Viscoelastic Properties of Physically Cross-Linked Networks. Transient Network Theory

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ABSTRACT: A simple model is introduced to describe the dynamics of physically cross-linked networks in which junctions are sufficiently weak to break and recombine in thermal fluctuations. The time-evolution equation under arbitrary macrodeformation is derived for the creation and annihilation of the junctions—and hence for the number of elastically effective polymer chains with a fixed end-to-end vector. We focus our attention specifically on the *unentangled networks* in which the molecular weight M_x between neighboring junctions is smaller than the entanglement molecular weight M_e, so that each chain obeys Rouse dynamics modified by sticky trapping centers rather than reptation. Stress–strain relation under shear and elongational deformation is detailed for a model network which is made up of polymers of uniform length with associating functional groups at their chain ends. On longer time scales than the junction breakage time, the total number of effective chains decreases with time—resulting in an intranetwork flow.

1. Introduction

In most polymer blends or solutions of practical interest, polymer chains carry specific groups interacting with each other by associative forces capable of forming bonds, and hence a description in terms of van der Waals type interaction—or χ *parameter* in lattice-theoretical terminology—is insufficient. These forces include hydrogen bonding, ionic association, stereocomplex formation, cross-linking by the crystalline segments, and solvent complexation. In most common cases the bonding energy is comparable to the thermal energy, so that the bond formation is reversible by the change in temperature or concentration. Thermodynamics of network formation and multiphase competition were studied by the present authors[1,2] to describe phase behavior peculiar to the polymer fluids interacting via specific associating forces. The present paper concerns dynamic properties of the thermoreversible networks (or *physical gels*) to study enhanced viscoelasticity due to the presence of the temporal junctions.

There has been an accumulation of evidences that networks with reversible junctions exhibit highly enhanced viscoelastic properties which are quite different from ordinary polymer melts. Typical examples of the experimental studies can be taken from biological macromolecules[3-5] in which networks are formed by hydrogen bonding. It turned out that a mechanical spectrum of dynamical moduli does not show any softening in low frequencies but is rather insensitive over a wide range of frequencies covering from 10^{-2} to 10^2 rad/s and also that relaxation of stress does not seem to obey a simple exponential decay but is rather well described by a power law.[4] It was also found that the complex viscosity is in most cases larger than the stationary viscosity when compared at the frequency which is the same as the stationary shear rate, thus suggesting a failure of the Cox–Merz rule.

Another example in current research is that of thermoplastic elastmers[6,7] in which synthetic polymers are cross-linked by specific associating groups. These include, in addition to the hydrogen bonding, charge (electron) transfer, ion pairing, acid–base interaction, dipole–aromatic ring interaction, and coordination with metallic ions. They range from strong ionic interactions to weak dispersive interactions. Viscoelastic measurements of ionomers,[8] for instance, revealed the following three characteristics: the glass temperature is increased due to the reduced mobility of a polymer chain as a result of the physical cross-linking, the rubbery plateau is extended, and a high-temperature mechanical loss appears due to the breakage and reorganization of the cross-links. Despite the vast amount of experimental data, no systematic theoretical study on the dynamics of reversible networks has been reported so far.

To get an idea of the dynamical mechanical properties of physically cross-linked networks, one must realize that there are two clearly distinct categories—that is, entangled networks and unentangled networks. In an *unentangled network* in which the average molecular weight M_x of a chain connecting the two neighboring temporal junctions is smaller than the entanglement molecular weight M_e, the major part of the stress is sustained by the elastically active chain strands spanning the junctions, while in an *entangled network* in which the opposite relation $M_x > M_e$ holds, localized entanglements play a role apparently similar to the cross-linked junctions.

The first systematic study on the reversible networks was the *transient network theory* developed by Green and Tobolsky,[9] in which stress relaxation in rubberlike polymer networks was treated by the kinetic theory of rubber elasticity suitably extended so as to allow for the creation and annihilation of junctions during the network deformation. In order to ensure a wider range of applicability, some arbitrary assumptions in their theory were later removed by Lodge[10] and Yamamoto[11] with the intention to apply it to the entangled melts[12] (rather than the reversible networks). In their studies, to describe the observed viscoelastic properties of ordinary polymer melts, localized entanglements were regarded as the temporal junctions which can be created and destroyed during the macroscopic deformation. Because of the lack of detailed knowledge about the molecular mechanism of junction generation (onset of entanglements), their theories, however, remain semiphenomenological.

Another stream of study of temporal networks concerns a model network whose history involves cross-links added in a certain stage, a part of which are subsequently removed so as not to be present in the final stage of deformation

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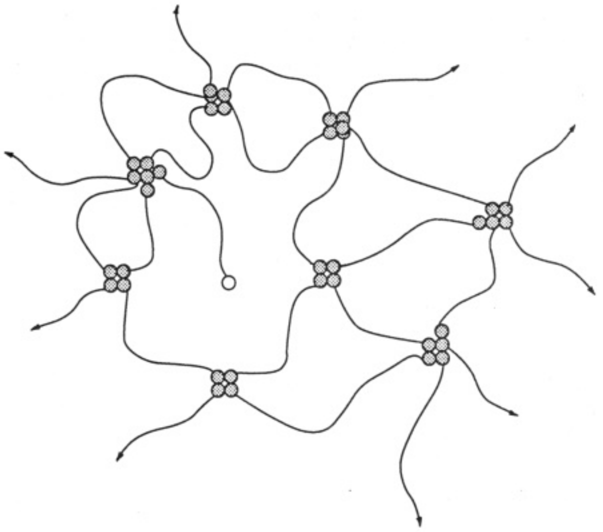

Figure 1. Model network made up of polymer chains with sticky end groups. A dangling end is shown by the open circle.

(*addition–subtraction network*). On the basis of such a model composite network, Flory[13] calculated the stress relaxation, finding that it obeys slow dynamics including a logarithmic dependence $\sigma(t)/\sigma(0) \sim 1/\beta t \log \beta t$, which is closer to a power law rather than an exponential. Flory's intuitive argument was later confirmed by Fricker[14] with minor modification through a replica calculation. Owing to the rather arbitrary assumption about chain creation and annihilation, the addition–subtraction network model provides no firm molecular base to describe the real physical gels.

Dependence of the final network properties on its construction history including more than two steps was elucidated by Baxandall and Edwards[15] starting from the first principles of statistical mechanics. In the special case where cross-links are successively introduced into a basis network in different stages of strains (a *multiadditional* network), explicit results on the elastic free energy and the structure factor were derived.

