ichikawa (8) in experiments with different mixtures of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$ together with VOCl_3 .

According to Junghanns, the aluminum compounds having the larger number of Cl atoms, i.e., $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$ and $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$, show the higher tendency to give completely amorphous copolymers in the compositional range of 65 to 75 mole % of ethylene (7). If larger groups are substituted for ethyl, no difference is noticed.

The dependence of the copolymer composition on the ethylene-pro-

pylene ratio in the reaction phase in the presence of different catalyst systems is shown in Figs. 1 and 2.

It has been shown (12) that if the catalyst $\text{Al}(\text{C}_2\text{H}_5)_3 + \text{VCl}_4$ is prepared in the presence of propylene alone and then used in the copolymerization, the copolymer formed is richer in propylene than when the catalyst is prepared in the presence of the ethylene-propylene mixture. By contrast, the copolymers obtained with a catalyst prepared in the presence of either ethylene alone or both monomers together have the same composition.

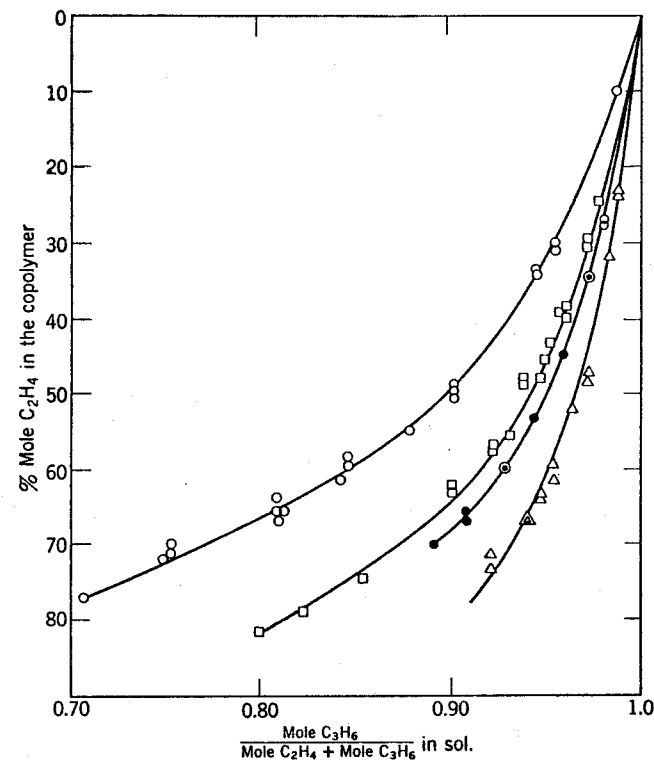


Fig. 1. Composition of ethylene-propylene copolymers plotted against the mole fraction of propylene in the total dissolved monomer for different catalyst systems prepared from hydrocarbon soluble transition metal compounds. ○, $\text{VCl}_4 + \text{AlR}_3$; □, $\text{VOCl}_3 + \text{AlR}_3$; ●, $\text{VAc}_3 + \text{AlR}_2\text{Cl}$; △, $\text{TiCl}_4 + \text{AlR}_3$.

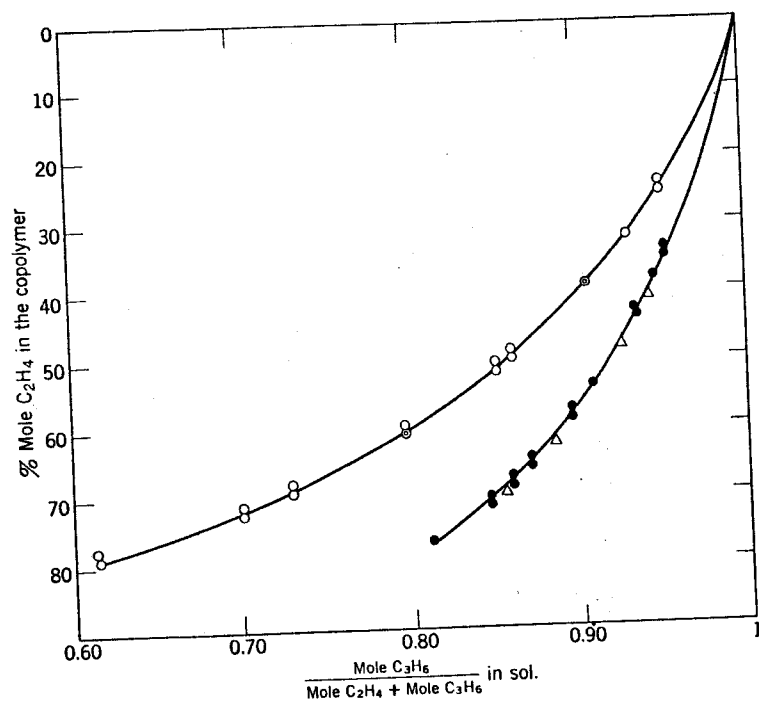


Fig. 2. Composition of ethylene-propylene copolymers plotted against the mole fraction of propylene in the total dissolved monomer for different catalyst systems prepared from hydrocarbon insoluble transition metal compounds. O, $\text{VCl}_3 + \text{AlR}_3$; ●, $\text{TiCl}_3 + \text{AlR}_3$; Δ , $\text{TiCl}_2 + \text{AlR}_3$.

