C' = penalty function constant
c_p = heat capacity
D = effective axial diffusivity
F = augmented function to be minimized
$\mathbf{f}(\mathbf{x})$ = nonlinear vector function
ΔH = heat of reaction
$\mathbf{I}$ = identity matrix
$\mathbf{J}$ = Jacobian matrix
K = Liapunov constant
l = length of reactor
N = number of stages
N_{Pe} = vl/D Peclet Number
Q = dimensionless activation energy
Q' = defined by Equation (17)
q = flow rate
r = reaction rate
T = temperature
t = time
U = heat transfer coefficient
V = reactor volume
$V(\mathbf{x})$ = Liapunov function
$\dot{V}(\mathbf{x})$ = time derivative—Liapunov function
v = fluid velocity
$\mathbf{x}$ = state vector
Δx_j = j^{th} length increment
y = defined by Equation (13)

Greek Letters

α = defined by Equation (25)
η = defined by Equation (13)
ρ = density
τ = defined by Equation (13)
τ_o = defined by Equation (13)

Subscripts

o = inlet
A = ambient
ss = steady state

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Network Rupture and the Flow of Concentrated Polymer Solutions

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Entanglement theories for polymer solutions resemble those developed for solid rubbers. These rubberlike theories are extremely successful qualitatively; they give a good indication of the type of response observed experimentally in concentrated solutions. Quantitatively the theories are not so useful; in general they predict constant viscosities in simple shearing motions and ever-increasing tensile stress in steady elongational flow.

If it is supposed that the lifetime of the entanglements is limited partly by a maximum allowable strain magnitude, and that the network ruptures locally whenever this magnitude is exceeded, greatly improved quantitative predictions are observed. For polyisobutylene-cetane solutions, where the critical strain magnitude appears to be about 3, excellent prediction of the steady shearing viscosity curve is available starting from the measured dynamical response to small sinusoidal strains and the critical strain magnitude. Normal stress effects are also well represented; in elongational flow the tensile stress shows a slight maximum. It thus appears that the notion of network rupture is useful in guiding the selection of continuum theories for polymer fluid description.

CONTINUUM THEORY FOR THE DESCRIPTION OF POLYMER FLUIDS

The hunt for nonlinear constitutive relations giving a realistic description of polymer melts and solution has been in progress since 1948; however, if one considers the early pioneering studies of variable viscosity, the search would date back to about 1920. To be acceptable, a constitutive equation is required to predict realistic results for the material to be described over whatever range of tests is currently available. The weakness of the purely continuum point of view seems to be that as the range of tests is extended there is no guarantee that any apparently satisfactory continuum equation will continue to prove useful; as more information continues to be built into the model a wider range of tests is required to test its predictive ability; failures in prediction then require more built-in information, more complex tests, and so on. As an example of this the continuum approaches of Macdonald and Bird (*1*) and Bogue (*2*) lead to acceptable responses in many flows but in an inertialess simple elongation they yield infinite stresses at finite extension rates: these are not observed experimentally (*3*).

In view of such problems it seems much more reasonable, as advocated by Lodge (*4*), to make use of the extensive knowledge of the molecular structure of polymer fluids as a guide towards suitable constitutive equations. This idea has been tried with varying success (*5* to *11*). The work of Lodge (*5*) and Hayashi (*6*) gives a constant shear viscosity function and hence is somewhat unrealistic. The theories of Bernstein, Kearsley, and Zapas (*7*), Kaye (*8*), and Ward and Jenkins (*9*) seem to be quite capable of reasonable predictions but are not easy to use. A discussion of some of these developments is given by Bogue and Doughty (*10*). The same difficulty in use, coupled with rather inaccurate predictions, has limited interest in Pao's work (*11*). The earlier work of Yamamoto (*12*) does yield a variable viscosity and a finite tensile viscosity, starting from a molecular network theory.

These papers, particularly Lodge's (*4*) development, illustrate that the use of the molecular theory of rubbery substances (*13*) provides a fairly realistic basis for constructing continuum rheological theories; these can then be improved by further molecular considerations. One advantage of this procedure is that it gives one more confidence in predictions for complex flows than one can hope to have from *ad hoc* continuum equations.

The present paper is considered by the author as a development arising from Lodge's (*4, 5*) theory using arguments based on molecular considerations where possible. One might view the developments in other ways but the aforementioned approach is believed to be most natural.

