Graphlike State of Matter. 10. Cyclization and Concentration of Elastically Active Network Chains in Polymer Networks†

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ABSTRACT: The spanning-tree approximation of the cascade theory is applied to the calculation of the number of elastically active network chains (EANCs) and elastically inactive cycles in the random cross-linking of linear primary chains of "most probable" distribution. A system of kinetic equations was developed to include terms to describe intermolecular cross-linking, plus intramolecular reaction in the sol and in the gel, together with the elastic reactivation of inactive cycles in the gel, as a function of cross-linking density. Computations show that by suitably rescaling the data to the gel point, the concentration of EANCs is effectively independent of cyclization up to appreciable degrees of cross-linking.

The contributions to a recent Discussion on Rubber Elasticity[2a] show that the statistical mechanics underlying the phenomenology are still beset by major perplexities. Even when we are certain that we are measuring true equilibrium moduli, their comparison with theory raises various controversial questions.[2b] The major ones center on: (1) the front factor in the equation of state; (2) the Gaussian approximation of the configurational statistics of network chains; (3) network flaws such as (a) loose material and chain ends; (b) cycles (loops) which waste cross-links, and the possible effect of thermodynamic volume exclusion on cyclization;[3] (c) entanglements of chains (an individual entanglement may lower the modulus but on average entanglements increase the modulus (Edwards[4])); and (4) the origin of the C_2 term in the equation of state.

The present work is concerned with the effects of cycles (see 3b), and it arose from recent attempts to estimate their effect theoretically. Our wider aim is to draw attention to the neglect in the field of rubber theory of strategies well tried in other fields of physical science. Several disturbances which individually contribute modest or second-order effects to a simple first-approximation theory may combine to render application of the simple theory hazardous and its refinements impossible.

The way forward is usually by experimental procedures which allow individual disturbances to be canceled out of the analysis by "superposition" procedures, the construction of master curves, etc. A general methodology seeks to identify the critical point associated with the phenomenon and to reduce physical properties to quantities, often dimensionless, relative to their critical values. Corresponding-state theories,[5,6] or the WLF transform,[7] are examples from polymer science. Indeed, the familiar ratio[8] $\langle r^2\rangle/\langle r_0^2\rangle$ (with $\langle r_0^2\rangle$ the dimensions in the reference state) in the modern form of the elastic equation of state cancels out configurational changes in Gaussian chains. For the statistics of network graphs, the relevant critical point is Flory's gel point, and conversion parameters reduced relative to their critical values have been used by a number of investigators. This reduction is known to be specially fruitful at very low conversions (near the gel point), as will be illustrated below.

Analogous procedures are used in other branches of physics which employ the same lattice graph model (the so-called percolation model[9,10]), giving different but appropriate interpretations to its statistical parameters. The analogies have been well set out by Stauffer[11] in tabular form.

† Affectionately dedicated to Dr. Maurice Huggins for his eightieth birthday.

It has been repeatedly emphasized[12-14] that the disturbances numbered above as (2) and (3c) theoretically vanish asymptotically at sufficiently low conversion past the gel point. Besides, such rubbery materials are highly diluted by their sol fractions, so that the C_2 term would also be asymptotically eliminated. To exploit these benefits, more exacting experimental techniques are required because of the real problems involved in making *equilibrium* measurements, and it is essential to *generalize* the common method for calculating the concentration N_e of active network chains. The generalization to a graph-theoretically more refined definition of the concentration is due to Scanlan[15] and independently to Case.[16] It extends the cruder procedures, based on the notion of the mean molecular weight $\overline{M}_c$ between cross-links and a chain-end correction, to situations covering all networks, including homopolycondensates, and later to networks obtained by an alternating mechanism involving more than one type of unit.[17,18] Equally important, it extends the older procedures into the low conversion range close to the gel point. The Scanlan–Case definition of an elastically active network chain (EANC) renders the earlier procedures obsolete because it is a generalization; it reduces asymptotically to the values based on $\overline{M}_c$, where this procedure is defined, at conversions as high as several times the critical value, which is the range of conversion usually studied. Unfortunately, in this range the disturbances (2), (3b), (3c), and (4) introduce complications.

Several investigators have questioned the importance of the Scanlan–Case method because they verified the asymptotic convergence to the older and more familiar theory within the ranges of relatively high conversions which they were studying, e.g., Treloar,[2b] Allen,[19] and Helfand and Tonelli.[20] The latter authors nevertheless are aware of the importance of this model at low conversions. At high conversions the more direct calculation, using $\overline{M}_c$ and the (correct form of) chain-end correction, is then quite in order as a mathematically justified approximation to the better theory. However, in the recent Discussion, Flory[21] criticized the Scanlan–Case concept on theoretical grounds. The objections which Flory raised in the Discussion would apply most strongly at high "conversion", where his own procedure, which he cites, is mathematically equivalent. The merit of the Scanlan–Case formulation is exemplified by its power to generalize into a single and simple equation (eq 31 of ref 12), classical formulas (including those of Flory) covering various kinds of systems by six different teams.[22] Because of misunderstandings, the basic theory was restated in simple terms in another lecture[13] published after the discussion.[29]

The calculation of the concentration N_e of EANCs is, then, by implication *universally* based on the statistics of a treelike

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model derived from the real network graph by treating ring closures as intermolecular links. Experimental tests amply justify such a treatment to a tolerable approximation. Tonelli and Helfand[23] argued that a better approximation to N_e was required in respect of certain loops which actually waste cross-links "before any properties of a rubber are seriously discussed". A second-approximation treatment for calculating all statistical parameters (including N_e) is already available. It is a perturbation treatment, based on spanning trees, but injecting the notion of Gaussian statistics for the rate of elastically inactive ring closures.[24–26] This perturbation model has been specifically denoted as "the spanning-tree approximation" for ring-chain competition processes,[27] and it is now briefly described.

In the presence of formation of elastically inactive cycles, two kinds of correlations affect the statistics of formations of links which cannot be treated exactly: (a) long-range configurational effects (in three-dimensional space) are approximated by some model like the Gaussian chain, and (b) the statistics of paths through the (one-dimensional) network, available for closure into cycles by formation of elastically inactive links. The latter situation is approximated by replacing the network by a spanning tree, i.e., a graph free from cycles, comprising the same set of points (atoms), and just enough lines (bonds) to link them into a single infinite branched molecule. After this restriction of the network to a tree, there is a unique path between any two atoms. The single statistical approximation involved in this stratagem is to equate the generating functions for the number of offspring (successor units) on successive generations from the first one upwards, so that $F_1 = F_2 = F_3 = \ldots$ Now F_1 is exactly calculable from (but not equal to) the link-probability generating function F_0 of the zeroth generation; viz.,

$$F_1(\theta) = F_0'(\theta)/F_0'(1)$$

where θ is the auxiliary variable of the generating functions. The relation $F_1 = F_2 = F_3 \ldots$ is exact asymptotically as the concentration of cycles formed falls to zero. The whole approximation treatment has been tested by computer calculation against the exact treatment of a bifunctional (non-gelling)[28] system and against experiments[27,29,30] and an excellent agreement was achieved. The spanning-tree approximation also gave results agreeing closely with exact calculations for the early stage of a potentially gelling polyfunctional system,[31] and it is believed that it represents the best available model for approximating ring-chain competition processes.

While the present authors and their co-workers have found the spanning-tree approximation very appropriate for treating ring-chain competition,[3,24–28,30–33] other workers seem to ignore it even where it would clearly solve their problems.[34] In case this reflects distrust of the underlying model, we note here that, in a special but representative case, the model reduces to one constructed by Neyman[35] in 1940 and now classical in pure and applied[36] statistics.

Up to the gel point the definition of cyclization is quite simple: a newly formed bond is considered intramolecular if its formation does not result in an increase in molecular weight. This happens if the two reacting functionalities are already connected via a sequence of chemical bonds. Beyond the gel point the above definition of cyclization becomes inadequate although it can still be applied to the sol, but within the gel all gel–gel reactions would have to be considered intramolecular. Instead we are interested only in such intramolecular bonds that cannot be elastically active and cannot contribute to the equilibrium elastic modulus of the gel. Such a point of view on post-gel cyclization has been developed historically and was made clear recently.[37]

In this paper, we shall apply the spanning-tree approximation to the calculation of wastage of links formed. In order to include cyclization with the other sources of wastage (treated exhaustively earlier[33]), we use the spanning-tree approximation. An intramolecular link is wasted unless it closes a cycle which includes an active network junction point (as defined by Scanlan). An active junction point is a point in the spanning tree from which at least three totally independent paths can be traced along the tree to the surface of the specimen. In the statistical calculation, the surface of the specimen is taken to lie at infinity. A chain is an active network chain if it links two active junction points, but does not harbour active junction points along its length. The requirement of total independence of the three paths from an active junction point to infinity will be relaxed only for the purpose of a small correction later (Appendix A2, part 3).

