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Topological Structure and Physical Properties of Permanently Cross-Linked Systems. 1. *s*-Functional, Homogeneous, Gaussian Systems

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ABSTRACT: Topological structure of homogeneous, permanently cross-linked systems has been described in terms of the distribution of various structural elements (single, double, etc., chains connecting pairs of junctions, free-end chains, loops, and void functionalities). For a system with *s*-functional junctions general formulas have been derived for the critical structure (gel point), chain-contraction coefficient, concentration of elastically effective junctions, modulus of elasticity, and gel fraction.

It was recognized many years ago that the topological structure of rubber networks affects their elasticity, gel-sol fraction, and other macroscopic properties. Flory,[2a] Tobolsky,[2b] Case,[3] Scanlan,[4] Mullins and Thomas,[5] Dobson and Gordon,[6] and others[7,8] introduced various corrections to the equations of rubber elasticity, to allow for the presence of elastically ineffective parts of cross-linked systems, due to free-end chains connected to cross-links with one end only. The present author discussed tetrafunctional networks with free-end chains and loops[9] and together with Klonowski[10] tried to derive information about the distribution of cross-links with various numbers of such structural elements from thermodynamic considerations (minimization of free energy)[10] to obtain "thermodynamically most probable structures". It was realized later that such an approach was not applicable to permanent, irreversible networks, as for such systems, no mechanism for thermodynamic optimization is available. Also, free-end chains and loops, discussed in the earlier papers, do not exhaust all topologically admissible types of structural elements, and analyses emphasizing only some types of junctions and neglecting others are rather arbitrary. Therefore, we have considered the problem once more to give a more systematic analysis of cross-linked systems with all topologically possible structural elements. The present analysis is an extension and generalization of the earlier treatment by the author and Klonowski[9,10] which now includes correction of errors resulting from the thermodynamic approach, inadmissible to permanently cross-linked systems. The present paper concerns cross-linked systems of any functionality, presents general classification of topologically possible defects, and derives general expressions for modulus of elasticity G, contraction coefficient A, critical structure (gel point), and gel fraction. Further papers in this series will deal with more specific network models for which the distribution functions will be derived from additional assumptions.

Characterization of Cross-Linked Structures

Consider a set of chains $\mathcal{C}$ (with cardinality N_c) and a set of *cross-links* (junctions) $\mathcal{J}$ (with cardinality N_j). Chains connected with their ends to cross-links form the system under consideration. There are several different ways in which the chains can be connected to various junctions. Considering a single cross-link one can distinguish several "structural elements" attached to it (Figure 1). *Uncross-linked* chains, strictly speaking, do not form part of the cross-linked system, but, being present in all real systems, contribute to their physical behavior. The elements which occupy a single functionality at each junction are: singlets, i.e., chains connected with their two ends to two different cross-links (s), free-end chains (f), i.e., chains connected with one end to one junction only, and void functionalities (v). The elements consuming two functionalities of each cross-link to which they are connected are: doublets (d), i.e., two chains connecting the same pair of junctions, and loops, (l), i.e., chains connected with both ends to the same cross-link. Triplets (t), quadruplets (q), and higher multiplet parallel groups of three, four, or more chains connecting the same pair of cross-links appear in systems of cross-links with higher functionalities.

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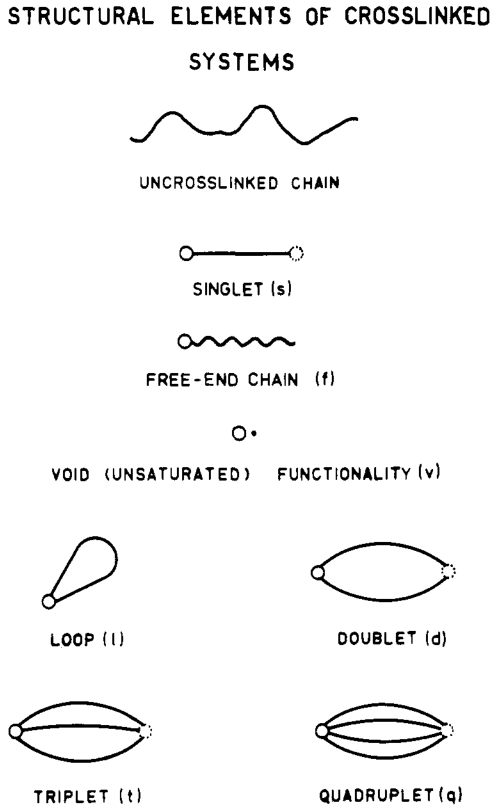

Figure 1. Topological elements appearing in cross-linked systems with maximum functionality $s \leq 4$.

