as used in this article, means gamma or electron radiation. This is because these are the forms of radiation used in by far the greater part of the work. In general, gamma and electron radiation are not differentiated in this article. Since one of the effects of gamma radiation is the production of relatively energetic electrons in the substance being irradiated, the general effects of the two types of radiation are similar.

Megarad. One million rads.

Molecular weight. High polymers generally have a range or distribution of molecular weights. In molecular-weight determinations an average is arrived at. The statistical nature of this average is determined by the experimental technique used.

Monomer. (i) A small molecule which can enter a reaction to form a large polymer molecule. (ii) A segment of the polymer that corresponds to the monomer molecule. In the case of polyethylene this would be —CH_2—CH_2—, which corresponds to ethylene, $CH_2 = CH_2$.

Number average molecular weight. The average molecular weight defined by

$$\overline{M}_n = \underset{i}{\Sigma} Xi\, Mi = \frac{\Sigma Ni\, Mi}{\Sigma Ni}$$

where Xi is the mole fraction of species i, Ni is the number of moles of species i, and Mi is the molecular weight of species i. It corresponds to the arithmetic mean molecular weight and is usually determined from measurement of osmotic pressure.

Polymer. A molecule of high molecular weight which is formed from the reaction of a number of smaller molecules called monomers.

Rad. A radiation-energy absorption of 100 ergs per gram of sample. This is equivalent to 6.24×10^{13} electron volts per gram. A rad is the unit of absorbed dose.

Sol fraction. The fraction of a polymer sample which can be dissolved in the appropriate solvent.

Weight average molecular weight. The average molecular weight given by

$$\overline{M}_w = \underset{i}{\Sigma} Wi\, Mi = \frac{\Sigma Ni\, Mi^2}{\Sigma Ni\, Mi}$$

where Wi is the weight fraction of species i and the other symbols have the meanings given under *Number average molecular weight.* It is usually determined by light scattering in solution. If all the molecules have the same weight, then $\overline{M}_n = \overline{M}_w$. For the "most probable molecular weight distribution,"

$$\overline{M}_w = 2\,\overline{M}_n$$

Synthetic Elastomers

Development of synthetic materials is accelerated by stereospecific polymerization catalysts.

J. B. Campbell

A major impetus in the development and large-scale manufacture of synthetic elastomers was the shortage of natural rubber in World War II. The synthetic elastomers have proved to be more than substitutes and today constitute more than 75 percent of the total elastomer consumption in the United States. This replacement is due partially to economic factors but also to the wider range of desirable structures and properties available through synthesis. Preparative methods in elastomer chemistry have increased steadily in scope, with especially remarkable advances during the past 8 years. This development has been accompanied by physical studies that have led to better understanding of the basic structural features needed in elastomeric high polymers. Scientific effort in the field of synthetic elastomers continues to expand in academic, government, and industrial laboratories.

Structural Requirements

An elastomer is usually regarded as a solid material which can be grossly elongated or distorted and which rapidly recovers, to essentially the original dimensions, after removal of the stress. This property results from the introduction of restraining cross-links between linear chains of high molecular weight that otherwise have high mobility. It is desirable to consider separately the structural requirements of the linear chains and those of the final elastic network, in line with the actual technology in the utilization of elastomers; the "raw," linear polymer is formed in the desired shape by heat and pressure and then cross-linked or vulcanized to a three-dimensional network.

High internal mobility is essential in elastomeric polymers; this requirement precludes significant crystallinity in the unstretched chains, which may be visualized as existing in randomly coiled configurations of maximum entropy. The tendency of polymers to crystallize is enhanced by high regularity in structure and strong intermolecular forces resulting from polar groupings. While many crystalline high polymers become rubber-like at temperatures above the melting point, T_m, the common classes of elastomers are amorphous at ambient temperatures. As a consequence, elastomeric structures tend to be irregular and nonpolar, and hydrocarbon polymers predominate.

Similarly, the need for chain flexibility requires that the elastomer be above the glass temperature T_g. This is the temperature below which "segments" of chains in the amorphous high polymer no longer move as a whole but are restricted because of local intramolecular and intermolecular forces. Below this temperature, the elastomer becomes, physically, a hard, more or less brittle glass. This transformation is not a phase transition, as crystallization is, but may be compared to the solidification of a liquid to a glass (*1*). Properties such as the thermal expansion coefficient and heat capacity show abrupt changes in the region of T_g. Figure 1 is a typical plot of relative length against temperature for a neoprene synthetic elastomer which has a T_g of −48°C (*2*). No simple correlation of chemical structure and glass-transition temperatures can be made. In general, when the structural units have high rotational barriers, high van der Waals interactions, and bulky or polar substituents, the glass temperature of the polymer is high (*1, 3*). Molecular weight (beyond a minimum point) and cross-linking have no major effect on T_g.

