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Elastically Effective Chains in Transient Gels with Multiple Junctions

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ABSTRACT: Most thermoreversible gels have multiple junctions combining more than two network chains. The number of chains bound together in a single junction is called the *multiplicity* of the junction. On the basis of the Scanlan−Case criterion, the numbers of elastically effective chains and effective junctions in thermoreversible gels with multiple junctions are calculated as functions of the polymer concentration and the temperature for several important types of multiplicity distribution. It is found that the number of elastically effective chains increases as the cube of the concentration deviation near the sol/gel transition concentration and reaches an asymptotic high-concentration region where it increases proportionally to the concentration. The result is compared with the observed elastic moduli of associating polymers.

I. Introduction

Associating polymers are polymers which carry small amounts of associating groups capable of forming aggregates in good solvents for the polymer backbone. Rheological properties of the transient networks formed by associating polymers have attracted much experimental and theoretical interest in recent years. Typical examples are networks in aqueous solutions of polymers end-capped with short hydrophobic chains at both ends, such as hydrophobic ethoxylated urethane (called HEUR)[1−3] and poly(propylene oxide)−poly(ethylene oxide)−poly(propylene oxide) triblock copolymers.[4−6] These polymers can act as model associating systems, but other networks formed by hydrophobically modified cellulose derivatives such as ethyl hydroxyethyl cellulose (called EHEC) in the presence of an ionic surfactant in water[7−10] and telechelic ionomers such as α,ω-sodium sulfonatopolyisoprene (called α,ω-NaPIPS) in organic solvents[11] are also important examples.

The dynamic properties of the associating polymers are generally studied by dynamic mechanical measurements. The simplest theory of transient networks in which the network junctions can break and recombine by thermal motion of the polymers and/or under applied deformation was proposed by Green and Tobolsky.[12] Their theory gives

$$G_\infty = \nu_{\text{eff}} k_B T \tag{1.1}$$

for the high-frequency storage modulus and

$$\eta(\dot{\gamma}) = G_\infty \tau \tag{1.2}$$

for the steady shear viscosity. Here, ν_{eff} is the number of elastically effective chains in the network, k_B the Boltzmann constant, T the absolute temperature, and τ a relaxation time. The viscosity is independent of the shear rate, $\dot{\gamma}$. The relaxation time (τ) is the reciprocal of the rate of chain-end disengagement from a junction.

More recently, one of us and Edwards[13,14] (hereafter referred to as TE) refined their theory to provide a detailed molecular−theoretical picture for the Maxwellian behavior of the dynamic mechanical moduli and also to account for the observed shear-rate dependence of the viscosity. TE derived the relation

$$\frac{\nu_{\text{eff}}}{\nu} = \frac{p/\beta_0}{1 + p/\beta_0} \tag{1.3}$$

for the fraction of the elastically effective chains relative to the total primary chains (ν) in the solution, where β_0 is the rate of chain disengagement from a junction (assumed here for simplicity to be independent of the chain extension) and p the rate of chain recombination into a junction. It was experimentally found that in some ideal cases the rheological time scale is governed by the disengagement rate (β_0) which obeys the activation type formula

$$\beta_0 = \omega_0 \exp(-E/k_B T) \tag{1.4}$$

where E is the activation energy for disengagement. The chain recombination rate (p) obviously depends on the distribution of network junctions around the chain, which should inevitably depend on the polymer concentration and the temperature. The number of elastically effective chains in the network (ν_{eff}) can directly be obtained from the measurement of the high-frequency storage modulus through the relation 1.1, so it would be meaningful to obtain information on the recombination rate through theoretical and experimental study of the number of effective chains. The main purpose of this paper is to derive the number of elastically effective chains and other structural network parameters, such as the number of effective junctions and dangling ends, *as a function of the temperature and the polymer concentration* and compare them with the experimental results reported.

In the work by Annable *et al.*,[2] the observed strong concentration dependence of the modulus near the gelation point was ascribed mainly to the formation of small loops which are dangling from the network matrix. They made a numerical simulation, but the complete classification of the loops and analytical calculation of their numbers in the network as functions of the thermodynamic variables were impossible. Instead, here we start from the conventional Scanlan−Case criterion[15,16] for a chain to be elastically effective. This criterion proposes that chains connected at both

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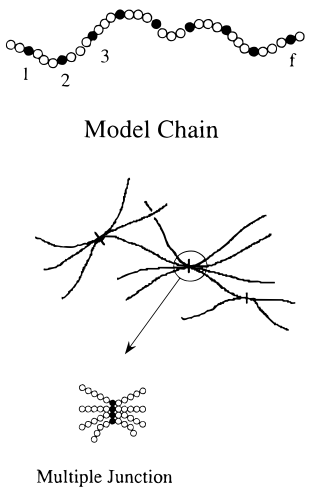

Figure 1. A model primary chain and network junctions. Each chain with n repeat units carries f functional groups capable of forming multiple junctions. The number of functional groups in a junction is called its multiplicity.

ends to junctions with at least three paths to the gel network are elastically effective. In fact networks cross-linked by covalent bonds (chemical gels) were extensively studied by this criterion. Later this work was extended by Pearson and Graessley[17] to deal with the networks with junctions in which more than two chains are combined (*i.e. multiple junctions*). All these works concern permanent cross-links so that the extent of reaction (α) is the unique parameter for the specification of the network structure. In physical gels with temporary junctions, however, the network structure is controlled by the thermodynamic requirements, so all characteristics should be described as functions of the thermodynamic variables such as the temperature, the polymer concentration, and the surfactant concentration. A pioneering attempt to do this was made by Clark and Ross-Murphy.[18] They applied the Scanlan–Case criterion to the physical networks formed by pairwise association of functional groups and expressed the modulus as a function of the polymer concentration. We start from their idea and derive a complete description of thermoreversible networks with junctions of arbitrary multiplicity.

