A Generalized Transient Network Model for Associative Polymer Networks

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ABSTRACT: A transient network model is described for a polymeric system consisting of linear chains, connected with temporary cross-links. The model is a reformulation and extension of a similar model which was presented recently [Wientjes, R. H. W.; Jongschaap, R. J. J.; Duits, M. H. G.; Mellema, J. A new transient network model for associative polymer networks. *J. Rheol.* **1999**, *43*, 375−391]. Contrary to common transient network models the interconnection between segments is explicitly taken into account. The dynamics of the system is also described by the state of a whole chain, instead of separate segments. As a result a prediction of the shape of relaxation spectra is possible. The model predicts broad spectra with long relaxation times, in particular for chains with many stickers. In the present formulation also systems with multiple types of stickers can be treated. In that case, plateau regions in dynamic moduli may appear.

1. Introduction

Transient network models are an important class of models, developed to describe the rheological behavior of polymer melts and solutions. The transient network concept was first proposed by Green and Tobolsky,[3] put in a tensorial format by Lodge[8] and Yamamoto,[16] and developed further by many others (see the book[1] for a review). Lately, there are a number of new developments in transient network models. First are improvements in order to describe nonlinear flow behavior,[10] then simulations, which have become an important tool for the investigation of transient networks,[4,13] and finally a combined transient network and reptation theory in the sticky reptation models of Rubinstein et al.[6,11,12]

Although the transient network concept was primarily developed to model entanglement in polymeric systems, the model may also be used to model the dynamics of weak gels, consisting of a network of chains with reversible cross-links. In the present paper we propose a new transient network model for this type of systems.

A special feature of this model is that the network segments are not treated as independent. Instead, the interconnection of segments in a chain is taken into account explicitly. As a result the present theory allows the prediction of relaxation spectra. This is fundamentally different from ordinary transient network models, where relaxation spectra are introduced by using the ad hoc concept of complexity of segments. Although a general constitutive equation is derived (eq 19 below), we will concentrate here on the linear viscoelastic behavior. In a recent paper,[14] we published a model based upon the same principles. In our present paper, the mathematical analysis, however, is reformulated and extended. We improve an assumption in our earlier paper about the stress contribution of newly created segments. As a result we now obtain different predictions. In the new formulation, we are able to treat also the case of multiple types of stickers. This turns out to be of significant influence.

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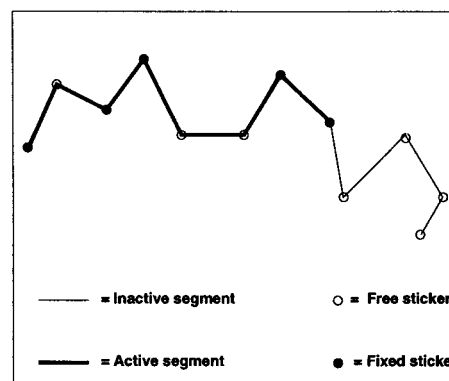
Figure 1. Chain with free and fixed stickers and active and inactive segments.

2. Model

We consider a system of linear flexible polymer chains with on each chain (see Figure 1) a finite number of *stickers* that can associate to form reversible cross-links. As a result, the whole system acts as a reversible gel of multiple connected chains. The stickers can exist in one of two states: *free* and *fixed*. The connection state of the whole chain will be specified by a variable s which determines the states of all stickers along a chain. The parts of a chain between stickers are called segments. All segments are equal and modeled by linear entropic springs. Segments which carry stress are called *active*. To specify the state of a segment i in a chain in state s we use a parameter v_s^i defined as

$$v_s^i = 1 \leftrightarrow \text{segment } i \text{ active in state } s$$

$$v_s^i = 0 \leftrightarrow \text{segment } i \text{ inactive in state } s \qquad (1)$$

This is not a dynamic variable but a constant which determines unambiguously the state of all segments for any value of the state variable s.

The environment of a chain is treated for the active segments as a tube, which prevents motions perpendicular to it. This tube constraint is similar to the one used in reptation dynamics.[2] In the present model,
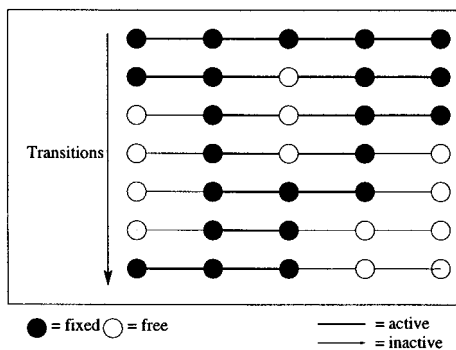
Figure 2. Change of state of segments due to changes of the state of stickers along the chain. A transition of a sticker from fixed to free results only in a loss of tension segment if that sticker defines the terminus of a succession of active segments.

contrary to the so-called sticky reptation models,[6] however, there is no motion of the chain along the tube. The main purpose of the tube is to retain the direction of active segments as long as they remain active, even when adjacent stickers are free. A transition of a sticker from fixed to free results only in a loss of tension in an adjacent segment if in that transition the segment becomes inactive. If, for example, the sticker in the middle of the chain in the fifth state displayed in Figure 2 becomes free, no change of stress takes place in the adjacent segments. If this occurs in the sixth state of the same figure, the stress in the segment left to that sticker will be released. This is a cooperative effect which is specific for our model and results in relatively long times in the stress relaxation spectrum. The nonactive segments are assumed to be always in their equilibrium distribution. This is similar to the common assumption of transient network theories,[7] that segments are created in the equilibrium distribution. This assumption which is obviously an oversimplification is retained to keep the analysis relatively simple. If a nonactive segment becomes active, its contribution to the stress is determined by its subsequent motion. The total contribution of active segments i in a state s is determined by the distribution function ψ_s^i. In the next section the coupled set of evolution equations by which the segment distribution functions are determined will be discussed. This is an improvement on our earlier paper,[14] where it was assumed that the distribution function of active segments was dependent only of the state s.