The intensity of formation of elastically inactive cycles in random cross-linking of primary chains was dealt with by Helfand and Tonelli.[19,23] They weighted the probability of closing an x-membered ring by the probability that none of the $x - 1$ segments bear a cross-link with an infinite continuation. As in other treatments (cf. ref 24–26, 38, and 39) Gaussian chain statistics was used for the ring-closure probability although corrections were used for small cycles.[20,23]

The original treatment[23] was criticized[40] (a) for the use of wrong cross-linking statistics and (b) for making no distinction between the cyclization probability within a free chain and an EANC where the chain ends are constrained by cross-links.

Objection (a) was partly corrected in the second paper[19] by using a modified Flory's expression for the fraction of "sterile" cross-links in the whole system. However, the use of an overall fraction of sterile cross-links as a weighting factor is incorrect, because one cannot find any elastically active cross-link in the sol or in the loose material tied to the gel. The importance of the objection (b) has been examined in the present work (Appendix A1): it has been found that the constraints imposed on chain ends by cross-links do decrease the cyclization probability but not as much as was expected.

Another serious objection is to be raised additionally. Cross-linking of primary chains is a kinetically controlled irreversible reaction and should be treated accordingly. What Helfand and Tonelli calculate refers only to differential fractions (increments) of wasted cross-links or EANCs formed at a given level of cross-linking. One should rather find the integral fractions solving the corresponding set of differential equations. It is easy to see that such a neglect would cause a serious error in treating stepwise reactions (where the differential fraction of ring-forming functionalities is zero at the start)[26,30–32] or in chain polymerisation.[33] In their reply to the criticism[40] mentioned above, Helfand and Tonelli[41] suggest that just such a kinetic approach based upon earlier work[37] could be used in place of their equilibrium approach. Turning to our spanning-tree model calculations, we have kept distinct the formation of cyclic links in the sol and in the gel. The transfer of certain links from the active to the inactive account introduced by Helfand and Tonelli is also incorporated in our calculation, as it should be, according to the definition of link wastage just given. A link in the gel may be wasted at the moment it is formed, because it closes a cycle devoid of active junction points. At a later stage (see Figure 1), formation of other links may cause the same pair of units to change its status, viz., when that cycle acquires an active junction point. In that case the link originally wasted should be transferred to the active account. Of course, such a correction factor can be made only on a statistical basis.

Our model is well structured for the strategy of canceling disturbances outlined in the introductory section; a suitable rescaling of data should render the concentration of EANCs independent of cyclization at least within experimental error.

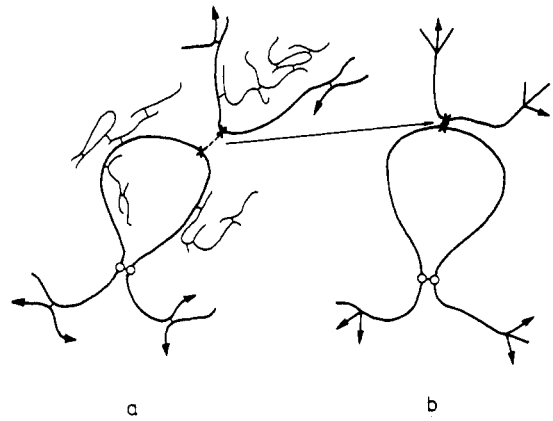

Figure 1. Activation of a cycle. An arrow denotes a path to infinity through the gel; (○) ring-closing functionality. (a) An ωC functionality on the ring reacting with another ωC functionality bearing two independent paths to infinity. (b) The cycle has become activated (pendant repeat units have been deleted for clarity).

Other effects may then become accessible to experimental test. For example, Helfand and Tonelli[19] "speculated that the elastically ineffective portion of the polymer acts like a diluent in decreasing . . . deviations from ideal elastic behavior", while Langley and Polmanteer,[42] among others, have stressed the importance of entanglements, and support their arguments by measurements of the sol fraction from γ-irradiated poly(dimethylsiloxane).

We have restricted ourselves in the numerical calculations to a system, very representative of practical applications, with the most probable (random) distribution of primary chains, and to Gaussian cyclization probability although a modification for short chains would be quite easy.

The Treelike Model for Cross-Linking of the Most Probable Distribution of Primary Chains

The most probable distribution of *linear* chains can be generated from bifunctional units (repeat units). If the chance of finding a functionality to form a bond is p, then the probability generating function (pgf) for the number of bonds issuing from the root ($F_0(\theta)$) and from units in the first and higher generations ($F_1(\theta)$) is (cf. ref 43)

$$F_0(\theta) = (1 - p + p\theta)^2 \tag{1}$$

$$F_1(\theta) = 1 - p + p\theta \tag{2}$$

which yield by standard procedures[44] the well known formulas for the number (P_n^0) and weight (P_w^0) average degree of polymerization:

$$P_n^0 = 1/(1 - p) \tag{3}$$

$$P_w^0 = (1 + p)/(1 - p) \tag{4}$$

If primary chains are cross-linked some of the repeat units are coupled by intermolecular cross-links and some links may be intramolecular. Let ν be the fraction of cross-linked repeat units and ν_ω, ν_σ, and ν_α the fractions of uncross-linked, intramolecularly cross-linked, and intermolecularly cross-linked repeat units, respectively ($\nu = \nu_\alpha + \nu_\sigma$). These units are supposed to bear free, ring-forming, and intermolecular functionalities and will also be referred to as ωC, σC, and αC functionalities. The degree of polymerization of primary chains is a function only of p.

Within the spanning-tree model, an ωC functionality has no offspring. The cyclization probability depends on the number of links between the two reacting functionalities and we should consider a possible contribution by cross-links

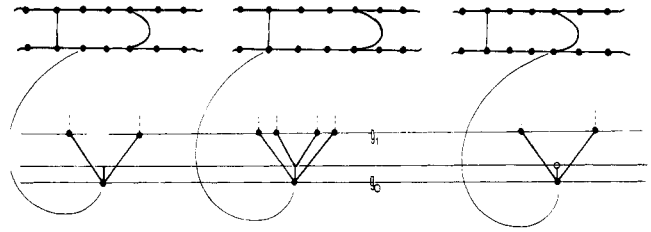

Figure 2. Mapping of repeat units into the graphlike state. Top: units on primary chains, with intermolecular cross-link between chains! and additional intramolecular cross-link ↄ , mapped into their molecular trees (bottom). The trees are rooted, from left to right: on a unit with an ωC functionality (unreacted), on an αC functionality, and on a σC functionality. The cross-link (center) on the generation denoted C is contracted so that generations g_0 and g_1 (P-type units) are the zeroth and first generation of the molecular trees.

themselves. Since the cross-link is often only one C–C bond and the cross-links are not numerous in the range of interest we disregard their contribution. Under such conditions molecular trees are constructed from units shown in Figure 2; i.e., by contracting away the cross-link, two previously two-functional units become a four-functional unit such as the one in the center.

Branched structures corresponding to cross-linking of primary chains are thus formally generated only via the P functionalities of the units in Figure 2. The pgf for the number of bonds issuing from such a unit in the root can be written as

$$F_0(\theta,\vartheta) = (\nu_\omega\vartheta_\omega + \nu_\sigma\vartheta_\sigma)(1 - p + p\theta)^2 + \nu_\alpha\vartheta_\alpha(1 - p + p\theta)^4 \tag{5}$$

with $\vartheta = (\vartheta_\omega,\vartheta_\sigma,\vartheta_\alpha)$ referring to C functionalities and the coefficients of ϑ_i for $\theta = 1$ are the fraction ν_i. The coefficients of θ^i ($\vartheta = 1$) refer to units with i offspring in the first generation. The pgf for the number of bonds issuing from the first and higher generations is

$$F_1(\theta,\vartheta) = (\nu_\omega\vartheta_\omega + \nu_\sigma\vartheta_\sigma)(1 - p + p\theta) + \nu_\alpha\vartheta_\alpha(1 - p + p\theta)^3 \tag{6}$$

The gel point is given by[43]

$$[\partial F_1(\theta,\vartheta)/\partial\theta]_{\theta=1,\vartheta=1} = 1 \tag{7}$$

which yields for the critical value of

$$\nu_{\alpha_c} = (1 - p)/2p = 1/(P_w^0 - 1) \tag{8}$$

The post-gel parameters are related to the extinction probability υ given by the lower positive root of the equation[44]

$$\upsilon = F_1(\upsilon,1) \tag{9}$$

i.e.,

$$\upsilon = (\nu_\omega + \nu_\sigma)(1 - p + p\upsilon) + \nu_\alpha(1 - p + p\upsilon)^3 \tag{10}$$