II. Model Network

We consider a model solution in which primary chains are dissolved in a solvent and associate with each other through the aggregation of functional groups sparsely embedded along the chain backbone (see Figure 1). The term "*functional group*" is used here for a group, or short polymer segment, capable of forming aggregates via noncovalent bonding. Typical examples are hydrogen-bonding groups and microcrystalline segments, but short hydrophobic side chains attached on water-soluble polymers are another important example of such functional groups. These groups can form thermoreversible junctions with variable multiplicity. The junction multiplicity (k) is defined by the number of the functional groups in the junction.[19,20] For example, $k = 2$ denotes a pairwise junction at which two functional groups are combined, and so on. A functional group which remains unassociated in the solution corresponds to $k = 1$.[19,20] Let n be the number of statistical repeat units (monomers) on a primary chain, and let f be the number of functional groups it carries.

In thermal equilibrium many junctions are formed in the solution, with a population distribution determined by thermodynamic requirements. We consider the post-gel regime of the solution where the sol part and a gel network coexist, generalizing the treatments of Flory[21] and of Pearson and Graessley.[17] Let w_k ($k = 2, 3, 4, ...$) be the junction distribution defined by the number of functional groups in k junctions divided by the total number of functional groups participating in the (real) junctions with $k \geq 2$. Let p_k ($k = 1, 2, 3, ...$) be the probability for a randomly chosen functional group to be in a k junction. Then the junction distribution is expressed as

$$w_k = p_k / \sum_{k \geq 2} p_k \tag{2.1}$$

The probability for a functional group to remain unassociated (p_1) can be expressed in terms of the extent of reaction (α) defined by

$$\alpha \equiv \sum_{k \geq 2} p_k \tag{2.2}$$

We then have $p_1 = 1 - \alpha$, and the relation

$$p_k = \alpha w_k \tag{2.3}$$

follows for $k \geq 2$.

We next consider the connectivity of a functional group to the gel network, following the theoretical treatment of Pearson and Graessley.[17] Let u be the probability that a randomly selected functional group is either unreacted or a part of the sol fraction. It is a function of the temperature and the concentration of the primary polymers for the given associative interaction. This quantity controls the probability ζ_i ($i = 0, 1, 2$) that such a randomly chosen unassociated functional group is connected to the gel network through i paths. (In this paper we use ζ_i for the path connectivity instead of p_i in the literature[17] to avoid confusion with junction probability p_k.) Explicitly, Pearson and Graessley showed that

$$\zeta_0 = \frac{1}{f} \sum_{m=1}^{f} u^{m-1} u^{f-m} = u^{f-1} \tag{2.4a}$$

$$\zeta_2 = \frac{1}{f} \sum_{m=1}^{f} (1 - u^{m-1})(1 - u^{f-m}) = 1 + u^{f-1} - \frac{2(1 - u^f)}{f(1 - u)} \tag{2.4b}$$

$$\zeta_1 = 1 - \zeta_0 - \zeta_2 = 2\left\{\frac{1 - u^f}{f(1 - u)} - u^{f-1}\right\} \tag{2.4c}$$

Let us next specify the junction type in more detail (see Figure 2). A junction of multiplicity k that is connected to the gel network through i paths is referred to as an (i, k) junction. Let $\mu_{i,k}$ be the number of junctions specified by the type (i, k) for $k = 1, 2, 3, 4, ...$ and for $0 \leq i \leq 2k$. The total number of junctions with multiplicity k in unit volume is given by

$$\mu_k = \sum_{i=0}^{2k} \mu_{i,k} = (f\nu\alpha)(w_k/k) \tag{2.5}$$

where ν is the total number of primary chains in unit volume. Pearson and Graessley[17] found that $\mu_{i,k}$ is given by

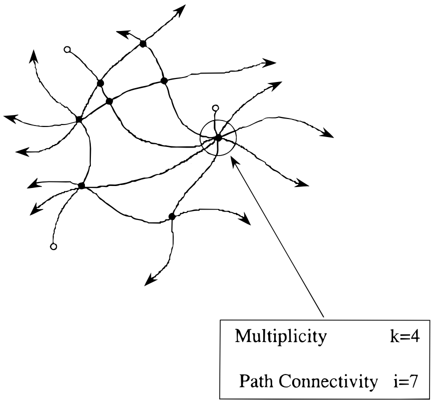

Figure 2. The classification of the junctions. A junction of multiplicity *k* connected to the network matrix through *i* paths is called a junction of the type (*i*, *k*). Open circles show the ends of primary chains.

$$\mu_{i,k} = (f\nu\alpha)w_k \sum_{0\le m\le i/2} \frac{(k-1)!}{(k-i+m)!(i-2m)!m!} (\zeta_0)^{k-i+m}(\zeta_1)^{i-2m}(\zeta_2)^{m} \tag{2.6}$$

by counting the number of ways to combine *k* functional groups on the separated chains into a junction of the type (*i*, *k*).

III. The Number of Elastically Effective Chains

We now study the sol fraction (S) in the postgel regime of our model solution. By definition the sol fraction is given by the sum of the two terms: the probability for a unreacted functional group not to be connected to the gel network and the probability for a reacted functional group to be connected only to the finite part. We thus find

$$S = (1-\alpha)\zeta_0 + \alpha\theta(\zeta_0)\zeta_0 \tag{3.1}$$

where the new function $\theta(x)$ is defined by

$$\theta(x) \equiv \sum_{k\ge 2} w_k x^{k-1} \tag{3.2}$$

Let us now introduce a function $u(x)$ by

$$u(x) = 1 - \alpha + \alpha\theta(x) \tag{3.3}$$

or equivalently

$$u(x) \equiv \sum_{k\ge 1} p_k x^{k-1} \tag{3.4}$$

At $x = \zeta_0$, this function gives the probability that a randomly chosen functional group is either unreacted or reacted with the functional groups which are connected only to the sol part. We thus confirm that the value $u(\zeta_0)$ is actually the probability u discussed in the section 2. By using this definition, eq 3.1 is transformed to

$$S = \zeta_0 u(\zeta_0) \tag{3.5}$$

On the other hand, we see that the sol fraction is also given by

$$S = u(\zeta_0)^f \tag{3.6}$$

since a chain belongs to the sol if all functional groups it carries are connected to the sol. These two different pictures lead to the same result if the path probability ζ_0 satisfies the algebraic equation

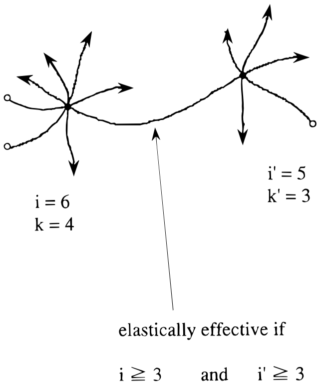

Figure 3. Scanlan–Case criterion for a network subchain to be elastically effective. A subchain connected to junctions with $i \ge 3$ at both ends is regarded as elastically effective.

$$x = u(x)^{f-1} \tag{3.7}$$

The smallest root must be taken if this equation has more than one solution. Hereafter we refer to the smallest root of this equation as x_1. In the special case of pairwise junction, this equation reduces to the conventional result of Flory:[21,22]

$$x = (1 - \alpha + \alpha x)^{f-1} \tag{3.8}$$

Once the sol fraction is found, the gel fraction is obtained by $G = 1 - S$.

