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A KINETIC NETWORK MODEL FOR NONLINEAR VISCOELASTIC FLOW PROPERT--ETC(U)
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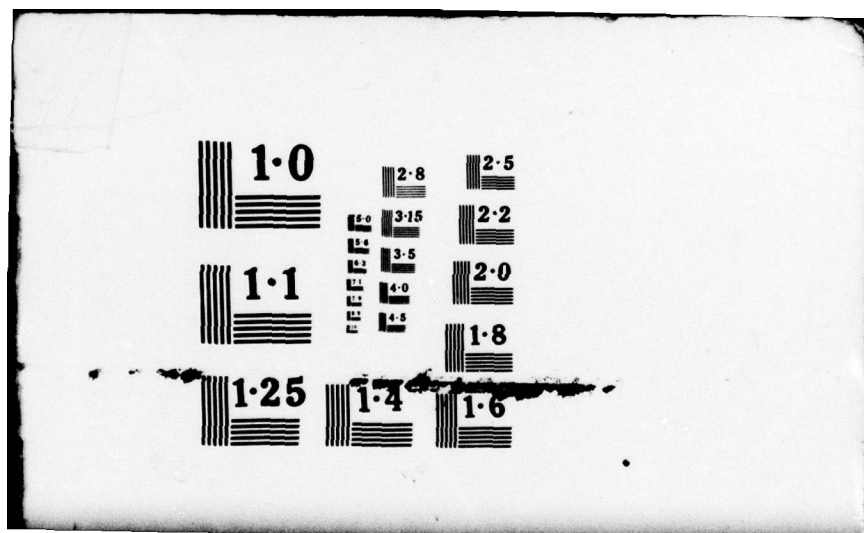
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6 A Kinetic Network Model

for Nonlinear Viscoelastic Flow Properties
of Entangled Monodisperse Polymers.

by

10 David/Soong ~~and~~ Mitchel/Shen

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Department of Chemical Engineering
Berkeley, California

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A KINETIC NETWORK MODEL FOR NONLINEAR VISCOELASTIC FLOW
PROPERTIES OF ENTANGLED MONODISPERSE POLYMERS

High polymers in concentrated solutions or in the melt exhibit shear-rate-dependent viscosity and normal stress differences. In transient flows upon inception of steady shear, the stress growth function of the polymer overshoots through a maximum and then decays to the steady-state value asymptotically for large shear rates. However, for small shear rates, it only increases monotonically to its limiting steady-state value. Upon cessation of steady shear, the stress relaxation function decreases monotonically to zero, the rate of which is higher for larger shear rates. These rheological properties have been interpreted by the shear-induced changes in the steady-state entanglement density in the polymer (1).

Lodge explained the nonlinear viscoelastic flow properties by a "rubberlike liquid" model, which however still predicted a shear-rate-independent viscosity and primary normal stress coefficient. Many modified theories (3-6) have since been proposed to refine this model. Most of them employ empirical expressions for the memory functions to give the rate-dependent properties. In this work, we shall propose a kinetic network model which appears to predict the observed nonlinear viscoelastic flow properties of entangled polymer systems.

The basic molecular mechanism of this model attributes the rate-dependence of viscosity and normal stress difference to the decrease in entanglement density with increasing shear rate. In a flow field, entanglements are being formed and disengaged

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→ constantly. The entanglement loss process is caused primarily by the imposed shear and is assumed to be proportional to the shear rate to a power a where

$$\dot{n}_l = k_l \dot{\gamma}^a n \quad (1)$$

where $\dot{n}_l$ is the entanglement loss rate, k_l is the rate constant, $\dot{\gamma}$ is the shear rate, n is the current number of entanglements along a representative chain, and $a (<1)$ accounts for the elastic nature of the polymer. The entanglement creation process, driven by thermal diffusion, is assumed to be independent of shear rate. ↩
In other words,

$$\dot{n}_c = (k_c / \lambda^a) (n_0 - n) \quad (2)$$

where $\dot{n}_c$ is the entanglement creation rate, k_c is the rate constant, λ is a characteristic time determined by the rate of diffusion, and is thus a function of molecular weight and temperature, a is the elasticity parameter, and n_0 is the saturation number of entanglements along a representative chain. $(n_0 - n)$ is the number of vacant sites where entanglements have been lost and can be likely regenerated.

