The Structure of Rubber Networks with Multifunctional Junctions

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ABSTRACT: The modulus of a rubber network depends on the number of elastically active strands (ν) and junctions (μ) in the network. Statistical methods for calculating ν and μ for random networks with tetrafunctional junctions have already been developed. In the present paper expressions are derived for ν and μ in random networks with junction functionalities other than four. There has been considerable discussion in the literature about which of two criteria, the Flory or the Scanlan–Case, should be used for counting the number of strands and junctions. Although each method leads to different values for ν and μ, it is demonstrated that the difference, $\nu - \mu$, is the same regardless of the criterion used. Other structural parameters pertaining to multifunctional networks are also calculated including the probability, according to the Langley criterion, that two randomly selected strands have a fixed topological relationship with each other.

There are three essentially separate aspects to the problem of relating the elasticity of rubber networks to their molecular structure. One is the fundamental relationship between elasticity and network connectivity for phantom networks, i.e., networks in which the strands interact only at the junction points. The second is the statistical problem of calculating the parameters needed to apply this theory to particular networks from the mechanisms of network formation. The third is the problem of chain entanglements, which is to say, the contributions to the modulus arising from interactions between strand contours. This paper deals mainly with the second problem but contains some comments on the third.

Recently one of us reported some results on networks of polybutadiene formed by radiation cross-linking.[1] In that study it was shown that network formation takes place both by tetrafunctional cross-linking and by polymerization of the unsaturated units in the polybutadiene chains. Such networks contain multifuctional junctions, and their structures are more complicated than networks which contain tetrafunctional links only. In this paper we derive statistical expressions for the structure of multifunctional networks. Although these expressions are derived specifically for polymerization cross-linking, we expect that they will also be useful for dealing with the structure of other multifunctional networks. Example materials of this type include block copolymers in which chain units cluster into glassy or crystalline domains, ionomer networks, and certain gels such as agarose where network formation occurs by aggregation.

In the second part of the article the structural parameters associated with mechanical properties are discussed. We review recent expressions for the free energy of phantom networks[2–5] and show how the parameters in these theories can be calculated for multifunctional networks. We apply the criterion of Langley[6] for calculating the contribution of entanglements to the modulus in multifunctional networks. Finally we develop expressions for structural parameters which may be important in the maximum extension and viscoelastic behavior of networks. Possible differences in mechanical behavior between multifunctional and simple tetrafunctional networks are discussed.

Sol–Gel Statistics

Consider a collection of N long primary chains, each containing r structural units, and assume that network formation proceeds by randomly linking the units of these molecules. A junction which unites two structural units has four strands leading away from it, i.e., its functionality, f, is equal to 4. A junction which unites j units requires $j - 1$ cross-links and has a functionality equal to $2j$ (Figure 1).

When the number of cross-links exceeds a certain critical value a fraction of the polymer molecules will be united into a macroscopic cluster having the structure of a three-dimensional network. The fraction of structural units in the network is the gel fraction, g, and the remainder comprises the sol fraction, $s = 1 - g$.

An expression for the sol fraction will be derived using a method due to Flory.[7] First two probabilities are defined: φ is the probability that a randomly selected noncross-linked unit belongs to the sol, and θ is the probability that a randomly selected cross-linked unit belongs to the sol. The sol fraction can then be expressed as

$$s = (1 - \alpha)\varphi + \alpha\theta \qquad (1)$$

where α is the fraction of all units which participate directly in cross-links. A junction belongs to the sol only if all the units it connects would belong to the sol in the absence of that junction. If there are no intramolecular cross-links in the sol, $\theta = \varphi^j$ for junctions which join j units. When junctions of different functionality are present,

$$\theta = \sum_{j=2}^{\infty} w_j \varphi^j$$

in which w_j is the fraction of cross-linked units located in junctions containing j units. Equation 1 can now be rewritten as

$$s = (1 - \alpha)\varphi + \alpha \sum_{j=2}^{\infty} w_j \varphi^j \qquad (2)$$

The probability υ that a randomly selected unit is not cross-linked or, if it is cross-linked, that the cross-link joins it only to units which are part of the sol is

$$\upsilon = 1 - \alpha + \alpha \sum_{j=2}^{\infty} w_j \varphi^{j-1} \qquad (3)$$