We now employ the aforementioned criterion of Scanlan[15] and Case[16] to decide whether a subchain connected to two junctions of the type (i, k) and (i', k') at its ends is elastically effective or not (see Figure 3): only subchains connected at both ends to junctions with at least three paths to the gel are elastically effective. We thus have i, $i' \ge 3$ for an effective chain. A junction with one path ($i = 1$) to the gel unites a group of subchains dangling from the network matrix the conformations of which are not affected by an applied stress. A junction with two paths ($i = 2$) to the gel merely extends the length of an effective subchain. We may call the junctions with $i \ge 3$ elastically effective junctions. An effective subchain is defined as a chain connected to two effective junctions at its both ends. We thus find

$$\mu_{\mathrm{eff}} = \sum_{k=2}^{\infty}\sum_{i=3}^{2k}\mu_{i,k} = (f\nu\alpha)\left[\int_{\zeta_0}^{1}\theta(x)\,\mathrm{d}x - (\zeta_1+\zeta_2)\theta(\zeta_0) - \frac{1}{2}(\zeta_1)^2\theta'(\zeta_0)\right] \tag{3.9}$$

for the number of elastically effective junctions in unit volume and

$$\nu_{\mathrm{eff}} = \frac{1}{2}\sum_{k=2}^{\infty}\sum_{i=3}^{2k} i\mu_{i,k} = \frac{1}{2}(f\nu\alpha)[(\zeta_1 + 2\zeta_2)(1-\theta(\zeta_0)) - (\zeta_1)^2\theta'(\zeta_0)] \tag{3.10}$$

for the number of elastically effective chains in unit volume, where $\theta'(x)$ is the derivative of the function $\theta(x)$. The essentially same result for ν_{eff} in the case of a single allowed multiplicity had been derived by Peniche-Covas *et al.* by an intuitive method.[23]

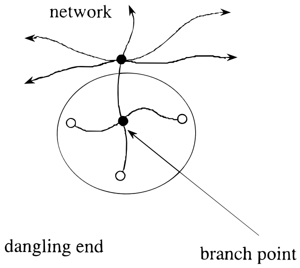

Figure 4. A dangling end with a single branch point and four subchains. It has three ends of the primary chains as indicated by circles.

Another important feature of the network is the number and structure of elastically inactive chains that are dangling from the network. We call them dangling ends. A dangling end may consist either of a single subchain or of a group of subchains connected by several branch points (see Figure 4). In thermoreversible gels, transitions from effective chains to dangling chains, and *vice versa*, are constantly taking place due to thermal motion and also to an applied deformation. The structure of a dangling end can be described by the number of subchains and branch points it contains. By definition, the number of dangling ends is given by

$$\nu_{\text{end}} = \sum_{k=2}^{\infty} \sum_{i=2}^{2k} (2k - i)\mu_{i,k} = (f\nu\alpha)[(\zeta_1 + 2\zeta_0)(1 - \theta(\zeta_0)) - 2\zeta_0\zeta_1\theta'(\zeta_0)] \quad (3.11)$$

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 branch points they have is then given by

$$\mu_b = (f\nu\alpha)\theta(\zeta_0)\zeta_1/\nu_{\text{end}} \quad (3.12)$$

All these equations are condensed descriptions of those derived by Pearson and Graessley.[17] Dušek and his coworkers[24] also used the Scanlan−Case criterion in their branching theory to address many aspects of loops and elastically effective and ineffective chains in the network. Although limited to the case of pairwise cross-linking, this method has an advantage over the above combinatorial method in introducing systematic corrections to the tree approximation.

More recently, the effect of junction multiplicity on the elastically effective chains was studied by te Nijenhuis.[25] His result reduces to the Morton−Ferry relationship[26] in the limit of pairwise cross-linking but differs from the above formula (3.10) derived on the basis of the Scanlan−Case criterion.

At this stage, we have to notice a special circumstance for the case of primary polymers carrying functional groups at their chain ends. Let us consider, for instance, telechelic polymers, *i.e.* polymers carrying only two functional groups, at both their ends ($f = 2$). Since a chain comes into, or goes out of, a junction with only one path (Figure 5), only the number i lying in the region $0 \leq i \leq k$ is allowed for the junction type (i, k). With the probability ζ_2 being identically zero, the combinatorial counting leads to

$$\mu_{i,k} = (f\nu\alpha)w_k\frac{(k-1)!}{i!(k-i)!}(\zeta_0)^{k-i}(\zeta_1)^i \quad (3.13)$$

in place of eq 2.6. Repeating all the calculations, we find that ν_{eff} and μ_{eff} remain the same, but the number of dangling ends becomes

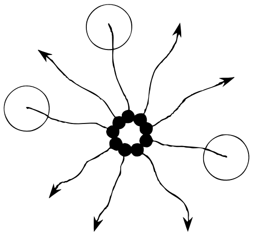

Figure 5. A junction formed by end-functional groups. Only one path comes out of each functional group in the junction. Circles show the dangling ends.

$$\nu_{\text{end}} = \sum_{k=2}^{\infty}\sum_{i=2}^{k}(k - i)\mu_{i,k} = (2\nu\alpha)\zeta_0[1 - \theta(\zeta_0) - \zeta_1\theta'(\zeta_0)] \quad \text{for telechelic chains only} \quad (3.14)$$

