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Theory of Nonlinear Viscoelasticity of Network Structure Based on the Tube Model

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In previous reports,[1] we presented a nonlinear network theory of viscoelasticity taking into account both chain slippage and change in the number of chains in the deformed state. In the theory, the chain breakage coefficient, the inverse of relaxation time for chain breakage, is treated as a function of the trace of strain tensor.

In another report,[2] we presented a constitutive equation of a network structure on the assumption of constant length transformation of the end-to-end vectors of segments. A segment means a part of polymer chain between two neighbouring junctions.

In this report, we treat the relaxation processes of a network system brought about only by chain breakage. We consider the relaxation processes of deformed state of a network structure, and introduce two processes, contraction of a segment in a tube and the translational diffusive motion of a polymer chain in a tube.

In the first, we consider the relaxation process at constant deformation of a polymer chain, in which each segment in a chain is deformed affinely. In our model terminal segments are broken at the terminal junctions and the broken segments are contracted to the original length in the tube, the tube still being in a deformed state. This short time relaxation process is termed the primary relaxation process. Therefore, the segment lost in the primary relaxation process has the same deformation as the tube, though it has the length in the stress free state and some part of tube disappears by a slip-out of the terminal segments by contraction. This successive segment-breakage and sudden contraction process, the primary relaxation process, corresponds to the contraction by slippage in the tube proposed by Doi,[5] as shown in the relation between the slip theory and chain breakage theory.[3,4]

The relaxation process subsequent to the primary one is the secondary relaxation process due the diffusive motion of the chain, in which each segment have the constant length deformation of the end-to-end vectors of segments. A terminal part of a polymer chain slips out through junctions by the diffusive motion in the secondary relaxation, and segments are lost, and then a long dangling chain is formed. After the dangling chain is re-crosslinked to other chains, segments are formed in the stress free state.

Next, we consider the number of these segments created in a time interval dt' at t' and remain unbroken until a later time t. Let the number of these segments in unit volume of the network structure be $n(t,t')dt'$. $n(t,t')$ is the rate of segment-creation at t' of survived segments in the time interval $(t-t')$, and is termed the "segment generating function". $n(t,t')$ is assumed to be a function of $(t-t')$.

The stress of the network structure at t is supported by the segments which are created before t and remain unbroken at t. Therefore, we can obtain the rheological equation of network structure by knowing the segment generating functions and the deformation of the end-to-end vectors of segments in the primary and the secondary relaxation processes.

In order to formulate a theory using the above concept, we make the following assumptions: (1) the number of segments in a polymer chain is constant, (2) segments are deformed affinely in the primary relaxation process, (3) the deformation of the end-to-end vector of a segment is the constant length transformation in the secondary relaxation process, (4) segments are reformed in the stress free state after the secondary relaxation process, (5) the segment generating function is a function of the time interval between the time in which segments are created and the present time, and (6) segments are Gaussian chains.

We consider the segment generating function $n_1(t,t')$ and $n_2(t,t')$ in the primary relaxation process and the secondary one, respectively.

We introduce $v_1(t,t')$ and $v_2(t,t')$ defined by

$$v_1(t,t')=\int_{-\infty}^{t'} n_1(t,t'')\,dt''$$
$$v_2(t,t')=\int_{-\infty}^{t'} n_2(t,t'')\,dt'' \quad (1)$$

$v_1(t,t')$ is the number of segments which are created before t' and participate in the primary relaxation process at t, $v_2(t,t')$ is the number of segments created before t' and participate in the secondary relaxation process at t, following the primary relaxation process before t. Since the rate of decrease of $v_1(t,t')$ is generally proportional to $v_1(t,t')$ and $v_1(t,t')$ depends only on the time interval $(t-t')$, we have,

$$\partial v_1(t,t')/\partial t=-\partial v_1(t,t')/\partial t'=-v_1(t,t')/\tau_1 \quad (2)$$

where τ_1 is the relaxation time of the primary relaxation process. Then we have

$$v_1(t,t')=v_0\,\mathrm{e}^{-(t-t')/\tau_1} \quad (3)$$

and

$$n_1(t,t')=\frac{\partial v_1(t,t')}{\partial t'}=\frac{v_0}{\tau_1}\mathrm{e}^{-(t-t')/\tau_1} \quad (4)$$

where v_0 is the number of segments in a unit volume of the network structure.

