

## The Shear Modulus of Flowing Polyethylene Melts

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### Synopsis

Tests on three low-density polyethylene melts over a range of temperatures and shear rates, using a Weissenberg rheogoniometer, have enabled the reduced shear modulus to be obtained as a function of shear rate at the initiation of shearing and at various subsequent stages. For the two polymers which gave plateau values of modulus during the course of shearing these were in good agreement with figures quoted in the literature, but the initial modulus (measured on one polymer) was an order of magnitude higher. This supports the view that a network structure exists in the polymer at rest and is disrupted in the early stages of shearing. It was not possible to obtain unequivocal evidence that the equilibrium modulus decreases with amount of shearing, as required by the hypothesis that rheological breakdown is caused by a reduction in molecular entanglements.

### INTRODUCTION

When polymer melts are continuously sheared they undergo a progressive change which has been termed "rheological breakdown." This is characterized by a reversible reduction in tangential, and especially normal, stress components with the amount of the shear applied at a constant rate, though temporary increases may occur at some stage of the process. This has been ascribed to partial disentanglement of the molecules during the shearing<sup>1-4</sup> but it has been difficult to reconcile this view with the increase in shear modulus of the melt with increasing shear.

The kinetic theory of elasticity gives the equilibrium shear modulus  $G$  of a crosslinked polymer as

$$G = \frac{1}{2} SNkT \quad (1)$$

where  $N$  is the number of crosslinks per unit volume,  $k$  is the Boltzmann constant,  $T$  the absolute temperature and  $S$  is the ratio of effective chains to crosslinks. This has been applied by several authors to flowing polymer melts without justifying such a course, although the system of continually changing crosslinks is very different from that for which eq. (1) was derived. Recently, however, Kaye<sup>5</sup> has modified Lodge's molecular theory<sup>6</sup> of flow of incompressible polymeric liquids by introducing the

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reasonable assumption that the lifetimes of the crosslinks are stress dependent. He finds that for steady laminar shearing:

$$P_{12}^2/(P_{11}-P_{22}) = 1/2 SNkT \quad (2)$$

where  $P_{11}$ ,  $P_{22}$  and  $P_{12}$  are components of the stress tensor with the usual orientation of axes.  $N$  is to be interpreted as the instantaneous concentration of crosslinks whether due to entanglements or secondary valency forces. This may be combined with the Weissenberg hypotheses,<sup>7</sup> which for these conditions can be written:

$$P_{12}^2/(P_{11}-P_{22}) = G \quad (3)$$

to give eq. (1) for polymeric liquids.

Unfortunately Lodge's theory and Kaye's modification of it make use of the two-network hypothesis which Flory<sup>8</sup> has shown to be inappropriate where crosslinks are being broken as well as formed. Nevertheless there is a good deal of evidence that Lodge's theory leads to qualitatively useful deductions, and it seems likely that this will be at least as true of Kaye's version. On this basis it was hoped that a quantitative study of the changes in shear modulus during the steady shearing of polyethylene melts would give qualitative information concerning the changes involved in rheological breakdown.

### Materials

Low-density polyethylenes were used because of the authors' interest in this material and because the work formed part of a wider programme, though it was recognized that linear polymers would have made interpretation of results somewhat easier. The following three polymers were used, and contained 0.1 percent antioxidant.

Polyethylene *A* Melt index 0.3—

Polyethylene *B* Melt index 0.3—Narrower molecular weight range than *A*.

Polyethylene *C* Melt index 7

### Apparatus and Method

All the experimental work was done on a Weissenberg rheogoniometer (Sangamo Controls Limited, model R.16). Except for a few tests at low shear rates, where 5 cm platens were used, the cone and plate were 2.5 cm diameter with a gap angle of 4 degrees. Disks of polymer were cut from sheet moulded to about 0.13 cm thick and were pressed between the heated cone and plate, the excess being trimmed off in the usual way. Torque and thrust were recorded on a U.V. recorder and the modulus during shearing obtained from the stress components by eq. (3). In addition the initial modulus  $G_0$  of the melt was determined for polymer *A* by the method of Vinogradov and Belkin<sup>9</sup> in which the slope of the shear stress/shear strain curve is measured at the origin. For this purpose a thick torsion bar was

used to minimize inertia forces, and a high gain on the transducer amplifier was combined with a high recorder chart speed.