THE MOLECULAR BASIS OF POLYMER FLUID BEHAVIOR

The books by Treloar (*13*), Bueche (*14*), and Ferry (*15*) summarize the theory of rubberlike elastic behavior and its application to polymer solutions. Each molecule is considered as a long, randomly oriented body moving under Brownian forces in the solvent. At low polymer concentrations, when the molecules are substantially independent, each polymer molecule may be considered as a series of jointed rods with viscous damping at the joints. The treatments of Rouse (*16*), Zimm (*17*), and Tschoegl and Ferry (*18, 19*) yield relaxation spectra in accordance with observations from dynamical tests at small strains providing polymers of uniform molecular weight are used. As concentrations and molecular weights become larger the molecules interact with one another and form temporary entanglements. A useful review of the entanglement concept is given by Porter and Johnson (*20*), which lends credibility to the concept of a polymer solution as an interconnected network held together by constantly forming and dissociating polymer entanglements. Surprisingly, perhaps, it has been shown (*15*) that the dynamical behavior for such concentrated solutions can be predicted quite well by Rouse-like theories merely by increasing the friction coefficient, or viscous resistance, to account for the proximity of other molecules. In brief, it may be said that a good deal is known about the dynamical response of the polymer network. For steady flows the situation is not so clear, and predictions of non-Newtonian viscosity continue to appear. The contributions of Yamamoto (*12*) have been mentioned; Bueche (*14*) describes his own extensive work in this field. Graessley (*21*) considers the dynamics of entanglement formulations by introducing a characteristic entanglement time. The entanglement density in the fluid depends on the ratio of the time that two molecules are near enough to form an entanglement to the entanglement time. This entanglement density is lowered by shearing. Although this theory looks quite reasonable for simple shearing, no attempt at generalization in an invariant manner to general flows was made. In some respect the ideas are similar to those of Yamamoto (*12*). Lodge sets out the assumptions made in his theory of flow [(*41*), p.118] and notes that the critical assumption as far as the predicted constancy of viscosity is concerned is the assumption that the flow has no effect on the balance of formation and dissolution of junctions. Removal of this hypothesis (*12*) yields a non-Newtonian viscosity.

The assumption that a multiple-network hypothesis may be used when linkages rupture has been discussed by Scanlan and Watson (*22*), Flory (*23*), and Scanlan (*24*). The multiple network hypothesis is an extension of the two-network theory originally used for cross-linked materials (*25*). In the two-network theory of rubber behavior stresses in the sample are considered as being due to the sum of forces in a number of initial cross-links after straining, plus the forces due to a second network of cross-links introduced in the strained state; the second network only contributes to the stress upon further straining, of course. The criticisms of the two-network theory when network rupture occurs (*22* to *24*) yield the result that the residual stress in a relaxing tensile sample is underestimated if the two-network theory is used; the extent of the error depends on the percentage of the cross-links undergoing rupture and reformation in the stretched state. It is difficult to form an estimate of the error occurring in Lodge's theory (*5*) due to this effect because the current network is supposed to consist of linkages of all ages in different states of strain. One might suppose that the effect is negligible if, after adding a small number of junctions, the network becomes homogenized before rupture so that the total number of ruptures and reformations occurring at any given time is infinitesimal. In this context the word homogenized implies that the new junctions rapidly become indistinguishable from the rest of the network. In consideration of other uncertainties present in the theory [for example, non-Gaussian chain behavior (*13*)] this effect will be supposed small; however, if at some stage of the polymer flow a large fraction of the network ruptures it may be necessary to recognize the effect of link ruptures on the viscosity.

At this point we introduce Lodge's (*4*) constitutive equation on which developments here are based, relating the stress matrix **T** to pressure (p) and the history of a strain matrix (**S**); $\mathbf{S}(t')$ measures the strain of a network element which joined the network at time t' relative to the present configuration as reference state.
Thus

$$\mathbf{T} = -p\mathbf{I} + \int_{-\infty}^{t} N(t-t')\mathbf{S}(t')dt' \qquad (1)$$

$N(t-t')dt'$ is proportional to the number of elements effectively joining the network at time t' which are still joined to the network at the present and **I** is the unit matrix. N depends on the polymer/solvent combination and temperature. According to the usual theory of rubber elasticity (*13*) $\mathbf{S}$ should be the Finger strain measure $\mathbf{B}$ which is related (*26*) to the ratio of size between areas of an element in the strained and unstrained conditions for incompressible media. Adoption of this measure of strain gives, in a shearing flow with velocity vector, $v = (\gamma y, 0, 0)$, the result $t_{yy} = t_{zz}$ (*5*). This is not usually observed in polymer fluids (*27* to *29*). However, it is also known from experiments on rubbers (*30*) that the appropriate measure of strain is not simply $\mathbf{B}$, but $\mathbf{B} + \beta\mathbf{C}$ where β is a constant and $\mathbf{C}$ is the Green strain measure which is related to $\mathbf{B}$ by the equation

$$\mathbf{B} + \mathbf{I} = (\mathbf{C} + \mathbf{I})^{-1} \tag{2}$$

For dry rubbers β is small and negative (~ -0.1 to -0.2), rising to zero in highly swollen rubber (*30*). Various possible causes for the divergence from simple kinetic theory are given by Gumbrell, et al. (*30*). One possibility is non-Gaussian behavior of the network links. Thomas (*31*) shows however that this theory leads to a positive value for the deviation from the simple kinetic theory, that is opposite of the experimental trend. For fluids it may readily be shown that the adoption of $(1 + \beta)\mathbf{B} + \beta\mathbf{C}$ as strain measure gives the result that in simple shearing the normal stress ratio is

$$\frac{t_{yy} - t_{zz}}{t_{xx} - t_{yy}} = \beta \tag{3}$$

Thus we will take $\beta \neq 0$ and

$$\mathbf{S} = (1 + \beta)\mathbf{B} + \beta\mathbf{C} \tag{4}$$

This modification of the strain measure is due to Lodge [see (*32*)].