C. Reactivity Ratios in Ethylene-Propylene Copolymerization

In the study of the reactivity ratios in ethylene-propylene copolymerization, the influence of the penultimate monomer unit on the reactivity of the chain end is generally neglected.

Table I shows the values of the reactivity ratios for ethylene-propylene copolymerizations in the presence of different catalyst systems. In every case the reactivity ratio of ethylene is much higher than that of propylene, as may be expected for anionic copolymerization. The product of the reactivity ratios is in many cases close to unity, as generally happens in ionic copolymerizations.

In the series of catalysts made from VOCl_3 , VCl_4 , and VCl_3 , the relative reactivity of ethylene generally decreases with decreasing vana-

dium valence. The same happens for catalysts based on TiCl_4 and TiCl_3 . In the presence of the latter compounds, the relative reactivity of ethylene is higher than in the presence of the corresponding vanadium compounds (VCl_4 and VCl_3 , respectively) under otherwise identical conditions.

The reactivity ratios have been shown to be practically independent of temperature in the range of -20 to 75°C (14,2).

D. Intrinsic Viscosity of Ethylene-Propylene Copolymers

Many factors influence the intrinsic viscosity of ethylene-propylene copolymers. The most important ones are examined below.

1. Polymerization Time

The intrinsic viscosity of ethylene-propylene copolymers increases with time in the presence of some catalyst systems, e.g., $\text{VAc}_3 + \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$

TABLE I
Monomer Reactivity Ratios for Ethylene-Propylene Copolymerization in the Presence of Different Catalyst Systems

Catalyst system	$r_{\text{C}_2\text{H}_4}$	$r_{\text{C}_3\text{H}_6}$	Ref.
$\text{VOCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_3$	17.95	0.065	13
$\text{VCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$	7.08	0.088	14
$\text{VCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_3$	5.61	0.145	15
$\text{VAc}_3 + \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$	15.0	0.04	2
$\text{TiCl}_4 + \text{Al}(\text{C}_2\text{H}_5)_3$	33.36	0.032	16
$\text{TiCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_3$	15.72	0.110	16
$\text{TiCl}_2 + \text{Al}(\text{C}_2\text{H}_5)_3$	15.72	0.110	16
$\text{VO}(\text{OR})\text{Cl}_2 + \text{AlC}_2\text{H}_5\text{Cl}_2$	17.5	0.05	1
$\text{VO}(\text{OR})_2, \text{VO}(\text{OR})_2\text{Cl}, \text{VO}(\text{OR})\text{Cl}_2 + \text{AlR}_2\text{Cl}, \text{AlRCl}_2^b$	17-28	—	5
$\text{VOCl}_3, \text{VCl}_4 + \text{AlR}_3, \text{AlR}_2\text{Cl}, \text{AlRCl}_2^b$	17-28	—	5
$\text{VO}(\text{O}-n\text{-C}_4\text{H}_9)_3 + \text{Al}(i\text{-C}_4\text{H}_9)_2\text{Cl}$	22.00	0.046	17
$\text{VO}(\text{OC}_2\text{H}_5)_2\text{Cl} + \text{Al}(i\text{-C}_4\text{H}_9)_2\text{Cl}$	18.90	0.056	17
$\text{VO}(\text{OC}_2\text{H}_5)\text{Cl}_2 + \text{Al}(i\text{-C}_4\text{H}_9)_2\text{Cl}$	16.80	0.055	17
$\text{VO}(\text{OC}_2\text{H}_5)_3 + \text{Al}(i\text{-C}_4\text{H}_9)_2\text{Cl}$	15.00	0.070	17
$\text{VCl}_4 + \text{HCl}_2\text{Al}(\text{O}(\text{C}_2\text{H}_5)_2)$	10.7	0.022	10

^a VAc_3 = vanadium trisacetylacetonate.

^b Any combination of an aluminum and vanadium compound.

^c The product $r_{\text{C}_2\text{H}_4} \cdot r_{\text{C}_3\text{H}_6}$ is equal to 1.

(2), VOCl_3 + alkyl aluminum dichloride or sesquichloride (7,18), $\text{VOCl}_2(\text{OR}) + \text{AlR}_2\text{Cl}$ or $\text{VCl}_4 + \text{AlR}_2\text{Cl}$ (18).

In the presence of other catalyst systems, such as $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_4$ aged at 60°C for 30 minutes and employed at 25°C (19), the copolymerization time hardly influences the intrinsic viscosity.

2. Temperature

Other factors being the same, the intrinsic viscosity of ethylene-propylene copolymers increases with decreasing polymerization temperature (7).