This equation has a trivial root $\upsilon = 1$ which can be eliminated and the solution for $\upsilon\langle 0,1\rangle$ becomes

$$\upsilon = [-\nu_\alpha p(3 - 2p) + \{\nu_\alpha^2 p^2(3 - 2p)^2 + 4\nu_\alpha p(1 - p)[\nu_\alpha(1 - p)^2 + 1 - \nu_\alpha]\}^{1/2}]/2\nu_\alpha p^2 \tag{11}$$

A bond issuing to higher generations may be a part of a finite (υ-type bond) or an infinite ($(1 - \upsilon)$-type bond) path. This occurs with probability υ and $1 - \upsilon$, respectively. The definition of υ given by eq 10 implies that we do not consider correlations between the bonds issuing from a unit in the root. In that case it is legitimate to replace F_0 by G_0 (cf. ref 17 and 18)

$$G_0(\theta,\vartheta) \equiv F_0(\upsilon\theta_\upsilon + (1 - \upsilon)\theta_{1-\upsilon},\vartheta) \tag{12}$$

with

$$\theta = (\theta_\upsilon, \theta_{1-\upsilon})$$

The coefficient of ${\theta_\upsilon}^i{\theta_{1-\upsilon}}^j$ ($\vartheta = 1$) is the probability of finding a unit in the root issuing i υ-type and j $(1-\upsilon)$-type bonds. The vectorial generating function for the offspring of a unit on generation 1 is then as follows:

$$\mathbf{G}_1(\theta_\upsilon, \vartheta) = \{G_{1\upsilon}(\theta_\upsilon, \vartheta), G_{1,1-\upsilon}(\theta_{1-\upsilon}, \vartheta)\} \tag{13}$$

where $\mathbf{G}_{1\upsilon}$ refers to a unit on generation 1 linked to a υ-type link from the root and $G_{1,1-\upsilon}$ to a $(1-\upsilon)$-type link. Accordingly,

$$G_{1\upsilon}(\theta, \vartheta) = G_1(\theta_\upsilon, 0, \vartheta)/(G_1(1,0,1)) \tag{14}$$

$$G_{1(1-\upsilon)}(\theta, \vartheta) = [G_1(\theta_\upsilon, \theta_{1-\upsilon}, \vartheta) - G_1(\theta_\upsilon, 0, \vartheta)] / [G_1(1,1,1) - G_1(1,0,1)] \tag{15}$$

The pgf's 14 and 15 will be useful for the statistics of cyclization within finite and infinite paths (Appendix A2).

The structural parameters of interest, the sol (w_s) and gel (w_g) fractions, the number of EANCs per repeat unit in the whole system (N_e) and in the gel (N_e'), are derived exactly from G_0; thus

$$w_s = G_0(1,0,1) = (1 - \nu_\alpha)(1 - p + p\upsilon)^2 + \nu_\alpha(1 - p + p\upsilon)^4 \tag{16}$$

$$w_g = 1 - w_s \tag{17}$$

For a network chain to be an EANC at least three independent paths must issue from each of its ends to infinity.[12] Using the identity

$$G_0(1, \theta_{1-\upsilon}, 1) \equiv T(\theta_{1-\upsilon}) \equiv \sum_{i=0}^{4} t_i {\theta_{1-\upsilon}}^i \tag{18}$$

the number of EANCs per repeat unit becomes (exactly)

$$N_e = \tfrac{1}{4} \sum_{i=3}^{4} i t_i \tag{19}$$

The multiplication factor $\frac{1}{4}$ (instead of $\frac{1}{2}$, cf. ref 12) arises from the fact that the F_0 and G_0 refer to contracted units (Figure 2) and each contracted unit with an αC functionality is composed of two repeat units. The sum in eq 19 can be expressed in terms of the first and second derivatives T' and T'' at $\theta_{1-\upsilon} = 1$ or 0 (cf. ref 12).

$$N_e = (\tfrac{1}{4})(T'(1) - T'(0) - T''(0)) \tag{20}$$

and substituting eq 5, 12, and 18 into eq 20 one gets

$$N_e = \nu_\alpha p^3(1-\upsilon)^3[3 - 2p(1-\upsilon)] \tag{21}$$

The number of EANCs per repeat unit in the gel is

$$N_e' = N_e/w_g \tag{21'}$$

Determination of ν_ω, ν_σ, and ν_α from the Kinetic Control of Cross-Linking

Cross-linking is a kinetically controlled irreversible reaction and the fractions ν_ω, ν_σ, and ν_α are obtained by solution of the three respective differential equations. Taking into account cyclization we will consider four contributions to the change of ν_i: (a) intermolecular cross-linking between any two ωC functionalities, (terms A), including those in the gel; (b) cyclization with sol (terms B); (c) cyclization within gel (this latter contribution includes intramolecular reaction in the loose material attached to the rest of the gel by one bond and intramolecular reaction within any one EANC; because of the comparatively small difference between cyclization within a free chain and within EANCs, especially for long EANCs, established in Appendix A1, the same Gaussian statistics is used for all these steps (terms C)); (d) activation of cycles (a σC functionality is transformed into an αC functionality if an ωC functionality on the respective cycle reacts intermolecularly with another ωC functionality already attached to the gel; the probability of activation thus depends on the size of the cycle (terms D); for more details of these latter three contributions see Appendix A2).

Allowing for all four contributions the set of differential equations for a change in ν_i is

$$-\mathrm{d}\nu_\omega/\mathrm{d}kt = A_\omega + B_\omega + C_\omega + D_\omega \tag{22}$$

$$-\mathrm{d}\nu_\sigma/\mathrm{d}kt = A_\sigma + B_\sigma + C_\sigma + D_\sigma \tag{23}$$

$$-\mathrm{d}\nu_\alpha/\mathrm{d}kt = A_\alpha + B_\alpha + C_\alpha + D_\alpha \tag{24}$$

where k is a rate constant and t is time; kt can be eliminated and ν_i expressed as a function of the total cross-linking density, ν.

Cross-linking is considered a bimolecular reaction in which two ωC functionalities must meet in a reaction volume δV around a randomly selected repeat unit. The chance of there finding an ωC functionality is $\nu_\omega \delta V$ and that of finding in δV another ωC functionality not connected with the former via a sequence of chemical bonds (in the absence of excluded volume effects) is $C_0{\nu_\omega}^2$, where C_0 is the average concentration of repeat units in moles per volume. For various types of cyclization reactions considered here the chance of finding an ωC functionality belonging to the specified root i is $(\nu_\omega)_i \delta V$ and the local concentration of ωC functionalities in δV supplied by a path or subtree j is $(C_0)_j$; $(C_0)_j$ is determined by the conformational statistics of the connecting sequence of bonds. If that sequence is approximated by a statistically equivalent Gaussian chain then

$$(C_0)_j = [(3/2\pi QL'^2)^{3/2}/N_A] \exp(xr)^{-3/2} m_{xj} \tag{25}$$

where Q is the number of main chain atoms in a statistical segment, L' is the length per main chain atom, N_A is Avogadro's number, r is the number of main chain atoms per repeat unit, and m_{xj} is the number of C functionalities x repeat units distant from the root on the jth path.

The factor

$$\Lambda \equiv (3/[2\pi QL'^2])^{3/2}/N_A \tag{26}$$

characterizes the intensity of cyclization. The structure of the differential equations is such that intermolecular terms contain C_0 and cyclization terms contain Λ as multiplicative factors.

Thus for the intermolecular terms one gets

$$A_\omega = {\nu_\omega}^2 C_0 \tag{27}$$

$$A_\sigma = 0 \tag{28}$$

$$A_\alpha = -{\nu_\omega}^2 C_0 \tag{29}$$

The relations for B, C, and D terms are derived in Appendix A2; $B_\alpha = C_\alpha = D_\omega = 0$.

Discussion

Using the preceding theory we have calculated the changes in the fraction of intramolecular cross-links

$$\sigma = \nu_\sigma/(\nu_\sigma + \nu_\alpha) \tag{30}$$

and concentration of EANCs in the whole system and in the gel for different dilutions. The input parameters have been chosen corresponding approximately to cross-linking of isoprene chains: $C_0 = 0.0134$ mol repeat units cm^{-3}, $(QL'^2)^{1/2} = 4.45 \times 10^{-8}$ cm (the characteristic ratio for *cis*-polyisoprene $\langle r_0^2 \rangle / nL^2 \simeq 4.7$, cf. ref 8), yielding $\Lambda = 6.22 \times 10^{-3}$ mol cm^{-3}, $r = 4$, $x_0 = 2$, and ${P_n}^0 = 1000$ ($p = 0.999$).