Complete information about the topology of a permanently cross-linked system without chain entanglement could be provided by a rectangular matrix $N_c \times N_j$ whose components (0 for no connection, 1 for single connection (one chain end to one junction), 2 for looplike connection (two ends to the same junction)) indicate which chains ($i = 1, 2, \ldots, N_c$) are connected to individual cross-links ($j = 1, 2, \ldots, N_j$). The characterization of all physical properties of the system would, in addition to the above matrix, require the knowledge of N_c molecular weights (or contour lengths) of the chains and information about chain entanglement, a $N_c \times N_c$ matrix of entanglement invariants.[11] This sums up to the information of the order of $N_c(2N_j + k + mN_c)$ bits, i.e., of the order of the square of the number of junctions N_j (or chains N_c) in the whole system. For a macroscopic sample of 1 cm^3 volume this number reaches 10^{35}–10^{43}. It is obvious that such a formulation exceeds all possibilities of computation and any tractable theory should be based on much more limited information. The assumption of homogeneity, stating that the probability of finding any type of cross-link (i.e., any admissible combination of structural elements indicated in Figure 1) is independent of its position in the cross-linked system, reduces the description of the whole system to the distribution of a finite number of junction types. In our earlier papers tetrafunctional systems with five[10] or eight[9] types of tetrafunctional junctions were discussed. The total number of topologically admissible cross-links for tetrafunctional systems involving seven structural elements is 34. Such a system will be discussed in the next paper.

With increasing maximum functionality of cross-links, s, the number of structural elements and their combinations (cross-link types) increases. Table I presents such data for maximum functionalities between 1 and 9. The junctions with $s = 1$ and 2 are not sensu stricto cross-links but can appear as mono- and divalent chemical groups capable of reacting with chain ends. Topological groups of cross-links mentioned in Table I correspond to various possible combinations of one, two, three, and more functional structural elements. E.g., for cross-links with maximum functionality, $s = 3$, three topological groups are possible: one three-functional element (group 3), one two-functional and one one-functional element (group 21), or three one-functional elements (group 111). The number of junction types (the last column in Table I) is the number of parameters required for the description of the structure of a homogeneous system. With additional assumptions about the randomness of distribution of individual structural elements leading to multinomial distribution of junction types, the information required for characterization of a system reduces to the fractions of functionalities occupied by individual structural elements (cf. the second column in Table I). The number of topological groups T (column 5 in Table I) is equal to the number of independent constants in the multinominal distribution. Some conformational considerations based on the assumption of "equilibrium conformation" make possible further reduction of the necessary information by expressing the fractions of loops, doublets, triplets, and higher multiplets through the fraction of singlets and moments of molecular weight distributions, thus leaving only a few parameters to be determined from experiment. We will discuss such simplified models in the next paper. Here we will concentrate on a general, homogeneous Gaussian system with any functionality of cross-links. The assumption about the Gaussian potential of chains is necessary for the calculation of the contraction coefficient.

In the class of homogeneous systems, i.e., ones without correlation between the structure of junctions, the topological structure will be completely characterized by J parameters n_k, viz., fractions of junctions (crosslinks) with a given configuration of structural elements. The number of different junction types for various functionalities is given in the last

Table I
Structural Characteristics of Cross-Linked Systems with Maximum Functionality, *s*

Max functionality, s	Structural elements[a]	The no. of structural elements $E(s)$	Topological groups	The no. of topological groups $T(s)$	The no. of junction types $J(s)$
1	s, f, v	3	1	1	3
2	s, f, v, d, l	5	2, 11	2	8
3	s, f, v, d, l, t	6	3, 21, 111	3	17
4	s, f, v, d, l, t, q	7	4, 31, 22, 211, 1111	5	34
5	s, f, v, d, l, t, q, m5	8	5, 41, 32, 311, 221, 2111, 11111	7	62
6	s, f, v, d, l, t, q, m5, m6	9	6, 51, . . . , 111111	11	109
7	s, f, v, d, l, t, q, m5, m6, m7	10	7, 61, . . . , 1111111	15	182
8	s, f, v, d, l, t, q, m5, m6, m7, m8	11	8, 71, . . . , 11111111	22	296
9	s, f, v, d, l, t, q, m5, m6, m7, m8, m9	12	9, 81, . . . , 111111111	30	466

[a] s = singlet, f = free-end chain, v = void functionality, l = loop, d = doublet, t = triplet, q = quadruplet, mk = higher multiplets.

