THE CHEMISTRY OF SYNTHETIC RUBBER*

RUDOLPH DEANIN**
University of Illinois, Urbana

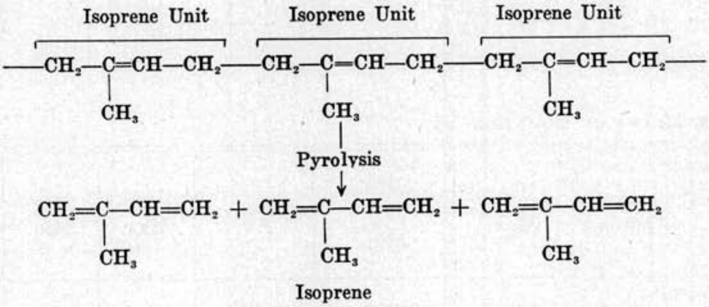
INTRODUCTION

In 1835 an obscure German chemist named Himly heated a sample of natural rubber and distilled out a volatile colorless liquid which was later named isoprene.[1]

During the next half century, several men reported the repolymerization of isoprene.[1, 2, 3] Then in 1882 Sir William Tilden suggested that if another and more economical source of isoprene were available, commercial polymerization of isoprene to synthetic rubber might be possible.[3]

While isoprene itself was not readily available in large quantities, several similar substances were.

Pyrolysis of Natural Rubber



$$\underbrace{-CH_2-\underset{CH_3}{C}=CH-CH_2}_{\text{Isoprene Unit}}-\underbrace{CH_2-\underset{CH_3}{C}=CH-CH_2}_{\text{Isoprene Unit}}-\underbrace{CH_2-\underset{CH_3}{C}=CH-CH_2}_{\text{Isoprene Unit}}-$$

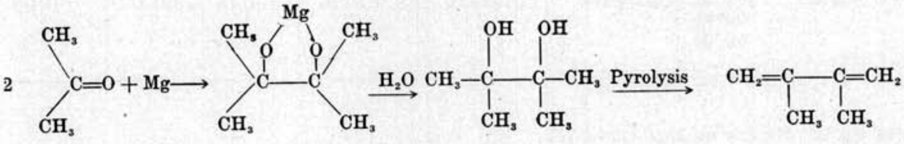
$$\downarrow \text{Pyrolysis}$$

$$CH_2=\underset{CH_3}{C}-CH=CH_2 + CH_2=\underset{CH_3}{C}-CH=CH_2 + CH_2=\underset{CH_3}{C}-CH=CH_2$$

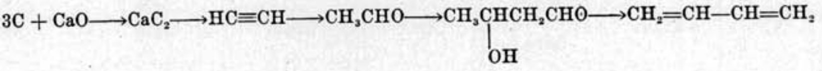
Isoprene

Preparation of Dienes

2,3-Dimethylbutadiene



Butadiene



$$3C + CaO \longrightarrow CaC_2 \longrightarrow HC\equiv CH \longrightarrow CH_3CHO \longrightarrow CH_3\underset{OH}{C}HCH_2CHO \longrightarrow CH_2=CH-CH=CH_2$$

$$2C_2H_5OH \longrightarrow CH_2=CH-CH=CH_2$$

$$\text{Petroleum} \xrightarrow[\text{Cracking}]{\text{Catalytic}} CH_2=CH-CH=CH_2$$

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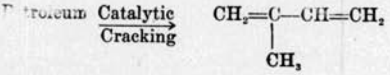
**Present address: Allied Chemical and Dye Corporation, Morristown, New Jersey.

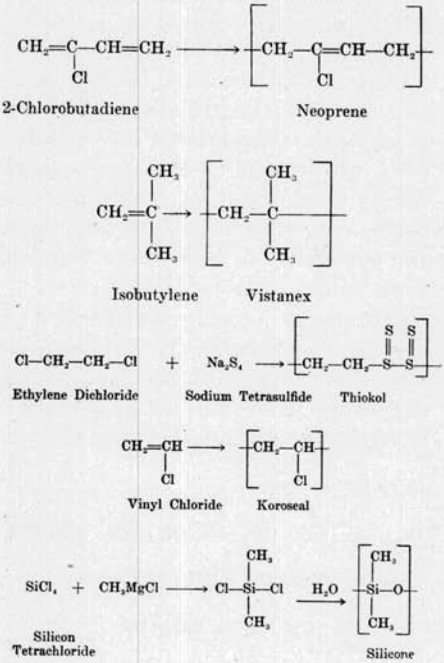
Isoprene



$$\text{Petroleum} \xrightarrow[\text{Cracking}]{\text{Catalytic}} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}CH{=}CH_2$$