It follows from the definition of υ that the sol fraction can also be expressed as

$$s = \upsilon^r = \left(1 - \alpha + \alpha \sum_{j=2}^{\infty} w_j \varphi^{j-i}\right)^r \qquad (4)$$

By rearranging and combining eq 2 and 4 it can be shown that $s = \varphi^{r/(r-1)}$ and hence for long primary chains $s \simeq \varphi$, allowing eq 4 to be rewritten

$$s = \left(1 - \alpha + \alpha \sum_{j=2}^{\infty} w_j s^{j-1}\right)^r \qquad (5)$$

a result first reported by Scott.[8]

If all the junctions are tetrafunctional, $w_j = 1$ ($j = 2$) and $w_j = 0$ ($j \neq 2$). Equation 5 simplifies to

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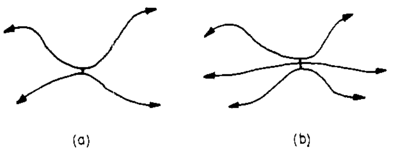

Figure 1. (a) A tetrafunctional junction uniting two chains with one cross-link. (b) A hexafunctional junction uniting three chains with two cross-links.

$$\begin{aligned} s &= (1-\alpha+\alpha s)^r \\ &= (1-\alpha g)^r \\ &= e^{-\alpha g r} \qquad (\alpha \ll 1) \end{aligned} \tag{5a}$$

These are the usual formulas reported in the literature.[9,10] If the junctions are formed by polymerization or by clustering of structural units into either glassy, crystalline, or ionic domains, there will be a distribution of functionalities and a distribution function, w_j, related to the mechanism and kinetics of the cross-linking process must be used. Some appropriate distribution functions are discussed in Appendix A.

Paths to the Gel

A randomly selected noncross-linked unit is connected to the gel by 0, 1, or 2 paths. Let the respective probabilities be p_0, p_1, and p_2. Expressions for each can be calculated as follows. If a unit is selected n units from one end of a primary chain r units long, the probability that this end is connected to the sol is υ^n. The probability that the other end is connected to the sol is υ^{r-n-1}. The probability that a randomly chosen uncross-linked unit has both ends connected to the sol is therefore

$$\begin{aligned} p_0 &= \frac{1}{r}\sum_{n=0}^{r-1} \upsilon^n \upsilon^{r-n-1} \\ &= \upsilon^{r-1} \end{aligned} \tag{6}$$

which is identical to the expression for φ (see eq 2 and 4).

The probability that a unit n units from one end of a primary chain is connected to the gel is $1-\upsilon^n$. The probability that the other end is connected to the gel is $1-\upsilon^{r-n-1}$. The probability that a randomly chosen uncross-linked unit has both ends connected to the gel is

$$\begin{aligned} p_2 &= \frac{1}{r}\sum_{n=0}^{r-1} (1-\upsilon^n)(1-\upsilon^{r-n-1}) \\ &= 1+\upsilon^{r-1} - 2(1-\upsilon^r)/r(1-\upsilon) \end{aligned} \tag{7}$$

From the normalization condition, $p_0 + p_1 + p_2 = 1$, we find

$$p_1 = 2\,[(1-\upsilon^r)/r(1-\upsilon) - \upsilon^{r-1}] \tag{8}$$

The expressions for p_0, p_1, and p_2 can be used to calculate a number of structural parameters related to the mechanical properties of the network.

(All of the formulas derived in the last two sections can be extended to the case where the polymer being cross-linked has an arbitrary distribution of molecular weights and to the case where chain scission occurs simultaneously with cross-linking. These generalizations are given in Appendix B.)