IV. Sol/Gel Transition with Junctions of Variable Multiplicity

The sol/gel transition point is defined by the point where the weight-average molecular weight of the clusters diverges. For polycondensation by multiple reaction the condition was found[19,20] to be given by

$$(f_{\text{w}} - 1)(\mu_{\text{w}} - 1) = 1 \quad (4.1)$$

where f_{w} is the weight-average functionality of the primary chains ($f_{\text{w}} = f$ for our model solution of monodisperse primary polymer chains), and

$$\mu_{\text{w}} \equiv \sum_{k\geq 1} kp_k \quad (4.2)$$

is the weight-average multiplicity of the junctions (including unreacted functional groups as $k = 1$ junctions). By definition (2.3), this average is given by

$$\mu_{\text{w}} = 1 + \alpha\theta'(1) \quad (4.3)$$

We therefore have

$$(f - 1)\alpha\theta'(1) = 1 \quad (4.4)$$

for the sol/gel transition condition. In the special case of a single allowed multiplicity, this equation reduces to the one found by Peniche-Covas *et al.*[23]

The weight-average multiplicity of the real junctions (excluding the unreacted functional groups) defined by

$$\langle k \rangle_{\text{w}} \equiv \sum_{k\geq 2} kw_k \quad (4.5)$$

is then given by

$$\langle k \rangle_{\text{w}} = 1 + \theta'(1) \quad (4.6)$$

This is often referred to as *average aggregation number* in the literature.

V. Network Characteristics as Functions of the Temperature and Concentration

So far we have presented all structural parameters of the network as functions of the extent of reaction (α) and the path probability (ζ_0). We now express them as functions of the thermodynamic variables such as the polymer concentration (ϕ) and the temperature (T). To do this we start from the definition (3.4) of the function $u(x)$.

In a previous paper[20] (referred to as TS) on the thermodynamic theory of gelation with multiple junctions, we studied interference between gelation and phase separation on the basis of the lattice-theoretical free energy of associating polymer solutions. By using Fukui-Yamabe's generalized tree statistics[19] for combinatorial counting, we derived the most probable distribution of clusters, and on this basis, we studied the solution properties. TS showed that the probability p_k of the k junction can be expressed as

$$p_k = K_k \psi^{k-1} p_1^k \tag{5.1}$$

due to the multiple-equilibrium conditions for the association–dissociation process, where K_k is the reaction constant for the formation of a k junction from separated k functional groups and ψ is the total number of functional groups in the solution. We have $\psi = f\nu$ for our model solution. Let us assume, as in TS, that the reaction constant takes the form

$$K_k = \gamma_k \lambda(T)^{k-1} \tag{5.2}$$

where $\lambda(T)$ is the association constant defined by

$$\lambda(T) \equiv \exp(-\beta \Delta g_0) \tag{5.3}$$

(where $\beta \equiv 1/k_B T$, the reciprocal temperature, Δg_0 is the standard free energy change for binding a functional group into a junction), and γ_k is the factor giving surface correction for the binding energy. On substitution of these definitions into eq 3.4, we find

$$u(x) = (1 - \alpha)\gamma(zx) \tag{5.4}$$

where a new function $\gamma(x)$ is defined by

$$\gamma(x) \equiv \sum_{k \geq 1} \gamma_k x^{k-1} \tag{5.5}$$

and the parameter z is defined by

$$z \equiv \lambda(T)\psi p_1 = \left(\frac{\lambda(T) f}{n}\phi\right)(1 - \alpha) \tag{5.6}$$

The volume fraction (ϕ) divided by the number of repeat units on a chain (n) gives the number of the primary chains in unit volume ($\nu = \phi/n$), and the parameter z depends only on the combination $\lambda(T)\nu$. In what follows, we therefore use $c \equiv \lambda(T)f\phi/n$ as a scaled polymer concentration. The parameter z is then given by

$$z = (1 - \alpha)c \tag{5.7}$$

which is essentially the number of functional groups remaining unassociated. From the definition of the function $\theta(x)$, we find

$$\theta(x) = \frac{1 - \alpha}{\alpha}[\gamma(zx) - 1] \tag{5.8}$$

and

$$w_k = \frac{1 - \alpha}{\alpha}\gamma_k z^{k-1} \tag{5.9}$$

The normalization condition $u(1) = 1$ then gives the relation

$$z\gamma(z) = c \tag{5.10}$$

or, equivalently,

$$1 - \alpha = 1/\gamma(z) \tag{5.11}$$

which was derived in TS. Solving this relation with respect to z, we find z, and hence α, as a function of the scaled concentration (c). Let us eliminate α from eq 5.8 by using the relation 5.11. We find

$$\theta(x) = (\gamma(zx) - 1)/(\gamma(z) - 1) \tag{5.12}$$

which gives the function $\theta(x)$ in terms of the concentration. Similarly, to find the zero path probability equation 3.7 is then transformed to

$$x = [\gamma(zx)/\gamma(z)]^{f-1} \tag{5.13}$$

The smallest solution (x_1) of this equation can now be found as a function of c.

Finally we can readily check that $\theta(1) = 1$ holds and its derivative is given by

$$\theta'(1) = \frac{\mathrm{d} \ln[\gamma(z) - 1]}{\mathrm{d} \ln z} \tag{5.14}$$

On substitution into the sol/gel transition criterion (eq 4.4) and by the use of the relation 5.7, we find

$$f' \frac{\mathrm{d} \ln \gamma(z)}{\mathrm{d} \ln z} = 1 \tag{5.15}$$

for finding the critical value of z as a function of the functionality and the multiplicity, where an abbreviation $f' \equiv f - 1$ has been used as in TS.

Before studying specific models of the junctions, we derive asymptotic forms of the network parameters in the extreme limit of complete reaction $\alpha \to 1$. In this limit the smallest root of eq 5.13 goes to zero ($x_1 \to 0$), and hence

$$\zeta_0 \to 0 \tag{5.16a}$$

$$\zeta_1 \to 2/f \tag{5.16b}$$

$$\zeta_2 \to 1 - 2/f \tag{5.16c}$$

The effective chains and junctions therefore show a limiting behavior

$$\frac{\nu_{\mathrm{eff}}}{\nu} \to f' - \frac{2}{f} w_2 \tag{5.17a}$$

$$\frac{\mu_{\mathrm{eff}}}{\nu} \to \frac{f}{\langle k \rangle_n} - \frac{2}{f} w_2 \tag{5.17b}$$

where $\langle k \rangle_n \equiv (\sum_{k \geq 2} w_k/k)^{-1}$ is the number-average junction multiplicity. For the dangling ends we find

$$\frac{\nu_{\mathrm{end}}}{\nu} \to 2 \tag{5.18}$$

as expected, because only the two ends of the primary chains remain dangling at the completion of association. In contrast, for telechelic polymers, we are led to the asymptotic behavior $\nu_{\mathrm{end}}/\nu \to 0$ from eq 3.14, again as expected.