3. Catalyst Concentration

Other factors being the same, the intrinsic viscosity of the copolymer decreases when the catalyst concentration is increased (see e.g., Ref. 2), a fact that agrees with the existence of transfer processes involving the catalyst.

4. Monomer Concentration

Other factors being the same, the intrinsic viscosity of the copolymer decreases with increasing monomer concentration.

5. Ethylene-Propylene Molar Ratio in the Reaction Phase

Other factors being the same, the intrinsic viscosity of the copolymer increases when the molar ratio of ethylene to propylene in the reacting phase is increased (see e.g., Ref. 1, 12).

6. Nature of the Alkyl Aluminum Compound

In the presence of some vanadium compounds, e.g., VCl_4 and VOCl_3 , at room temperature, the highest viscosities are obtained in the presence of $\text{Al}(\text{C}_2\text{H}_5)_3$, $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3$, and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ (7). These results have been confirmed by Ichikawa (8) using mixtures of $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ and $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$ with VOCl_3 at a constant Al/V molar ratio of 20.

7. Alkyl Aluminum Compound/Transition Metal Compound Molar Ratio

In the presence of some catalyst systems, such as $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} + \text{VAc}_3$ (2) or $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_4$, aged at 60°C for 30 min and employed at 25°C , and with the concentration of the vanadium compound and other factors being kept constant, the intrinsic viscosity decreases when the molar ratio of alkyl aluminum compound to vanadium compound is increased.

In the presence of the catalyst system $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2 + \text{VOCl}_3$, and $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3 + \text{VOCl}_3$ (20), the intrinsic viscosity increases when the Al/V ratio increases up to 15. If this ratio is further increased, the intrinsic viscosity decreases in the case of the first catalyst system but remains constant in the case of the second.

If $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$ mixtures are employed at a constant Al/V ratio of 20, the intrinsic viscosity of the copolymers is lower than that obtained from employing $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ or $\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$ alone.

When tetrachloroethylene is used as solvent and $\text{VOCl}_3 + \text{Al}(i\text{-C}_4\text{H}_9)_3$ or $\text{VOCl}_3 + \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ as the catalyst, an increase in Al/V ratio has no influence on the intrinsic viscosity (8). In heptane, on the other hand, an increase in $\text{Al}(i\text{-C}_4\text{H}_9)_3/\text{VOCl}_3$ ratio increases the intrinsic viscosity.

In hexane and benzene, maxima in intrinsic viscosity are observed for $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VOCl}_3$ ratios of 5 and 15, respectively.

In the presence of the catalyst system $\text{HCl}_2\text{Al}\cdot\text{O}(\text{C}_2\text{H}_5)_2 + \text{VCl}_4$ in benzene, the intrinsic viscosity increases as the Al/V ratio is increased from 3 to 10.

8. Aging of the Catalyst

Other factors being constant, for some catalyst systems, such as $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_4$, aging does not exert any influence on the intrinsic viscosity of the copolymer.

For other catalyst systems, such as $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl} + \text{VAc}_3$ (2) or $\text{VOCl}_3 +$ alkyl aluminum dichloride or sesquichloride (7), the intrinsic viscosity of the copolymer increases when the aging time of the catalyst is increased.

E. Kinetics of Ethylene-Propylene Copolymerization in the Presence of the Catalyst System $\text{VCl}_4 + \text{Al}(\text{C}_6\text{H}_{13})_3$

A systematic kinetic study of the ethylene-propylene copolymerization in the presence of catalysts prepared from $\text{Al}(\text{C}_6\text{H}_{13})_3$ and VCl_4 was carried out by Natta and co-workers (19).

When low monomer and catalyst concentrations were used so that the effects of mass and heat transfer phenomena could be neglected, the following results were obtained:

1. The activity of the catalyst decreases with time. However, if the catalyst is aged in the absence of monomer for a certain period of time (30 min) at 60°C , further aging in the temperature range of $0-40^\circ\text{C}$ does not influence the activity (Fig. 3).

2. The activity of the stabilized catalyst depends on the molar ratio

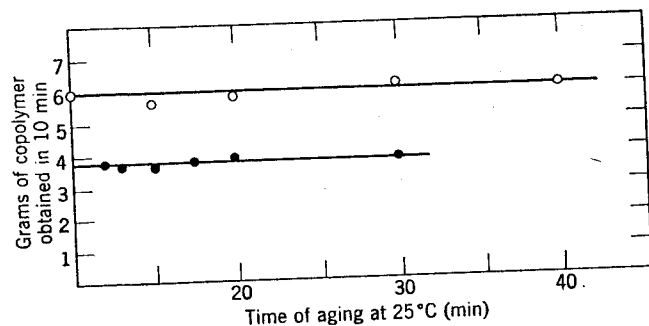


Fig. 3. Independence of activity with time for $\text{Al}(\text{C}_6\text{H}_{13})_3\text{-VCl}_4$ catalysts aged at 60°C for 30 min. Polymerization temperature = 25°C ; absolute pressure = 1 atm; solvent: *n*-heptane, 410 cm^3 ; $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{VCl}_4$ mole ratio = 2.5; $\text{C}_2\text{H}_6/\text{C}_2\text{H}_4$ mole ratio in the gaseous feed = 2.15. ●, V (g vanadium present in the catalytic system) = 0.0299; polymerization time = 10 min; ○, V = 0.0449; polymerization time = 6 min.

between the two reagents used for its preparation. The highest activity is obtained for a molar ratio $\text{Al}(\text{C}_6\text{H}_{13})_3/\text{VCl}_4$ of about 2.5.

