

## Nonlinear Viscoelastic Behavior of Polymer Melts

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### Introduction

The general theory of linear viscoelasticity,<sup>1</sup> based on Maxwell's relaxation theory, has been applied with considerable success to the behavior of various materials under small stresses. A nonlinear generalization of the theory should be highly useful in order to describe the viscoelastic behavior under circumstances where the deformations are large, e.g., in the case of flow of polymer melts. Prandtl<sup>2</sup> was one of the first to try to evolve a general theory of nonlinear viscoelasticity based on a semimolecular model. He was able to predict quantitatively the stress dependence of flow and relaxation phenomena, but no experimental verification of the theory seems to have been attempted at the time. It can be shown however that, as far as the influence of shear stress on viscosity is concerned, Prandtl's result, under certain simplifying conditions, is similar to that derived by Weissenberg<sup>3</sup> with the aid of a more formal mathematical theory. An identical expression was deduced by Eyring<sup>4</sup> from his theory of rate processes and, in its most general form, was shown to describe correctly a large number of experimental results.<sup>5-7</sup>

More recently Brinkman and Schwarzl<sup>8,9</sup> have elaborated a somewhat different model in order to describe nonlinear creep of viscoelastic solids. Here again the influence of stress is similar to that predicted by the older theories treating non-Newtonian flow.

It is the object of this paper to present a set of equations, derived from Eyring's theory, which describe nonlinear flow and relaxation in terms of a characteristic relaxation spectrum to be determined from measurements in a region where the behavior is approximately linear. The method will be used to interpret the behavior in simple shear of a number of various polymer melts.

### Experimental

All measurements were made by means of the Saint-Gobain microconsistometer, a cone-and-plate viscometer designed by Kepes.<sup>10</sup> After preliminary centrifugation at 5000 rpm of the sample of molten polymer under a N<sub>2</sub> atmosphere, the sample was placed in the viscometer and its flow curve measured at constant temperature. The torque exerted on the conical surface was determined for increasing values of the shear rate  $\dot{\gamma}$  ranging

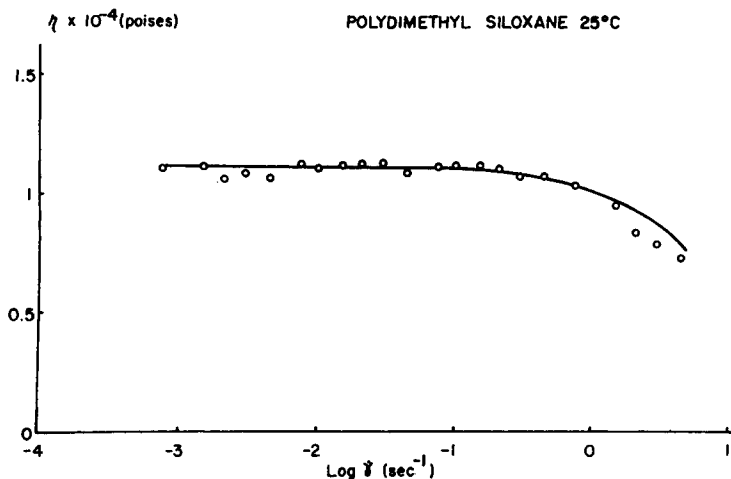


Fig. 1. Viscosity of polydimethylsiloxane as a function of shear rate: (O) experimental values; (—) curve calculated from relaxation spectrum.

from  $10^{-4}$  to  $10^2$   $\text{sec}^{-1}$ . Shear stress  $\sigma$  and viscosity ( $\eta = \sigma/\dot{\gamma}$ ) were calculated from the observed values of the torque. The torsion head consisting of five superposed torsion wires of decreasing diameter, made it possible to determine shear stresses in the range of  $10^1$ – $10^6$  dynes/cm.<sup>2</sup> Relaxation of shear stress at constant deformation after the rotation had been stopped was determined by measuring the torque as a function of time without displacement of the cone.<sup>7,10</sup> During all measurements the sample was surrounded by an  $\text{N}_2$  atmosphere in order to prevent any oxidative degradation of the polymer. Results of the flow and relaxation measurements of various polymer melts are plotted in Figures 1–10.

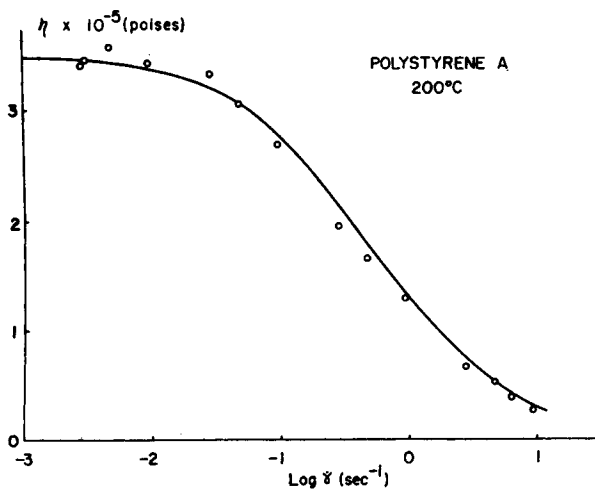


Fig. 2. Viscosity of polystyrene A as a function of shear rate: (O) experimental values; (—) curve calculated from relaxation spectrum.

