Network Theory for Nonlinear Viscoelasticity. Elastic Recoil

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(Received November 11, 1978)

ABSTRACT: A molecular network theory developed by one of the authors (Y.T.) is applied to an elastic recoil which is one of the nonlinear viscoelastic phenomena of concentrated polymer systems. The integral equation for the constrained recovery on the removal of shear stress following steady shear flow is numerically solved with assuming that the solution for the shear strain is approximately described by a function of time t , as $\gamma(t) = \gamma_e - (\gamma_e - \gamma_i) \exp(-\alpha t)$, where α is a positive constant, γ_e an ultimate shear recovery and γ_i the instantaneous shear recovery determined by the rate of shear $\dot{\gamma}$ in the steady shear flow before recovery. The result of this numerical calculation proves that the ultimate recovery increases with $\dot{\gamma}$ and is larger than the value of $s(= \Delta\sigma_{n1}/2\sigma_s)$, where σ_s and $\Delta\sigma_{n1}$ are the shear stress and the first normal stress difference in the steady flow, respectively.

KEY WORDS Network Theory / Nonlinear / Viscoelasticity / Shear Flow / Concentrated Polymer System / Elastic Recoil /

Extensive phenomenological consideration has recently been given to the nonlinear viscoelasticity of concentrated polymer systems, although a molecular theory is less progressive. In previous papers^{1,2} many of the nonlinear viscoelastic properties of concentrated polymer systems were qualitatively explained by a semimolecular theory developed by one of the authors (Y.T.) on the basis of Yamamoto's weak network theory.³ The elastic recoil has not yet been fully investigated by the semimolecular theory because of its lengthy numerical calculation since the result of the elastic recoil is analytically expressed by an

integral equation². In this paper we have numerically solved the integral equation for the elastic constrained recovery of shear stress following the steady shear flow.

THEORETICAL

According to Yamamoto's weak network theory, the chain distribution function $F(\mathbf{h}, N, t)(\mathbf{h}(\xi, \eta, \zeta)$, end-to-end distance vector of the chain between the two network junctions; N , number of segments; t , time) is given by

$$F(\mathbf{h}, N, t) = \frac{1}{|\mathbf{e}(t)|} F(\mathbf{e}^{-1}(t)\mathbf{h}, N, 0) \exp \left[- \int_0^t \beta(\mathbf{e}(t')\mathbf{e}^{-1}(t)\mathbf{h}, N) dt' \right] + \frac{1}{|\mathbf{e}(t)|} \int_0^t |\mathbf{e}(t')| G(\mathbf{e}(t')\mathbf{e}^{-1}(t)\mathbf{h}, N, t') \times \exp \left[- \int_{t'}^t \beta(\mathbf{e}(t'')\mathbf{e}^{-1}(t)\mathbf{h}, N) dt'' \right] dt' \quad (1)$$

where $G(\mathbf{h}, N, t)$ is the chain-reformation function, $\beta(\mathbf{h}, N)$ the chain-breakage coefficient, and $\mathbf{e}(t)$ the deformation tensor. The stress-deformation-time relation in integral form is,

$$\sigma(t) = \mathbf{e}(t) \mathbf{S}(t) \mathbf{e}^+(t) + P \mathbf{1} \quad (2)$$

$$\mathbf{S}(t) = \mathbf{S}_0(t) + \int_0^t \mathbf{e}^{-1}(t') \mathbf{T}(t, t') \mathbf{e}^{+1}(t') dt' \quad (3)$$

$$S_0(t) = \sum_N \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (\mathbf{h}\mathbf{h}) \left(\frac{1}{r} \frac{d\phi}{dr} \right)_{r=|e(t)\mathbf{h}|} F(\mathbf{h}, N, 0) \exp \left[- \int_0^t \beta(e(t')\mathbf{h}, N) dt' \right] d\mathbf{h} \quad (4)$$

$$T(t, t') = \sum_N \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} (\mathbf{h}\mathbf{h}) \left(\frac{1}{r} \frac{d\phi}{dr} \right)_{r=|e(t)e^{-1}(t')\mathbf{h}|} G(\mathbf{h}, N, t') \exp \left[- \int_{t'}^t \beta(e(t'')e^{-1}(t')\mathbf{h}, N) dt'' \right] d\mathbf{h} \quad (5)$$

where ϕ is the free energy of chain, $(\mathbf{h}\mathbf{h})$ is a tensor

$$(\mathbf{h}\mathbf{h}) = \begin{pmatrix} \xi^2 & \xi\eta & \xi\zeta \\ \eta\xi & \eta^2 & \eta\zeta \\ \zeta\xi & \zeta\eta & \zeta^2 \end{pmatrix} \quad (6)$$

and P is the inner pressure from the internal energy.