The ranges of temperature and shear rate used in the continuous shearing experiments were as follows:

Polymer	Temperature Range (°C)	Shear Rate Range (s <sup>-1</sup> )
A	156-200	0.0177-1.77
B	151-210	0.177-5.61
C	120-150	0.282-448

Polymers *A* and *B* were tested in an atmosphere of nitrogen, but in the case of polymer *C* it was found possible to omit this because of the lower temperature and shorter test periods.

### Results

With polyethylenes *A* and *B* the maximum rate of shear was determined by the tendency for the sample to break up at high stresses, and in any case slight loss of material from the gap commenced at a shear in the region of 100. This proved a severe restriction in studying rheological breakdown, and polymer *C* was included in the tests since it gave closely reproducible stress measurements at shears up to about 1000. Beyond this, reproducibility deteriorated suggesting that shearing was no longer uniform. A lag of about 50 msec between the signal from the servo transducer and the

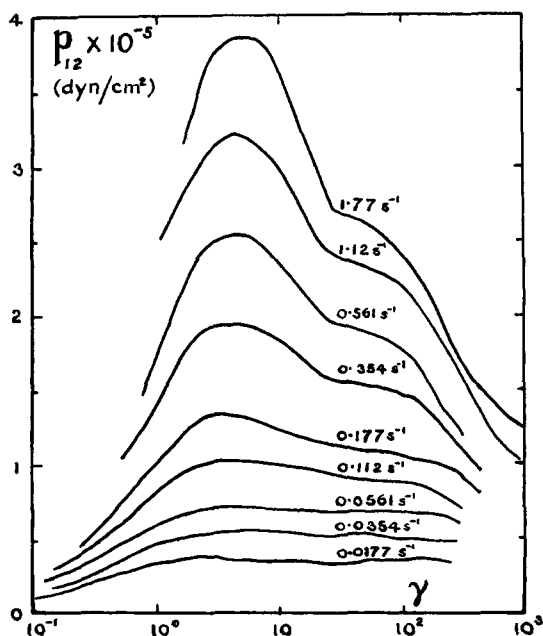


Fig. 1. Polymer *A* at 180°C. Shear dependence of tangential stress.

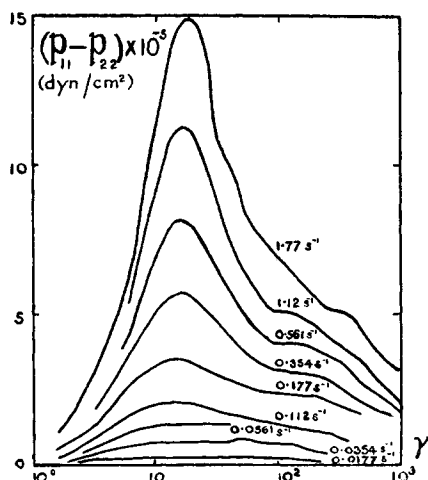


Fig. 2. Polymer A at 180°C. Shear dependence of normal stress.

operation of the servo motor invalidated the initial normal stress measurements at high shear rates. Also much above 100  $\text{s}^{-1}$  difficulty was experienced in obtaining sufficiently quick response of the servo system to the rapidly changing normal stress at low shears, without introducing "hunting," so that further loss of data in the early stages of shearing resulted.

Typical curves showing the variation of  $P_{12}$  and of  $P_{11}-P_{22}$  with applied shear during constant-rate shearing are shown in Figures 1-4, and are essentially similar to those obtained previously for low-density polyethylene.

