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THE RELATIONSHIP BETWEEN ELASTICITY AND STRUCTURE OF MACROMOLECULAR NETWORKS: OUTLINE OF A NEW APPROACH

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THE RELATIONSHIP BETWEEN ELASTICITY AND STRUCTURE
IN MACROMOLECULAR NETWORDS: OUTLINE OF A NEW APPROACH

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A new approach has been proposed with a view toward
remedying the inadequacies that shed serious doubt
on the ability of the classic statistical theory to
provide a reasonable definition of the structure of
macromolecular networks, and particularly that of
rubber vulcanizates.

On an experimental basis, it has been found that a
traction test at high temperature would conveniently
supply reversible contraction-elongation relations,
provided the adhesion of annular cylinders to the disks
is eliminated by a quick rotation of the latter.
From the theoretical point of view, th replacement
of the "related" hypothesis by that of a less direct
connection of the links of the networkds with the
elastic continuum that they constitute will eliminate
the anomalies that have remained unexplained thus far.
The proposed model actually reproduces the experimental
traction curves much more accurately, while accounting
for the apparent conformity with classical theory of
the vulcanizates, both in the compressed and the
swelled state, without resorting to hypothetical supra-
structures.

As Professor Morton (Ref. 1) emphasized last year, the

evolution of elastomer thechnology will henceforth be largely

determined by progress in the knowledge of the relationships of

structures and properties, which, with reference to the recent

past, reflect the effects of stereospecific polymerization.

Spectacular as this discovery was, one must not lose sight of the fact that rubber undergoes extremely complex transformations during fabrication as well as in use, so that in spite of the great contribution already made by science to that industry, there still remains a considerably margin of empiricism. This paradoxic nature of certain aspects of this situation is particularly striking in the case of vulcanization; and one of the most serious obstacles to the understanding of this necessary stage before the product can be used certainly resides in a still insufficient knowledge of the high elasticity of rubber.

The basic causes of the phenomenon were explained long ago as a result of the work of pioneers such as Guth, Tobisky, Flory, Treloar, Gee, Rivil, and others. But the current theories of rubber elasticity still leave some important questions unanswered, which justifies the various attempts being made, such as that discussed below, to attact the problem from a new angle.

I. STRENGTHS AND WEAKNESSES OF THE CLASSICAL THEORY OF ELASTICITY OF MACROMOLECULAR NETWORKS.

First, let us go over the familiar concept of rubber elasticity: how did it come to be directly associated with the existence of a macromolecular network, ideally of a permanent nature, at least in the absence of chemical reactions such as oxidation, for example. Since it is not possible to review here all aspects

of this vast subject, we shall limit ourselves to considering

the equilibrium contraction-deformation relations and the effects

of swelling by a solvent. In the process, we shall try to bring

out the points on which the majority of authors appear to be

substantially in agreement as well as those that are still

controversial.

In general, it can be said that the type of elasticity in

question is characterized by the possibility of achieving, with-

out the exertion of significant force, considerably reversible

deformations which exceed the dimensions of the material at

rest by several magnitudes. Furthermore, the return to the

original state appears to be almost instantaneous as soon as

the material is left alone.

Originally manifested mainly by natural rubber, this peculia-

rity can now be found in various synthetic products, but the

deformation and reversibility described above don't become

evident until all of the following three conditions exist(Ref. 2):

a)   great freedom of rotation on their valence cones of the

atoms situated at articulation points A_1, A_2, A_3, A_4 ... of the

long molecular chains that constitute the material (Fig. 1).

b)   weak secondary interaction forces among the latter.

c)   permanent interlocking of the chains at a small number

of sufficiently spaced points.

Because of the first two conditions, these macromolecules can, except at very low temperatures, randomly adopt a great number of conformations, from the most compact to the loosest, in a short period of time with respect to the observation period; when the third condition is fulfilled the local topology of the network thus created is statistically fixed but does not counteract a thermal motion comparable, at the atomic level, to that existing in fluids.

Otherwise, despite the fact that its importance for other mechanical properties depends directly on the cohesiveness of the material (breaking load, resistance to tearing or abrasion), the regularity of the molecular structure of the chains has only a limited effect on the elasticity of the vulcanizates, principally through a possible development of crystallization evoked by the stretching.