For example, bimolecular reduction of acetone produced pinacol hydrate, which was then dehydrated to 2, 3-dimethylbutadiene; this formed the basis of the German synthetic "Methyl Rubber" during the first World War. Later 1, 3-butadiene became available from several sources in large quantities and is now the most important material in synthetic rubber production. Very recently even isoprene became commercially available, but contemporary industrial practice heavily favors the use of butadiene for general purpose synthetic rubber.[4]

Other Synthetic Rubbers



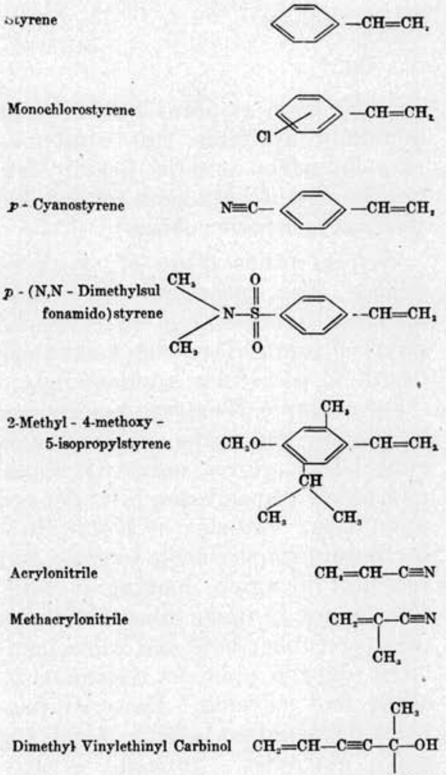
Several other types of synthetic rubber are produced in small amounts because they have special physical properties which make them useful in particular applications.[4]

For example, Neoprene has high oil resistance, and many of its uses in rubber hose, gloves, industrial shoes, and power transmission belts depend upon this. Vistanex or Butyl Rubber is very impermeable to gases and resistant to aging, making it valuable for use in inner tubes. Thiokol's uses for rubber hose and cable insulation depend upon its resistance to aging and solvents. Koroseal provides transparent elastic films for many purposes. Silicone greatly outlasts other rubbers in high temperature gaskets and similar uses. The present discussion, however, will be limited to butadiene polymers, which form the major portion of synthetic rubber production today.

THE GR-S POLYMERIZATION SYSTEM

The physical properties of butadiene synthetic rubber are improved greatly by copolymerizing butadiene with various vinyl comonomers.

Comonomers

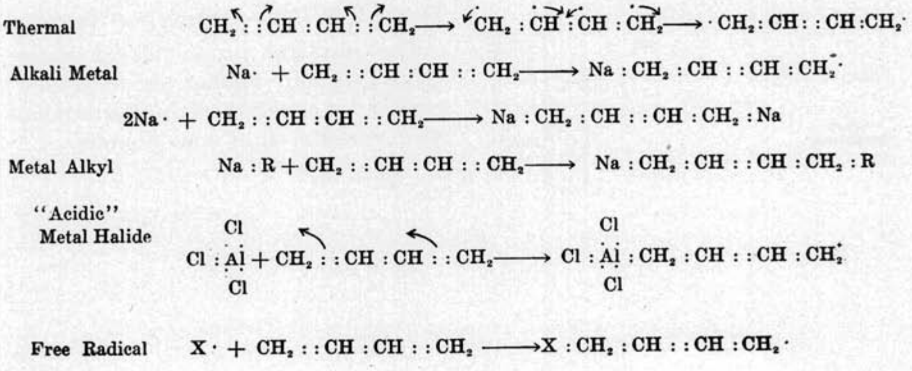


While styrene is the most common comonomer in GR-S rubber, many substituted styrenes have been used experimentally to determine whether they may produce improved synthetic rubber.[5] For example, monochlorostyrene is available in moderate quantities and has produced tires which wear considerably longer than GR-S. One *p*-cyanostyrene copolymer produced excellent preliminary tests, but this comonomer is so difficult to prepare that no further studies of it have been attempted. Attempts to produce superior synthetic rubber have led to the investigation of even such complex comonomers as *p*-(N, N-dimethylsulfonamido) styrene and 2-methyl-4-methoxy-5-isopropylstyrene.