An assumption of the Gaussian chain gives

$$\phi(|\mathbf{h}|, N, T) = (3kT/2)(|\mathbf{h}|^2/a^2N) \quad (7)$$

where T is the absolute temperature and a is the effective length of a segment. We adopt the following $G(\mathbf{h}, N, t)$ and $\beta(\mathbf{h}, N)$

$$G(\mathbf{h}, N, t) = G_0 \exp \left(- \frac{3h^2}{2Na^2} \right) \quad (8)$$

$$\beta(\mathbf{h}, N) = \left(\frac{\beta_0}{Na^2} \right) h^2 \quad (9)$$

according to the previous treatment,^{2,3} where G_0 and β_0 are positive constants, and the distribution of N is neglected.

CONSTRAINED RECOVERY

Measurement of the recovery in polymer liquids after shear flow have usually been made under circumstances not permitting any change in the separation of shearing surfaces to take place. We now suppose that the liquid undergoes the steady shear flow of shear rate $\dot{\gamma}$, described by the deformation tensor

$$\mathbf{e} = \begin{pmatrix} 1 & \dot{\gamma}t & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (10)$$

At time $t=0$, the tangential traction on the shearing planes is made and kept at zero and the liquid is constrained so that any subsequent strain will be a shear with the same shearing planes as in the steady shear flow. Let the shear recovery of strain be described by the deformation tensor

$$\mathbf{e} = \begin{pmatrix} 0 & -\gamma(t) & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (11)$$

The strain-time relation in the constrained recovery is schematically shown in Figure 1. The $\gamma(t)$ consists of an instantaneous recovery γ_i which occurs immediately after the removal of the stress and a delayed recovery which includes any subsequent gradual change in the strain. The ultimate recovery γ_o is regarded as the sum of the instantaneous recovery and the total delayed recovery.

To calculate $\gamma(t)$, we will first determine the chain distribution function $F(\mathbf{h}, N, 0)$ under the steady shear flow of the shear rate $\dot{\gamma}$ throughout the interval $-\infty < t \leq 0$.

Substitution of eq 10 into eq 1 with infinite t leads to,

Figure 1. Schematic representation of elastic recoil.

$$F(\mathbf{h}, N, 0)_{\dot{\gamma}} = G_0 \int_0^{\infty} \exp[-A\mathbf{h}^2 + B\xi\eta - C\eta^2] d\delta \quad (12)$$

$$A = \left(\frac{3}{2} + \beta_0 \delta \right) / Na^2 \quad (13)$$

$$B = (\beta_0 \dot{\gamma} \delta^2 + 3\dot{\gamma} \delta) / Na^2 \quad (14)$$

$$C = \left(\frac{1}{3} \beta_0 \dot{\gamma}^2 \delta^3 + \frac{3}{2} \dot{\gamma}^2 \delta^2 \right) / Na^2 \quad (15)$$

This $F(\mathbf{h}, N, 0)_{\dot{\gamma}}$ is adopted as an initial chain distribution function. From eq 2, 3, and 11, the shear stress $\sigma_s(t)$ and the first normal stress difference $\Delta\sigma_{n1}(t)$ are calculated as follows.

$$\sigma_s(t) = S_{012}(t) - \gamma(t)S_{022}(t) + \int_0^t [T_{12}(t, t') + \{\gamma(t') - \gamma(t)\}T_{22}(t, t')] dt' \quad (16)$$

$$\begin{aligned} \Delta\sigma_{n1}(t) = & S_{011}(t) - S_{022}(t) - 2\gamma(t)S_{012}(t) + \gamma(t)^2 S_{022}(t) + \int_0^t [T_{11}(t, t') - T_{22}(t, t') + 2\{\gamma(t') - \gamma(t)\}T_{12}(t, t') \\ & + \{\gamma(t') - \gamma(t)\}^2 T_{22}(t, t')] dt' \end{aligned} \quad (17)$$