Still, the distribution and the average value of the molecular masses before vulcanization play only a minor role from this point of view in comparison with the number of bonds in the network that are brought out by the much more important effect of vulcanization on the modulus. The explanation for this is provided by the famous experiment of Meyer and Ferri (Ref. 3), according to which the tension of a sufficiently stretched rubber fiber is essentially proportional to the absolute temperature. It is deduced from this that rubber elasticity is scarcely dependent on variations of potential energy, as is the case with

rigid solids, such as crystals, metals, or glasses, but rather on the kinetic energy of the various segments of the chains produced by the thermal molecular motion.

Thus, despite the incomparably greater density of polymers, a basic analogy exists between the hydrostatic compressibility of gases and the variations in form of a rubber specimen acted on by directional forces. In both cases, the elastic reactions of the material are directly related to the great number of internal molecular configurations that are possible, that is, to the entropy of these systems.

Putting aside for the moment the mathematical developments resulting from this "mechanical statistic" of macromolecular networks, the simple fact remains that all macroscopic deformation modifies the original symmetry and, as a result, increases the degree of order of a swarming mass of indefinitely ramified chains.

This easily explains that even very large deformations could be produced in the rubber without significant variations in volume, and without the need for a large expenditure of energy; the universal tendency to return to the most disturbed state possible, and consequently the most probably one, accounts equally well for the spontaneous resumption of elasticity of the vulcani-zates and for their negligible, if not zero, permanent deformation (Ref. 2).

Knowing that the above formula correctly accounts for the nature of the phenomenon, we could visualize models of molecular

networks on similar statistical bases, and felt a growing need
to relate their theoretical behavior to that of actual vulcanizates.
Among the different criteria that permit such a comparison, the
contraction-deformation relations at constant temperature are ge-
nerally used the most because of their sensitivity and convenience.
In theiry, it does not matter which type of effect is chosen in
this case; however, in practice, a state of homogenous deformation
is more difficult to acheive in contraction or shearing stress than
in monoaxial expansion, and this is the reason for the preference
for simple traction tests, although they are not sufficient by them-
selves to define completely the intrinsic elastic properties.

As an example, Figure 2 shows the results of such a comparison
for one of the most realistic models suggested thus far, by Treloar
(Ref. 2), which conveniently reproduces the general course of the
entire experimental traction curve, with its progressive transition
from the shallow slopes found at average elongations to the sudden
rise preceding the rupture.

However, a much more thorough investigation is indispenable for
a quantitative identification which will permit a precise analysis
of the relations between the molecular structure and the mechanical
properties. Because the simplifying hypotheses are less and less
justified as the importance of the deformation increases, one is
led to attribute greater significance to a coincidence in the re-
gion of average deformations. Unfortunately, as is evident from
Figure 2, an irreducible separation of the curves is nearly always
observed, and the deviation, which already amounts to 20% among the
force values at 100% elongation, thus makes any tentative identification

completely arbitrary under these conditions.

Yet, at the time when Flory related the reticulation density to the equilibrium model (Ref. 4), this disagreement was not clearly evident. Despite the objections that must have resulted from it, the bases established by Flory are still applied extensively even today, which can be explained by the fact that swelling by a solvent appears to make the vulcanization pass into an ideal state governed by the laws of the classic statistical theory (Ref. 5). Since the latter postulates a direct relationship between the reticulation density and the maximum distension, this simple determination is considered as the mean standard for characterizing the structure of a network (Refs. 6 and 7), even though certain authors prefer to rely on the value of the modules in order to avoid the systematic errors that an insufficiently precise knowledge of the polymer-solvent interaction coefficient might give rise to (Ref. 8).

But the most serious criticism of these methods concerns their basic premises themselves. Both assume, in effect, that the deviations from statistical theory come from sort of a mechanism unrelated to the entropic process, and that a simple dilution (Refs. 7 and 9), or perhaps even the fact of causing compression instead of elongation (Refs. 10 and 11), are enough to eliminate them. More specifically, according to a recent thesis by Blockland, the semicrystalline bundles of chains, analogous to Kargin's "supra-structures," would interfere with the statistics of conformity of the static amorphous phase, and this mechanism would account for the quantitative agreement claimed by the author (Ref. 12). Yet, it is not at all

certain that the secondary structures that would be destroyed by the swelling actually exists, and the best agreement of the results with respect to swelled vulcanizates is perhaps in reality entirely fortuitous, as we shall show later.