A flexible polymer of high molecular weight must be cross-linked or vulcanized to prevent permanent flow and to obtain elastic recovery. In a typical elastomer containing a carbon-carbon "backbone," short cross-links are inserted randomly to give an average spacing of 400 to 800 chain carbon atoms between cross-links. The result is one "infinite" network in which the cross-linking structures constitute very little of the total mass. In Fig. 2, typical stress-strain curves (elongation and recovery) are shown for vulcanized and unvulcanized specimens of a neoprene synthetic elastomer in the "gum" state

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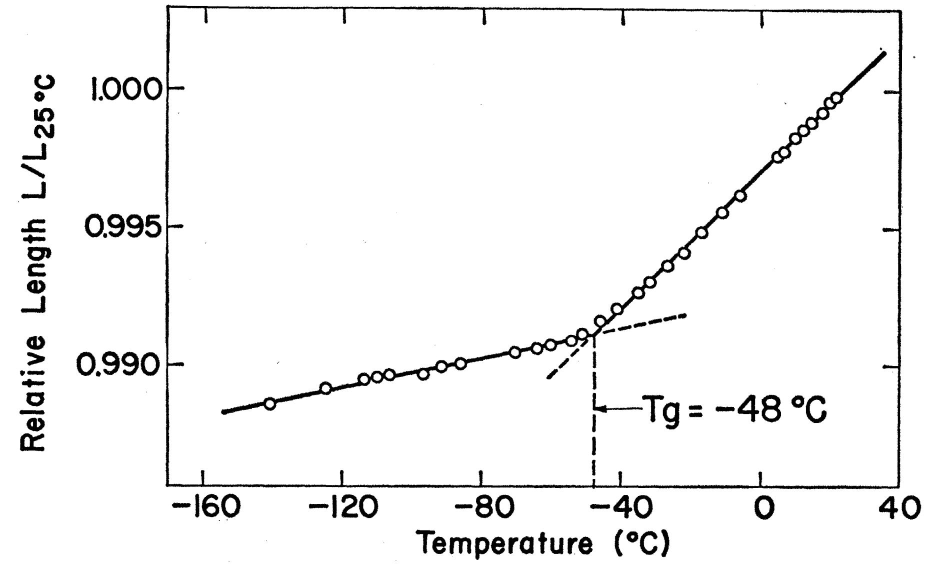


Fig. 1. Determination of the glass temperature, T_g, of a vulcanized neoprene synthetic elastomer containing 35 percent of carbon black filler.

(the state that occurs when no carbon black or other filler is used). The vulcanized specimen recovers almost completely, with low hysteresis loss, while the unvulcanized specimen suffers gross permanent deformation. The polymer physics (*1, 4*) of elastomer networks is outside the scope of this article, but several important features of vulcanized structures should be mentioned. In the curve for the vulcanized specimen (Fig. 2) the stress rises slowly until the elongation is about 200 to 300 percent, and heat is evolved during this extension. In studies of natural rubber and several synthetics it has been established that with such moderate elongations the heat evolved is nearly equal to the work required for extension, and, accordingly, the elastic force is due almost entirely to a decrease in entropy arising from orientation of the random chains of the elastomer.

At high elongations the curve for the vulcanized specimen rises more steeply and the evolution of heat is intensified. That heat is evolved can be verified by the classic experiment of rapidly stretching a "rubber band" lightly across one's lips; the warmth is readily apparent. This behavior in vulcanizates in the gum state is characteristic of natural rubber and those synthetics which crystallize at sufficiently high elongations. The formation of crystalline regions (10 to 30 percent at maximum elongation) has been demonstrated by x-ray diffraction studies; the increase in the evolution of heat results from the associated latent heat. The crystalline regions also act as additional cross-links, restraining the amorphous sections of chain and accentuating the elastic force resulting from further elongation. On removal of the stress, the crystalline regions melt, and the original dimensions obtain.

In the cross-linking of linear polymers of finite molecular weight, two types of network chains are formed. Internal or "effective" chains are those which are bound at each end in a cross-linkage and which contribute toward elastic recovery. However, some terminal chains are produced which are bound at only one end in a cross-linkage, the free end being the terminus of the original linear polymer. A terminal chain, or "loose end," is not elastically effective in providing a restoring force for equilibrium deformations, since it is free to flow and relieve the imposed strain. Flory (*1*) has derived the following equation of state for rubbery elasticity, which relates the numbers of loose ends, total chains, and effective chains:

$$\nu_e/V = \nu/V(1-2M_c/\overline{M})$$

where ν_e/V is the number of effective chains per unit volume, ν/V is the total number of chains per unit volume, and $(1 - 2M_c/\overline{M})$ is a function of the number of loose ends where M_c is the molecular weight of an effective chain and $\overline{M}$ is the primary molecular weight of the uncross-linked polymer. Under conditions which are not destructive of the cross-links, the properties of a cross-linked network are essentially independent of the chemical nature of the cross-links, which may be regarded as structural restraining points (*5*).

