10^6 statistically verified pseudorandom numbers, $\{\epsilon_j^1\}$ and the set 2 of 10^5 random numbers $\{\epsilon_k^2\}$ generated physically. The mixing was done by applying the algorithm

$$\epsilon_i = (\epsilon_j^1 + \epsilon_k^2) \bmod (2^{31} - 1)$$

Possible repetition of the same pairs (j, k) has been algorithmically excluded.

A program for simulation of the polymerization has been written in PL/1 for the IBM/370 computer, Model 135. The use of the described method of information storage allowed systems to be computed with a starting number of monomer units up to approximately $N = 5 \times 10^5$ (depending on the reactivities K_i) with 520 kilobytes of core memory. It is higher by more than one order of magnitude compared to the method storing separately each monomer unit.[11] The time consumption for a random reaction ($K_0 = K_1 = K_2$) and for the system size $N = 30\,000$ is 350 s for $B = 10$, 301 s ($B = 30$), and 451 s ($B = 300$); for $N = 100\,000$ it is 1250 s for $B = 100$.

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Elastic Activity of Imperfect Networks

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ABSTRACT: The number of elastically effective chains in an elastomeric network is $\nu_{eff} = 2\xi$, where ξ is the number of independent circuits, or the cycle rank of the network. This universal measure of network connectivity applies regardless of the functionalities of the junctions, of their statistical distribution, and of the distribution of free ends of chains in an imperfect network. It is unambiguously related according to $\xi = \nu_a - \mu_a$ to the number μ_a of "active" junctions arbitrarily identified as those joined by three or more paths to the network and the number ν_a of active chains attached at both ends to active junctions. The number ν_a of active chains thus defined is not, however, a proper substitute for ν_{eff}.

Introduction

The stored elastic free energy of a phantom network[1] of Gaussian chains is expressed rigorously by[2,3]

$$\Delta A_{el} = (\xi/2)kT(\sum_{i=1,2,3} \lambda_i^2 - 3) \quad (1)$$

where λ_1, λ_2, and λ_3 are extension ratios along principal axes of the strain relative to the undeformed state of reference and ξ is the cycle rank of the network[3,4] or the number of independent circuits it contains. These circuits are assumed to be long, many chains being included in each of them. Otherwise stated, this qualification on the use of ξ as a universal measure of network connectivity requires that the number of short, circuitous paths shall be negligible, a condition usually fulfilled in densely interpenetrating networks.[4] The elastic response of the network is then uniquely determined by ξ; the number of junctions, their functionalities, and imperfections due to free (unattached) ends of chains are subsumed in ξ.

The cycle rank can be equated to the difference between the number ν of chains and the number ψ of labeled points in the network. These quantities are more fully defined in Figure 1. Junctions are represented in this figure by filled circles, free ends of chains by open circles. Their sum is ψ, the total number of labeled points. Junctions may be of any functionality $\phi \geq 2$. Labeling of bifunctional "junctions" is optional; inclusion of those with $\phi > 2$ is obligatory.

A chain is defined, in the usual way,[5,6] as the sequence of units bounded by consecutively labeled points along the given path. In the terminology of graph theory, the chains are edges and the labeled points are vertices of a connected graph. It follows that

$$\xi = \nu - \psi + 1$$

or, for a macroscopic network,

$$\xi = \nu - \psi \quad (2)$$

The quantities ν and ψ refer exclusively to the network; coexisting material (sol) of finite molecular size is not to be included in their evaluation.

Scanlan[7] and Case[8] have defined an active junction as one joined by at least three paths to the gel network; see Figure 1. A junction connected to the network by only one path imposes no constraints that cannot be dissipated by diffusional relaxations. One with two paths to the network merely subdivides a chain into two chains without imposing permanent constraints beyond those due to the junctions at the ends of the undivided chain. Junctions with only two paths to the network are therefore relegated to the inactive category according to the Scanlan–Case criteria. Scanlan[7] and Case[8] define an active chain as one terminated by active junctions at both of its ends.

Pearson and Graessley[9] have shown that for a randomly interconnected network whose junctions are of even functionality (ϕ even[10])

$$\xi = \nu_a - \mu_a \quad (3)$$

where ν_a and μ_a are the numbers of "active" chains and "active" junctions as defined by Scanlan[7] and Case.[8] The

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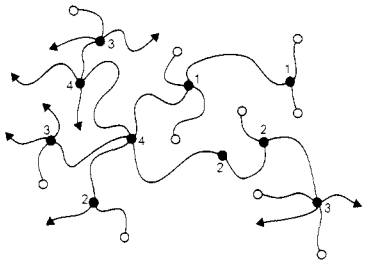

Figure 1. Schematic representation of a portion of a network. Junctions are shown by filled circles, chain ends by open circles. Arrows identify chains leading to the network by paths not included in the diagram. Each numeral denotes the number of paths to the network from the junction so labeled.

simple proof presented below generalizes this result. The principal objective of the present paper is to clarify the essential distinction between active chains according to the Scanlan–Case definitions and the number ν_{eff} of effective chains relevant to rubber elasticity theory.

