Hydrogenation.—A suspension of 0.26 g. of platinum oxide in 15 cc. of ethyl acetate was shaken with hydrogen until the reduction was complete. After adding 0.14 g. of the fulvene the shaking was continued until no more hydrogen was absorbed. The solution became colorless long before hydrogenation was complete. The substance combined with 62 cc. of hydrogen instead of 65 cc. calculated for 5 double linkages and the product no longer reduced a solution of permanganate in acetone. In a similar experiment it was found that the solution became colorless when two atoms of hydrogen had been absorbed. The operation was interrupted at this stage and the product was isolated in the usual manner. A solution of the resulting colorless oil in piperidine rapidly developed color when it was shaken with air and the residue that was left after removing the solvent gave the characteristic color reactions of the fulvene.

Reaction with Maleic Anhydride.—A solution of 4.8 g. of the fulvene in 10 cc. of pure benzene was treated with 2.0 g. of maleic anhydride. A reaction accompanied by slight evolution of heat occurred at once. The color of the solution, originally orange, darkened rapidly and became a very dark red when the mixture was warmed for a few minutes on a steam-bath. Quinone, which like maleic anhydride forms beautifully crystalline addition products with cyclopentadiene, caused the same color changes as the anhydride, but no crystalline addition products could be obtained with either of these substances.

Fulvene from α-Ionone, II.—Condensation of pure α-ionone with cyclopentadiene by the same procedure that was used with the β-isomer resulted in a product which boiled at 107–109° under 5 mm. The yield was 76%.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.9; H, 10.1. Found: C, 89.5; H, 10.2.

This fulvene is likewise a viscous, orange-colored oil which rapidly absorbs oxygen from the air. Like the β-isomer it becomes colorless after absorbing two atoms of hydrogen and requires 10 atoms of hydrogen for complete saturation. Like its isomer, also, it is regenerated when a piperidine solution of the dihydro addition product is shaken with air. The color produced by antimony chloride is a shade of blue slightly different from that obtained with the β-isomer.

Fulvene from Pseudo-ionone, III.—This fulvene was obtained like the others but owing to resinification during distillation the yield of pure product was much lower—38%. It boiled at 139–141° under 0.5 mm.

Anal. Calcd. for $C_{18}H_{24}$: C, 89.9; H, 10.1. Found: C, 89.6; H, 10.2.

The fulvene is a viscous, red oil. It becomes colorless after combining with two atoms of hydrogen and requires 12 atoms for complete saturation. Its behavior toward maleic anhydride is the same as that of the other fulvenes of this series and like the others it develops a blue color with antimony chloride.

Summary

The paper contains a description of the method that was found best for condensing the ionones with cyclopentadiene and a brief description of the resulting fulvenes.

CAMBRIDGE, MASS. RECEIVED OCTOBER 17, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE OHIO STATE UNIVERSITY]

The Structure of Rubber and the Mechanism of Elastic Stretching

BY EDWARD MACK, JR.

Rubber seems to be unique in the magnitude of its elastic extensibility. No adequate explanation of its behavior has ever been given.

The supposition that mere high molecular weight alone can account for pronounced elastic properties is not permissible. High molecular weight may be *necessary* but it is not a *sufficient* condition. In any elastic-stretch effect, at all comparable in magnitude with that of rubber, we must necessarily expect to find *two* features present, whatever the particular mechanisms may be by means of which these two features are achieved, namely: (I) there must be some mechanism whereby the molecules involved can change their width and depth dimensions into length, upon the application of a stretching force; and (II) there must be some mechanism for automatic retraction.

The closest approach to a satisfactory picture is perhaps Kirchhof's assumption of a spiral[1] molecule, later developed by Fikentscher and Mark,[2] Hauser[3] and others. Although this explanation may have provided satisfactorily for (I), it has been weak and defective in the more essential particular, since it has failed to indicate any operable mechanism for automatic retraction.

In the first place, when we examine into the potentialities of the rubber molecule in a search for centers of attractive force sufficiently cogent to implement a mechanism for compulsory folding, we are practically limited to a consideration of two possibilities: either (a) that the residual

[1] Kirchhof, *Kolloid Z.*, **30**, 176 (1922); *Kolloidchem. Beihefte*, **16**, 47 (1922).

[2] Fikentscher and Mark, *Kautschuk*, **6**, 2 (1930); *Rub. Chem. and Tech.*, **3**, 201 (1930).

[3] Hauser, 76th Meeting of the American Chemical Society, and *Ind. Eng. Chem.*, **21**, 249 (1929).

valences of the double bonds (the effective force assumed by Fikentscher and Mark), or (b) that the van der Waals attractive forces between hydrogen atoms (on the surfaces of the molecules) act in this capacity. Possibility (a) may be eliminated as being extremely improbable in itself, and far less probable than (b), on the following grounds. (1) When the rubber molecule is extended, the double bonds are spaced much too far apart to permit the van der Waals forces (or any other forces such as residual chemical forces) between neighbor double bonds to become operative. Such forces fall off extremely rapidly with increasing distance between centers of attraction; and it is not easy to see how the double bond valences theory can surmount this serious difficulty. (2) If the residual valences of the double bonds are in fact such powerful centers of attraction one would expect the boiling point of liquid ethylene, $H_2C{=}CH_2$, to be much higher than that of liquid ethane, $H_3C{-}CH_3$. But on the contrary, the boiling point of ethylene is lower, only about 169.4° A., whereas that of ethane is about 184.9° A. Thus it seems clear that two hydrogen atoms (attached to adjacent carbon atoms within a molecule) attract neighbor hydrogen atoms more strongly than the residual valences of a double bond attract neighbor double bonds and neighbor hydrogen atoms. (3) Staudinger[4] and Leupold, who claim to have shown that practically completely hydrogenated rubber still possesses to a considerable extent the elastic properties of natural rubber, attempt to score the point that the double bonds, therefore, cannot be an essential part of the retractive mechanism. The validity of this criticism, of course, depends on the reliability of their own conclusions. No quantitative data have as yet been presented either as to the degree of hydrogenation of their product or as to the degree of its elastic extensibility.

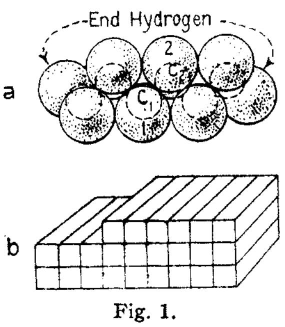
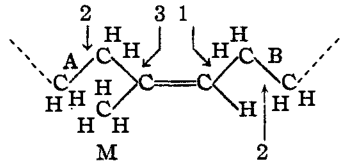


Fig. 1.

We know that the van der Waals forces of attraction between hydrogen atoms (attached to carbon atoms), thus —C—H:::H—C—, are quite large, as is made evident by the magnitude of heats of fusion and heats of vaporization of *normal* hydrocarbon chain molecules, for example. Figure 1a, shows a model of *n*-hexane. The carbon atoms (radius 0.77 Å.) are attached together at tetrahedral angles, and form the backbone of the molecule. The hydrogen atoms (of equilibrium domain radius 1.29 Å.)[5] are attached to the carbon atoms (C—H internuclear distance 1.08 Å.) at tetrahedral angles also, and they form an outer skin or sheath which envelops the carbon chain completely. Behind every hydrogen atom in the drawing (except the end hydrogens) there lies another hydrogen atom, to form the pair of hydrogens on each carbon, CH_2. When such a molecule escapes by evaporation from a liquid surface, as in Fig. 1b, the van der Waals contacts must be broken, on the average, at about 15 hydrogen atoms, although possibly about 20, where the bottom surface of the molecule, one side surface and one end, contact with neighbor molecules lying in the surface of the liquid. It makes no difference whether the surface molecules are lying flat or standing vertically in the surface. Since the molar heat of vaporization of *n*-hexane at 0° is 7675 cal.,[6] the energy required to drag 1 gram-atom of hydrogen (bonded to carbon, C—H) off a hydrocarbon surface would be about 500 cal. at room temperature (7675 ÷ 15 = 512). This value will be used later to calculate the work of stretching rubber.