In this paper, and subsequent ones, we consider dynamic properties of physical gels in the unentangled regime. We propose a new type of transient network theory to ensure a molecular picture which is suitable to describe real networks in which cross-links are actually generated and destroyed. We find a specific form of the junction generation function, which is dependent on the number of active chains present at the moment of linkage—and hence dependent on the macrodeformation at the same moment. Stationary viscoelasticity, dynamic linear response, stress relaxation, and transient phenomena including stress overshoot are explored in this series of papers. The relation to the Flory's work is also discussed.

2. Models of Transient Networks

The model we consider in this paper is a network made up of n polymer chains with uniform molecular weight M (or the number of monomers N), each connected to the junctions through sticky functional groups attached on both ends (see Figure 1). Junctions comprised of an arbitrary number of chain ends are allowed. We assume $M \ll M_e$, so that the effect of the external force can spread over the entire network through the junctions without any topological hindrance. There are two kinds of chains in the network: elastically active chains and dangling chains. A chain whose both ends are connected to the separate junctions—shown by filled circles in Figure 1—is called an *elastically active* (or *effective*) chain because stress is transmitted from one junction to another along this chain, while a chain with either end attached to any junction—shown by a open circle in Figure 1—is called a *dangling* chain because it is almost free from the effect of external forces. (The stress transfer by a dangling chain is made only through friction with its surrounding chains, which is negligibly small compared with that made by the deformation of active chains under the unentangled assumption.)

If one end of an active chain snaps from a junction due to thermal motion or a tension caused by the external force, the chain relaxes into an equilibrium state and becomes dangling after a lapse of the single-chain relaxation time τ (which is on the order of a Rouse relaxation time). It is the change in macroscopic properties of the network on a time scale slower than τ that is the concern of this paper.

2.1. Chain Distribution Function.

We start from the assumption that viscoelastic properties of our network on a slower time scale than τ are controlled by the elastically active chains. The first thing we must do is to derive a time-evolution equation for the number of active chains under a macroscopic deformation.

Consider a time-dependent deformation described by the tensor $\hat{\lambda}(t)$, which is exerted on the network at time $t = 0$ and evolves with arbitrary time dependence. In order to derive a dynamic equation on a time scale larger than τ, let us choose a time interval Δt, which is small enough from a macroscopic point of view but still larger compared to τ, and let us divide the continuous time into discrete steps by using this unit Δt such that the jth time is given by $t_j \equiv j\Delta t$ ($j = 0, 1, 2, ...$). The deformation tensor $\hat{\lambda}(t)$ can be transformed into a product of small successive deformations

$$\hat{\lambda}(t) = \prod_{j=1}^{n} \hat{\gamma}_j \tag{2.1}$$

where the jth deformation $\hat{\gamma}_j$ is defined by

$$\hat{\gamma}_j \equiv \hat{\lambda}(t_j)\cdot\hat{\lambda}(t_{j-1})^{-1} \tag{2.2}$$

Consider next the chain distribution function $F_n(\mathbf{r}_n)$ which is defined by

$$F_n(\mathbf{r}_n)\,\mathrm{d}\mathbf{r}_n \equiv \left\{ \begin{array}{l} \text{the number of elastically effective} \\ \text{chains whose end-to-end vectors fall} \\ \text{on the small volume } (\mathbf{r}_n, \mathbf{r}_n + \mathrm{d}\mathbf{r}_n) \\ \text{after } n\text{th deformation} \end{array} \right. \tag{2.3}$$

The total number ν_n of the chains which remain active is then given by

$$\nu_n \equiv \int \mathrm{d}\mathbf{r}_n\, F_n(\mathbf{r}_n) \tag{2.4}$$

In order to define our problem clearly, we introduce two fundamental assumptions on the chain configuration at this stage:

(i) All chains are Gaussian in the stress-free state.

(ii) An end-to-end vector of any active chain deforms affinely to the macroscopic deformation tensor.

Both of these assumptions could be removed by introducing a more realistic chain model appropriate to describe large deformations and also by considering the fluctuation in the junction position. These are outside the scope of the present paper.

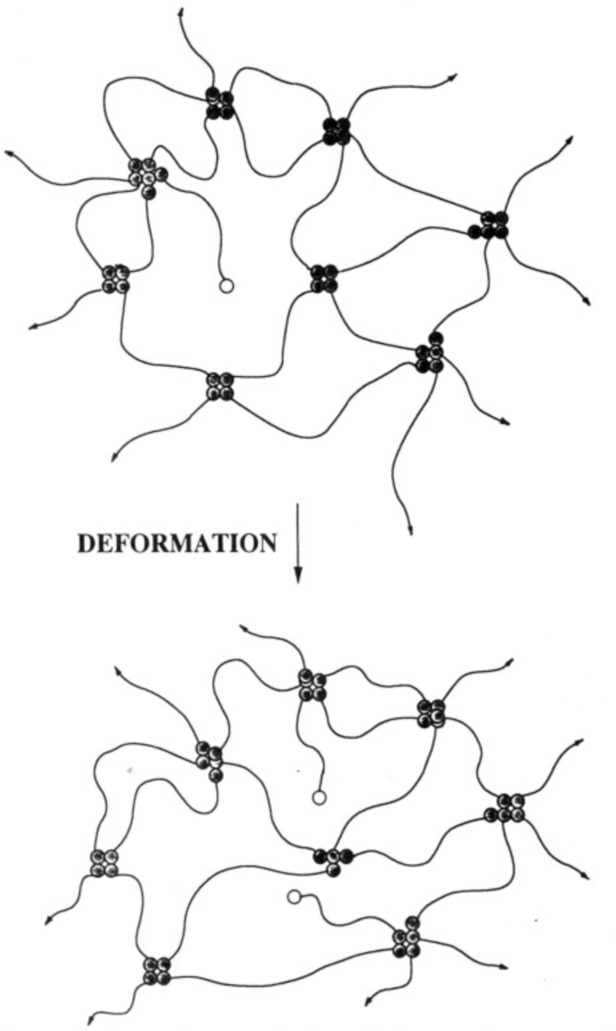

Figure 2. Internal reorganization of the transient network induced by a macroscopic deformation. Chains suffering from high tension snap from the junctions and form dangling ends, while some dangling chains catch sticky junctions in the course of thermal movement.