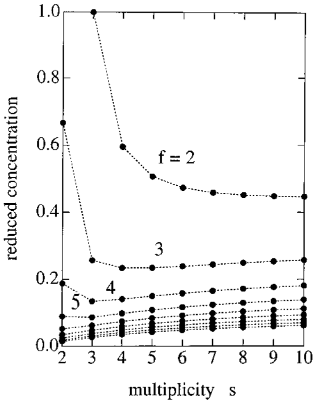

Figure 6. The sol/gel transition concentration plotted against the junction multiplicity. The functionality f is varied from curve to curve. It is a monotonically decreasing function of the multiplicity s for the functionality $f = 2$, but has an optimal s for $f = 3, 4, 5$. For f larger than 5, is steadily increases with s.

A. Fixed Multiplicity Model. The first model we study allows only one fixed number (s) of functional groups in a junction. We therefore have only $k = 1$ (unreacted) and $k = s$ (reacted). Since $w_s = 1$ with other w_k being zero, we find $\theta(x) = x^{s'}$, where $s' \equiv s - 1$, and

$$\gamma(z) = 1 + z^{s'} \tag{5.19}$$

The relation 5.10 is transformed into

$$\frac{\lambda(T)}{n}\phi = S_1(\alpha) \tag{5.20}$$

where a new function $S_1(\alpha)$ is defined by

$$S_1(\alpha) \equiv \frac{\alpha^{1/s'}}{f(1-\alpha)^{s/s'}} \tag{5.21}$$

This function reduces to the first moment of the Stockmayer distribution function[27] in the case of pairwise association $s = 2$. Solving this equation with respect to the extent α of reaction, we now find it as a function of the temperature and the polymer concentration. At the sol/gel transtion point we find

$$\alpha^* = 1/f's' \tag{5.22}$$

for the critical extent of reaction and

$$\frac{\lambda(T)}{n}\phi^* = \frac{f's'}{f(f's'-1)^{s/s'}} \tag{5.23}$$

for the (reduced) critical polymer concentration. This critical concentration is plotted in Figure 6 as a function of the multiplicity. The functionality f is changed from curve to curve. It turns out that, for $f = 2$, the critical concentration is a decreasing function of s (gelation is easier for higher multiplicity, as it should be), but for f larger than 5, it is an increasing function of s (gelation is easier for lower multiplicity). For $f = 3, 4, 5$, there is an optimal value of s for gelation. Detailed comparison of this result to the experimental sol/gel transition concentration has recently been made by one of the authors and Nishinari.[28]

Now, the equation to find x_1 takes the form

$$x = (1 - \alpha + \alpha x^{s'})^{f'} \tag{5.24}$$

the solution of which is formally given by

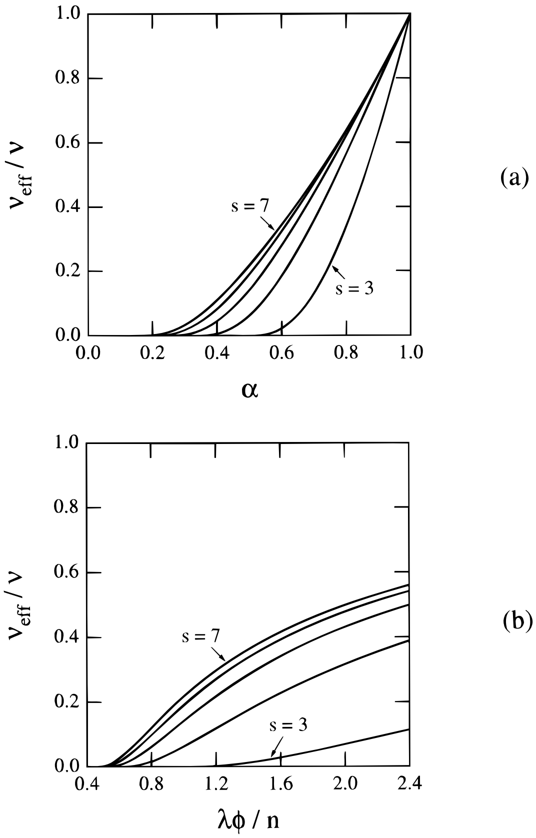

Figure 7. The number of elastically effective chains (relative to the total number of chains) as a function of the extent of reaction (a), and of the reduced concentration (b). The multiplicity is changed from curve to curve, while the functionality is fixed at $f = 2$. Each curve rises in cubic power of the concentration deviation from the transition point and approaches unity at the high limit of the concentration.

$$x_1 = \left[\frac{\alpha'(1-\alpha)}{\alpha(1-\alpha')}\right]^{1/s'} \tag{5.25}$$

Here α' is a solution of the equation

$$(\alpha')^{1/s'}(1-\alpha')^{f'-1/s'} = \alpha^{1/s'}(1-\alpha)^{f'-1/s'} \tag{5.26}$$

that lies in the pregel regime ($\alpha' < \alpha^*$) for a given value of α ($>\alpha^*$). This smaller root refers to the average extent of the reaction in the sol. Our method thus reduces to the conventional treatment of the postgel regime by Flory[21,22] in the special case of pairwise association $s = 2$ for $f \geq 3$. The elastically effective chains in physical gels for this case were calculated by Clark and Ross-Murphy.[18]

We now examine the opposite case where polymers carry only two functional groups $f = 2$ but form multiple junctions with $s \geq 3$. We find $\zeta_0 = x_1$, $\zeta_1 = 1 - x_1$, and $\zeta_2 = 0$. The last relation, $\zeta_2 = 0$, is obvious because an unreacted functional group on a chain can only be connected to the gel through the chain carrying it (*i.e.* $i = 1$) in the special case of $f = 2$. The number of effective chains now becomes

$$\nu_{eff}/\nu = \alpha(1 - x_1)(1 - s'x_1^{s''} + s''x_1^{s'}) \tag{5.27}$$

Similarly the number of effective junctions and of dangling ends take the form

$$\mu_{eff}/\nu = (2\alpha/s)[1 - (x_1^{s''}/2)(s's''x_1^2 - 2ss''x_1 + ss')] \tag{5.28}$$