The Number of Elastically Active Strands

The criterion for deciding whether a strand is elastically active is due to Scanlan[11] and Case.[12] They propose that only strands connected at both ends to junctions with at least three paths to gel are active. A junction with zero paths or one path to the gel unites strands whose equilibrium configuration is not affected by an applied strain. A junction with two paths to the gel merely extends the length of an active strand. Deriving specific expressions from the Scanlan–Case criterion requires the use of another network parameter. Let c_{ij} be the number of network junctions uniting j units which have i paths to gel ($0 \le i \le 2j$). By an application of the multinomial theorem (see Appendix C) we find

$$c_{ij} = n_j \sum_{0\le k\le i/2} \frac{j!}{(j-i+k)!(i-2k)!k!} \times p_0^{\,j-i+k} p_1^{\,i-2k} p_2^{\,k} \tag{9}$$

where n_j is the number of network junctions containing j cross-linked units:

$$n_j = \alpha r N w_j / j \tag{10}$$

The number of elastically active strands is found by summing all paths to the gel from junctions where $i \ge 3$ and dividing by 2 since each of these strands is connected to two junctions.

$$\nu = {}^1\!/\!_2 \sum_{j=2}^{\infty} \sum_{i=3}^{2j} i c_{ij} \tag{11}$$

With eq 9 and 10 and the identity

$$\sum_{i=3}^{2j} i c_{ij} = \sum_{i=0}^{2j} i c_{ij} - \sum_{i=0}^{2} i c_{ij}$$

this expression becomes

$$\nu = {}^1\!/\!_2 \alpha r N \left[2p_2 \sum_{j=2}^{\infty} w_j (1 - p_0^{\,j-1}) + p_1 \sum_{j=2}^{\infty} w_j (1 - p_0^{\,j-1} - (j-1) p_0^{\,j-2} p_1) \right] \tag{12}$$

Equation 12 has a physically simple interpretation. It is twice the number of cross-linked units with two paths to the gel, multiplied by the probability that they are cross-linked to units with at least one path to the gel, plus the number of cross-linked units with one path to the gel, multiplied by the probability that they are cross-linked to units with at least two paths to the gel. The factor ½ again corrects for the double counting of all strands.

The number of elastically active network junctions is

$$\mu = \sum_{j=2}^{\infty} \sum_{i=3}^{2j} c_{ij} \tag{13}$$

Using eq 9 and 10 again, this expression reduces to

$$\mu = \alpha r N \left[\sum_{j=2}^{\infty} (w_j/j)(1 - p_0^{\,j} - j p_0^{\,j-1} p_1 - j p_0^{\,j-1} p_2 - {}^1\!/\!_2\, j(j-1) p_0^{\,j-2} p_1^{\,2}) \right] \tag{14}$$

which is the total number of junctions minus those with only 0, 1, or 2 paths to the gel. For the special case of tetrafunctional cross-linking the expressions for ν and μ simplify to

$$\nu = {}^1\!/\!_2 \alpha r N (3 p_1 p_2 + 2 p_2^{\,2}) \tag{15}$$

$$\mu = {}^1\!/\!_2 \alpha r N (2 p_1 p_2 + p_2^{\,2}) \tag{16}$$

results that have been previously given by Langley.[13]

Gordon and Ross-Murphy[14] have also reported an expression for ν applying to multifunctional networks in which all of the junctions have the same functionality. Although their equation is numerically equivalent to our eq 12, it has a different form. This difference comes from the choice of an extinction probability. Whereas we have chosen φ, the probability that a randomly chosen uncross-linked unit is part of a finite structure (sol molecule), they have chosen the probability that a randomly selected cross-linked unit is connected via cross-links to a finite number of additional units. In our nomenclature this probability is equal to φ^{j-1}.

We conclude this section by deriving two types of limiting relationships, one which applies at low cross-link densities just beyond the gelation threshold and the other at high cross-link densities when the transformation to gel is nearly complete.

Let $\epsilon = (\alpha - \alpha_c)/\alpha_c$ be a parameter which measures the distance from the gel point. Here $\alpha_c = [(f_w/2 - 1)(r - 1)]^{-1}$ is the critical density of cross-linked units at gelation and

$$f_w = 2 \sum_{j=2}^{\infty} j w_j$$

is the weight-average number of strands leading away from a randomly selected junction. Then at low cross-link densities

$$g \sim \epsilon \tag{17}$$

$$p_2 \sim \epsilon^2 \tag{18}$$

$$\nu \sim \epsilon^3 \tag{19}$$

$$\mu \sim \epsilon^3 \tag{20}$$

$$L \sim \epsilon^{-1} \tag{21}$$

where L is the average number of structural units in an active strand. The exponents in eq 17–21 are a result of the basic assumption used in sol–gel statistics; the number of intramolecular cross-links in finite size molecules is negligibly small. Use of this assumption leads to a network whose local connectivity is treelike in nature and hence to exponents that are exactly the same as those found for other gelation (percolation) problems which take place on treelike lattices.[15,16] Recent theoretical work by de Gennes indicates that neglecting intramolecular cross-links is a valid assumption for high molecular weight polymers.[17]

