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Some Recent Contributions to Synthetic Rubber Research*

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Introduction

WHEN the war put an end to shipments of natural rubber from the Far East, it became evident that synthetic chemistry would be called upon to fill the gap in our supply of this strategic material. We know now how effectively the emergency was met. In less than three years the production of Buna S type synthetic rubber alone had risen to exceed our total prewar comsumption of natural rubber. Few, however, realize the magnitude of the effort and the extent of the cooperation between groups of experts that was essential for the achievement of this success.

Rubber companies in this country had been experimenting with synthetic substitutes for natural rubber for some time before the present war began. None of these products, however, was sufficiently advanced either from the stand-point of raw materials or in regard to the knowledge of its properties, to warrant production on a large scale as a substitute for natural rubber during the emergency. In 1942, following the advice of the Baruch Committee, we decided to place chief reliance on Buna S, the butadiene-styrene synthetic rubber which the Germans developed about 1934. In addition, considerable support was given to the domestic synthetics, Neoprene, Thiokol and Butyl. The latter rubbers, however, were not considered as useful for tires as Buna S.

Making Buna S in this country and fabricating it were not simple, however. The Germans had kept the details of the process secret and restricted shipments of the product. Besides, as we have since found out, the German chemists did not have any too complete control of the process themselves and the type of rubber made by them, as shown by samples obtained indirectly, was not satisfactory for use on American processing machinery. Our engineers and research men were therefore faced with the problem of setting up a process on an enormous scale to turn out a product which could be used in our tire plants and which would give satisfactory service on the road. Fortunately for us, a few companies had acquired enough knowledge

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both from German sources and from their own researches to warrant taking the gamble.

As a part of the large program laid out under the auspices of the Government in 1942, provision was made for a cooperative research and development effort to parallel and to contribute to the constructional program designed to provide the much needed rubber. A large number of company laboratories as well as universities contributed to this research. The Bell Telephone Laboratories because of its past contributions in this field of synthetic polymers was asked to participate in this program. The present discussion is intended to describe part of the Bell Laboratories investigations directed toward the improvement of Buna S type rubber, particularly work relating to the characterization and control of the final copolymer.

In order to present the material in a logical and understandable form to readers unfamiliar with the subject-matter, brief mention will be made of the history of the synthetic rubber problem and of progress in the knowledge of polymeric substances during recent years.

The Problem of Synthetic Rubber

The problem of synthesizing natural rubber is almost as old as man's curiosity about the nature of rubber itself which began when Faraday in 1826 first showed it to be a hydrocarbon having the formula $C_{10}H_{16}$. Experiments done by Williams in 1860, in which he obtained isoprene from natural rubber and by Bouchardat in 1879, who showed that isoprene could be polymerized to a rubber-like material, represent about as close as we have come to synthesizing natural rubber in spite of many subsequent efforts. In 1910 particularly, when the price of natural rubber reached $3 per pound, considerable pressure was exerted to bring about this synthesis. Although the chemist failed in this quest his very failure, analyzed in the light of more recent studies on other polymers as well as rubber, has had its virtues. It has emphasized the importance of chemical structure, that is the precise organization of the atoms composing the rubber molecules (in addition to simply the nature of these atoms) in determining the ultimate properties of a polymer.

Although natural rubber eluded synthesis, the early organic chemical work nevertheless laid the basis for our present synthetic rubber. Curiously, much of this pioneering research on synthetic rubber was done in England with the support of strong proponents of natural rubber. However, Germany and Russia were also active contributors. The United States later achieved fame by bringing forth two of the most promising rubbers yet produced, Neoprene and Butyl. The early foreign synthetics were based on the polymerization of hydrocarbons such as 1-methyl butadiene and 2,3

dimethyl butadiene and butadiene itself. They were undoubtedly "rubbers" of a sort but there could be no question about their inferiority to the natural product. Even today the Russians persist in making their synthetic rubber from butadiene and, although there have been improvements, the polymer is still subject inherently to the same fundamental difficulties of structure that existed when it was first synthesized by Lebedev in 1911.

The deficiencies in the early synthetic rubbers and the difficulty of synthesizing natural rubber were appreciated in Germany where in the period 1935–39 several plants were constructed to manufacture synthetic rubber, including Buna S, on a large scale. By polymerizing together butadiene and styrene instead of butadiene alone they achieved several advantages over previous synthetic rubbers. The fact that the best opinion in this country decided in favor of imitating German Buna S, shows that progress in Germany was indeed substantial. As we have already indicated, however, improvements were necessary in both the German product and process if it was to be satisfactory for our use. The product developed in this country and now being currently produced at the rate of nearly 700,000 tons per year, although prepared from the same starting materials as German Buna S, therefore differs from the latter in many important respects. The name Government Rubber-Styrene, abbreviated GR-S, has been given to this product.

History of the Development of Ideas of Composition and Structure of Polimers

All rubbers, both natural and synthetic, as well as all organic plastics and fibers belong to a class of substances called polymers. We now know that they are constructed of large molecules, in turn built up of simple atomic patterns (repeating units) joined end to end. Surprisingly, it was not until about fifteen years ago that this idea gained general acceptance among chemists. Since that time truly remarkable research progress on polymers has been made. It is not our object to present a full account of this work here. Most of it was carried on independently of its application to the synthetic rubber problem but nevertheless has had a profound effect upon it. A brief review of the growth of the present concepts of natural and synthetic polymers will, however, help to emphasize the significance of the more recent researches on synthetic rubber.

For a long time chemists believed that naturally occurring polymers like natural rubber, cellulose and silk were indefinite chemical compounds in which the arrangement of the atoms was so complex as to defy analysis. As has been mentioned, Faraday had shown in the case of natural rubber that carbon and hydrogen atoms were present in the ratio of 16 hydrogens

for every 10 carbons. It was not until much later that it was postulated that rubber, inasmuch as it had the same hydrogen to carbon ratio as isoprene obtainable from it, was a compound in which many isoprene groups were in some manner combined together. Thus, Harries about 1904 was inclined to regard rubber as a sort of association complex representing a combination of relatively small ring molecules held together by van der Waals' attractions[1]. This same view of polymers as associations of small molecules was also applied to cellulose by well-known carbohydrate chemists both in England and in Germany.

The influence of the contemporary colloid chemists helped to promote this idea. Even the term "micelle", applied by them to soap and other aggregates, which are in fact van der Waal's or ionic associations, was unfortunately adopted to describe the structure of many of the organic polymers. In addition, early x-ray studies on natural polymers, because of a misinterpretation of the diffraction patterns, lent further support to these views. For some reason or other it was not appreciated by workers in the field that the x-ray unit cell did not necessarily mark the boundaries of the organic molecule. Hence, since the unit cells appeared to be small, many erroneously concluded that the molecules were small also. It is to Sponsler and Dore[2], working in this country in 1926 on the x-ray structure of cellulose fibers, that we must give thanks for being the first to realize the incorrectness of the older x-ray deductions and to postulate a long primary valence chain structure for cellulose.

The realization that natural organic polymers really consisted of very long chains of primary valence bound atoms, in the strictly organic chemical sense, came surprisingly slowly. Staudinger in Germany beginning about 1926 was most insistent on this view[3], although others including Meyer and Mark were developing the same conception. As early as 1910 Pickle in England had conceived of such a chain type of molecule for natural rubber but unfortunately did not follow it up. As the idea of molecules of large size grew, it became more and more popular to try to measure them. Also there was much effort given to working out the details of the "crystal structure" of the natural products insofar as they could be regarded as crystalline. Here again was an opportunity for argument which is still going on today: just what do we mean by the term "crystalline" when applied to these substances? The answer seems to be that we have all degrees of organization of the molecules, or more correctly parts of molecules, in polymers from the completely chaotic or amorphous in some to highly ordered or what may be called crystalline arrangement in others. We shall have occasion to come back to this subject in our later discussion.

It was logical that the interest of scientists in the constitution and structure of polymers should be lavished on naturally occurring high polymers

rather than on the synthetic ones. But strangely enough it has been the synthetic polymers which have really led us to a more complete understanding of the natural substances and particularly to the explanation of why polymers have the properties they do.

The early work on synthetic polymers, as we have seen, centered around the constitution of natural rubber and efforts to duplicate it. Soon, however, organic chemists found they could make better products from other dienes than they could from isoprene which seemed to be the progenitor of natural rubber. The approach was necessarily empirical—one of trying out a variety of reaction conditions on the chemical compound to be polymerized and studying the properties of the final product as compared to natural rubber. Nearly always the comparison was disappointing. Following this procedure the Germans and the Russians developed their respective competitors for natural rubber from 1910 to the present time. The organic chemistry of polymerization, the reactions whereby the simple unsaturated compounds join up into longer molecules, was, however, very imperfectly understood in 1910 and still is not clear today.

Perhaps it was for this reason that some organic chemists decided to build large molecules by methods in which they had acquired great confidence in regard to how the atoms come together. Emil Fischer, the first of this group, succeeded in synthesizing a polypeptide molecule of known composition and known organic structure which, although smaller in size than the natural proteins, nevertheless was very large compared to the usual organic molecules. This was in 1906. About 20 years later the matter was again opened up in a more general way by Staudinger and his collaborators who synthesized chains built up of alternate carbon and oxygen atoms, the polyoxymethylenes, and showed how such large molecules could give rise to a pseudo-crystalline type of crystal lattice. Then came the simple and beautiful work of W. H. Carothers and his collaborators beginning in 1928, which led to the development of nylon. These compounds and the linear polyesters, which Carothers had (by improvement of the methods of Vorländer[4] and others) prepared, because they were known to contain long chain molecules of definite structure and composition, were ideal compounds to examine in order to determine what factors were truly responsible for observed polymer behaviors. In this way it was hoped to explain the outstanding toughness, high tensile strength, rubberiness, peculiar softening and flow properties and a host of other characteristics of polymers which make these materials so important in life processes and technology. Researches along these lines have indeed shown that the way the various units are combined and the regularity of the atomic arrangements in the units themselves have a profound effect on properties.