3. Evolution Equations

Like in classical transient network theory[7,16] the rheological properties of the system are determined by the creation, loss, and motion of segments. Of primary interest are the evolution in time of the density $\Psi_s^i(\mathbf{q}_i, t)$ of chain segments number i of a chain in state s in an infinitesimal three-dimensional volume element $d^3\mathbf{q}_i$ in the segment-configuration space, and the number density n_s of chains in state s. We also define a one-chain probability density ψ_s^i by

$$\Psi_s^i(\mathbf{q}_i, t) = n_s \psi_s^i(\mathbf{q}_i, t) \qquad (2)$$

The evolution equation of segments is assumed to be

$$\frac{\partial \Psi_s^i}{\partial t} = -\nu_s^i \frac{\partial}{\partial \mathbf{q}_i} \cdot (\Psi_s^i \dot{\mathbf{q}}_i) + \sum_{s' \neq s} (A_{ss'} \Psi_{s'}^i - A_{s's} \Psi_s^i) \qquad (3)$$

The first term in the right-hand side is the convective part. Because of the factor ν_s^i this term is nonzero only for active segments, in accordance with the assumption that the inactive segments are always in equilibrium. The motion $\dot{\mathbf{q}}$ of the active segments is assumed to be affine, so

$$\dot{\mathbf{q}}_i = \mathbf{L} \cdot \mathbf{q}_i \qquad (4)$$

where $\mathbf{L} = (\nabla \mathbf{v})^T$, the velocity gradient tensor.

The last term in eq 3 defines the kinetic contributions. $A_{s's}$ is the transition rate of a chain for transition from state s to state s'.

By integration of eq 3 a rate equation for n_s, the density of chains in state s, is obtained:

$$\dot{n}_s = \sum_{s' \neq s} A_{ss'} n_{s'} + A_{s',s} n_s \qquad (5)$$

This kind of gain−loss equation is called a master equation.[5] For the transition probabilities it can be proved[9] that

$$A_{s,s} = -\sum_{s' \neq s} A_{s's} \qquad (6)$$

This allows us to write eq 5 in a more compact form:

$$\dot{n}_s = \sum_{s'} A_{ss'} n_{s'} \qquad (7)$$

Here the summation over s' extends over the whole range of states, including $s' = s$.

From eqs 2, 3, and 5 we obtain for the one-chain distribution function ψ_s^i

$$\frac{\partial \psi_s^i}{\partial t} = -\nu_s^i \frac{\partial}{\partial \mathbf{q}_i} \cdot (\psi_s^i \dot{\mathbf{q}}_i) + \sum_{s'} \frac{n_{s'}}{n_s} A_{ss'} (\psi_{s'}^i - \psi_s^i) \qquad (8)$$

and by multiplication with ν_s^i using the identity $\nu_s^i \nu_s^i = \nu_s^i$ (no summation) and separating in the last term contributions with segment i active and contributions with segment i inactive in the state s' and using our model assumption that free segments are always in the equilibrium distribution ψ^0, after some rearrangement the following evolution equation for ψ_s^i:

$$\nu_s^i \frac{\partial \psi_s^i}{\partial t} = -\nu_s^i \frac{\partial}{\partial \mathbf{q}_i} (\psi_s^i \dot{\mathbf{q}}_i) +$$

$$\sum_{s'} \frac{n_{s'}}{n_s} A_{ss'} \nu_s^i (1 - \nu_{s'}^i)(\psi^0 - \psi_s^i) +$$

$$\sum_{s'} \frac{n_{s'}}{n_s} A_{ss'} \nu_s^i \nu_{s'}^i (\psi_{s'}^i - \psi_s^i) \qquad (9)$$

The first summation are transitions from *inactive* to *active*; the second summation transitions from *active* to *active* segments.

4. Constitutive Equation

The macroscopic stress tensor **T** is the sum of contributions of the active segments, so

$$\mathbf{T} = \sum_s \sum_i \nu_s^i \mathbf{T}_s^i \qquad (10)$$

where

$$\mathbf{T}_s^i = n_s \kappa (\mathbf{S}_s^i - \boldsymbol{S}^0) \qquad (11)$$

with κ the segments-spring constant,

$$\mathbf{S}_s^i = \langle \mathbf{qq} \rangle_s^i = \int \mathbf{qq} \psi_s^i d^3 \mathbf{q} \qquad (12)$$

the second moment of the segment distribution function ψ_s^i, and $\boldsymbol{S}^0$ the equilibrium value

$$\boldsymbol{S}^0 = \langle \mathbf{qq} \rangle^0 = \frac{kT}{\kappa} \mathbf{1} \qquad (13)$$

This is essentially the so-called *Kramers form*[1] of the polymer contribution to the stress tensor.