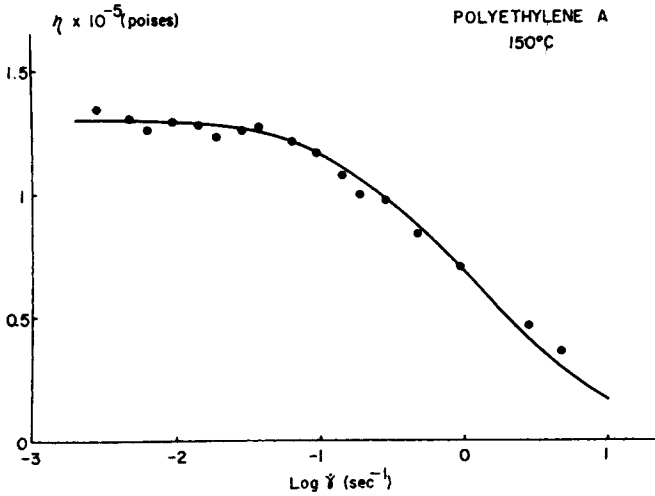


Fig. 3. Viscosity of polyethylene A as a function of shear rate: (●) experimental values; (—) curve calculated from relaxation spectrum.

### Nonlinear Relaxation Theory

The nonlinearity of general relaxation theories like those of Prandtl<sup>2</sup> and of Eyring<sup>4</sup> arises from the influence of the external force on the potential barriers separating the equilibrium positions of molecules or molecular groups. Under certain simplifying assumptions (all potential barriers

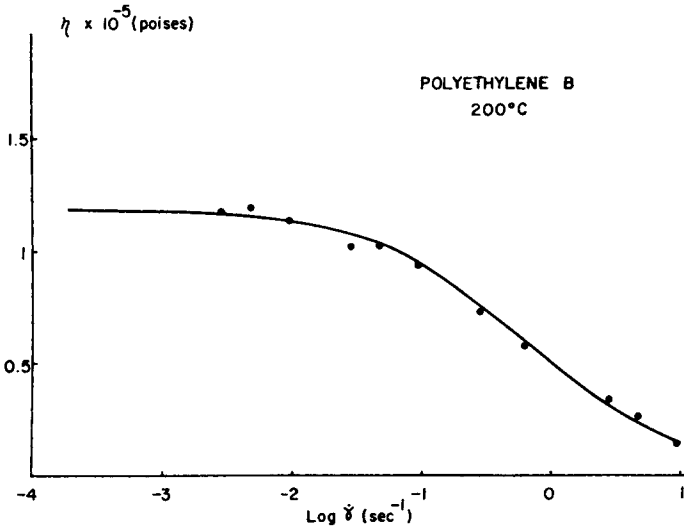


Fig. 4. Viscosity of polyethylene B as a function of shear rate: (●) experimental values; (—) curve calculated from relaxation spectrum.

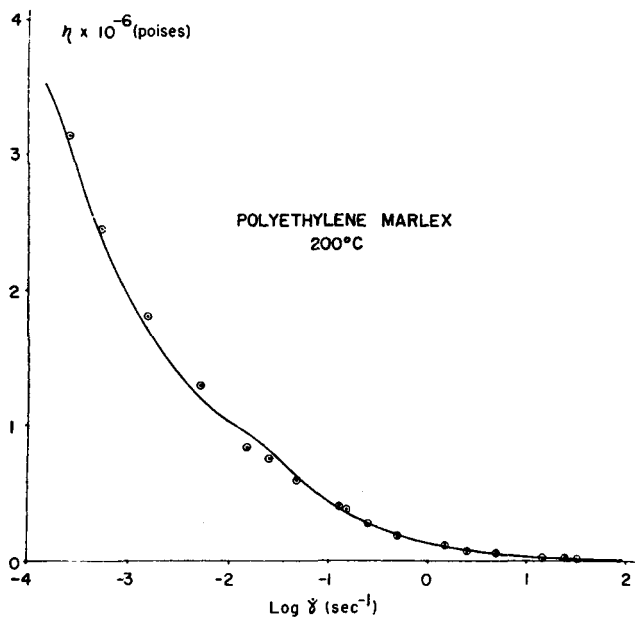


Fig. 5. Viscosity of Marlex polyethylene as a function of shear rate: (O) experimental values; (—) curve fitted by means of Ree and Eyring's trial-and-error method.

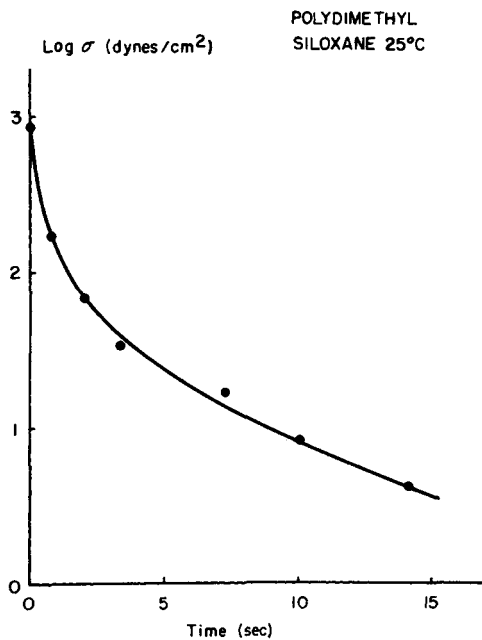


Fig. 6. Stress relaxation in polydimethylsiloxane: (●) experimental values; (—) curve fitted by means of Prony's method.