This work has also emphasized the importance of size and linearity of the

chain molecules on polymer behavior. For example, the length of the molecules which are present in a polymer is of critical importance to certain properties such as mechanical strength. These facts, as well as the necessity for order in the arrangement of the molecular units along the chains were not appreciated by the early organic workers. That Carothers realized what many of the older organic chemists did not realize is indicated by his statement made in 1934 that the problem of physically characterizing polymers in significant numerical units is of the utmost importance and that it should receive more attention jointly from physicists and chemists.

Some Physico-Chemical Features of Polymers

We have seen very briefly how the quest for the origin of properties of rubbers and polymeric substances in general led of necessity to a study of the intimate details of chain molecule structure on the one hand and a study of the general characteristics of large molecules on the other. Before taking up the specific researches on GR-S synthetic rubber, however, it will be helpful to pursue somewhat further the ideas on the formation and constitution of polymers.

There are two general chemical processes by which polymer molecules are formed, namely polymerization and polycondensation. Chemists, at times, use the first term to represent all processes leading to the formation of large molecules but it is more convenient to distinguish two processes even though the difference between them is academic in some cases. In polymerization, chemical molecules called the monomers, become "activated" either by heat energy or by means of special chemical compounds. In this state they spontaneously grow at the expense of their unactivated neighbors until the growth of the chains is abruptly terminated, either by active chains coming together or by a transfer of energy to other, often foreign, molecules. The entire growth reaction for any given chain usually takes but a fraction of a second for completion. When two or more different monomers capable of polymerization enter together into the same chain molecule formation the process is referred to as "copolymerization".

In polycondensation, identical or non-identical molecules react to give large molecules just as in polymerization. The difference is that in the former reaction a molecule of water (or other substance) is evolved each time a new molecule is added to the growing chain system. Also the reaction resulting in chain growth is step-wise in the sense that each added molecule follows the same steps in reacting that are followed by any other. No special type of activation on the end of the growing chain is necessary. Finally, since there is no activated growth, the phenomena of termination in the sense used above in connection with polymerization do not exist.

Both kinds of polymers are important technically. Thus polystyrene is a

polymerization type of polymer. Nylon on the other hand is a polycondensation polymer. Buna S type synthetic rubber is a polymerization copolymer because it is formed by polymerizing together styrene and butadiene monomers.

One of the important characteristics about reactions leading to the formation of polymers is that they result not in molecules of the same size but in a statistical distribution or mixture of molecules of various sizes. These molecular weight distributions, as they are called, in special cases can be

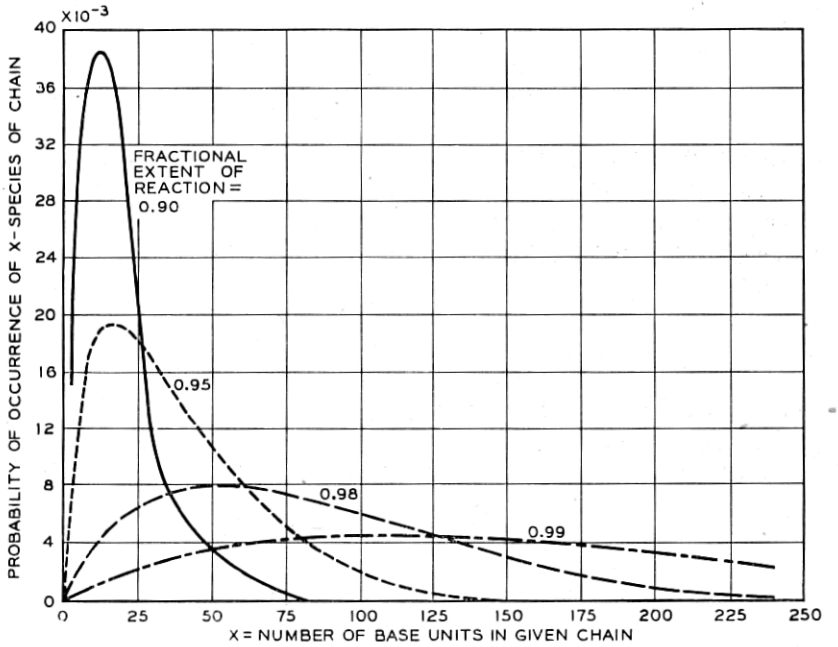


Fig. 1.—Curves showing frequency distribution of molecule species of different chain lengths for linear polyesters (Flory—reference 5).

calculated from the nature of the reaction. In other instances this is not possible, although experimentally it is often possible to arrive at an approximate curve representing a given polymer distribution. Figure 1 shows a series of curves for a linear polyester in which the reaction conditions are such that the calculated curves[5] represent very closely the actual distribution of molecules present. The curves represent the weight fraction of each molecular species present in the mixture at the extent of reaction shown on each curve.

It is customary to speak of an "average molecular weight" therefore in characterizing these polymer mixtures. Several different types of averages

are used for convenience. The two most frequently employed are what are termed the "number average" and the "weight average". If osmotic pressure measurements are made on solutions of the polymer and extrapolated to zero concentration these will lead to a number average molecular weight figure. This average represents what we would obtain if we sorted out the molecules according to molecular weight and counted them. Multiplying each molecular weight (m_1) by the number present (n_1) and dividing by the total number of molecules we obtain the number average molecular weight ($\overline{M}_n$) or stated mathematically

$$\overline{M}_n = \frac{\Sigma m_i n_i}{\Sigma n_i} = \frac{1}{\Sigma \frac{f_i}{m_i}} \tag{1}$$

where f_i is the weight fraction of species of molecular weight, m_i.

Usually the osmotic pressure measurements are difficult to carry out and a simpler measurement, that of dilute solution viscosity (DSV) is performed. This determination consists in measuring the relative viscosity of a solution of the polymer at one given low concentration and calculating

$$(DSV) = \frac{\ln \eta_r}{c} \tag{2}$$

where η_r is relative viscosity and c is the concentration in grams per 100 ml. of solution. A more fundamental quantity usually differing little from the DSV value is the so-called intrinsic viscosity. This is defined as $[\eta] = \frac{\ln \eta_r}{c_{c \to o}}$. Measurements are made at several concentrations and extrapolated to zero concentration just as for osmotic pressure. From this value a molecular weight, which may be referred to as a viscosity average molecular weight, can be calculated from the empirical expression $[\eta] = K(\overline{M}_v)^a$ where both K and a are constants over a fairly wide range, and which must be independently determined. In some polymer distributions this viscosity average is very close to the weight average defined by

$$\overline{M}_w = \frac{\Sigma w_i m_i}{\Sigma n_i m_i} = \Sigma f_i m_i \tag{3}$$

where m_i is again the molecular weight of each species and f_i is the weight fraction in which it is present in the mixture. In the example of Fig. 1 the number averages are indicated by the maxima of the various curves. Here the viscosity and weight averages are identical.

In polymers an equally important consideration with molecular size distribution is chain molecule structure. It is convenient to distinguish between micro-chain structure and macro-chain structure. By micro-chain

structure we mean the detailed architecture of the chain molecule over distances of the order of length of the repeating unit. The kind of atoms involved in the unit and their spatial arrangement in regard to atoms in the same chain as well as in the neighboring chains are included in this definition. It is the micro-chain structure which determines entirely the chemical properties of the polymer and to a large extent the physical properties as well. Thus, the influence of solvents, oxidizability, hardness at a given temperature, softening point, ability to crystallize are determined largely by the micro-structure of the polymer.

Macro-chain structure on the other hand refers to the long range form of the chain molecule. It ignores composition and concerns itself with the nature of the molecule as a whole and with its interconnections to other molecules.

Certain terminology has grown up in this connection which can be conveniently defined at this time. We speak of "linear" polymers when primary valence bonds can be traced through the molecules from one end to the other without passing over the same atoms twice. We say "branched" molecules are present when the process of tracing leads us into one or more offshoots from the main chain. When the degree of branching becomes excessive the molecules may become insoluble in good solvents for the linear or slightly branched molecules. When nteworks of molecules are present we say the polymer is "netted" or "cross-linked". In this instance closed paths may be traced and the smaller the paths, the "tighter" or more "intense" is the netting. Netted chain molecule systems are invariably insoluble. Insoluble polymers whether because of intense branching or netting are called "gel". We speak of micro-gel when the gel particles (molecules) are microscopic or smaller in size (say less than 1μ) and of macro-gel when the particles are large.[6] Usually macro-gel as well as the micro-gel is associated with soluble molecule species. These latter are referred to as "sol" and represent the linear or the less branched molecular components of the mixture. The complete description of every molecule present in a polymer mixture is thus a very difficult if not impossible task. We are thus forced to employ a statistical treatment.

In the case of copolymers, still other considerations arise. There is the probability that the reacting components will not react with one another at the same rates they do with themselves. When this occurs the composition of the molecules in the mixture varies, some containing more of one component than others do. Also the order in which the components are arranged along the chains may vary molecule to molecule. Such circumstances of course give rise to varying properties in the copolymer mixture. We shall have occasion to consider these questions below in connection with the development of GR-S.

Early Status of GR-S Synthetic Rubber

The process by which GR-S type synthetic rubber is made is known as the emulsion polymerization process. In it, butadiene and styrene in the proper proportions are emulsified in water with small amounts of catalysts and substances called modifiers which serve to control the plasticity of the polymer. During the reaction period of from ten to twenty hours about three-fourths of the butadiene and styrene are converted into the synthetic rubber. The reaction occurs in such a way that very minute particles are formed and the resulting synthetic latex is suggestive of natural latex. To obtain the rubber itself the latex is coagulated with acid and sodium chloride or with aluminum sulfate and the coagulum washed. After drying the rubber crumbs are baled and shipped to the fabricating factories. The above brief sketch of course does not provide an idea of the many complexities which arise in practice nor of the many process variations which can be used to control the final properties of the rubber. A complete treatment of this subject falls outside the scope of this paper.