In the second place, if we examine the rubber molecule for a possible mechanism for extensibility, it would seem that we are limited entirely to rotation on C—C bonds (and to the extremely small molecule extension due to slight bending of bonds). In the accompanying structural formula of a section of the *extended* rubber molecule chain, the C—C bonds are numbered 1, 2, 3 to correspond with the scheme used in the model of Fikentscher and Mark. Rotations about bonds 1 and 3 are easy and free. The angles through which the two respective rotations occur, namely, the rotation of C_2H_4 group A on bond 3 and of C_2H_4 group B on bond 1, are determined by structural features within the formula section,



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(4) Staudinger and Leupold, *Ber.*, **67**, 304 (1934); *Rub. Chem. and Tech.*, **7**, 496 (1934).

(5) Mack, THIS JOURNAL, **54**, 2141 (1932).

(6) "Int. Crit. Tables."

to be explained presently. Rotation on bond 2, within the $\overset{\mathrm{H\ \ H}}{\underset{\mathrm{H\ \ H}}{\mathrm{C{-}C}}}$ groups, cannot occur, or perhaps, more correctly, it does not occur. It is not so much the steric hindrance of the large-sized hydrogen atoms that prevents this rotation, but rather the strong van der Waals forces of attraction between the hydrogen atoms on the two neighbor groups. In Fig. 1a, hydrogen atom 1 and the hydrogen atom directly behind 1, both attached to carbon atom C_1, are tightly locked to hydrogen atom 2 and the hydrogen atom directly behind it, both of which are attached to carbon atom C_2. It requires a strong impulse to cause rotation over these potential humps, unless, of course, a better hydrogen-to-hydrogen contact could be established by rotation. It is not apparent how any such betterment could be achieved by rotation on bond 2 of the C_2H_4 groups in the rubber molecule, and it is extremely probable that these groups act as fairly rigid blocs.

Function of the Double Bond.—The function of the double bond is two-fold. (1) It provides enough free space about the doubly bonded carbon atoms, $^{3}{>}C{=}C{<}^{1}$, to permit free rotation on bonds 3 and 1. (2) It functions in such a way as to throw the C_2H_4 groups either into the *cis* or *trans* positions. The unique elastic properties of natural rubber develop only when the C_2H_4 groups are *cis*.

Mechanism of Elastic Stretch

The details of this mechanism may be explained by reference to approximately scale drawings of the molecule models. In Fig. 2I, is given what we may call a side view. The double-bonded carbon atoms, ${>}C{=}C{<}$, are shown at the middle, with the single bonds radiating at 120° angles, all in the plane of the paper. Attached to one of these bonds is the single hydrogen atom H_s; attached to another (lower left) is the methyl group, carrying three hydrogen atoms (directly behind H_m lies another hydrogen which we shall designate as H'_m). All of the hydrogen atoms, except H_s, are attached to their respective carbon atoms at tetrahedral angles. The various atoms occupy the positions shown, in I, when the rubber molecule is *extended*.

The methyl group is free to rotate, but it orients itself as indicated because one of its hydrogen atoms will then contact with H_s, whereas if it turns so as to present two hydrogen atoms to H_s, no contacting occurs. Thus the two hydrogen atoms, H_m and H'_m, place themselves just beneath C_2H_4 group A, and contact respectively with hydrogen atoms a_1 and a'_1 (which is behind a_1) of group A. A top view, looking down on the eight hydrogen atoms of groups A and B is given in II.

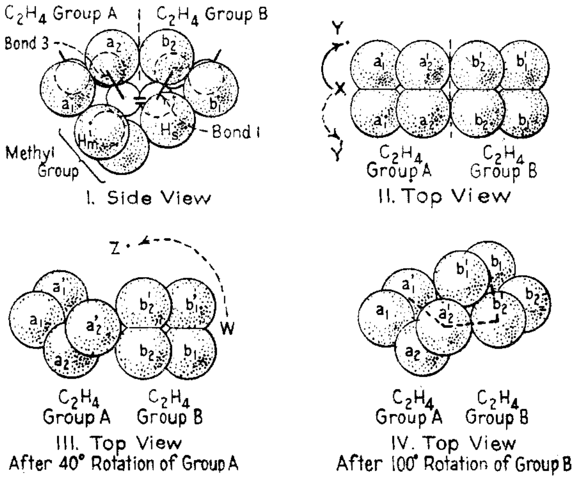

Fig. 2.

Now, when the retraction mechanism operates, two things happen. First, Group A rotates through approximately 40°. Let us set up a reference point on the paper (in II), marked Y. Then the part of the C_2H_4 group A indicated by X turns around (on bond 3) so that X is brought close to Y, as shown in III. The reason for the rotation is the achievement of a larger number of hydrogen-to-hydrogen contacts after the rotation. In the extended configuration, in II, there are *four* hydrogen contacts made by group A, namely, a_2 with b_2, a'_2 with b'_2, a_1 with H_m, and a'_1 with H'_m. But after the rotation, in III, group A makes *six* hydrogen contacts, namely, a'_2 contacts with both b_2 and b'_2, a_2 contacts with H_m, a_1 contacts with both H_m and H'_m, and a'_1 contacts with H'_m. Therefore position III has the advantage over position II in affording *two more* hydrogen contacts. The impelling force which causes the rotation is the van der Waals attraction between hydrogen atoms; and the plausibility of our appeal to these forces is very great because they are required to operate over only extremely small distances, less than 1 Å.

Secondly, *after* group A has turned, group B then executes a rotation through about 100° (from W to Z in III), to give the final completely retracted form shown in IV. In the configuration of III, group B makes *four* hydrogen-to-hydrogen contacts, both b_2 and b_2' with a_2', and both b_1 and b_1' with H_s (beneath). In IV, group B makes *five* hydrogen osculations, namely, b_1 and b_2 both contact H_s, b_1' contacts a_1', b_1' contacts a_2' and b_2' contacts a_2'. Configuration IV represents an improvement of *one* contact over III. The van der Waals forces of attraction of both a_1' and a_2' (in III) for b_1' are required to function over a considerable distance, about 3 Å. But it is extremely likely that the oscillation of group B about bond 1, due to thermal agitation, would bring b_1' well within range of these forces. If group A rotated initially clockwise, as in III, then group B would rotate counter-clockwise; but if group A rotated toward Y′ then group B would rotate clockwise to contact with it.