The value of $v_2(t,t')$ is obtained by counting those segments which were created before t' and remain in the primary relaxation process at t'' and then proceed to the secondary relaxation process from t'' to t. Accordingly, letting τ_2 be the relaxation time of the secondary relaxation process, we have

$$v_2(t,t')=\int_{t'}^{t} n_1(t'',t')\mathrm{e}^{-(t-t'')/\tau_2}\,dt''$$
$$=\frac{v_0\tau_2}{\tau_2-\tau_1}(\mathrm{e}^{-(t-t')/\tau_2}-\mathrm{e}^{-(t-t')/\tau_1}) \quad (5)$$

and

$$n_2(t,t')=\frac{\partial v_2(t,t')}{\partial t'}$$
$$=\frac{v_0\tau_2}{\tau_2-\tau_1}\left(\frac{\mathrm{e}^{-(t-t')/\tau_2}}{\tau_2}-\frac{\mathrm{e}^{-(t-t')/\tau_1}}{\tau_1}\right) \quad (6)$$

For the system containing the primary and secondary relaxation processes, the stress is expressed as

$$\boldsymbol{\sigma}(t)=\frac{3kT}{a^2}\int_{-\infty}^{t}[n_1(t,t')\langle(\boldsymbol{r}(t,t')\boldsymbol{r}(t,t'))\rangle$$
$$+n_2(t,t')\langle(\boldsymbol{r}(t,t')\boldsymbol{r}(t,t'))\rangle]\,dt'-P\mathbf{1} \quad (7)$$

where $\boldsymbol{r}(t,t')$ is the end-to-end vector at t of a segment created at t', a is the end-to-end distance of a segment in the stress free state, $(\boldsymbol{rr})$ is the dyad, $\langle\ \rangle$ is the average with respect to the network structure, the subscripts 1 and 2 indicate the quantities in the primary relaxation process and the secondary one, respectively.

Let the relative deformation tensor at t with respect to t' be $\gamma(t,t')$. The deformation of the end-to-end vector $r(t')$ in the primary relaxation process between t' and t is given by

$$r(t,t')=\gamma(t,t')\cdot r(t') \quad (8)$$

from assumption 2, and the deformation in the secondary relaxation process between t' and t is expressed as

$$r(t,t')=\frac{\gamma(t,t')\cdot r(t')}{|\gamma(t,t')\cdot u(t')|}$$
$$u(t')=r(t')/a \quad (9)$$

from assumption 2. Then we have, from eq 7,

$$\sigma(t)=G_0\int_{-\infty}^{t}\left[\frac{e^{-(t-t')/\tau_1}}{\tau_1}\lambda(t,t')+\frac{\tau_2}{\tau_2-\tau_1}\times\left(\frac{e^{-(t-t')/\tau_2}}{\tau_2}-\frac{e^{-(t-t')/\tau_1}}{\tau_1}\right)\frac{3\lambda(t,t')}{\mathrm{Tr}.\lambda(t,t')}\right]dt'-\mathbf{P1} \quad (10)$$

where

$$\left.\begin{aligned}\lambda(t,t')&=\gamma(t,t')\cdot\gamma^{+}(t,t')\\ G_0&=\nu_0 kT\end{aligned}\right\} \quad (11)$$

Equation 10 is a simplification of that of Doi[5], and is easily applied to practical problems.

Stress Relaxation

When a constant shear deformation γ_0 is given at $t=0$, the shear stress is given by

$$\left.\begin{aligned}\sigma_{xy}(t)&=\gamma_0 G(\gamma_0,t)\\ G(\gamma_0,t)&=G_0\left[e^{-t/\tau_1}+\frac{\tau_2}{\tau_2-\tau_1}\times\left(\frac{3}{3+\gamma_0^2}\right)(e^{-t/\tau_2}-e^{-t/\tau_1})\right]\end{aligned}\right\} \quad (12)$$

The relaxation modulus *versus* time relation in log–log plot is shown in Figure 1, the number on each curve is the value of γ_0. The curves have their shoulders in the transition region from the primary relaxation to the secondary one. Similar results were obtained by experiments of Fukuda *et al.*[6]

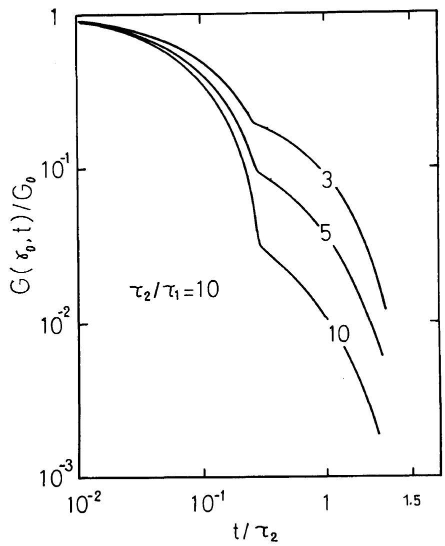

Figure 1. Logarithmic plots of relaxation modulus against time. The number on each curve is the value of γ_0. Curves have shoulders in the transition region from the primary relaxation process to the secondary one.