It appears that the normal stress ratio is small (*28, 29*) for several polymer solutions; more evidence is urgently needed here. Perhaps the work of Isihara, et al. (*33*) is applicable here and the small second normal stress difference $t_{yy} - t_{zz}$ is due to non-Gaussian chain statistics. Certainly one may expect some linkages to be very highly strained in the network. Hence the amendment of the strain measure as suggested, with a relatively small value of $|\beta|(\overset{=}{<} 1/2)$ seems reasonable; clearly, without the non-Gaussian effect one might expect solutions to behave like highly swollen rubbers.

The function $N(\tau)$ governs the response to a small sinusoidal shear strain; from such tests $N(\tau)$ can easily be found (*15*). Usually a sum of exponentials is considered to be a sufficiently accurate approximation for N. With discrete time constants λ_n the form

$$N(\tau) = \sum \frac{a_n}{\lambda_n^2} e^{-\tau/\lambda_n} + \eta_\infty \delta'(\tau) \tag{5}$$

may be used. The a_n and λ_n may be assigned in terms of the Rouse (*16*), Zimm (*17*) or other molecular theory if desired (*1*). η_∞ is the limiting viscosity at very high shear rates; it is of the order of the solvent viscosity. $\delta'(\tau)$ is the formal derivative of the delta function (*34*). In the Lodge model, the response is still deficient in that the viscosity is constant and does not decrease with shear rate. Means for rectifying this are now discussed.

THE NETWORK RUPTURE HYPOTHESIS

Some of the schemes for introducing variable viscosity into network theories have already been discussed. Kaye (*35*) discusses the idea of allowing the rate of breakage of cross-links to become stress-dependent. The disadvantage of this scheme is that the constitutive equation does not give the stress explicitly when the flow field and particle trajectories are known; the function N in Equation (1) now depends on stress. Consequently the author is unable to treat easily any flow except simple shear. Tanner and Simmons (*36*) suppose that network rupture occurs at a given strain magnitude; this apparently crude hypothesis not only gives the stress explicitly in terms of the strain history but also seems to be quite successful quantitatively. A test of this theory for combined simple and sinusoidal shearing has been given elsewhere (*36*). In this theory no infinite stresses arise in elongational flows (*36*).

It is now convenient to review some of the basic evidence for adopting the network rupture theory. Previously, (*36*) we have hypothesized that rupture must occur when the network strain reaches a sufficient magnitude; that this magnitude is a statistical quantity should perhaps be emphasized although it will be idealized below as being a definite determinate quantity.

Some idea of orders of magnitude for rupture of systems with various amounts of permanent cross-linking may be found in the literature. Landel and Fedors (*37*) find that SBR material that is not cross-linked ruptured in tension with a most probable extension ratio of about 6.7. Raw rubber (*38*) shows a wide variety of rupture strains depending on molecular weight, strain rate, and temperature. Generally the rupture strains are between 3 and 10. Some low density polythenes (*39*) show rupture at about 400% elongation over a wide range of temperature; in another work (*40*) one sees that a small amount of cross-linking increases the rupture strain. It should be noted that the rupture strain depends somewhat on the rate of extension (*40*); at 25°C. for a Viton B gum vulcanizate a slightly higher breaking strain was found for more rapid tests. The same is true for a cross-linked GR-S rubber [(*15*), p. 441]; however at some temperatures this rate trend is reversed. In both the above cases the uniaxial strains at rupture were about 3 to 4 at 25°C.

It seems that rupture extension ratios of order 3 to 10 are to be expected with typical solid polymers. Little seems to be known about rupture in more complex stress patterns but it seems plausible that the maximum principal extension ratio is the main governing factor. Williams (*41*) says that it is impossible to give a universal criterion for rupture at present but that in many cases the maximum strain is a reasonable criterion. In many cases the maximum principal strain will be little different numerically from the sum of the principal strains, that is the first invariant of the strain matrix; this will be true provided the largest principal strain is much bigger than the other two. In general one may expect that the rupture criterion will be at least a function of two nonzero invariants of $\mathbf{S}$; in the absence of more definite information from the above evidence we adopt the following simplest criterion for network rupture in flowing solutions. Rupture is supposed to occur when

$$tr\ \mathbf{S} = (1 + 2\beta)\, B^2 \tag{6}$$

where $tr\ \mathbf{S}$ is the sum of the principal strains and B is a number expected to be of order 10 and which is probably temperature and rate dependent. The factor $(1 + 2\beta)$ is inserted for convenience. In simple shearing flows it is of no consequence since $tr\ \mathbf{B} = tr\ \mathbf{C}$ but in elongational flows it makes some difference to the results if β is not small. Returning to Equation (1) we now suppose that the function $N(\tau)$ may be expressed in the form (5). It is clear that an exponentially small number of junctions that were formed in the distant past persist and in many steady flows (for example simple shearing) these junctions have large strains of ever increasing magnitude. In the network rupture theory these residual junctions are wiped out as the strain magnitude reaches the critical value. In many cases