### Time/Temperature Superposition

Although it is usual to obtain the shear modulus of polymers as a function of logarithmic time or frequency in creep, relaxation, or dynamic tests, it is to be expected that a similar type of relationship exists between the shear modulus during continuous shearing, and logarithmic shear rate. This was implied by Vinogradov and Belkin<sup>9</sup> and has also been pointed out by Blyler and Huseby.<sup>10</sup>

In agreement with previous findings<sup>1</sup> a plot of  $P_{11}-P_{22}$  against  $P_{12}$  at constant shear  $\gamma$  is found to give, to a first approximation, a single curve (Figs. 5 and 6), not depending separately on temperature and shear rate, which may therefore be assumed to have equivalent effects. (The systematic deviation of the 200°C points in Figure 5 is believed to be due to slight oxidation of the polyethylene in spite of the nitrogen atmosphere.) The W.L.F. reduction formula is normally applicable only up to about 100°C above the glass transition temperature, but according to West et al.<sup>11</sup> it is valid at least up to 200°C for linear polyethylene. In the present work it is used as a convenient method of combining results obtained at different temperatures without detailed enquiry into the extent of its applicability.

By this means a reduced curve for the initial shear modulus  $G_0$  has been plotted in Figure 7. There is a moderate amount of spread in the results, attributable to experimental difficulties, but the form of the curve is clearly similar to those obtained by Vinogradov and Belkin, with a plateau value of about  $9 \times 10^5$  dyn/cm<sup>2</sup>, and this shows evidence of a reduction with increasing temperature, though not to the same extent as noted by these authors.

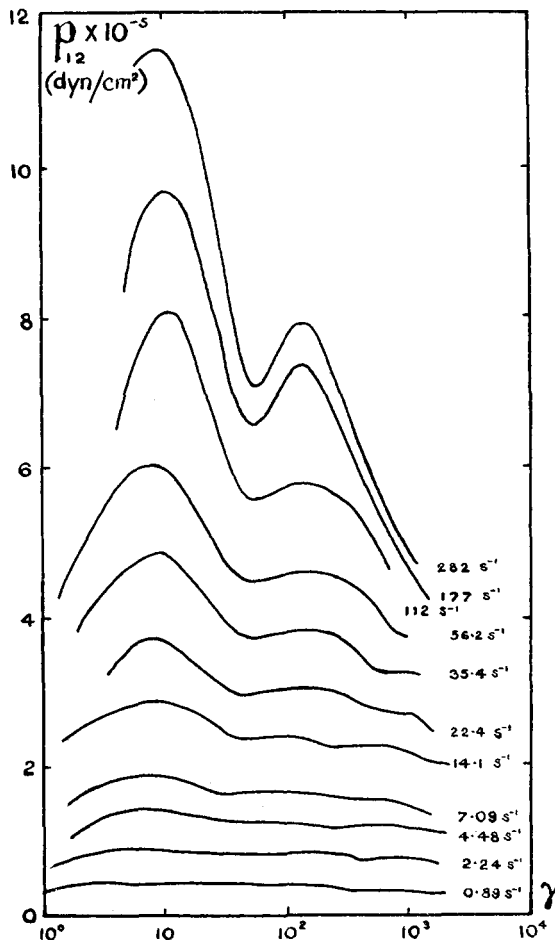


Fig. 3. Polymer C: platen temperature 135°C. Shear dependence of tangential stress.

As may be seen from Figures 5 and 6, where values of  $G$  have been plotted from the average curves relating the stress components, the stress increases with the modulus. Since rheological breakdown has been shown to depend mainly upon the stress and the applied shear, it is evident that modulus/shear rate curves at large shears will represent a series of different stages of rheological breakdown. Nevertheless, so long as the applied shear is con-