3. At constant ethylene-propylene ratio, the copolymerization rate is first order with respect to catalyst and overall monomer concentration.
4. The overall monomer concentration being constant, the polymerization rate increases very rapidly with increasing ethylene concentration.
5. The activation energies of the four elementary copolymerization reactions are practically the same (6600 cal/mol).

In some copolymerizations carried out with the aid of catalysts acting through an anionic coordinated mechanism (e.g., copolymerization of propylene with butene-1 (21), of some vinylaromatic monomers (22), of ethylene with propylene in the presence of catalysts prepared from solid halides of Ti or V), r_1 (or the reciprocal of r_2)* is almost equal to the ratio between the homopolymerization rates of monomers 1 and 2. This relationship is not observed for the corresponding polymerizations of ethylene and propylene in the presence of the catalyst system $\text{Al}(\text{C}_6\text{H}_{13})_3 + \text{VCl}_4$. In this case the ratio between the homopolymerization rates of ethylene and propylene is much higher than the reactivity ratio of ethylene. Neither this fact nor the considerable increase in the copolymerization rate obtained by increasing the ethylene/propylene ratio in reacting phase can be explained only on the basis of the values of the

* See footnote on page 681.

propagation constants. It is, therefore, also necessary to take into account that a variation in the total number of growing chains may result from a variation in the ethylene propylene ratio. This variation in the number of growing chains can be explained as the consequence of the existence of active centers capable of homopolymerizing ethylene, but which are rather inert as soon as a propylene unit has been added (23). In the latter case the activity will not be lost irreversibly, but propagation will occur at such a slow rate as to be practically negligible. Propylene will be able to add to growing chains formed by such centers only when the monomer unit added immediately before is ethylene.

This phenomenon has also been confirmed by direct measurement of the number of active centers (capable of originating growing chains) present in the homopolymerization of ethylene and propylene with the catalyst systems $\text{VCl}_3 + \text{AlR}_3$ and $\text{TiCl}_4 + \text{AlR}_3$. Further proof is given by the possibility of preparing ethylene-propylene copolymers with catalysts that cannot start the homopolymerization of propylene but are active in the homopolymerization of ethylene.

By recognizing the variation in the number of the growing chains as indicated above and relating the polymerization rates to the same concentration of growing chains, the ratio between the homopolymerization rates of ethylene and propylene is almost the same as the reactivity ratio for ethylene.

F. Ethylene-Propylene Copolymerization Rate in the Presence of Different Catalyst Systems

Using catalyst systems prepared from VOCl_3 and alkyl aluminum dichloride or sesquichloride, Junghanns and co-workers (7) have studied the influence of different parameters connected with the catalyst preparation on the copolymerization rate. A loss in activity with time occurs both when the catalyst is prepared in the presence of the monomers and when it is kept some time under nitrogen before being added to the monomers. The loss in activity is faster in the former case, however. In the absence of the monomers, the catalyst activity decreases more slowly if the A/V ratio is increased from 5 to 40. As the catalyst activity decreases, a corresponding decrease in the vanadium valence also takes place.

The temperature scarcely influences the rate of decrease in activity, at least not between 20 and 40°C .

The polymerization rate increases if the ethylene-propylene ratio increases. If the monomer concentrations are kept constant, an increase

in temperature causes an increase in polymerization rate. An increase in total monomer concentration at constant monomer ratio increases the polymerization rate.

In the presence of VOCl_3 -based catalysts and with $\text{Al}(i\text{-C}_4\text{H}_9)_3$ or $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ as the alkylaluminum (8), an increase in yield calculated on VOCl_3 is always observed if the Al/V ratio is increased from 1 up to a certain maximum value that varies with the nature of the catalyst and the solvent. Beyond that value, no further increase in yield is observed.

Using the catalyst systems $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2 + \text{VOCl}_3$ or $\text{Al}_2(\text{C}_2\text{H}_5)_3\text{Cl}_3 + \text{VOCl}_3$, Kelly and co-workers (20) found that an increase in the Al/V molar ratio causes an increase in the catalyst efficiency. If the Al/V ratio is kept constant at 20 and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}-\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ mixtures of different composition are employed, a maximum catalyst efficiency is found for an $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}:\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}_2$ molar ratio of 2/3.

If mixtures of trialkyl aluminum compounds and AlBr_3 are employed in the preparation of the catalyst, the molar ratio of $\text{AlBr}_3/\text{AlR}_3$ must not exceed 2:1, otherwise very poor copolymer yields are obtained (20). An increase in propylene content in the feed at constant total monomer concentration causes a decrease in the polymerization rate and in the intrinsic viscosity of the copolymer. Similar results have been obtained by Ichikawa (8).