Compounding, Processing, and Vaulcanization

A perfect elastic network would be one having no loose ends, one resulting from a linear or raw polymer of infinite molecular weight prior to cross-linking. Such a network would be desirable from the standpoint of properties of the vulcanizate, but in actuality the upper limit of molecular weight (more precisely, the molecular-weight distribution) of the raw polymer is dictated by considerations of compounding and processing; various fillers and vulcanizing aids must be dispersed intimately in the polymer, and the resulting "compound" must be readily amenable to molding or extrusion to obtain the shape of the final vulcanizate. The higher the molecular weight of the raw polymer, the higher the viscosity of the compound (because of the greater mechanical entanglement of the amorphous chains), and the more difficult the processing.

Reinforcing fillers, primarily colloidal carbon blacks, are added to most elastomer compounds and often constitute 50 percent or more, by weight, of the compound. The effects vary with the specific elastomer and filler combination, but in general there is an increase in stiffness, tensile strength, tear resistance, and abrasion resistance. Reinforcing fillers are particularly needed to produce useful mechanical properties in those synthetic elastomers which do not crystallize on stretching. Figure 3 shows a stress-strain curve for a gum vulcanizate of styrene-butadiene rubber and a curve for a corresponding vulcanizate containing reinforcing black (30 percent by weight).

A great body of empirical and theoretical knowledge on the interaction of the elastomer and reinforcing fillers has been developed. It is now recognized that primary chemical bonds are formed between the hydrocarbon chains and active groupings on the surface of the black particle. Free radicals, formed during the mechanical milling or mixing and subsequent vulcanization, appear to play a major role in this bonding (*6*). The bonds so formed constitute additional points of restraint in the vulcanizate.

Vulcanization or "curing" of elastomers can be accomplished with any of a variety of reagents. Preferred systems have been developed for specific compounds and specific applications of each type of elastomer. One basic consideration is the "safety," during processing, of the compound containing the curing reagents. A significant number of cross-links must not be formed at the temperatures prevailing during the milling, mixing, or extrusion steps of processing; the compound must remain plastic in order to be formed smoothly into the desired shape. However, rapid formation of cross-links *is* desired when the shaped compound is subsequently heated in the vulcanization step; here, the selected method of vulcanization represents a compromise between considerations of safety and rate of cross-linkage.

To obtain a stable vulcanizate with adequate mechanical properties, one may use a compound that contains numerous components in addition to reinforcing fillers and curing reagents. These may be antioxidants, plasticizers, diluent oils and softeners, tackifiers, inert clay fillers, coloring pigments, and so on. It must be emphasized that the "rubbery" properties of the vulcanizate are a function of the whole system and of the complex interaction of these components.

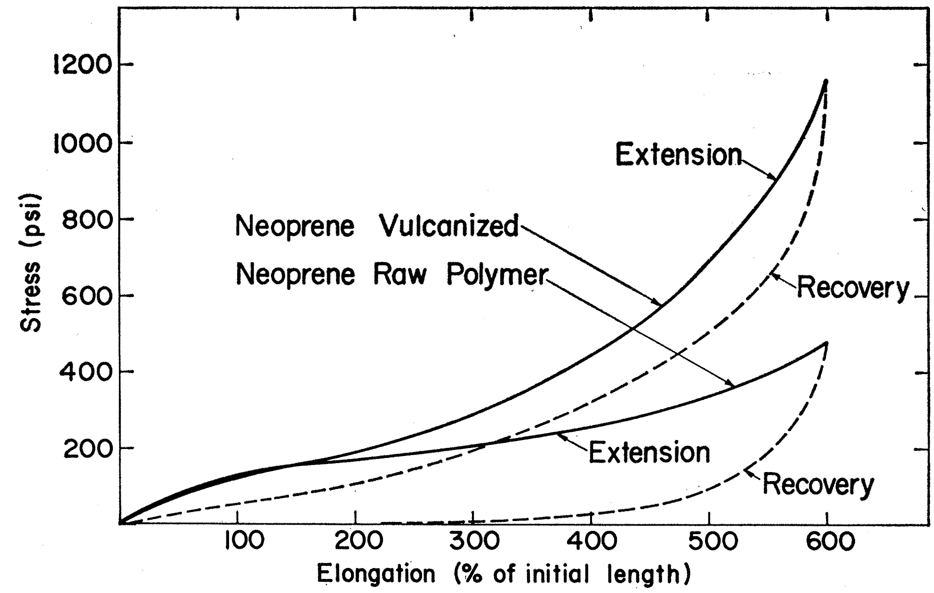
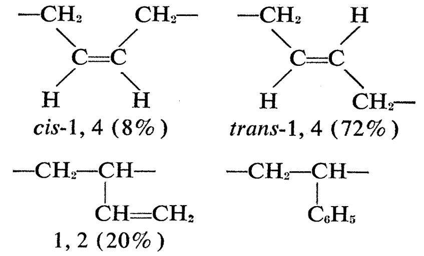


