1. INTRODUCTION

Self-assembly and rheological properties of the transient networks made up of telechelic associating polymers have attracted much experimental and theoretical interest in recent years. Telechelic associating polymers are water-soluble polymers carrying short hydrophobic chains attached at their chain ends. Typical examples are hydrophobic ethoxylated urethane (called HEUR), hydrophobic poly(N-isopropylacrylamide)(tel-PNIPAM), hydrophobic poly(2-isopropyl-2-oxazoline)(tel-PIPOZ) etc. These telechelic polymers form flower micelles at low polymer concentration. With increase in the concentration, micelles are connected to each other by bridge chains. The solutions eventually change to networks with micellar junctions, which allow association and dissociation of the hydrophobic chain ends.

The rheological properties of associating polymers are commonly studied by dynamic mechanical measurements. A simple theory of the transient networks in which network junctions can break and recombine by thermal motion and/or under applied deformation was proposed by Green and Tobolsky, and later developed by Lodge and Yamamoto. The fundamental assumption of TE theory is the affine deformation of the network junctions as in the classical theory of rubber elasticity; the end-to-end vector of a bridge chain connecting the neighboring micellar junctions deforms affinely to the macroscopic deformation tensor. TE derived the master curve for the dynamic moduli of a Maxwell fluid with a well-characterized single relaxation time.

More recently, Tanaka and Koga studied the effects of fluctuation and diffusion of the network junctions by considering non-affine deformation. Koga et al discussed the effect of the tension along the chain on the disengagement rate, and studied the normal stresses as well as the shear stress.
of the main chains under flows has not been explicitly taken into account. However, in the networks of temperature-sensitive polymers, such as tel-PNIPAM and tel-PIPOZ, effect of chain collapse is expected to be drastic, in particular, near the coil–globule transition temperature. To cope with such conformational transition of the main chains, we develop in this paper a new transient network model which can incorporate the transition of the main chain between two conformation states A and B (two-state model), one of which (B) is taken as a reference conformation such as a random coil, and the other (A) is a collapsed state.

2. MODEL TRANSIENT NETWORKS

Consider a networks made up of telechelic polymers whose main-chains consist of the polymers capable of taking either the collapsed state (referred to as A-state) or the random-coil state (referred to as B-state), and whose end-chains form micellar network junctions by hydrophobic aggregation. We regard the random conformation of the chain as the reference state. We mainly concern in this paper the partially collapsed conformation of the chain for the A-state, but we can treat other conformations such as partial helix, sheet, rod, etc equally well. The timescale of the conformation transition is described by the reaction rate, and hence depends on the free energy barrier between the two states.

The end-chains are assumed to undergo association–dissociation process by thermal motion of the chains and/or under external forces. The timescale of this process is described by the average life time of the end groups in the junctions. Chains in the network are then classified into four categories: elastically effective A-chains (A state with both ends connected to the junctions, referred to as EA), dangling A-chains (A state with free one end, DA), elastically effective B-chains (random coils with its both ends connected to the junctions, EB), and dangling B-chains (random coils with one free end, DB) (see Figure 1).

The transition from EA to EB is assumed to take place with the reaction rate \( k(r) \), and for the reverse transition with the reaction rate \( k'(r) \). They depend on the end-to-end vector \( r \) connecting the two network junctions, and hence on the tension along the chain. Because A/B transition is mainly caused by the tension along the chain, the transition between DA and DB is assumed to be so slow that it is neglected.

To study the rheological properties of the transient model network, we start from the time-development equations for the number of elastically effective chains, and of dangling chains, under arbitrary time-dependent deformation \( \dot{\lambda}(t) \)

\[
\begin{align*}
\frac{\partial \psi_A}{\partial t} + \nabla \cdot (\mathbf{v}_A \psi_A) &= - (\beta_A + k) \psi_A + k' \psi_B + \alpha_A \phi_A \\
\frac{\partial \psi_B}{\partial t} + \nabla \cdot (\mathbf{v}_B \psi_B) &= - (\beta_B + k') \psi_B + k \psi_A + \alpha_B \phi_B \\
\frac{\partial \phi_A}{\partial t} &= - \alpha_A \phi_A + \beta_A \psi_A \\
\frac{\partial \phi_B}{\partial t} &= - \alpha_B \phi_B + \beta_B \psi_B
\end{align*}
\]

(2.1a)  (2.1b)  (2.1c)  (2.1d)

where \( \psi_A(r, t) \), \( \psi_B(r, t) \) are the number of EA and of EB chains in the network at time \( t \) whose end-to-end vector is specified by \( r \), and \( \phi_A(r, t) \), \( \phi_B(r, t) \) are those for the dangling chains. The effective chains are assumed to deform affinely to the external deformation, and hence we have

\[
\mathbf{v}_A(t) = \mathbf{v}_B(t) = \frac{d\dot{\lambda}(t)}{dt} \cdot \dot{\lambda}(t)^{-1} \cdot r
\]

(2.2)

for the deformation velocities.