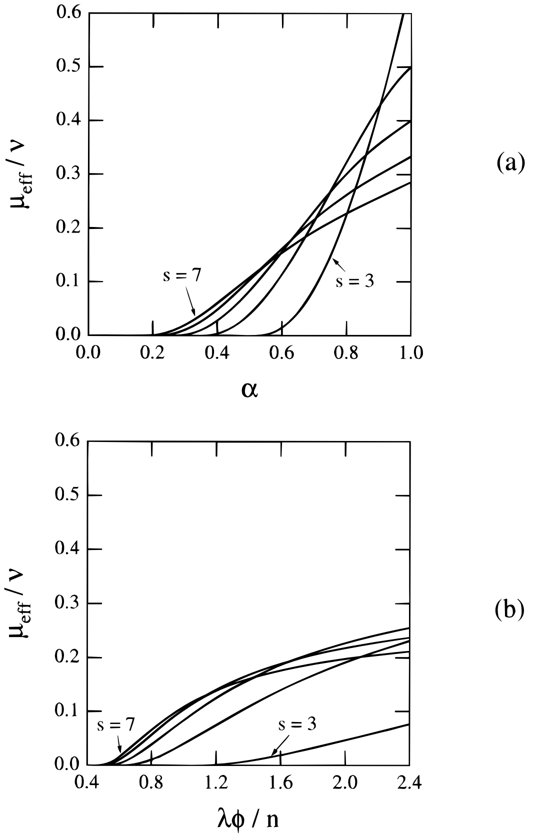

Figure 8. The number of elastically effective junctions as a function of the extent of reaction (a) and of the reduced concentration (b). The multiplicity is changed from curve to curve, while the functionality is fixed at $f = 2$. Each curve rises in cubic power of the concentration deviation from the transition point and approaches $2/s$ at the high limit of the concentration.

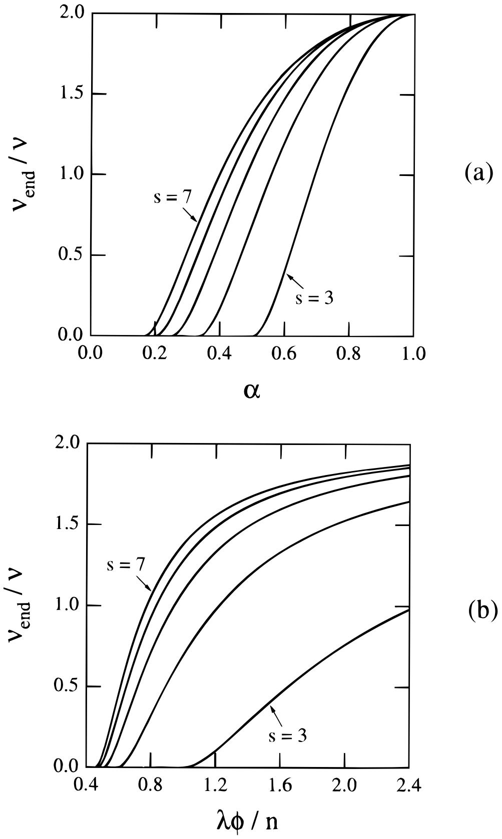

Figure 9. The number of dangling ends as a function of the extent of reaction (a) and of the reduced concentration (b). The multiplicity is changed from curve to curve, while the functionality is fixed at $f = 2$. All curves approach 2 at the high limit of the concentration because only both ends of each chain remain dangling in this limit.

and

$$\nu_{end}/\nu = (2\alpha)[1 + x_1 - (2s - 1)x_1^{s'} + (2s - 3)x_1^{s}] \tag{5.29}$$

The slightly modified form

$$\nu_{end}/\nu = (2\alpha)(1 - s'x_1^{s''} + s''x_1^{s'})x_1 \tag{5.30}$$

must be used for telechelic polymers.

Figure 7 shows the number of elastically effective chains for $f = 2$ with s varied from curve to curve as a function of the extent of reaction (part a) and of the reduced concentration (part b). The critical behavior obeys the mean-field scaling law

$$\nu_{eff}/\nu \simeq (\phi - \phi^*)^t \tag{5.31}$$

with $t = 3$. The cubic power comes of course from the mean-field treatment (tree statistics). According to percolation theory, we should expect a smaller power, $t = 1.7$.[29] At the completion of the reaction, $\alpha = 1$ (and hence $\lambda\phi/n \rightarrow \infty$), and the curves asymptotically reach unity. The number of effective chains is proportional to the polymer concentration in this region.

Figure 8 shows the number of elastically effective network junctions as a function of the extent of reaction (a) and of the reduced concentration (b). Each curve rises as the cube of the concentration deviation from the gel point and reaches a finite value $2/s$ at high concentration. The number of dangling ends and the average number of branch points in each dangling end are shown in Figures 9 and 10. All curves for the dangling ends reach 2, and all curves for the branch points vanish at the limit of high concentration (or completion of association), because only both ends of the primary chains can remain dangling in this limit.

The simplest model network is the one formed by bifunctional ($f = 2$) primary chains with triple junctions ($s = 3$). In this special case, we find $\alpha' = 1 - \alpha$, where α is the root of the third order algebraic equation $c^2\alpha^3 + \alpha - 1 = 0$. The larger one lying in $0 \leq \alpha \leq 1$ must be chosen for α in order for α' to be the smaller root of eq 5.26. All network properties are analytically expressed. We have, for example, $\zeta_0 = (1 - \alpha)/\alpha$, $\zeta_1 = (2\alpha - 1)/\alpha$, $\zeta_2 = 0$, and

$$\nu_{eff}/\nu = (2\alpha - 1)^3/\alpha^2 \tag{5.32a}$$

$$\mu_{eff}/\nu = 2(2\alpha - 1)^3/3\alpha^3 \tag{5.32b}$$

Since the critical extent of reaction is given by $\alpha^* = 1/2$, the cubic power near above the sol/gel transition point is evident.