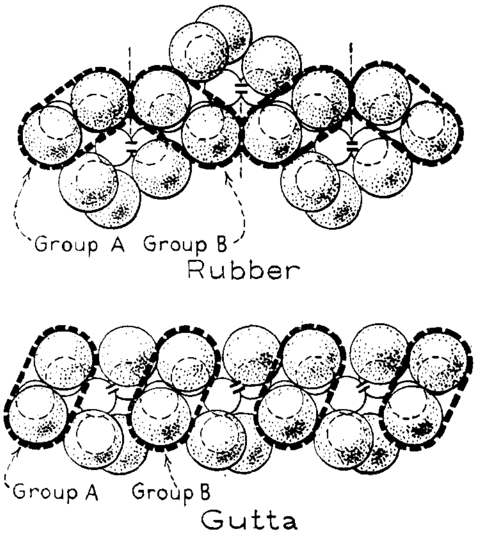

Fig. 3.

Thus, the retracted form IV possesses altogether *three* more hydrogen-to-hydrogen contacts internally, within the configuration, than the extended form II. By pulling out the retracted and folded form we do work against the van der Waals forces of attraction, residing in the extra hydrogen contacts, and store potential energy (of bond rotation). Upon release of the stretching force, rotation automatically occurs to the retracted form, a condition of smaller potential energy. In somewhat different words, and by analogy with the evaporation of hydrocarbon molecules from a liquid surface, we may say that in the stretching process three atoms of hydrogen are dragged off a virtually liquid surface, and in retraction three atoms of hydrogen spontaneously condense, for that portion of the rubber molecule shown in Fig. 2. If we wish to coin a name for the mechanism by which the rubber molecule extends and retracts we might therefore appropriately call it a "hydrogen-evaporation-condensation" process. The mechanism resembles evaporation $\rightleftarrows$ condensation rather than melting $\rightleftarrows$ crystallization because when a hydrocarbon molecule escapes by evaporation from a hydrocarbon surface, all of the hydrogen-to-hydrogen contacts that are broken, are broken completely, as is also true of the present rubber stretch mechanism; whereas when such a molecule leaves a crystal lattice and passes into a melt, the number of hydrogen-to-hydrogen contacts may be somewhat diminished, but the significant change is that the extra load of kinetic energy which the molecule has acquired prevents it from being retained rigidly in the lattice.

Since group A, in Fig. 2, functions as a group B for the next pair of doubly bonded carbon atoms in the rubber chain, lying to the left, and since group B functions as a group A to the right, there will be an improvement of three hydrogen contacts, in passing from the extended to retracted form, for every double bond throughout the length of the whole rubber molecule. Since we already know approximately the energy required to evaporate a gram-atom of hydrocarbon-hydrogen, we have available the basis for a calculation of the work required to stretch rubber, if we can estimate the number of double bonds, or of C_5H_8 groups in unit volume of rubber. Before we proceed to this calculation, however, it would be well to discuss the gutta molecule, as well as the shape of the rubber molecule and the problem of degree of elongation.

The Gutta or Balata Molecule.—The important difference between the rubber and gutta molecules may be illustrated in Fig. 3. Both molecules are shown *extended.* In rubber, it is the fact that the A and B groups are in the *cis* position, and are consequently tilted *toward* one another, that allows group B, rotating through about 100°, to make an improved hydrogen-to-hydrogen contact with group A (which has itself rotated through about 40°). In gutta the A and B groups are *trans.* Group B is not tilted toward A, but lies parallel to it, and no amount of turning of B will bring it any nearer to A. Nor does rotation of any sort improve the hydrogen contacting of group B in any manner. It already makes four hydrogen contacts, two with the hydrogen atom of the methyl group, and two with the single hydrogen atom *trans* with respect to the methyl group. It unquestionably retains this fixed position permanently (with respect to the hydrogen atom and methyl group lying to its left).

However, group A in the gutta molecule does rotate through 40°, as in the case of rubber; although it is to be noted that there is a gain of only *one* hydrogen contact in this rotation, as compared with *two* in rubber. For, while the lower end of group A in the gutta molecule, Fig. 3, gains two contacts with the methyl group in executing the 40° rotation, it loses one contact with the single hydrogen atom (*trans* with respect to the methyl). It is to be kept in mind that every one of the C_2H_4 groups in gutta acts as an A group to the right and as a B group to the left, with the result that the C_5H_8 are rigid blocs, turning through 40° on bond 3 (see Fig. 2).

Thus the total retractive effect in gutta would be only one-third as large as in rubber, per C_5H_8 group, and in gutta the extensibility would be quite small because the rotation through only 40° would not affect the length appreciably. The 50:50 chance of 40° rotation of the C_5H_8 group either clockwise or counter-clockwise would thus probably lead to a zig-zag molecule with a long axis which is straight for the most part, but occasionally bent into long arcs, or into gross zig-zags. A tangled mass of such molecules, all of them possessing slight extensibility, could well exhibit the slightly elastic behavior characteristic of gutta.

Shape of the Rubber Molecule and the Problem of Elongation.—It is extremely difficult to demonstrate the shape possibilities of the rubber molecule chain without the aid of 3-dimensional scale models. But a rough idea of the possibilities may be conveyed diagrammatically. In Fig. 2IV, the directions in which the three 2-carbon sections, C—C, C═C and C—C, lie as viewed from above, after the 40° and 100° rotations have occurred, are indicated by the heavy dotted lines. Remembering that the 40° rotation may occur in either direction, let us consider Fig. 4, where the C═C section is represented thus ═══. At (a) a zig-zag shape is shown, obtained by allowing the 40° rotations to occur alternately along the chain, first in one direction and then in the other. Such a retracted shape pulls out to almost twice its initial length. In (b) the 40° rotation on ═══ f is in the same direction as on ═══ d; on ═══h it is opposite. ═══ f is directed up out of the plane of the paper (in b). Thes ection g lies above e, and i lies above g. This shape has an elongation of about 4.

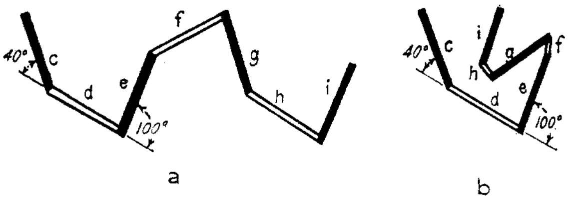

Fig. 4.

Obviously with about 1000 C_5H_8 groups per molecule (molecular weight about 68,000) and with the potentiality of either clockwise or counter-clockwise 40° rotation for every C_5H_8 group, there will be an enormous number of possible shapes, in fact 2^{1000}, except in so far as the crowding by neighbor molecule strands prevents the formation of otherwise possible shapes. True spirals would probably not be produced, at least not if the 40° and 100° rotations are compulsory. But if the 100° rotation is frequently prevented from attaining its full value by the interference of vicinal groups on neighbor molecules, so that the rotation takes place through only 50 to 75° (on condition that a betterment of hydrogen contact is obtained with the neighbor groups), tight or loose spirals of various degrees of pitch might be formed. This is not very likely; one would rather expect to find folded zig-zags and "S"-shaped forms of various sorts.

Nor does x-ray examination of retracted rubber give us any help at all at present in connection with molecule shape. The x-ray diffraction pattern of retracted rubber resembles the typical liquid or amorphous pattern. All we could hope to get out of it would be that, already knowing the structure of the C_5H_8 link, we could attempt to justify this structure from the x-ray data; that is, we could treat the retracted rubber as a liquid made up of C_5H_8 groups. In the completely, or largely, extended form of the molecule, the x-ray interferences from the regularly spaced C_5H_8 groups along the whole length of the straightened molecule lying in the direction of stretch would produce a typical uni-axial x-ray pattern, as indeed it does. But we know this much already anyhow, for extended rubber, at least by deduction from the geometrical considerations here presented. The x-ray work has, of course, emphasized the point that the arrangement of the parts of the molecule is random in retracted rubber, and anisotropic in extended rubber. However, there would seem to be no justification for an interpretation of the diffraction pattern of retracted rubber as indication of the presence of spirals. This may be the true solution, but it is ambiguous; there may be many other solutions which fit the x-ray data equally well.