Acrylonitrile is another comonomer frequently used in industry. Preliminary studies indicate that methacrylonitrile may be far superior for tires, but this comonomer is practically unavailable for further tests at present.[6] Dimethyl vinylethinyl carbinol is an example of another comonomer which may offer the possibility of improving physical properties.[7]

Butadiene copolymerizes very slowly, even under the influence of heat and pressure. With the addition of proper catalysts—or activators—the polymerization reaction may be

Catalysis of Butadiene Polymerization



Thermal $CH_2::CH:CH::CH_2 \longrightarrow \cdot CH_2:CH:CH:CH_2 \longrightarrow \cdot CH_2:CH::CH:CH_2\cdot$

Alkali Metal $Na\cdot + CH_2::CH:CH::CH_2 \longrightarrow Na:CH_2:CH::CH:CH_2\cdot$

$2Na\cdot + CH_2::CH:CH::CH_2 \longrightarrow Na:CH_2:CH::CH:CH_2:Na$

Metal Alkyl $Na:R + CH_2::CH:CH::CH_2 \longrightarrow Na:CH_2:CH::CH:CH_2:R$

"Acidic" Metal Halide $Cl:\overset{Cl}{\underset{Cl}{Al}} + CH_2::CH:CH::CH_2 \longrightarrow Cl:\overset{Cl}{\underset{Cl}{Al}}:CH_2:CH::CH:CH_2\cdot$

Free Radical $X\cdot + CH_2::CH:CH::CH_2 \longrightarrow X:CH_2:CH::CH:CH_2\cdot$

carried out readily under a wide variety of conditions.

Thus alkali metals,[8] alkali metal alkyls,[9] or so-called "acidic" metal halides[10] may be used to activate the carbon-carbon double bonds and thus catalyze extremely rapid butadiene polymerization. The synthetic rubber industry has generally preferred to use activators which decompose tc yield free radicals which initiate the polymerization reaction.

Free Radical Activators

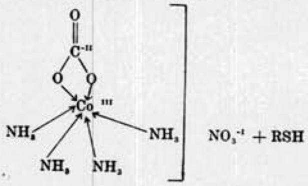
$$H{-}O{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{-}O{-}O{-}\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}{-}O{-}H$$

$K_3Fe(CN)_6 + RSH$

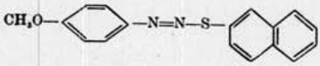
$H_2O_2 + \left[Fe_x^{III}(P_2O_7)_y^{-IV}\right]^{-z}$

ROOH + Other Ingredients

$O_2 + \cdot\left[Fe_x^{II}Fe_y^{III}(P_2O_7)_z^{-IV}\right]^{-w} + RSH$



$NO_3^{-1} + RSH$



$+ \left[Fe_x^{II}(P_2O_7)_y^{-IV}\right]^{-z}$

While a number of types of activators have been developed,[7, 11] the chemistry of activation is very obscure and poorly understood. A survey of some of the activators frequently used indicates that most of them are good oxidizing agents, and suggests that initiation of polymerization may involve some oxidation reaction; but the specificity of these activator systems emphasizes the complexity and obscurity of this reaction.

The polymerization may be carried out in the vapor or bulk (liquid) phase,[8] in solution, [9, 10] suspension, or emulsion[12].

While the Russian synthetic rubber industry has concentrated upon vapor or liquid phase polymerization of butadiene using sodium catalyst, American and German synthetic rubber production is based upon emulsion copolymerization of butadiene with other comonomers, using free radical activators.

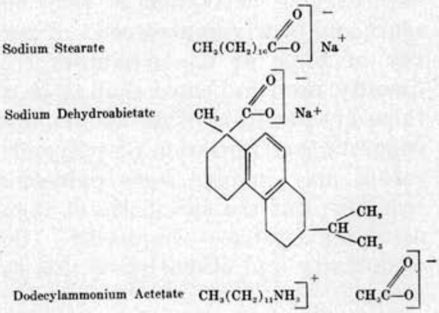
To disperse the organic monomer liquid in water various emulsifiers have been used.