When the Baruch Committee advised "bulling through" the synthetic program on the basis of Buna S type rubber, it fixed the chemical composition of the product to a very great extent. We knew then, or shortly afterward, that we would be required to use approximately 690,000 tons of butadiene and 197,500 tons of styrene per year to produce the coplymer rubber. Whatever other components might be employed would be available in only insignificant quantities by comparison. One element of choice remained as far as chemical composition was concerned, namely the proportions in which the two components might be used. German Buna S is supposed to consist of 75 parts by weight of butadiene to 25 parts of styrene but, as we shall see later, this ratio does not determine the ratio actually present in the final copolymer which is a function of reaction variables as well as the initial ratio of the ingredients. Consequently it was necessary to examine the composition of the final copolymer and to control it at the proper ratio of butadiene to styrene. The chemical composition was not the only factor to be controlled, however, since as we have seen, the properties of polymers unlike ordinary chemical compounds depend as much if not more on the chain structure. This is of course not only dependent on the nature of the starting ingredients but also on the manner in which they are combined into the chain.

At the time intensive work was undertaken in this country on Buna S type synthetic rubber little attention had been given to its characterization by physico-chemical means. The usual physical testing procedures involving the preparation of compounds by mixing in pigments and vulcanizing were of course being employed to supply useful information about the

copolymer produced and the vulcanization properties possessed by it. What was needed, however, were more precise and revealing tests, and tests which could be carried out directly on the copolymer itself. No ordinary chemical methods such as are applicable to the usual type of synthetic chemicals apply, for reasons which should be evident from our previous discussion. New methods of characterization designed to insure uniformity and satisfactory quality in the GR-S copolymer were required.

The precise and early control of the copolymer was of utmost importance. Non-uniformity in the product may cause serious troubles in fabricating operations such as are employed in tire plants, wire coating factories, adhesives manufacture, etc. Furthermore, with a varying product it often cannot be determined whether the trouble, when it occurs, is in the copolymer or in the method of fabrication being used.

What are the characteristics which must be controlled to insure a satisfactory product? To answer this question it was necessary to investigate a variety of GR-S copolymers and to conduct service tests on them in order to determine their practical performance. Some of these tests, particularly those on tires, have been very extensive. Some of the characteristics of the copolymer which experience has taught should be measured and controlled are:

1. The over-all or average styrene content in the butadiene-styrene copolymer.

   This necessitates (1) a method of separating the pure copolymer (which is the rubber-like component) from non-rubber components such as soap, salts, insoluble matter etc., and (2) a suitable method for determining the styrene content of the purified copolymer.
2. The percentage soap, fatty acids and low molecular butadiene-styrene compounds in the rubber.
3. The amount of "gel" fraction, if present, and the swelling volume of the gel.[7]
4. The average molecular size of the "sol" or soluble fraction of the copolymer.
5. The degree of branching of the sol molecules.
6. The molecular weight distribution of the sol.

In addition to the above tests on the final copolymer, control tests which can be used during the polymerization to tell when the reaction has progressed to the proper point were needed. In the following paragraphs we will take up in some detail the problem of characterization and attempt to show the basis on which methods have been evolved to control some of the quantities listed above.

Composition of GR-S and Its Determination

Given a piece of GR-S synthetic rubber, our first task from the standpoint of determining its chemical composition is to separate the pure copolymer which is responsible for the rubber-like properties from the non-rubber constituents. The latter comprise soaps or other emulsifying agents, fatty acids, salts, antioxidant and low molecular weight, non-rubbery butadiene-styrene products to the extent of several percent. Some of these minor ingredients, like the antioxidant, are essential whereas others play no important role subsequent to polymerization. All, however, must be separated from the copolymer before it can be properly evaluated. The analysis for the non-rubber components after separation is fairly straightforward and standard and will not be gone into here.

It has been found that the azeotrope of toluene and ethyl alcohol which consists of approximately 30 parts by volume of toluene to 70 parts by volume of alcohol is an excellent extractant for the non-rubber compounds and hence may be used to effect a separation[8, 9]. The procedure for isolating the copolymer is simply to place a quantity, say 10 grams, of the GR-S in an extraction thimble supported in an extraction flask as shown in Fig. 2. Another, more rapid, procedure is to reflux the azeotrope over the rubber for two hours, when extraction has been found to be essentially complete. This method is now used in the Standard Specification for all GR-S. The pure copolymer, left as residue, is the product to which we now turn our attention.

As has been mentioned, the ratio in which butadiene and styrene are employed in the starting mixture does not determine either the ratio in the whole copolymer at a given stage of reaction or the ratio present in any given chain molecule of the copolymer. Therefore the starting ratio cannot be relied upon to control the composition of the final copolymer. Experiments show that under certain process conditions large differences in composition between different fractions of the copolymer do occur. Even under the best conditions theoretical considerations predict that variations must occur between molecules since the ratio of the reactants is continuously changing during the reaction.

Let us examine the chemistry of the process for a moment to try better to understand why these variations are possible. When styrene (S) reacts with itself polystyrene (S_x) is formed. Analogously polybutadiene (B_y) is formed in the case of butadiene (B). In GR-S both styrene and butadiene react to give a copolymer.

When a quantity of styrene undergoes polymerization, a distribution consisting of various numbers of long chain molecules of various lengths is formed. Thus, if we start with N_1 molecules of styrene, S, the polymeriza-

tion reaction results in the formation of molecules of polystyrene by the addition of S to S in chain fashion. The result may be expressed as follows:

$$N_1S \rightarrow a_1S_1 + a_2S_2 + a_3S_3 + \cdots + a_nS_n \qquad (4)$$

where each term represents a group of styrene molecules containing $1, 2 \cdots n$ styrene units, n assuming values up to several thousand depending on the

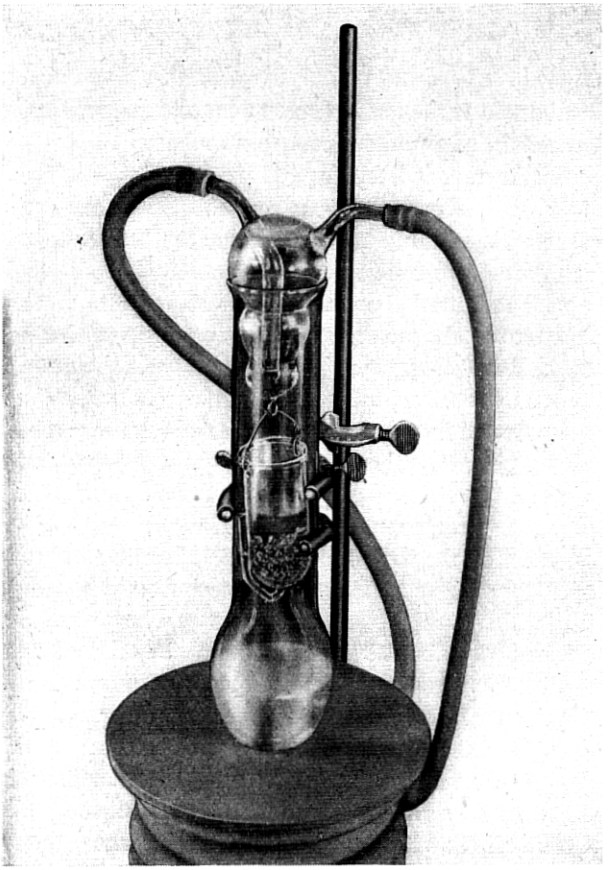


Fig. 2.—Apparatus for extracting non-rubber components from GR-S.

reaction conditions. If N_1 is very large there are of course many molecules, a_n, formed of the length corresponding to each value of n. In fact, $a_1 + 2\,a_2 + 3\,a_3 + \cdots + na_n = N_1$. The first term in (4) allows for the molecules which do not react, the second represents the dimers, the third the trimers, etc.

In an analogous way we may consider N_2 molecules of butadiene, B, to polymerize into chain molecules of various lengths:

$$N_2B \rightarrow b_1B_1 + b_2B_2 + b_3B_3 + \cdots + b_nB_m . \tag{5}$$

Now if styrene and butadiene molecules react together, as in the production of GR-S, we can represent their copolymerization as the insertion of the styrene chains (or portions of them) of (4) at random points in the butadiene chains of (5) to form chains S_jB_k. That is

$$N_1S + N_2B \rightarrow \Sigma\ a_iS_jB_k \tag{6}$$

where j and k take on a variety of integral values and in any particular chain the arrangement of S and B units is probably random.

In practice, in the reaction represented by (6), N_2/N_1 has the value of approximately 6 since 75 parts by weight of butadiene are employed to 25 parts of styrene. Each chain molecule therefore would be expected to contain about 6 butadiene residues to each one of styrene. It is actually found, however, as indicated above that the starting ratio is not adhered to throughout the reaction, the molecules formed early being richer in butadiene and those formed later being poorer in butadiene than the starting ratio of 6 to 1. But, not only is the ratio B_k/S_j a variable from molecule to molecule of the copolymer formed but also their sequence along the chain is variable. Thus, in equation (6), even when equal numbers of styrene and butadiene molecules are present, a strict alternation is apparently not maintained but "strings" of one pure component or the other, form.

In the GR-S reaction the *weight* ratio of butadiene to styrene in the first molecules formed may be as high as 4:1 or more from a starting charge of ratio 3:1. Thus, the average weight percentage of styrene in the GR-S copolymer first formed is about 8% below that in the original charge (25%) and increases with conversion so that at the point where the reaction is stopped the copolymer forming contains about 29% styrene. Analogously there is evidence to show that in GR-S no regular sequence of butadiene and styrene along the chain molecules exists but rather a more or less random entrance of the two residues into the molecules with a frequency approximating the 6 to 1 ratio, as the extent of combination (percentage conversion) of the two ingredients approaches completion where obviously the two must become equal. Figure 3 illustrates this behavior for a typical sample prepared in the laboratory. An integral curve showing the cumulative percentage styrene and a differential curve representing the percentage styrene in the increment of the copolymer are illustrated.