Analysis and Discussion

Let all "trees" pendant to the network through one path only, including single chains with one end free (denoted by open circles in Figure 1), be removed. Further, let all superfluous labels at points representing "junctions" having a functionality of only two be eliminated. Then ψ is reduced to μ_a and ν to ν_a; i.e., all of the remaining junctions are active junctions and all of the remaining chains are active chains in the Scanlan–Case sense.

In this process, the reductions in ν and in the number of labeled points are equal; i.e.

$$\psi - \mu_a = \nu - \nu_a \tag{4}$$

This follows because each tree removed has an equal number of labeled points and chains, and elimination of a superfluous label lowers both ψ and ν by unity. Combination of eq 4 with eq 2 gives eq 3. Thus, the latter relationship is generalized to networks of any kind. The functionalities of the junctions may be odd as well as even, and the combination of units by junctions is not required to occur in any prescribed manner; specifically, it need not occur at random.

Each independent circuit effectively contributes two chains to the network. Hence, the number of effective chains is

$$\nu_{eff} = 2\xi \tag{5}$$

It is important to observe that, in general,

$$\nu_a \neq \nu_{eff} \tag{6}$$

Identification of ν_a with ν_{eff} is legitimate only in a perfect network, i.e., a network devoid of free chain ends. In such a network

$$\nu_{eff} = \phi\mu_\phi/2 = \nu_a \tag{7}$$

The nonequivalence of active and effective chains in imperfect networks may be illustrated by considering the incremental changes in ν_a and in $2\xi = \nu_{eff}$ that occur when two free ends, topologically remote in the network, are joined. Following the chain leading from one of these free ends toward the network, we note the number of pathways to the network from the next junction offering two or more pathways to the network; see Figure 1. Let the numbers thus found by following the chains extending from the respective free ends be i and i'. The increase $\Delta\nu_a$ in the number of active chains, according to the Scanlan–Case criteria, resulting from joining the pair of free ends is half of the sum of the increases in the numbers of active chains attached to the two identified junctions. Results for various values of i and i' are given in the last column of Table I. The cycle rank is increased by $\Delta\xi = 1$ for formation of a junction by fusion of any pair of free ends. The corresponding increase in the number of effective chains is invariably $\Delta\nu_{eff} = 2$. It does not depend on the local topology of the network connections, as the Scanlan–Case criteria would require and as the figures in the last column of Table I might suggest.

Table I
Increases in the Number of Active Chains

i	i'	$\Delta\nu_a$
2	2	3
2	≥ 3	2
≥ 3	≥ 3	1

The consequences of increasing the network connectivity through combination of other pairs of labeled points, one or both of which is a junction, may be similarly analyzed. The change is $\Delta\nu_{eff} = 2\Delta\xi = 2$ for any combination. On the other hand, $\Delta\nu_a$ depends on the topologies of the network in the neighborhoods of the respective labeled points. The numbers of active chains as defined by Scanlan[7] and Case[8] depend therefore on the incidences of the various topologies and, hence, on the statistics of interlinking in the given network.

Differences between ν_a and ν_{eff} are illustrated by calculations of Scanlan[7] for tetrafunctional networks formed by (i) random cross-linking of chains having the "most probable" distribution of lengths and (ii) chains of uniform length. For imperfect tetrafunctional networks, eq 5 yields the familiar relation[5,6,11]

$$\nu_{eff} = \mu_4 - N \tag{8}$$

where μ_4 in the number of cross-linkages and N is the number of primary molecules, or

$$\nu_{eff} = \nu_0(1 - 2M_c/\bar{M}_n) \tag{9}$$

where ν_0 is the total number of chains in the network, M_c is the average molecular weight of a chain, and $\bar{M}_n$ is the average molecular weight of the primary molecules. The difference between ν_{eff} calculated according to these alternative equations and ν_a put forward by Scanlan and Case as the proper measure of the number of elastically effective chains is substantial according to Scanlan's calculations.[7] These comparisons underscore the importance of avoiding confusion of ν_a with ν_{eff}.

References and Notes

(1) A phantom network is defined[3] as a hypothetical one consisting of chains that are subject only to those constraints that arise directly from the connectivity of the network, impingements of chains and junctions on one another being of no consequence. Thus, the chains, in response to the perturbation of their configurations by the strain, act only upon the junctions to which they are connected. They are otherwise devoid of material properties and, hence, do not interfere with one another. These characteristics of a phantom network hold at all deformations.

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(10) Pearson and Graessley[9] define j as the number of units joined at a junction of even functionality. Hence, ϕ as here defined is twice the j used by Pearson and Graessley to characterize networks of even functionality.

(11) See ref 6, pp 462–4.