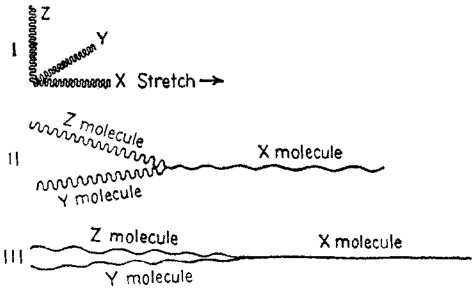

Fig. 5.

It is not easy to predict what the elongation of the average molecule would be. But in view of the probability that close-packed chain sections would be favored because of the severe space restrictions imposed by neighbors, it would not be unfair to assure an average elongation of about 3. The degree of elongation possible with any particular molecule depends not only on its shape, but also on its original position, occupied in the matrix of the rubber with respect to the direction in which the piece of rubber is eventually stretched (to consider only uni-directional stretching). From the well-known fact that a piece of rubber is isotropic with respect to stretch, unless it has been milled or racked or been given violent mechanical uni-directional treatment of some sort, it follows that the general orientation of any chosen molecular axis, such as the long axis, must be perfectly random and haphazard. In other words, we not only have a practically infinite number of possible molecule shapes, but we also have them tangled together in a practically infinite number of different directions. It is possible to obtain an approximate analysis of the situation, nevertheless, in the following manner.

Let us suppose that in a small cubical volume of rubber we have three molecules of average shape, and each of potential elongation equal to 3, arranged along three rectangular coördinates, x, y and z, as shown in Fig. 5I. The direction x is parallel to the direction in which stretching is to occur, y is perpendicular to the plane of the paper. All of the other molecules, lying in an enormous number of different directions in the solid angle subtended by x, y and z axes, will exhibit an average elongation behavior which will be approximately the same as the combined effect produced by stretching these three molecules. The initial length of this small cube of rubber is the length of the x-molecule, and we may set it equal to 1.

Upon the application of the stretching force, the x-molecule will unwind first since, because of its more favorable orientation, it is more susceptible to the unwinding leverage at its rotatable link joints. In II of Fig. 5, the x-molecule is shown practically completely straightened out to almost three times its initial length. During this earlier portion of the stretch, as the length of the rubber piece increases, and its cross section diminishes, the axes of the y- and z-molecules will ride around with the mass of rubber, and will line up more and more in the direction of stretching (if slippage is prevented). As they do so these molecules will themselves begin to unwind, and will eventually be straightened out almost completely in the line of stretch, as shown in III. In this way the original length of 1 will become extended to a final length of about 6. It should be pointed out that the length of the z-molecule will *not* be added to the length of the y-molecule, to give a total elongation of about 9. For, as the cross section diminishes, as width and depth both transform themselves into length, the z-molecule will be performing the same function in the width dimension which the y-molecule is simultaneously performing in the depth dimension; and the two molecules will finally, at the end of the stretching, be lined up as two practically parallel strands, side by side.

At any rate it would seem to follow logically on these geometrical grounds that the elongation of a macroscopic piece of rubber will be very nearly *twice* the elongation of its average molecule, oriented with its long axis in the direction in which the stretching force is applied. Furthermore, this conclusion is valid no matter in what direction one chooses to stretch the piece of rubber, since the rectangular and mutually perpendicular reference axes, x, y and z, may be shifted to any desired position to accommodate the direction of stretch, because of the isotropic character of the rubber. It would not be quite fair to claim that an elongation substantially in agreement with the observed elongation has thus been predicted. The average molecular elongation of about 3 was only a rough guess. (It might well be 4 or 5.) We may say, however, that there is clearly a sufficient and probable range of rubber molecule shapes, and of rubber molecule elongations, to provide the basis for an explanation of how rubber can be made to stretch as much as it is observed to stretch.

The Work of Stretching Rubber

During the first stages of the stretching process it has been observed that a much smaller force is required to produce a given extension of rubber than during the later stages, that is, if applied stretching force is plotted against elongation (as in Fig. 7), the curve rises more and more steeply toward the end of the stretch. The explanation of this stress-strain curve would seem to be as follows.

It is to be kept in mind that the retractive force at any stage of stretching depends on the population of bond rotation mechanisms that have been unwound at that stage, since van der Waals forces at all of these are tugging to achieve retraction. In Fig. 5, the unwinding of the x-molecules would in itself give an extension from an initial length of 1 up to about 3, and this would be still further increased by the mere partial riding around of the y-molecules and the z-molecules to give a total extension of about 4, without having unwound more than about one-third of the number of the 100° rotation mechanisms (B groups), which would of course unwind before the A groups (40°), because only one hydrogen contact is involved. Thus, only about one-ninth of the total hydrogen contacts would have been broken at this stage. The plot of this first portion of the stretch is given by the line x (100°), in Fig. 6.

Upon still further stretching, the y- and z-molecules unwind, and result in an extension in length up to a total of perhaps 5.5. But to unwind them a much larger stretching force must be applied because these two kinds of molecules provide twice as many hydrogen contacts (100° rotation) as the x-molecules. Furthermore, if twice the stretching force is applied, the unwinding leverage would take hold on the A groups (40°) of the x-molecules, so that by the time the length had increased to 5.5 times the initial length, five-ninths of the total hydrogen contacts would have been broken. The plot of this stage is indicated by the line x (40°); y, z (100°).

Then the A groups of the y- and z- molecules unwind, bringing the length up to perhaps 5.9, with the breaking of the remaining four-ninths of the hydrogen contacts, indicated by the line y, z (40°). Superimposed on this last increment in the stretching force, and perhaps to some extent on some of the earlier increments, just before the breaking load is reached, would be a considerable force required to do work of lateral compression, of pushing molecules together sidewise into awkward positions, of forcing contacting atoms of neighbor molecules together until repulsive forces develop, and perhaps also of bond bending.

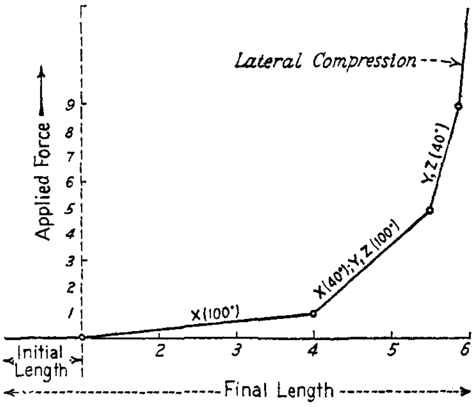

Fig. 6.

The foregoing analysis is very rough. For example, the line x (100°) would really rise more steeply, since many molecules oriented out of the line of stretch would almost immediately become subject to the unwinding leverage. However, the general shape features of the stress-strain curve emerge from these geometrical considerations.