It must be left to future research to determine how important the molecule to molecule variations in styrene content are in terms of useful properties

and to devise ways of eliminating them if necessary. For the present, we are perhaps justified in assuming that these variations can be neglected. The control considered here therefore relates to the over-all or average composition of the copolymer.

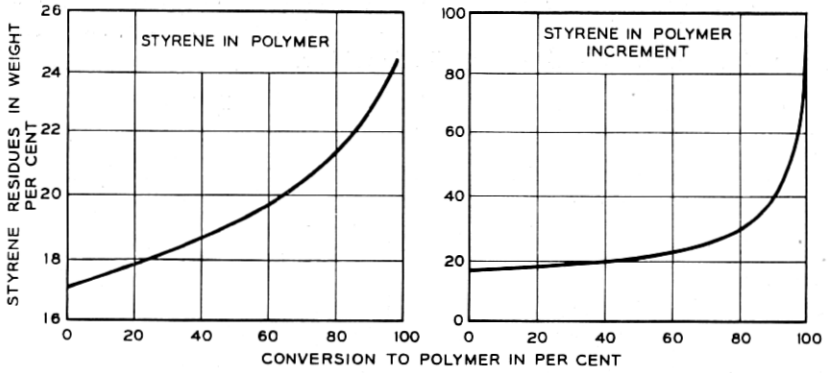


Fig. 3.—*Left:* Cumulative percentage by weight of styrene in the copolymer as a function of percentage conversion for an initial 25 percent styrene charge. *Right:* Percentage by weight of styrene in the polymer forming at any instant as a function of conversion for an initial 25 percent styrene charge.

Determination of Styrene Content

Many suggestions involving both chemical and physico-chemical methods for measuring the average styrene content of GR-S copolymers have been proposed. Physico-chemical methods when applicable have an advantage in speed and precision over straight chemical methods and therefore have been more carefully examined. Both ultra-violet absorption[10] and refraction[8] have been shown to be applicable but since the absorption method is much more sensitive to impurities, the refraction method has proven the most general. It has the advantage also that it can be employed with polymers containing considerable gel fraction.

The refraction method is based on the fact that the styrene residues in the copolymer provide a greater contribution to the refraction of light passing through the solid or a solution of the solid than do the butadiene residues. Early work at the Bell Laboratories showed that the determination of the refractive index of the solid *unpurified* copolymer led to errors. In addition, the determination of the refractive index even of purified polymers was not precise if much gel was present, as frequently was the case with the early synthetic product. As a consequence a method, based on the use of the interferometer, was developed[8, 10]. The procedure is to disperse 2.4 grams of the pure copolymer in benzene, transfer the contents to the interferometer

cell and make a reading of the change in refraction compared to the pure benzene. This value, with the help of a curve relating styrene content to refraction, enables the true styrene content to be determined. The curve of refraction as a function of styrene content must be constructed beforehand and is shown in Fig. 4. This curve is obtained by measuring the refraction of pure polystyrene on the one hand and polybutadiene on the other. Checks also were made by independent methods of estimating composition in the range of the usual Buna S-type synthetic rubber.

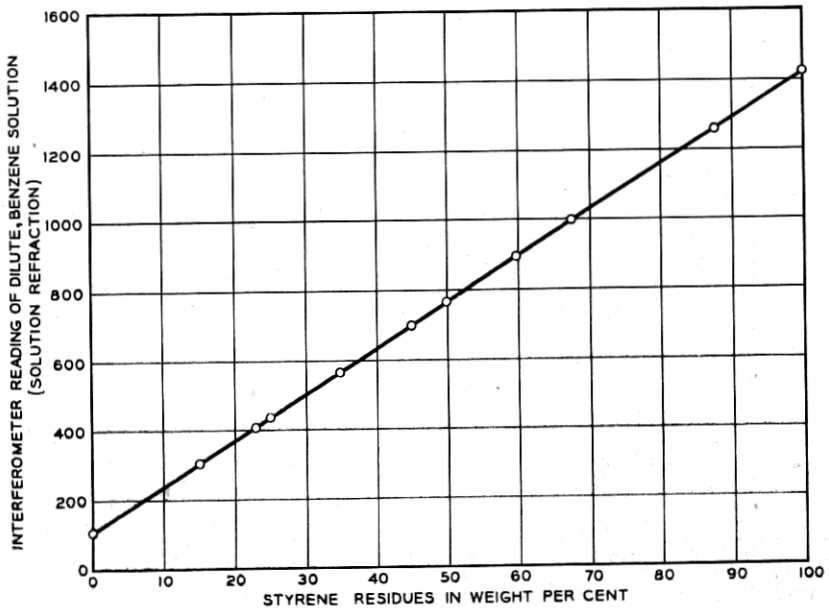


Fig. 4.—Refraction as a function of styrene content for solutions in benzene of polymers containing known percentages of styrene.

Through the use of this method it has been possible to control the styrene content of the copolymer to about ± 0.2 weight percent styrene residues, which is amply close for all purposes. Figure 5 shows the apparatus employed in this determination, the interferometer. More recently, it has been possible to employ a simpler procedure where a milling of the copolymer is introduced to remedy difficulties early encountered in the determination of the refractive index directly on the solid[11]. Although not as precise as the interferometer method, this method is shorter and as a consequence is finding application in process control. It is safe to say that today, with these methods, the control of the average composition of GR-S procuced in this country is now entirely adequate for all purposes.

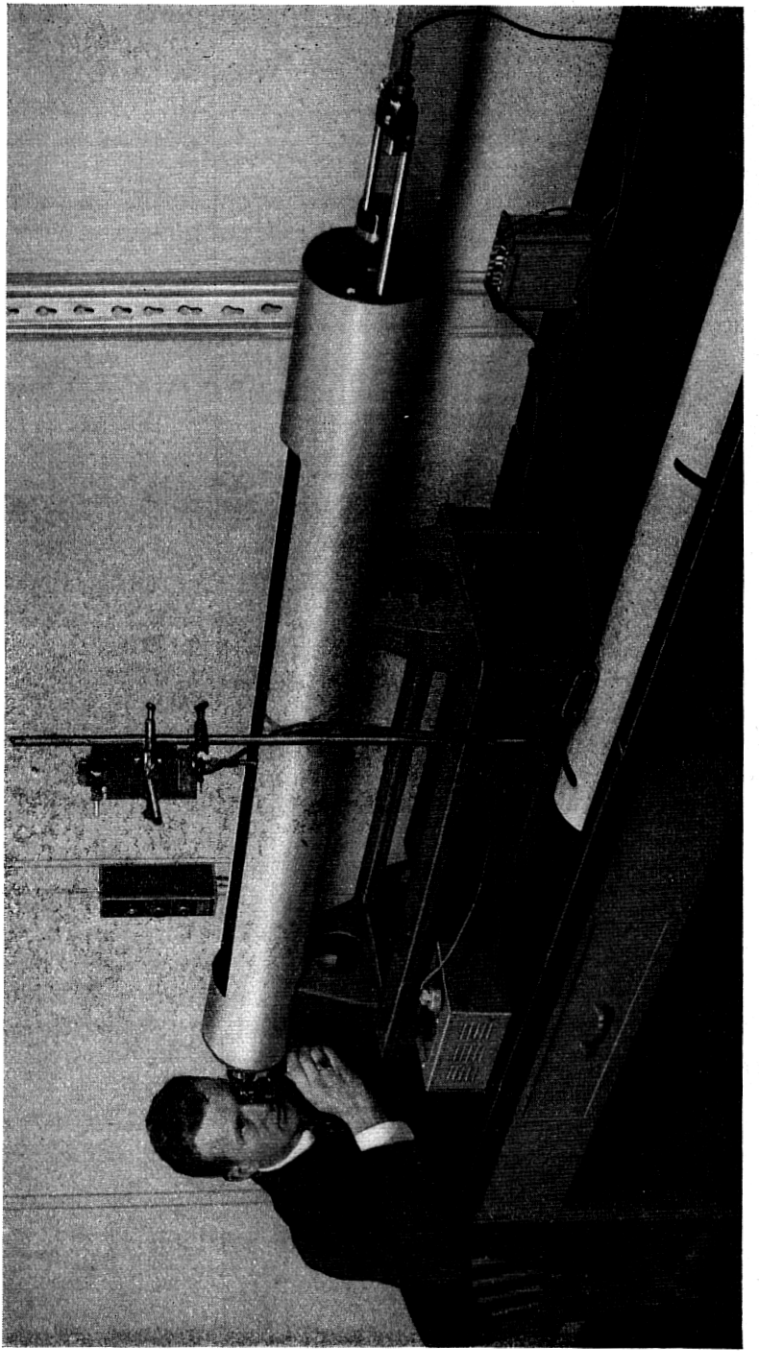


Fig. 5.—Interferometer used in the determination of styrene content of synthetic rubber from refraction.

Molecular Weight Distribution in GR-S

Unlike the linear polyesters whose molecular weight distributions can be calculated from simple assumptions (Fig. 1), the distribution of molecular sizes present in polymerization polymers cannot, at the present state of our knowledge at least, be accurately predicted. With linear polymers of uniform composition it is possible to determine experimentally the approximate molecular weight distribution by fractional precipitation of the dissolved polymer from dilute solution. This procedure, to yield good results, must be carried out under very careful control, and requires considerable time. The usual procedure is to prepare a solution of the polymer to be studied and add to it portions of a precipitant. The successive fractions of the whole polymer precipitated are then examined for average molecular weight by some suitable method. This procedure can give only a crude separation but often furnishes useful information. More accurate results require the use of very dilute solutions and the precipitation is best carried out by lowering the temperature to produce insolubility at each step. The experimental distribution curve is then obtained by plotting as ordinate the weight fraction and as abscissa the average molecular weight (weight average or number average) corresponding to each fraction. In this way an integral curve is obtained which on differentiation gives differential curves of the type shown in Fig. 1.