By assumption ii we have

$$\mathbf{r}_n = \hat{\gamma}_n\cdot\mathbf{r}_{n-1} = \ldots = \hat{\lambda}(t_n)\cdot\mathbf{r}_0 \tag{2.5}$$

where $\mathbf{r}_0$ is a chain vector in the initial state. Next we consider the change in the number of active chains in a small interval Δt after the ith deformation $\hat{\gamma}_i$ is given to the system (see Figure 2). Conventional affine network theory[16] for a network with permanent cross-links assumes that the number of chains is conserved; that is

$$F_i(\mathbf{r}_i)\,\mathrm{d}\mathbf{r}_i = F_{i-1}(\mathbf{r}_{i-1})\,\mathrm{d}\mathbf{r}_{i-1} \tag{2.6}$$

In our temporal network, however, active chains are temporarily created and annihilated, and, as a result, the number of chains with a given end vector is a function of time. In order to consider how an active chain is broken into a dangling one, let us consider the tension along the chain. It seems plausible to suppose that either end of the chain snaps from the junction to which it is attached as soon as the tension supported by the chain exceeds a critical value. This critical value is related to the strength of the junction and hence the free energy Δf of the bond formation. Since the tension is proportional to the end-to-end distance in a Gaussian chain, it follows that there should be a critical end-to-end distance r^* above which an active chain snaps from the junction. This distance — *cutoff length*—is proportional to $\exp(\Delta f/k_BT)$. An active chain, whose end-to-end distance $|\mathbf{r}|$ lies below r^*, still has the probability to break by random thermal motion at the very moment when the fluctuation due to the Brownian movement concentrates by chance to the extent that its instantaneous tension exceeds the critical value. Let $\beta(\mathbf{r})$ be the probability per unit time for such an event to occur. It is a steadily increasing function of r and called the *chain breakage probability* in the conventional transient network theory.[9-11] The number of chains which remain active after $\hat{\gamma}_i$ is therefore reduced to

$$\theta(r^*-r)[1-\beta(\mathbf{r}_i)\Delta t]F_{i-1}(\mathbf{r}_{i-1})\,\mathrm{d}\mathbf{r}_{i-1} \tag{2.7}$$

for our temporal network.

We next consider the molecular process of how an active chain is created. A dangling chain, after relaxing into the equilibrium state, can capture one of the junctions in its neighborhood by its reactive dangling end (see Figure 2). Let p be the *recombination rate*—that is, the probability per unit time for such a recombination to take place. The number of active chains Δn_i produced during the time interval Δt in the ith step must be proportional to the number of the dangling chains; hence, we have

$$\Delta n_i = p\Delta t(n - \nu_i) \tag{2.8}$$

because there are a total of $n - \nu_i$ dangling chains in this stage. Since each dangling chain is Gaussian, the number

$$\Delta n_i f_0(\mathbf{r}_i)\,\mathrm{d}\mathbf{r}_i \tag{2.9}$$

of active chains is generated in the volume $(\mathbf{r}_i, \mathbf{r}_i + \mathrm{d}\mathbf{r}_i)$, where

$$f_0(\mathbf{r}) = \left(\frac{3}{2\pi Na^2}\right)^{3/2}\exp\left(-\frac{3r^2}{2Na^2}\right) \tag{2.10}$$

is a Gaussian chain distribution, whose average end distance is given by $\langle r^2\rangle_0 = Na^2$. The probability p depends on the molecular weight of the chain, temperature, and reactivity of the end groups.

Putting (2.7) and (2.9) together, we finally come to a recursion relation

$$F_i(\mathbf{r}_i)\,\mathrm{d}\mathbf{r}_i = \theta(r^*-r_i)[1-\beta(\mathbf{r}_i)\Delta t]F_{i-1}(\mathbf{r}_{i-1})\,\mathrm{d}\mathbf{r}_{i-1} + \Delta n_i f_0(\mathbf{r}_i)\,\mathrm{d}\mathbf{r}_i \tag{2.11}$$

from which our theory starts. This equation relates the chain distribution function at an arbitrary stage to one a step earlier. By iteration we can express it in terms of the initial distribution.

2.2. Initial Value Problem. Iterating the recursion relation from the first step to the nth, we find a relation

$$F_n(\mathbf{r}_n)\,\mathrm{d}\mathbf{r}_n = \zeta_{n,1}F_0(\mathbf{r}_0)\,\mathrm{d}\mathbf{r}_0 + \sum_{i=1}^{n}\zeta_{n,i}\Delta n_i f_0(\mathbf{r}_i)\,\mathrm{d}\mathbf{r}_i \tag{2.12}$$

where $\zeta_{n,i}$ is defined by

$$\zeta_{n,i} \equiv \prod_{j=i}^{n}\theta(r^*-r_j)[1-\beta(\mathbf{r}_j)\Delta t] \tag{2.13}$$

This relation gives the chain distribution function at an arbitrary step under a given initial distribution.

We next take the $\Delta t \to 0$ limit to obtain the continuous-time counterpart of this relation. The discrete time n is replaced by the continuous one defined by $t \equiv n\Delta t$, and we have a time-dependent distribution function $F(\mathbf{r},t)$ instead of $F_n(\mathbf{r}_n)$. The limit leads to the equation

$$F(\mathbf{r},t)\,\mathrm{d}\mathbf{r} = \Theta(\mathbf{r},t;\mathbf{r}_0,0)\,F(\mathbf{r}_0,0) + \int_0^t\Theta(\mathbf{r},t;\mathbf{r}',t')\,m(t')\,f_0(\mathbf{r}')\,\mathrm{d}\mathbf{r}' \tag{2.14}$$

where the two-point function Θ is defined by

$$\Theta(\mathbf{r},t;\mathbf{r}',t') \equiv [\lim_{\Delta t\to 0} \prod_{j=i}^{n} \theta(r^*-r_j)] \exp[-\int_{t'}^{t} \beta(\mathbf{r}_{t'',t'})\,\mathrm{d}t''] \tag{2.15}$$

This function provides the *survival probability*—that is, the probability for a given active chain with $\mathbf{r}'$ at time t' to remain active until time t when it has an end vector $\mathbf{r}$. The front factor has arisen from the existence of a cutoff length. In the following we absorb it into β by taking β to include a term $-[\ln \theta(r^*-r_{t'',t'})]/\tau$, so that it diverges as soon as the end distance exceeds r^*. Thanks to the affine assumption, $\mathbf{r}$ is related uniquely to $\mathbf{r}'$ through the equation

$$\mathbf{r} = \hat{\lambda}(t)\cdot\hat{\lambda}(t')^{-1}\cdot\mathbf{r}' \tag{2.16}$$

The first term in (2.14) therefore gives the number of chains which, being active in the initial state, survive until time t. The function $m(t)$ in the second term of (2.14) is the number of active chains created in a unit time:

$$m(t) \equiv \lim_{\Delta t\to 0} \frac{\Delta n}{\Delta t} = p(n - \nu(t)) \tag{2.17}$$

This term therefore gives the number of active chains which are created at time t' with end-to-end vecotr $\mathbf{r}'$ and remain active until t. Since this term depends on the space integral of $F(\mathbf{r}',t')$ through $\nu(t')$, (2.14) is not an explicit solution of the initial value problem, but it gives rather an *integral equation* for $F(\mathbf{r},t)$.