To obtain this result, the force in an active segment with a segment vector $\mathbf{q}_i$ of a chain in state s has been taken to be

$$\mathbf{f}_s^i = \kappa \mathbf{q}_i \qquad (14)$$

This is an approximation. In fact, for a series of connected active segments, with free stickers at the interconnections, due to equilibration of forces, the force in all segments will be the same. This force will depend on the total extension of these segments. Moreover, the free stickers will also move from the positions determined by the assumption of affine motion and no longer coincide with the connections between the tube elements. To include this in an analytical formulation of our model, if possible, would be very cumbersome. We expect, however, that eq 14 can be used as an approximation for the spring forces and that the free stickers always follow the positions, determined by the assumed affine motion. At least, in a treatment of linear viscoelastic behavior, which is the main issue of our present paper, these approximations are expected to be sufficient.

From eqs 9, 12, and 13 the following evolution equation for $\mathbf{S}_s^i$ is obtained

$$\frac{\delta}{\delta t}(\mathbf{S}_s^i - \boldsymbol{S}^0) + \sum_{s'} \beta_{ss'}^i (\mathbf{S}_{s'}^i - \boldsymbol{S}^0) = 2 \frac{kT}{\kappa} \mathbf{D} \qquad (15)$$

where $\delta/\delta t$ is an upper convective derivative (so $\delta/\delta t \boldsymbol{S}^0 = -2kT/\kappa \mathbf{D}$) and

$$\beta_{ss'}^i = \frac{n_s}{n_s} \nu_s^i \delta_{ss'} + \frac{n_{s'}}{n_s} B_{ss'}^i \qquad (16)$$

with

$$B_{ss'}^i = -A_{ss'} \nu_s^i \nu_{s'}^i \qquad (17)$$

We refer to Appendix A for details of the derivation of these results.

From eqs 15 and 18 the following differential equation for $\mathbf{T}_s^i$ is obtained:

$$\frac{\delta}{\delta t}\left(\frac{\mathbf{T}_s^i}{n_s}\right) + \sum_{s'} \beta_{ss'}^i \frac{\mathbf{T}_{s'}^i}{n_{s'}} = 2kT\mathbf{D} \qquad (18)$$

With eqs 16 and 17 this may also be written as

$$\frac{\delta}{\delta t}\mathbf{T}_s^i + \sum_{s'} B_{ss'}^i \mathbf{T}_{s'}^i = 2n_s kT\mathbf{D} \qquad (19)$$

The equations eqs 7, 10 and 18 or 19 provide a complete set of constitutive equations of the model. We see that the constitutive behavior is determined mainly by the matrix $A_{ss'}$ of transition rate coefficients which determines by eq 7 the rate of change of number densities of the states n_s of the chains and the matrices $\beta_{ss'}^i$ or $B_{ss'}^i$ occurring in the stress tensor expressions. The matrices $\beta_{ss'}^i$ or $B_{ss'}^i$ also contain information about the chain connectivity in the matrix ν_s^i. Because of these features the present model is able to give more detailed predictions about, in particular the linear viscoelastic behavior of the system than the common transient network models. In the next section, we will discuss in some detail how in our model the relaxation spectra are predicted explicitly.

5. Linear Viscoelastic Behavior

For the analysis of linear viscoelastic response we use a linearized version of eq 19 with an ordinary time derivative and for all n_s the equilibrium values: n_s^0. Instead of the whole stress tensor, we only consider the shear stress component $\tau = T_{12}$. In a one-dimensional representation, the differential equation for the contributions τ_s^i to the stress $\tau = \sum_s \sum_i \nu_s^i \tau_s^i$ then becomes

$$\dot{\tau}_s^i + \sum_{s'} B_{ss'}^i \tau_{s'}^i = n_s^0 kT\dot{\gamma} \qquad (20)$$

If all eigenvalues of the matrix $[B^i]$ are distinct, the following transformations can be used to decouple the equations in eq 20

$$\tilde{B}_{ss'}^i = P_{st}^{i-1} B_{tu}^i P_{us'}^i = \mathrm{diag}(b_1^i, b_2^i, \ldots) \qquad (21)$$

$$\tilde{\tau}_s^i = P_{ss'}^{i-1} \tau_{s'}^i \qquad (22)$$

Then eq 20 becomes

$$\dot{\tilde{\tau}}_s^i + b_s^i \tilde{\tau}_s^i = \sum_{s'} P_{ss'}^{i-1} n_{s'}^0 kT\dot{\gamma} \qquad (23)$$