The dissociation rate \( \beta_i(r)(i = A, B) \) is the probability for the end group of an effective chain of the type \( i \) to dissociate from the junction per unit time. Similarly, the recombination rate \( \alpha_i(r) \) is the probability for the free end of a dangling chain of the type \( i \) to associate into the junction. In addition to these conventional treatments of the transient networks, we have introduced new reaction rates \( k \) and \( k' \) for the transition between A and B states. The reaction rate \( k(r) \) is the transition probability per unit time for an EA chain to change to an EB chain, and \( k'(r) \) is vice versa. They both depend on the end-to-end vector \( r \) because the conformation change is driven by the

![Fig. 1. Model network consisting of the chains of four categories: effective A (EA), dangling A (DA), effective B (EA), dangling B (DB). The transition between the effective A and effective B is assumed to take place with the reaction rate \( k \) and \( k' \).](image-url)
The total numbers of E-chains and D-chains at time $t$ are given by the integrations as

$$\nu_i(t) = \int \psi_i(r, t) \, dr \quad (2.3a)$$

$$\mu_i(t) = \int \phi_i(r, t) \, dr \quad (2.3b)$$

for $i = A, B$.

3. EQUILIBRIUM STATES AND DETAILED BALANCE CONDITION

First, we consider the equilibrium state under no deformation $\lambda(t) = 0$. By putting $\partial/\partial t = 0$, the equations reduce to

$$-(\beta_A + k)p_A + k'\psi_A + \alpha_A\phi_A = 0 \quad (3.1a)$$

$$-(\beta_A + k')\psi_A + k'\psi_B + \alpha_A\phi_A = 0 \quad (3.1b)$$

$$-\alpha_A\phi_A + \beta_A\psi_A = 0 \quad (3.1c)$$

$$-\alpha_B\phi_B + \beta_B\psi_B = 0 \quad (3.1d)$$

From the last two equations, we have

$$\psi_A(r) = \frac{\alpha_A}{\beta_A} \phi_A(r) \quad (3.2a)$$

$$\psi_B(r) = \frac{\alpha_B}{\beta_B} \phi_B(r) \quad (3.2b)$$

Substituting into the first two equations, we find the reaction rate $k$ and its reverse rate $k'$ must satisfy the relation

$$\frac{k'}{k} = \frac{\alpha_A\beta_B\phi_A}{\alpha_B\beta_A\phi_B} \quad (3.3)$$

This serves as the detailed balance condition to ensure the unique equilibrium state. In what follows, we write this ratio as $\kappa$. We then have

$$k'(r) = \kappa(r)k(r) \quad (3.4)$$

The equilibrium chain distribution functions can be written in terms of the tension of the chains. For the dangling chains, they are

$$\phi_i'(r) = \mu_i\phi_i(r) \quad (3.5)$$

for $i = A, B$, where $\mu_i$ are the equilibrium numbers of the dangling chains of each type, and

$$\Phi_i(r) = C_i \exp \left[ - \int_0^r f_i(r) \cdot dr \right] \quad (3.6)$$

are the normalized probability distributions for the end-to-end vector $r$ of the dangling chains. The force $f_i(r)$ as functions of the end-to-end vector are regarded as the known properties.

Similarly, we can write

$$\psi_i'(r) = \nu_i\psi_i(r) \quad (3.7)$$

and

$$\Psi_i(r) = C_i \exp \left[ - \int_0^r F_i(r) \cdot dr \right] \quad (3.8)$$

for the effective chains. The tension $F_i$ are different from $f_i$ because of the existence of end-chain dissociation–association processes. From the equilibrium solutions (3.2a) and (3.2b), we have the relation

$$F_i(r) = f_i(r) - \nabla \ln \left( \frac{\alpha_i(r)}{\beta_i(r)} \right) \quad (3.9)$$

for $i = A, B$.