2.3. Differential Equation. In order to find the differential equation equivalent to this integral expression, we next consider a short time interval between t and $t + \Delta t$. Since the end vector $\mathbf{r}$ is mapped onto $\mathbf{r}' = \hat{\lambda}(t+\Delta t)\cdot\hat{\lambda}(t)^{-1}\cdot\mathbf{r}$ during this small interval, the difference $\Delta\mathbf{r} \equiv \mathbf{r}' - \mathbf{r}$ takes the value

$$\Delta\mathbf{r} = \hat{\Lambda}(t)\cdot\mathbf{r}\Delta t \tag{2.18}$$

to first order in Δt, where the tensor $\hat{\Lambda}(t)$ is defined by $\hat{\Lambda}(t) \equiv (\mathrm{d}\hat{\lambda}(t)/\mathrm{d}t)\cdot\hat{\lambda}(t)^{-1}$. In other words, the rate of change $\mathbf{v}$ in the end vector per unit time is given by

$$\mathbf{v} = \hat{\Lambda}(t)\cdot\mathbf{r} \tag{2.19}$$

The recursion relation connecting the distribution function at t' with the one at t, when expanded in powers of Δt, gives a differential equation

$$\frac{\partial F}{\partial t} + \nabla\cdot(F\mathbf{v}) = G(\mathbf{r},t) - \beta(\mathbf{r})\,F(\mathbf{r},t) \tag{2.20}$$

The first term G on the right-hand side describes the change due to the creation of active chains; it is called the *chain generation function*. It is given by

$$G(\mathbf{r},t) = m(t)\,f_0(\mathbf{r}) = p(n - \nu(t))f_0(\mathbf{r}) \tag{2.21}$$

The second term describes the decrease due to junction breakage; β is called the *chain breakage rate*. Equation 2.20 is the same as the one derived by Yamamoto[11] for an entangled melt but differs fundamentally in that our equation includes a chain generation function depending on the number of active chains $\nu(t)$—and hence the space integral of $F(\mathbf{r},t)$—at the very moment when chains are created. In fact it provides an integrodifferential equation for $F(\mathbf{r},t)$.

2.4. Initial Equilibrium Distribution. In the following we consider an *aged system*—that is, a network which is kept quiescent with no external perturbation for a sufficiently long time, so that it remains intact in an equilibrium state. Since $\partial F/\partial t = 0$ and $\hat{\Lambda}(t) = 0$ by definition for an aged system, (2.20) gives a balance

$$p(n - \nu_0)f_0(\mathbf{r}) = \beta(\mathbf{r})\,F(\mathbf{r},0) \tag{2.22}$$

for the initial distribution, where $\nu_0 \equiv \int F(\mathbf{r},0)\,\mathrm{d}\mathbf{r}$ is the number of active chains in the initial equilibrium. This balancing condition requires that $F(\mathbf{r},0)$ must be proportional to $f_0(\mathbf{r})/\beta(\mathbf{r})$. Correct normalization gives $F(\mathbf{r},0) = \nu_0 f(\mathbf{r},0)$, where

$$f(\mathbf{r},0) \equiv f_0(\mathbf{r})/\zeta_0\beta(\mathbf{r}) \tag{2.23}$$

with

$$\zeta_0 \equiv \int \frac{f_0(\mathbf{r})}{\beta(\mathbf{r})}\,\mathrm{d}\mathbf{r} \tag{2.24}$$

being the normalization constant. The initial distribution is therefore *not Gaussian* if the chain breakage rate β depends on the end-to-end distance. Substituting this form for f into (2.22), we find

$$\nu_0 = \frac{p\zeta_0}{1 + p\zeta_0}n \tag{2.25}$$

Among the total n of the chains forming the network, the fraction $p\zeta_0/(1 + p\zeta_0)$ turns out to be active.

3. Number of Active Chains

To get an idea of how an aged network evolves under a macroscopic deformation, let us first consider the time development of the number of active chains. Spatial integration of (2.14) gives

$$\nu(t) = \nu_{\mathrm{in}}(t) + p\int_0^t \zeta(t;t')[n - \nu(t')]\,\mathrm{d}t' \tag{3.1}$$

where

$$\nu_{\mathrm{in}}(t) \equiv \int \Theta(\mathbf{r},t;\mathbf{r}_0,0)\,F(\mathbf{r}_0,0)\,\mathrm{d}\mathbf{r}_0 \tag{3.2}$$

and

$$\zeta(t;t') \equiv \int \Theta(\mathbf{r},t;\mathbf{r}',t')\,f_0(\mathbf{r}')\,\mathrm{d}\mathbf{r}' \tag{3.3}$$

The first term $\nu_{\mathrm{in}}(t)$ gives the number of chains which were initially active and remain active until time t. (Subscript in indicates that it depends on the initial distribution.) It is therefore a steadily decreasing function of the time, vanishing at $t = \infty$ in most cases. (It can reach a finite value at $t = \infty$ when the chain breakage rate $\beta(\mathbf{r})$ vanishes in a certain finite region of r. The detailed viscoelastic properties of a network falling into this category will be studied in a subsequent paper in this series.) The function $\zeta(t;t')$ gives the survival probability averaged over the distribution at the creation time t' (Gaussian chains are created); it is a function of the time difference $t - t'$ provided that the deformation tensor has translational invariance in time. By differentiating (3.1) with respect to time, we find

$$\frac{\mathrm{d}\nu}{\mathrm{d}t} = \left(\frac{\mathrm{d}\nu}{\mathrm{d}t}\right)_{\mathrm{gen}} + \left(\frac{\mathrm{d}\nu}{\mathrm{d}t}\right)_{\mathrm{des}} \tag{3.4}$$

where

$$\left(\frac{\mathrm{d}\nu}{\mathrm{d}t}\right)_{\mathrm{gen}} \equiv p[n - \nu(t)] \tag{3.5}$$

is the number of active chains generated in a unit time, and

$$\left(\frac{\mathrm{d}\nu}{\mathrm{d}t}\right)_{\mathrm{des}} \equiv \frac{\mathrm{d}\nu_{\mathrm{in}}}{\mathrm{d}t} + p\int_0^t \frac{\partial\zeta(t;t')}{\partial t}[n - \nu(t')]\,\mathrm{d}t' \tag{3.6}$$

is the number of active chains which are destroyed in a unit time. (Note that $\partial\zeta(t;t')/\partial t < 0$.)