At steady state, the creation rate equals the loss rate ($\dot{n}_c = \dot{n}_l$) and the entanglement density stays constant. Equating Eqs. 1 and 2, we have

$$P \equiv n/n_0 = \frac{1}{1 + (k_l/k_c) (\lambda \dot{\gamma})^a} \quad (3)$$

Eq. 3 describes the probability for entanglements to exist at different shear rates. The viscous drag from the entanglements is believed to be the major source of contribution to polymer viscosity (1). Therefore, to a good approximation, the reduced

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viscosity as a function of shear rate is also given by

$$\frac{\eta(\dot{\gamma})}{\eta_0} = \frac{1}{1 + (k_\ell/k_c) (\lambda \dot{\gamma})^a} \quad (4)$$

where η_0 is the zero-shear-rate viscosity of the polymeric fluid.

The normal stresses come from the elastic energy stored in the system, and are primarily sustained by pairs of entanglements, because the elastic deformation energy can be trapped in between these slowly moving points. The primary normal stress difference should thus be proportional to the square of the probability for individual entanglements to remain under the flow situation, which in turn corresponds to the probability for pairs of entanglements to exist simultaneously. In other words,

$$\tau_{11}(\dot{\gamma}) - \tau_{22}(\dot{\gamma}) = -\theta \left(\frac{\dot{\gamma}}{1 + (k_\ell/k_c) (\lambda \dot{\gamma})^a} \right)^2 \quad (5)$$

where θ is a proportionality constant which determines the value of primary normal stress difference. The reduced viscosity and primary normal stress difference as functions of shear rate calculated by Eqs. 4 and 5 for a equals to 0.85 is given in Fig. 1. The curves show qualitatively the expected trend.

Under transient flow conditions, such as inception and cessation of steady shear, the entanglement probability P becomes a function of time which also has some parametric dependence on shear rate. It can still be calculated by the following differential equation governing the relationship between the change of entanglements to the two competing rate processes, i.e.,

$$\dot{n} = \dot{n}_c - \dot{n}_l \quad (6)$$

where $\dot{n}$ is the rate of change of entanglements. Inserting the expressions for entanglement creation and loss rates, Eq. 6 can be integrated to give for start-up experiments.

$$P(t; \dot{\gamma}_0) = P_\infty(\dot{\gamma}_0) + (1 - P_\infty(\dot{\gamma}_0)) \exp\left(\frac{-k_l \dot{\gamma}_0^a t}{1 - P_\infty(\dot{\gamma}_0)}\right) \quad (7)$$

where $P_\infty(\dot{\gamma}_0)$ is the steady-state entanglement probability; and for stress relaxation experiments.

$$P(t; \dot{\gamma}_0) = 1 - (1 - P_\infty(\dot{\gamma}_0)) \exp\left(-\frac{k_c}{\lambda^a} t\right) \quad (8)$$

where $P_\infty(\dot{\gamma})$ is again the steady-state entanglement probability, in this case, before the flow is stopped.

Polymer network possesses certain elastic characteristics. When it is suddenly deformed upon the inception of steady shear, the shear stress born by an average entanglement first increases with time rapidly and then gradually levels off towards the steady-state value. A Maxwellian model is assumed to represent this behavior, i.e.,

$$\frac{\sigma(t; \dot{\gamma}_0)}{\sigma_\infty(\dot{\gamma}_0)} = 1 - \exp(-t/\tau) \quad (9)$$

where $\sigma(t; \dot{\gamma}_0)$ and $\sigma_\infty(\dot{\gamma}_0)$ are the current average stress and the final steady-state stress carried by individual entanglements respectively, and τ is the system time constant. The macroscopic stress exerted by the fluid is given by the product of the average microstress supported by a remaining entanglement and the number of such stress-bearing entanglements. The

normalized shear stress growth functions thus calculated are presented in Fig. 2. The curves qualitatively reproduce the expected behavior. Quantitative comparison of this theory with experimental data is now being investigated, the results of which will be reported in forthcoming publications.