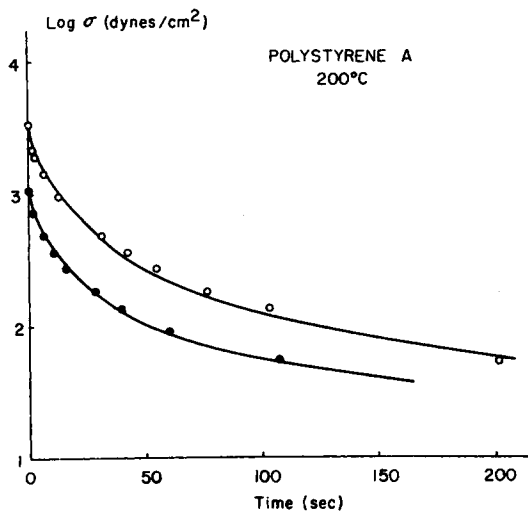


Fig. 7. Stress relaxation in polystyrene A: (O, ●) experimental values; lower curve fitted by graphical analysis; upper curve calculated from relaxation spectrum.

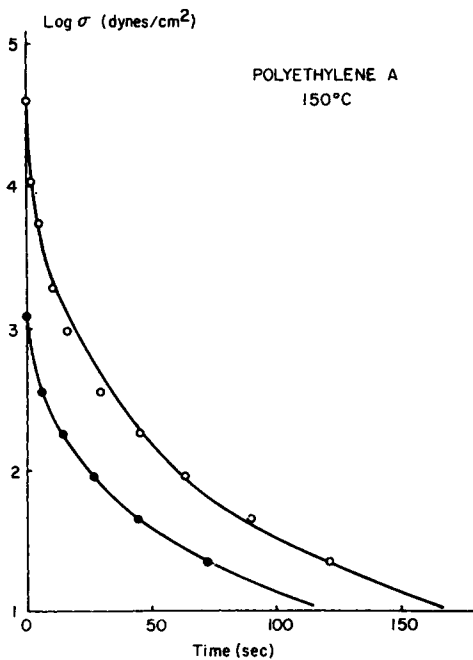


Fig. 8. Stress relaxation in polyethylene A: (O, ●) experimental values; lower curve fitted by graphical analysis; upper curve calculated from relaxation spectrum.

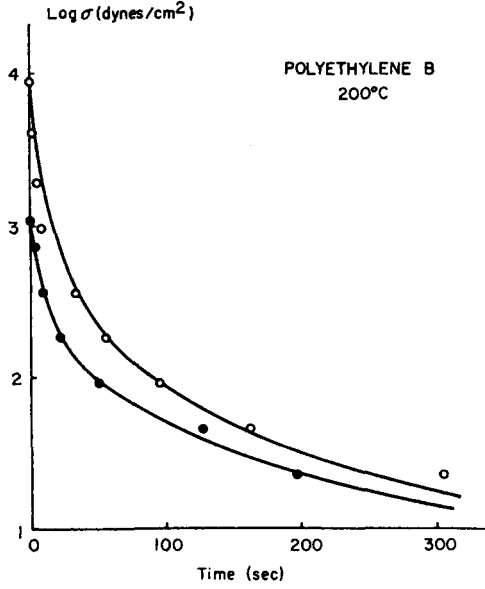


Fig. 9. Stress relaxation in polyethylene B: (O, ●) experimental values; lower curve fitted by graphical analysis; upper curve calculated from relaxation spectrum.

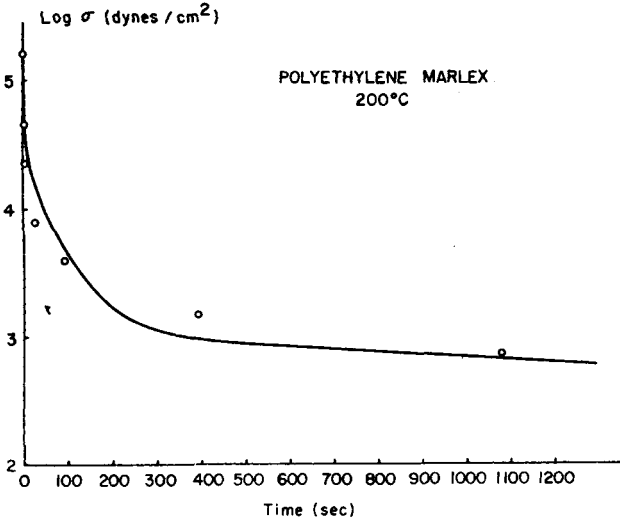


Fig. 10. Stress relaxation in Marlex polyethylene: (O) experimental values; (—) curve calculated from relaxation spectrum (derived from flow curve).

identical and symmetrical) the following expression for the viscosity in simple shear flow has been derived:

$$\eta = \sigma/\dot{\gamma} = \beta\sigma/\sinh(\alpha\sigma) \quad (1)$$

where  $\alpha$  and  $\beta$  are functions of molecular parameters.

According to Eyring's theory:

$$\alpha = \lambda_2\lambda_3\lambda/2kT$$

and

$$\beta = \lambda_1/2\lambda K_0 \quad (2)$$

$\lambda$  is the average distance between the equilibrium positions (the width of the potential barrier),  $\lambda_2$  is the distance between neighboring molecules in the same direction as  $\lambda$  (direction of motion),  $\lambda_3$  the distance between neighboring molecules in the shearing planes but perpendicular to the direction of motion, whereas  $\lambda_1$  is the analogous distance perpendicular to the shearing planes.