In addition, troublesome contradictions appear when one compares the reticulation densities either by the above methods or by chemical analyses (Refs. 7, 13, 14, and 15). In order to get around this latter problem, it is currently admitted that the interconnections of the chains act as localized juncture points by attaching to the covalent intermolecular linkages (Refs. 13, 14, 15, 16, 17). This concept is, in our opinion, too rudimentary, since this type of molecular interaction should rather occur in a diffuse fashion along the chains. The concept also appears to exclude the translation of its effect on the elastic behavior to the equilibrium by means of a pure and simple identification of the obviously transitory junctures with permanent chemical linkages.

The fact that rubber elasticity is within the province of probabilistic concepts (Refs. 18 and 19), cannot be contested, but a satisfactory quantitative interpretation of the deviations from statistical theory is still lacking (Ref. 20). In order to clarify this problem, it would be desirable to begin by improving the measurement techinques which thus far leave much to be desired.

II. A PRELIMINARY CONDITION: OBTAINING REVERSIBLE DEFORMATIONS

General experience, and even too superficial an examination of data in the laboratory, often leave the wrong impression that rubber is a more or less perfectly elastic material,

endowed with a practically reversible mechanical behavior, just like the ideal substance considered in the statistical theory of elasticity. In fact, however, the strict equilibrium conditions required are generally very difficult to fulfill, so that most authors resort to laborious thermomechanical conditioning (Ref. 21), with little guarantee of success.

In the case of traction tests at great elongations, hysteresis phenomena to guard against are, in addition to aging by oxidation or post-vulcanization, the intrinsic viscoelasticity of polymers (Ref. 22) and possibly partial crystallization beyond a critical expansion depending on temperature (Ref. 23). Their combined effects are manifested in particular by the significant deviations that are always observed at ambient temperature between the in-and-out branches of a traction cycle at constant speed, as shown in Figure 3 for a pure gum vulcanizate of dicumyle cis-polyisoprene peroxide.

When it was necessary to work under truly reversible conditions at our laboratory, we asked ourselves whether our objective was not a myth, at least for isothermal cycles of great amplitude. In fact, according to certain researchers, any significant deformation would not only modify the statistical conformity of the molecular chains but should also provoke either a rupture of labile linkages equivalent to a permanet degradation (Ref. 24), or a slipping of the interconnecting points of the chains incompatible with a well defined macroscopic form at rest (Ref. 21). Thinking along the same lines, the "Mullins effect," by which one often designates this apparent

mechanical softening of rubber, has also been attributed to rear-rangements of the networks, as well as to local crystallization of short, very elongated chains.

Contrary to these viewpoints, a study of the viscoelastic relaxation of vulcanizates has, in the meantime, convinced us that at least up to elongations of 100% their tension ultimately tends toward the same limit when a similar expansion is gradually obtained with either increasing or decreasing deformation values (Ref. 26). Consequently, this limit corresponds to a state of equilibrium for a given elongation. However, it cannot be measured directly in this fashion except in the case of highly reticulated vulcanizates, since the relaxation of slightly vulcanized rubbers is relatively much slower and would require about ten years, according to their kinetics, before approaching equilibrium.

In addition, the relaxation test does not lend itself well to the study of reversible contraction-deformation relations, which leads us to reconsider the possibilities of the traction test. In this regard, there were reasons to hope that a high temperature elevation, around 100°C, for example, would accelerate the viscoelastic processes to the point of rendering them negligible in the course of the traction cycles at average speeds. Furthermore, crystallization is unlikely to occur in this temperature region, even at great elongations (Ref. 23). Therefore, a means was devised, both simple and rapid, of obtain-ing the desired information provided that certain time limits due to the rate of aging at high temperatures were not exceeded.