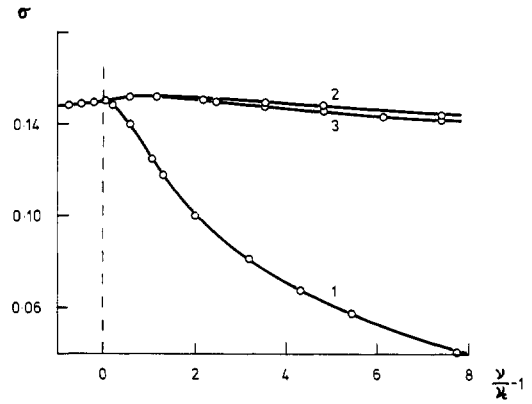

Figure 3. Fraction of cross-links closing elastically inactive cycles plotted against reduced cross-linking density $(\nu/\nu_c) - 1$: (1) cyclization only within sol (terms $C = D = 0$); (2) cyclization within sol and gel (D terms = 0); (3) as for (2) but including activation of cycles (D terms); $v_0 = 1$ (bulk state); other parameters as in text.

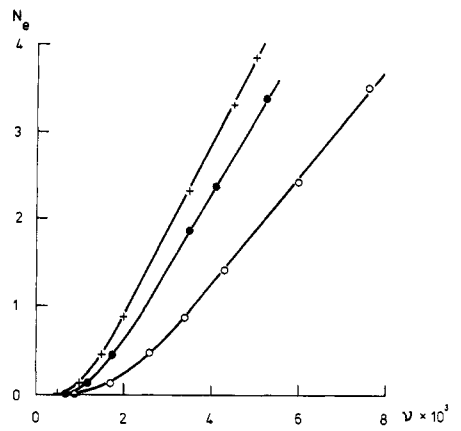

Figure 4. N_e is the number of elastically active network chains per number average primary chain as a function of ν: (×) no cyclization; (●) $v_0 = 1$; (○) $v_0 = 0.25$; other input parameters as in text.

Table I
Effect of Dilution on Critical Conversion Parameters

v_0	$10^4\nu_c$	σ_c (eq 30)
no rings	5.01	0
1.0	5.88	0.151
0.75	6.18	0.191
0.50	6.78	0.262
0.25	8.56	0.415

The three differential equations were solved by a fourth-order Kutta–Merson method with automatic error control exactly as described previously.[30-32] Close to the gel point (i.e., as $w \simeq$ unity) sums of the form $\Sigma_{x=1}^{\infty} w^x(x)^{-3/2}$ (cf. (A2-4), (A2-24), and, e.g., (A2-49)) converge very slowly. In this case we use the series due to Lindelof for evaluating[31] the *modified* Riemann ζ function

$$R(w) \equiv \sum_{x=1}^{\infty} w^x/x^{3/2} \quad (\equiv \zeta(3/2) \text{ when } w = 1)$$

when $w \simeq 1$. The program for the solution of the rate equations was encoded in Algol-60 for a DEC System-10 computer using double length arithmetic (word length in single precision = 27 bits) at the University of Essex Computer Centre.

To trace the effect of cyclization in the sol and gel and of activation of cycles, the B, C, and D terms have been successively switched on in the differential eq 22–24. Up to the gel point only A and B terms are operative so that a single set of cross-linking densities ν_c $(=\nu_{\sigma c} + \nu_{\alpha c})$ at the gel point is obtained for different dilutions v_0, $C_0 = 0.0134v_0$ (Table I).

The following conclusions can be extracted from results obtained on the chosen model systems (cf. Figures 3–6).

(a) The σ fraction. (1) The increase in σ up to the gel point is very small which is characteristic for cross-linking of long primary chains. Ring closing between different chains (multiple cross-linking) is very weak compared with cyclization within the same chain because of the small number of intermolecular cross-links.

(2) Beyond the gel point the contribution to σ due to cyclization in the sol rapidly decreases along with the decrease in the sol fraction.

(3) After inclusion of cyclization in the gel one observes a continuous increase in σ passing through the gel point with an inflexion point at the gel point, and a flat maximum beyond the gel point. Such a shape corresponds to a maximum in $d\nu_\sigma/d\nu$ vs. ν at the gel point.

(4) The activation of cycles has a comparatively weak effect on σ especially at low ν; at $\nu/\nu_c \simeq 9$ it amounts to ~2% (Figure 3), at ten times higher ν corresponding to one cross-linked unit per 15–20 repeat units it lowers ν_σ by ~5%, but would become more pronounced if we passed to still higher cross-linking densities. The main reason for the comparatively weak contribution is an abundance of small rings over larger ones so that the average concentration of ωC functionalities (uncross-linked segments) belonging to rings is small. However, the approximation used in calculation of the ring-size distribution in the gel may also be partly responsible. The largest rings and the broadest distribution was assumed (eq A2-49) to exist at the gel point (where $y = 1$). This may not be exact, although the largest rings are certainly being formed in the critical region.

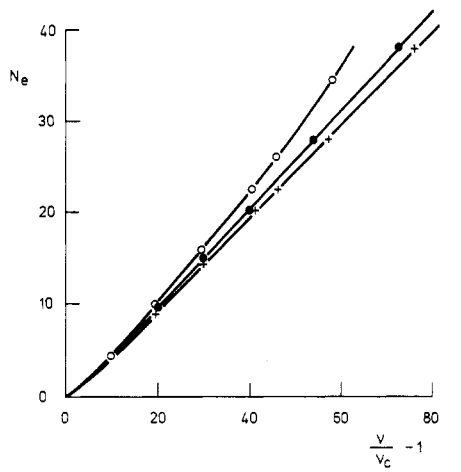

Figure 5. As in Figure 4 except N_e plotted against $((\nu/\nu_c) - 1)$ to illustrate the success of the rescaling.

(b) Concentration of Elastically Active Network Chains. If plotted against the total cross-linking density ν the concentrations of EANCs N_e or N_e' for the ring-free case and at different dilutions yield different curves (Figure 4). The relative wastage of cross-links in elastically inactive loops is of course highest close to the gel point; e.g., at $\nu = 4 \times 10^{-3}$ it amounts to ~20% for the bulk rubber and ~60% for the 25% solution, results which agree well with those calculated from the equilibrium approach.[20] However, if we replot N_e or N_e' as a function of $(\nu/\nu_c) - 1$ (Figure 5) we get almost coinciding curves with a difference for the two extremes $\nu/\nu_c \approx 10$ not higher than 5%. At higher cross-linking densities the differences become progressively larger (about 6% for the bulk rubber and 25% for $v_0 = 0.25$) when $(\nu/\nu_c) - 1 \simeq 60$, but so densely cross-linked rubbers are rarely met in practice.

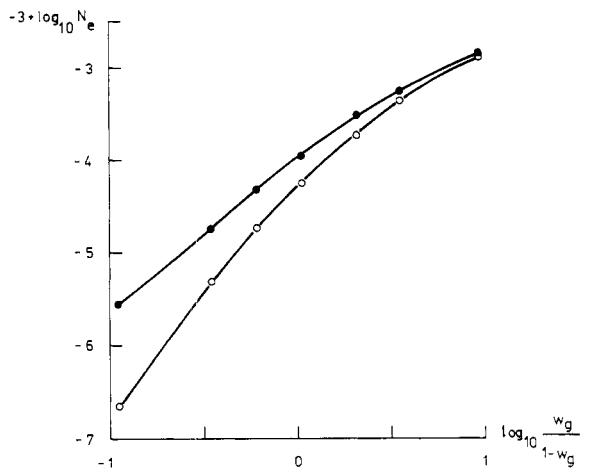

Figure 6. N_e (●) for the whole system and N_e' (○) for the gel as a function of log $(w_g/(1 - w_g))$, where w_g is the gel fraction.

Even better independence of the cyclization extent is obtained if N_e or N_e' are plotted against the gel fraction. Even at $w_g \approx 0.9$ the difference corresponding to the two extremes does not exceed 0.2%. Figure 6 shows single generalized plots for all cases studied. Close to the gel point N_e is proportional to $((\nu/\nu_c) - 1)^3$ or w_g^3 and N_e' to $((\nu/\nu_c) - 1)^2$ or w_g^2.

The success of the rescaling procedure is very important for testing of the theories of rubber elasticity and for the separation of the effect of intermolecular interactions (entanglements) on the equilibrium modulus. Considerations about the amount of cyclization can be almost fully eliminated except for the single piece of information supplied by the shift of the gel point over the theoretical value. Such invariance was found also for systems obtained by stepwise alternating polyaddition.[45]

Acknowledgments. S. B. R.-M. thanks the Science Research Council for financial support.

Appendix A1

Cyclization Within an Elastically Active Network Chain. It can be expected that the probability of forming an intramolecular cross-link between the ath and bth segment of a polymer chain of n segments will depend on the positional freedom of the chain ends. For a free chain (with no constraints imposed on its ends) obeying Gaussian statistics the well-known $-3/2$ power law[38] is valid; i.e., the probability of closing a loop of $|b - a|$ segments is proportional to $|b - a|^{-3/2}$. Let us consider the situation if the positional freedom of chain ends differs from that for a free chain.