In GR-S, such a fractionation procedure is complicated by the fact that all of the molecules of the copolymer are not of the same type. For as we have seen we may encounter differences not only in structure between molecules but also in composition either of which alone will, independently of molecular size *per se*, influence solubility.

In fact experiments have shown that fractions separated from GR-S actually do exhibit differences in styrene content attesting to the special complications of determining molecular distributions in copolymers by this method. In spite of this, fractionations of GR-S have been made which no doubt have qualitative value. As a result of such experiments it has been found that molecular size distribution in GR-S is highly dependent on impurities present during the reaction as well as on other factors. When, however, the process and raw materials are suitably controlled it is likely that the shape of the curve does not vary greatly. Under these circumstances the number average molecular weight determined by osmotic pressure furnishes a measure of molecule size.

If the molecules are not too highly branched, we may employ viscosity measurements to furnish a "viscosity average" molecular weight. Since the latter measurements are the simplest to make they are generally employed[12], although care must be used to insure proper interpretation of results. In general, the average molecular weight given by the viscosity will

fall nearer to the low molecular weight end of the distribution curve than does the true weight average molecular weight. Only for a homogeneous system does it coincide with the number average value. Hence, the difference between the two can be used as a rough measure of the broadness of the distribution.

Light scattering from solutions offers possibly an absolute way of getting the true weight average value. If the molecules are small compared to the

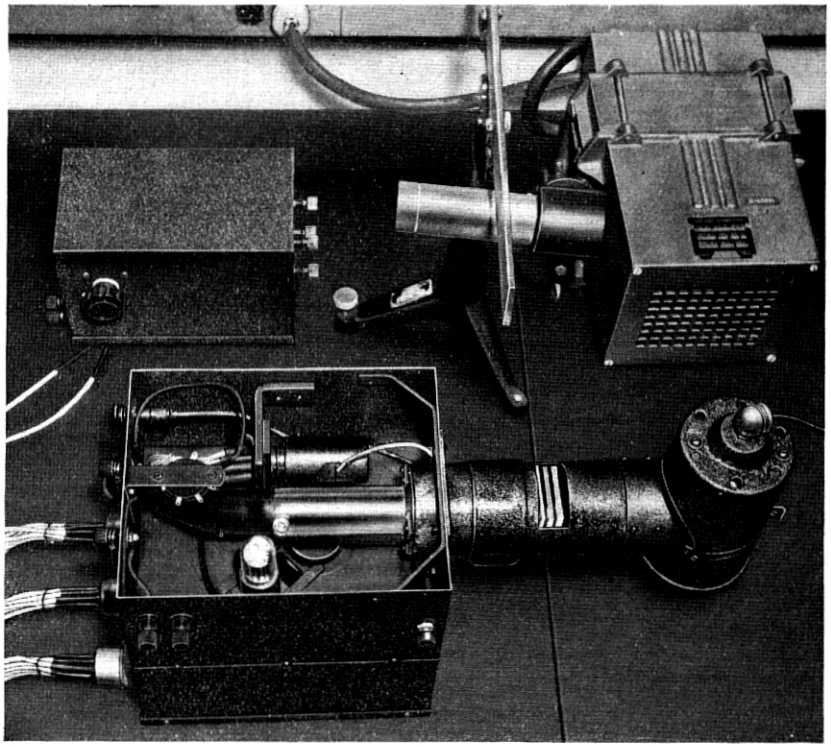


Fig. 6.—Apparatus for measuring the intensity of scattered light from solutions of polymers

wavelength of the light used and solutions of various dilutions are employed, measurements of turbidity τ, i.e. the fraction of the total light scattered per cm. of path, allow the weight average molecular weight $\overline{M}_w$ to be calculated according to

$$\overline{M}_w = \frac{1}{H(c/\tau)_o}$$

where H is a constant, c is the concentration and $(c/\tau)_o$ is the value found by extrapolation to zero concentration[13]. Further study of this method is

required before direct results can be obtained on GR-S. An apparatus employing electron multiplier tubes for measurement of the intensity of the scattered light, which was developed in the Laboratories, is being used to study this new technique. Its original form is illustrated in Fig. 6. Likewise, photographic determination of scattered light has established good correlation with independent molecular weight evaluation of certain other polymers[14].

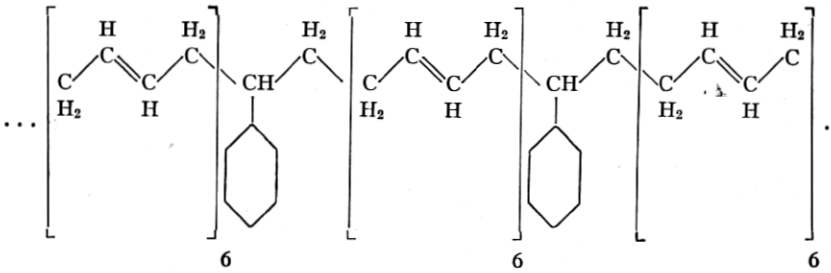
The distribution of molecule sizes in GR-S has a profound influence on its properties. It is controversial still as to whether a uniform or non-uniform distribution is desirable for all considerations. The presence of low molecular material favors ease of processing but depreciates properties. High molecular material behaves the opposite. It is customary to regard the viscosity, either of the rubber itself or the dilute solution viscosity, as a measure of the average molecular weight. While this assumption is not wholly true, it is partly justified because the shape of the distribution curve as commonly measured for GR-S is roughly constant. When osmotic measurements can be made sufficiently accurately, the number average molecular weight together with the viscosity average provides a more precise measure of the distributions present.

Chain Structure of GR-S and Its Characterization

As for simple polymers, the chain structure of GR-S is best considered from two points of view: the micro-structure and the macro-structure. The micro-structure, which has already been briefly discussed, is concerned with the kinds of atoms forming the chain, their arrangement in space and the manner in which they pack with the atoms of neighboring chain molecules. It is this structure which is all-important in determining the nature of the forces between molecules and, in turn, the intrinsic rubber-like properties of the polymer. The micro-structure also determines the chemical properties of the compound. The macro-structure, on the other hand, is not dependent on the kind of atoms in the polymer or their immediate relation to each other but with the length of the chain molecules, their general shape and the extent to which they are joined with the other molecules (netted) or what were originally other molecules in the material. It is the macro-structure which plays the chief role in plasticity and viscosity of the rubber during processing, its smoothness or roughness during extrusion, the extent to which it elongates or creeps on stretching and the extent to which it swells in solvents.

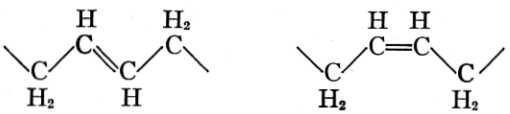
Let us approach the problem of the micro-chain structure of GR-S by considering the possibilities from the organic structural point of view. In the formation of GR-S about 6 butadiene molecules combine with each styrene molecule. In (9) butadiene is shown in brackets and styrene residues

are between them. There are at least four important ways in which the chain structure of GR-S can deviate from the simplest structure, namely



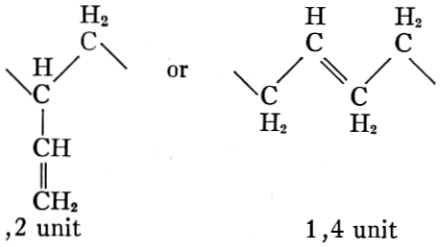
(9)

which would arise from a regular addition of butadiene and styrene. In the first place, as noted before, the styrene and butadiene units can be badly mixed up in the chain and not arranged in any special order. Secondly, the butadiene or the styrene units may be reversed end for end in the chains. This will make no difference in the case of the butadiene provided the molecule has a center of symmetry but this is probably not the case. Again, the butadiene residue may assume either the well-known *cis* or the *trans* configurations shown in (10) because of the double bond present in it.



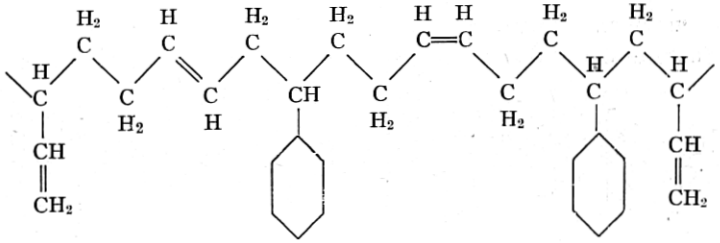
(10)

Finally, the butadiene unit may be combined into the chain as a 1,2 or as a 1,4 unit. In the former case a vinyl group is appended to the chain molecule whereas in the latter it is absent:



(11)

If these possibilities are considered, one representation of the chain molecule over a distance we should consider within the definition of micro is as follows:



(12)

Obviously many other combinations are possible which are even more involved.

There is considerable chemical as well as physical evidence to support the presence of all of these possibilities in the GR-S molecule. It is probable that the butadiene and styrene units enter the chain in an irregular manner, although, as we have seen, one molecule may acquire more total styrene or butadiene than another. The occurrence of *cis* and *trans* forms and head-to-tail arrangements is also irregular. The 1,2 and 1,4 butadiene structures likewise may occur randomly although the amount of 1,2 structure appears to vary somewhat depending on the type of reaction. It is not possible to review here the detailed evidence for the randomness and for the occurrence of these various features. The fact that x-rays when diffracted from stretched or cooled samples of GR-S fail to show evidence of crystalline or even of imperfectly crystalline material is proof that a disordered chain structure exists. X-rays, however, do not specify the cause of this disorder.