The observed work of stretching rubber can be accounted for as follows. The over-all dimensions of the C_5H_8 group are about 6 × 5 × 4.4 Å., giving a volume of about 132×10^{-24} cc. On the supposition that a 1 cm.^{3} of rubber is made up of such closely packed groups, there would be 7.6×10^{21} C_5H_8 groups present (*i. e.*, $1 \div 132 \times 10^{-24} = 7.6 \times 10^{21}$). This is 0.0125 gram-molecules of C_5H_8 (*i. e.*, $7.6 \times 10^{21} \div 6.06 \times 10^{23} = 0.0125$). This would yield a density for rubber a little greater than 0.85 (*i. e.*, 0.0125 × 68.06 = 0.851), as compared with a density for natural rubber of about 0.9. Actually, of course, in natural rubber a certain amount of useless material is present, partially polymerized or partially broken-down molecules and the mingling of this material of relatively low molecular weight into the crevices and interstices of the rubber matrix could readily produce a slightly enhanced density.

Since *three* hydrogen-to-hydrogen contacts are broken in every C_5H_8 group, there would be 0.0375 gram-atom of hydrogen "evaporated" upon complete stretching of 1 cm.^{3} of natural rubber. As calculated previously, about 500 cal. are required to drag one gram-atom of hydrogen (C—H) off a hydrocarbon surface. Consequently, the predicted work of stretching 1 cm.^{3} of rubber is about 18.75 cal. or, in mechanical units, about 800 kg.-cm. This compares favorably with the 275–550 kg.-cm. actually observed for natural rubber and vulcanized rubber as shown, for example, in Fig. 7. It is to be remembered that the predicted value was for almost "perfect" rubber; there may well be not as many as 7.6×10^{21} C_5H_8 groups in 1 cm.^{3}. Furthermore, not quite all of the A groups on y- and z-molecules may be unwound when break occurs; the value of 500 cal. may be a little too large; and the fraction of the total work attributable to lateral compression (indicated by the unshaded area in Fig. 7) is uncertain. The total work of stretching is to be portioned out to the various stages, as energy areas, in accordance with the shape of the stress-strain curve.

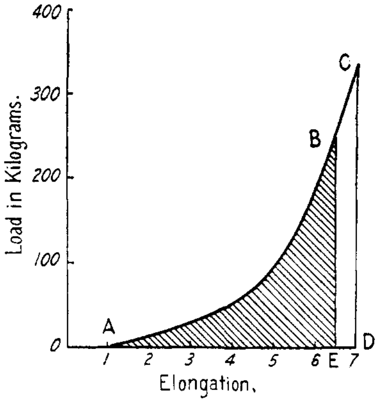

Fig. 7.

Two other matters now deserve consideration.

(1) In the Fikentscher and Mark model[2] theory, where the implementing force for retraction was assumed by its authors to be the residual valences of the double bonds, the retractive mechanism should obviously be destroyed by even an only fairly complete saturation of the double bonds with hydrogen. In terms of the present theory, however, we would expect substantial elastic properties if, after hydrogenation, a residue of a few double bonds per molecule is left. The point may be clarified with the aid of Fig. 8. After hydrogenation the molecule would lie in straight line sections like regular *normal* hydrocarbon chains (like Fig. 1) except for the side-chain CH_3 groups and except for the few double bond van der Waals mechanism "joints" scattered randomly along the length of the molecule. In these straight sections of the chain, as we have represented them in the drawing, there would be perhaps 100–150 of the original C_5H_8 groups. The molecule would have a vastly smaller range of possible shapes than the original rubber molecule, but it could coil into spirals or zig-zags, or S-shapes. The extensibility of a tangled matrix of such molecules, randomly shaped and randomly oriented, would approach that of rubber; indeed the elongation could well be as large as in rubber, were it not for the probably more severe restrictions imposed by lateral compression. The behavior along the x, y and z directions would be the same as that already described.

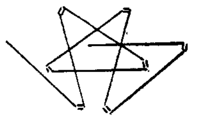

Fig. 8.

The strength of such a hydro-rubber would be very small as far as the unwinding of the small population of groups A and B is concerned. For this reason the first portion of the stress-strain curve would be very flat. But because of the development of lateral compression relatively early in the elongation, the curve would soon rise sharply to appreciably large values of applied stretching force.

Whether or not this prediction of some considerable elastic properties for hydrogenated rubber is substantiated by the facts depends on whether or not Staudinger's more recent conclusions are corroborated.

(2) It is to be expected that a slight improvement in the hydrogen contacting, around the external surfaces of the C_5H_8 groups, would come about during the later stages of stretching, since it would then be easier for the straightened anisotropic molecule strands to contact more perfectly with neighbors than in the random arrangement

of the retracted condition. It might therefore be supposed that such an improvement in hydrogen-to-hydrogen contacting would prevent retraction. It is very doubtful whether the gain in the number of intermolecular contacts is anything like as large as the loss in intramolecular contacts resulting from the unwinding of the A and B groups, and furthermore it seems likely that the improvement in hydrogen contacting laterally between molecules at certain points is largely offset by the development of restoring repulsive forces due to lateral compressions at other points. It is difficult to evaluate the factors of the situation. It is possible, but doubtful, that this improved hydrogen contacting may operate to diminish the work of stretching rubber, and thus be one of the factors in causing the discrepancy between the predicted and the observed work of stretching.

Heat Effects in Rubber

It is well known that rubber, stretched and still loaded, will retract appreciably and lift the load, when the rubber is warmed. This is to be expected. The addition of heat would amplify the oscillation about the rotatable joints scattered along the length of the extended rubber molecules, particularly so in the extended state where van der Waals forces are tugging strongly to effect retraction. The time-averaged length of the molecules would of course become shorter, and partial retraction would occur. It is to be remembered also that near complete extension the more or less parallel molecule strands are pushed together tightly in lateral compression, and any increase in thermal agitation would produce a forced lateral expansion and a longitudinal contraction.

Retracted rubber, on the other hand, would *expand* (isotropically) when warmed, because of amplified oscillation at the turning bonds, but not very readily because of the resistance offered by the *folded* van der Waals mechanism "joints." If heated sufficiently, however, the time-averaged positions of the joints would be almost completely *unwound*, and the rubber would lose its elastic properties and assume the characteristics of a viscous "tacky" liquid. If the heating be not carried too far, the rubber would regain essentially its initial properties upon cooling; but if unduly heated, thermal decomposition would disorganize the matrix and leave it permanently "sticky."

If largely extended rubber is chilled sufficiently it will not retract when the stretching load is removed; although if it is allowed to warm up again, it will, at a characteristic temperature, jump suddenly back into retracted form. The extended molecule strands, lying together side by side, and pushed together by severe lateral compression, undoubtedly become locked in position at certain points by the fitting together of protruding atoms and groups into notches and re-entrant angles, since even the completely extended molecule presents a surface contour which is zig-zag (see Fig. 3). Upon release of the stretching load, before normal retraction can then set in at room temperature, the tense molecules are dependent upon thermal agitation to disengage these mechanical obstructions to longitudinal motion. It is thus readily apparent how a fairly small drop in temperature could "freeze-in" the surfaces of the molecules and cut the thermal agitation sufficiently so that it would not be large enough to unlock the neighbor molecule strands.

The so-called *Joule* effect deserves consideration. Natural rubber and chloroprene rubber (but not other synthetic rubbers) upon extension become *warm*, and upon retraction either with or without load, become *cool*. Bock and Bostroem[7] very ingeniously calculated the heat effect for different degrees of elongation from their calorimeter measurements of the heat of swelling of rubber in benzene. They examined finely divided unstretched rubber, and rubber stretched to various degrees and stabilized by cooling to 8° (and also finely divided), and found a liberation of heat roughly proportional to the amount of elongation. For example at 658% and 821% elongation, the heats evolved were 5.24 and 6.80 calories per gram of rubber.