James and Guth[46,47] showed that the distribution of chain-end separation around the most probable value in a perfect network of Gaussian chains is also Gaussian and gave arguments that the positional freedom of cross-links (junctions) does not differ much from that of a segment in the network. We will explore the extremal situations when the cross-links are fixed in their most probable positions and when their positional freedom corresponds to that of ends of a free chain. The reality is expected between these two extremes.

First consider a network chain of n segments in three dimensions whose end segments are parts of elastically active cross-links and have coordinates $\bar{x}_1$ (x_1,y_1,z_1) and $\bar{x}_4$ (x_4,y_4,z_4), respectively. Let the bond between the pth and $(p + 1)$th segment be located at $\bar{x}_2$ and that between the $(p + q)$th and $(p + q + 1)$th segment be located at $\bar{x}_3$ (Figure 7).

For Gaussian chains the number of possible arrangements for state I relative to those bonds at $\bar{x}_2$ and $\bar{x}_3$ are positionally constrained by the chain connectivity only,

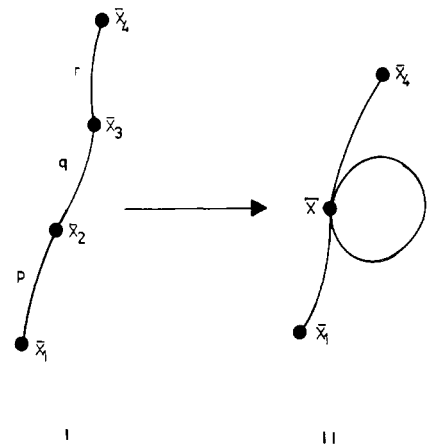

Figure 7. Ring closure in a chain.

$$W(n,p,q,\bar{x}_i) = W'(n,p,q,\bar{x}_i) \Big/ \int\int_{-\infty}^{\infty} W'(n,p,q,\bar{x}_i)\, d\bar{x}_2\, d\bar{x}_3 \tag{A1-1}$$

where

$$W'(n,p,q,\bar{x}_i) = A_p{}^3 A_q{}^3 A_r{}^3 \exp[-B_p{}^2(\bar{x}_1 - \bar{x}_2)^2 - B_q{}^2(\bar{x}_2 - \bar{x}_3)^2 - B_r{}^2(\bar{x}_3 - \bar{x}_4)^2] \tag{A1-2}$$

where $A_k = B_k/\pi^{1/2}$ and $B_k = 3/2kL^2$ and k is the number of segments and L is the length of a segment. The integral in eq A1-1 corresponds to the number of conformations of a chain of n segments, viz.,

$$A_n{}^3 \exp[-B_n{}^2(\xi^2 + \eta^2 + \zeta^2)] \tag{A1-3}$$

whose mean-square end-to-end separation distance is given by

$$\xi^2 = (x_1 - x_4)^2, \quad \eta^2 = (y_1 - y_4)^2, \quad \zeta^2 = (z_1 - z_4)^2$$

Let us consider the reduction in the number of possible rearrangements if a q-membered loop is formed (state II). This corresponds to $\bar{x}_2 = \bar{x}_3 = \bar{X}$; substituting this condition into eq A1-1 and integrating over dX we get the probability of cyclization

$$P_c(n,q) = (A_q A_{n-q}/A_n)^3 \times \exp[-(B_{n-q}{}^2 - B_n{}^2)(\xi^2 + \eta^2 + \zeta^2)] \tag{A1-4}$$

or using the definition of A_k and B_k

$$P_c(n,q) = \lambda^{3/2}\{n/[q(n-q)]\}^{3/2} \times \exp(\{-\lambda q/[n(n-q)]\}(\xi^2 + \eta^2 + \zeta^2)) \tag{A1-5}$$

with $\lambda = 3/2L^2$.

It is seen (as is intuitively obvious) that the chance for cyclization does not depend on the position of the ring along the chain and depends only on its size q and length of the chain n.

Assuming along with James and Guth that the distribution of chain ends extension is Gaussian around the most probable position (ξ_0,η_0,ζ_0) and given by

$$W_E = A_E{}^3 \exp\{-B_E{}^2[(\xi - \xi_0)^2 + (\eta - \eta_0)^2 + (\zeta - \zeta_0)^2]\} \tag{A1-6}$$

the cyclization probability becomes

$$P_{cE}(n,q) = \int\int\int_{-\infty}^{\infty} P_c(n,q) W_E \, d\xi \, d\eta \, d\zeta \tag{A1-7}$$

The result of integration is

$$P_{cE}(n,q) = (A_q A_{n-q} A_E/A_n)^3 (\pi/(B_{n-q}{}^2 - B_n{}^2 + B_E{}^2))^{3/2} \times \exp\{[B_E{}^4/(B_{n-q}{}^2 - B_n{}^2 + B_E{}^2) - B_E{}^2](\xi_0{}^2 + \eta_0{}^2 + \zeta_0{}^2)\} \tag{A1-8}$$

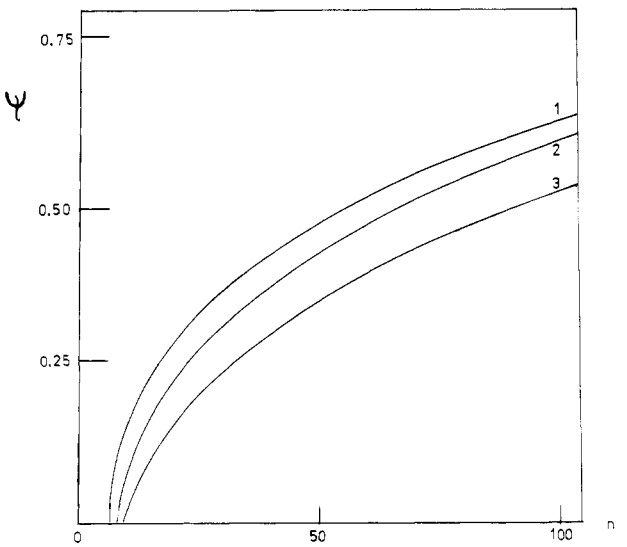

Figure 8. Relative cyclization probability ψ plotted against chain-length n: (1) free chain; (2) chain with fixed end points; (3) chain with Gaussian distribution of end point distances around the most probable distance.

or using a reduced length of the cycle $Q = q/n$

$$P_{cE}(n,q) = \lambda^{3/2}(QS)^{-3/2} \exp\{-(\lambda Q/S)(\xi_0^2 + \eta_0^2 + \xi_0^2)\} \quad \text{(A1-9)}$$

where

$$S = QE + (1 - Q)n$$

For a free chain whose ends are not constrained by cross-links $E = n$ and $\xi_0 = \eta_0 = \zeta_0 = 0$, eq A1-9 correctly gives

$$P_c(q) = \lambda^{3/2} q^{-3/2} \quad \text{(A1-10)}$$

For fixed chain ends with separation $\xi_0^2 + \eta_0^2 + \zeta_0^2 = nL^2$ and $E = 0$ (δ-function separation W_E)

$$P_c(n,q) = \lambda^{3/2}[q(1 - Q)]^{-3/2} \exp\{-3Q/2(1 - Q)\} \quad \text{(A1-11)}$$

For chain-end extension distribution around the mean distance $\xi_0^2 + \eta_0^2 + \zeta_0^2 = nL^2$ and with E = n as for a free chain

$$P_c(n,q) = \lambda^{3/2} q^{-3/2} \exp\{-3Q/2\} \quad \text{(A1-12)}$$

It can be seen that $P_c(n,q)$ approaches the situation in a free chain when Q goes to zero, i.e., when n is high enough. In long network chains the probability of ring closure is therefore not sensitive to the constraints imposed on chain ends.

The Mean Cyclization Probability $\bar{P}_c$. On an n-membered chain, loops may be formed of different lengths connecting different segments. If we consider all possible couplings along the chain (cf. ref 3 and 31) we get

$$\bar{P}_c(n) = [2/(n - 1)] \sum_{q=q_0}^{n-2} (n - q - 1) P_c(n,q) \quad \text{(A1-13)}$$

where q_0 is the number of segments in the smallest possible ring. Figure 8 illustrates the change in the reduced mean cyclization probability ψ.

$$\psi = \bar{P}_c(n)/\bar{P}_c(\infty) \quad \text{(A1-14)}$$

where $P_c(\infty)$ corresponds to an infinite chain; $q_0 = 5$ has been chosen. It is seen that the chance for cyclization is the highest in a free chain. If the positional freedom allowed for cross-links is equal to that of ends of a free chain the chance for cyclization falls: for short chains ($n = 10$) it is lower by a factor of ~2 while for $n = 100$ it is lower only by ~25%. The condition of fixed cross-links yields an intermediate curve so that the real situation is expected between curves 3 and 2.