At high cross-link densities, limiting relationships for the network parameters can be expressed in terms of $\gamma = \alpha r$, the average number of cross-linked units per primary chain. We find

$$g = 1 - e^{-\gamma} \tag{22}$$

$$p_2 = 1 - 2/\gamma + e^{-\gamma} \tag{23}$$

$$\nu = (\gamma - 1)N \tag{24}$$

$$\mu = \gamma N \sum_{j=2}^{\infty} w_j/j = 2\gamma N/f_n \tag{25}$$

$$L = r/\gamma \tag{26}$$

where f_n is the number-average number of strands leading away from a junction. Rubber networks that are used in mechanical applications typically have values of $\gamma \gg 1$, a region in which these asymptotic forms (eq 22–26) should be valid.[18]

Number of Fundamental Circuits in a Network

Flory[4] has recently published an expression for the elastic free energy of a phantom rubber network. He reports that the modulus is proportional to $\nu' - \mu'$ where ν' and μ' are the numbers of strands and junctions in the network regardless of how many connections they have to the gel. On the other hand Graessley[3] has reported that the modulus should be proportional to $\nu - \mu$, where ν and μ are defined by the Scanlan–Case criterion. We intend to show that $\nu' - \mu'$ equals $\nu - \mu$. Although a proof using results from graph theory[19] could be given, we have chosen instead a simpler one that makes use of the nomenclature introduced above.

As noted by Flory,[4] in any connected graph the number of fundamental circuits, ξ, is equal to the difference between the number of edges and the number of vertices plus one. In a rubber network the vertices are the junctions and the terminal ends of polymer chains; the edges are the polymer strands which connect these vertices. Hence

$$\xi = \nu' - \mu' + 1 \tag{27}$$

Each cross-linked unit that is introduced divides a primary chain, producing one new network strand. The total number of network strands then is equal to the number of cross-linked units plus the number of primary chains in the network

$$\nu' = \sum_{j=2}^{\infty} \sum_{i=1}^{2j} j c_{ij} + N_g \tag{28}$$

where the subscript g on N indicates that only chains in the network (gel) are counted. The number of vertices equals the number of junctions plus the number of chain ends

$$\mu' = \sum_{j=2}^{\infty} \sum_{i=1}^{2j} c_{ij} + 2N_g \tag{29}$$

Finally, the number of primary chains in the network is just one-half the number of free ends

$$N_g = {}^1\!/_2 \sum_{j=2}^{\infty} \left[\sum_{i=2}^{2j} (2j - i)c_{ij} + (2j - 2)c_{1j} \right] \tag{30}$$

where $2j - i$ is the number of ends contributed by a junction with two or more paths to the gel ($i \geq 2$) and $2j - 2$ is the number of additional ends contributed by a junction with just one path to the gel. Combining the last three equations

$$\nu' - \mu' = {}^1\!/_2 \sum_{j=2}^{\infty} \sum_{i=3}^{2j} (i - 2)c_{ij} = \nu - \mu \tag{31}$$

Thus the Flory and Graessley expressions are the same, and the number of fundamental circuits in a rubber network (ξ) is equal to $\nu' - \mu'$ or $\nu - \mu$.[20]

The number of fundamental circuits and the number of active strands in networks with different functionalities are shown in Figures 2 and 3 as functions of the reduced cross-link density α/α_c.