$2K_0$  is the total number of jumps per unit time across the potential barrier in both directions and in absence of any external force. In the most simple case

$$K_0 = (kT/h) \exp \{ \Delta S/k \} \exp \{ -\Delta H/kT \} \quad (3)$$

where  $h$  is the Planck constant,  $k$  the Boltzmann constant, and  $\Delta S$  and  $\Delta H$  the activation entropy and enthalpy, respectively. When the shearing is suddenly stopped, part of the molecules or molecular groups will occupy nonequilibrium positions. Reestablishment of equilibrium would result in a more or less important shear recovery if the external force is suppressed at the same time as the shearing. If, on the other hand, the total shear deformation is kept constant, as is the case in our experiments, shear stress will be gradually released as a result of the rearrangement of the molecules. Stress relaxation may be described by the general Maxwell formula:

$$-d\sigma/dt = \sigma/\tau \quad (4)$$

where  $\tau$  is the relaxation time.

In linear theory  $\tau$  is considered as a constant, but in general, as already suggested by Maxwell himself,  $\tau$  will be a decreasing function of the stress. Eyring's theory of rate processes has been used to predict different expressions for the stress dependence of relaxation time. In one of the most recent publications<sup>11</sup> it is proposed that the stress dependence obeys a hyperbolic sine law:

$$\tau = [2K_0 \sinh(\alpha\sigma)]^{-1} \quad (5)$$

This expression or its approximate form for high stresses where  $\sinh(\alpha\sigma) \approx \frac{1}{2} \exp \{ \alpha\sigma \}$ , is claimed to hold in certain cases, but it should logically break down for low stresses, since it predicts an infinitely long relaxation time if the stress tends to zero. A more general expression may be derived if one assumes that at constant total deformation all molecular jumps, independent of their direction, contribute to the relaxation of stress.

Adopting Eyring's one-dimensional model, the jump frequency in the forward direction is equal to  $K_0 \exp \{ \alpha \sigma \}$  and in the backward direction equal to  $K_0 \exp \{ -\alpha \sigma \}$ . The relaxation time, supposed to be equal to the inverse of the total jump frequency, may be written now as:

$$\tau = [2K_0 \cosh (\alpha \sigma)]^{-1} \quad (6)$$

For small stresses,  $\alpha \sigma \ll 1$ , and the relaxation time will be approximately constant:

$$\tau^0 = 1/2K_0 = \beta \lambda / \lambda_1 \quad (7)$$

The value of the shear modulus as defined by Maxwell:  $G = \eta / \tau$  is given by eqs. (1) and (6):

$$G = \lambda_1 \sigma / \lambda \tanh (\alpha \sigma) \quad (8)$$

According to eq. (8) the shear modulus increases with stress and tends to infinity, whereas the viscosity and the relaxation time decrease with stress and tend to zero [see eqs. (1) and (6)].

For small values of stress,  $\alpha \sigma \ll 1$ , the shear modulus approaches a limiting value:

$$G^0 = \lambda_1 / \lambda \alpha \quad (9)$$

With the aid of eq. (8) the following expression for the recoverable shear strain during flow may be obtained:

$$\gamma_e = \sigma / G = (\lambda / \lambda_1) \tanh (\alpha \sigma) \quad (10)$$

Equation (10) shows that the recoverable shear strain increases with stress but, in contrast to the shear modulus, the recoverable strain approaches a limiting value  $\Gamma$  for very high stresses:

$$\Gamma = \lim_{\sigma \rightarrow \infty} \gamma_e = \lambda / \lambda_1 \quad (11)$$

Equations (6)–(11) can be used now to express the parameters of the nonlinear model in terms of limiting values and of stress:

$$\tau = \tau^0 / \cosh (\sigma / G^0 \Gamma) \quad (12)$$

$$G = \sigma / \Gamma \tanh (\sigma / G^0 \Gamma) \quad (13)$$

$$\eta = \sigma \tau^0 / \Gamma \sinh (\sigma / G^0 \Gamma) \quad (14)$$

$$\gamma_e = \Gamma \tanh (\sigma / G^0 \Gamma) \quad (15)$$

Brinkman and Schwarzl<sup>8,9</sup> have developed a nonlinear theory of viscoelasticity based on a similar one-dimensional model in which the crossing of a potential barrier is considered as a diffusion process. This theory has been used to describe the creep behavior of a viscoelastic solid without irreversible flow. For very small stresses, the diffusion model behaves as a linear Kelvin-Voigt solid, but at higher stresses creep becomes nonlinear. If all potential barriers are identical and symmetrical, the nonlinear be-



havior in shear can be described by the following expressions for the retardation time  $\theta$  and the compliance  $J$ :

$$\theta = \theta^0 / \cosh(\sigma J^0 / \epsilon) \quad (16)$$

$$J (= 1/G) = (\epsilon / \sigma) \tanh(\sigma J^0 / \epsilon) \quad (17)$$

The (elastic) deformation is equal to:

$$\gamma_e = \sigma J = \epsilon \tanh(\sigma J^0 / \epsilon) \quad (18)$$

where

$$\epsilon = \lim_{\sigma \rightarrow \infty} \gamma_e \quad (19)$$

$\theta^0$  and  $J^0$  are the limiting values of the retardation time and the shear compliance for zero stress. Equations (16)–(19) are formally identical to those derived above for the nonlinear Maxwell liquid. In both cases nonlinear behavior is described by the same hyperbolic functions of stress and limiting parameter values.