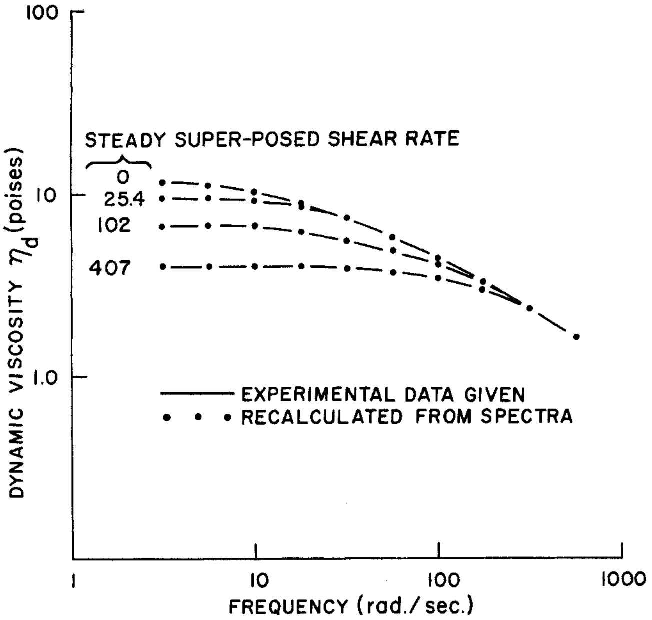

Fig. 1. Dynamic viscosity for 5.4% polyisobutylene-cetane solution with and without superposed steady shearing.

this causes the lower infinite limit in (1) to be replaced by a finite limit. Simple shearing provides an example; here the velocity field is v = $(\gamma y, 0, 0)$; then if $t - t' = \tau$, we find (*4*)

$$\mathbf{B} = \begin{bmatrix} \gamma^2\tau^2 & \gamma\tau & 0 \\ \gamma\tau & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}; \quad \mathbf{C} = \begin{bmatrix} 0 & -\gamma\tau & 0 \\ -\gamma\tau & \gamma^2\tau^2 & 0 \\ 0 & 0 & 0 \end{bmatrix} \tag{7}$$

Thus from (6) and (4) rupture occurs when

$$\gamma^2(t-t')^2 = B^2 \tag{8}$$

and Equation (1) becomes

$$\mathbf{T} = -p\mathbf{I} + \int_{t-\tau_R}^{t} N(t-t')\, \mathbf{S}(t')\, dt' \tag{9}$$

where $\tau_R = B/\gamma$. With $N(\tau)$ given as in (5) we find the viscosity function $\eta_s(\gamma)$ as (*36*)

$$\eta_s = \eta_\infty + \sum_n a_n \left[1 - \left(1 + \frac{B}{\lambda_n \gamma} \right) \exp\,(-B/\lambda_n\gamma) \right] \tag{10}$$

while the dynamic viscosity $\eta_d (\equiv G''/\omega)$ takes the well-known form (*15*)

$$\eta_d = \eta_\infty + \sum_n a_n/(1 + \lambda_n{}^2\omega^2) \tag{11}$$

B may thus be found from a comparison of the dynamic and steady shear viscosity curves. For polymer solutions of sharply defined molecular weight the a_n and λ_n values may be assigned theoretically; for wider known distributions of molecular weight some progress can be made (*42*); here it is assumed that the a_n and λ_n are found empirically from dynamic small strain measurements. An expression for the first normal stress difference $t_{xx} - t_{yy}$ $(\equiv N_1)$ may readily be developed; we find (*36*):

$$\frac{t_{xx} - t_{yy}}{\gamma^2} = \sum_n a_n\lambda_n \left[2 - \left(2 + \frac{2B}{\lambda_n\gamma} + \left[\frac{B}{\lambda_n\gamma} \right]^2 \right) \exp\,(-B/\lambda_n\gamma) \right] \tag{12}$$

This completes the basic theory for a shearing flow and an application showing the method of finding the various parameters is now given.

A COMPARISON WITH EXPERIMENTAL DATA

Simmons (*43*, *44*) has performed some experiments with 5.4% polyisobutylene cetane solution obtaining dynamic viscosities (η_d) and elastic moduli (G') not only in the fluid at rest but also when the sample is undergoing shearing; in this case the velocity field is of the form v = $\{\gamma y, 0, a\omega y \cos \omega t\}$. The results are shown in Figures 1 and 2; the numbers attached to the curves denote the value of the steady shear rate γ. From the curves with zero shear rate the a_n values were assigned using a numerical iterative procedure similar to that used by Hopkins (*45*). It was found that the Rouse type of theoretical curves (*16*) did not give a very good fit as the polyisobutylene sample did not have a sharp molecular weight distribution, hence the λ_n were assigned logarithmically, four per decade, as in Table 1. The values of Table 1 correspond to a relaxation spectrum of discrete lines. This is convenient for subsequent calculations.