4. LINEAR RESPONSE OF THE NETWORK UNDER OSCILLATORY SHEAR FLOW

To study linear response of the network under small oscillatory shear flow along $x$ axis, we consider the deformation tensor

$$\lambda(t) = \begin{bmatrix} 1 & \epsilon e^{i\omega t} & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (4.1)$$

where $\omega$ is the frequency of oscillation, and the amplitude $\epsilon$ of the oscillation is assumed to be small. The affine velocity vector (2.2) is given by

$$v(t) = \begin{bmatrix} \epsilon e^{i\omega t} e^{i\omega t} \\ 0 \\ 0 \end{bmatrix} \quad (4.2)$$

The distribution function of the end-to-end vector of the effective chains is then changed to

$$\psi_i(r, t) = \psi_i'(r)\{1 + \epsilon \eta_i(r, t)\} \quad (4.3)$$

up to the first order of the deformation amplitude $\epsilon$. On the contrary, the distribution function of the dangling chains remains the same within the first order of $\epsilon$. Its correction is of the second order $\phi_d(r, t) = \phi_d'(r) + O(\epsilon^2)$

Substituting these forms into eqs (2.1a) and (2.1b), we obtain the equations for the linear deviations $\eta_i(r, t)$
\[
\frac{\partial \eta_A}{\partial t} + (\beta_A + k) \eta_A - k' R(r) \eta_B = i \omega y e^{i \omega t} F_{A,x}
\]
\[
\frac{\partial \eta_B}{\partial t} + (\beta_B + k') \eta_A - k R(r) \eta_A = -i \omega y e^{i \omega t} F_{B,x}
\]
where
\[
R(r) \equiv \frac{\psi_A^*(r)}{\psi_B^*(r)}
\]
and \(F_{i,x}\) is the \(x\)-component of the tension (3.9) for an effective chain of the type \(i\).

To solve these coupled eqns, we introduce the amplitude for \(\eta\) as
\[
\eta_A(r, t) = A(r) e^{i \omega t}, \quad \eta_B(r, t) = B(r) e^{i \omega t}
\]
On substitution into eqns (4.4a) and (4.4b), we find
\[
\begin{bmatrix}
i \omega + \beta_A + k, & -k \\
-k', & i \omega + \beta_B + k'
\end{bmatrix}
\begin{bmatrix}A \\ B\end{bmatrix}
= i \omega y \begin{bmatrix}F_{A,x} \\ F_{B,x}\end{bmatrix}
\]
Solving these eqns for \(A\) and \(B\), we have
\[
\begin{bmatrix}A \\ B\end{bmatrix} = i \omega y \frac{\begin{bmatrix}(i \omega + \beta_B + k')F_{A,x} + k F_{B,x} \\ k' F_{A,x} + (i \omega + \beta_A + k) F_{B,x}\end{bmatrix}}{D(r, \omega)}
\]
where
\[
D(r, \omega) \equiv (i \omega + \beta_A + k)(i \omega + \beta_B + k') - k k'
= \alpha^2 - \omega^2 + i \beta \omega
\]
is the determinant of the matrix. The new parameters \(\alpha\) and \(\beta\) have been introduced by the definitions
\[
\alpha(r) \equiv (\beta_A \beta_B + k \beta_B + k' \beta_A)^{1/2}
\]
and
\[
\beta(r) \equiv \beta_A + \beta_B + k + k'
\]
All these parameters depend on the chain vector \(r\).

Since we have two kinds of elastically effective chains, we can calculate the stress by adding each contribution in the linear regime. From the formula for the stress, the \((i, j)\) component is given by
\[
\sigma_{i,j}(t) a^3 = \int \delta r \left[ (x_i f_{A,j}) \psi_A^*(r, t) + (x_i f_{B,j}) \psi_B^*(r, t) \right]
\]
For the linear response, we have
\[
\sigma_{x,y}(t) a^3 = \epsilon \int \delta r \left[ (x f_{A,y}) \psi_A^*(r, t) \eta_A(r, t) + (x f_{B,y}) \psi_B^*(r, t) \eta_B(r, t) \right]
\]
The complex modulus is defined by the response to the deformation (4.1) in the form
\[
\sigma_{x,y}(t) a^3 = \epsilon G(\omega) e^{i \omega t}
\]
Substituting (4.6) into the stress (4.13), and comparing with the definition of modulus, we find
\[
G(\omega) = \int dr \frac{i \omega}{D(r, \omega)} \left\{ \phi_A^*(r) Q_A(r, \omega) + \phi_B^*(r) Q_B(r, \omega) \right\}
\]
where
\[
Q_A(r, \omega) \equiv \frac{\alpha_A}{\beta_A} \left[ (i \omega + \beta_B + k') (x f_{A,y}) (y f_{A,x}) + k (x f_{B,y}) (y f_{B,x}) \right]
\]
\[
Q_B(r, \omega) \equiv \frac{\alpha_B}{\beta_B} \left[ k' (x f_{A,y}) (y f_{A,x}) + (i \omega + \beta_A + k) (x f_{B,y}) (y f_{B,x}) \right]
\]
We have eliminated the unknown \(\psi_i^*(r)\) in favor of the known distribution functions \(\phi_i^*(r)\). In these equations, we have the detailed balance condition (3.4) between \(k\) and \(k'\).