These curves can be compared with the experimental data on the high frequency dynamic modulus for HEUR measured by Annable *et al.*[2] Their experimental data for HEUR C16/35K (end-capped with $C_{16}H_{33}$, molecular weight 35 000, Figure 19 in ref 2) are replotted in Figure 11. If we choose $c^* = 1.0\%$ for the weight concentration at gelation, the scaling power at the critical region gives $t = 1.6$, close to the percolation value. But since this power depends sensitively on how we choose c^*, more

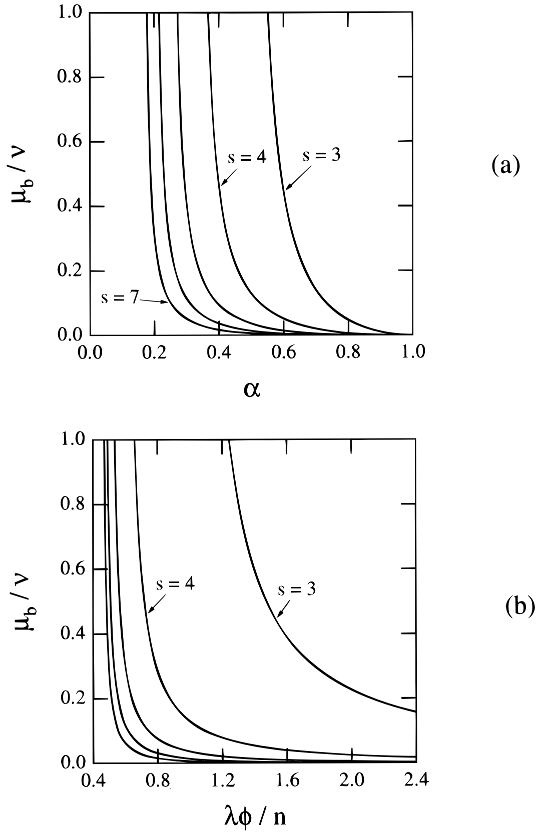

Figure 10. The average number of branch points in a dangling end as a function of the extent of reaction (a) and of the reduced concentration (b). The multiplicity is changed from curve to curve, while the functionality is fixed at $f = 2$.

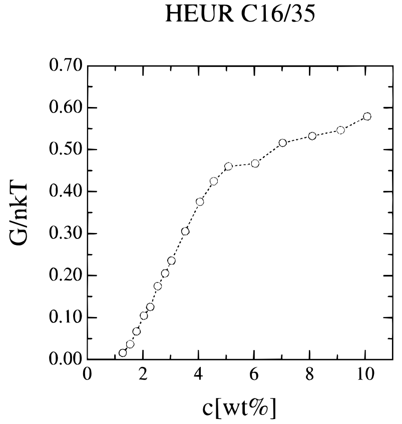

Figure 11. The high-frequency storage modulus of HEUR 16C/35K measured by Annable *et al.* is replotted against concentration on the linear scale. If one choose $c^* = 1.0$ wt % for the gelation concentration, the initial slope is estimated to be 1.6.

detailed experimental examination in the critical region is eagerly required. In Figure 12 fitting the experimental curve by our theoretical calculation is attempted. Because of the temperature prefactor $\lambda(T)$ and also the difference in the unit of the polymer concentration, we have horizontally shifted the experimental data. Although fitting by a single theoretical curve with a fixed multiplicity is impossible because of the existence of polydispersity in the multiplicity, our theory produces correct behavior over a wide range of the concentration.

Another simple case is the pairwise association $s = 2$ for arbitrary functionality f. The number of elastically effective chains was calculated by Clark and Ross-Murphy.[18] Their result can be reproduced by choosing

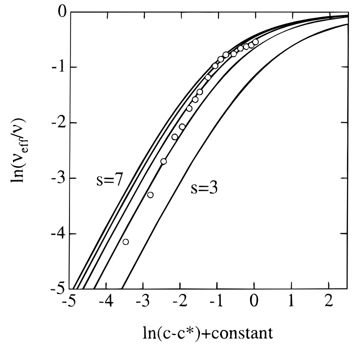

Figure 12. Comparison of the HEUR 16C/35K data with the theoretical calculation. The experimental data are horizontally shifted.

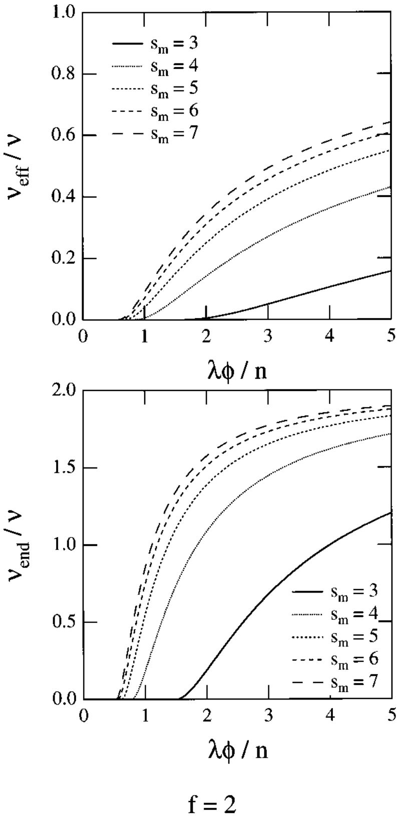

Figure 13. The number of elastically effective chains and dangling ends in the saturating junction model as a function of the scaled polymer concentration for primary polymers of functionality 2. The maximum multiplicity (s_m) is varied from curve to curve.