Fourier transformation gives

$$\hat{\tilde{\tau}}_s^i = \frac{\lambda_s^i}{1 + i\omega\lambda_s^i} \sum_{s''} P_{ss''}^{i-1} n_{s''}^0 kT\hat{\dot{\gamma}} \qquad (24)$$
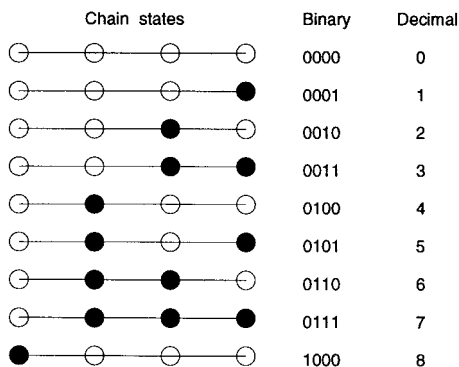
with the relaxation times

$$\lambda_s^i = \frac{1}{b_s^i} \qquad (25)$$

After transformation to the original variables we finally obtain

$$\hat{\tau}_s^i = G_{s'}^i \frac{\lambda_{s'}^i}{1 + i\omega\lambda_{s'}^i} \hat{\dot{\gamma}} \qquad (26)$$

with

Figure 3. State numbers s of states for the case of a chain with three segments.

$$G_{s'}^i = kT \sum_s \sum_{s'} v_s^j P_{ss'}^j P_{s's''}^{j-1} n_{s'}^0 \qquad (27)$$

The corresponding storage and loss moduli are

$$G'(\omega) = \sum_i \sum_s G_s^i \frac{\omega^2 \lambda_s^{i2}}{1 + \omega^2 \lambda_s^{i2}} \qquad (28)$$

$$G''(\omega) = \sum_i \sum_s G_s^i \frac{\omega \lambda_s^i}{1 + \omega^2 \lambda_s^{i2}} \qquad (29)$$

5.1. The Matrixes A and ν. To apply the results derived in the previous section, we need explicit expressions for the elements of the matrices $A_{ss'}$ and v_s^i. To that end a consistent numbering of stickers, segments, and states is needed, and we will use a scheme based upon the binary representation of numbers. The state number s will be chosen such that the digits 1 in its binary representation correspond to fixed and digits 0 to free stickers. In Figure 3 this is illustrated for eight states of a chain of three segments. In accordance with this numbering, we will also number the segments from right to left so for a state with state number s such that $2^{k+1} < s < 2^k$ the highest value of the number of a fixed sticker is k. Noting that for states with an odd value of the state number s the right-end sticker is fixed and that multiplication of s by a factor 2^j corresponds to shift of the pattern of free and fixed stickers with j steps to the left we see that for states with $2^{k+1} < s$ and $s = m2^j$ where m is an odd number, the segments with numbers between j and k are active. In this way the nonzero values of the matrix v_s^i are readily obtained.

Next, the transition matrix $A_{ss'}$ has to be constructed. To that end we define a matrix

$$K = \begin{bmatrix} 1 & g \\ h & 1 \end{bmatrix} \qquad (30)$$

where g is the transition rate for transition of a sticker from free to fixed and h the transition rate for transition of a sticker from fixed to free.

For the two states of a "chain" consisting of one sticker, by using eq 6, we obtain for the transition matrix

$$A^{(1)} = \begin{bmatrix} -h & g \\ h & -g \end{bmatrix} \qquad (31)$$

By making use of the Kronecker product

$$K \otimes K = \begin{bmatrix} 1 & g & g & g^2 \\ h & 1 & gh & g \\ h & gh & 1 & g \\ h^2 & h & h & 1 \end{bmatrix} \qquad (32)$$

the A matrix for the case of two stickers is obtained in a similar manner:

$$A^{(2)} =$$
$$\begin{bmatrix} -2h - h^2 & g & g & g^2 \\ h & -g - h - gh & gh & g \\ h & gh & -g - h - gh & g \\ h^2 & h & h & -2g - g^2 \end{bmatrix}$$
$$(33)$$

In general

$$A_{ij}^{(N)} = K^{\otimes N} + (1 - \sum_k K_{ik}^{\otimes N}) \delta_{ij} \qquad (34)$$

where $K^{\otimes N}$ denotes an n-fold Kronecker product. Expressions for higher order v and A matrices are readily constructed numerically with algorithms based upon these rules.

A similar procedure is possible for systems with *different types of stickers* if they are arranged in some regular pattern which is repeated along the chain. In that case the same procedure is valid, with the only difference that instead of the 2 × 2 matrix K a bigger matrix has to be used as building blocks for the A matrix.

5.2. Examples. We will show now some examples of predictions of linear viscoelastic behavior according to the present model. A drawback of the method, outlined above, is that the number of states increases rapidly with the number of stickers and a considerable amount of computer time and memory is required for the analysis. This may be reduced eventually by making use of special algorithms, but at present we only performed calculations for relatively few stickers. This, however is sufficient to illustrate some characteristic features of the model.

We use a chain with up to eight stickers. First the case of equal stickers will be discussed and after that also the case of a chain with two types of stickers. Finally, we also use a different method, namely a straightforward simulation of the creation, loss and deformation according to the present model for an ensemble of chains. In this way also results for larger numbers of stickers can be obtained.