It is well known that the linear viscoelastic behavior of many materials under small stresses cannot be accounted for by a single value of the time constant and the modulus (or compliance). A discrete relaxation spectrum or a continuous distribution function of relaxation times has generally to be introduced in order to describe the experiments. It will be shown in the next section that all experimental results reported in this paper can be satisfactorily described by means of a characteristic relaxation spectrum the stress dependence of which is given by eqs. (12) and (13).

### Experimental Verification of the Nonlinear Relaxation Theory

It is generally assumed that the deformation of a macromolecular system results from translational and rotational displacements of more or less voluminous backbone segments and side groups. Each group of identical subunits is, at a given temperature, completely characterized by a relaxation time ( $\tau_i^0$ ) and an elasticity modulus ( $G_i^0$ ) as far as linear behavior is concerned. In order to describe nonlinear behavior, a third parameter  $\Gamma_i$  is necessary as shown by eqs. (12)–(15). This parameter is equal to the limiting value of the recoverable deformation of a subunit at infinitely high stress, and, according to Eyring's theory, it can be expressed as the ratio  $\lambda/\lambda_1$ , which is equal to the ratio of the distance between two equilibrium positions in the direction of shear and the dimension of a subunit perpendicular to the shear planes. We have assumed, as a first approximation, that this ratio is equal to 1 for all subunits concerned. In that case the eqs. (20) and (21) should hold:

In shear flow:

$$\sigma = \Sigma \sigma_i = \Sigma G_i^0 \sinh^{-1}(\tau_i^0 \dot{\gamma}) \quad (20)$$

In relaxation at constant deformation:

$$-d\sigma/dt = -d\Sigma \sigma_i/dt = \Sigma(\sigma_i/\tau_i^0) \cosh(\sigma_i/G_i^0) \quad (21)$$

If  $\sigma_i/G_i^0 \ll 1$ , the relaxation equation becomes, in a first approximation, linear:

$$-d\sigma/dt \simeq \Sigma \sigma_i/\tau_i^0$$

or

$$\sigma(t) = \Sigma \sigma_i(0) \exp \{ -t/\tau_i^0 \} \quad (22)$$

where  $\sigma_i(0)$  is the stress due to the  $i$ th group of subunits for  $t = 0$ .

The observed relaxation curves for the lowest stresses, i.e.,  $\sigma(0) \sim 10^3$  dynes/cm.<sup>2</sup>, have been decomposed in three or four exponential curves in order to calculate the relaxation spectrum according to eq. (22). In a semilogarithmic plot each exponential curve is represented by a straight line the slope of which is equal to  $-1/\tau_i^0$  and whose intercept on the ordinate is equal to  $\ln \sigma_i(0)$ . The values of  $G_i^0$  have been calculated from eq. (20) which may be written as:

$$G_i^0 = \sigma_i(0)/\sinh^{-1}(\tau_i^0\dot{\gamma}) \quad (23)$$

For small stresses, i.e., in the approximately linear region, the eq. (23) may be reduced to:

$$G_i^0 \simeq (0)_i\sigma/\tau_i^0\dot{\gamma} \quad (24)$$

The values of  $\tau_i^0$  and  $G_i^0$  obtained in this way for a number of polymers are given in Table I. The variation of viscosity with rate of shear, as calculated from the relaxation spectrum, is shown in Figures 1-4. The curves in these figures have been calculated by means of the eq. (25):

$$\eta = (1/\dot{\gamma})\Sigma G_i^0 \sinh^{-1}(\tau_i^0\dot{\gamma}) \quad (25)$$

It is obvious that the agreement between theory and experiment is remarkably good.

The nonlinear relaxation curves in Figures 7-10 have also been calculated from the relaxation spectrum by means of a graphical integration of eq. (21) for each term:

$$\tau_i^0 \int_{Z(0)}^{Z(t)} dZ/Z \cosh Z = t \quad (26)$$

where  $Z(t) = \sigma_i(t)/G_i^0$  and  $Z(0) = \sinh^{-1}(\tau_i^0\dot{\gamma})$ .

The value of the shear stress at any time is then obtained by summing up the calculated partial stresses:  $\sigma(t) = \Sigma \sigma_i(t)$ .

The most pronounced nonlinear behavior was observed in the case of the high density polyethylene Marlex for which no stresses low enough to be described by the linear relaxation eq. (22) have been attained. The relaxation spectrum of this polymer, given in Table I, has been calculated from the observed flow curve (Fig. 5) by means of the trial-and-error method described by Ree and Eyring,<sup>5</sup> and by applying eqs. (7) and (9), in which  $\lambda/\lambda_1$  has again been assumed to be equal to 1.\* The relaxation

\* Ree and Eyring have also defined a parameter  $x$  representing the fractional area on a shear surface occupied by a group of identical subunits. From an experimental point of view this parameter is inseparable from the shear modulus of a subunit. We have, therefore, assumed all  $x_i$ 's to be equal to 1 in accordance with the generally accepted phenomenological treatments of viscoelastic behavior.