Fig. 2. Effect of vulcanization or cross-linking on the stress-strain behavior of a neoprene synthetic elastomer containing no fillers.

Styrene-Butadiene Rubber

Attempts to synthesize general-purpose hydrocarbon elastomers began in the last century and centered around the homopolymerization of the simple dienes, isoprene and 1,4-butadiene. The synthesis of natural rubber, *cis*-1,4-polyisoprene, received particular attention. Polymers with adequate physical properties were not obtained until the 1930's, when reinforced styrene-butadiene copolymers were developed, primarily in Germany, through the use of emulsion polymerization methods (*7*). In the United States during World War II, an intense effort was made to develop and manufacture such elastomers. Today, styrene-butadiene rubber alone makes up more than 50 percent of all elastomers consumed in this country, the major use being for tires for passenger automobiles. No advantage results from the use of isoprene rather than butadiene, which is readily obtainable through the thermal cracking and dehydrogenation of C-4 hydrocarbon fractions.

The designation *styrene-butadiene rubber* covers a family of copolymers, the most important of which is a random copolymer containing 25 percent styrene. The linear backbone contains the following structural units, which indicate the multiple routes by which the butadiene monomer is incorporated.



The relative amounts of the butadiene moieties vary somewhat with the conditions of polymerization, and typical values are given.

The manufacture of styrene-butadiene rubber is based on polymerization, by free-radical catalysis, in aqueous emulsion systems. This well-studied method (*8*) gives rapid polymerization rates and high molecular weights, and the low viscosity of the medium facilitates removal of the heat of polymerization. One less well known feature of the method is the control of molecular weight by the use of "modifiers" such as dodecylmercaptan. Termination of the growth of a given polymer chain occurs by a chain transfer process,

$$R\cdot + C_{12}H_{25}SH \rightarrow R{-}H + C_{12}H_{25}S\cdot$$

The growing chain radical $R\cdot$ terminates by abstraction of a hydrogen atom from the mercaptan and loses capacity for further growth. The $C_{12}H_{25}S\cdot$ radical formed then reacts with the monomer and initiates another growing chain. In the absence of such a transfer mechanism the raw polymer may have too high a molecular weight and, in a practical sense, be tough and unworkable.

Sulfur has played a major role in the vulcanization of unsaturated elastomers since Charles Goodyear's initial success in developing the method in 1839. The technique for styrene-butadiene rubber is similar to that for natural rubber; sulfur is utilized, together with an "accelerator" and an "activator," to achieve a rapid rate of cross-linking. Numerous organic compounds function as accelerators; two important classes are (i) derivatives of 2-mercaptobenzothiazole and (ii) dithiocarbamate compounds. The activators are usually metallic oxides, such as zinc oxide. The complex chemistry of sulfur vulcanization (*9*) is not yet understood completely, but the point of initial attack appears to be an allylic hydrogen. In this sense, each unsaturated diene unit in the polymer is a potential site of cross-linking. The cross-links formed between chains are primarily sulfide and disulfide groupings.

Specialty Elastomers

A variety of commercial elastomers have been developed to obtain improved physical properties or chemical resistance, or both, under environmental conditions where natural rubber and styrene-butadiene rubber are inadequate. The older special-purpose polymers are,