When copolymerizations are carried out with the catalyst system $\text{VAc}_3 + \text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$ at 25°C (2), the overall polymerization rate depends on the molar ratio of the two catalyst components, and the highest activity is found for $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ ratios close to 3.5.

The catalyst ages, both if it is employed in the copolymerization and if it is kept at 25°C under nitrogen for some time before being added to the monomer mixture.

If the preparation of the catalyst and the copolymerization are carried out at temperatures below 0°C , the catalyst activity decreases much more slowly than at 25°C .

When the catalyst activity is plotted versus the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ molar ratio for experiments carried out at -20°C , no definite maximum is noticeable in contrast to what is observed at 25°C . The catalyst activity increases considerably if the $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}/\text{VAc}_3$ molar ratio is increased from 3 to 4, and increases slightly if the same ratio is varied from 4 to 20.

At -20°C , the copolymer yields obtained in a given time and with catalysts aged under the same conditions are directly proportional to the

catalyst concentration, i.e., the copolymerization rate is first order with respect to the catalyst concentration.

If the $\text{C}_3\text{H}_6/\text{C}_2\text{H}_4$ ratio and other factors are kept constant, the copolymerization rate is first order with respect to the monomer concentration.

All other conditions being equal, the copolymerization rate increases remarkably if the $\text{C}_2\text{H}_4/\text{C}_3\text{H}_6$ molar ratio in the feed is increased.

III. ETHYLENE-PROPYLENE TERPOLYMERS

Ethylene-propylene copolymers cannot be vulcanized by the conventional processes used for diene rubbers or for butyl rubber because of the absence of groups that can react with sulfur.

Since the hydrogen atom of the tertiary carbon atoms is particularly reactive toward free radicals, ethylene-propylene copolymers can be vulcanized with organic peroxides. Crosslinking takes place by combination of free radicals belonging to different polymer chains (see e.g., Ref. 24 and literature cited there).

As rubber users are traditionally accustomed to vulcanize with recipes based on sulfur and accelerators, many investigators (of which the authors of this chapter were among the first) have studied the introduction of double bonds into every copolymer molecule during the polymerization. In this way terpolymers containing a small amount of double bonds capable of being vulcanized with traditional methods used for low unsaturation rubbers (such as butyl rubber) are obtained.

Although many linear or cyclic diolefins may be copolymerized with ethylene and propylene, not all of them are suitable for producing good synthetic rubbers. First of all, they must be able to polymerize in such a manner that the distribution of the double bonds becomes random. This is probably one of the reasons why conjugated diolefins give terpolymers whose vulcanizates generally exhibit modest properties.

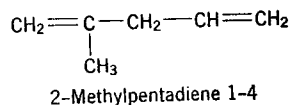
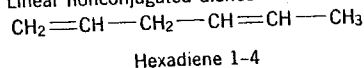
The use of acetylene and its homologs as termonomers does not give good results owing to the tendency of these monomers to react with alkylaluminums and thus deactivate the catalyst.

In order to avoid the formation of branches or crosslinks during or after the terpolymerization, the residual double bond of the diene entering the polymer chain should not react further during the polymerization and the subsequent polymer recovery steps.

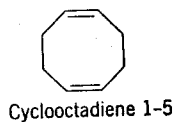
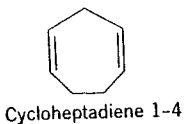
A number of classes of nonconjugated polyenes suitable for the synthesis of ethylene-propylene terpolymers have been found (Fig. 4) (25-29).

The factors regulating the intrinsic viscosity of ethylene-propylene

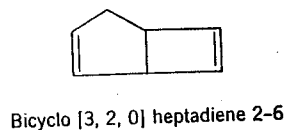
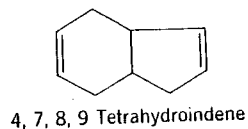
1 Linear nonconjugated dienes



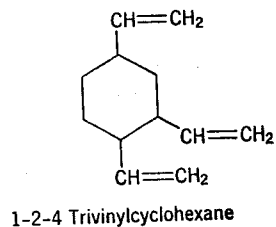
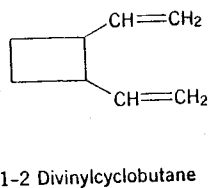
2 Monocyclic diolefins



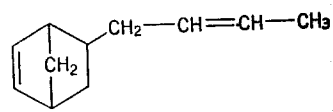
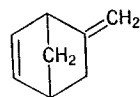
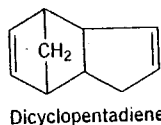
3 Bicyclic diolefins



4 Polyalkenylcycloalkanes



5 Norbornene derivatives



6 Linear trienes

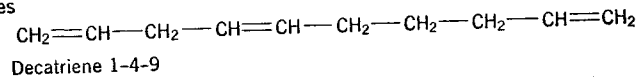


Fig. 4. Classes of termonomers suitable for making ethylene-propylene terpolymers.