If there is no transition between \(A\) and \(B\) state, we have \(k = k'=0\), so that the modulus reduces to the sum of the Maxwell elements, each corresponding to \(A\) and \(B\) state. However, for finite transition rates, there are interferences between them.

5. RELATION TO THE BURGERS MODEL

So far we have allowed an arbitrary chain vector dependence of the dissociation and association rates. To obtain specific results, let us confine in what follows to the simplest case of the constant rates. Also, let us assume the reaction rate \(k\) from \(A\) state to \(B\) is also a constant. (The reverse rate \(k'\) depends on \(r\) to ensure the correct equilibrium.) The effect of the chain tension on the transition rate can be included to the analysis, but only at the expense of more combursome calculation.

We then have
\[
G(\omega) = \frac{4 \pi}{15} \nu_0 k_B T \int_0^\infty dr r^4 \Phi_0(r) \frac{i \omega [P(r) + i \omega Q(r)]}{\alpha(r)^2 - \omega^2 + i \beta(r) \omega}
\]
where \(B\) state is assumed to be Gaussian, and
\[
\nu_0 \equiv \alpha_B \mu_B^2 / \beta_B
\]
is the equilibrium number of effective \(B\) chains, and
\[
\Phi_0(r) = C_n e^{-r^2/2na^2}
\]
is the distribution of the end vector of a Gaussian chain with \(n\) statistical units. Other factors are
Since the main contribution to the integrals comes from the spherical region with radius of $n^{1/2}a$ around the origin of the coordinates, we can replace $\kappa(r)$ in the integrand by its value $\kappa_0 \equiv \kappa(0)$ at the origin. Within this approximation, we have

$$G(\omega) = \nu_0 k_B T Q \times$$

$$\frac{[\beta(P/Q) - (\alpha^2 - \omega^2)]\omega^2 + [\beta \omega^2 + (P/Q)(\alpha^2 - \omega^2)]\omega}{\beta^2 \omega^2 + (\alpha^2 - \omega^2)^2}$$

(5.4)

where we have

$$P = [\beta_B + k(1 + \kappa_0)]\kappa_0 g_{AA}$$

$$Q = \kappa_0 g_{AA} + g_{BB}$$

(5.5a, 5.5b)

after integration, with the definitions

$$g_{AA} = \frac{4\pi}{15} \int_0^\infty drr^4 \Phi_0(r) f_A(r)^2$$

$$g_{BB} = \frac{4\pi}{15} \int_0^\infty drr^4 \Phi_0(r) f_B(r)^2$$

(5.6a, 5.6b)

We can now clearly see that our transient network gives the dynamic mechanical modulus of the Burgers model. In the Burgers model, a Maxwell element with modulus $R_1$ and viscosity $\eta_1$ is connected to a Voigt element with $R_2$ and $\eta_2$ in series. Comparing with the standard description of the model,2) we find that the phenomenological elastic moduli and viscosities of the Burgers model are related to our molecular parameters through the equations

$$\eta_1 \left( \frac{1}{R_1} + \frac{1}{R_2} \right) + \frac{\eta_2}{R_2} = \frac{\beta}{\alpha^2}$$

(5.7a)

$$\frac{\eta_1 \eta_2}{R_1 R_2} = \frac{1}{\alpha^2}$$

(5.7b)

$$\eta_1 = P$$

(5.7c)

$$\frac{\eta_1 \eta_2}{R_2} = Q$$

(5.7d)

The relaxation time of the Maxwell element is therefore given by

$$\tau_1 = \frac{\eta_1}{R_1} = \frac{P}{Q\alpha^2}$$

(5.8)

and that of the Voigt element is

$$\tau_2 = \frac{\eta_2}{R_2} = \frac{Q}{P}$$

(5.9)