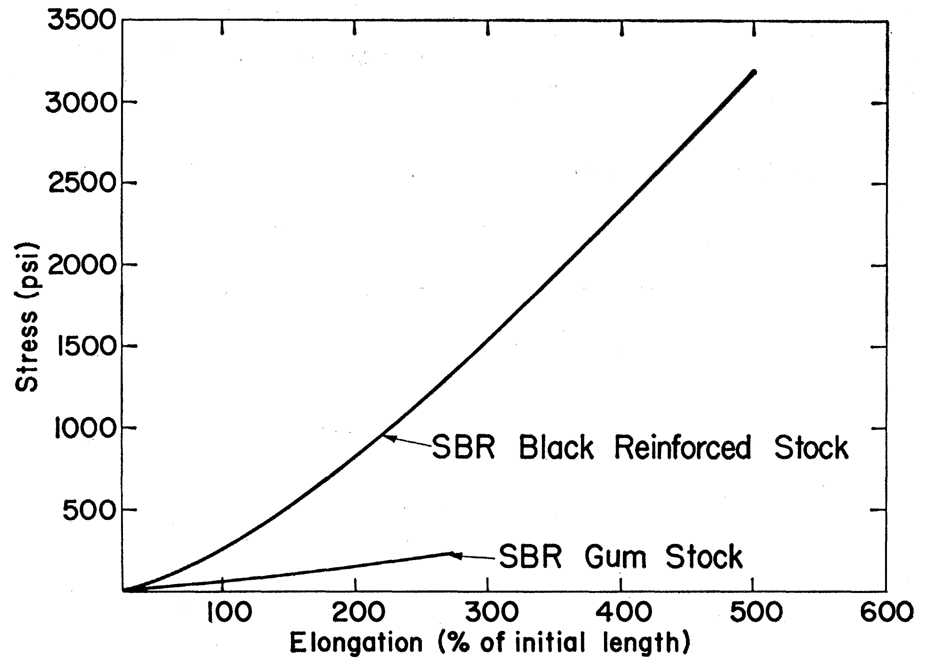
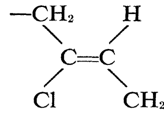


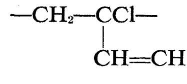
Fig. 3. Effect of reinforcement with 30 percent carbon black on the stress-strain behavior of vulcanizates of styrene-butadiene rubber.

to a considerable extent, derived from conjugated diene monomers, but the more recently developed materials depart from this pattern.

Neoprenes (*10*), developed in 1931, were the first synthetic elastomers manufactured in the United States; they are polymers of chloroprene, 2-chloro-1,3-butadiene. This monomer is more reactive than 1,3-butadiene, and polymerizations are readily obtained in free-radical emulsion systems. About 90 percent of the chloroprene enters in the *trans*-1,4 form; the corresponding chlorine atoms are of the vinyl type and relatively inert. A number of other structures appear which include a small amount of active allylic chloride from 1,2-polymerization. Examples of such structures are the following:



trans-1, 4 (90%)



$$\underset{\mathrm{CH{=}CH_2}}{\mathrm{—CH_2—CCl—}}$$

1, 2 (1%)

The neoprenes crystallize readily on stretching and do not require reinforcement to obtain high tensile strength. They may be vulcanized by the use of metal oxides in conjunction with bifunctional reagents which react with the allylic chloride. A major function of the metal oxide is to neutralize the hydrochloric acid formed.

The chlorinated-olefin backbone of neoprene is less reactive than the backbone of styrene-butadiene rubber and natural rubber, and the vulcanizates are more resistant to ozone and oxidative degradation. Moreover, because of the high chlorine content, the swelling in oils and hydrocarbon solvents is less.

The nitrile rubbers (*11*) are a family of copolymers of butadiene and acrylonitrile; the more important members contain 25 to 35 percent of acrylonitrile. As with styrene-butadiene rubber, the nitrile rubbers were developed initially in Germany in the 1930's, through free-radical emulsion polymerization. Sulfur is used in their vulcanization, as well as accelerators similar to those used for styrene-butadiene rubber. It is primarily because of their resistance to oils that the nitrile rubbers are used extensively. Higher resistance, or lessened swelling, is obtained as the content of polar nitrile groups is increased, but at the expense of flexibility at low temperatures. There is a linear relationship between the glass temperature and the acrylonitrile content.

Butyl rubbers (*12*) are copolymers of isobutylene that contain 1.5 to 4.5 percent of isoprene to provide unsaturated vulcanization sites. Manufacture is by cationic polymerization at −95°C in methyl chloride diluent; aluminum chloride is used as a catalyst. Polymer formation is very rapid, and the heat of formation is removed by vaporization of the methyl chloride. The isoprene is incorporated almost entirely in a 1,4- structure; the resulting unsaturation is in the polymer backbone. Because of the limited unsaturation, butyl rubbers have greater stability against attack of ozone and oxygen than styrene-butadiene rubber and natural rubber, but they offer fewer sites for cross-linking. Vulcanization of butyl rubbers requires relatively higher temperatures, more time, and active accelerators. Butyl rubber crystallizes on stretching, and no enhancement of tensile strength is obtained through using reinforcing fillers, although the latter do give higher moduli and increased resistance to abrasion. As compared to other elastomers, butyl is outstanding in its low permeability to gases.