In order to look at the shape of the spectrum itself a box spectrum using boxes of variable height (four per decade) was assumed. Previous attempts (*36*) to find the changes in relaxation spectra due to shearing indicated that the changes are quite dramatic. A cut-off of the long relaxation times by shearing was evident, but the steepness of the cut-off was difficult to establish. To show this a hypothetical example of a uniform spectrum extending from zero to $\tau = 0.01$ sec. was assumed and the calculated rigidity was found to be

$$G''(\omega) = 10^4 \arctan\,(\omega/100) \tag{13}$$

corresponding to $\eta_o = 100$ poises. Figures 3 and 4 show how closely the data recalculated from the spectrum found by the iterative method approximates the original data of Equation (13) and how difficult it is to detect very steep steps. The relation between $H(\lambda)$ and $N(\tau)$ is the usual one (*15*):

$$N(\tau) = \int_o^\infty \frac{H}{\lambda^2} e^{-\tau/\lambda d\lambda} \tag{14}$$

Some smoothing procedures to avoid wild oscillations in the iterative calculations were introduced (*46*); the ele-

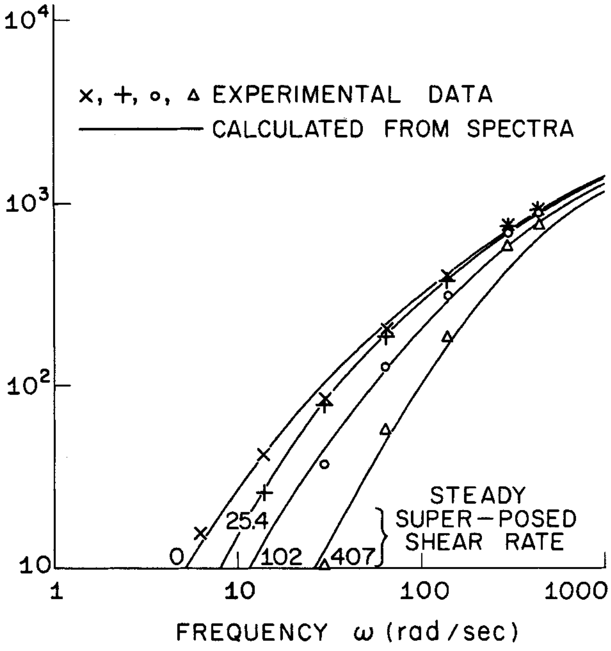

Fig. 2. Dynamic elasticity data for 5.4% polyisobutylene solution with and without superposed steady shearing.

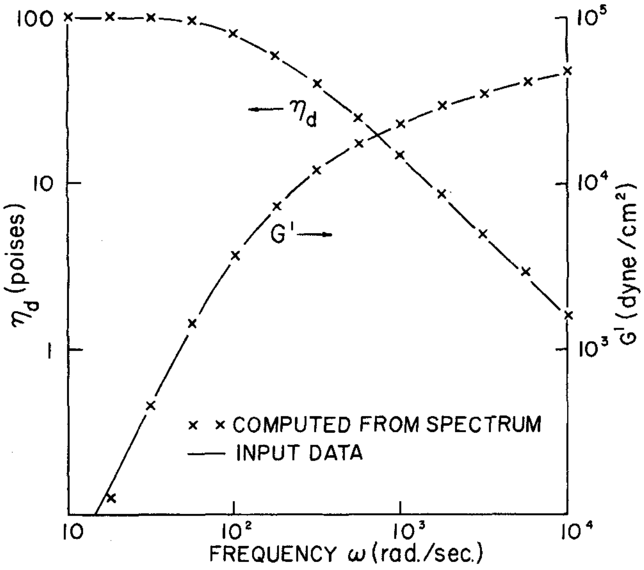

Fig. 3. Dynamic viscosity and elasticity data computed from a step spectrum.

Table 1. Line Relaxation Spectrum of 5.4% Polyisobutylene-Cetane Solution

n	a_n (poises)	λ_n (sec.)
1	0.0001	0.316
2	0.1741	0.178
3	1.751	0.100
4	1.956	0.0562
5	2.184	0.0316
6	1.197	0.0178
7	1.211	0.0100
8	0.957	0.00562
9	0.649	0.00316
10	0.954	0.00178
11	0.486	0.00100
12	0.001	0.000562
13	0.164	0.000316
14	0.021	0.000178
15	0.237	0.000100

For the present experimental data (up to $\omega \sim$ 1,000 rad./sec.) one could alternatively eliminate time constants 12, 13, 14, and 15 and substitute a limiting viscosity $\eta_\infty \approx 0.423$ poises.