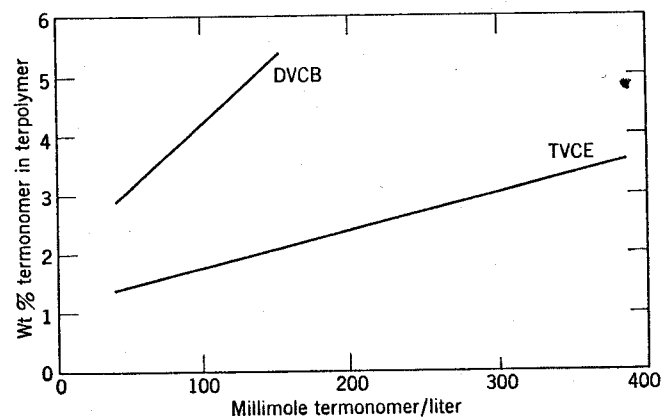


Fig. 5. Weight percentage of *trans*-1,4 divinylcyclobutane (DVCB) and 1,2,4 trivinylcyclohexane (TVCE) in terpolymer as a function of termonomer concentration in the liquid phase.

terpolymers are the same as for the binary copolymers. The rate of terpolymerization is generally lower than that of the diene-free copolymerization (4). The content of termonomer in the terpolymer increases, as can be predicted, if its relative concentration in the reacting phase is increased (Fig. 5).

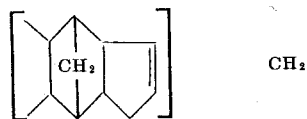
Whereas monoolefins are generally fed continuously throughout the terpolymerization, all the termonomer can often be added at the beginning of it, depending on its low rate of conversion.

However, if the termonomer is particularly reactive, continuous or periodic addition of it throughout the polymerization may be desirable or even necessary to prevent undesirably high termonomer conversions (4).

It has often been observed that, if the concentrations of ethylene and propylene in the feed are kept constant and the diene termonomer concentration is increased, unlike in the case when the termonomer is another alpha-olefin, e.g., butene-1, the ethylene to propylene ratio in the terpolymer increases. This phenomenon has been observed in the case of linear, non-conjugated diolefins (25), 1,5-cyclooctadiene (26) (Fig. 6) and dicyclopentadiene (25,30). However, the way in which the monomers are added can limit the extent to which it appears (4).

The termonomer most studied is dicyclopentadiene (25,4,30,31). As

the norbornene-type double bond is the more reactive, the monomer unit is



(25,30). However, in some cases the second double bond reacts, too (31), giving rise to branching.

The monomer unit formed from a certain termonomer in terpolymerization is often different from that formed in its homopolymerization. This is for example the case for 1,5-cyclooctadiene (32,26), 2-methylene-5-norbornene (cationic systems) (33,33a), and 1-methyl-1,5-cyclooctadiene (34) (Fig. 7).

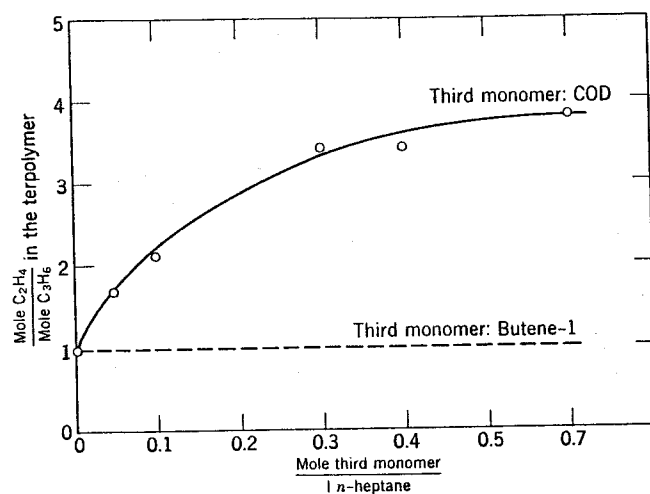


Fig. 6. Copolymerization of ethylene and propylene with a third monomer. Dependence of C_2H_4/C_3H_6 molar ratio in the terpolymer on the concentration of the third monomer in the reacting phase. Solid line: ethylene-propylene-cyclooctadiene-1.5 terpolymerization. Experimental conditions: polymerization temperature = $-10^\circ C$; abs. pressure = 1 atm; solvent, *n*-heptane; C_3H_6/C_2H_4 mole ratio in the gaseous feed = 2; $VCl_4 = 0.5$ mmole/l; $Al(C_2H_5)_2Cl/VCl_4$ mole ratio = 5; dotted line: ethylene-propylene-butene-1 terpolymerization. Experimental conditions: polymerization temperature = $25^\circ C$; abs. pressure = 1 atm; solvent, *n*-heptane; C_3H_6/C_2H_4 mole ratio in the gaseous feed = 2; $VCl_4 =$ mmole/l; $Al(C_2H_5)_2/VCl_4$ mole ratio = 2.5.