TABLE I  
Relaxation Spectra of Various Polymer Melts

Polymer	$\bar{M}_w^a$	$(\bar{r}^2)^{1/2}$ A, b	Temp., °C.	$G_1^0$ , dynes/ cm. <sup>2</sup>	$G_2^0$ , dynes/ cm. <sup>2</sup>	$G_3^0$ , dynes/ cm. <sup>2</sup>	$G_4^0$ , dynes/ cm. <sup>2</sup>	$\tau_1^0$ , sec.	$\tau_2^0$ , sec.	$\tau_3^0$ , sec.	$\tau_4^0$ , sec.	$\Delta H_{\sigma\sigma}$ , kcal. mole
Polydimethyl- siloxane	227,300	280	25	$2.85 \times 10^4$	$2.26 \times 10^2$	$10^2$	240	0.28	1	4	—	3.0
Polystyrene A	400,000	387	200	$6 \times 10^4$	$9.7 \times 10^2$	$10^2$	214	2.5	17	165	—	25.0
Polyethylene A	683,000	2000	150	$4 \times 10^4$	$3.4 \times 10^2$	$10^2$	126.7	2	12.5	62.5	—	10.8
Polyethylene B	1,350,000	2100	200	$5.2 \times 10^4$	$7.25 \times 10^2$	$10^2$	410	50	0.6	8.2	40	230
Polyethylene (Marlex)	88,500	664	200	$7.6 \times 10^4$	$1.44 \times 10^4$	$10^4$	377	0.8	57.5	8500	—	9.4

<sup>a</sup> Weight-average molecular weight determined by light scattering in solution.

<sup>b</sup> Root-mean-square radius of gyration was determined in benzene for the dimethylsiloxane and polystyrene, and in tetralin for the polyethylenes.

spectrum obtained in this way has been used to calculate the nonlinear relaxation curve of Figure 10, which appears to be in fair agreement with the observed relaxation behavior. The calculated nonlinear relaxation curves of Figures 7, 8, and 9 also show a rather good agreement with experiment.

### Discussion

The nonlinear viscoelastic behavior of various polymer melts is shown to be adequately described by a discrete relaxation spectrum the stress dependence of which may be derived from the theory of rate processes. Until now, the validity of rate theory in the field of non-Newtonian flow of polymers had been demonstrated only in an empirical way, but the results reported in this paper show definitely that the characteristic parameters, in a first approximation, may be derived directly from relaxation experiments. However, these results could only be obtained by assuming that, for all deformation modes, the parameter  $\Gamma$  is equal to 1. It is not obvious at all that this assumption should be strictly valid for all polymers investigated. As a matter of fact, in some of the cases reported the agreement between flow and relaxation curves would be still better if some of the  $\Gamma_i$ 's were assumed to be somewhat different from 1. The limited accuracy of the experimental data, in particular those concerning the relaxation of stress does not permit us to make any firm statement about the real values of the  $\Gamma_i$ 's, but the data seem to suggest that the  $\Gamma_i$ 's of the most voluminous flow units (which are associated with the longer relaxation times) may be somewhat smaller than 1, whereas the  $\Gamma_i$ 's of the smallest flow units (whose relative contribution to the stress increases with the rate of shear) might be larger than 1.

As we have already shown,  $\Gamma$  is equal to the limiting value of the recoverable strain of the flow unit at infinitely high stress or, according to Eyring, equal to the ratio of the distance between two equilibrium positions in the direction of shear and the dimension of the flow unit perpendicular to the shear planes. At relatively high shear rates, flow is due principally to the displacements of small flow units; if these flow units are anisodimensional and oriented in the direction of shear  $\Gamma$  might be larger than 1 which seems actually to be the case. Confirmation of this hypothesis has, however, to await more precise experimental results providing quantitative information on the value of  $\Gamma$  for the different flow units. Analysis of the flow curve in terms of the generalized Ree-Eyring equation:  $\sigma = \Sigma G_i^0 \Gamma_i \sinh^{-1} (\tau_i^0 \dot{\gamma} / \Gamma_i)$  will lead to a set of values for  $G_i^0 \Gamma_i$  and  $\tau_i^0 / \Gamma_i$ .

On the other hand,  $G_i^0$  and  $\tau_i^0$  may be evaluated directly from the (approximately) linear relaxation curve, as shown in this paper. In this way, two values (which, obviously, should be identical) will be obtained for every  $\Gamma_i$ . It should be emphasized, however, that the graphical analysis of the flow curve is a rather inaccurate procedure which becomes practically impossible to handle in the case of closely spaced relaxation times. Graphical analysis of the linear relaxation curve, on the other hand, is relatively simple although somewhat arbitrary.<sup>12</sup>

A sum of exponentials may, however, be resolved by means of mathematical procedures<sup>13-15</sup>; in fact, the relaxation spectrum of the polydimethylsiloxane (see Table I) has been obtained by Prony's method of analysis with the aid of a LGP-30 computer (Royal McBee). The relative merits of this and other mathematical procedures are actually under study.

As to the influence of temperature we have already shown in an earlier paper<sup>7</sup> that our experimental results are in agreement with Ree and Eyring's analysis<sup>5</sup> of a limited set of data obtained by other authors.

In a temperature range between 150 and 300°C., polymer flow may be described by a single value of the activation enthalpy at constant stress ( $\Delta H_s$ ) independent of temperature and independent of stress. This means that for the different flow units of a given polymer, the difference in relaxation time is only due to a difference in activation entropy which, according to Ree and Eyring, should be explained by the fact that for large flow units the entanglement coupling of molecular chains belonging to adjacent units is more important than for the smaller ones.