The apparatus used is a special dynamometer which records, if necessary up to near-rupture conditions, the tension-elongation cycles to which ring-shaped cylinders are subjected at temperatures ranging between 30 and 120°C (Fig. 4).

The deformation of the specimen is caused by the displacement of a movable disk by another, static disk with a constant translation movement. As usual, the fixed disk idles on its axis in order to equalize the tensions in each of the rectilinear strands of the ring. An auxiliary motor causes the other disk to turn with an angular velocity that can be regulated at will, which differs from similar normalized devices in which the rotation of the disks is controlled by their spacing and is therefore dependent on the velocity of elongation of the cylinder.

This conceptual detail, which might appear superfluous at first glance, has been shown to be indispensable in use to ensure a direct kinetic relationship between the spacing of the disks and the elongation of the neutral fiber of the ring, as shown in Fig. 5a. The latter indicates the obviously anomalous results found in comparing, for a low though normal rotation velocity, the hysteresis curves corresponding to a homogeneous series of vulcanizates of dicumylecis-polyisoprene peroxide.

Since these vulcanizates covered a large range of reticulation densities, it was found after a preliminary study of their relaxation kinetics that the energy dissipated during each traction cycle should have lessened as the quantity of the vulcanization agent introduced was increased: no appreciable difference could be discerned.

This apparent contradiction is due to an "artifact" that seems to have remained unnoticed until now and is connected with the adhesion of rubber to the orifices of the disks. Under certain conditions, this tends to cause elongation gradients along the momentarily curved portions of the cylinder, which then become more or, on the contrary, less deformed than the rectilinear strands, depending on whether the disks are in the process of moving apart or together (Fig. 6). In this case, the average elongation, calculated from the total length of the neutral fiber, is not exactly equal to the elongation of the strands, on which the traction force measured at a given instant depends directly. In addition, since the direction of the error thus committed is reversed for the in-and-out branches of a deformation cycle, an apparent hysteresis effect is caused in a purely artificial manner.

To remedy this problem, it is fortunately sufficient, as was indicated by the computation, to impose a minimum linear drive velocity on the disks, a function of the expansion velocity of the ring. As soon as the elongation exceeds about 30%, the deformation becomes practically uniform along the neutral fiber, and this time a logical classification according to the importance of the hysteresis cycles in traction is obtained (Fig. 5b). Thanks to this simple modification, experimental data reflecting the true traction properties for the four above-mentioned vulcanizates have thus been systematically gathered between 30 and 120°C.

The presumed reduction in area of the cycles observed when the temperature rises is due partly to thermodynamic conditions that become increasingly less favorable to the crystallization of the stereospecific polymer studied, and partly to the normal lessening of molecular friction of viscoelastic origin (Figs. 3 and 5b).

Thus, an elevated test temperature combined with a rapid rotation of the dynamometer disks makes it possible to obtain traction-elongation curves that are sufficiently reversible to justify a structural analysis.

III. A NEW MODEL: THE NETWORK OF CHAINS INDIRECTLY COUPLED TO AN ELASTIC CONTINUUM

Besides the references to the possible "supra-structures" mentioned earlier (Refs. 12 and 27), refinements of the statistical theory have also been proposed to account for variations in entropy or internal energy due to local molecular interactions (Refs. 20, 28), or to the orientation of the rigid elements of the network, such as the bonds (bridging linkages) or very short links (Ref. 29). These different developments all rest on the intangible principle that, except for great deformations, the chains of the network are clustered like the individual macromolecules of a high polymer in dilute solution.

Two rules logically follow from this which simplify the mathematical treatment considerably:

a) The statistic of chains may be considered gaussian at small and average deformations, with no correction for "covolume"

or interactions at great distance being necessary in the case of polymer groups, according to Flory (Ref. 19).

b) The average distances between the juncture points of the network vary in a "related" manner as a function of the macroscopic deformations, in agreement with the geometric law governing the displacements of the different points of a simple elastic continuum (Ref. 2).