Synthetic elastomers which have been recently developed for more specialized applications include the silicones and fluorine-containing polymers. The silicone rubbers (*13*), containing the highly flexible silicon-oxygen backbone, have remarkably constant properties over a wide temperature range and retain flexibility down to −80°C and lower. Fluorocarbon elastomers have been synthesized (*14*) through the copolymerization of vinylidene fluoride and perfluoropropylene and are usable at temperatures of 200° to 250°C. In addition, they have outstanding resistance to a variety of oils and chemicals.

Chlorosulfonated polyethylene (*15*) is an elastomer obtained by the conversion of a crystalline precursor of high molecular weight. The substitution of polyethylene with Cl_2 and SO_2 is effected in a free-radical process to introduce approximately one chlorine atom for every seven carbon atoms and one $—SO_2Cl$ grouping for every 90 carbon atoms. The chlorine atoms interfere with chain regularity to such an extent that crystallinity is destroyed. The reactive $—SO_2Cl$ sites are available for cross-linking. The elastomer is completely saturated and extremely resistant to ozone and oxygen.

Fluid Elastomer Systems

In the past 5 years there has been remarkable progress in the development of fluid elastomer systems in which fluid precursors polymerize "in place" in the absence of solvent and diluents to give, in one operation, a vulcanizate of the final shape desired. Polyurethane systems (*16*) based on diisocyanates such as 2,4-tolylenediisocyanate predominate.

The fundamental polymerization reaction is

$$n\,\mathrm{OCN{-}}R\mathrm{{-}NCO} + n\,\mathrm{HO{-}}R'\mathrm{{-}OH} \rightarrow [\mathrm{{-}OOCNH}R\mathrm{NHCOO}R'\mathrm{{-}}]_n$$

where HO—R'—OH is a fluid bifunctional "prepolymer" of molecular weight in the range 1000 to 3000. A corresponding spacing of the resultant urethane groupings along the high-polymer chain is obtained. Intermolecular and hydrogen bonding between these groupings affords effective cross-links at room temperature, and additional covalent cross-linking can be achieved by incorporating small amounts of tri- or tetrafunctional components in the polymerization. The prepolymers are linear polyether or polyester structures in which hydroxyl end groups are readily obtained.

With fluid systems the high-energy requirements associated with conventional rubber mills and mixers are avoided, and fluid systems are of unique value for filling intricate voids with elastomer. The most important application is the manufacture of urethane foams. In this process the fluid components are foamed with a suitable gas, and the catalyzed polymerization is effected rapidly in place.

Stereospecific Polymerization

The most significant advances in elastomer chemistry in recent years have resulted from the discovery of polymerization methods which afford controlled specificity in the stereoisomerism of hydrocarbon polymer chains (*17*). A variety of methods are known, but the most versatile are based on the coordination catalysts reported by Ziegler (*18*) and Natta (*19*). A vast number of coordination catalyst systems have been disclosed (*20*). Such systems are usually obtained from the combination of a compound of a transition metal from groups IVB to VIII and an organometallic compound of a metal from groups I to III in the periodic table. Titanium tetrachloride and vanadium oxytrichloride are typical examples of transition metal compounds, and aluminum alkyls are the most important of the organometallic compounds used. Essential features are vacant inner-shell *d*-orbitals which can coordinate with π electrons of a double bond and a metal-carbon bond. The catalysts can be used in the polymerization of both simple olefins and conjugated diolefins. The detailed nature of the catalysts and the mechanism of polymerization are currently subjects of great interest.

Reinvestigation by means of the new stereospecific polymerization methods of the homopolymerization of diene monomers has been highly rewarding. One of the most interesting achievements is the long-sought synthesis of *cis*-1,4-polyisoprene, which closely simulates natural rubber in structure and properties (*21*). Two methods are available: (i) coordination catalysis and (ii) catalysis by lithium and its compounds. The coordination catalysts are highly specific, and a small change in catalyst composition can have a profound effect on the detailed structure of the polyisoprene (*22*). High *cis*- content (approaching 98 percent in natural rubber) is necessary to obtain a high degree of crystallization on stretching. The optimum catalyst appears to be a combination of titanium tetrachloride and a trialkyl aluminum compound. The polymerization is normally effected in hydrocarbon solvents which do not coordinate with the catalyst and destroy its activity. Similarly, the polymerization is extremely sensitive to trace impurities which may interact with the catalyst, particularly to air and moisture.