The solution of the integral equation (3.1) can easily be found by the method of Laplace transformation. Let

$$\tilde{\nu}(s) \equiv \int_0^\infty e^{-st}\nu(t)\,\mathrm{d}t \qquad (3.7)$$

be the Laplace transform of $\nu(t)$. Equation 3.1 then gives

$$\tilde{\nu}(s) = \frac{np\tilde{\zeta}(s) + s\tilde{\nu}_{\mathrm{in}}(s)}{s[1 + p\tilde{\zeta}(s)]} \qquad (3.8)$$

in the Laplace space. It should be mapped back onto real time by using the explicit form of the initial distribution for an aged system. As far as the stationary viscoelastic properties are concerned, however, it is sufficient to find a solution at $t = \infty$. The simple pole at $s = 0$ gives

$$\nu(t = \infty) = \frac{np\tilde{\zeta}(0)}{1 + p\tilde{\zeta}(0)} \qquad (3.9)$$

for the number of active chains which is reached after infinite time. ($\tilde{\nu}_{\mathrm{in}}(0)$ has been assumed to be finite, because it is a rapidly decaying function.) Similarly we find that the number of active chains generated in a unit time is given by

$$\tilde{m}(s) = p\frac{n - s\tilde{\nu}_{\mathrm{in}}(s)}{s[1 + p\tilde{\zeta}(s)]} \qquad (3.10)$$

and hence we have for the steady state

$$m(t{=}\infty) = \frac{np}{1 + p\tilde{\zeta}(0)} \qquad (3.11)$$

4. Stress–Strain Relation

We next study how physical properties change with time. Let $\phi(\mathbf{r})$ be an arbitrary scalar quantity associated with each chain having the end vector $\mathbf{r}$. For instance, the elastic free energy stored in a single chain is an important quantity to be considered. It takes the form

$$\phi(r) = \frac{3kT}{2Na^2}r^2 \qquad (4.1)$$

for a Gaussian chain with N statistical units. Since we have $F(\mathbf{r},t)\,\mathrm{d}\mathbf{r}$ active chains at time t, time development of such a physical quantity can be found by integration: $\Phi(t) \equiv \int \mathrm{d}\mathbf{r}\ \phi(\mathbf{r})\ F(\mathbf{r},t)$. Substituting into (2.14), we find

$$\Phi(t) = \Phi_{\mathrm{in}}(t) + p\int_0^t \phi(t;t')[n - \nu(t')]\,\mathrm{d}t' \qquad (4.2)$$

where the two functions

$$\Phi_{\mathrm{in}}(t) \equiv \int \phi(\mathbf{r})\ \Theta(\mathbf{r},t;\mathbf{r}_0,0)\ F(\mathbf{r}_0,0)\ \mathrm{d}\mathbf{r}_0 \qquad (4.3)$$

and

$$\phi(t;t') \equiv \int \phi(\mathbf{r})\ \Theta(\mathbf{r},t;\mathbf{r}',t')\ f_0(\mathbf{r}')\ \mathrm{d}\mathbf{r}' \qquad (4.4)$$

are defined in a manner similar to those for the number of chains. The physical meaning of each term is obvious.

In order to study the network properties we assume here, as in the conventional transient network theory,[9-11] that the free energy of the entire network is given by the sum of the free energy stored in each individual chain and the internal energy caused by the molecular interactions between the chain segments. The latter is assumed to depend only on the density ρ of the segments. It is proportional to $nN/V(t)$, where $V(t)$ is the instantaneous volume of the system at time t. The volume change under deformation is given by $V(t) = V_0|\hat{\lambda}(t)|$ in terms of the initial volume V_0 and the determinant of the strain tensor. This assumption leads to the total free energy

$$\Phi_{\mathrm{total}}(t) = \Phi(t) + E(|\hat{\lambda}(t)|) \qquad (4.5)$$

where E represents the internal free energy due to the chain interaction.

The stress tensor corresponding to a given deformation $\lambda(t)$ is readily derived by differentiation

$$\hat{\Sigma}(t) = \lim_{\hat{\Delta}\to 0}\,[\Phi_{\mathrm{total}}((\hat{1} + \hat{\Delta})\cdot\hat{\lambda}) - \Phi_{\mathrm{total}}(\hat{\lambda})]\cdot\hat{\Delta}^{-1}$$

which explicitly gives for our transient network

$$\hat{\Sigma}(t) = \int \mathrm{d}\mathbf{r}\left(\frac{\phi'(r)}{r}\right)\mathbf{r}^{\mathrm{t}}\mathbf{r}F(\mathbf{r},t) - P\hat{1} = 3kT\frac{\langle\mathbf{r}^{\mathrm{t}}\mathbf{r}\rangle_t}{\langle r^2\rangle_0} - P\hat{1} \qquad (4.6)$$

where $\langle\mathbf{r}^{\mathrm{t}}\mathbf{r}\rangle_t$ is the instantaneous average of a dyadic $\mathbf{r}^{\mathrm{t}}\mathbf{r}$ at time t, and P is the isotropic pressure. (Superscript t indicates the transpose of a vector.) The pressure term $P\hat{1}$ comes from the internal energy. Substituting the integral form for $F(\mathbf{r},t)$, we find

$$\hat{\Sigma}(t) = \hat{\Sigma}_{\mathrm{in}}(t) + p\int_0^t \hat{\sigma}(t;t')[n - \nu(t')]\,\mathrm{d}t' - P\hat{1} \qquad (4.7)$$

for the time development of the stress tensor, where

$$\hat{\Sigma}_{\mathrm{in}} \equiv \int\left(\frac{\phi'(r)}{r}\right)\mathbf{r}^{\mathrm{t}}\mathbf{r}\Theta(\mathbf{r},t;\mathbf{r}_0,0)\ F(\mathbf{r}_0,0)\ \mathrm{d}\mathbf{r}_0 \qquad (4.8)$$

is the stress sustained by the initially active chains, and

$$\hat{\sigma}(t;t') \equiv \int\left(\frac{\phi'(r)}{r}\right)\mathbf{r}^{\mathrm{t}}\mathbf{r}\Theta(\mathbf{r},t;\mathbf{r}',t')\ f_0(\mathbf{r}')\ \mathrm{d}\mathbf{r}' \qquad (4.9)$$

is the time propagator for the stress survival. In the case where there is translational invariance in time, we find the solution in the Laplace space

$$\tilde{\Sigma}(s) = \tilde{\Sigma}_{\mathrm{in}}(s) + \tilde{m}(s)\,\tilde{\sigma}(s) - \tilde{P}(s)\hat{1} \qquad (4.10)$$

with $\tilde{m}(s)$ being given by (3.10). The stationary stress reached in the $t \to \infty$ limit is then given by

$$\hat{\Sigma}(t{=}\infty) = \frac{pn}{1 + p\tilde{\zeta}(0)}\tilde{\sigma}(0) - P(t{=}\infty)\hat{1} \qquad (4.11)$$

The isotropic pressure stays constant under a volume-conserving deformation $\hat{\lambda}(t)$ for which $|\hat{\lambda}(t)| = 1$ holds, but there should be a coupling between the chain elasticity and the segment interaction when the volume is not conserved during the deformation.