The evolution of heat is probably due to two effects: first, the improved intermolecular hydrogen contacting, following stretching. Since these contacts do not have to perform much external work in establishing themselves, but are brought about by a mechanically driven crowding together and alignment of molecules, heat would be evolved. The effect is akin to the Joule–Thomson effect in a hydrocarbon vapor. Since, however, the improvement in hydrogen contacting between neighbor molecules is probably really very slight, as we have already previously sug-

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(7) Bock and Bostroem, *Gummi-Ztg.*, **41**, 1112 (1927).

gested, it is to be doubted whether this is an important factor in the Joule effect.

Second, and more significantly, the evolution of the heat is closely analogous to the evolution of a heat of crystallization, particularly of a liquid which is forced to crystallize above its normal freezing point by application of pressure. The freezing point of isoprene, C_5H_8, is −120°. By the application of sufficient pressure we can raise its freezing point practically as much as we wish. This results because the applied pressure restricts the amplitude of the thermal motions of the molecules by squeezing the molecules together. If, with suitably delicate manipulating tools, we could grasp the two ends of a liquid isoprene molecule and hold it fixed, it would "freeze" far more easily than when possessed of its full quota of thermal agitation. In effect, this is really what happens to the C_5H_8 groups, polymerized to form a rubber molecule chain. They are fastened at both their ends, and the thermal motion of a C_5H_8 group is practically restricted to rotation about bonds. Consequently the individual groups freeze more easily than free isoprene molecules, although the groups are still "liquid" in retracted rubber at room temperature.

If, however, we still further restrict the thermal motions, and indeed practically remove the possibility of rotation on the bonds by stretching the molecules taut, and if in addition we squeeze the molecules together tightly in lateral compression, we may raise the freezing point sufficiently to cause crystallization at room temperature, whereupon the heat of crystallization is evolved. Upon release of the restraints, melting occurs and the heat of fusion is absorbed.

Further, it is likely that only the C_2H_4 groups B freeze. The A groups unwind with difficulty and most of them are unwound only near the end of the stretch. Even then the tendency of the A groups to rotate into retracted form is not much more than just balanced by the stretching load, and they are therefore ideally conditioned for appreciable amplitude of rotational oscillation, and are by no means held tautly stretched. The molar heat of fusion per CH_2 group is about 1000 cal.[8] Therefore, for a mole of B group it would be about 2000 calories, and for the number of moles of B group in 1 g. of rubber (or 1 g. of C_5H_8) it would be about 29 cal. ($2000 \div 68 = 29$). This is to be compared with 6.8 cal. actually found by Bock and Bostroem, above. The meaning of this ratio of predicted to observed heat effect, 29:6.8, probably is that only about one-fourth, or one-third, of the B groups crystallize, namely, those on the x-molecules, initially oriented near the line of stretch. These are the only ones eventually pulled taut enough to freeze. These groups straighten out first, and thereafter are subjected to the full force of the increasing stretching load which gradually tautens them more and more effectually, while the other B groups on y- and z-molecules are still being unwound, and never sufficiently tautened to freeze.

Accordingly, we would expect the Joule effect to increase at lower temperatures, since more of the groups would be able to freeze, and to decrease at higher temperatures. It is probably the junk materials, more or less oily sirupy hydrocarbon materials of relatively low molecular weight, that are responsible for preventing the development of the Joule effect in the synthetic rubbers (except in chloroprene). Such foreign molecules *lower* the freezing point, by interfering with the complete unwinding of the rubber molecules. For the same reason they prevent the development of the anisotropic x-ray pattern.

Attention should be directed to another interesting effect. If stretched rubber is allowed to retract without load, the van der Waals forces at the rotation joints would do very little work, merely that of retracting the unloaded rubber. Hence considerable heat should be liberated, an appreciable fraction of the energy of stretching. This liberated heat would partially neutralize the cooling effect. But when rubber is allowed to retract reversibly under load, the van der Waals joints would have to perform external work, and no heat would be released by them, and hence the cooling effect would be greater. Indeed this larger cooling effect under loaded retraction (adiabatic) has also been predicted on thermodynamic grounds by Gerke.[9]

Factors Controlling *cis* and *trans* Addition

In certain plants, natural processes seem able to lay down molecules of rubber, in others, molecules of gutta, with the C_2H_4 groups in rubber largely or wholly *cis*, and in gutta *trans*. In synthetic rubbers, however, mixtures of *cis* and *trans* configurations result. We may discuss the factors which determine *cis* and *trans* addition in

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[8] King and Garner, *J. Chem. Soc.*, 1450 (1934).

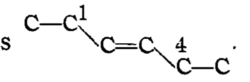
[9] Gerke, *J. Ind. Eng. Chem.*, **22**, 73 (1930).

polymerization, taking butadiene as an illustration.

Butadiene is a flat molecule. All of its atomic nuclei, 4C and 6H, lie in a single plane. A scale drawing of the model is given in Fig. 9. There is a double bond between C_1 and C_2 and also between C_3 and C_4. Between C_2 and C_3 the bond is single. Free rotation can unquestionably occur about this single bond, C_2—C_3, in the butadiene molecule. But when butadiene polymerizes by end union, the bond between C_2 and C_3 becomes a double bond (and of course C_1—C_2 and C_3—C_4 become single bonds) and thereafter no rotation whatever can take place on the double bond $C_2{=}C_3$.

Let us suppose that in the butadiene molecule, either one of the C_2H_3 groups, or both, happens to be rotating or oscillating rapidly about the single bond C_2—C_3. If, then, at any particular instant the electron bond shift between the various atoms is ready to occur, it will not occur at any and all phases of the bond rotation, but only within the narrow range of phase in which all four carbon atoms happen to be exactly, or nearly, *in the same plane* (since the four carbon atoms of the polymerized molecule also lie in a single plane). There are apparently two such phase instants, the one shown in Fig. 9, and one which is a half revolution, 180°, different. As a matter of fact, however, while the two C_2H_3 groups can lie as shown in Fig. 9, they *cannot* rotate into the other position 180° apart because of the bumping of hydrogen atom H_4' against hydrogen atom H_1 and the almost simultaneous bumping of hydrogen atom H_3 against hydrogen atom H_2. The possible rotation is through an angle of only about 145° instead of 180°, and thus fails by about 35° of bringing all four carbon atoms (or the fourth carbon atom) into the single plane.

Both of these configurations of the two halves of the butadiene molecule, the one shown in Fig. 9 and the one 145° different, have a decided preferential existence, as compared with the other phase configurations. The reason for this is that in these two positions the best hydrogen-to-hydrogen contacts are made. In Fig. 9, there is a contact between H_2 and H_4' and between H_1 and H_3; in the 145° position there is contact, as we have already indicated, between H_4' and H_1 and between H_3 and H_2. In other words, *van der Waals forces, operating within the molecule, determine the most probable configurations.* To knock the two halves of the molecule out of these favored positions, and set them into oscillation, would require the action of fairly violent thermal agitation.