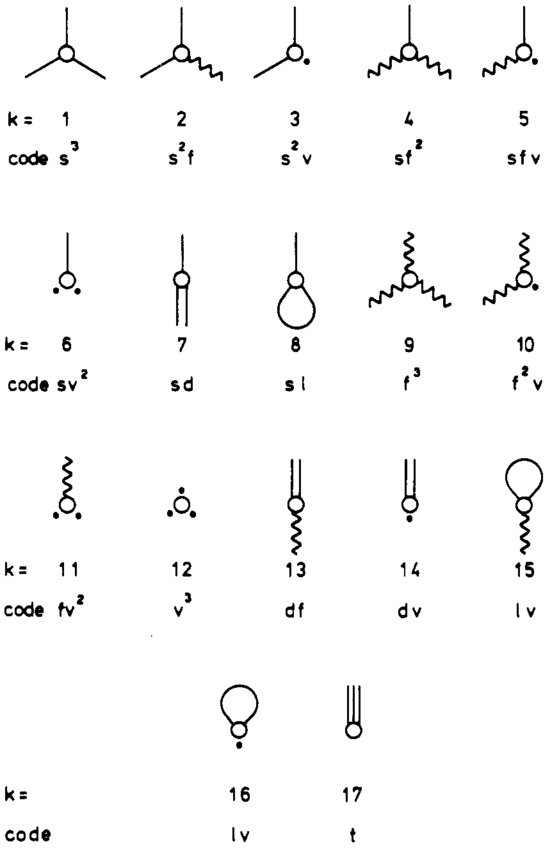

Figure 2. Topologically distinguishable types of junctions in trifunctional systems.

Table II
The Groups of Junctions with 0, 1, 2, and 3 Paths in a Cross-Linked System with Maximum Functionality $s = 3$

No. of paths, m	Junction types (code)	Fraction of junctions in the group, $\tilde{n}^{(m)}$
0	f^3, f^2v, fv^2, v^3, lf, lv, t	$\tilde{n}^{(0)} = n_9 + n_{10} + n_{11} + n_{12} + n_{15} + n_{16} + n_{17}$
1	sf^2, sfv, sv^2, sl, df, dv	$\tilde{n}^{(1)} = n_4 + n_5 + n_6 + n_8 + n_{13} + n_{14}$
2	s^2f, s^2v, sd	$\tilde{n}^{(2)} = n_2 + n_3 + n_7$
3	s^3	$\tilde{n}^{(3)} = n_1$

column of Table I. The same formalism was used in our earlier papers[7,8] but not all junction types were considered. The fractions n_k are normalized so that

$$\sum_{k=1}^{J} n_k = 1 \tag{1}$$

An example illustrating this notation for trifunctional systems is given in Figure 2. The individual junction types are, for higher clarity, labeled with the symbols of structural elements (s, f, v, etc.) in powers indicating the number of identical elements appearing in the same junction. So, s^3 denotes the junction with three singlet chains, fv^2 denotes one with one free-end chain and two void functionalities, etc. The J types of cross-links will be further subdivided into $(s + 1)$ disjoint groups, dependently on how many (m) independent paths, whether single or multiple, connect each junction to other junctions. Generally, also these fractions, $\tilde{n}^{(m)}$ ($m = 0, 1, \ldots, s$), are normalized to unity,

$$\sum_{m=0}^{s} \tilde{n}^{(m)} = 1 \tag{2}$$

For any given functionality s, the fractions $\tilde{n}^{(m)}$ can be expressed as sums of corresponding fractions of junctions n_k. Table II illustrates the relations for trifunctional systems ($s = 3$; $m = 0, 1, 2, 3$; $k = 1, 2, \ldots, 17$).

The junction with one triplet ($k = 17$, code t) has been classified in the group $m = 0$ because the tract issuing from it invariably ends in the adjacent junction and does not contribute to the construction of the gel part of the system.

In the following sections of this paper we will derive expressions for the fundamental physical characteristics of an s-functional, homogeneous Gaussian system in terms of the fractions n_k and $\tilde{n}^{(m)}$ of various junctions.

Modulus of Elasticity G and the Contraction Factor A

The statistical theory of rubber elasticity[9] yields for network systems composed of Gaussian chains the modulus G in the form

$$G = kTN_{\mathrm{c,ef}}A_{\mathrm{ef}} \tag{3}$$

where $N_{\mathrm{c,ef}}$ is the number of elastically effective network chains in unit volume of the system, A_{ef} is the average contraction of these chains

$$A_{\mathrm{ef}} = \langle h^2/\langle h_0^2\rangle\rangle_{\mathrm{ef}} \tag{4}$$

h and h_0 are chain end-to-end distances in the unstressed cross-linked state and in the uncross-linked state (unperturbed chain), respectively.