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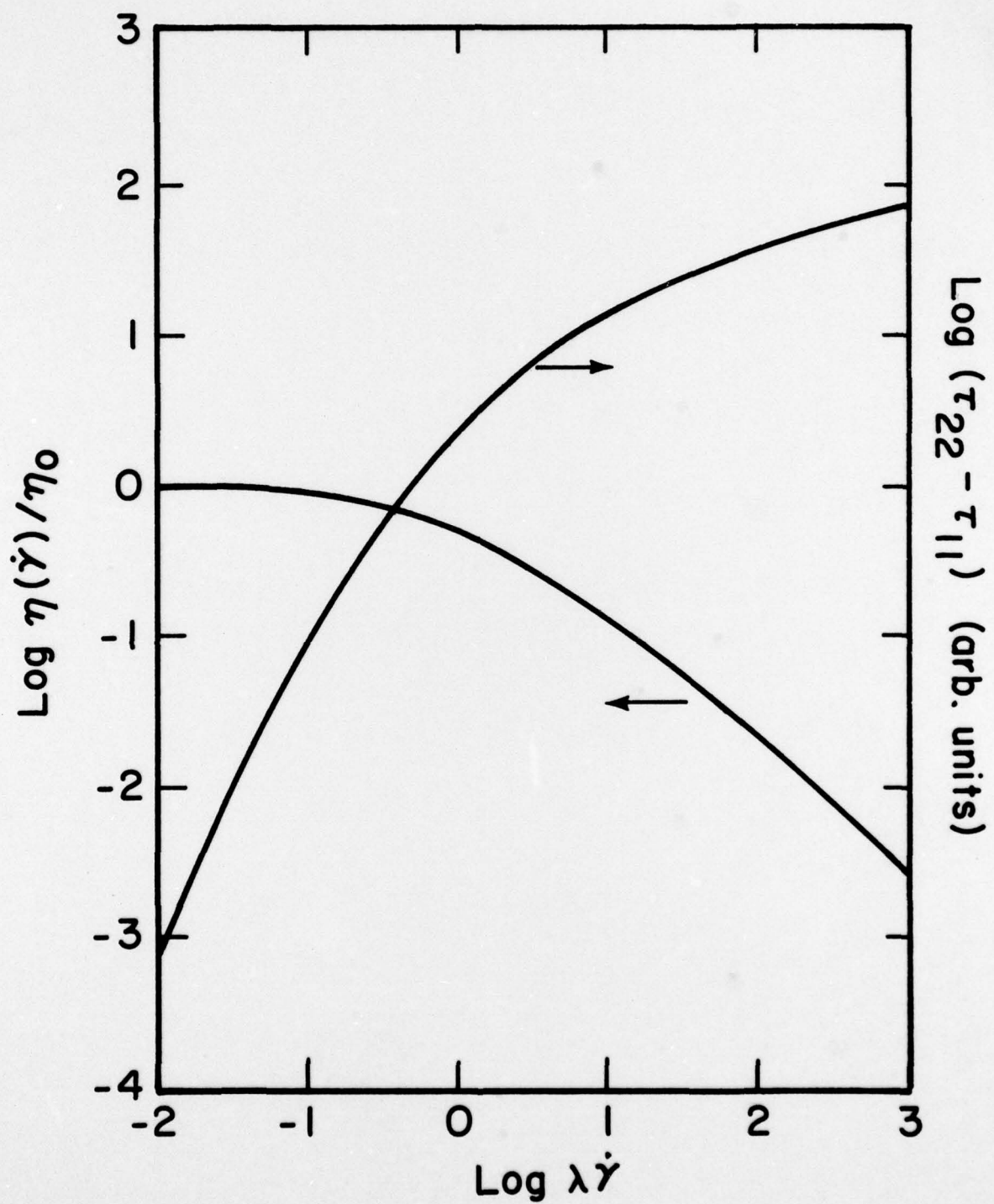
David Soong