In America ordinary fatty acid soaps[13] and certain rosin soaps (essentially sodium dehydroabietate)[14] are most commonly used, and other emulsifiers such as amine soaps have also been investigated.[15] In Germany, scarcity of natural soaps led to the use of various synthetic emulsifiers, such as Mersolat and Nekal.[16]

Polymerization Media

VAPOR	BULK	SOLUTION	SUSPENSION	EMULSION
Monomer	Monomer	Monomer	Monomer	Monomer
	Comonomer	Comonomer	Comonomer	Comonomer
		Solvent	Water	Water
			Protective Colloid	Emulsifier
Catalyst	Catalyst	Catalysts	Catalysts	Catalysts
				Modifier

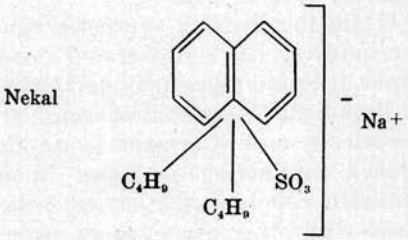
American Emulsifiers



$$\left[CH_3(CH_2)_{16}C{\overset{O}{\lVert}}-O\right]^- Na^+$$

$$\left[CH_3(CH_2)_{11}NH_3\right]^+ \left[CH_3C{\overset{O}{\lVert}}-O\right]^-$$

German Emulsifiers



Mersolat $\left[C_{14-17}H_{29-35}SO_3\right]^- Na+$

THE GR-S POLYMERIZATION REACTION

When soap dissolves in water it forms plate-shaped or spherical micelles.[17]

The monomer is emulsified as droplets of organic liquid surrounded by soap molecules and suspended in the aqueous phase. Monomer in these droplets diffuses gradually into the soap micelle, where intimate interphase contact permits the activators to initiate the polymerization reaction. As the reaction proceeds, continuous diffusion of monomer into the micelle and polymerization there converts the micelle into a polymer-monomer particle surrounded by a layer of soap molecules which stabilize the latex. Eventually the monomer droplets are all consumed, and only the polymer-monomer particles remain. Then further polymerization of the monomer decreases its concentration in the particles, and the rate of polymerization decreases gradually as the reaction approaches completion.[18]

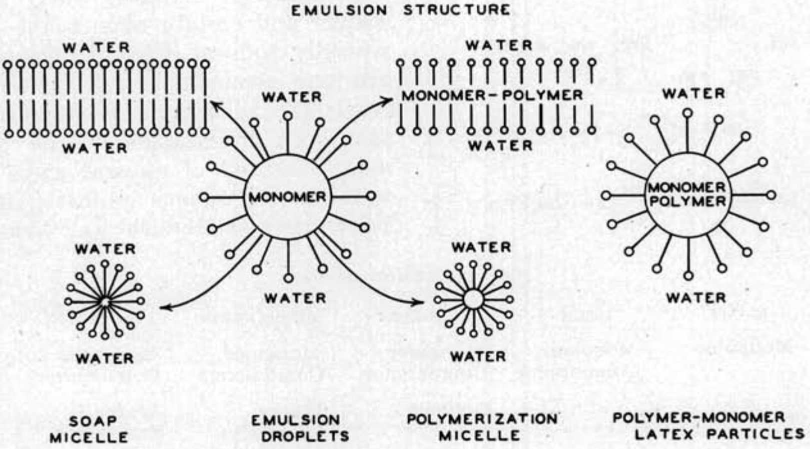
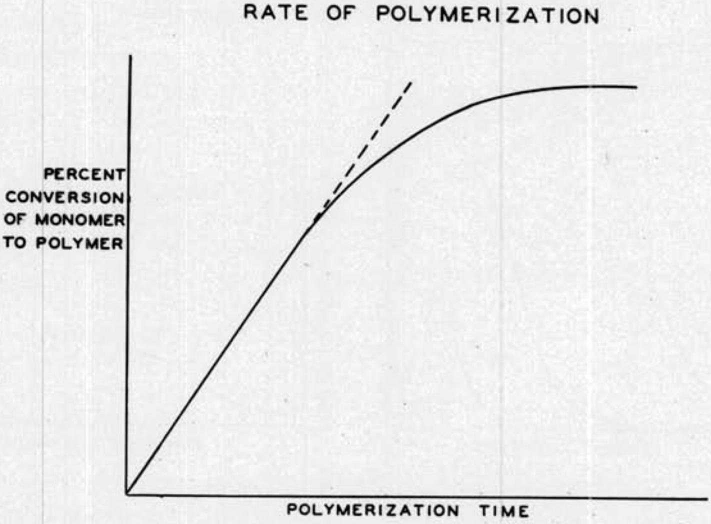