However, as has already been noted by various authors (Refs. 30, 31), the very existence of a permanent network implies, from a conformation-statistical point of view, much more severe restrictions than those normally imposed in a state of solution. In fact, the chain elements of such systems are more or less trapped since they are obviously incapable of passing through one another in the manner of the "phantom threads" ideally assumed in theory (Fig. 7). Furthermore, the interconnections of the chains that are often briefly assimilated at actual points of juncture are implicitely included in this category of topological interactions, which will probably be the object of future basic investigations (Ref. 32).

Nevertheless, the progressive nature of the chemical reactions that produce the networks provide, in our opinion, what may be an even more imperative reason for questioning the above principle of maximum bending of the chains (Ref. 33). In effect, successive ramifications of growing chains take place in the course of the polymerization of low-molecular-weight compounds or, in a more classical manner, the reticulation of macromolecules that are already very long, and numerous completely

closed circuits are bound to form even during the first stages
of these reactions. The chains included in these loops naturally
lose a part of their freedom of movement, and this effect must
be compensated for by an expansion of the loops. The consequence
of this process is that a substantial fraction of the chains of
the network must become a part of these first distended loops,
whatever the mechanism of the reticulation may be. The two hypo-
theses founded on this basis are then no longer valid, and to
replace them with less restrictive relations, the following semi-
empirical approach is proposed as applied to an ideal network
of chains formed, as usual, by n freely articulated segments
of equal length.

As far as their statistic of conformation is concerned, that
of Kuhn and Grun (Ref. 34), which has already been used by
Treloar (Ref. 35), can be adopted to account, by means of an
anisotropic model, for the stiffening of vulcanizates at great
elongations, as abstracted by the gaussian theory. As for the
law of deplacement of juncture points, it poses a more difficult
question. Basically, one should be able to find it by minimi-
zing the free energy of the aggregate of the chains; but, except
in the gaussian case, the erratic variations in length and
orientation of the links of the networks complicate a problem
which could only be solved by a regular "tetrahedral model"
(Ref. 35).

To get around this difficulty, at least in a formal fashion,
let us consider, among all the possible random paths that can be
followed along the chains of a network, a continuous circuit, such

that ABCDEF unite two jucture points immediately adjacent to A
and F for a path of minimum length (Fig. 8). The distance of
points A and F fluctuates continuously as a result of the thermal
movement; but its average value d_o in the undeformed state is
given by the relation

$$d_o = \left(\frac{N}{2}\right)^{-1/3}$$

where N is the number of links per volume unit.

On the other hand, Case and Wargin have already calculated
the probability of encountering the number q of links along this
minimum circuit as a function of the volume including the
extremities A and F, of the length nl of the links, and of the
"functionality" of the network - that is, the number of branches
emanating from each juncture point (Ref. 36). It is evident
from this work that, even for highly reticulated vulcanizates,
the value of q should be at least equal to 5 or 6, and the total
length of the circuit should consequently be considerably greater
than that of a single link. Accordingly, after a deformation, the
new distance d between A and F should not be sensitive to the
local topological irregularities; its length and average ovienta-
tion will thus vary as if the extremities A and F were merely
two points belonging to a similar elastic medium.

The average distance r between the link extremities, such
as A and B or D and E, on the other hand, should depend on these

irregularities for a nongaussian network. Still, its expression
as a function of deformation is not known, and one is forced to
substitute a judiciously selected empiric relation r(d), the
simplest, or course, is the equation of the tangent to the curve
of the unknown connection at a point defined by $r = r_o$ which
corresponds to the state of rest (Fig. 9).

In the first approximation, the expression for the relative
distribution of links r/nl may be written as

$$\frac{r}{nl} = \frac{r_o}{nl} + a \left[\frac{d}{d_o} - 1 \right] \qquad \text{(II)}$$

where d/d_o is given by the incompressible and isotropic relations
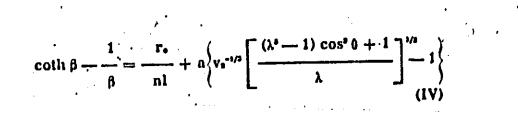of the mechanism of continuous media.