Work on synthetic linear polymers of known composition has demonstrated that relatively minute structural changes are able to cause marked disorder in polymer systems[16, 17]. It is not surprising, therefore, to find that GR-S copolymer is disordered. The important question is: what effect has the disorder on the properties and, if it is deleterious, what can be done about improving the chain structure? Without going into detailed arguments there is good reason to believe that an ordered chain structure is desirable for the best properties in a rubber. Only then is it possible for the chain molecules to pack together into crystalline-like regions on stretching and thus provide the resistance to tearing and breaking that are required. Natural rubber possesses this characteristic to an outstanding degree and polychloroprene and polyisobutylene when vulcanized also show considerable crystalline behavior on stretching. Other factors, such as the rate at which crystalline regions develop, are likewise important[17]. But the crucial requirement for toughness is the development of the crystalline type of forces on stressing.

It must be admitted that no great progress in reducing the chain disorder of GR-S has been attained as yet. Obviously, complete order because of the hybrid nature of the polymer is impossible. This was realized at the

outset of the research program and for that reason emphasis was placed on improving the macro-structure where obvious changes could be effected. We shall consider this phase of the work next.

We have already seen how the chain molecules of GR-S vary in size and in composition. They may vary also in over-all shape. Branching and cross-linking leading eventually to net-work formation may result during the chain growth or termination reactions. In this way variously shaped molecules may arise. Obviously the situation may become very complex and in reality we may have to do with mixtures where all types of molecular species are present at once.

What influence on the properties of the final compounded and vulcanized rubber do these various branched and netted chain structures have? It was not recognified at first that the gel part of GR-S was particularly different from the sol in its effect on ultimate properties. This was because no reliable measurements of sol or gel had been made and because sol and gel behaved differently during the compounding and processing steps[7, 12]. Some workers also did not appreciate that natural rubber and GR-S behave very differently in regard to the effect of processing on their ultimate properties.

It has since been established that the sol-gel properties are of importance both in the processing and in the final properties of GR-S synthetic rubber. It turns out that the amount of the sol and its molecular weight distribution and the amount of the gel and its swelling volume, which is a measure of the intensity of netting, enables us to make predictions as to what properties a given sample of rubber will exhibit during processing and in the final product[18]. This does not mean that other features of the sol and gel are unimportant. For example, methods of estimating the degree of branching (by means of concentrated solution viscosity)[6, 12] of the soluble portion have been worked out which undoubtedly will be useful if a more refined control proves desirable.

It is possible to make GR-S type rubber which is completely soluble. Such a product requires to be characterized only as to molecular weight distribution, composition and perhaps degree of branching. If the distribution of sol is such that there is an excess of low molecular material, the copolymer besides being soft and difficult to handle, provides cured stocks which have low tensile strength, poor tear and abrasion resistance, poor resistance to the growth of cracks and high hysteresis loss. If, on the other hand, an excess of high molecular material is present in the sol the copolymer is very stiff[18] and cannot be handled in the subsequent compounding and processing procedures. Aside from this difficulty its ultimate properties seem to be superior the higher the average molecular weight. When all considerations of properties and processing requirements are taken into

account a copolymer containing as nearly linear molecules as possible and having neither an excess of high or low molecular fraction is probably preferable.

Gel GR-S, depending on its swelling volume (see below), is a tough material totally lacking in plasticity. Swelling volumes as low as 10 are hardly distinguishable from vulcanized gum GR-S and in fact resemble it structurally because vulcanization is actually a special kind of gel formation. Ordinarily the swelling volumes of gel in GR-S range between 20-150[17, 18].

Commercial GR-S may contain both sol and gel, although the trend is to eliminate gel altogether. When large amounts of gel of moderate swelling volume are present the product is hard to mix, although it may extrude smoothly, and after processing, particularly if done hot, it is likely to give products which have higher modulus than copolymer free from gel, and to show poor resistance to cutting and crack growth—properties of great significance in tires and other applications.[18] It is therefore important that we should be able to determine sol and gel in the presence of each other. This need is particularly great in the case of characterization of copolymers after they have been subjected to processing and compounding[18]—treatments which often are responsible for profound changes in its molecular structure.

Methods of Characterization of Sol and Gel

Considerable work has been done at the Laboratories on methods for determining the sol-gel properties of polymers and in investigating the effects of various after treatments of the copolymers on their sol-gel characteristics[6, 18]. Figure 7 shows the type of apparatus employed for effecting the sol-gel separation[7]. The weighed copolymer sample is thoroughly dried, cut into small pieces and distributed on stainless steel screens contained in the bulb of the apparatus. About the 100 ml. of benzene is added and the parts assembled. After 24 hours or more standing without disturbance, the benzene containing the soluble part of the copolymer is carefully withdrawn by opening the stop-cock very slightly. The weight of the swollen gel left on the screens is obtained from the difference between the weight of the assembly after draining off the solution and its original weight. This divided by the original weight of the unswollen gel gives the swelling volume (SV) of the material. The slight density correction can be neglected.

The dilute solution viscosity is determined directly on 5 cc. of the solution withdrawn from the vessel and is calculated from equation (2). The concentration c is determined by evaporating a known volume of the solution and weighing the solid left after evaporation of the benzene. Figure 8 shows the viscometers and bath employed for the measurements of the relative viscosity. A variation of the dilute viscosity method adopted for

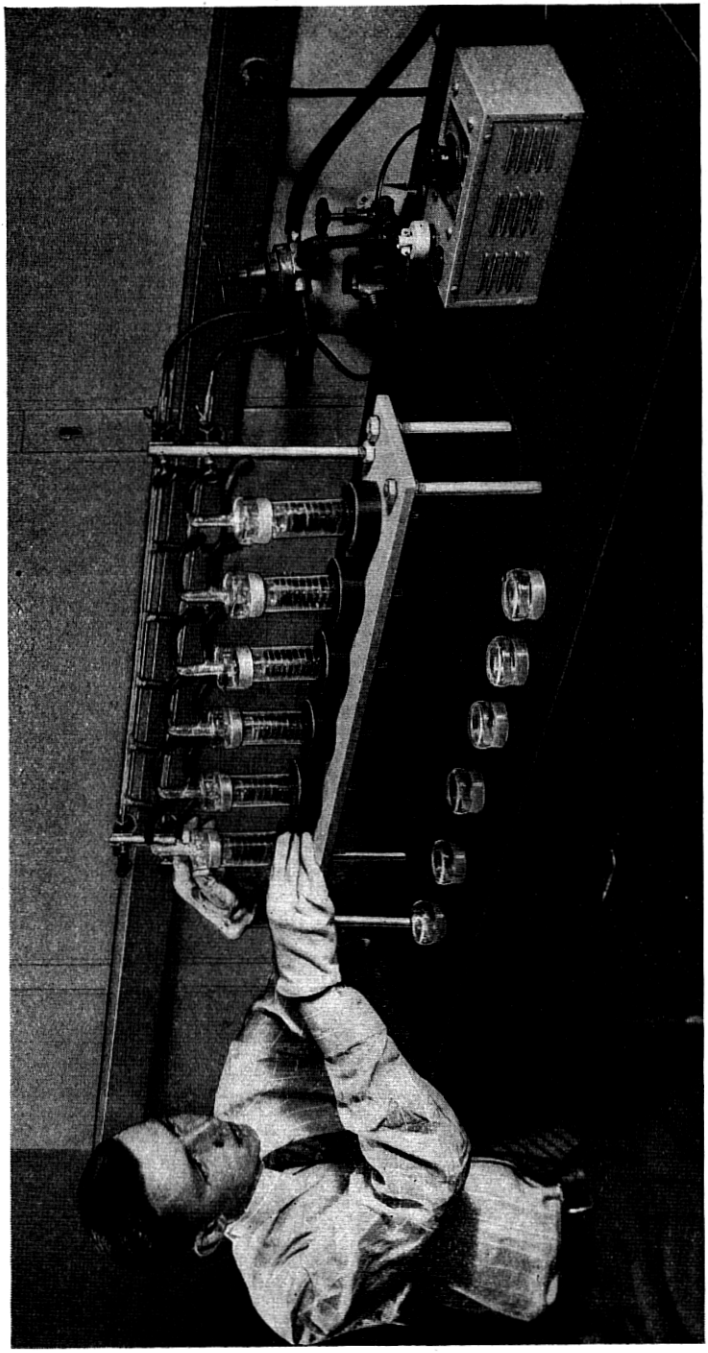


Fig. 7.—Apparatus employed in the determination of the sol-gel content of synthetic rubber.

use directly on latex has been employed as a control during the synthesis of GR-S[19]. This test, referred to as the vistex test, consists in adding 1 ml. of the latex sample to be examined to 100 ml. of a solvent having both hydrophobic and hydrophilic properties, such as a mixture of 70 parts (by volume) of xylene with 30 of pyridine, or 60 of benzene and 40 of *t*-butanol. The clear solution is run through the viscometer in the usual manner and the relative viscosity used as a measure of extent of reaction. The test has the