Lithium and lithium alkyls are unique among alkali metal catalysts in that they polymerize isoprene selectively to the *cis*-1,4 isomer. The greater selectivity of lithium as compared to sodium or potassium is related to its stronger complexing power, and cyclic complexes have been formulated to account for the steric control obtained. As with coordination catalysis, the polymerization is sensitive to the nature of the solvent, and small amounts of polar materials completely destroy the stereospecificity. Lithium catalysts are effective in butadiene polymerizations, but stereospecificity is not obtained.

Natural rubber has remained the elastomer of choice for the construction of heavy-duty tires for trucks, buses, and aircraft, because of its superior ability to dissipate heat and its longer life, as compared to styrene-butadiene rubber. Tire tests with synthetic *cis*-1,4-polyisoprene indicate that this elastomer is comparable to natural rubber in these respects, suggesting that the role of the latter may further decline.

By the proper choice of coordination catalyst, 1,4-polybutadienes can be obtained whose fine structure varies from 98 percent *cis*- to essentially 100 percent *trans*-. As with isoprene, polymers with high content of *cis*- forms offer the best elastomeric properties; the all-*trans*-1,4-polybutadiene is a crystalline material that melts at 135° to 145°C! Maximum contents of the *cis*- forms are obtained with catalysts derived from aluminum alkyls in combination with titanium tetraiodide or cobalt chloride. The polymer is being commercialized at a rapid rate because of its flexibility at low temperatures and its high resistance to abrasion when used in tires. *cis*-1,4-Polybutadiene may also partially replace natural rubber, and this event may influence greatly the development of synthetic *cis*-1,4-polyisoprene.

Ethylene-Propylene Elastomers

Coordination catalysis has been the means of obtaining, for the first time, high polymers of propylene and higher olefins. Stereoisomerism exists, and two regular arrangements have been synthesized by Natta (*22*). One is "isotactic" polypropylene (melting point, 170°C), in which successive units of a given chain possess the same configuration (all *d* or all *l*). The other is "syndiotactic" polypropylene (melting point, 183°C), in which *d* and *l* units alternate along the polymer chain. These regular polymers are highly crystalline, but "atactic" polypropylene, in which there is a random distribution of *d* and *l* units, is amorphous. Similarly, random copolymers of ethylene and propylene are amorphous and elastomeric and can contain from about 35 to 65 percent of either monomer.

Ethylene-propylene elastomers are produced from the cheapest and most readily available olefin raw materials, and the reinforced vulcanizates have desirable physical properties. Because of the completely saturated backbone, they have excellent resistance to ozone, oxygen, heat, and other degrading agents which attack unsaturated groupings in a chain, causing cleavage and loss of molecular weight. In turn, this stability makes vulcanization difficult, and energetic reagents such as peroxides are required. However, terpolymers produced from ethylene, propylene, and certain *nonconjugated* dienes have been developed recently which permit conventional sulfur vulcanization (*23*). The diene component contains dissimilar double bonds such that only one double bond enters into the polymerization; the other double bond remains in a grouping pendant to the polymer backbone. The pendant double bonds serve as cross-linkage sites in sulfur vulcanization but prevent unsaturation in the polymer backbone, where degrading agents cause chain cleavage and loss of desirable physical properties.

Technological evaluation of ethylene-propylene elastomers is being made to an increasing degree, and materials of this class will be produced in commercial quantities in 1963.

Summary

Elastomers are produced by the controlled cross-linking of linear, flexible chains of polymers of high molecular weight. The structures must be above the glass temperature, and they must be amorphous in the unstretched state. At moderate elongations, the elastic force is due almost entirely to a decrease in entropy. At higher elongations, partial crystallization may occur; if it does not, reinforcement with fillers of colloidal carbon black is required. The physical properties of an elastomer are modified greatly by interaction with the fillers and other components of the vulcanizate.

Synthetic elastomers have largely replaced natural rubber in the United States since World War II. Currently the major product of general usage is styrene-butadiene rubber, a copolymer manufactured by free-radical emulsion polymerization. It is vulcanized with sulfur and requires reinforcement. A number of other synthetic elastomers have been developed for improved performance at elevated temperatures and in the presence of oxygen, ozone, oils, chemicals, and so on. They represent a variety of structures, methods of synthesis, and methods of vulcanization.

The homopolymerization of isoprene in the all-*cis*- configuration has been achieved with the advent of stereospecific polymerization methods. This synthetic *cis*-1,4-polyisoprene appears to be fully equivalent to natural rubber. With the newer catalysts, *cis*-1,4-polybutadiene and the new ethylene-propylene copolymers have also been produced. It is anticipated that the commercial importance of these new synthetic elastomers will increase rapidly.