From these relations, we can find that the longer one (slow mode) of the two relaxation times of the Burgers model is given by

$$\tau_0 = \tau_1 + \frac{\eta_1}{R_2} = \frac{\beta}{\alpha^2}$$

(5.10)

and the shorter one (fast mode) has

$$\tau_m = \sqrt{\tau_1 \tau_2} = \frac{1}{\alpha}$$

(5.11)

To ensure how relaxation of the network is governed by the molecular parameters, we show again the explicit forms of $\alpha$ and $\beta$:

$$\alpha^2 = \beta_A \beta_B + k(\beta_B + \beta_A \kappa_0)$$

(5.12a)

$$\beta = \beta_A + \beta_B + k(1 + \kappa_0)$$

(5.12b)

We solve these equations with respect to the parameters of the Burgers model, and express them in terms of molecular characteristics. The results are
In the high frequency region \( \omega >> \tau_m^{-1} \), the storage modulus shows a plateau of the Maxwell level \( G'(\omega) \sim \nu_0 Q \) (independent of the reaction rate \( k \)), while it has another plateau of the Voigt level \( G'(\omega) \sim \nu_0 R_2 = \nu_0(\beta - P/Q - \alpha^2/\omega) \) in the intermediate frequency region \( \tau_0^{-1} << \omega << \tau_m^{-1} \). For frequencies lower than \( \tau_0^{-1} \), it behaves as \( G'(\omega) \sim \nu_0(\beta - P/Q - \alpha^2/\omega^2) \).

The loss modulus shows in general two peaks corresponding to each mode, and the viscosity behaves as \( \eta(\omega) \sim \nu_0(\beta - P/Q - \alpha^2/\omega^2) \) in the high frequency region, while it has a Newtonian value \( \eta_0 \equiv \eta(0) = \nu_0 \beta/P \) in the low frequency limit.

To see how the parameter \( \kappa_0 \) depends on the chain conformation, let us consider that the conformation A has a densely packed globule consisting of a contiguous sequence of the monomers with length \( \zeta \) on the chain (Figure 1). The total length \( n \) in terms of the number of the repeat units then reduces to the effective one \( n^* = n - \zeta \) corresponding to the random-coil part. The Gaussian assumption (5.2) then gives (5.14)

\[
\kappa_0 = C_{n^*}/C_n = (n/(n - \zeta))^{3/2}
\]

For larger globules, \( \kappa_0 \) is smaller, so that both modes have shorter relaxation times. Because the tension along the main chain grows larger more easily if the effective length of the chain is smaller, dissociation of the end chains takes place more often, and hence the stress relaxation time becomes shorter.

### 6. EFFECT OF THE CONFORMATION TRANSITION ON THE PLATEAU MODULUS AND THE RELAXATION TIME

We first consider the limit where the time scale of the conformational change is much slower than the duration time of the chain ends in the junctions. We have the condition \( k << \beta_A/\beta_B \), so that the network consists of the independent effective chains of each type. The slow mode has the relaxation time \( \tau_0 = 1/\beta_A + 1/\beta_B \), while the fast mode has \( 1/\sqrt{\beta_A \beta_B} \). The modulus is a simple sum of those of the Maxwell fluid of each type with the weight proportional to the number of chains \( \nu_A \) and \( \nu_B \).

Now, we introduce the coupling of these two Maxwell fluids through the finite reaction rate. Figure 3 shows how the two relaxation times are modulated by the reaction rate for a fixed parameter \( \kappa_0 \) of the detailed balance. They both decrease with \( k \), so that stress relaxation is accelerated with the conformational change.

In the limit of fast reaction, the fast mode (end-chain dissociation) disappears as \( \tau_m \sim 1/\sqrt{k} \). Only frequent conformation transition between A and B remains. Relaxation is possible only by the end-chain dissociation. The main chains take average conformation of A and B with their equilibrium statistical weights. The chain tension of such averaged conformations has a wide plateau region in the end-to-end distance, where chain segments are reeled out from the globules at a constant tension. The characteristic time approaches the asymptotic value of the average \((1 + \kappa_0/\beta_A + \kappa_0/\beta_B)\).

In Figure 3, we have fixed for simplicity the chain dissociation rates as \( \beta_A = \lambda \beta_0, \beta_B = \beta_0 \), and used the value \( \kappa_0 = 2^{3/2} \) for the globule of half chain length.