the function $\gamma(x)$ in eq 5.5 as $\gamma(x) = 1 + x$. We find α as

$$\alpha = \frac{1}{2c}(1 + 2c - \sqrt{1 + 4c}) \qquad (5.33)$$

in an explicit form from eq 5.20. The critical values are $\alpha^* = 1/f'$ and $c^* = (f'')^{f''}/(f')^{f'}$. Straightforward calculation leads to the result

$$\nu_{\text{eff}}/\nu = f\alpha(3\zeta_1 + 2\zeta_2)\zeta_2/2 \qquad (5.34a)$$

$$\mu_{\text{eff}}/\nu = f\alpha(2\zeta_1 + \zeta_2)\zeta_2/2 \qquad (5.34b)$$

where ζ values are given by eqs 2.4a–c with x_1 being the root of eq 3.8. The above formulae for the effective chains and junctions were first derived by Langley and Polmanteer.[30] For trifunctional ($f = 3$) primary chains, we find explicitly

$$\nu_{\rm eff}/\nu = (2\alpha - 1)^3(5 - \alpha)/3\alpha^3 \qquad (5.35a)$$

$$\mu_{\rm eff}/\nu = (2\alpha - 1)^3/\alpha^2 \qquad (5.35b)$$

B. Variable Multiplicity Model. We now allow junctions to take a wide range of multiplicities. TS considered two important models of variable multiplicity. In thermoreversible gels with junctions formed by ionic dipolar interaction or hydrophobic aggregation, the space surrounding a junction is densely packed with polymer chains, so its multiplicity has an upper limit ($s_{\rm m}$) due to steric hindrance among the chains. For such *saturating junctions*, the multiplicity is allowed to take a limited range $k = 1, 2, ..., s_{\rm m}$. We then find

$$\gamma(z) = (1 - z^{s_{\rm m}})/(1 - z), \qquad (5.36)$$

and

$$\theta(x) = x(1 - z)(1 - z^{s_{\rm m}}x^{s_{\rm m}})/(1 - zx)(1 - z^{s_{\rm m}}) \qquad (5.37)$$

for the necessary functions to calculate network properties. Here we have neglected the surface correction to the junction free energy and put $\gamma_{\rm k} = 1$ for all k allowed. For $s_{\rm m} = 2$, the calculation reduces to the $s = 2$ case of the fixed multiplicity model studied above.

In contrast, in gels with microcrystalline junctions, the size of a junction is controlled by the nucleation process of the crystallites. For a crystallite to remain thermodynamically stable, its size must exceed the critical value s_0, which depends on the degree of supercooling and also on the thermal history of the sample treatment. A junction is therefore allowed to take the multiplicity $k = 1$ (unreacted) and $k = s_0, s_0 + 1, ...,$ although extremely high multiplicities are highly improbable. For such junctions with a minimum multiplicity, we find

$$\gamma(z) = 1 + z^{s_0'}/(1 - z) \qquad (5.38)$$

and

$$\theta(x) = x^{s_0'}(1 - z)/(1 - zx) \qquad (5.39)$$

where $s_0' \equiv s_0 - 1$ as above.

Figure 13 shows the number of elastically effective chains and dangling ends in the saturating junction model as a function of the scaled polymer concentration for primary polymers of functionality 2. The maximum multiplicity $s_{\rm m}$ is varied from curve to curve. Because junctions of $k = 2$ in the saturating junction models with $f = 2$ merely extend the length of effective chains, the relative number of effective chains cannot reach unity even in the limit of complete reaction. Although $f = 2$, this calculation is done for nontelechelic polymers, so $\nu_{\rm end}/\nu$ tends to 2 (both ends per chain) for all maximum multiplicities in the limit of complete reaction as is expected.

Figure 14 shows the number of elastically effective chains and dangling ends in the minimum-junction model. The minimum multiplicity (s_0) is varied from curve to curve for a fixed functionality $f = 2$. The particular case of $s_0 = 2$ gives a gel network the junction multiplicity of which is allowed to take any value.

The importance of polydispersity in the junction multiplicity may be examined by comparing these theoretical calculations with experimental data on the temperature and concentration dependence of the gel fraction and storage moduli. A full analysis will be done awaiting the detailed measurements in the postgel regime.

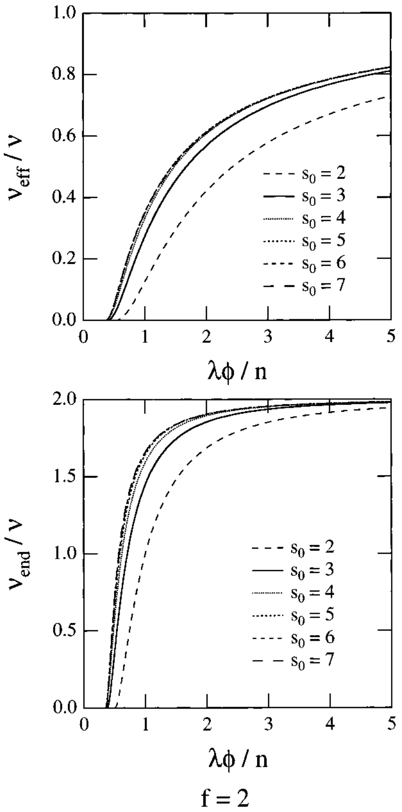

Figure 14. The number of elastically effective chains and dangling ends in the minimum-junction model. The minimum multiplicity (s_0) is varied from curve to curve for a fixed functionality $f = 2$.

VI. Conclusions and Discussion

On the basis of our recent theory of thermoreversible gelation with junctions of variable multiplicity, we have derived the number of elastically effective chains and other important network parameters as functions of the temperature and the polymer concentration. They are shown to be functions of a reduced concentration [$c \equiv \lambda(T)f\phi/n$] within the scheme of the multiple tree statistics. For instance, the number of effective chains can be expressed by a universal curve

$$\nu_{\rm eff}/\nu = \Phi(c) \qquad (6.1)$$

for a given associative interaction. The experimental data at different temperatures are therefore expected to be superimposed on a single master curve by a simple horizontal shift.

Theoretical calculations for several simple models of multipicity were compared with recent experiments on associating polymers. In transient networks of associating polymers, the average number of effective chains is decided by the balance between the chain disengagement rate β_0 and the chain recombination rate p. The equilibrium number is given by eq 1.3. Near the gelation concentration, the recombination rate is small compared to unity so we may write

$$p/\beta_0 \simeq \Phi(c) \qquad (6.2)$$

The chain recombination rate must of course be proportional to the number of effective junctions around the reactive chain end, which is essentially proportional to the number of effective chains in this region. On the other hand, the condition $p/\beta_0 \gg 1$ holds for sufficiently high concentrations so that ν_{eff}/ν approaches unity. The Scanlan−Case criterion, including these two extreme regions, produces the correct concentration dependence of the network parameters.

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