Physical Properties of Multifunctional Networks

At the present time there is no first-principles molecular theory for predicting the equilibrium modulus of a network which contains chain entanglements. However, a number of semiempirical methods[6,21] have proven to be quite successful in correlating experimental measurements of the modulus with network structure.[1,13,22,23] We discuss one of these methods which is due to Langley.[6]

When a high molecular weight uncross-linked polymer is tested under dynamic conditions the modulus remains essentially constant over a wide range of frequencies. The usual explanation is that a network of entanglements is present and the lifetime of the entangled states for the chains is longer than the experimental time scale. It seems plausible that a portion of this transient network could be permanently fixed or trapped by the addition of cross-links. In this case the modulus of a cross-linked entangled network will be greater than that of a phantom network with the same structure. If it is further assumed that the entanglement effect is simply additive, then the shear modulus, G, should be the sum of two parts: one from the strands which join the junctions, G_c, and one from trapped entanglements, G_e.

The contribution from the strands can be expressed as

$$G_c = \Phi(\nu - \mu)kT/V_0 \tag{32}$$

where Φ is a factor which depends on the connectivity of the network[24] and presumably is of order unity. V_0 is the volume of the network in the unstrained state.

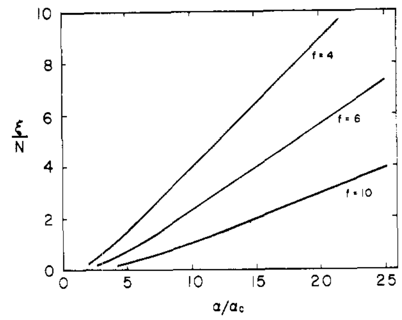

Figure 2. The number of fundamental circuits per primary chain vs. α/α_c for networks with tetrafunctional, hexafunctional, and decafunctional junctions. The asymptotic behavior of ξ is $\xi/N = [(\alpha/\alpha_c)/j] - 1$.

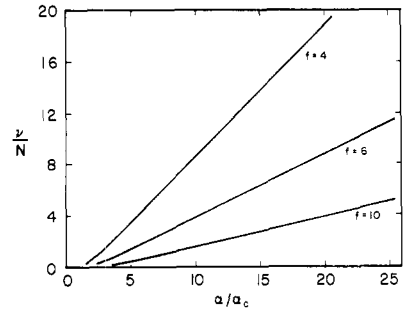

Figure 3. The number of elastically active strands per primary chain vs. α/α_c for networks with tetrafunctional, hexafunctional, and decafunctional junctions. The asymptotic behavior of ν is $\nu/N = [(\alpha/\alpha_c)/(j-1)] - 1$.

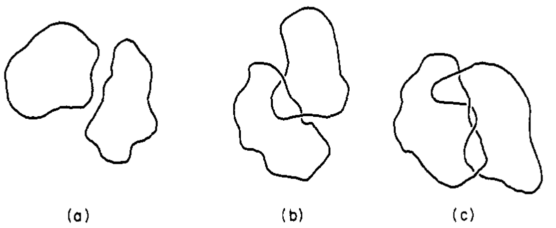

Figure 4. Three topological relationships between two closed loops: (a) not entwined, (b) once entwined, (c) twice entwined.

The contribution from entanglements is approximated as

$$G_e = T_e G_N{}^0 \tag{33}$$

where $G_N{}^0$ is the plateau modulus obtained from dynamic shear measurements on the uncross-linked system and T_e is a suitably chosen trapping factor. Langley suggested that T_e is equal to the probability that all four paths from a randomly chosen pair of units lead to the gel. From the definition of p_2,

$$T_e = p_2{}^2 \tag{34}$$

The entanglement trapping factor T_e can be interpreted in an alternate way. A structural unit that is part of an active network strand (with probability p_2) is also part of a closed circuit which in turn has a fixed topological relationship with all other closed circuits in the network (see Figure 4). Hence $p_2{}^2$ is the probability that two randomly chosen units are part of structures whose pairwise topological arrangement has been made permanent by the cross-linking process.

In Figure 5 T_e is plotted as a function of α/α_c for networks with tetrafunctional, hexafunctional, and decafunctional junctions. Figures 2 and 5 show that the moduli of entangled networks at equal values of α/α_c should decrease with increasing junction functionality.

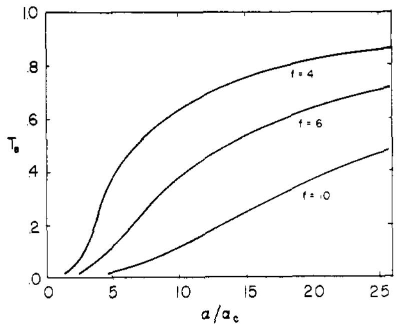

Figure 5. The trapping factor, T_e, for networks with tetrafunctional, hexafunctional, and decafunctional junctions.