In any cross-linked system the total set of chains $\mathcal{C}$ and the total set of cross-links (junctions), $\mathcal{J}$, can be divided into three disjoint parts: $\mathcal{C}_{\mathrm{sol}} \subset \mathcal{C}$ and $\mathcal{J}_{\mathrm{sol}} \subset \mathcal{J}$ are chains and junctions in the sol fraction of the system, i.e., in the part which is soluble and not connected to the elastically effective network. $\mathcal{C}_{\mathrm{gel,ef}} \subset \mathcal{C}$ and $\mathcal{J}_{\mathrm{gel,ef}} \subset \mathcal{J}$ are chains and junctions in the elastically effective part of the gel. A junction belongs to the elastically effective part of the gel if it is connected by at least three independent paths along network chains to the boundary of the macroscopic sample.[3-5] From each end of an elastically effective chain at least two independent paths should lead to the boundary.

$\mathcal{C}_{\mathrm{gel,inef}} \subset \mathcal{C}$ and $\mathcal{J}_{\mathrm{gel,inef}} \subset \mathcal{J}$ correspond to those fragments of the system which are connected to the elastically effective gel in just one junction. The chains $\mathcal{C}_{\mathrm{gel,inef}}$ and the junctions $\mathcal{J}_{\mathrm{gel,inef}}$ do not affect elastic properties of the network but contribute to the insoluble (gel) fraction of the system.

The three sets of chains are disjoint, i.e.,

$$\mathcal{C}_{\mathrm{sol}} \cap (\mathcal{C}_{\mathrm{gel,ef}} \cup \mathcal{C}_{\mathrm{gel,inef}}) = \emptyset \tag{5a}$$

$$\mathcal{C}_{\mathrm{gel,ef}} \cap \mathcal{C}_{\mathrm{gel,inef}} = \emptyset \tag{5b}$$

and the same applies to the sets of junctions:

$$\mathcal{J}_{\mathrm{sol}} \cap (\mathcal{J}_{\mathrm{gel,ef}} \cup \mathcal{J}_{\mathrm{gel,inef}}) = \emptyset \tag{6a}$$

$$\mathcal{J}_{\mathrm{gel,ef}} \cap \mathcal{J}_{\mathrm{gel,inef}} = \emptyset \tag{6b}$$

In the equation for modulus G (eq 3) two characteristics are controlled by topological structure of the system: the contraction coefficient of the elastically effective part of the gel, A_{ef}, and the concentration of elastically effective network chains, $N_{\mathrm{c,ef}}$. To calculate the coefficient A_{ef} one has to average the sum of squared end-to-end distances $h_i^{\,2}$ of $N_{\mathrm{c,ef}}$ chains belonging to the set $\mathcal{C}_{\mathrm{gel,ef}}$ over the appropriate configuration distribution function of all N_{j} junctions in the system $\rho(\mathbf{U})$.

$$A_{\mathrm{ef}} = \frac{1}{N_{\mathrm{c,ef}}} \int \ldots \int \sum_{i \in \mathcal{C}_{\mathrm{gel,ef}}} [h_i^{\,2}(\mathbf{U})/\langle h_{i0}^{\,2}\rangle]\rho(\mathbf{U})\,\mathrm{d}\mathbf{U} \tag{7}$$

$\mathbf{U} = (\mathbf{u}_1, \mathbf{u}_2, \ldots, \mathbf{u}_{N_{\mathrm{j}}})$ is a multivector composed of N_{j} radii vectors $\mathbf{u}_k$ of all cross-links (junctions) in the system. Taking into account that, with Gaussian chains the free energy of the system at any configuration of cross-links, $\mathbf{U}$, reads

$$F(\mathbf{U}) = (3kT/2) \sum_{i \in \mathcal{C}} [h_i^2(\mathbf{U})/\langle h_{i0}^2 \rangle] \tag{8}$$

the Boltzmann distribution of configurations $\rho(\mathbf{U})$ results in the form

$$\rho(\mathbf{U}) = \exp[-\tfrac{3}{2} \sum_{i \in \mathcal{C}} [h_i^2(\mathbf{U})/\langle h_{i0}^2 \rangle]/ \int \exp[-\tfrac{3}{2} \sum_{i \in \mathcal{C}} [h_i^2(\mathbf{U})/\langle h_{i0}^2 \rangle] \, d\mathbf{U} \tag{9}$$

and, consequently, the contraction coefficient A_{ef} reduces to

$$A_{\mathrm{ef}} = \frac{1}{N_{\mathrm{c,ef}}} \int \sum_{i \in \mathcal{C}_{\mathrm{gel,ef}}} [h_i^2(\mathbf{U})/\langle h_{i0}^2 \rangle] \times \exp[-\tfrac{3}{2} \sum_{i \in \mathcal{C}} h_i^2(\mathbf{U})/\langle h_{i0}^2 \rangle] \, d\mathbf{U} / \int \exp[-\tfrac{3}{2} \sum_{i \in \mathcal{C}} h_i^2(\mathbf{U})/\langle h_{i0}^2 \rangle] \, d\mathbf{U} \tag{10}$$