Combining Eq. II and Kuhn and Grün's statistic, the deriva-
tion of the energy function deduced from the variation in entropy
yields, in the case of an expansion-compression λ(*), the fol-
lwoing tension-elongation relation, which is valid for the
swelled as well as the dry state:

$$f = \frac{1}{2} akNnTv_s^{1/3}\lambda^{-1/3} \int_0^{\pi/2} \beta \frac{(1 + 2\lambda^3)\cos^2\theta - 1}{[(\lambda^3 - 1)\cos^2\theta + 1]^{1/3}} \sin\theta \, d\theta \qquad \text{(III)}$$

where β represents a transcendental function of λ occurring
equally, as shown by Langevin, for the analogous phenomena of

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*The coefficient of expansion λ is equal to the quotient of
the length in the expended state times the length in the state of
rest.

magnetic or electric saturation, such that

$$\coth \beta - \frac{1}{\beta} = \frac{r_e}{nl} + a\left\{v_s^{-1/3}\left[\frac{(\lambda^3 - 1)\cos^2\theta + 1}{\lambda}\right]^{1/2} - 1\right\}$$

(IV)

Here, κ indicates the Boltzmann constant, T the absolute temperature, v_2 the volumetric polymer fraction in the distended network, and θ a variable of integration in polar coordinates.

Until now, it has not been possible to calculate the above integral, since this generally requires the use of an ordinate. Meanwhile, in order to get an idea of the form of the corresponding tension-elongation curves, we can use the results obtained earlier with a mathematically simpler model possessing the same principal characteristics, except that it does not take into account in an equally realistic way the change in orientation of the chains during deformation (Ref. 33). Although this approximation introduces a few quantitative differences, the general form of the curves appears to be correctly presented (Ref. 37).

Figure 10 shows the reaction of the model to the dry state ($v_2 = 1$) as a function of $1/\lambda$ for expansion and of λ for compression; this change of variables facilitates the representation. In the ordinates, we have substituted the logarithm of $f/2kTNn$ ($\lambda - \lambda - 2$) for the force since it depends only on λ for a network of gaussian chains. As was to be expected, the gaussian

behavior is easily discernible at small and average deformations for curve 1, which correspond to a similar connection; on the other hand, when the distribution of chains in the undeformed state increases, the curves change direction radically. Instead of the long plateau, they now have two minimums clearly separated by a flattened maximum located in the compression zone.

In general, a remarkable agreement with the experimental curves-atypical example of which is presented above in Figure 10 (Ref. 38)--is observed in the vast region of deformation under consideration.

Statistical theory thus revised now accounts not only for the sharp slope that is nearly always observed in this type of diagram between 10 and 150% elongation but also for the different behavior in compression. The latter, according to the present model, now approaches an ideal gaussian state as has been suggested by certain authors.

The same comments apply when we consider the effect of a distention $1/v_2$ on the theoretical tension-elongation relations (Fig. 11).

One notes, in fact, an apparent elimination of the deviations of the classic statistical theory for sufficiently large swelling rates, in agreement, for exaple, with the experimental results of Mullins (Ref. 39) (Fig. 11). It is therefore not necessary to resort to the destruction of hypothetical oriented structures to explain this fact, which, in this context, is merely

an immediate consequence of a more significant isotropic distribution of the chains under the effect of swelling.

In support of this new interpretation, we might add that it also accounts for a recent observation made by Tobolsky and Sperling (Ref. 40). According to them, the relationship of the slightly elongated modules of a polydimethyl siloxane vulcanizate, measured respectively in the dry or swelled state, varies as $v_2{}^{2/3}$ rather than $v_2{}^{1/3}$ according to gaussian theory, or as the square of the latter quantity.

IV. A RELATED QUESTION: THE RETICULATION DENSITY

Thus far, r_o/nl, a, and the product Nn are the only structural parameters whose values are yielded directly through the identification of Eq. III with the experimental traction curves as represented by the logarithmic diagram of Fig. 10. At a difference of r_o/nl, the physical significance of the other parameters was apparent only if similar accuracies were used in the model.