Elongational Flow

When a steady elongational flow with a constant elongation rate a is given at $t=0$, the stress acting on the elongational direction becomes

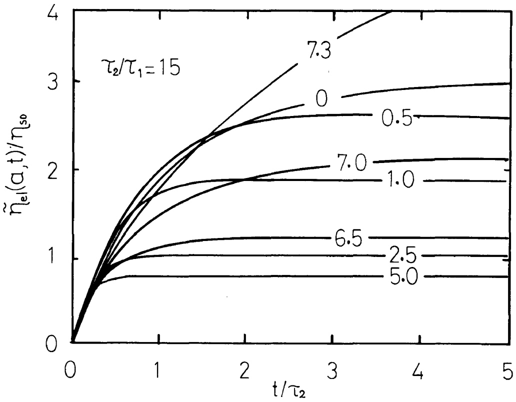

Figure 2. Stress growth at the onset of the steady elongational flow. The number on each curve is the value of the elongation rate, and η_{s0}, the steady shear viscosity.

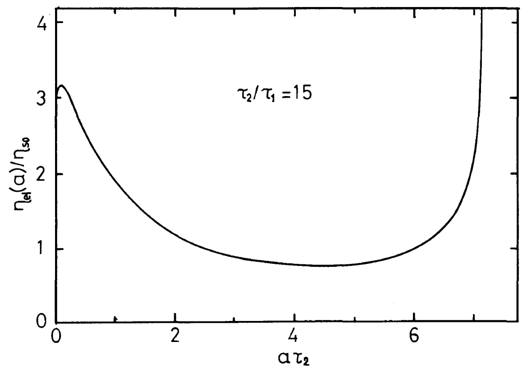

Figure 3. Elongational viscosity plotted against elongation rate predicted from Figure 2. As the elongation rate increases, it increases a little at the beginning, and passing a small maximum it decreases nearly in inverse proportion to the elongation rate and finally increases sharply.

$$\left.\begin{aligned}\sigma_{xx}(t)&=G_0F_{el}(a,t)\\ F_{el}(a,t)&=\int_0^t\left[a\,e^{-x/\tau_1}e^{2ax}(2+e^{-3ax})\right.\\ &\quad+\frac{\tau_2}{\tau_2-\tau_1}(e^{-x/\tau_2}-e^{-x/\tau_1})\\ &\quad\left.\times\frac{d}{dx}\left(\frac{1-e^{-3ax}}{1+2e^{-3ax}}\right)\right]dx\end{aligned}\right\}\quad(13)$$

We introduce $\tilde{\eta}_{el}(a,t)$ by

$$\tilde{\eta}_{el}(a,t)=\sigma_{xx}(t)/a \quad (14)$$

The $\tilde{\eta}_{el}(a,t)$ versus time relation is shown in Figure 2, η_{so} is the stready shear viscosity. $\tilde{\eta}_{el}(a,t)$ increases with time monotonously and tends to a stationary value for each a, which is the elongational viscosity or the tensile viscosity. The elongational viscosity $\eta_{el}(a)$ is given by

$$\eta_{el}(a)=\tilde{\eta}_{el}(a,\infty) \quad (15)$$

In Figure 3 $\eta_{el}(a)$ is plotted against elongation rate. The elongational viscosity has a small maximum at a very small a and it decreases nearly in inverse proportion to a and increases sharply again near at $a=1/2\tau_1$. The small maximum in our theory comes from the transition that the viscosity changes from the increase due to the linear term to the decrease due to the nonlinear term. The second sharp increase also results from the linear term originating in the primary relaxation process. However, in such a high elongation rate as $1/2\tau_1$, whether segments are deformed affinely even in the primary relaxation process is doubtful, and therefore, the second increase in elongational viscosity has a meaning only as a prediction by the theory containing the linear and nonlinear relaxation processes, and complicated flow properties[7] are not explained.

The results for other kinds of simple deformation are omitted, since no new results other than given in the previous report[2] were obtained.

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