The stress tensor in (4.11) provides the most general starting equation for the study of stationary viscoelasticity. For instance, if one considers a simple shear flow with constant shear rate for which the deformation tensor is given by

$$\hat{\lambda}(t) = \begin{pmatrix} 1 & \dot{\gamma}t & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \qquad (4.12)$$

($\dot{\gamma}$ being the constant shear rate), we have $\hat{\lambda}(t)\cdot\mathbf{r} = {}^{\mathrm{t}}(x + \dot{\gamma}yt,\ y,\ z)$ and hence

$$\tilde{\zeta}(0) = \int_0^\infty \mathrm{d}t\ \langle\exp[-\int_0^t \beta[[(x + \dot{\gamma}yt')^2 + y^2 + z^2]]^{1/2}\,\mathrm{d}t']\rangle_0 \qquad (4.13)$$

for an isotropic chain breakage rate for which $\beta(\mathbf{r})$ depends only on $|\mathbf{r}|$. The stationary shear viscosity defined by η_{st}-

$(\dot{\gamma}) \equiv \Sigma_{xy}(\infty)/\dot{\gamma}$ is then explicitly given by the formula

$$\eta_{\mathrm{st}}(\dot{\gamma}) = \frac{pn}{\dot{\gamma}[1 + p\tilde{\zeta}(0)]}\tilde{\sigma}_{xy}(0) \tag{4.14}$$

where

$$\tilde{\sigma}_{xy}(0) = \frac{3kT}{\langle r^2\rangle_0}\int_0^\infty \mathrm{d}t \, \langle (x + \dot{\gamma}yt)y \exp[-\int_0^t \beta[[(x + \dot{\gamma}yt')^2 + y^2 + z^2]]^{1/2}\,\mathrm{d}t']\rangle_0 \tag{4.15}$$

Similar formulae can be found for a uniaxial elongational flow for which

$$\hat{\lambda}(t) = \begin{pmatrix} e^{-\dot{\epsilon}t}/2 & 0 & 0 \\ 0 & e^{-\dot{\epsilon}t/2} & 0 \\ 0 & 0 & e^{\dot{\epsilon}t} \end{pmatrix} \tag{4.16}$$

($\dot{\epsilon}$ being a constant elongational rate). A detailed study on the viscosity and normal stresses for specific models of the chain breakage rate $\beta(r)$ will be reported in the next paper in this series.

5. Linear Response of the Transient Network

Stress measurements against small deformation have frequently been used to probe the viscoelasticity of physical gels in a linear regime.[4,5] We consider in this section the linear response of our model transient networks to small oscillatory strains. To find the dynamical moduli, let us suppose that a small oscillatory deformation

$$\hat{\lambda}(t) = \hat{1} + \hat{\epsilon}\sin\omega t \qquad (0 \le t) \tag{5.1}$$

is given to an aged network. For instance, the infinitesimal tensor $\hat{\epsilon}$ takes the form

$$\hat{\epsilon} = \begin{pmatrix} 0 & \epsilon & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{5.2}$$

for a shear deformation and

$$\hat{\epsilon} = \begin{pmatrix} -\epsilon/2 & 0 & 0 \\ 0 & -\epsilon/2 & 0 \\ 0 & 0 & \epsilon \end{pmatrix} \tag{5.3}$$

for an elongational deformation along the z direction.

To find the stress reached after a lapse of the transient process, we have to pick up the *secular terms* included in (4.7). A secular term is a term which remains oscillating without decay in the long-time limit $t \to \infty$. The first term $\hat{\Sigma}_{\mathrm{in}}(t)$, which carries a memory of the initial distribution, eventually decays as time goes on. The number of active chains $\nu(t')$ in the second term can be replaced by the stationary value $\nu(\infty)$ given by (3.9) as far as the long-time limit is concerned, which, for a small deformation, turns out to be

$$\nu(\infty) = \nu_0 + O(\epsilon^2) \tag{5.4}$$

when expanded in powers of ϵ, provided that the breakage rate β is isotropic. Carrying out the integral and discarding the decaying terms, we find the steadily oscillating stress in the linear regime. For instance, the shear deformation gives

$$\Sigma_{xy}(t) = \epsilon\nu_0 kT[g_1(\omega)\sin\omega t + g_2(\omega)\cos\omega t] + O(\epsilon^2) \tag{5.5}$$

for the shear stress, where the functions g_i are defined by

$$g_1(\omega) \equiv \frac{1}{\zeta_0\langle r^2\rangle_0}\left\langle \frac{\omega^2 r^2}{\beta(\beta^2 + \omega^2)}\left[1 - \frac{2r\beta\beta'}{5(\beta^2 + \omega^2)}\right]\right\rangle_0 \tag{5.6a}$$

$$g_2(\omega) \equiv \frac{1}{\zeta_0\langle r^2\rangle_0}\left\langle \frac{\omega r^2}{\beta^2 + \omega^2}\left[1 + \frac{(\omega^2 - \beta^2)r\beta'}{5\beta(\beta^2 + \omega^2)}\right]\right\rangle_0 \tag{5.6b}$$

(β' being the derivative of β). The shear storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ are therefore given by

$$G'(\omega) = \nu_0 kTg_1(\omega) \tag{5.7a}$$

$$G''(\omega) = \nu_0 kTg_2(\omega) \tag{5.7b}$$

The second term in g_1 gives softening of the storage modulus due to the increase of the chain breakage rate at higher stretching, while that in g_2 changes its sign at $\omega = \beta$, giving inhomogeneous correction to the loss modulus.

Similar calculations for the elongational deformation prove that elongational moduli are exactly 3 times larger than the shear moduli for all frequencies.

Although a detailed examination of these formulae will be discussed in a subsequent paper, a few conclusions, irrespective of the specific form of $\beta(r)$, are immediately available from these expressions:

(1) Dynamical moduli depend on the chain generation rate p only through the initial number ν_0 of the active chains.