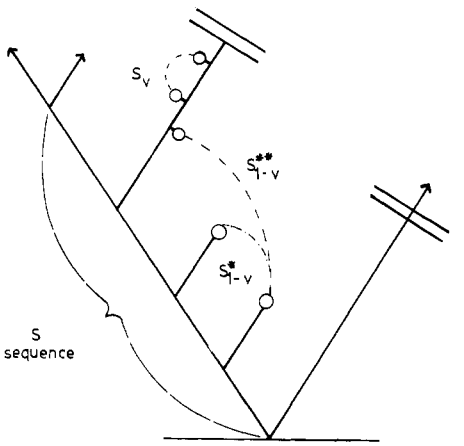

Figure 9. To illustrate the different S-type cyclization terms: ∓ finite path; (↑) infinite path; (⇑) finite or infinite path; (○) σ functionality.

It is worth mentioning that a replacement of the summation in eq A1-13 by integration within limits $q_0 - 1/2$ and $n - 2 + 1/2$ gives a good agreement with direct summation (the error was about 3% for $n = 10$ and <1% for $n = 100$). The integration of (A1-13) with $P_c(n,q)$ (eq A1-11) is trivial and with $P_c(n,q)$ (eq A1-12) it yields

$$\bar{P}_c(n) = \lambda^{3/2}[2/(n - 1)]\{z^{1/2}(n - 1)[\Gamma(-1/2, z(q_0 - 1/2)) - \Gamma(-1/2, 3(1 - z)/2)] - z^{-1/2}[\Gamma(1/2, z(q_0 - 1/2)) - \Gamma(1/2, 3(1 - z)/2)]\} \quad \text{(A1-15)}$$

where $z = 3/2n$ and $\Gamma(k,l)$ is the incomplete Γ function.

Appendix A2

Evaluation of Cyclization Terms and Cycle-Activation Terms in the Rate Equations 27–29. (1) Cyclization in the Sol. The terms in the rate equations to be evaluated are the nine denoted B, C, D with subscripts ω, σ, α in eq 22–24 (for the A terms see eq 27–29). Of these the B terms concern cyclization rates within the sol (see Figure 9). By definition

$$B_\alpha = 0 \quad \text{(A2-1)}$$

and because each cycle formed in the sol consumes one pair of free functionalities

$$B_\omega = -B_\sigma \quad \text{(A2-2)}$$

It remains to find B_σ. We see from eq 23 that B_σ should be the product of two (normalized) concentrations times a reciprocal volume term for dimensional consistency. The two concentrations represent (a) the fraction

$$[\partial^2 G_0(\theta_v, 0, \vartheta)/(\partial\theta_v\, \partial\vartheta_\omega)]_{\theta_v=1,\vartheta=1} = 2\nu_\omega p v(1 - p + pv) \quad \text{(A2-3)}$$

of units which are in the sol and bear a free functionality, where G_0 is given by (12) and (b) the mean number S_v of reaction partners available for the units just described under (a). When the latter are placed on generation zero of a family tree, the reaction partners counted by S_v lie on the generations above generation zero. Then[22-24]

$$S_v = G_{1v}{}^\omega \sum_{x=x_0}^{\infty} (G_{1v}{}^v)^{x-1}(xr)^{-3/2} \qquad (x_0 > 0) \quad \text{(A2-4)}$$

where

$$G_{1v}{}^v = [\partial G_{1v}/\partial\theta_v]_{\theta_v=1,\vartheta=1} = p[\nu_\omega + \nu_\sigma + 3\nu_\alpha(1 - p + pv)^2] \quad \text{(A2-5)}$$

and

$$G_{1\upsilon}{}^{\omega} = [\partial G_{1\upsilon}/\partial\theta_{\omega}]_{\theta_{\upsilon}=1,\vartheta=1} = \nu_{\omega}(1 - p + p\upsilon)/\upsilon \tag{A2-6}$$

with $G_{1\upsilon}$ given according to (14) by

$$G_{1\upsilon}(\boldsymbol{\theta},\boldsymbol{\vartheta}) = (\nu_{\omega}\vartheta_{\omega} + \nu_{\sigma}\vartheta_{\sigma}) \times (1 - p + p[\upsilon\theta_{\upsilon} + (1 - \upsilon)\theta_{1-\upsilon}]) + \nu_{\alpha}\vartheta_{\alpha}(1 - p + p[\upsilon\theta_{\upsilon} + (1 - \upsilon)\theta_{1-\upsilon}])^3 \tag{A2-7}$$

The summation in (A2-4) is over all the generations and implements[22–24] the weightings appropriate for the chance of collision between the two ends of a Gaussian subchain to close a ring of size (xr) bonds (comprising x units of r bonds each); the chance of such a collision being effective is proportional to the reciprocal volume

$$\Lambda = (3/(2\pi QL'^2))^{3/2}/N_{\mathrm{A}} \tag{26}$$

Hence using eq A2-3, A2-4, and 26, B_{σ} is given by

$$B_{\sigma} = -2\Lambda\nu_{\omega}(1 - p + p\upsilon)p\upsilon G_{1\upsilon}{}^{\omega} \sum_{x=x_0}^{\infty} (G_{1\upsilon}{}^{\upsilon})^{x-1}(xr)^{-3/2} \tag{A2-8}$$

(2) Cyclization in the Gel. Units in the gel must have at least one path to infinity. The various types of such units in the root are generated by the difference

$$G_{0g} = G_0(\theta_{\upsilon},\theta_{1-\upsilon},\vartheta) - G_0(\theta_{\upsilon},0,\vartheta) \tag{A2-9}$$

(The above generating function is not normalized as the *sum of sol plus gel* species is defined to be unity.) Again by definition

$$C_{\alpha} = 0 \tag{A2-10}$$

and

$$C_{\omega} = -C_{\sigma} \tag{A2-11}$$

The term C_{σ} is the sum of two terms

$$C_{\sigma} = (C_{\sigma})_{\upsilon} + (C_{\sigma})_{1-\upsilon} \tag{A2-12}$$

Here $(C_{\sigma})_{\upsilon}$ is the rate of cyclization between a unit on a finite subtree chosen as the root at random and a unit on the same finite subtree on a higher generation; this is cyclization within loose material attached to the gel whereas $(C_{\sigma})_{1-\upsilon}$ is the rate of cyclization in the remainder of the gel. $(C_{\sigma})_{\upsilon}$ may be written down in a similar manner to cyclization in the sol (previous section)

$$(C_{\omega})_{\upsilon} = -(C_{\sigma})_{\upsilon} = \Lambda M_{\upsilon}S_{\upsilon} \tag{A2-13}$$

where M_{υ} is the fraction of units in the system which are in the gel, bear a free functionality, and are on a finite subtree and is given by eq A2-14, Λ and S_{υ} are given by eq 26 and A2-5, respectively, and

$$M_{\upsilon} = [\partial^2 G_{0g}/\partial\theta_{\upsilon}\partial\vartheta_{\omega}]_{\theta=1,\vartheta=1} = 2\nu_{\omega}p^2\upsilon(1 - \upsilon) \tag{A2-14}$$

Similarly

$$-(C_{\sigma})_{1-\upsilon} = \Lambda M_{1-\upsilon}S_{1-\upsilon} \tag{A2-15}$$

with

$$M_{1-\upsilon} = [\partial^2 G_{0g}/\partial\theta_{1-\upsilon}\partial\vartheta_{\omega}]_{\theta=1,\vartheta=1} = 2\nu_{\omega}p(1 - \upsilon) \tag{A2-16}$$

$\Lambda S_{1-\upsilon}$ is the local concentration of unreacted C functionalities supplied by sequences of (a) units along a single path to infinity starting from a chosen root unit (such sequences will be denoted by S sequences) and (b) units on a finite subtree rooted on a unit belonging to an S sequence.