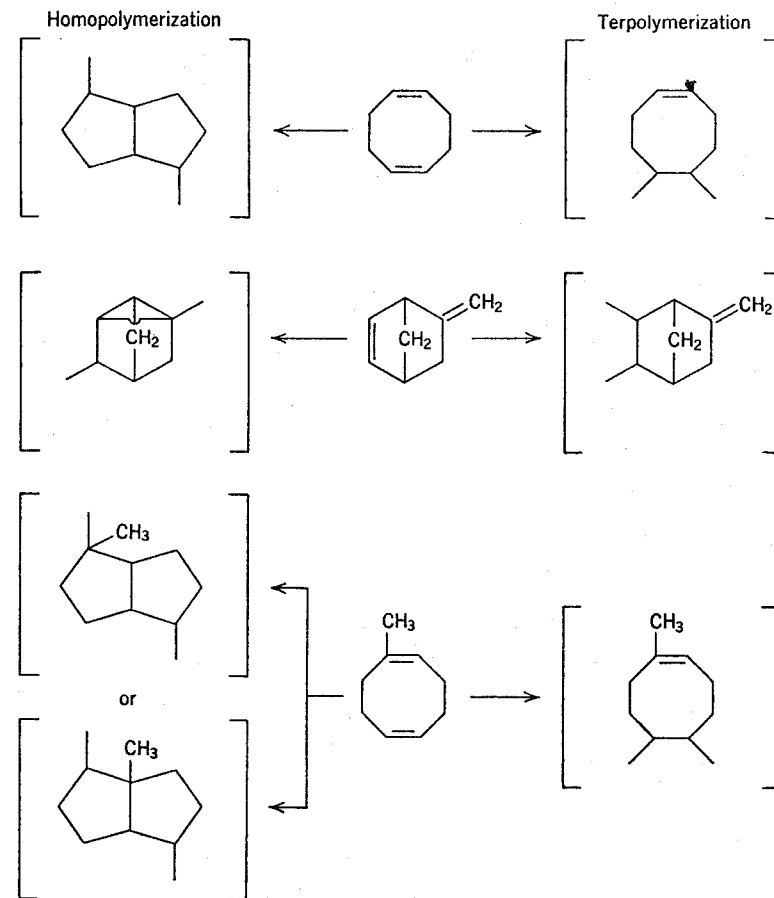


Fig. 7. Monomer units formed from certain cyclic monomers in homopolymerization and in terpolymerization with ethylene and propylene.

IV. DETERMINATION OF THE COMPOSITION OF ETHYLENE-PROPYLENE COPOLYMERS

A. Radiochemical Method

When radioactive ethylene (3) is used in ethylene-propylene copolymerization, the ethylene weight percentage in the copolymer is given by the ratio of the specific activity of the copolymer to that of the polyethylene obtained from the same ethylene.

B. IR Spectrographic Method

When adopting this method, which is the most general and important one for determination of the copolymer composition, one must distinguish between two cases depending on whether the copolymer is or is not soluble in solvents suitable for IR spectroscopic examination (e.g., carbon tetrachloride).

In the former case, the analysis is rather simple (3); measurement of the optical density of the absorption band at 7.25μ , due to methyl groups, makes it possible to calculate the amount of propylene units present. The value of the extinction coefficient used is the average of the values obtained from measurement on various solutions of atactic polypropylene.

A limitation to this method is that ethylene-propylene copolymers sometimes give rise to seemingly homogeneous solutions, which, however, also contain swollen copolymer particles. In such cases, the measurement should be carried out in the solid state (i.e., on pieces of thin film obtained by molding the copolymer).

According to the method proposed by Gössl (35), the ratio

$$R = \frac{E_{13.9}}{E_{8.6}}$$

between the extinction coefficients at 13.9μ and 8.6μ , respectively, is used. The band at 13.9μ is attributed to sequences of methylene groups from ethylene units and the band at 8.6μ to methyl groups from propylene units.

The calibration curve was obtained from measurements on samples completely soluble in carbon tetrachloride, whose propylene content could be determined with the help of the band at 7.25μ .

The method proposed by Wei (36) uses the ratio:

$$R' = \frac{E_{8.7}}{E_{13.9}}$$

The logarithm of this ratio is a linear function of the mole percent of propylene in the copolymer.

The method proposed by Ciampelli and co-workers (37) uses the ratio between the intensities of the bands at 8.6μ , whose intensity is proportional to the propylene content, and 2.32μ , whose intensity is proportional to the number of carbon-hydrogen bonds present in the copolymer and therefore practically proportional to the thickness of the film under

examination regardless of its composition. The calibration curve was obtained with samples containing C^{14} -ethylene.

A near infrared method proposed by Bucci and Simonazzi (38) uses the intensity ratio between the shoulder at 1692μ attributable to the methyl groups, and the maximum at about 1764μ , attributable to the methylene groups. The ratio is a linear function of the copolymer composition.