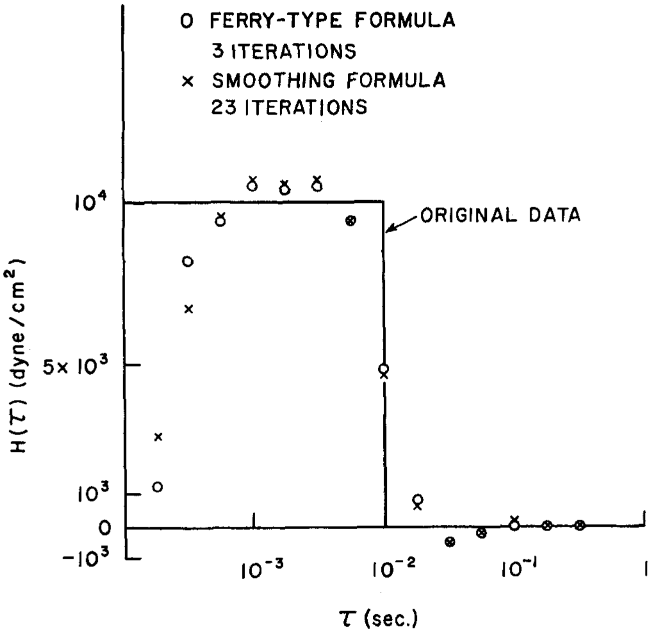

Fig. 4. Step spectra approximations from iterative calculations.

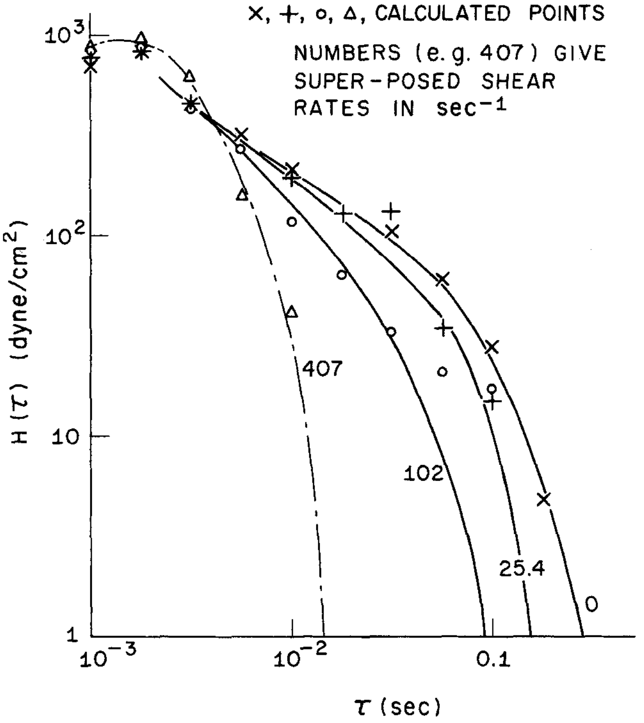

Fig. 5. Spectra for 5.4% polyisobutylene-cetane solution.

mentary methods of spectral calculation (*15, 36*) are not really adequate for sharply cut-off spectra but numerical iterative procedures are able to deal with these cases quite well.

Returning to the experimental data for the polyisobutylene-cetane solution Figure 5 shows the distortion and cut-off of the spectra by shearing. From Figure 4 we define a spectral cut-off time τ_c as $\tau_1/1.8$ where τ_1 is the time where $H(\tau) = 1$ dyne/sq. cm. Figure 6 shows the product $\gamma\tau_c$. Analysis of other data (*44*) also shows a rough proportionality of τ_c to $1/\gamma$ for several concentrations of polyisobutylene-cetane and sodium carboxymethylcellulose/water solutions and all relaxation times greater than $\sim 5/\gamma$ seem to be cut off by shearing. Typical cut-offs are predicted by the network rupture theory and a dis-

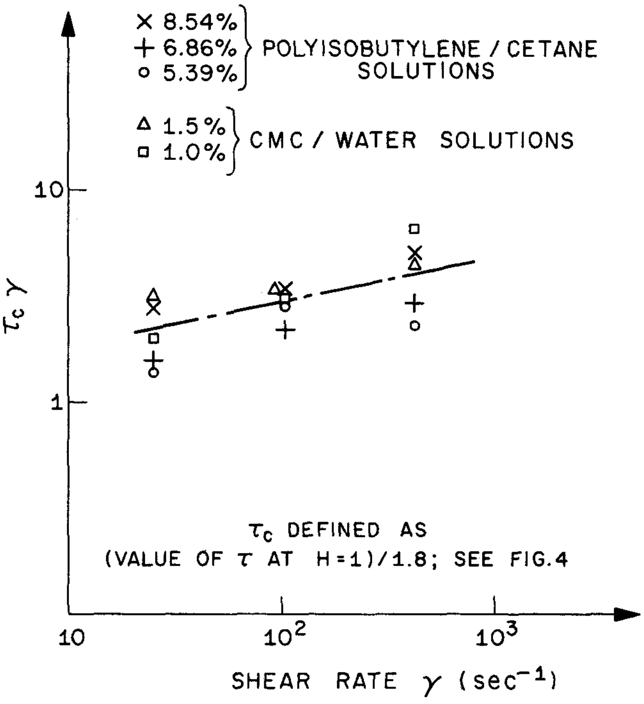

Fig. 6. Spectral cutoff times for various polymer-solvent combinations.