It can be noticed that the only difference between the sum of h_i^2 in the exponents and that in the preexponential term lies in the range of summation. In the exponents appear sums over the whole set of chains $\mathcal{C}$ while in the preexponential term only the subset $\mathcal{C}_{\mathrm{gel,ef}}$ is considered. Because the subsets of chains are disjoint (eq 5a,b) it can be written

$$\sum_{i \in \mathcal{C}} h_i^2(\mathbf{U})/\langle h_{i0}^2 \rangle = \sum_{i \in \mathcal{C}_{\mathrm{gel,ef}}} h_i^2(\mathbf{U})/\langle h_{i0}^2 \rangle + \sum_{i \in (\mathcal{C}_{\mathrm{gel,inef}} \cup \mathcal{C}_{\mathrm{sol}})} h_i^2(\mathbf{U})/\langle h_{i0}^2 \rangle \tag{11}$$

At the same time, because also the subsets of junctions are disjoint (eq 6a,b), the multivector $\mathbf{U}$ splits into three multivectors of lower ranks

$$\mathbf{U} = (\mathbf{U}_{\mathrm{sol}}, \mathbf{U}_{\mathrm{gel,ef}}, \mathbf{U}_{\mathrm{gel,inef}}) \tag{12}$$

composed of radii vectors of the junctions belonging to the subsets $\mathcal{J}_{\mathrm{sol}}$, $\mathcal{J}_{\mathrm{gel,ef}}$, and $\mathcal{J}_{\mathrm{gel,inef}}$, respectively. Therefore, the end-to-end vectors from the $\mathcal{C}_{\mathrm{sol}}$ become functions of the vector $\mathbf{U}_{\mathrm{sol}}$ alone, those from the set $\mathcal{C}_{\mathrm{gel,ef}}$ become functions of $\mathbf{U}_{\mathrm{gel,ef}}$, etc. This reduces the expression for A_{ef} to

$$A_{\mathrm{ef}} = \frac{1}{N_{\mathrm{c,ef}}} \int \sum_{i \in \mathcal{C}_{\mathrm{gel,ef}}} [h_i^2(\mathbf{U}_{\mathrm{gel,ef}})/\langle h_{i0}^2 \rangle] \exp[-\tfrac{3}{2} \sum_{i \in \mathcal{C}_{\mathrm{gel,ef}}} h_i^2(\mathbf{U}_{\mathrm{gel,ef}})/\langle h_{i0}^2 \rangle] \, d\mathbf{U}_{\mathrm{gel,ef}} / \int \exp[-\tfrac{3}{2} \sum_{i \in \mathcal{C}_{\mathrm{gel,ef}}} h_i^2(\mathbf{U}_{\mathrm{gel,ef}})/\langle h_{i0}^2 \rangle] \, d\mathbf{U}_{\mathrm{gel,ef}} \tag{13}$$

Now, in eq 13 both in exponents and in the preexponential term appears the same sum of h_i^2 taken over the elastically effective part of the gel. We will make use of the fact that the end-to-end vectors $\mathbf{h}_i$ are linear functions of the multivector $\mathbf{U}_{\mathrm{gel,ef}}$ and, consequently, the sum of $\mathbf{h}_i^2(\mathbf{U}_{\mathrm{gel,ef}})$ is a positive definite, quadratic form of $\mathbf{U}_{\mathrm{gel,ef}}$. For such a form there exists a linear transformation $\mathbf{P}$

$$\mathbf{U}_{\mathrm{gel,ef}} \rightarrow \mathbf{P}\mathbf{U}_{\mathrm{gel,ef}} = \mathbf{Q} \tag{14}$$

which reduces the quadratic form to the canonical form

$$\sum_{i \in \mathcal{C}_{\mathrm{gel,ef}}} h_i^2/\langle h_{i0}^2 \rangle = \sum_{i=1} Q_i^2 \tag{15}$$