C. Mass Spectrographic Analysis of Products Obtained by Pyrolysis

Bua and Manaresi (39) set up an analytical method based on the pyrolysis of ethylene-propylene copolymers followed by mass spectrographic analysis of the products thus obtained. A drawback of this method is the considerable length of time required for the analysis. Its possible field of application is rather limited, therefore.

D. Relationship between the Composition of Ethylene-Propylene Copolymers and the Temperature of Minimum Rebound

The methylene sequences in ethylene-propylene copolymers constitute the most flexible part of the amorphous macromolecule; while the propylene sequences by contrast are the least flexible ones. By increasing the ethylene content in amorphous copolymers, one increases the flexibility of the macromolecule; thus a higher rebound is obtained at any given temperature.

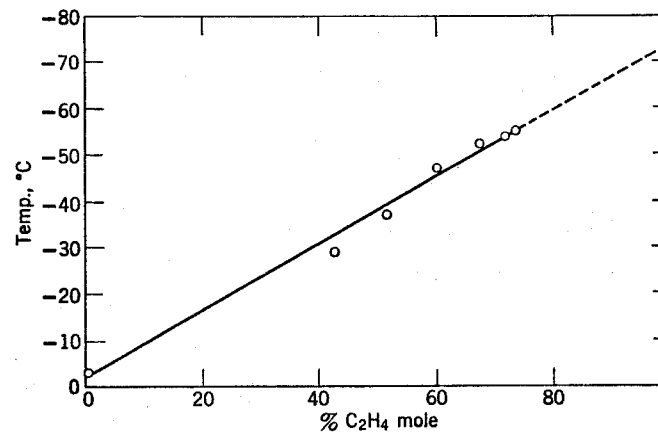


Fig. 8. Temperature of minimum rebound as a function of ethylene content for ethylene-propylene copolymers of varying composition.

A quantitative relationship between the ethylene content of the copolymer and the rebound value at or slightly below room temperature cannot be obtained easily, especially with uncured samples. In fact, the rebound value can be influenced by the viscosity of the copolymer, which is, in turn, a function of the average molecular weight.

At temperatures much below room temperature, the influence of the molecular weight becomes negligible; therefore, the rebound value is a function only of the copolymer composition. If the temperature of minimum rebound is used as a variable, it appears to be a linear function of the ethylene content (Fig. 8) (40).

V. DETERMINATION OF THE COMPOSITION OF ETHYLENE-PROPYLENE TERPOLYMERS

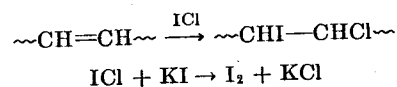
A. Propylene Content

Although no detailed study of the determination of the propylene content in ethylene-propylene terpolymers has been published, it may be assumed that the determination can be carried out by using the same bands and the same techniques as in the case of binary ethylene-propylene copolymers.

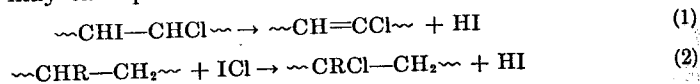
B. Unsaturation Content

1. Iodometric Method

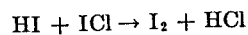
The determination of unsaturation in ethylene-propylene terpolymers by the ICl method has been thoroughly described by Hank (41) and Tunnicliffe and co-workers (42). According to the first author, an excess of ICl is added to a CS₂ or CCl₄ solution of the terpolymer. After about 1 hr, KI and water are added. Iodine formed in the reaction between KI and unreacted ICl is titrated with sodium thiosulfate.



As a blank, an ethylene-propylene copolymer solution is employed. Two side reactions may take place: HI elimination (1) and substitution (2):

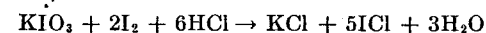


HI then reacts with excess ICl to give iodine:



While the first reaction does not disturb the determination of unsatura-

tion, the second reaction gives too high unsaturation values. The extent of the two side reactions can be judged by titration of I₂ with KIO₃:



To determine the reliability of the ICl method, terpolymers containing radioactive dicyclopentadiene were prepared. The iodometric values agreed well with those obtained by the radiochemical method.

According to the related method of Tunnicliffe et al. (42), measured portions of a CCl₄ solution of terpolymer containing excess ICl are removed at regular intervals and titrated as described above. The values so obtained are then extrapolated to zero time. Also in this case a control should be carried out with terpolymers containing labeled dicyclopentadiene.

The ICl method is suitable also for the analysis of 1,4-hexadiene terpolymers, but not for 1,5-cyclooctadiene terpolymers, in which extensive HI elimination and further ICl addition takes place.

2. Infrared Method

The unsaturation content of dicyclopentadiene terpolymers can be determined (41) from the intensity ratio between the band at 6.22 μ, due to the double bond contained in the cyclopentene ring, and the band at 2.32 μ, proportional to the thickness of the terpolymer film. Calibration curves can be obtained with the help of terpolymers whose unsaturation content has been established by other methods, e.g., by the ICl method.

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