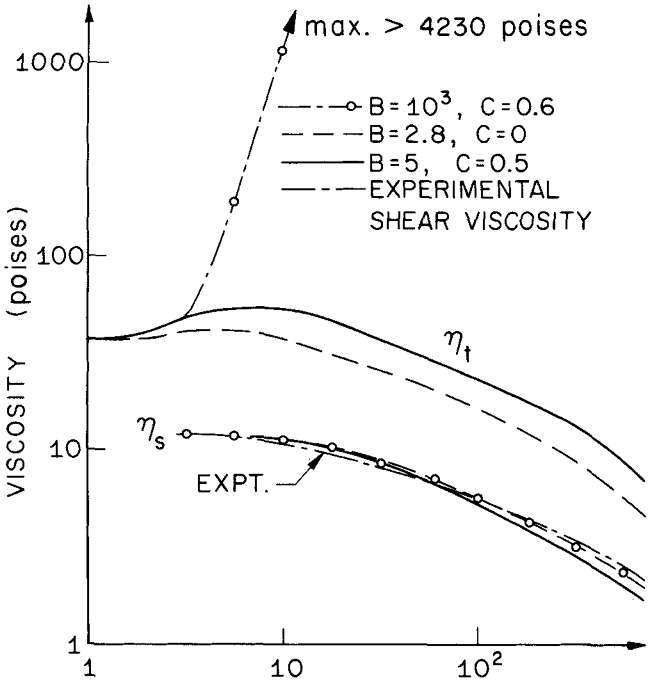

Fig. 7. Rupture theory viscosity predictions and experimental comparison.

cussion of the combined shearing motion is given elsewhere (*36*).

Using the values of Table 1 we may calculate the steady shear viscosity and the first normal stress difference, $t_{xx} - t_{yy}$, for various values of B. Figures 7 and 8 show these results for the 5.4% solution. The optimum value of B to obtain agreement with experiment appears to be about 2.8.

Figure 7 shows the computed tensile viscosity (Trouton viscosity) η_t for this fluid. The kinematics of this flow have been described by Lodge (*4*). The velocity field has the form $\mathbf{v} = (Gx, -Gy/2, -Gz/2)$ and the matrices **B** and **C** are found from

$$(\mathbf{B}+\mathbf{I}) = (\mathbf{C}+\mathbf{I})^{-1} = \begin{bmatrix} \exp 2G\tau & 0 & 0 \\ 0 & \exp - G\tau & 0 \\ 0 & 0 & \exp - G\tau \end{bmatrix} \tag{15}$$

The rupture criterion (6), setting $G(t - t') = \overline{B}$ [Equation (8)] then becomes

$$(1 + 2\beta)(B^2 + 3) = (1 + \beta)(\exp 2\overline{B} + 2\exp - \overline{B}) + \beta(\exp - 2\overline{B} + 2\exp \overline{B}) \tag{16}$$

For the particular fluid under discussion we take $\beta = 0.6$ (*28*)* and $B = 2.8$ as reasonable mean values. Solution of (16) then gives $\overline{B} \sim 1.23$. For very large values of B, (16) becomes

$$\overline{B} \sim \frac{1 + 2\beta}{1 + \beta} \ln B \tag{17}$$

The history integral (9) may now be computed (*36*) and for the spectrum of Table 1 the results are shown in Figure 7. There is a maximum in the tensile viscosity curve, but stresses remain finite.

Many simple integral theories (*1, 4*) predict infinite stresses for extensional rates greater than half of the (longest relaxation time)$^{-1}$. The present author does not consider this prediction (or the converse prediction of a limiting shear rate) to be realistic. When B becomes very large typical results are as shown in Figure 7 where a computation has been carried out for $B = 10^3$. In order to introduce a realistic shear dependent viscosity the kernel $N(t - t')$ has also been permitted to vary with the shear rate (or extension rate) in the manner used by Bird and Macdonald (*1*). A parameter c then occurs in the computation and its value has been chosen to be 0.6 so that with $B = 10^3$ the shear viscosity curve is practically identical to that for the simple rupture theory with $B = 2.8$. Both of these extremes (large B, $c = 0.6$, or $B = 2.8$, $c = 0$) yield rather poor agreement with experimental values of the first normal stress difference, Figure 8. More satisfactory agreement can be obtained by combining the molecular ideas of Graessley (*21*) with the rupture theory. This appears to amount to using the Macdonald-Bird (*1*) factors $1/(1 + c^2\lambda_n^2\gamma^2)$, which multiply the nth elements of $N(\tau)$, to allow for the effect of shearing on junction formation; the value of c is fixed at ½, however, and is not a free parameter. With $B = 5$, $c = 0.5$, the 5.4% polyisobutylene-cetane behavior is well represented in shear flow qualitatively and quantitatively. Note the increased maximum in the predicted elongation viscosity, Figure 7. The discrepancy between the normal stress data of Markovitz and Brown and twice the rigidity $[2G'(\omega)]$ at low shear rates is noted with this fluid; the normal stresses are more nearly equal to G' at the lowest rates available (not shown). This discrepancy cannot be resolved within the present theory or within other simple integral theories; however, more experiments are needed at this point. With this in mind, it is considered by the author that the theory is reasonably successful quantitatively. It may be used in a tentative explanation of the results of Ballman (*3*) in extensional flows.