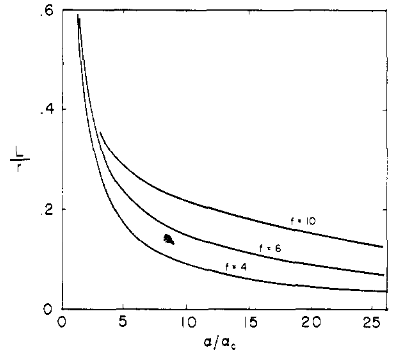

Figure 6. The ratio of the average length of a network strand to the length of a primary chain vs. α/α_c for networks with tetrafunctional, hexafunctional, and decafunctional junctions.

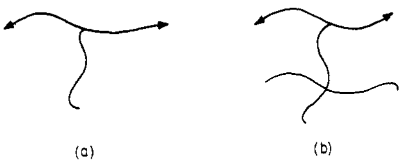

Figure 7. (a) A linear dangling end. (b) A dangling end with one tetrafunctional branch point.

An important structural feature of a network is L, the average number of units in an active strand. This parameter should be closely related to the maximum extensibility and hence to the tensile strength of a rubber network. Using definitions given above we obtain

$$L = p_2 rN/\nu \tag{35}$$

where the numerator is the total number of units in active strands. In Figure 6 L is given as a function of α/α_c for networks of various functionality.

Another important feature of a rubber network is the concentration and structure of inactive strands that are connected to it (dangling ends). These strands probably play an important role in the hysteritic behavior of dynamically loaded networks and in the creep and stress relaxation behavior of statically loaded networks.[25] For example, if a network is stretched rapidly both the network strands and the dangling ends will be extended in an approximately affine manner.[26,27] However, the latter will eventually relax to equilibrium configurations which are the same as those for the unstretched network. If this process takes place by a reptation-like process, then the length and branched structure of the ends will have a strong influence on the time required for relaxation.[28,29]

The nature of the dangling ends can be described in part by three parameters: (1) the number of ends, (2) the average number of units in an end, and (3) the average number of branch points on an end (see Figure 7).

The number of dangling ends is

$$\nu_{\text{end}} = \sum_{j=2}^{\infty} \sum_{i=2}^{2j} (2j-1)c_{ij}$$

$$= \alpha r N \sum_{j=2}^{\infty} w_j \, [2p_0(1-p_0^{j-1}) - (2j-1)\,p_0^{j-1}p_1 + p_1] \quad (36)$$

The summation is taken over junctions for which $i \geq 2$ because a junction with only one path to the gel is just a branch point on an already counted dangling end.

The average number of units in a dangling end is

$$L_{\text{end}} = p_1 r N/\nu_{\text{end}} \quad (37)$$

and the average number of branch points per dangling end is

$$B_{\text{end}} = \frac{\sum_{j=2}^{\infty} c_{1j}}{\nu_{\text{end}}} = \frac{\alpha r N \sum_{j=2}^{\infty} w_j p_0^{j-1} p_1}{\nu_{\text{end}}} \quad (38)$$

For monodisperse polymers cross-linked in the absence of chain scission, the number of dangling ends per primary chain and the number of branch points per dangling end quickly converge to 2 and 0, respectively.

In Figures 8 and 9, the weight fraction of dangling ends and the average length of a dangling end are plotted as functions of the reduced cross-link density, α/α_c. In certain applications for rubber networks it might be advantageous to absorb energy in a certain frequency range. Hence the presence of dangling ends would be quite desirable. In other applications the hysteritic losses associated with these ends might lead to an unwanted temperature rise and hence a need for networks with very few dangling structures.

Summary

A number of statistical relationships have been derived for calculating the structure of rubber networks with multifunctional junctions. Some of these quantities appear as parameters in the molecular theory of elastic energy in phantom networks. Others relate to Langley's trapping factor for the entanglement contribution to the modulus, to the maximum extensibility, and to the viscoelastic properties of networks.