Inserting $F(\mathbf{h}, N, 0)_{\dot{\gamma}}$ of eq 12 into $F(\mathbf{h}, N, 0)$ of eq 4 and integrating eq 4 with $\mathbf{h}$ by the use of eq 11, we have

$$S_{011}(t) = C_0 \int_0^{\infty} \frac{C_s}{D_s \sqrt{A_s D_s}} d\delta \quad \left(C_0 = \frac{3kTG_0}{2Na^2} \pi \sqrt{\pi} \right) \quad (18)$$

$$S_{012}(t) = C_0 \int_0^{\infty} \frac{B_s}{D_s \sqrt{A_s D_s}} d\delta \quad (19)$$

$$S_{022}(t) = C_0 \int_0^{\infty} \frac{\sqrt{A_s}}{D_s \sqrt{D_s}} d\delta \quad (20)$$

where

$$A_s = A + \beta_0 t / Na^2 \quad (21)$$

$$B_s = \frac{1}{2} B + \beta_0 \int_0^t \dot{\gamma}(t) dt' / Na^2 \quad (22)$$

$$C_s = A_s + \beta_0 \int_0^t \dot{\gamma}(t) dt' / Na^2 + C \quad (23)$$

$$D_s = A_s C_s - B_s^2 \quad (24)$$

The eq 5 and 11 give

$$T_{11}(t) = C_0 \frac{C_t}{D_t \sqrt{A_t D_t}} \quad (25)$$

$$T_{12}(t) = C_0 \frac{B_t}{D_t \sqrt{A_t D_t}} \quad (26)$$

$$T_{22}(t) = C_0 \frac{\sqrt{A_t}}{D_t \sqrt{D_t}} \quad (27)$$

where

$$A_t = \left\{ \frac{3}{2} + \beta_0(t-t') \right\} / Na^2 \quad (28)$$

$$B_t = \beta_0 \left\{ \int_{t'}^t \gamma(t'') dt'' - \gamma(t')(t-t') \right\} / Na^2 \quad (29)$$

$$C_t = A_t + \beta_0 \left\{ \gamma(t')^2(t-t') - 2\gamma(t') \int_{t'}^t \gamma(t'') dt'' + \int_{t'}^t \gamma(t'')^2 dt'' \right\} / Na^2 \quad (30)$$

$$D_t = A_t C_t - B_t^2 \quad (31)$$

Under the condition of $\sigma_s = 0$ in eq 16, $\gamma(t)$ satisfies the integral equation,

$$S_{012}(t) - \gamma(t)S_{022}(t) + \int_0^t [T_{12}(t, t') + \{\gamma(t') - \gamma(t)\} T_{22}(t, t')] dt' = 0 \quad (32)$$

The instantaneous recovery γ_i is obtained from eq 32 with $t=0$ and $\gamma(0)=\gamma_i$. When the shear stress σ_s is made zero, there is an instantaneous shear recovery of a magnitude,

$$\gamma_i(\dot{\gamma}) = \frac{S_{012}(0)}{S_{022}(0)} \quad (33)$$

$$S_{012}(0) = \int_0^\infty \frac{B}{2D\sqrt{AD}} d\delta \quad S_{022} = \int_0^\infty \frac{\sqrt{A}}{D\sqrt{D}} d\delta = \mu_0 \quad (34)$$

and an instantaneous decrease in the value of $\Delta\sigma_{n1}$ by an amount

$$\gamma_i^2 S_{022}(0) - 2\gamma_i S_{012}(0) = \frac{S_{012}(0)^2}{\mu_0} \quad (35)$$

where μ_0 is an instantaneous shear modulus.

NUMERICAL CALCULATION

The instantaneous recovery γ_i is calculated by performing the numerical integral of eq 34 for the given values of $\dot{\gamma}$.