Now, if the bond shift occurs when the configuration is that of Fig. 9, the two carbon atoms C_1 and C_4 are in the *trans* positions across $C_2{=}C_3$, and when end union occurs, the two C_2H_4 groups are *trans*, thus  $\mathrm{C{-}C^{1}\diagdown C{=}C\diagdown^{4} C{-}C}$. On the other hand, if the bond shift occurs during the 145° configuration, then C_1 and C_4 are *cis*. However, while the chance of existence of the two configurations of butadiene is probably about 50:50, the ease with which the configuration of Fig. 9 polymerizes is considerably greater. The 145° configuration must probably wait for thermal agitation to drive the C_2H_3 group simultaneously through approximately 35° into the plane. It is difficult to evaluate the relative probabilities of formation of the *trans* and *cis* products. The proportion of *trans* to *cis* might be 55:45, 75:25 or 95:5. At any rate, it is fairly certain that the *trans* form would predominate.

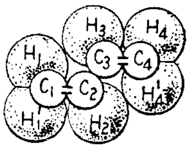
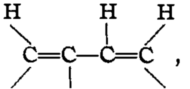
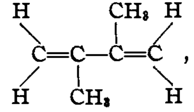
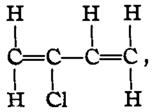
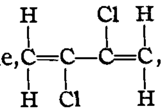


Fig. 9.

We need not carry through similar demonstrations here for the other substances which may be polymerized to produce rubber-like materials. It can readily be shown with scale models, using the same geometrical principles, that: (1) for isoprene,  $\mathrm{\overset{H}{\underset{H}{C}}{=}\underset{CH_3}{C}{-}\overset{H}{C}{=}\overset{H}{\underset{H}{C}}}$, the ratio of *trans* and *cis* is practically 50:50, possibly 60:40; (2) for dimethyl-butadiene,  $\mathrm{\overset{H}{\underset{H}{C}}{=}\underset{CH_3}{C}{-}\overset{CH_3}{C}{=}\overset{H}{\underset{H}{C}}}$, the ratio of *trans* to *cis* is practically the same as for butadiene; (3) for chloroprene,  $\mathrm{\overset{H}{\underset{H}{C}}{=}\underset{Cl}{C}{-}\overset{H}{C}{=}\overset{H}{\underset{H}{C}}}$, the ratio of *trans* to *cis* is probably about 60:40, as in isoprene; (4) for dichlorobutadiene,  $\mathrm{\overset{H}{\underset{H}{C}}{=}\underset{Cl}{C}{-}\overset{Cl}{C}{=}\overset{H}{\underset{H}{C}}}$, the ratio of *trans* to *cis* is possibly about 40:60; that is, the *cis* predominates. This prediction is made on the basis that not only are the two halves of the molecule more nearly in the same plane when Cl touches Cl and H touches H, but also because the van der Waals attraction between Cl and Cl is probably so much greater than between Cl and H, that the *cis* position giving the van der Waals contacts Cl· · · · · Cl and H · · · · · H is almost certainly more favored than the *trans* position giving the van der Waals contacts Cl · · · H and Cl · · · H.

Properties of Synthetic Rubbers

Finally, it might be interesting to predict the properties of the various synthetic rubbers, on the basis of the foregoing theory. The matching of prediction against fact cannot be very satisfyingly specific and detailed both because of the only semi-quantitative character of our theory and because of the obscurity of the facts and the spread in the claims and contentions made by various investigators in connection with the properties of their products.

Butadiene Rubber.—In butadiene rubber the A group does not rotate through 40°, since there is no CH_3 group beneath it, but only a single hydrogen atom. The contacts between a_1 and a_1' and the single hydrogen, in Fig. 10, are *two*, and are not improved, but spoiled, by rotation. Group B rotates through about 80°, either clockwise or counterclockwise, to establish *one* more hydrogen contact, as shown in the figure. (Of course, B could equally well remain fixed in retracted form and A rotate through 80°, but *both* A and B would not rotate, because the best contacting is achieved if one remains fixed.) With a gain of only one hydrogen contact per double bond, the work of stretching this rubber would therefore be small. The retractive mechanism functions only when the two C_2H_4 groups are *cis*, and thus with a preponderant population of *trans* configurations along the polymerized chain, the work of stretching and the retractive power become still further reduced.

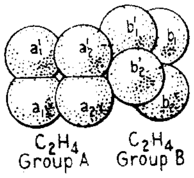
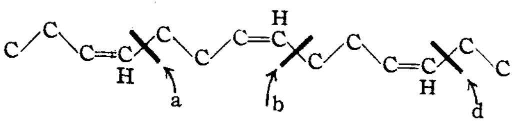


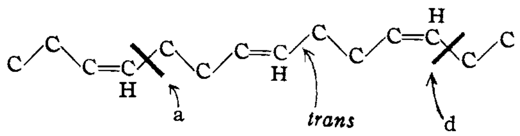
Fig. 10.

This sacrifice of strength at the *trans* configurations is accompanied however by a gain in elongation. If the butadiene rubber were composed entirely of *cis* configurations, as in the first formula below, it would have substantially the same elongation as the molecule of natural rubber, about 3, previously suggested. Let us make this point clear by means of carbon chain formulas.

cis-butadiene-rubber



cis- and *trans*-butadiene-rubber

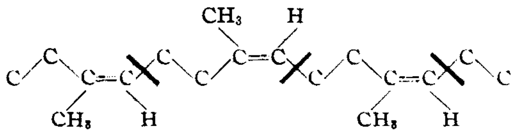


In the *cis*-rubber the C_5H_8 links rotate about the *Cis* planes, a, b and d, as shown in the formula. (*Cis* is capitalized to distinguish the relationship across the ends of a C_5H_8 group from that across $\rangle C{=}C\langle$). The interposition of the *trans* bonding between the two a and d rotation planes, which then become *Cis* with respect to each other, as shown in the synthetic rubber formula, produces a profound change in the shape possibilities for the molecule. (1) Not only is the link from a to d twice as long as the normal link, but (2) the non-compulsory rotation of the *trans* bond, which may occur because of crowding by neighbor groups and neighbor molecules, is *Trans* with respect to a and *Cis* with respect to d. Both of these features result in allowing the molecule to twist its links much more frequently into a closely packed folded chain, and hence may increase greatly the elongation of the average molecule, and hence also of the rubber.

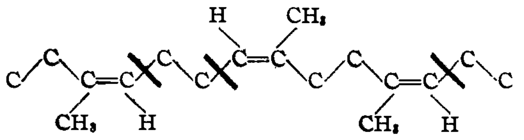
It should be noted, finally, that the proportion of junk material, partially polymerized molecules, is certain to be far greater in butadiene than in natural rubber.

Isoprene Rubber.—The properties of this rubber would be the same as natural rubber, except for the more abundant junk molecules, and except for the preponderance of *trans* configuration, in which case, as we have previously pointed out, the 100° rotation of the B group does not function. The elongation may well be greater than in natural rubber because of inversion.

Not inverted (*cis*, *Cis*)



Inverted (*cis, Trans*)



In the non-inverted, *cis* C_2H_4 type, the regular 100° group B rotation occurs across the ends of C_5H_8 links, and is *Cis*. But in the inverted, *cis* C_2H_4 type, this rotation occurs across the ends of short links, C_2H_4, and long C_8H_{12} links, interspersed, and is *Trans*. In the above structures the planes of rotation are indicated by heavy slanting lines. It is perhaps obvious from these structures, and is easily demonstrated with models, that inversion develops different shape possibilities for the retracted rubber molecule, and very decidedly improves the chances of spiraling and *more compact* zig-zagging.