Acknowledgments. The authors are grateful for many helpful discussions with Mr. Luc Dossin during the course of this work and for valuable suggestions by Professor J. D. Ferry on the manuscript. This work was supported in part by grants from the Exxon Chemical Co. and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Appendix A

Experimental Determination of α and w_j. The structure of a rubber network is determined by the molecular weight of the primary chains, the fraction of cross-linked units α, and the cross-link functionality distribution w_j. We describe an experimental method for determining α and w_j from the gel curve.

A collection of samples is prepared with a known initial molecular weight and differing in cross-link density. The sol fraction of each is measured by standard techniques.[30] With this information and eq 2 and 4, α and w_j can be determined for each sample as follows. Depending on the method used to prepare the samples, α will usually be proportional to the amount of cross-linking agent used, the radiation dose received, or the time of reaction. Furthermore, a knowledge of the mechanism of cross-linking may suggest a form for w_j. For example, if cross-linking takes place by polymerization of double bonds in the backbone of the polymer chain, w_j might be given by

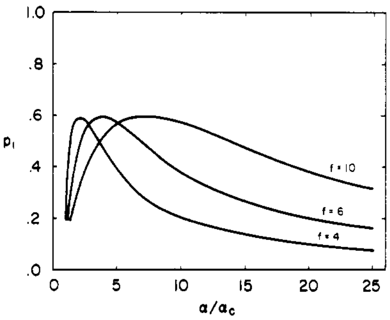

Figure 8. The weight fraction of dangling ends in a network vs. the reduced cross-link density (α/α_c) for networks with different junction functionalities.[4,6,10]

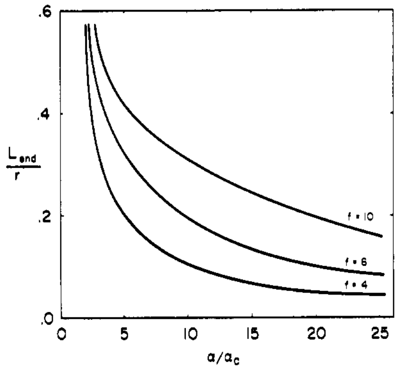

Figure 9. The ratio of the length of a dangling end to the length of a primary chain vs. the reduced cross-link density (α/α_c) for networks with different junction functionalities.[4,6,10]

$$w_j = \frac{j}{\varkappa 2}\left[\frac{\varkappa - 1}{\varkappa}\right]^{j-1} \quad (A1)$$

which applies for termination by disproportionation, or

$$w_j = \frac{j(j-1)}{2\varkappa^3}\left[\frac{\varkappa - 1}{\varkappa}\right]^{j-2} \quad (A2)$$

which applies for termination by recombination. The parameter $\varkappa$ is the kinetic chain length of the reaction in each case.

Likewise, if the cross-linking reaction yields junctions that all have the same functionality, f, then

$$w_j = 1 \qquad (2j = f)$$

$$w_j = 0 \qquad (2j \neq f) \quad (A3)$$

Finally, if cross-linking occurs by clustering of structural units into domains, a study of the nucleation and growth mechanism may suggest an appropriate distribution function. In all these cases the proportionality constant for cross-link formation and a parameter characterizing the junction functionality distribution could be determined by a regression analysis of the gel curve using eq 2 and 4, and thus the structural parameters of each network could be calculated.

Appendix B

Simultaneous Cross-Linking and Chain Scission for Primary Chains of Arbitrary Distribution. The expressions for s, p_0, p_1, and p_2 were derived for the case where all primary chains contain the same number of units, r. This restriction is easily removed. The case of an arbitrary distribution of primary chain lengths is treated by operating on the right-hand side of eq 2, 6, 7, and 8 with

$$\sum_{r=1}^{\infty} W_r$$

where W_r is the fraction of structural units in chains of length r. For example, eq 6 for p_0 becomes ($\varphi = p_0$)

$$p_0 = \sum_{r=1}^{\infty} W_r \left(1 - \alpha + \alpha \sum_{j=2}^{\infty} w_j \varphi^{j-1}\right)^{r-1} = \varphi \quad \text{(B1)}$$