References

1. P. J. Flory, *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, N.Y., 1953).
2. R. Garrett, unpublished data.
3. R. F. Boyer and R. S. Spencer, in *Scientific Progress in the Field of Rubber and Synthetic Elastomers* (vol. 2 of *Advances in Colloid Science*), H. Mark and G. S. Whitby, Eds. (Interscience, New York, 1946), pp. 1–57.
4. L. R. G. Treloar, *Physics of Rubber Elasticity* (Oxford Univ. Press, New York, 1958); F. Bueche, *Physical Properties of Polymers* (Interscience, New York, 1962); J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, 1961); A. V. Tobolsky, *Properties and Structure of Polymers* (Wiley, New York, 1960).
5. E. F. Cluff and E. K. Gladding, *J. Appl. Polymer Sci.* **3**, 290 (1960).
6. D. Parkinson, *Reinforcement of Rubbers* (Lakeman, London, 1957).
7. R. F. Dunbrook, in *Synthetic Rubber*, G. S. Whitby, Ed. (Wiley, New York, 1954), pp. 32–55.
8. F. A. Bovey, I. M. Kolthoff, A. I. Medalia, E. J. Meehan, *Emulsion Polymerization* (Interscience, New York, 1955); H. L. Williams, in *Polymer Processes* (vol. 10 of *High Polymers*), C. E. Schildknecht, Ed. (Interscience, New York, 1956), p. 111.
9. J. R. Shelton and E. T. McDonel, *Proceedings of the International Rubber Conference, Washington, D.C.* (1959), pp. 596–603; D. Craig, *Rubber Chem. Technol.* **30**, 129 (1957).
10. A. M. Neal and L. R. Mayo, in *Synthetic Rubber*, G. S. Whitby, Ed. (Wiley, New York, 1954), pp. 767–793.
11. W. L. Semon, *ibid.*, pp. 794–837.
12. R. M. Thomas and W. J. Sparks, *ibid.*, pp. 838–891.
13. F. M. Lewis, *Rubber Chem. Technol.* **35**, 1222 (1962).
14. S. Dixon, D. R. Rexford, J. S. Rugg, *Ind. Eng. Chem.* **49**, 1687 (1957).
15. W. F. Busse and F. W. Billmeyer, Jr., *J. Polymer Sci.* **12**, 599 (1954).
16. J. H. Saunders, *The Polyurethanes* (vol. 16, part 1, of *High Polymers*) (Interscience, New York, 1962).
17. W. Cooper, in *Progress in High Polymers*, J. C. Robb and F. W. Peaker, Eds. (Academic Press, New York, 1961), pp. 281–340; C. E. H. Bawn and A. Ledwith, *Quart. Rev. London* **16**, 361 (1962).
18. K. Ziegler, E. Holzkamp, H. Breil, H. Martin, *Angew. Chem.* **67**, 541 (1955).
19. G. Natta, *ibid.* **68**, 393 (1956); *Chem. Ind. London* **1957**, 1520 (1957); *J. Polymer Sci.* **16**, 143 (1955).
20. N. G. Gaylord and H. F. Mark, *Linear and Stereoregular Addition Polymers* (Interscience, New York, 1959).
21. J. D. D'Ianni, *Rubber Chem. Technol.* **34**, 361 (1961).
22. G. Natta, *Makromol. Chem.* **35**, 94 (1960).
23. E. K. Gladding, J. W. Collette, B. S. Fisher, *Ind. Eng. Chem. Prod. Res. Develop.* **1**, 65 (1962); J. J. Verbanc, M. S. Fawcett, E. J. Goldberg, *ibid.*, p. 70.

Undergraduate Institutions and the Production of Scientists

The talented student's decision to become a scientist can be influenced by the type of college he attends.

Alexander W. Astin

The number of undergraduate students who abandon plans to pursue a career in science far exceeds the number who decide to enter science from other fields. Hence, the number of qualified individuals who are available to enter fields in which there is already a shortage of trained manpower tends to be reduced. The factors in the student's undergraduate college experience which affect his motivation to pursue a career in science therefore seem worthy of investigation (*1*).

Among the factors which may influence a student's decision to pursue a career in science at graduation are his personal characteristics at the time he enters college and the type of college he attends. But it is difficult to study the influence of the institution, since students are not distributed randomly among different types of colleges. Under these conditions, variations among institutions with respect to the career plans of their graduates may reflect differences in the kinds of student bodies initially recruited, differences in the effects of the institutions themselves, or some combination of these two factors.

The importance of using rigorous research designs in attempting to compare the effects of different types of colleges on student performance is clearly illustrated by the history of the "Ph.D. productivity" problem. In the earliest studies (*2*) it was found that undergraduate institutions differed markedly

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