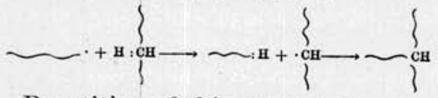
FIG. 1



RATE OF POLYMERIZATION

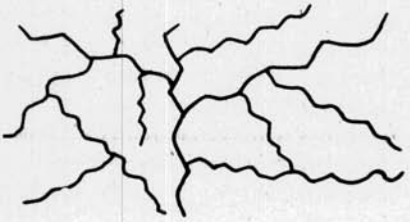
FIG. 2

As the polymerization reaction proceeds, the concentrations of the reactants and the physical conditions of the system change, and the molecular structure and physical properties of the resulting polymer vary continuously.[19] The growing polymer molecule may attack another polymer molecule, probably at the carbon-hydrogen bond adjacent to a vinyl group, and this chain transfer reaction produces a new free radical which grows into a cross-linked three-dimensional molecule.[20]



$$\sim\!\sim\cdot + H:CH \longrightarrow \sim\!\sim:H + \cdot CH \longrightarrow \sim\!\sim CH$$

Repetition of this cross-linking reaction produces a "pincushion" shape polymer molecule.



If a modifying agent is used to regulate the growth of these cross-linked molecules, it terminates the growing molecules by a chain transfer reaction.[21]

$$\sim\!\sim\cdot + RS:H \longrightarrow \sim\!\sim:H + RS\cdot \longrightarrow RS\sim\!\sim$$

As the modifier is consumed during the reaction, its concentration decreases and its effectiveness becomes less and less. The decreased frequency of chain transfer permits the molecular weight to rise, but it also permits more extensive cross-linking to form large three-dimensional molecules which are insoluble in benzene and are known as gel.[22] As the modifier concentration is decreased, gel formation increases rapidly. Molecular weight, which is measured by the intrinsic viscosity of the dilute benzene solution, increases as the modifier concentration decreases, as long as the rubber is entirely soluble; but when part of the rubber is excluded from the benzene solution as gel, the intrinsic

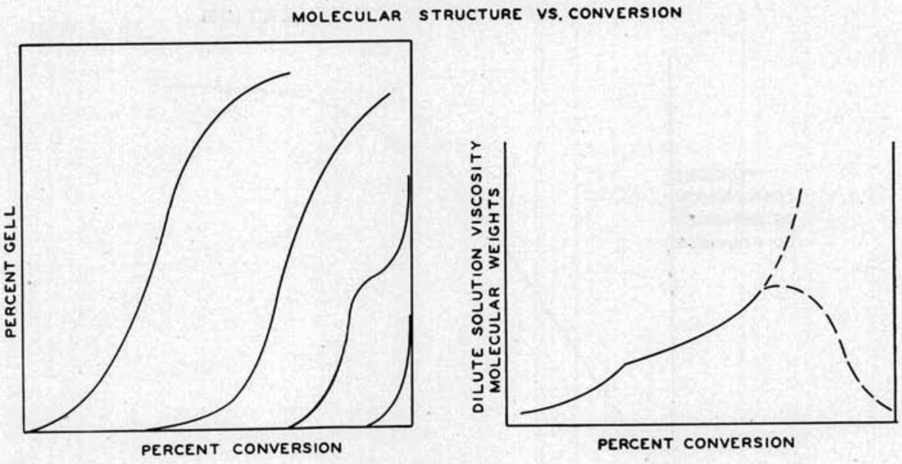


FIG. 3.

viscosity drops, while the actual molecular weight probably rises very rapidly.