(2) Nonuniform dependence of the chain breakage rate on the end distance crucially affects the mechanical moduli, leading to the deviation from the conventional form for the superposition of the Maxwell elements, each having the relaxation time $\beta(r)^{-1}$.

(3) There is no obvious reason for the dynamic viscosity $\eta(\omega)$ obtained from the dynamic moduli by the relation

$$\eta(\omega) = \frac{G''(\omega)}{\omega} \quad \text{or} \quad \eta^*(\omega) = \left[\frac{G'(\omega)^2 + G''(\omega)^2}{\omega}\right]^{1/2}$$

to agree with the stationary viscosity $\eta_{\mathrm{st}}(\dot{\gamma})$ found in the preceding section (eq 4.14) when it is compared at the frequency ω which is the same as the shear rate $\dot{\gamma}$. (The two agree at $\omega = \dot{\gamma} = 0$ as they should.)

6. Nonlinear Stress Relaxation

Another frequent experimental measurement concerns the long-time behavior of the stress after a sudden deformation followed by constant strain. To find a fundamental formula for the stress relaxation, we consider a stepwise deformation

$$\hat{\lambda}(t) = \hat{\lambda}\theta(t) \tag{6.1}$$

given at $t = 0$ on an aged network, where $\hat{\lambda}$ is a constant strain tensor. The number of active chains changes according to (3.1), but under such a stepwise deformation the initial term takes the form

$$\nu_{\mathrm{in}}(t) = \frac{\nu_0}{\zeta_0}\left\langle \frac{e^{-\beta(|\hat{\lambda}\cdot r|)t}}{\beta(r)}\right\rangle_0 \tag{6.2}$$

while the survival function is given by

$$\zeta(t;t') = (e^{-\beta(r)(t-t')}\rangle_0 \quad \text{for} \quad 0 < t' \le t \tag{6.3}$$

If we consider a particular limiting situation where the chain breakage rate takes a constant value β_0 independent of the end distance, the network has a single relaxation time β_0^{-1}, so that the number of the initially active chains decreases according to the exponential law, while the total number ν_0 of active chains remains constant. In more realistic cases where $\beta(r)$ is a steadily increasing function of r, however, the system has a mechanical spectrum of the relaxation times:

$$H(\tau) = \tau\left\langle \frac{\delta(\tau - \beta(|\hat{\lambda}\cdot\mathbf{r}|)^{-1})}{\beta(r)} \right\rangle_0 \tag{6.4}$$

may lead to a nonexponential relaxation depending on the detailed form of $\beta(r)$. The long-time decay of stress can be derived from (4.7). The stress supported by the chains which are initially active decays according to the law

$$\hat{\Sigma}_{\mathrm{in}}(t) = \frac{3\nu_0 kT}{\zeta_0 \langle r^2\rangle_0}\hat{\lambda}\cdot\left\langle (\mathbf{r}\,{}^{t}\mathbf{r})\frac{e^{-\beta(|\hat{\lambda}\cdot\mathbf{r}|)t}}{\beta(r)} \right\rangle_0 \cdot {}^{t}\hat{\lambda} \tag{6.5}$$

which has the same spectrum as (6.4). The superscript "t" on the left shoulder of a physical tensor (or vector) indicates its transpose. Therefore, as pointed out by Yamamoto,[11] our model is similar to the phenomenological Maxwell model with multiple relaxation times, each corresponding to the reciprocal of the chain breakage rate.

The second and third terms in (4.7) have no effect on the stress relaxation because both terms have the same value in the diagonal elements and have no off-diagonal element. Specifically the stress survival function takes the form

$$\hat{\sigma}(t;t') = \sigma_0(t-t')\hat{1} \tag{6.6}$$

with

$$\sigma_0(t) \equiv \frac{kT}{\langle r^2\rangle_0}\langle r^2 e^{-\beta(r)t}\rangle_0 \tag{6.7}$$

For each specific deformation $\hat{\lambda}$, we can find a detailed description of the stress relaxation function. For instance, for a shear deformation

$$\hat{\lambda} = \begin{pmatrix} 1 & \lambda & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \tag{6.8}$$

we have

$$\Sigma_{xy}(t) = \frac{3\nu_0 kT}{\zeta_0\langle r^2\rangle_0}\left\langle (x+\lambda y)y\frac{e^{[-\beta((x+\lambda y)^2+y^2+z^2)t]^{1/2}}}{\beta(r)} \right\rangle_0 \tag{6.9}$$

A detailed examination on the shear and elongational deformation will, however, be reported in a subsequent paper.

7. Conclusion and Discussion

We have developed a dynamical theory of a physically cross-linked network in the unentangled regime. The simple model introduced here has a main advantage in that it provides a clear molecular picture for the internal reorganization of the network structure in terms of the two molecular parameters: the chain breakage rate $\beta(r)$ and the chain recombination rate p. This network model permits calculation of dynamical properties—irrespective of transient or stationary ones—by the combination of these two parameters. The equation obtained for the time development of the elastically active chains has some elements in common with the conventional transient network theory, but it is fundamentally different in that it includes the chain generation function which depends on the instantaneous total number of chains and hence on the time history of the macroscopic deformation from the initial state to the very moment considered.

In order to find how these two parameters depend on molecular characteristics such as the molecular weight of the polymer, chain stiffness, or strength of the associating force among the end groups, analysis of single-chain motion in the network is required. In the unentangled regime considered here, the motion of a single chain basically obeys Rouse dynamics, properly modified by sticky trapping centers distributed around it. The terminal relaxation time—which can be represented by $\beta(\mathbf{r}=0)^{-1}$—is hence expected to be proportional to $\tau_x M^2$, where τ_x is the lifetime of a bond formed between the reactive groups which are not attached on the polymer chains.[17]