In that regard, one must take into consideration the volume mass ρ of the polymer, which is slightly higher than that of the material capable of accumulating elastically mechanical energy because of the existence of defects in the network such as entirely independent elements (sol fraction*), and chain ends or "hanging" loops connected to the rest of the network only by

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*The sol fraction is also sometimetimes used to evaluate the reticulation density (Refs. 41, 42); however, even if one accepts quite arbitrary hypotheses on the length distribution of the links and the relative probabilities of dissociation and reti-

single point (Ref. 19). In equalizing this quantity with the product of the total number of chain segments, under the constraint for their mass m_s, we have

$$N \cdot n \cdot m = g \cdot \varrho \qquad (V)$$

where g is a coefficient of correction, generally somewhat lower than unit, which takes into account the diluting effect due to the above defects. Thus, the experimental data would supply, if g is known, mass m, of the "equivalent statistical segment" that characterizes the flexibility of the chains; this can also be obtained from the flow birefringence of polymer solutions.

On the other hand, it is not possible to estimate separately on these bases alone the respective values of N and n. The same situation would exist in the case of gaussian theory if one did not assume that the dispersion of the links of the network in the state of rest is the same as that of free chains of equal lengths (Refs. 2, 43): one could not then determine the reticulation indices defined by the number of links N nor the average molecular mass $M_c = nm_s$ between bridging linkages. As far as the present model is concerned, this hypothesis, which scarcely appears compatible with the interactions of the chains in the midst of a macromolecular network, is obviously excluded.

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culation of the chains, the low accuracy of determining residuals of extraction by a solvent is a major inconvenience, particularly in the presence of deterioration products.

Let us now consider the minimum circuit shown in Figure 8, and let us assume that the vector joining the extremities A and F is simply oriented in the same direction as a traction force tending toward infinity. This obliges the network to assume an expansion limit λm, as predicted by Eqs. III and IV. Physically, this limit reflects the impossibility of imposing on any link of the network a dispersion greater than its own developed length. Once this critical state has been attained, since extremities A and F are an integral part of the continuum, the only configuration that this most exposed circuit could take is a straight line now that the longest combined circuits ending at the same points of juncture are statistically sinuous. In this state, the maximum relative dispersion of q links qln/d_o, becomes equal to the expansion limit λm, and consequently, Eqs. I and V result in

$$N = \frac{1}{4}\left(\frac{q.l.g.\varrho}{\lambda m.m_s}\right)^{1/n} \qquad \text{(VI)}$$

This relation shows that the reticulation density N can be evaluated from experimental data since, in principle, these supply all of the necessary terms except for the number q of links of the minimum circuit, which can be determined from Case's theory (Ref. 36).

V. FUTURE CONSEQUENCES

The present methods of determining the structural characteristics of macromolecular networks are based on a statistical theory of elasticity which imperfectly translates the mechanical

properties of these materials; but it appears that this can be remedied on the basis of certain less restrictive postulates. The necessary experimental data could, on the other hand, be used, under reversible conditions more compatible with the theory, for traction tests made at high temperatures.

What, then, are the chances of success for a method whose relatively complex mathematical formalism is nevertheless accessible to modern methods of numerical calculation? This is precisely the question that should be answerable by a systematic study of this type applied to various types of vulcanizates and supplemented by other data obtained using the appropriate techniques of analytical chemistry.

At any rate, the remarkable agreement already demonstrated with respect to the existing literature promises to result in a more thorough knowledge of the topology of networks.

F I G U R E S

1.   Rotation of atoms in a paraffin molecule on the valence conas.

2.   Differences between the classic statistical theory and the actual elastic behavior of vulcanizates.

                  experimental curve;
                  consistently gaussian chains;
                  nongaussian chains with great deformations.

3.   Hysteresis cycle of a pure gum vulcanizate. Temperature $30^{\circ}C$; expansion velocity 2.5% per second.

4.   Recording dynamometer.

5.   Hysteresis cycles of cis-polyisoprene vulcanizates for various reticulation densities for a peroxide. Temperature $120^{\circ}C$; expansion velocity 2.5% per second.

6.   Schematic distribution of elongation along an annular cylinder according to the rotation velocity of the disks.

7.   Dispersion caused in a "closed circuit" by its interactions with the chains crossing it.

8.   Schematic presentation of a minimum circuit along the chains of a network for various states of deformation.

9.   Curve of network link connection to the elastic continuum.

10.   Elasticity of dry macromolecular networks.

11.   Elasticity of expanded macromolecular networks.