As for the delayed recovery, we approximately solve eq 32 by assuming that the solution is given by

$$\gamma(t) = \gamma_e - (\gamma_e - \gamma_i) \exp(-\alpha t) \quad (36)$$

where, γ_e is the value of $\gamma(t)$ in the limit of $t \rightarrow \infty$ and α the relaxation rate when $\gamma(t)$ approaches infinitely to the limiting value γ_e . The delayed recovery is satisfactorily characterized by the two parameters α and ε , where $\varepsilon = (\gamma_e - \gamma_i)/\gamma_i$. For the first approximation, it is reasonable to solve eq 32 by using eq 36, instead of seeking a numerical solution of eq 32.

In general, when the memory function is a single exponential, there exists no delayed recovery, and when the memory function is constructed by the sum of more than two exponentials, the delayed

recovery appears. The simplest case in the latter system gives a delayed recovery in which the memory function is the sum of the two exponentials. Our approximation corresponds to the adoption of such a simple case. The proof that if the memory function is constructed by the sum of two exponentials, eq 36 hold will be found in a textbook by Lodge.⁵

A set of two parameters α and ε is numerically determined by the method of the Least Squares so that $\gamma(t)$ of eq 36 approximately satisfies eq 32. The eq 16, 19–24, 26–31 and 36 give

$$\sigma_s(t; \alpha, \varepsilon) = \int_0^\infty \frac{B_s - \gamma(t)A_s}{D_s \sqrt{D_s A_s}} d\delta + \int_0^t \frac{B_t + \{\gamma(t') - \gamma(t)\}A_t}{D_t \sqrt{A_t D_t}} dt' \quad (37)$$

where

$$A_s = A + \beta_0 t \quad (38)$$

$$B_s - \gamma(t)A_s = -\gamma_1 A + \frac{1}{2}B + \varepsilon \gamma_1 \left\{ -\left(A + \frac{\beta_0}{\alpha}\right) + \left(A + \frac{\beta_0}{\alpha} + \beta_0 t\right) \exp(-\alpha t) \right\} \quad (39)$$

$$D_s = D + \frac{\beta_0 \varepsilon \gamma_1}{\alpha} \left\{ -\left(\frac{3}{2}\varepsilon + 2\right) \gamma_1 A + B - \frac{\beta_0 \varepsilon \gamma_1}{\alpha} \right\} + \beta_0 \left[\{(1 + \varepsilon)^2 \gamma_1^2 + 2\} A - (1 + \varepsilon) \gamma_1 B + C + \frac{\beta_0 \varepsilon^2 \gamma_1^2}{2\alpha} + \beta_0 t \right] t \\ + \frac{2\beta_0 \varepsilon \gamma_1}{\alpha} \left\{ (1 + \varepsilon) \gamma_1 A - \frac{1}{2}B + \frac{\beta_0 \varepsilon \gamma_1}{\alpha} \right\} \exp(-\alpha t) - \frac{\beta_0 \varepsilon^2 \gamma_1^2}{\alpha} \left(\frac{1}{2}A + \frac{\beta_0}{\alpha} + \frac{1}{2}\beta_0 t \right) \exp(-2\alpha t) \quad (40)$$

$$A_t = \frac{3}{2} + \beta_0(t - t') \quad (41)$$

$$B_t + \{\gamma(t') - \gamma(t)\}A_t = \left(\frac{3}{2} + \frac{\beta_0}{\alpha} \right) \varepsilon \gamma_1 \{ \exp(-\alpha t) - \exp(-\alpha t') \} + \beta_0 \varepsilon \gamma_1 (t - t') \exp(-\alpha t) \quad (42)$$

$$D_t = \left\{ \frac{3}{2} + \beta_0(t - t') \right\}^2 + \frac{3}{2} \beta_0 \varepsilon^2 \gamma_1^2 \left[\frac{1}{\alpha} \left\{ -\frac{1}{2} \exp(-2\alpha t) \right. \right. \\ \left. \left. + 2 \exp(-\alpha t - \alpha t') - \frac{3}{2} \exp(-2\alpha t') \right\} + (t - t') \exp(-2\alpha t') \right] \\ + \frac{\beta_0 \varepsilon^2 \gamma_1^2}{\alpha} \left[\frac{1}{2} (t - t') \{ \exp(-2\alpha t') - \exp(-2\alpha t) \} - \frac{1}{\alpha} \{ \exp(-2\alpha t) + \exp(-2\alpha t') - \exp(-\alpha t - \alpha t') \} \right] \quad (43)$$