The number of new variables Q_i is equal to the number of independent components of the vector $\mathbf{U}_{\mathrm{gel,ef}}$. The total number of elastically effective junctions (the cardinality of the subset $\mathcal{J}_{\mathrm{gel,ef}}$) is $N_{\mathrm{j,ef}}$. Translation of the whole system of junctions should not affect the results, so we will choose one of these junctions as the origin of the radii vectors $\mathbf{u}_k$. This reduces the number of independent junctions (and the number of degrees of freedom) to $N_{\mathrm{j,ef}} - 1$. Substituting eq 15 into eq 13 we obtain the general expression for the contraction factor

$$A_{\mathrm{ef}} = (N_{\mathrm{j,ef}} - 1)/N_{\mathrm{c,ef}} \tag{16}$$

The above result (eq 16) stating that the contraction coefficient is equal to the number of degrees of freedom per network chain seems reasonable. Similar considerations carried out for the ineffective part of the gel or for the sol fraction lead to the same relation and it can be written generally

$$A = (N_{\mathrm{j}} - 1)/N_{\mathrm{c}} \tag{17}$$

where A is the contraction factor average for any Gaussian system composed of N_{j} junctions and N_{c} chains. For non-Gaussian systems, the free energy $F(\mathbf{U})$, eq 8, will include terms higher than quadratic and reduction of the exponents to the canonical form and separation of variables will not be possible.

Equation 17 is valid for systems with any topology and any functionality. For an *ideal s-functional network* the number of chains N_{c} is proportional to the number of junctions N_{j}

$$N_{\mathrm{c}} = (s/2)N_{\mathrm{j}} \tag{18}$$

and

$$A = (2/s) - 1/N_{\mathrm{c}} \rightarrow 2/s \tag{19}$$

This result reduces to $A = \tfrac{1}{2}$ for ideal tetrafunctional systems and to $\tfrac{2}{3}$ for ideal trifunctional systems. $A = \tfrac{1}{2}$ for tetrafunctional systems has been derived in other ways by James and Guth,[12] Ronca and Allegra,[13] and Eichinger.[14] On the other hand, for cross-linked systems with *treelike topology* the number of chains N_{c} is

$$N_{\mathrm{c}} = N_{\mathrm{j}} - 1 \tag{20}$$

and

$$A = 1 \tag{21}$$

without respect to functionality. For real systems the contraction of the elastically effective part of the gel will be intermediate between the ideal case (eq 19) and the treelike extreme (eq 21).

$$1 \geq A \geq 2/s \tag{22}$$

In a recent paper Graessley[15] derived a contraction factor A for Gaussian networks, using apparently a similar method to that used above. His result

$$A = (s - 2)/s \tag{23}$$

was apparently due to special topology of the networks which were assumed to be composed of fragments of trees with some junctions constrained (and hence removed as integration variables). It is not clear how microscopic treelike fragments can be constrained inside of the cross-linked system and what kind of real networks can be described with the aid of that model.

Substituting A_{ef} from eq 16 to eq 3 one obtains the modulus of elasticity G in the form

$$G = kT\,(N_{\mathrm{j,ef}} - 1) \rightarrow kTN_{\mathrm{j,ef}} \tag{24}$$

It is evident that the modulus is controlled by the number of elastically effective *network junctions* rather than *network chains* as assumed in our earlier papers.[9,10]

The suggestion that modulus of elasticity of polymer networks should be expressed in terms of effective network junctions rather than network chains has been put forward earlier by other authors (cf. ref 7). The fact that in the earlier formulas for tetrafunctional junctions the modulus was proportional to $2N_j$ (rather than to N_j in our eq 24) indicates that it was simply a result of conversion of the number of network chains into the number of cross-links (junctions) with contraction factor $A = 1$. With the assumption of $A = 1$, for ideal s-functional networks the modulus at constant number of cross-links N_j would be proportional to junction functionality, s

$$G = kTN_c = (s/2)kTN_j$$

while our results show that the possible effect of functionality is completely compensated by the contraction factor $A = N_j/N_c$

$$G = kTN_cA = kTN_j$$

independently of s.

The Number of Elastically Effective Network Junctions, $N_{j,ef}$, Gel Point, and Gel Fraction

The calculation of the elastically effective junctions, fraction of junctions forming the gel, and its elastically effective part is based on the consideration of the continuity of a single path in the cross-linked system, starting from a randomly chosen junction and propagating along the network chains infinitely (practically: until it reaches the boundary of the system), or being terminated at some point (junction) without connection to other junctions. This problem has been discussed in our earlier paper (ref 10, Appendix) for limited network models on the basis of the theory of cascade processes. We will use the same method here for the more general class of s-functional, homogeneous networks describable in terms of the junction distribution function $\tilde{n}^{(m)}$ $(m = 0, 1, \ldots, s)$.