PHYSICAL PROPERTIES OF GR-S SYNTHETIC RUBBER

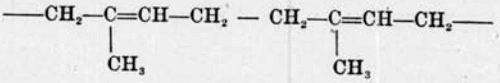
Corresponding with these changes in molecular structure there is a gradual change in physical properties.[23] As the molecular weight increases, the synthetic polymer resembles natural rubber more closely and the physical properties improve. Extensive gel formation however produces a structure quite different from natural rubber, and has a detrimental effect on physical properties. At high conversions, when gel formation becomes serious, Mooney viscosity increases, while processability and ease of breakdown decrease; these all indicate the formation of tough rubber which is difficult to process. Rebound (resilience) improves; but tensile strength, elastic elongation, rate of crack growth during flexing, and modulus all become worse, signifying a deterioration of rubber-like properties. Thus polymerization conditions must be carefully controlled to produce polymers with the desired physical properties.

Even at its best, however, synthetic rubber is very different from natural rubber, and much of this difference is believed to be due to differences in molecular structure.[24]

Natural rubber contains a 2-methyl group placed at regular intervals along the polymer chain, while polybutadiene does not. The position of monomer units in the polymer chain is very regular in natural rubber, whereas it is a random mixture of 1, 2- and 1, 4-addition in synthetic rubber, and would be even worse in synthetic polyisoprene. The occasional units of vinyl monomers add to the heterogeneity of the synthetic rubber molecule. Furthermore, in natural rubber the arrangement of the atoms at the double bonds is always *cis,* while in synthetic rubber it is a mixture of *cis* and *trans.*[25] Natural rubber contains long linear molecules, while synthetic rubber contains a heterogeneous mixture of cross-linked three-dimensional molecular structures. Finally the molec-

Molecular Differences Between Natural and Synthetic Rubber

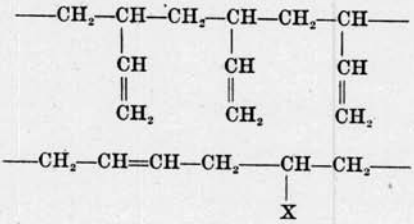
Natural Rubber



$$\mathrm{-\!-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}=CH-CH_2-\!-}$$

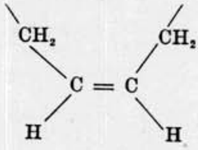
Synthetic Rubber

$$\mathrm{-\!-CH_2-CH=CH-CH_2-CH_2-CH=CH-CH_2-\!-}$$

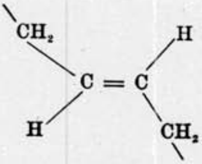


$$\mathrm{-\!-CH_2-\underset{\underset{\displaystyle CH_2}{\underset{\|}{\displaystyle CH}}}{\underset{|}{CH}}-CH_2-\underset{\underset{\displaystyle CH_2}{\underset{\|}{\displaystyle CH}}}{\underset{|}{CH}}-CH_2-\underset{\underset{\displaystyle CH_2}{\underset{\|}{\displaystyle CH}}}{\underset{|}{CH}}-\!-}$$

$$\mathrm{-\!-CH_2-CH=CH-CH_2-\underset{\displaystyle X}{\underset{|}{CH}}-CH_2-\!-}$$



Cis



Trans

ular weight distribution is very different in the natural and synthetic polymers: natural rubber is more homogeneous, has less low-molecular weight material and a higher average molecular weight; while synthetic rubber has more low-molecular weight material, is more heterogeneous, and has a lower average molecular weight.[22, 26] All these differences contribute to the great difference between the two in processability and physical properties.

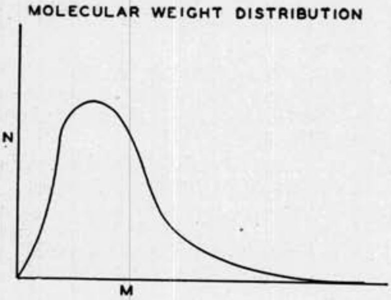


FIG. 4

Consequently we cannot call butadiene polymers "rubber substitutes" in the sense that they must resemble and replace natural rubber. Rather, we must recognize that synthetic polymers are distinctly different from natural rubber, and that therefore their processing, physical properties, and resulting uses must be designed to use them to best advantage, rather than merely to make them a bad substitute for something entirely different. During the war years, the urgent need for a rubber substitute prevented this functional approach; and consequently the future of synthetic rubber, in competition with natural rubber, is still uncertain. On the other hand, the special synthetics, which were developed and applied specifically where they were superior, are certainly here to stay, and will become more and more important as they are developed further by industrial research.

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