We define the function $Z(\alpha, \varepsilon)$ as

$$Z(\alpha, \varepsilon) = \sum_{i=1}^n \sigma_s^2(t_i; \alpha, \varepsilon) \quad (44)$$

The $\sigma_s^2(t_i; \alpha, \varepsilon)$ at each time t_i is summed up on the principle of the method of Least Squares and $Z(\alpha, \varepsilon)$ is minimized for a given value of $\dot{\gamma}$ as a function of α and ε . As n increases, the time axis is divided into shorter interval ($t_i - t_{i-1}$) and the number of division increase. For each fixed n thus determined, the minimum point in $\alpha - \varepsilon$ space is searched for over the time range of $t = 10^{-3}$ to 10^3 on the logarithmic scale. This procedure is repeated for increasing n until the minimum point of $Z(\alpha, \varepsilon)$ is found to change no longer.

RESULTS AND DISCUSSION

In Figure 2 the values of γ_e , s and $2s$ are plotted against $\dot{\gamma}$, where s is defined by $s = \Delta\sigma_{n1}/2\sigma_s$, ($\Delta\sigma_{n1} = S_{011}(0) - S_{022}(0)$, $\sigma_s = S_{012}(0)$), and the values of γ_1 , γ_e , s , α and ε are listed for various

shear rates $\dot{\gamma}$ in Table I. ($\beta_0 = 1$) As is shown in Figure 3 an experimental study reports⁴ that γ_e is an increasing function of $\dot{\gamma}$, and γ_e is nearly equal to the value of s in the region of linearity ($\dot{\gamma} \ll 1$) and is higher than s as $\dot{\gamma}$ increases. Figure 2 shows that our results are qualitatively in good agreement

Figure 2. γ_e , s and $2s$ vs. $\dot{\gamma}$ curves ($\beta_0=1$).

Table I. Values of γ_1 , γ_e , s , α , ϵ for various $\dot{\gamma}$ ($\beta_0=1$)

$\dot{\gamma}$	γ_1	γ_e	s	α	ϵ
10^{-2}	0.01611	0.0483	0.0872	0.0272	1.99
10^{-1}	0.126	0.243	0.268	0.533	0.931
1	0.631	0.808	0.759	1.29	0.281
10	1.92	2.06	1.89	5.10	0.0739
10^2	4.57	4.72	4.32	30.6	0.0335

Figure 3. Experimental curves of γ_e , s and $2s$ vs. $\dot{\gamma}$ for polyisobutylene at 100°C by Vinogradov, *et al.*; taken from ref 4.

with the experiment. The difference between γ_e and s at the left-hand side in Figure 2 can be regarded as the degree of error due to the present approximation, since γ_e has to coincide theoretically with s at $t \rightarrow 0$ in itself.

We have dealt with the constrained recovery following the steady shear flow because it is easy to compare it with experimental studies. The constrained recovery is distinguished from the free recovery⁵ in which the liquid undergoes a steady shear flow and stress is suddenly made zero or isotropic. Two other kinds of elastic recoveries are measured in an unsteady state⁶. One is during the stress development before shear flow becomes a steady state and the other is during the stress relaxation after cessation of steady shear flow. The most essential feature of the elastic recoil, however, may be satisfactorily discussed by the constrained recovery after following the steady shear flow which we have dealt with.

Throughout previous¹ and the present papers, we have studied various typical nonlinear viscoelastic phenomena of concentrated polymer systems in shear flow and have explained these by our semimolecular network model. The theory is constructed for the convenience of calculating the stress for a given deformation. On the contrary, since only the elastic recoil requires calculation of deformation for a given stress, we have to solve the integral equation numerically, which involves a lengthy and tedious calculation. The fairly good agreements between the results of our theory and experiments prove the justification of this network model. The problem under elongational flow still remains unsolved by this model.

Acknowledgements. This work was partly supported by a Grant-in-Aid for Scientific Research 165210 from the Ministry of Education. The numerical calculations were performed on a HITAC 8700-8800 system at the computer center at the University of Tokyo.

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