$$S_{1-\upsilon} = S_{1-\upsilon}{}^{*} + S_{1-\upsilon}{}^{**} \tag{A2-17}$$

$\Lambda S_{1-\upsilon}{}^{*}$ is the concentration of reaction partners within the S sequence whereas $\Lambda S_{1-\upsilon}{}^{**}$ is the corresponding concentration of reaction partners on a finite subtree rooted on an S sequence (see Figure 9). In order to calculate these respective terms we thus have to find the probability that a particular S sequence should have length x, i.e., that the first junction point from which two or more paths issue to infinity lies at distance x units along the path from the root. This probability we denote p_x. (The S sequence always terminates at an active junction point when the single path to infinity filters into two or more such paths; the chance of an S sequence terminating at the surface of the particle can be neglected.) The respective contributions from ωC functionalities directly attached to the S sequence and residing on finite subtrees rooted on the S sequence are derived from the pgf $G_{1(1-\upsilon)}$ (eq 15). For the required units, issuing one and only one $(1\text{-}\upsilon)$-type bond, we may write for them the pgf $I(\boldsymbol{\theta},\boldsymbol{\vartheta})$

$$I(\boldsymbol{\theta},\boldsymbol{\vartheta}) \equiv \theta_{1-\upsilon}\left(\frac{\partial G_{1(1-\upsilon)}}{\partial\theta_{1-\upsilon}}\right)_{\theta_{1-\upsilon}=0} \Bigg/ \left(\frac{\partial G_{1(1-\upsilon)}}{\partial\theta_{1-\upsilon}}\right)_{\theta_{\upsilon}=1,\theta_{1-\upsilon}=0,\vartheta=1} = [(\nu_{\omega}\vartheta_{\omega} + \nu_{\sigma}\vartheta_{\sigma} + 3\nu_{\alpha}\vartheta_{\alpha})(1 - p + p\upsilon\theta_{\upsilon})^2]\theta_{1-\upsilon}/\mu \tag{A2-18}$$

where

$$\mu = \nu_{\omega} + \nu_{\sigma} + 3\nu_{\alpha}(1 - p + p\upsilon)^2 \tag{A2-19}$$

The number of νC functionalities per unit of the S sequence I^{ω} is then

$$I^{\omega} \equiv (\partial I(\boldsymbol{\theta},\boldsymbol{\vartheta})/\partial\vartheta_{\omega})_{\boldsymbol{\theta}=1,\vartheta=1} = \nu_{\omega}/\mu \tag{A2-20}$$

and of issuing υ-type bonds I^{υ}

$$I^{\upsilon} \equiv (\partial I(\boldsymbol{\theta},\boldsymbol{\vartheta})/\partial\theta_{\upsilon})_{\boldsymbol{\theta}=1,\vartheta=1} = 6\nu_{\alpha}(1 - p + p\upsilon)/\mu \tag{A2-21}$$

The local concentration of ωC functionalities supplied by units of the S sequence is then

$$S_{1-\upsilon}{}^{*} = I^{\omega} \sum_{x=x_0}^{\infty} p_x(rx)^{-3/2} \tag{A2-22}$$

Considering cyclization with ωC functionalities on attached finite subtrees we note that then the ring cannot be smaller than $2r$. First we consider the case $x_0 \leqslant 2$. Considering units in the first generation, the contribution of C functionalities supplied by the issuing subtrees is proportional to

$$\sum_{z=1}^{\infty} (G_{1\upsilon}{}^{\upsilon})^{z-1}[(z + 1)r]^{-3/2}$$

from a unit on the second generation to

$$\sum_{z=1}^{\infty} (G_{1\upsilon}{}^{\upsilon})^{z-1}[(z + 2)r]^{-3/2}, \text{ etc.}$$

so that the contribution from all possible finite subtrees attached to the S sequence is given by

$$S_{1-\upsilon}{}^{**} = I^{\upsilon}G_{1\upsilon}{}^{w} \sum_{x=1}^{\infty} p_x \sum_{z=1}^{\infty} (G_{1\upsilon}{}^{\upsilon})^{z-1}[(z + x)r]^{-3/2} \tag{A2-23}$$

If $x_0 \leqslant 3$ some of the free functionalities close to the root become inactive in cyclization and then

$$S_{1-\upsilon}{}^{**} = I^{\upsilon}G_{1\upsilon}{}^{\omega}\left\{\sum_{x=1}^{x_0-1} p_x \sum_{z=x_0}^{\infty} (G_{1\upsilon}{}^{\upsilon})^{z-x-1}(zr)^{-3/2} + \sum_{x=x_0}^{\infty} p_x \sum_{z=1}^{\infty} (G_{1\upsilon}{}^{\upsilon})^{z-1}[(z + x)r]^{-3/2}\right\} \tag{A2-24}$$

($G_{1\upsilon}{}^{\upsilon}$ and $G_{1\upsilon}{}^{\omega}$ are given by eq A2-5 and A2-6.)

The probability p_x is derived from the pgf $G_{1(1-\upsilon)}$ eq 15 which is written now in the equivalent form as a sum.

$$G_{1(1-\upsilon)}(\boldsymbol{\theta},1) = \sum_{i=0}\sum_{j=1} p_{ij}\theta_\upsilon{}^i\theta_{1-\upsilon}{}^j \qquad \text{(A2-25)}$$

The fraction of units in the first generation with only a single path to infinity (only one $(1-\upsilon)$-type bond) is given by

$$\sum p_{i1} \Big/ \sum_i\sum_j p_{ij} = p\mu \qquad \text{(A2-26)}$$

and for the second and higher generations (for $g \geq 1$ each p_{ij} unit issues j $(1-\upsilon)$ bonds) we have

$$\sum_i p_{i1} \Big/ \sum_i\sum_j j p_{ij} = \mu/(1+2\nu_\alpha) \equiv y \qquad \text{(A2-27)}$$

Since we have to consider the probability of $x-1$ such successive events we have

$$p_x = p\mu y^{x-1} \qquad \text{(A2-28)}$$

Substituting from eq 8, A2-19, and A2-27 we see that at the gel point ($\upsilon = 1$) $p_x = 1$ for all x, as it should be.

The form of the distribution p_x (eq A2-28) as a geometric series ("Flory distribution") renders it invariant to short circuiting by pendant cycles (Figure 1b), so that the apparent omission of this complication from our derivation is justified. This invariance to short circuiting arises from the spanning-tree approximation (we have in fact only ring forming functionalities in trees, not cycles); i.e., the p_x distribution holds asymptotically in the limit of zero cyclization.

(3) Activation of Cycles. For a network chain to be active, according to the Case–Scanlan definition there must be at least three independent paths to infinity from each of the two junction points at the extremities of the EANC (see Figure 1). By way of refinement, when an unreacted C functionality on a ring in the gel reacts with another unreacted C functionality in the gel, the ring is assumed to be converted into (at most) two EANCs. We refer to this as a step which activates the cycle and our model takes this into account by transferring pairs of functionalities previously classified as σ ring-closing functionalities into the category of α functionalities. Such a pair of α functionalities will contribute at most a pair of EANCs, and N_e (the number of EANCs *per repeat unit*) will be increased, because of the dependence of N_e upon ν_α, the conversion parameter (eq 11 and 21).

The D_i, cycle activation terms, are given by

$$D_\omega = 0 \qquad \text{(A2-29)}$$

$$D_\sigma = C_0\Gamma_\sigma\Gamma_\omega\mathcal{R} \qquad \text{(A2-30)}$$

$$D_\alpha = D_\sigma \qquad \text{(A2-31)}$$

Here the fraction Γ_σ of σC functionalities on units in the gel is obtained in the usual way from the pgf G_0 (eq 12) and is equal to

$$(\partial G_0/\partial\vartheta_\sigma)_{\boldsymbol{\theta}=1,\vartheta=1} - (\partial G_0/\partial\vartheta_\sigma)_{\theta_\upsilon=1,\theta_{1-\upsilon}=0,\vartheta=1}$$
$$\equiv \Gamma_\sigma = \nu_\sigma(1-(1-p+p\upsilon)^2) \qquad \text{(A2-32)}$$

Γ_ω is the fraction of ωC functionalities per unit in the gel and $\mathcal{R}$ is the average number of functionalities per ring in the gel. Γ_ω is obtained in the same way as in eq A2-32

$$\Gamma_\omega = \nu_\omega(1-(1-p+p\upsilon)^2) \qquad \text{(A2-33)}$$

The average number of ωC functionalities per cycle, $\mathcal{R}$, is a sum of products of (a) the number of repeat units of the ring able to carry an ωC functionality (ring units), $x-1$, (b) the number fraction of rings in the gel of size x,$n_{\sigma g}(x)$, (c) the number of ωC functionalities per ring unit, Z, over all possible ring sizes x:

$$\mathcal{R} = \sum_x (x-1)n_{\sigma_g}(x)Z \qquad \text{(A2-34)}$$

In calculating Z let us recollect that (a) σC functionalities must have their partners on units being parts of finite or infinite paths and (b) from each of the $x-1$ ring units at least two P bonds must issue and either one or both have to be $(1-\upsilon)$-type bonds. We now construct the pgf for the number of C functionalities and issuing υ-type bonds from ring units, $C(\theta_\upsilon,\vartheta)$ satisfying the above conditions. For that purpose the pgf G_0 (eq 12) is rewritten in the form

$$G_0(\boldsymbol{\theta},\vartheta) = \sum_{i=0,j=0}\sum k_{ij}(\vartheta)\theta_\upsilon{}^i\theta_{1-\upsilon}{}^j \qquad \text{(A2-35)}$$

and the relevant terms (with $\theta_{1-v} = 1$) are $k_{i1}\theta_\upsilon{}^i/\theta_\upsilon$ and $k_{i2}\theta_\upsilon{}^i$ (the first corresponds to finding the partner of a σC functionality on a finite subtree and the other on an infinite path):

$$C(\theta_\upsilon,\vartheta) = \sum_i (k_{i1}\theta_\upsilon{}^{i-1} + k_{i2}\theta_\upsilon{}^i)/\mathcal{N}$$
$$= \left[\frac{1}{\theta_\upsilon}\left\{\left(\frac{\partial G_0}{\partial\theta_{1-\upsilon}}\right)_{\theta_{1-\upsilon}=0} - \left(\frac{\partial G_0}{\partial\theta_{1-\upsilon}}\right)_{\theta_{1-\upsilon}=\theta_\upsilon=0}\right\} + \frac{1}{2}\left(\frac{\partial^2 G_0}{\partial\theta_{1-\upsilon}{}^2}\right)_{\theta_{1-\upsilon}=0}\right]\Big/\mathcal{N} \qquad \text{(A2-36)}$$

where $\mathcal{N}$ is the normalizer.