Dimethylbutadiene Rubber.—Here both C_2H_4 groups function as A groups, whether they are *cis* or *trans*, rotating through 40°. There is a chance of one-half that they will turn toward one another, that is, one clockwise and the other counter-clockwise, and also a probability of one-half that they will *not* turn toward one another, that is, both clockwise or both counter-clockwise. In the former case the molecule becomes considerably shortened, and consequently acquires a fairly large elongation; in the latter case, the elongation is extremely small, only about as large as in a gutta molecule. The average elongation behavior, then, for a rubber matrix could be readily predicted. The work of stretching would be large, since all of the C_2H_4 groups function, and every one establishes *two* more hydrogen contacts in retraction. No inversion is possible. The junk factor, of course, must be considered.

One further point should be noted. The introduction of two C_2H_4 groups, whether *cis* or *trans*, on to $>C=C<$, together with two CH_3 groups, crowds these groups together very severely, particularly when groups A and B are unwound into extended form. In fact, it is only because of the possibility of some bond bending, and the "mashing" in of the hydrogen atom domain[10] that the structure, especially in extended form, can exist. It would be natural to expect, then, that this rubber would be sluggish in retraction, but that its "snap" would improve at higher temperatures, with the assistance of increased thermal agitation. Whitby and Katz say:[11] "It was observed that, when warmed, the specimens of methyl rubber largely lost their sluggishness."

Dichlorobutadiene Rubber (?).—In this polymerized product the C_2H_4 groups, whether *cis* or *trans*, are not crowded by the two chlorine atoms, as they are by CH_3 groups in methyl rubber. The product, however, should *not* possess any rubber-like properties, and should not be called rubber at all. Both C_2H_4 groups, whether *cis* or *trans*, are rigidly locked in extended position, each by contacts between two hydrogen atoms and a chlorine atom. No rotation of either group A or group B would be possible.

Chloroprene Rubber.—In the case of chloroprene rubber we are in the fortunate situation of possessing a fairly abundant mass of facts, much less obscure than in the case of other synthetic rubbers, supplied in the main in the brilliant original paper of Carothers,[12] Williams, Collins and Kirby.

When the C_2H_4 group B, in α-polychloroprene, or in μ-polychloroprene, is *cis* with respect to group A, it functions exactly as in butadiene rubber: the angle of rotation is again about 80°, and the magnitude of the van der Waals retractive force is probably essentially the same. The only difference in the entire situation is that group A is held much more firmly in its extended position (non-rotating) by the Cl atom than it is in butadiene rubber by the hydrogen atom. This, however, makes no difference in the general result, as long as group B is free to execute its 80° rotation, as it is.

When group B is *trans* to A it also functions as retractive mechanism. The geometry of the arrangement can best be demonstrated with scale models, but the effect may be explained by means of the following structural formulas.

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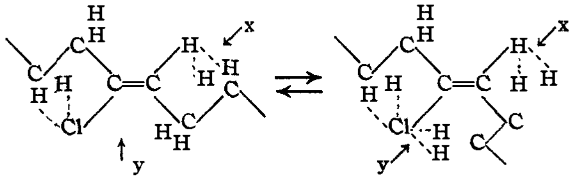
(10) In the models employed, the hydrogen atom is assumed to possess spherical symmetry, at least in its outer domain, like other atoms. The hard spherical surface of its electron domain (merely a token for the equilibrium distance of approach between hydrogen nuclei) may however be invaded by another atom making a sufficiently violent impact. In this sense the domain may be penetrated, or distorted, or "mashed" in from the room-temperature equilibrium radius of 1.29 Å. to perhaps about 1.0 Å. (see Ref. 5).

In this paper the C=C internuclear distance has been taken as about 1.45 Å., instead of a possibly more probable smaller value, more like the 1.2 Å. used by Meyer and Mark, "Der Aufbau der Hochpolymeren Organischen Naturstoffe," Akademische Verlagsgesellschaft, Leipzig, 1930, pp. 189–206. This was done to facilitate the two-dimensional representation of the models in the drawings, and to allow me to avoid discussion of the hydrogen domain penetration. The difference is small, and does not disturb the qualitative or the semi-quantitative aspects of the present theory.

(11) Whitby and Katz, *Can. J. Research*, **6**, 398 (1932); *Rub. Chem. Tech.*, **5**, 566 (1932).

(12) Carothers, Williams, Collins and Kirby, THIS JOURNAL, **53**, 4203 (1931).



Extended Retracted

In the extended form two good hydrogen contacts occur at x, but none at y between the Cl and the two hydrogens of group B. But in the retracted form, *involving a rotation of group B through 180°*, possibly accompanied by a small rotation on bond 2 of group B, not only is the hydrogen contacting at x just as good as before, but additional contacts are made between two hydrogen atoms of group B and the Cl atom, at y. (Internuclear distance C—H is 1.08 Å., C—Cl is 1.91 Å.; domain radius of H is 1.29 Å., of Cl is 1.51 Å., at room temperature.) The van der Waals attraction between Cl and H is very much stronger than the attraction between H and H. This is clearly indicated by a comparison of the boiling points for CH_4, $CHCl_3$, CH_2Cl_2, $CHCl_3$, CCl_4 and other chlorinated hydrocarbon molecules. It would not be difficult to calculate empirically the work of extension of this *trans* Cl . . . . . H "joint," in the same manner as done previously for the retraction mechanism in natural rubber. But we shall be content with this qualitative demonstration. The work of stretching would be large.

There is every reason to believe that there are irregularities along the chains of α- and μ-polychloroprene, that is, both inversion and a mixture of *cis* and *trans* configurations,[13] the latter in a proportion something like that predicted in the previous section on polymerization to *cis* and *trans* forms. These irregularities would lead to a large elongation, as suggested previously.

Since polychloroprene polymerizes extremely rapidly, relatively, there should be very little junk material present when the rubber is recovered. The Joule effect should appear, that is, some of the C_2H_4 B groups should freeze, upon stretching, at least those of the x-molecules, oriented initially near the direction of stretch, and possibly only the *cis* B groups, because their retractive pull is less than that of the *trans* B groups.

A future discussion of the factors involved in vulcanization, and perhaps also a discussion of the catalysis of polymerization, are contemplated.

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Summary

A theory of the mechanism of elastic stretch in rubber is described. It is christened a "hydrogen-evaporation-condensation" mechanism. In an attempt to develop a unified theory of rubber behavior, some of the more important properties of the various forms of rubber are discussed, from the point of view of strict adherence to the principles of geometry and of structural organic chemistry. Among the topics discussed are: shape of the rubber molecule, the work of stretching rubber, the shape of the stress-strain curve, heat effects in rubber (including the Joule effect), Staudinger's hydrogenated rubber, factors controlling *cis* and *trans* addition, x-ray diffraction pattern, properties of synthetic rubbers, inversion and sluggishness.

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(13) It is probably not permissible for Carothers, Williams, Collins and Kirby (Ref. 12) to draw the conclusion, from their x-ray diffraction pattern (their Fig. 1), that "the polychloroprene is freer from irregularities in the structure of its molecules than other synthetic rubbers." In the first place, the absence of sharp x-ray patterns in the case of other synthetic rubbers is to be partly accounted for in terms of the abundant junk materials present, as well as in terms of irregularities. In the second place, their x-ray diagram is far from being "sharp." Its spots are quite diffuse.