If network formation is accomplished by reaction with peroxides or exposure to radiation, it is likely that chain scission will occur simultaneously with cross-linking. Equation B1 can be modified for this case by using in place of W_r an altered distribution function $W_r(\beta)$ where β is the fraction of bonds between units that have been scissioned. An expression for $W_r(\beta)$ for initially linear chains has been given by Montroll.[31]

$$W_r(\beta) = W_r(0)(1-\beta)^{r-1} + r\beta(1-\beta)^{r-1} \times \sum_{l=r+1}^{\infty} \frac{W_l(0)}{l}\left[2 + \beta(l - r - 1)\right] \quad \text{(B2)}$$

where $W_r(0)$ is the initial chain length distribution.

Let

$$1 - \sum_{j=2}^{\infty} w_j \varphi^{j-1} = \tau$$

and then substitute (B2) into (B1)

$$\varphi = \sum_{r=1}^{\infty} W_r(0)(1-\beta)^{r-1}(1-\alpha\tau)^{r-1} + \beta \sum_{r=1}^{\infty} r(1-\beta)^{r-1}(1-\alpha\tau)^{r-1} \sum_{l=r+1}^{\infty} \times \frac{W_l(0)}{l}\left[2 + \beta(l - r - 1)\right] \quad \text{(B3)}$$

One of the summations in the second term can be completed after reversing the order of summation. Combining the remaining terms we have

$$\varphi = 1 - \sum_{r=1}^{\infty} W_r(0) \left\{2\lambda\left[1 - \frac{1-(1-\zeta)^r}{r\zeta}\right] - \lambda^2\left[1 - \frac{2 - 2(1-\zeta)^r}{r\zeta} + (1-\zeta)^{r-1}\right]\right\} \quad \text{(B4)}$$

where $1 - \zeta = (1-\beta)(1-\alpha\tau)$ and $\lambda = \alpha\tau/\zeta$. In obtaining eq B4 we have made use of the fact that in typical cross-linked polymers α and $\beta \ll 1$ permitting the approximation $\zeta = \beta + \alpha\tau - \beta\alpha\tau \simeq \beta + \alpha\tau$. For the special case of tetrafunctional cross-linking eq B4 can be rearranged to results obtained before by Inokuti[32] and Langley.[6]

The procedure followed in deriving eq B4 can also be applied to the equations for p_1 and p_2 with the results

$$p_1 = 2 - 2\varphi - \sum_{r=1}^{\infty} W_r(0)\left\{2\lambda\left[1 - \frac{1-(1-\zeta)^r}{r\zeta}\right]\right\} \quad \text{(B5)}$$

$$p_2 = \varphi - 1 + \sum_{r=1}^{\infty} W_r(0)\left\{2\lambda\left[1 - \frac{1-(1-\zeta)^r}{r\zeta}\right]\right\} \quad \text{(B6)}$$

It should be noted that if chain scission does occur the equations for calculating the number of active strands and other network parameters will not be altered, apart from the requirement that the new results for p_0, p_1, and p_2 be substituted.

Appendix C

Derivation of Equation 9. Consider a junction which ties together j chains, and let t_{ij} be the probability that i paths lead from this junction to the gel. If in the absence of the given junction l_0 of the chains have no paths to the gel (l_1, one, and l_2, two), then t_{ij} will be given by the multinominal distribution

$$t_{ij} = \Sigma'' \frac{j!}{l_0!\, l_1!\, l_2!} p_0^{l_0} p_1^{l_1} p_2^{l_2} \quad \text{(C1)}$$

where the double prime indicates the summation is over all sets of l_0, l_1, and l_2 subject to the two conditions $l_0 + l_1 + l_2 = j$ and $l_1 + 2l_2 = i$. Using these two constraints to eliminate l_0 and l_1 and letting $l_2 = k$ we have

$$t_{ij} = \sum_{0 \le k \le i/2} \frac{j!}{(j-i+k)!(i-2k)!k!} p_0^{j-i+k} p_1^{i-2k} p_2^{k} \quad \text{(C2)}$$

The number of junctions uniting j chains and having i paths to the gel is

$$c_{ij} = n_j t_{ij} \quad \text{(C3)}$$

which is eq 9.

References and Notes

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