A second, somewhat more surprising conclusion may be drawn from the observed invariance of  $\Delta H_s$ . This means, in fact, that the moduli  $G_s$  are independent of temperature, at least in the range of temperatures investigated. If the elasticity of polymer melts is attributed to the presence of molecular entanglements (see below) the modulus should, according to the kinetic theory of rubberlike elasticity, be proportional to the absolute temperature if the number of entanglements were independent of temperature. This number will, however, decrease with increasing temperature and the latter effect appears to compensate exactly the theoretical increase of modulus. This will, of course, not necessarily be the case for higher temperatures where the moduli might be expected to be lower.

Measurements of the complex shear modulus in polyethylene melts have recently been reported<sup>16</sup> which also show a negligible small influence of the temperature on the real part of the modulus.

In all molecular theories of polymer flow one admits<sup>17-20</sup> the existence of transient networks whose junctions are attributed to molecular entanglements or secondary forces. The modulus of elasticity should then be equal to:<sup>19</sup>

$$G^0 = snkT \quad (27)$$

where  $n$  is the number of network junctions per unit of volume and  $s$  the ratio of network chains to network junctions. If the junctions are tetrafunctional,  $s$  is equal to 2. In terms of Eyring's parameters the shear modulus of a flow unit is equal to:

$$G^0 = 2kT/\Gamma\lambda\lambda_2\lambda_3 \quad (28)$$

as follows from eqs. (2), (9), and (11).

The denominator in eq. (28) is of the same order of magnitude as the volume of the flow unit. A comparison of eqs. (27) and (28) might induce

one to consider the volume of a flow unit to be identical with the volume associated with a network junction. The molecular mechanism of polymer flow may then be depicted as follows. On shearing the polymer the network is strained, altering its configurational entropy and thereby giving rise to stress. Slippage and (ultimately) chain disentanglement in the network junctions leads to a continuous relaxation and recreation of stress during flow. The motion of all segments belonging to a network chain has to be coordinated in order to assure the contribution of the chain to the energy dissipation in the network. At low rates of shear this coordination can take place over considerable distances (some thousands of Angstrom) but when the shear rate increases, the only configurational rearrangements able to keep pace with the imposed macroscopic deformation are those coordinated over shorter distances that are the shorter the higher the shear rate. In other words, the total stress is to be considered as a sum of partial stresses, each of which is due to the deformation of a network having more or less widely spaced junction points. For increasing shear rates the relative contribution of the networks with most widely spaced junction points decreases gradually. Equally, the relative contribution of each network to the dissipated energy decreases gradually with increasing shear rate. Application of eq. (28) to the experimental results reported in this paper shows that the viscosity at the highest shear rates is principally due to the deformation of a network having junction points separated by about 100 A. in the average. Referring to what has been said earlier about the probable value of  $\Gamma$  one might suppose that the average distance between the junction points of this network in the direction of shear is larger than the distance perpendicular to the planes of shear.

After cessation of flow, the molecular chains will rearrange in order to adopt the most probable configuration compatible with the imposed, constantly held strain. This rearrangement will most rapidly take place by segmental motions coordinated over small distances and leading to total release of stress in the networks with closely spaced junction points. Complete stress relaxation will only be reached after reestablishment of the most probable configuration of all molecular chains, by means of a coordinated motion of widely spaced junction points. The mathematical formulation of the behavior of the transient network model has been developed in considerable detail by Yamamoto<sup>18</sup> and, independently, by Lodge.<sup>19</sup> Our discussion seems to suggest that the network theory may also furnish a molecular interpretation of the parameters in the Eyring-Ree relaxation theory if the activated state of the flow units is identified with the deformed state of parts of the transient network. Taking account of the fact that the activation enthalpy of all flow units is the same, in a first approximation, it does not seem necessary to assume that different flow units correspond to different networks, each characterized by the particular nature of its junction loci. The existence of one single type of network might be assumed whose subdivision in more or less voluminous flow units is however not necessarily unique.

Although the behavior of the network, in that case, still might be described by means of a discrete relaxation spectrum, a detailed discussion of the observed spectra given in Table I is not yet warranted in view of the more or less arbitrary character of the analytical procedures employed. It is hoped that the mathematical methods actually under study will yield in the near future less ambiguous information on the relaxation spectrum. Arbitrary analysis of the experimental data might also be avoided by introduction of continuous distribution functions.

Finally it should be remarked that in most of the polymers studied a particular kind of network appears to exist at rest which breaks down as soon as the shear strain exceeds a certain limiting value. This phenomenon can be observed by following the evolution of stress during the first instants after application of the constant shear rate. Before attaining its equilibrium value the stress passes through a maximum, the difference between maximum and equilibrium value being the larger, the higher the shear rate. The limited number of observations effected so far seem to indicate that the maximum stress is attained for a certain characteristic value of the strain which is somewhat dependent on the shear rate. Similar observations have been reported by other authors<sup>21-23</sup> in the case of polymer melts and solutions. The nature of the linkages forming this network has not yet been elucidated but it has been observed that the rate of reformation of the network is rather rapid, the time necessary to build up the thixotropic structure after cessation of flow being in the order of 5-10 sec. for the vinyl polymers discussed in this paper. As the time necessary for breakdown is of the same order of magnitude, results of flow measurements in relatively short capillaries should be regarded with circumspection, especially at high shear rates when the time spent in the capillary may be shorter than the time necessary for breakdown of the thixotropic structure. Apparent viscosity values obtained in this way will be substantially higher than the equilibrium values determined by means of, e.g., a cone-and-plate viscometer as used in our investigations.