For the creation and loss rates g and h we use an Arrhenius type of equation

$$g, h \sim \alpha e^{E_t/kT} \qquad (35)$$

where α^{-1} is a characteristic time, k is the Boltzmann constant, T is the absolute temperature, and the index $t = g$ is used for creation and $t = h$ is used for loss processes. For the calculations we take $\alpha = 1$ and express the activation energies E_t in units kT. The results shown here are renormalized to the number of segments per chain. In Figure 4 the relaxation spectrum is given for the cases of 5 and 8 stickers with $E_g = 3$ and $E_h = 5$ as calculated with eq 21, 25, and 27. We see that the spectrum is relatively wide and we also note the rapid growth of the number of relaxation times with
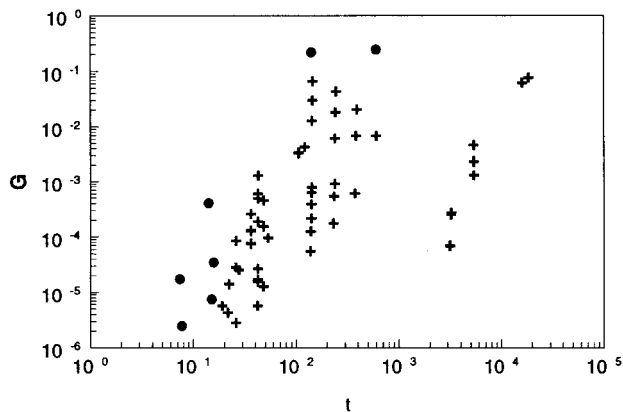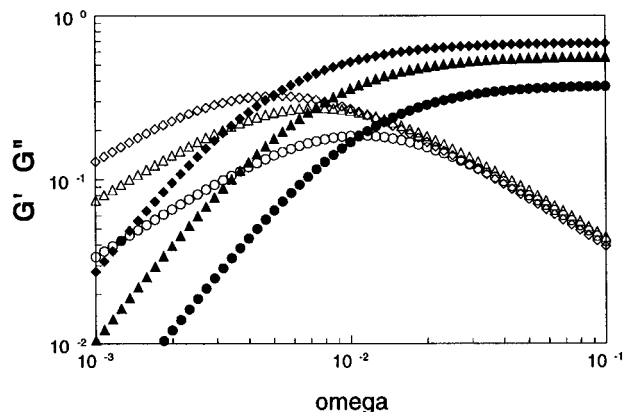
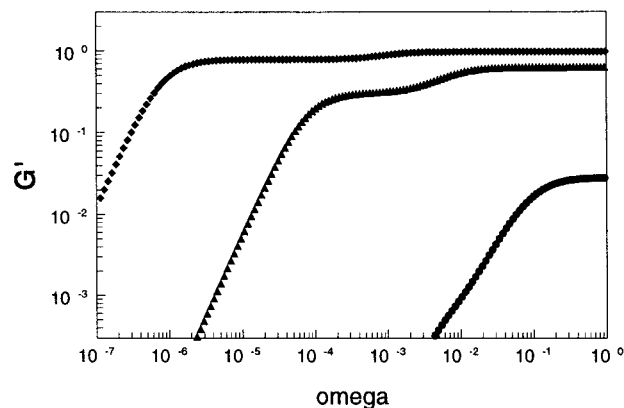**Figure 4.** Relaxation spectra $E_g = 3$, $E_h = 5$: (●) $N = 5$; (+) $N = 8$.
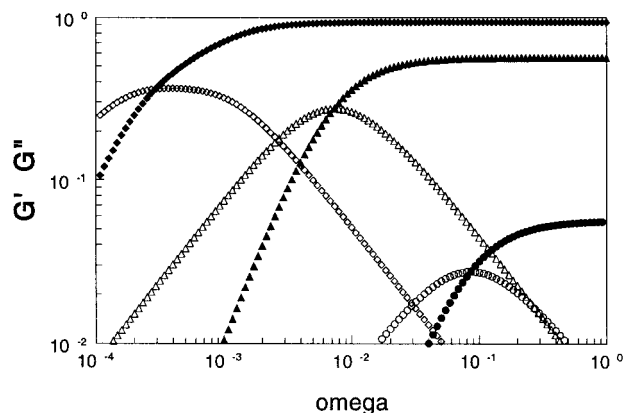
Figure 5. Viscoelastic moduli for 5 stickers per chain and $E_g = 5$, open symbols designate G'', closed symbols G', $E_h = 3$ (○), $E_h = 5$ (△), and $E_h = 7$ (◇).

Figure 6. Viscoelastic moduli for $E_g = 5$ and $E_h = 5$. Open symbols designate G'' and closed symbols G': (○) $N = 3$; (△) $N = 5$; (◇) $N = 7$.


Figure 7. Two types of stickers, $N = 6$, $E_{g \text{ weak}} = 5$, $E_{g \text{ strong}} = 10$: (●) $E_{h \text{ weak}} = 3$, $E_{h \text{ strong}} = 6$; (▲) $E_{h \text{ weak}} = 5$, $E_{h \text{ strong}} = 10$; (◆) $E_{h \text{ weak}} = 7$, $E_{h \text{ strong}} = 14$.