The probability of extinction, e, i.e., the probability that a single path will terminate somewhere, is different from the unity solution of the equation[16]

$$e = F_1(e) \qquad 0 < e < 1 \tag{25}$$

where $F_1(e)$ is the probability generating function for the transition from the ith generation to the $(i + 1)$ generation. In terms of the fractions of junctions with $0, 1, \ldots, m$ paths, $\tilde{n}^{(m)}$, the generating function F_1 reads

$$F_1(e) = \sum_{m=1}^{s} m\tilde{n}^{(m)}e^{m-1} / \sum_{m=1}^{s} m\tilde{n}^{(m)} \tag{26}$$

With simple rearrangements and after division by $(e - 1)$, eq 25 reduces to the form

$$\sum_{k=1}^{s-2} \sum_{m=k+2}^{s} m\tilde{n}^{(m)}e^{k} = \tilde{n}^{(1)} \tag{27}$$

Equation 27 presents an algebraic equation of the $(s - 2)$ degree. For trifunctional and tetrafunctional systems the solutions read simply

$$e = \tilde{n}^{(1)}/3\tilde{n}^{(3)} \tag{27a}$$

and

$$e = \tfrac{1}{2}[(1 + 3\tilde{n}^{(3)}/4\tilde{n}^{(4)})^2 + \tilde{n}^{(1)}/\tilde{n}^{(4)}]^{1/2} - \tfrac{1}{2}(1 + 3\tilde{n}^{(3)}/4\tilde{n}^{(4)}) \tag{27b}$$

and for higher s can be obtained numerically. The critical structure of the system, i.e., one which corresponds to the transition from the collection of finite aggregates (sol) to infinite aggregates (gel) reads

$$e < 1 \quad \text{or} \quad \tilde{n}^{(1)} < \sum_{k=1}^{s-2} \sum_{m=k+2}^{s} m\tilde{n}^{(m)} \tag{28}$$

It can be noticed that the gelation condition (eq 28) defines the relation between the maximum concentration of one-path junctions and junctions with three or more paths. Junctions without any paths, $\tilde{n}^{(0)}$, and those with two paths, $\tilde{n}^{(2)}$, do not affect the critical condition.

To find the concentration of elastically effective junctions, i.e., ones from which at least three paths lead to infinity (boundary of the sample), we have to consider all possibilities of successful configurations in the classes $\tilde{n}^{(3)}, \tilde{n}^{(4)}, \ldots, \tilde{n}^{(s)}$ with the result

$$N_{j,ef} = N_j \sum_{m=3}^{s} \sum_{k=3}^{m} \tilde{n}^{(m)} \binom{m}{k} (1 - e)^k e^{m-k} \tag{29}$$

Similarly, the concentration of junctions in the gel fraction (i.e., concentration of junctions which have at least one path leading to infinity) is

$$N_{j,gel} = N_j \sum_{k=1}^{s} \tilde{n}^{(k)}(1 - e^k) \tag{30}$$

N_j in eq 29 and 30 is the total concentration of junctions in the system. It can be shown that the critical condition for gelation (eq 28) is the necessary and sufficient condition for the appearance of gel and, at the same time, for the appearance of the elastically effective fraction

$$e < 1 \Leftrightarrow N_{j,gel} > 0 \tag{31}$$

$$e < 1 \Leftrightarrow N_{j,ef} > 0$$

For trifunctional systems eq 29 and 30 yield respectively

$$N_{j,ef}/N_j = \tilde{n}^{(3)}(1 - e)^3 \tag{29a}$$

$$N_{j,gel}/N_j = (1 - e)[\tilde{n}^{(1)} + \tilde{n}^{(2)} \times (1 + e) + \tilde{n}^{(3)}(1 + e + e^2)] \tag{30a}$$

It is evident that the number of elastically effective junctions $N_{j,ef}$ grows more steeply with $(1 - e)$ than does $N_{j,gel}$.

The function of elastically effective junctions $N_{j,ef}$ from eq 29 can be substituted to eq 24 and the modulus G expressed through the distribution of junctions with various numbers of paths, $\tilde{n}^{(m)}$

$$G = kTN_jf[\tilde{n}^{(m)}, e(\tilde{n}^{(m)})] \tag{32}$$

No information about molecular weights or more detailed structure of junctions is needed. The same applies to the critical condition of gelation, eq 28.

On the other hand, the mass fraction of the gel or the fraction of network chains in the gel requires more information. If u_k is the number of network chains per junction of the kth type (the classification into $J(s)$ topologically distinguishable junction types is meant, cf. Figure 2 and Table I) and $p_k(e)$ is the probability that the junction k is connected to the gel with at least one path, then

$$N_{c,gel}/N_j = \sum_{k=1}^{J(s)} n_k p_k u_k \tag{33}$$

or

$$N_{c,gel}/N_c = \sum_{k=1}^{J(s)} n_k p_k u_k / \sum_{k=1}^{J(s)} n_k u_k \tag{34}$$

where N_j and N_c are total concentrations of junctions and chains in the system. The probabilities p_k depend on the class to which the k-type junction belongs. If the kth type belongs to the class m (i.e., there are m independent paths issuing from the junction), the probability p_k reads

$$p_k(e;m) = 1 - e^m \tag{35}$$

The number of chains per junction, u_k, depends on the fine structure of the junction. For a monodisperse system resulting