We next briefly discuss the relation between our recursion relation for the elastically active chains and Flory's addition–substraction network theory.[13,14] In Flory's theory a part of the initially introduced cross-links (hence active chains) is removed after the first deformation $\hat{\gamma}_1$, and some new junctions are introduced. The total network is then deformed in accordance with another tensor $\hat{\gamma}_2$. The number of active chains changes from $\nu_0 f_0(\mathbf{r}_0)\,d\mathbf{r}_0$ to

$$F_1(\mathbf{r}_1)\,d\mathbf{r}_1 = (\nu_0 - \Delta n)f_0(\mathbf{r}_0)\,d\mathbf{r}_0 + \nu_1 g(\mathbf{r}_1)\,d\mathbf{r}_1 \tag{7.1}$$

in the first step, where ν_1 chains are added and Δn chains are removed. The distribution function $g(\mathbf{r}_1)$ of the added chain is not known at this stage. The end-to-end vector $\mathbf{r}_1$ is related to $\mathbf{r}_0$ as $\mathbf{r}_1 = \hat{\gamma}_1\cdot\mathbf{r}_0$ from the assumption of affineness. In the final deformation $\hat{\gamma}_2$, the number of chains is conserved so that $F_2(\mathbf{r}_2)\,d\mathbf{r}_2 = F_1(\mathbf{r}_1)\,d\mathbf{r}_1$ holds. Since the total deformation is given by $\hat{\lambda} = \hat{\gamma}_2\cdot\hat{\gamma}_1$, the free energy of the network must be

$$\Phi_{\mathrm{network}} = \int \phi(\mathbf{r}_2)\,F_2(\mathbf{r}_2)\,d\mathbf{r}_2 = (\nu_0 - \Delta n)I(\hat{\lambda}) + \nu_1\int \phi(\mathbf{r}_2)\,g(\mathbf{r}_1)\,d\mathbf{r}_1 \tag{7.2}$$

where $I(\hat{\lambda})$ is the first invariant of the deformation $\hat{\lambda}$. Flory proposed that this free energy should be given by

$$(\nu_0 - \Delta n + \phi n_1)I(\hat{\lambda}) + (1-\phi)n_1 I(\hat{\gamma}_2) \tag{7.3}$$

where ϕ is a factor depending on the fraction of the added chains relative to the total chains. His argument immediately leads to the result

$$g(\mathbf{r}_1)\,d\mathbf{r}_1 = \phi f_0(\mathbf{r}_0)\,d\mathbf{r}_0 + (1-\phi)f_0(\mathbf{r}_1)\,d\mathbf{r}_1 \tag{7.4}$$

The distribution of the added chains is a mixture of the relaxed ones ($f_0(\mathbf{r}_1)$) and the strained ones ($f_0(\mathbf{r}_0)$). In other words, the network behaves as if a fraction ϕ of the chains cross-linked in the relaxed state had been transferred to the ones cross-linked under the strain $\hat{\gamma}_1$. The distribution of the added chains partially preserves the memory of the original network. In reality, however, chains to be eliminated are not randomly chosen, but there should be a selection rule; a chain which is stretched more has a higher probability to break. Moreover, addition of cross-links takes place where there is a functional group ready to form a bond. In our model network, a chain with one free end is released from strain to return to an equilibrium configuration within the single-chain relaxation time τ, so that, on a longer time scale than τ, it loses the memory of the effect of a strain it has suffered one step earlier. Thus effect of the memory transfer has been neglected.

The model we proposed in this paper does not cover the important regime where M_x is much larger than M_e so that chain entanglements play essential roles in the dynamics. In that regime we have, in addition to the reversible bonds, effective junctions formed by the localized chain entanglements which can persist longer than the lifetime of the association. Starting from the tube model[18] of the entangled melts, molecular motion through an entangled temporal network was studied by Gonzalez[19] by introducing the concept of *hindered reptation*—that is, reptation modified by the distribution of sticky trapping centers around the confining tube. The work has recently been reexamined and corrected by Leibler et al.[20] in order to account for the observed longest relaxation time in the model thermoplastic elastomers. Detailed viscoelastic properties in the entangled regime are, however, still open to study.

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References and Notes

(1) (a) Tanaka, F. *Macromolecules* **1989**, *22*, 1988. (b) Tanaka, F. *Macromolecules* **1990**, *23*, 3784, 3790.
(2) Tanaka, F.; Matsuyama, A. *Phys. Rev. Lett.* **1989**, *62*, 2759.
(3) Clark, A. H.; Ross-Murphy. S. B. *Br. Polym. J.* **1985**, *17*, 164.
(4) Clark, A. H.; Ross-Murphy, S. B. *Adv. Polym. Sci.* **1987**, *83*, 57.
(5) Richardson, R. K.; Ross-Murphy, S. B. *Int. J. Macromol.* **1987**, *9*, 257.
(6) Russo, P. S., Ed. *Reversible Polymer Gels and Related Systems*; ACS Symposium Series 350; American Chemical Society: Washington, DC, 1987.
(7) Utracki, L. A., Weiss, R. A., Eds. *Multiphase Polymers: Blends and Ionomers*; ACS Symposium Series 395; American Chemical Society: Washington, DC, 1989.
(8) (a) Rundberg, R. D.; Makowski, H. S.; Westerman, L. *Adv. Chem. Ser.* **1980**, *187*, 67. (b) Fitzgerald, J. J.; Kim, D.; Weiss, R. A. *J. Polym. Sci., Polym. Lett. Ed.* **1986**, *24*, 263. (c) Bazuin, C. G. Reference 7, p 476.
(9) Green, M. S.; Tobolsky, A. V. *J. Chem. Phys.* **1946**, *14*, 80.
(10) Lodge, A. S. *Trans. Faraday Soc.* **1956**, *52*, 120.
(11) Yamamoto, M. *J. Phys. Soc. Jpn.* **1956**, *11*, 413; **1957**, *12*, 1148; **1958**, *13*, 1200.
(12) For a review of the transient network theory, see: (a) Bird, R. B.; Curtiss, C. F.; Armstrong, R. C.; Hassager, O. *Dynamics of Polymeric Liquids*; John Wiley & Sons, Inc.: New York, 1987; Vol. 2, Chapter 20, p 353. (b) Larson, R. G. *Constitutive Equations for Polymer Melts and Solutions*; Butterworth Publishers: Stoneham, MA, 1988; section 6.3, p 168. An earlier network model (Acierno, D.; La Manta, F. P.; Marrucci, G.; Rizzo, G.; Titomanlio, G. *J. Non-Newtonian Fluid Mech.* **1976**, *1*, 125) permits the number of network chains to be nonconstant.
(13) Flory, P. J. *Trans. Faraday Soc.* **1960**, *56*, 722.
(14) Fricker, H. S. *Proc. R. Soc. London* **1973**, *A335*, 267, 289.
(15) Baxandall, L. G.; Edwards, S. F. *Macromolecules* **1988**, *21*, 1763.
(16) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; Chapter 9.
(17) Baxandall, L. G. *Macromolecules* **1989**, *22*, 1982.
(18) Doi, M. D.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford University Press: Oxford, U.K., 1986.
(19) Gonzalez, A. E. *Polymer* **1983**, *24*, 77; **1984**, *25*, 1469.
(20) Leibler, L.; Rubinstein, M.; Colby, R. H. *Macromolecules*, **1991**, *24*, 4701.