increasing N. In particular, for the case of eight stickers, it can be seen that the relaxation times can be divided into two groups of relaxation processes. The largest relaxation times are about 2×10^4, which correspond to relaxation process where two bonds breakup simultaneously. The second group is the group around 1×10^2, which is the breakup time of one sticker. This group consist of many different relaxation times, divided into two subgroups. First, there is the relaxation process where chain segments relax after a process of breakup of several stickers in succession. The corresponding relaxation time grows roughly in a linear way with the number of bonds that have to break for such a process. Second, there are often various ways for the same number of bonds to break (either simultaneously or in succession). This will cause the relaxation time to be proportional to the number of possible ways of breaking. In Figure 5 the moduli G' and G'' are given for a chain of five stickers, a creation energy of $E_g = 5$, and three different values of the loss energy, $E_h = 3$, 5, and 7. We note (in particular for high values of E_h) the relatively flat slope in the low-frequency region of the moduli curves, which is an indication of a broad spectrum. We see that the value of the plateau modulus increases for higher values of E_h. This is also what should be expected, since a high value of E_h implies a longer average lifetime of the chains, which means higher stresses. For higher values of E_h we also see a shift of the curves to the left, which corresponds to longer relaxation times. This is also in accordance with the longer lifetimes of the chains. In Figure 6 the viscoelastic moduli are presented for the case that $E_g = E_h = 5$

and three different values of N: $N = 3$, 5, and 7. We see a strong increase of the moduli values with the number of stickers. This is characteristic of the present model where the connectivity of the chains is taken into account. If a sticker becomes free, this will not always mean a loss of stress. Only for stickers that terminate a succession of active segments is such the case. The probability of such an occurrence does not depend on N, but for larger N the fraction of such stickers is simply smaller. This increase in the number of multiconnected states for higher N also contributes to shift the relaxation spectrum to larger times; this causes the shift of curves to the left. Roughly the mean relaxation time scales with the number of stickers. In Figure 7 the effect of different types of stickers is illustrated. Here we consider the viscoelastic moduli for the case of two type of stickers: strong $E_g = 10$, $E_h = 2$ and weak $E_g = 5$, $E_h = 1$ for the cases $E_h = 3$, 5, and 7. We see that in this manner it is possible to obtain G' curves with different plateaus and G'' curves with multiple maxima.

Although the example here is given to show some features of our model, it should be noted that application for the case of two types of stickers is part of our current research on the rheological behavior of guar gum solutions.[15]

Again, we see for higher values of E_h larger moduli and a shift of the curves to longer time ranges.

In Figure 8 the results of direct simulations are compared with the results obtained with the analytical method discussed above. In this simulation, the relax-
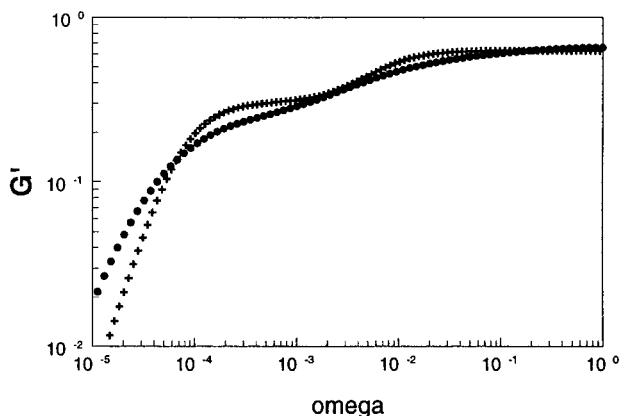
Figure 8. Comparison of simulation and analytical results $N = 6$, $E_g = 5$, $E_h = 5$: (+) analytical; (●) simulation.

Figure 9. Simulation results for one type of stickers, $E_g = 5$, $E_h = 5$: (●) $N = 2$; (▲) $N = 4$; (◆) $N = 8$; (◇) $N = 16$.

Figure 10. Simulation results for two type of stickers, random placement of strong and weak stickers (1:1), $E_{g\ \text{weak}} = 5$, $E_{h\ \text{weak}} = 5$, $E_{g\ \text{strong}} = 10$, $E_{h\ \text{strong}} = 10$: (●) $N = 2$; (▲) $N = 4$; (◆) $N = 8$; (◇) $N = 16$.

ation spectrum is obtained from single chain simulations. During these simulations, the lengths and orientations of chain segments are kept constant. This is allowed, since the linear relaxation behavior is determined only by the breakup and formation of bonds. A step strain experiment is simulated: a chain, randomly placed in a given state performs a virtual step strain. As a consequence all active chain segments obtain a given extension and orientation and a given stress.
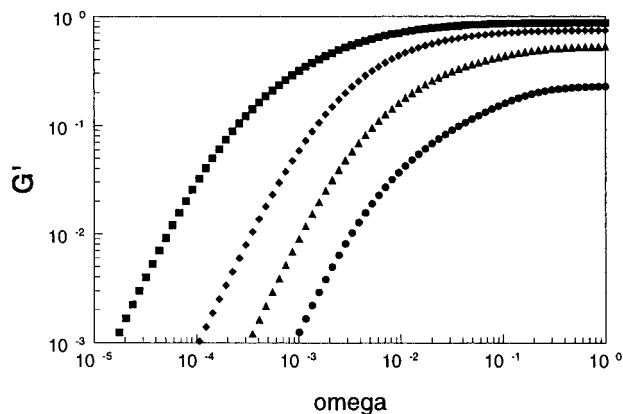
During a simulation time step, the stickers have a given probability, determined by the activation energies, to change their state (free, fixed). By this process, particular chain segments become inactive and lose their preferred orientation and stress. When chain segments become inactive the corresponding relaxation time and number of segments that becomes inactive is stored. In the stress relaxation experiment. inactive segments will not contribute to the stress any more, even if they become active again. The process of changing states of stickers is repeated until all stress contributions are lost. The simulation is repeated for many randomly chosen chains and the time values and stress losses of the various chains are collected. In this way, the relaxation spectrum is obtained.