CONCLUSION

Although the present theory of network rupture has a molecular motivation, and the idea of stress or strain-induced rupture is intuitively appealing, it is clear that attempts to refine and clarify these concepts should be made. These should preferably look closely at the molecular aspects; as an example of this form of attack one may

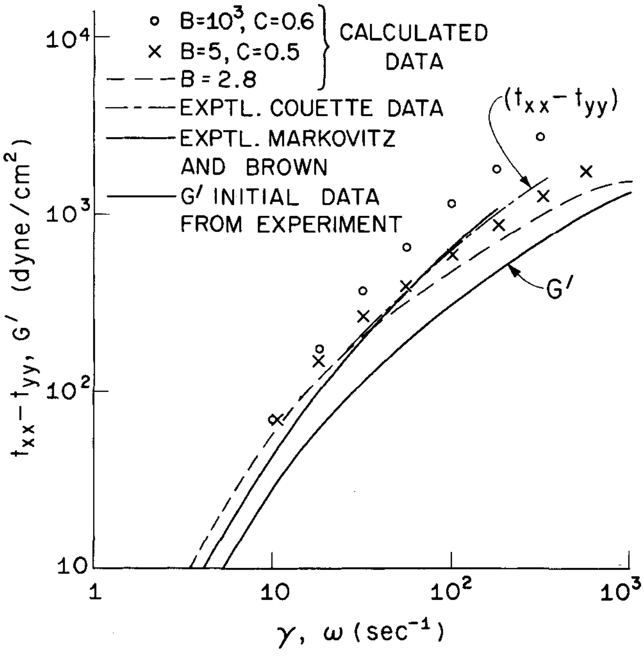

Fig. 8. Rupture theory normal stress difference predictions and comparison with experiments.

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* This value may need revision (*29*).

cite a recent paper (*47*) on the formation of junctions. Questions that can be asked include:

1. How does the rupture strain depend on stress field, temperature, concentration, etc.?
2. How is the formation of junctions [that is $N(\tau)$] influenced by shearing? This question has been investigated (*12, 21*) but without taking into account the possibility of network rupture.
3. What form of strain measure **S** and what rupture criterion should be used?

It may be noted that an encouraging feature of the present theory is the prediction of a finite tensile viscosity at all finite extensional rates. It is not clear why theories which predict infinite stresses in extension and pure shearing were ever considered reasonable. Recognizing this, we can also see that unless molecular theories leading to infinite integrals of the form (1) include rupture (or kernel modification) to remove the infinite limit (or ensure convergence), then some kinematic history which would be quite realizable physically can always be found which will cause divergence of the integrals. This presupposes that the memory function is not precisely zero at any arbitrarily large value of $(t - t')$. If N is precisely zero for $(t - t') > \tau_R$ (say), then the results of the theory are formally indistinguishable from the rupture hypothesis at least in the flows examined here. The rupture hypothesis seems more natural to the author, but some modification of $N(t - t')$ by the shearing is to be expected. Thus although the rupture hypothesis seems qualitatively and quantitatively successful insofar as it has been tried here and elsewhere (*36, 44*) more testing and research is thought to be needed.

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NOTATION

a_n = strength of contribution of nth time constant (poises)
B = rupture strain
$\mathbf{B}$ = Finger strain matrix
$\mathbf{C}$ = Green strain matrix
c = constant governing junction formations
G', G'' = complex moduli components (dyne/sq. cm.)
H = relaxation spectrum (dyne/sq. cm.)
$\mathbf{I}$ = unit matrix
n = integer
N = junction density function (dyne/sq. cm.)
P = pressure (dyne/sq. cm.)
t = time (sec.)
$\mathbf{T}$ = stress matrix (dyne/sq. cm.)
t_{xx}, etc. = components of $\mathbf{T}$ (dyne/sq. cm.)
$\mathbf{S}$ = strain matrix in general
$\mathbf{v}$ = velocity vector (cm./sec.)

Greek Letters

β = normal stress ratio, Equation (3)
γ = rate of shearing (sec.$^{-1}$)
δ' = derivative of delta function
λ_n = time constant (sec.)
$\eta_\infty, \eta_d, \eta_s, \eta_t$ = viscosities; limiting, dynamic, shearing and tensile respectively (poises)
τ_R = rupture time (sec.)
ω = frequency (rad./sec.)

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