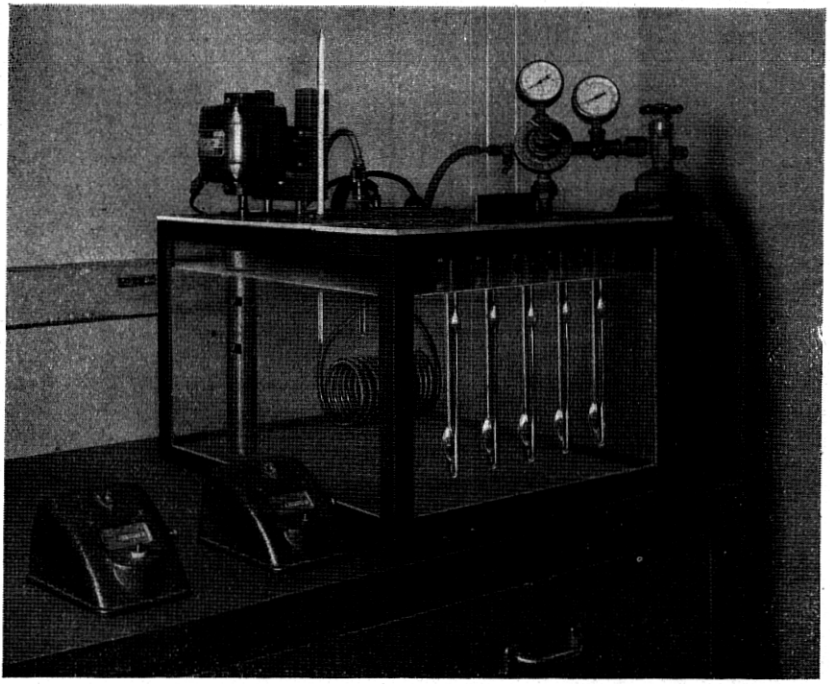


Fig. 8.—Viscometers and bath used for the determination of dilute solution viscosity of polymer solutions.

advantage of great speed, thus providing control of the reaction, step by step. Figure 9 shows the apparatus employed in the determination of concentrated solution viscosity (*CSV*).[20] In this measurement a 15 percent solution of the copolymer in xylene is made by weighing the required quantity of GR-S into a test-tube adding the precise volume of xylene and stoppering. The solution is homogenized by moving a steel armature through it in the test-tube by means of a strong electro-magnet. A trace of acetic acid is added to eliminate thixotropic effects. After complete dispersion has been effected the viscosity is determined by the falling ball

method. Branched copolymers show inordinately high concentrated solution viscosities. The latter may therefore be employed as a measure of degree of branching or approach to gelation when supplemented by dilute solution viscosity measurements. Furthermore, the power required to maintain the armature stationary as measured by the current passing through the magnet furnishes data useful in predicting how a given copolymer sample will process.

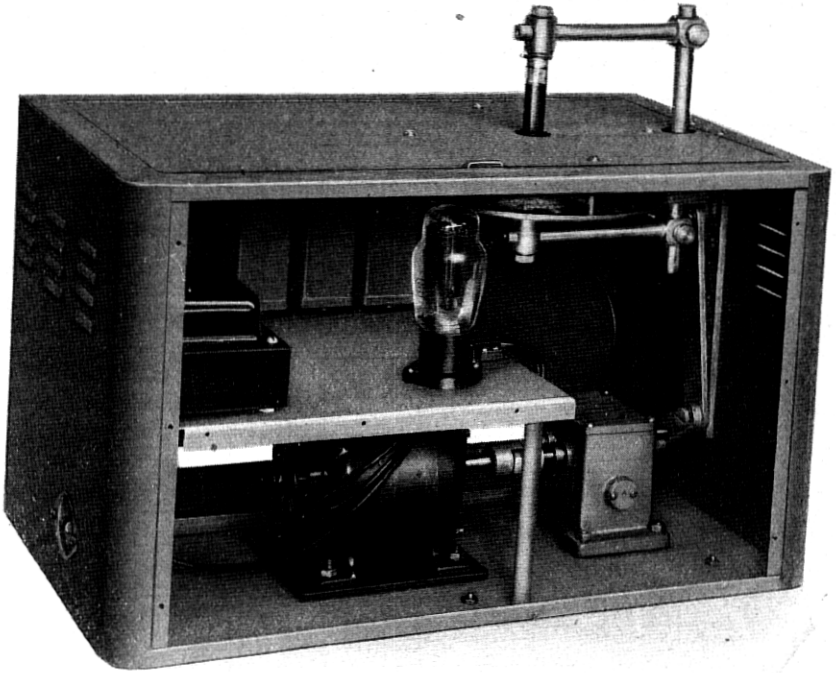


Fig. 9.—Apparatus employed to effect the solution of synthetic rubber prior to the determination of concentrated solution viscosity.

Application of Sol-Gel Methods to Control Processing

In addition to their application to the control of synthetic rubber in production, the sol-gel methods of characterizing the copolymer which have been briefly described above are of very great use in elucidating what happens during the processing of the rubber[18]. By the term "processing" is meant the operations which are carried out on the copolymer subsequent to its manufacture and prior to its vulcanization into its final form. These operations involve working the rubber on machinery (plastication) in order to render it soft and satisfactory for mixing in pigments and for extrusion

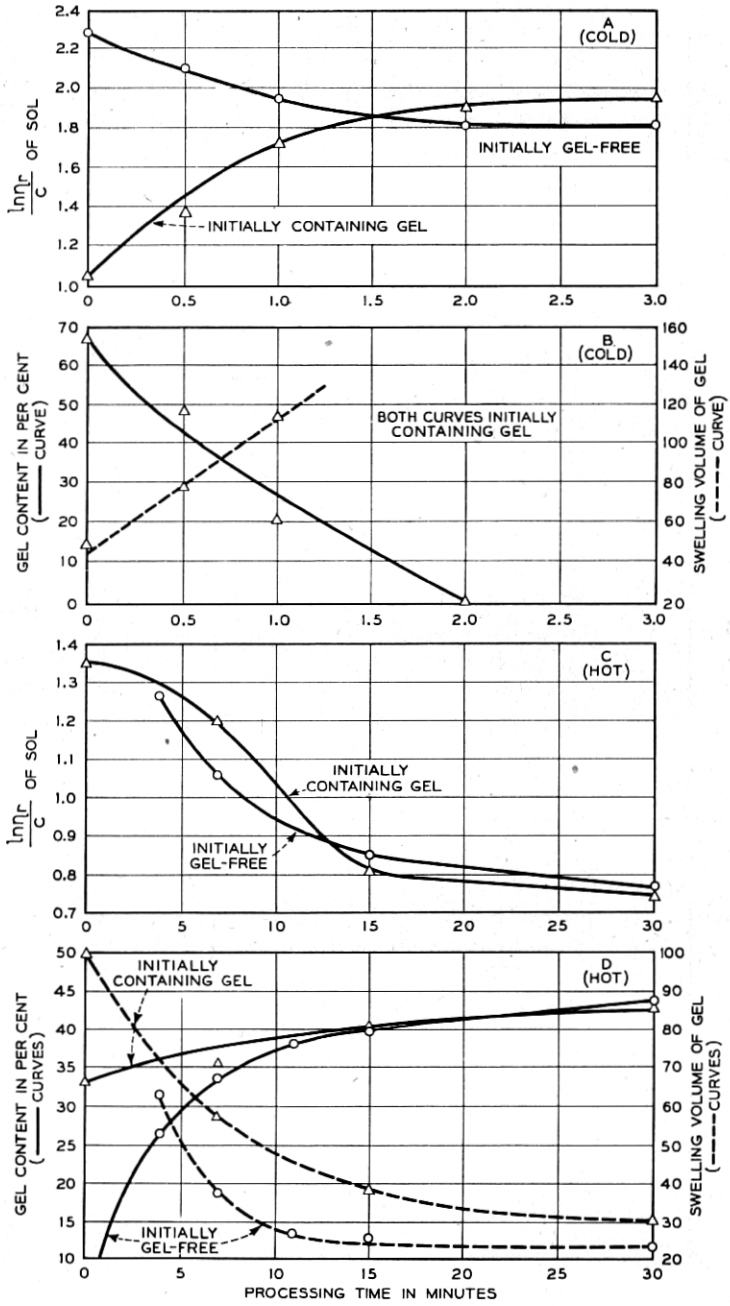


Fig. 10.—Curves showing change in solution viscosity $\left(\frac{\ln \eta_r}{c}\right)$ of sol, gel content, and swelling volume of gel with time of milling. Both cold (A and B) and hot (C and D) milling are shown for samples of synthetic rubber containing no gel and gel of low swelling volume.

and molding. Several different types of machines are employed including mills, calenders, Banbury mixers and extrusion machines. At every stage and particularly in Banbury mixing, where carbon black is generally mixed in, the copolymer undergoes changes which affect its performance in the finished product. This is especially true if, as nearly always happens in practice, considerable heat is developed during the operation. Indeed, it is frequently true that processing operations have more to do with the ultimate rubber properties than do factors in the production of the copolymer itself[18]. It is only fairly recently that this point has been sufficiently emphasized and considerable progress made in controlling the processing steps to the same extent as the polymerization is now controlled.

To see what happens during processing of the copolymer let us assume we subject two extreme types of GR-S, one containing no gel and one containing gel of rather low swelling volume, to a typical hot processing treatment consisting of hot mastication and Banbury mixing in of carbon black.[18] In addition, in order to exhibit differences in processing let us consider the effects of cold processing on the same two samples. As is evident from Fig. 10 which summarizes the results,[18] hot processing tends to build up gel and decrease its swelling volume in both of the rubber samples. The dilute solution viscosity on the other hand falls. This behavior although of advantage to subsequent extrusion and calendering operations is definitely opposed to securing the best mechanical properties in the final rubber. Cold processing has the opposite effect on the samples. Thus, the copolymer not containing gel is little affected, whereas the gel in the other is broken down and gives rise to a higher dilute solution viscosity.

In processing, therefore, important changes in the chain structure of the copolymer are brought about. Under certain circumstances, these are beneficial, but since most processing involves considerable heat development the changes are usually detrimental. It is of the utmost importance therefore that a type of copolymer is produced which is compatible with the type of processing machinery already installed in industry. In addition, uniformity of the copolymer is of very great significance if control of processing operations is to be achieved, for such control cannot be attained with a variable starting material.