We see significant differences with the analytical results, in particular over a long time range. These difference are caused by errors, due to the relatively small number (typically 100) of chains used in the simulations. On the other hand, the simulation results still give a reasonable approximation of the magnitude and shape of G'. This offers the possibility to extend the range of N values. This is illustrated in Figures 9 and 10 for the storage modulus G' for the cases of one and two types of stickers and $N = 2, 4, 8,$ and 16.
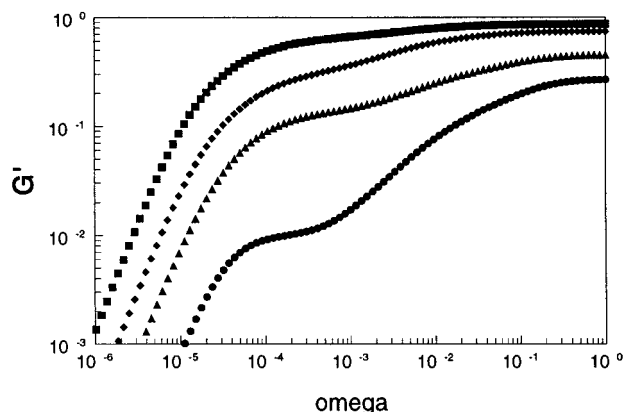
Note that in Figure 10 two plateaus are visible for the case of two stickers. This is a result of the random placement of strong and weak stickers. Sometimes a chain with two strong stickers is simulated, and then the relaxation time becomes large. In the analytical solution, the plateau at low frequencies would not be present here. For a large number of stickers, the difference between the one and two type sticker behavior becomes less. However the behavior in the case of one sticker remains smooth compared to the case of two stickers.

6. Concluding Remarks

In this paper, a network model is presented which is essentially different from common transient network models in the sense that the stress release in segments is treated as a cooperative process. If a sticker becomes free, the stress in the adjacent segments is not always released; this will happen only for segments which become free in the sense indicated in Figure 1. In other cases, the stress in the segment will remain the same. Physically this leads to broad spectra with long relaxation times, in particular for chains with many segments. This is qualitatively in accordance with the observed behavior of polymer gels.

Formally, the dynamics of the system is primarily described by the state s of the whole chain, and not, as in ordinary transient network models, by the state of independent segments. A drawback of this representation is that the number of states increases rapidly with the number of stickers, so with modest computing resources, only chains with relatively few stickers can be analyzed. For that case, as has been shown in the previous section, the main features of the model can already be demonstrated adequately. We have discussed the linear viscoelastic behavior of the chain with up to eight stickers for a few values for the creation and loss rates. It has been shown that the model predicts a wide relaxation spectrum with a shape determined by the underlying kinetics. This is essentially different from ordinary transient network models, where the shape of the relaxation spectrum is introduced ad hoc by the concept of complexity[7] of segments.

The shape of the spectrum alters if different types of stickers are introduced. We have seen how in that case

plateau regions in the dynamic viscoelastic moduli may appear. This feature may be used by the modeling of particular systems such as gels of biopolymers. In an earlier paper,[14] moduli with plateau values were also obtained for the case of one type of stickers. This, however appears to be the result of the crude approximations in the mathematical analysis, which have been improved in the present formulation.

In the work of Leibler, Rubinstein, and Colby[6] [LRC] the dynamics of a temporary network with reversible cross-links is described by a sticky reptation model. In the LRC model, a reptational diffusion takes place if parts of the chain become free (in an earlier treatment of Gonzalez,[3] it was required for a reptation step that the whole chain was free). Stress relaxation is modeled as in classical reptation theory and takes place at a characteristic time T_d, the disengagement time of the whole chain. Two important time scales in the LRC model also are the average lifetime τ of the stickers and the disengagement time T_d. As a result the model predicts essentially two plateau regions in $G'(\omega)$.

Our model is in a sense complementary to the LRC model. We neglect reptation completely and attribute the stress relaxation solely to the stress release in free segments at the chain ends, which is assumed to be instantaneous. We assume that in a transient gel this mechanism of stress release is far more important than the slow stress relaxation due to (sticky) reptation and that the only fundamental process is the creation and loss of individual stickers. Interconnection of segments is taken into account and that the relaxation spectrum is derived explicitly. As a result, our model (for one type of stickers) predicts no extra plateau region in $G'(\omega)$ but only a broadening for frequencies below the characteristic time of the stickers, whereas the LRC model predicts a plateau between this region and frequencies corresponding to the reptation (disengagement) time scale. The first part of the LRC relaxation spectrum (belonging to their characteristic time τ) is independent of the molecular weight. We, on the other hand, find a relaxation spectrum which strongly depends on the number of stickers and also of the molecular weight.

It should be noted also that currently no explicit derivation of relaxation behavior based upon the sticky reptation model is available. The LRC model provides a detailed analysis of the diffusion of the chain along the tube but only a crude estimation of the of the relaxation behavior, based upon classical reptation theory and the obtained results for the characteristic time scales. A rigorous treatment should be based upon the stress contributions in the chain segments.

Finally if should be noted that contrary to LRC, our model, although based upon rather crude approximations, predicts a closed constitutive equation.