Table III
Probabilities of the Attachment to Gel, p_k, and the Numbers of Chains Per Junction, u_k, for Individual Types of Trifunctional Junctions

Junction type, k	Code	No. of paths, m	p_k	u_k
1	s^3	3	$1 - e^3$	3/2
2	s^{2}f	2	$1 - e^2$	2
3	s^{2}v	2	$1 - e^2$	1
4	sf^2	1	$1 - e$	1/2
5	sfv	1	$1 - e$	3/2
6	sv^2	1	$1 - e$	1/2
7	sd	2	$1 - e^2$	3/2
8	sl	1	$1 - e$	3/2
9	f^3	0	0	3
10	f^{2}v	0	0	2
11	fv^2	0	0	1
12	v^3	0	0	0
13	df	1	$1 - e$	2
14	dv	1	$1 - e$	1
15	lf	0	0	2
16	lv	0	0	1
17	t	0	0	3/2

from end-to-end connection of identical chains to a multifunctional cross-linking agent, the mass and the number of chains at any junction depend on the number and type of structure elements. Each singlet contributes with one-half chain, free-end chain with 1, void functionality with 0, a loop with 1, a doublet, triplet, and a k-multiplet with 1, 3/2, and k/2 chains, respectively. This makes possible calculation of gel fraction provided that the topological structure of the system, i.e., the junction type distribution function n_k [$k = 1, 2, \ldots, J(s)$], is known. The values of p_k and u_k for all 17 junction types possible in a trifunctional system are given in Table III.

Discussion

The considerations included in this paper seem to form a basis for the development of more specific models. Classification of all possible topological elements in the structure of cross-links removes the arbitrariness involved in earlier treatments due to emphasizing only some structural features and neglecting others. The introduction of the void functionality (v) as a formal structural element of a cross-link makes possible consideration of systems with a distribution of effective functionalities: s is a *potential*, maximum functionality of each crosslink, clearly determined by its chemical structure while the *effective* functionality depends on what kind of structural elements saturate these potential valences. For the systems considered in this paper, the critical structure (gel point), the contraction coefficient (A), and the modulus of elasticity (G) are determined solely by the distribution of junctions according to the number of independent paths connecting each junction to other junctions, $\tilde{n}^{(m)}$. More detailed information is required for the calculation of the mass fraction of the gel and mass fraction of the elastically effective part of the gel. The information about the distribution of junction types, $\tilde{n}^{(m)}$ or n_k, can be obtained from various sources, including kinetics of the cross-linking process and thermodynamic considerations of chain conformation in the conditions of cross-linking. The way in which the distribution functions are derived from kinetic or other data is of primary importance for the understanding and rational prediction of the macroscopic behavior of networks; the amount of information available empirically is very scanty and practically limited to the modulus G, swelling coefficient, and gel fraction. These data can be matched by different structural models using many parameters. This explains the apparent success of many incomplete and even self-inconsistent models which, using a number of adjustable parameters, can be made to fit the few experimental data quite well. The predictive value of a structural theory depends on the way in which the structure is derived from the information about the system and its formation rather than by the apparent consistency of the predictions with the few experimentally measured properties. We will discuss this problem in one of the next papers.

The class of cross-linked systems discussed in this paper is also limited. Three assumptions are responsible for this. The assumed Gaussian statistics of individual network chains limit the applicability of the model to systems with not too high cross-link densities (not too short network chains) and not too high deformations of the system. The homogeneity, stating that the structure can be adequately described in terms of the configuration of a single junction (cross-link), is a model assumption which cannot be proved to be true, although it seems reasonable as a natural first approximation. One can, in principle, build up a theory in terms of the distribution of configuration of pairs, triads of junctions, etc. This would result in the considerable increase in the number of parameters of the theory. E.g., introduction of pair distribution for trifunctional systems, instead of 17 types of junctions shown in Figure 2, would bring seven types of junctions without any connection to others, $m = 0$, and 43 distinguishable pairs of junctions. Extension of the present, correlationless model to pair or higher correlations would be possible should an indication that such an extension is necessary arise. The more important point concerns neglect of entanglements. The great importance of entanglements entrapped between permanent junctions both for equilibrium elasticity and transient behavior seems to be beyond any doubt. The theory of entanglement is, however, very far behind the theory of rubber elasticity based on permanent cross-links and we could not find any way of treating this problem on the level of strictness comparable to that possible for the topology of permanent junctions. The problem is additionally complicated by the fact that the contribution of entanglements to equilibrium elasticity is not equal to that of permanent junctions and therefore not additive.[17] This problem requires intensive theoretical and experimental studies.

References and Notes

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