We next consider the high-frequency limit of the modulus. From (5.4), we find that the high-frequency plateau modulus is given by

\[
G_0 = \nu_0 Q k_B T
\]

where \( \nu_0 \) is the equilibrium number \( \nu_0 \) of the effective chains of the reference conformation. Let us express it in terms of the total number of chains

\[
\rho = \nu_A + \nu_B + \mu_A + \mu_B
\]

![Fig. 3. The relaxation times, \( \tau_0 \) and \( \tau_m \), plotted as functions of the reduced reaction rate \( k/\beta_0 \) for three values of the ratio \( \lambda = \beta_1/\beta_0 \). The parameter \( \kappa_0 \) is fixed at \( \kappa_0 = 2^{3/2} \).](image-url)
in the network. By the integration of the detailed balance condition (3.3) over the chain vector, we find $\mu_A = \left( \frac{\alpha_B}{\beta_B} \frac{\beta_A}{\alpha_A} \right) \kappa_0 + \left( 1 + \frac{\alpha_B}{\beta_B} \right) \mu_B$ (6.3) Substituting into $\nu_0$ of (5.1), we find (6.4) It depends on the ratio $\beta/\alpha$ of the dissociation-association process of the end chains.$^{4}$ In Figure 4 we show a typical frequency profile (the reduced value $G(\omega)/G_0$) of the Burgers model. we have fixed the chain dissociation rates as $\beta_B = \lambda \beta_0$, $\beta_B = \beta_0$, and used the value $\kappa_0 = 2^{3/2}$ for the globule of half chain length. In the symmetric case of $\lambda = 1$ where dissociation rates of the chains are the same, the loss modulus shows a symmetry around $\omega_0/\beta_0 = 1$. The precise profile is given by $G'(\omega) = G \left[ F\left( \bar{\omega} \right) \right]$, and $G''(\omega) = G \left[ F\left( \bar{\omega} \right) \right]$, where $\bar{\omega} = \omega_0/\beta_0$ is the scaled frequency, and (6.5) is the amplitude. The effect of the reaction rate is included in $K(k) = 1+(1+\kappa_0)(k/\beta_0)$. The loss tangent is tan $\delta(\omega) = \beta_0/\omega$ as in the Maxwell model. But the shape is narrower. If there is no transition, we have $K(k) = 1$, so that $F(\bar{\omega})$ reduces to the simple Maxwell form (6.6) For the slower dissociation rate $\lambda = 0.1$ of A-chains, there is a shoulder at the high frequency side ($\tau_0$) of the main peak at $\tau_m$. For the faster dissociation rate $\lambda = 10$, the shoulder appears at the low frequency side ($\tau_m$) of the main peak at $\tau_m$. Therefore, by looking into the fine structure in the frequency spectrum of the loss modulus near the collapse transition, we may have chance to study thermo-sensitive rheology of the water-soluble polymers.

7. CONCLUSIONS AND DISCUSSION

We have developed a new transient network model for the telechelic polymers whose main chains change their conformation between two different ones A and B (two-state model) with a finite reaction rate. Although these conformation changes can include any ones, such as coil–globule transition, coil–helix transition, coil–rod transition etc, we focused on the coil–globule transition of the temperature sensitive water-soluble polymers, in particular tel-PNIPAM, near their transition point.$^{23}$ Under the simple assumption of constant dissociation rates of the chain ends, we have found that the stress is released in two different relaxation modes with a slow and fast relaxation time due to the coupling of the conformation change and end-chain dissociation. In the limit of low reaction rate, these modes decouple from each other, resulting in the independent relaxation corresponding to the dissociation of the chain ends on each state. In the limit of high reaction rate, the slow mode gives the average relaxation time of the end-chain dissociation, while the fast mode disappears. The complex modulus has the frequency spectrum of the Burgers model, and shows fine structures depending on the reaction rate. Detailed comparison with experimental data of tel-PNIPAM gives information on the mechanical strength of globules and time-scale of the coil–globule transition.

Fig. 4. The storage and loss modulus of the transient network plotted against reduced frequency. Parameters are fixed at $\kappa_0 = 2^{3/2}$, $R = 0.7$, $k_0/\beta_0 = 0.2$, $\beta_A = \lambda \beta_0$, $\beta_B = \beta_0$. 

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Improvement of the present model is possible for several directions. The first one is to allow chain-vector dependence of the dissociation rates, as well as of the reaction rate. This is a necessary prerequisite for the study of nonlinear rheology.

The second one is to introduce the transition between the conformation DA and DB by introducing the reaction rate $k_2$, $k'_2$. They have been neglected because the conformation change is expected to be mainly driven by the chain tension along the effective chains. Detailed study of these effects, together with examination of the experimental data, will be reported in our forthcoming paper.

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