An obvious extension of our present model is an analysis of nonlinear rheological behavior. This will not be undertaken, however, in this paper. The advantage of our present analysis of linear viscoelastic behavior is that some specific results are obtained, with only a few a model assumptions.

As in classical network theory, the extension to the nonlinear regime may proceed by introducing (rate of) strain or stress dependent creation and loss rates, nonaffine motion, etc. This is possible, in principle, but this requires the introduction of extra model parameters. On the other hand, it should be noted that the fact that we are able to derive an explicit analytical constitutive equation provides at least a starting point for nonlinear constitutive modeling. In approaches such as the LRC model, where no constitutive equation is derived, such is impossible.

Instead of phenomenological and empirical constitutive modeling, we would prefer however to extend the numerical treatment used in connection with our Figures 9 and 10. In that treatment, physically realistic properties can be attributed to individual stickers and also more realistic segment force laws than our eq 17 can be introduced. The only price that has to be paid here is that with such modifications the model will be no longer have a closed analytical form. Such, however, is an exception in rheological modeling, anyhow.

Additional refinement of the model is possible. In particular, the assumption that released segments transfer instantaneously into their equilibrium state is rather artificial. It would be more realistic to introduce here some kind of reptation time for the chain ends. Although such is probably possible, we did not introduce this. The assumption is in the spirit of classical transient network theory, moreover, since the main contribution to the stress is due to the active segments, and thus, we do not expect a substantial improvement of the model by this refinement.

Other modifications could be introduced: the introduction of additional mechanisms such as stress release, nonaffine motion, etc. We still believe, however, that the basis principles as outlined in this paper are the essential elements describing the linear viscoelastic behavior of weak polymer gels.

Appendix A. Derivation of equation eq 15

By eqs 9, 12, and 13

$$\frac{\delta}{\delta t}\mathbf{S}_s^i + \zeta_s^i(\mathbf{S}_s^i - \boldsymbol{S}^0) = \sum_{s'}\chi_{ss'}^i(\mathbf{S}_{s'}^i - \mathbf{S}_s^i) \qquad (36)$$

with

$$\zeta_s^i = \sum_{s'}\frac{n_{s'}}{n_s}A_{ss'}\nu_s^i(1 - \nu_{s'}^i) \qquad (37)$$

and

$$\chi_{ss'}^i = \frac{n_{s'}}{n_s}A_{ss'}\nu_s^i \nu_{s'}^i \qquad (38)$$

so

$$\frac{\delta}{\delta t}(\mathbf{S}_s^i - \boldsymbol{S}^0) + \zeta_s^i(\mathbf{S}_s^i - \boldsymbol{S}^0) + \sum_{s'}\chi_{ss'}^i(\mathbf{S}_s^i - \boldsymbol{S}^0) =$$

$$\sum_{s'}\chi_{ss'}^i(\mathbf{S}_{s'}^i - \boldsymbol{S}^0) + 2\frac{kT}{\kappa}\mathbf{II}$$

$$\frac{\delta}{\delta t}(\mathbf{S}_s^i - \boldsymbol{S}^0) + \sum_{s'}\zeta_s^i\delta_{ss'}(\mathbf{S}_{s'}^i - \boldsymbol{S}^0) +$$

$$\sum_{s'}\sum_{s''}\chi_{s's''}^i\delta_{ss'}(\mathbf{S}_{s'}^i - \boldsymbol{S}^0) = \sum_{s'}\chi_{ss'}^i(\mathbf{S}_{s'}^i - \boldsymbol{S}^0) + 2\frac{kT}{\kappa}\mathbf{II}$$

$$\frac{\delta}{\delta t}(\mathbf{S}_s^i - \boldsymbol{S}_0) + \sum_{s'}\beta_{ss'}^i(\mathbf{S}_{s'}^i - \boldsymbol{S}^0) = 2\frac{kT}{\kappa}\mathbf{D}$$

where $\delta/\delta t$ is an upper convective derivative (so $(\delta/\delta t)\boldsymbol{S}^0 = -2(kT/\kappa)\mathbf{D}$) and

$$\beta^i_{ss'} = (\zeta^i_{s'} + \sum_{s''}\chi^i_{s's''})\delta_{ss'} - \chi^i_{ss'}$$

$$= \sum_{s''}\frac{n_{s''}}{n_{s'}}A_{s's''}(\nu^i_{s'}(1 - \nu^i_{s'}) + \nu^i_{s'}\,\nu^i_{s''})\delta_{ss'} - \frac{n_{s'}}{n_s}A_{ss'}\nu^i_s\,\nu^i_{s'}$$

$$= \sum_{s''}\frac{n_{s''}}{n_{s'}}A_{s's''}\nu^i_{s'}\delta_{ss'} - \frac{n_{s'}}{n_s}A_{ss'}\nu^i_s\,\nu^i_{s'}$$

$$= \sum_{s''}\frac{n_{s''}}{n_s}A_{ss'}\nu^i_s\delta_{ss'} - \frac{n_{s'}}{n_s}A_{ss'}\nu^i_s\,\nu^i_{s'}$$

$$= \frac{n_s}{n_s}\nu^i_s\delta_{ss'} - \frac{n_{s'}}{n_s}B^i_{ss'}$$

References and Notes

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