We wish to thank Mrs. J. Lesavre and P. Duffaud of this laboratory for their analysis of some of the relaxation curves by means of Prony's method, Dr. E. R. Howells (I.C.I. Plastics Division) for providing some of the samples, and Mr. R. Prechner for performing the experimental work.

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### Synopsis

With the aid of Eyring's rate theory a set of equations is derived describing the nonlinear viscoelastic behavior of a generalized Maxwell liquid in simple shear. It is shown that this behavior may be completely described by a stress- and temperature-dependent relaxation spectrum which, in a first approximation, becomes independent of stress if the latter tends to zero. Each term of the discrete relaxation spectrum is characterized by a relaxation time, a shear modulus, and a dimensionless parameter  $\Gamma$  equal to the limiting value of a recoverable strain at infinitely high stress. All  $\Gamma$ 's disappear from the relevant equations if the stress tends to zero. Similar expressions describing nonlinear behavior of a generalized Kelvin-Voigt solid may be derived from Schwarzl and Brinkman's diffusion theory. The theory is used to interpret the observed nonlinear flow and relaxation behavior of a number of various polymer melts. The polymers have been studied under well-defined hydrodynamical and thermal conditions in a cone-and-plate viscometer. In a first approximation, all  $\Gamma$ 's have been supposed equal to 1. The theoretical flow and relaxation curves calculated from the observed relaxation spectrum are in fair agreement with the experimental ones. Finally it is shown that the observed behavior may also be interpreted in terms of the transient network theory if the activated state of a flow unit is identified with the strained state of more or less voluminous parts of the molecular network in a polymer melt.

### Résumé

A partir de la théorie d'Eyring, on déduit un ensemble d'équations pour décrire le comportement viscoélastique non-linéaire en cisaillement simple d'un liquide de Maxwell généralisé. On a pu montrer que ce comportement peut être complètement décrit par un spectre de relaxation dépendant de la contrainte et de la température, lequel devient en première approximation indépendant de la contrainte lorsque cette dernière tend vers zéro. Chaque terme du spectre discontinu de relaxation est caractérisé par un temps de relaxation, un module de cisaillement et un paramètre sans dimensions  $\Gamma$  égal à



la valeur limite d'une déformation récupérable pour des contraintes infiniment grandes. Tous les  $\Gamma_i$  disparaissent des équations précédentes si la contrainte tend vers zéro. Des expressions analogues décrivant le comportement non-linéaire d'un solide de Kelvin-Voigt généralisé peuvent être déduites de la théorie de la diffusion de Schwarzl et Brinkman. La théorie sert à interpréter l'écoulement non-linéaire observé et le mécanisme de relaxation de différents polymères fondus. Les polymères ont été étudiés dans des conditions hydrodynamiques et thermiques bien définies à l'aide d'un viscosimètre à cône et plan. En 1ère approximation, tous les  $\Gamma_i$  ont été supposés égaux à 1. L'écoulement théorique et les courbes de relaxation calculées à partir du spectre de relaxation observé sont en accord avec les valeurs expérimentales. Enfin on a montré que le comportement observé peut également être interprété à l'aide de la théorie du réseau transitoire si l'état activé d'une unité d'écoulement est identifié à l'état déformé d'une maille plus ou moins grande du réseau moléculaire dans le polymère fondu.

### Zusammenfassung

Mit Hilfe der Eyringschen Geschwindigkeitstheorie wird ein Gleichungssystem abgeleitet, mit welchem das nichtlineare, viskoelastische Verhalten einer verallgemeinerten Maxwell-Flüssigkeit bei einfacher Scherung beschrieben werden kann. Es wird gezeigt, dass dieses Verhalten vollständig durch ein spannungs- und temperaturabhängiges Relaxationsspektrum beschrieben werden kann, das in erster Näherung bei Annäherung an die Spannung Null von der Spannung unabhängig wird. Jeder Term des diskreten Relaxationsspektrums wird durch eine Relaxationszeit, einen Schubmodul und einen dimensionslosen Parameter  $\Gamma_i$ , entsprechend dem Grenzwert der reversiblen Verformung für unendlich grosse Spannung, charakterisiert. Wenn die Spannung gegen Null geht, verschwinden die  $\Gamma_i$ -Werte aus den entsprechenden Gleichungen. Ähnliche Ausdrücke können für das nichtlineare Verhalten eines verallgemeinerten Kelvin-Voigt-Festkörpers aus der Diffusionstheorie von Schwarzl und Brinkman abgeleitet werden. Die Theorie wird zur Deutung des beobachteten, nichtlinearen Fließ- und Relaxationsverhaltens einer Reihe verschiedener Polymerschmelzen benützt. Die Polymeren wurden unter wohldefinierten hydrodynamischen und thermischen Bedingungen in einem Kegel-Platteviskosimeter untersucht. In erster Annäherung wurde angenommen, dass alle  $\Gamma_i$ -Werte gleich eins sind. Die aus dem beobachteten Relaxationsspektrum berechneten theoretischen Fließ- und Relaxationskurven stimmen mit den experimentell erhaltenen gut überein. Schliesslich wird gezeigt, dass das beobachtete Verhalten auch mit der Theorie der instabilen Netzwerkbildung erklärt werden kann, unter der Voraussetzung, dass der aktivierte Zustand der Fließeinheit mit dem verformten Zustand mehr oder weniger voluminöser Teile des Molekülnetzwerkes in einer Polymerschmelze identifiziert wird.

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