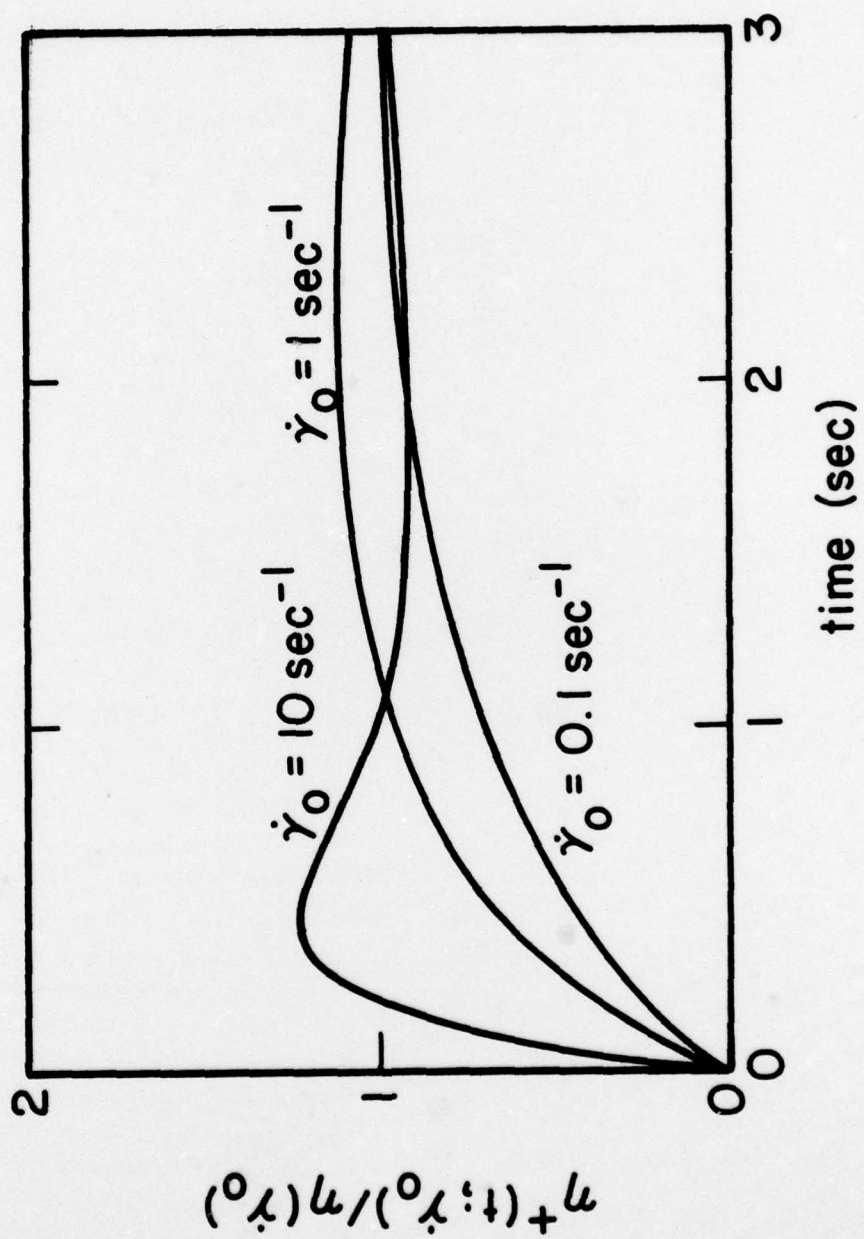
Mitchel Shen

Department of Chemical Engineering
University of California, Berkeley
Berkeley, California 94720

CAPTIONS

1. Theoretical curves of log reduced viscosity and primary normal stress difference vs log reduced shear rate, where λ is the characteristic time, and a is the elasticity parameter. (The ratio k_ℓ/k_c is taken as 1, and $a = 0.85$)
2. Normalized stress growth function for three different shear rates calculated by the theory. The parameters used are $a = 0.85$, $k_\ell = 0.3$, $k_\ell/k_c \lambda^a = 1$, $\tau = 0.5$.





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