The number of ωC functionalities, U_ω, per ring unit is

$$U_\omega = (\partial C(\boldsymbol{\theta},\vartheta)/\partial\vartheta_\omega)_{\boldsymbol{\theta}=1,\vartheta=1} = \nu_\omega(1-\upsilon)p^2(1+\upsilon)/\mathcal{N} \qquad \text{(A2-37)}$$

and the number of issuing υ-type bonds

$$U_\upsilon = (\partial C(\boldsymbol{\theta},\vartheta)/\partial\theta_\upsilon)_{\boldsymbol{\theta}=1,\vartheta=1}$$
$$= \nu_\alpha p^3\upsilon(1-\upsilon)\{4\upsilon(3(1-p)+2p\upsilon) + 12(1-\upsilon)(1-p+p\upsilon)\}/\mathcal{N} \qquad \text{(A2-38)}$$

with

$$\mathcal{N} = p^2\upsilon(1-\upsilon)\{2(1-\nu_\alpha) + 4\nu_\alpha[3(1-p)^2 + 3(1-p)p\upsilon + p^2\upsilon]\} + (1-\upsilon)^2p^2\{1-\nu_\alpha + 6\nu_\alpha(1-p+p\upsilon)\} \qquad \text{(A2-39)}$$

Each finite subtree issuing from a ring unit contributes to the number of ωC functionalities by

$$G_{1\upsilon}{}^\omega \sum_{x=1}^{\infty} (G_{1\upsilon}{}^\upsilon)^{x-1} = G_{1\upsilon}{}^\omega/(1-G_{1\upsilon}{}^\upsilon)$$
$$= \nu_\omega(1-p+p\upsilon)/\upsilon(1-p\mu) \qquad \text{(A2-40)}$$

Using eq A2-37 and A2-40, $\mathcal{R}$ in eq A2-34 is obtained:

$$\mathcal{R} = [U_\omega + U_\upsilon G_{1\upsilon}{}^\omega/(1-G_{1\upsilon}{}^\upsilon)]\sum_x (x-1)n_{\sigma g}(x) \qquad \text{(A2-41)}$$

In order to calculate the approximate ring-size distribution in the gel, $n_{\sigma g}(x)$, we use a perturbation method. For weak cyclization $n_\sigma(x)$ is obtained at the gel point directly from the differential eq 23 and 24 with $\upsilon = 1$ using eq 29 and A2-3

$$\mathrm{d}\nu_\sigma(x)/\mathrm{d}\nu_\alpha = 2(\Lambda/c_0)p(p+2\nu_\alpha p)^{x-1}(rx)^{-3/2} \qquad \text{(A2-42)}$$

where $\nu_\sigma(x)$ is the number fraction of σC functionalities belonging to x-membered rings. Substituting $Z \equiv p + 2p\nu_\alpha$ and integrating one obtains the value of $\nu_\sigma(x)$ at the gel point

$$\nu_{\sigma c}(x) = [(\Lambda/C_0)(xr)^{-3/2}/p\nu_{\alpha c}]\int_{Z=p}^{1} Z^{x-1}\,\mathrm{d}Z \qquad \text{(A2-43)}$$

which yields the number fraction distribution of ring sizes at the gel point

$$n_{\sigma c}(x) = \frac{x^{-5/2}(1-p^x)}{\sum_{x=x_0}^{\infty} x^{-5/2}(1-p^x)} \qquad \text{(A2-44)}$$

This distribution reduces to that obtained by Gordon and Scantlebury for the nonrandom equilibrium polycondensation of a trifunctional monomer,[22] when $p = 0$.

Beyond the gel point elastically inactive rings must not contain elastically active units with three independent paths to infinity. Their number increases, however, with increasing cross-linking density, which means that newly formed inactive rings are smaller and the activation process selectively activates larger rings (cf. eq A2-34). We *assume* that (1) the size of such rings decreases beyond the gel point and (2) the size distribution in the gel close to the gel point is the same as in the sol. Both assumptions may make the distribution fall sharper with increasing x than in reality and somewhat underestimate the activation process.

In the gel, rings have been formed by reaction of ωC functionalities in the root with those on issuing finite and infinite paths. The fraction of such issuing paths, ξ_v and ξ_{1-v}, respectively, ($\xi_v + \xi_{1-v} = 1$) is easily obtained from the pgf G_0 (eq 17).

$$\xi_v = v/(1 + v), \qquad \xi_{1-v} = 1/(1 + v) \tag{A2-45}$$

To find an x-membered ring, an x-1 membered sequence should be terminated by a unit bearing a σC functionality. The probability of finding such a terminating unit on a finite subtree is

$$G_{1v}{}^{\sigma} \equiv (\partial G_{1v}/\partial \vartheta_{\sigma})_{\theta=1,\vartheta=1} = \nu_{\sigma}(1 - p + pv)/v$$

and on an infinite sequence

$$G_1{}^{\sigma}(1 - v) \equiv (\partial G_1(1 - v)/\partial \vartheta_{\sigma})_{\theta=1,\vartheta=1} = \nu_{\sigma} p$$

Considering a finite subtree the probability of finding an x-membered ring is proportional to $G_{1v}{}^{\sigma}(G_{1v}{}^{v})^{x-1}$ and the same probability rescaled to the corresponding probability at the gel point, P_v, is then

$$P_v = (\nu_{\sigma}/\nu_{\sigma c})y^{x-1}(1 - p + pv)/v \tag{A2-46}$$

For a ring closed within a sequence with infinite continuation to be elastically inactive, the sequence must be effectively unbranched with a single continuation to infinity (cf. S sequence defined in section A2(2)). The probability of existence of such a ring is therefore proportional to $G_1{}^{\sigma}{}_{(1-v)}y^{x-1}$ and if this probability is taken relative to that at the gel point, P_{1-v}, then

$$P_{1-v} = (\nu_{\sigma}/\nu_{\sigma c})y^{x-1} \tag{A2-47}$$

Therefore the ring-size distribution in the gel beyond the gel point is given by

$$n_{\sigma g}(x) = n_{\sigma c}(x)(\xi_v P_v + \xi_{1-v}P_{1-v})/\mathcal{N}' \tag{A2-48}$$

where $\mathcal{N}'$ is a normalizer.

Since both P_v and P_{1-v} are proportional to y^{x-1}

$$n_{\sigma g}(x) = x^{-5/2}(1 - p^x)y^{x-1} \Big/ \sum_{x=x_0}^{\infty} x^{-5/2}(1 - p^x)y^{x-1} \tag{A2-49}$$

and the sum appearing in eq A2-41 is

$$\sum_{x=x_0}^{\infty}(x - 1)n_{\sigma g}(x) = \sum_{x=x_0}^{\infty}(x - 1)x^{-5/2}(1 - p^x)y^{x-1} \Big/ \sum_{x=x_0}^{\infty} x^{-5/2}(1 - p^x)y^{x-1} \tag{A2-50}$$

For $x_0 = 1$ the first term is zero, because the smallest ring does not bear any unreacted ωC functionality.

Substituting from eq A2-30, A2-32, A2-39, A2-41, and A2-50 we then have our final result for D_{σ}

$$D_{\sigma} = C_0\nu_{\sigma}\nu_{\omega}[1 - (1 - p + pv)^2]^2[U_{\omega} + U_v G_{1v}{}^{\omega}/(1 - G_{1v}{}^{v})] \sum_{x=x_0}^{\infty}(x - 1)x^{-5/2}(1 - p^x)y^{x-1} \Big/ \sum_{x=x_0}^{\infty} x^{-5/2}(1 - p^x)y^{x-1} \tag{A2-51}$$

with U_{ω}, U_v, $(G_{1v}{}^{\omega}/1 - G_{1v}{}^{v})$, and y given by (A2-37), (A2-38), (A2-40), and (A2-27), respectively.

References and Notes

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