The processing step which involves the mixing in of carbon black (or other pigment) is perhaps the most important. Unfortunately, the presence of the carbon black makes it impossible to employ the usual sol-gel analysis because a new kind of insolubility enters.[18, 21] In addition to the primary valence gel discussed up to this point, a secondary valence combination involving the carbon black and the large sol molecules forms. This is not immediately distinguishable from the first type of gel unless we have other reason to know that the latter is absent and does not form during the

mixing operation. This phenomenon of the insolubilization of natural rubber by carbon black has been known for some time.[22] Only recently, however, has its relation to the structural features of GR-S copolymer become apparent.[21] Work is now underway to allow an estimation of both types of gel in the presence of one another. When this is achieved the analysis of the reactions occurring during compounding will be further facilitated.

Chain Structure and Polymer Properties

We have now reviewed some of the molecular complexities which are involved in the synthesis of GR-S synthetic rubber. It remains to discuss more in detail the influence of chain structure on the properties we associate with rubber-like behavior. We might begin by asking ourselves two questions: (1) What makes a polymer exhibit rubber-like properties? (2) What composition and chain structure are desirable in a rubber? The first question involves a discussion of the theory of rubber-like elasticity. The answer to the second involves an inquiry into the specific use to which the material is to be applied. Since most of our rubber is employed in tires let us consider the special requirements for that use.

Taking up the first question, we fall immediately into the pit of having to define what a rubber is and how it differs from a plastic. Originally rubber meant "natural rubber". When synthetics with rubber-like properties appeared we adopted the term "synthetic rubber" to describe them. Some have objected (unsuccessfully) to the use of this term because it implies synthetic natural rubber and have proposed the word "elastomer" instead. Others have gone still further and suggested other terms (usually ending in mer) for various plastics and rubber-like materials.

All of these new names seem unnecessary. Polymer is the inclusive term. The term rubber simply has come to mean a polymer which at ordinary temperatures has properties like natural rubber. A plastic is a polymer which at ordinary temperatures is hard and which usually becomes soft and deformable at higher temperatures. Such terms as rubber-like plastic or glass-like plastic are frequently employed. This kind of terminology is admittedly loose but it often tells just as much in familiar words as does the newly proposed nomenclature.

The significant fact is that there is a perfectly consistent and orderly relationship between the properties of polymers and their chemical composition and structure. Fundamentally, the major factor which determines whether a long chain polymer will be a rubber or a plastic is the magnitude of the forces acting between chain molecules. If the forces between polymer molecules are low, the polymer is a rubber; if they are high, it is a plastic. And obviously since these forces can be regulated nicely there are all grada-

tions from the hardest to softest polymer. A rubber therefore may be regarded simply as a soft plastic—one in which the forces between chains are very low—with one important distinction, namely that soft plastics to show rubber-like properties must be "vulcanized" i.e. a few very strong inter-chain linkages must be established to prevent slippage. Some plastics can be vulcanized, too, but here the inter-chain forces are high anyway and the few additional strong bonds are not essential. However, the usual inter-chain forces in plastics being of the van der Waals' type are very susceptible to temperature. Consequently, if we weaken them by raising the temperature we can, provided the plastic is "vulcanized", cause it to acquire rubber-like properties at the higher temperature. So the distinction between rubbers and plastics is in the last analysis slight.

We still have not answered the question as to what causes a polymer to exhibit rubber-like properties. In fact it was only during the last 10 years or so[23] that the answer has been known, which is surprising, because it is simply "temperature". Contrary to previous views, forces between atoms in the same chain have little to do with the long range retraction phenomenon shown by rubbers, at least at elongations up to about 200%. The stretched polymer returns because of the thermal heat motion in the mass which seeks to restore the elongated chain molecules to their more stable, kinked-up configurations. The molecules, through their vulcanization points, communicate their retraction behavior to the entire mass. Thus theory agrees with experience that the chemical constitution of the polymer is of secondary significance. As long as chain molecules are present which are capable of kinking-up by rotations about chemical bonds, as long as the forces between molecules are not large compared to the thermal energy, and as long as the molecules are interconnected at points so as not to slip, we shall have a rubber-like substance whether we call it a rubber or a plastic or an elastomer.

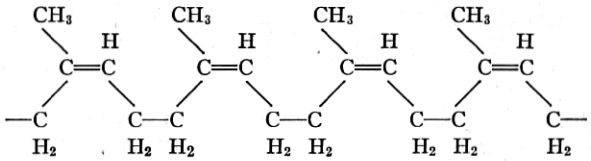
Coming to our second question, it might now take the form: what composition and chain structure are desirable in a rubber for tires? We shall see that the qualitative views expressed above must be altered if we are to explain the more intimate properties of rubber involved in this application. We have already seen from the sol-gel discussion what some of these refinements are. There are certain differences between GR-S type synthetic rubber and natural rubber, however, which go back even farther and involve the manner in which the molecules pack and slip over one another during deformation. These have geen discussed above under micro-structure.

Man learns largely by imitation and our knowledge of rubber-like behavior has been no exception. Natural rubber possesses amazing qualities which no synthetic product has yet been able entirely to duplicate, although we have found in many cases ways to overcome weaknesses in synthetic rubbers by round-about means. For example, the hysteresis loss in vulcanized

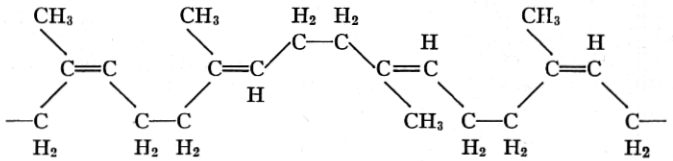
natural rubber, i.e. the heat generated per cycle of reversible stretching, is less than any synthetic rubber of comparable gum tensile strength. The resistance to crack growth of vulcanized natural rubber, particularly in gum, i.e. unfilled form, is better than any synthetic of comparable low-temperature flexibility.

What are the causes of these differences? We can make synthetic rubbers from hydrocarbons (in fact from isoprene itself) which judged simply from the composition should have the same interchain forces acting as in natural rubber. That this is not so is shown by the fact that polyisoprene in all the properties which would fit it for a tire rubber is much inferior to natural rubber. We are forced to conclude that it is the form of the individual isoprene units (*cis* or *trans*) and the way in which they are placed in the chain that determines.

In stretched natural rubber we are convinced that units are orderly arranged in the *cis* configuration as follows:



In polyisoprene on the other hand they are probably in random disorder:



We might expect then that the interchain forces, which change so critically with distance, are less of a match for the thermal energy in synthetic polyisoprene than in natural rubber. The high degree of molecular uniformity in natural rubber, as X-rays show, gives rise to a crystallization on stretching which is entirely absent from polyisoprene (see Fig. 11). Even before crystallization as such has progressed far (it starts in nuclei and these multiply throughout the mass) the interchain forces have prepared for and compensated in an effective way for the increased effect of stress tearing the chains apart and the increased thermal energy tending to weaken the interchain forces. We may look upon natural rubber as a substance which progressively and automatically transforms itself to a plastic as it is elongated. It is these crystallization phenomena which are responsible for high gum tensile strength[17] and outstanding resistance to the growth of cracks.

To return to our question and ask once more what structure we desire in a rubber for tires we see that although we cannot quite write an order in terms of a chemical formula we can state general requirements. We want a polymer in which the interchain forces are as low as possible to give us low hysteresis. At the same time we want regularity of chain molecules to provide a minimum loss of cohesion with rising temperature and rising elongation. To a chemist this sounds like an order for natural rubber and the design of Buna S which we were forced to imitate in the emergency seems wrong. If research can iron out some of this irregularity, a further improvement in our product perhaps can be achieved. The chemist by the clever trick of adding styrene to butadiene has provided himself a way he can

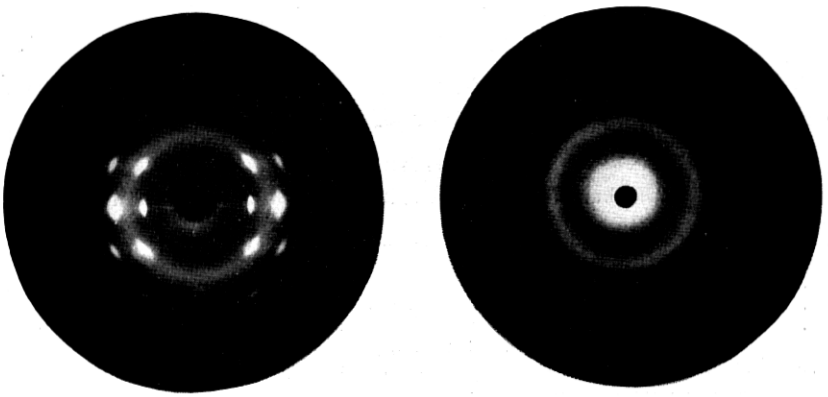


Fig. 11.—X-Ray photographs of natural rubber, stretched (left) and synthetic polyisoprene, stretched (right).

regulate the interchain forces and therefore the degree of rubberiness of Buna S. He is able to make it harder and stronger at will by increasing the amount of styrene, something nature is unable to do. But his task is not finished until he can control also the order and the packing of his molecules or devise some equally clever way of getting the interchain forces to behave.

Conclusion

We have attempted to review some of the problems arising out of the effort to achieve the best possible Buna S type rubber for our war emergency and to show how they have been attacked. We have also tried to give a simple account of some of the theories underlying the behavior of polymers. The story of synthetic rubber is of course much broader both in theory and practice than we have indicated.

Future synthetic polymers will be devised to meet the intimate requirements of many diverse applications. Engineering will be more precise and control of our materials will be based more on scientific methods. It is romantic to read from a recent popular book "you see him in his shirt sleeves cutting off a piece of rubber with his knife, smelling it, biting it and stretching it. Then he either looks satisfied or worried. Laboratory reports give him a complete report on the sample but a prodigious memory and a sixth sense born of years at his job often tell him whether the rubber will make a good tire." But this is hardly the way the future engineer will judge. It is hoped that the present account has helped to point out how scientific methods are being applied and how research can supply a safe guide to the wise control and application of synthetic materials.

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