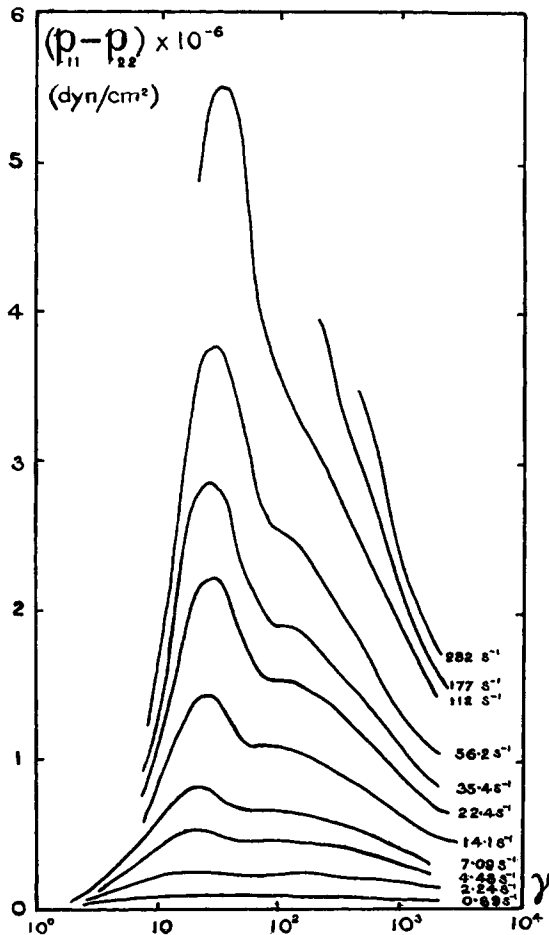


Fig. 4. Polymer *C*: platen temperature 135°C. Shear dependence of normal stress.

stant, superposition is still possible since the horizontal shift is essentially at constant  $G$  and therefore constant rheological breakdown.

Because of the comparatively rapid changes in stress at small applied shears, especially at high shear rates, the validity of eq. (3) in these regions is questionable since it assumes steady conditions, but at a shear of 50 these changes have slowed down sufficiently for this objection to be considered unimportant. The composite modulus/shear rate curves for the three polymers are shown in Figures 8–10 for shears of 50 and 300 in the case of *A* and *B*, and of 100 and 1000 for polymer *C*. The same W.L.F. constants were used at different stages of shearing.

#### Effect of Amount of Shear

At a shear of 50 polymer *A* shows a plateau value of  $8 \times 10^4$  dyn/cm<sup>2</sup> which is an order of magnitude lower than the plateau value of  $G_0$ . This is

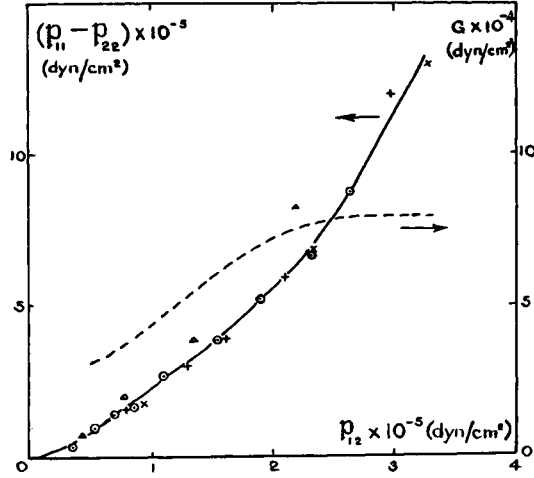


Fig. 5. Polymer A. Dependence of normal stress and shear modulus on tangential stress at constant applied shear. (X), 156°C; (+), 165°C; (o), 180°C; ( $\Delta$ ) 200°C.

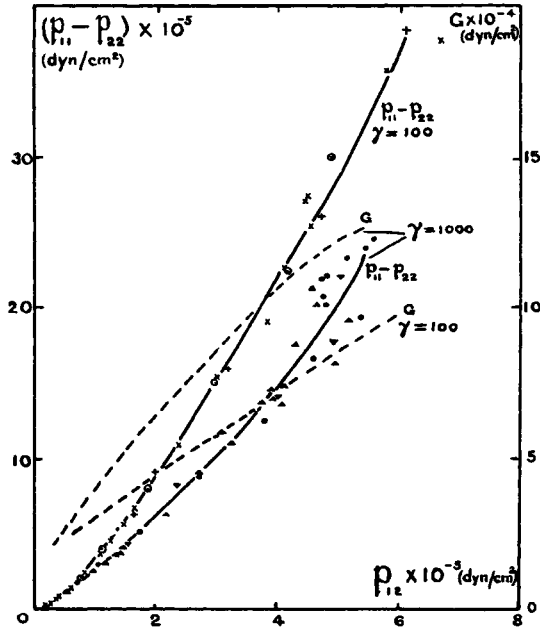


Fig. 6. Polymer C. Dependence of normal stress and shear modulus on tangential stress at constant applied shear. (Points refer to normal stress.)

$\gamma = 10^2$	$\gamma = 10^3$	platen temp.
+	$\blacktriangledown$	120°C
x	$\blacktriangle$	135°
o	$\bullet$	150°

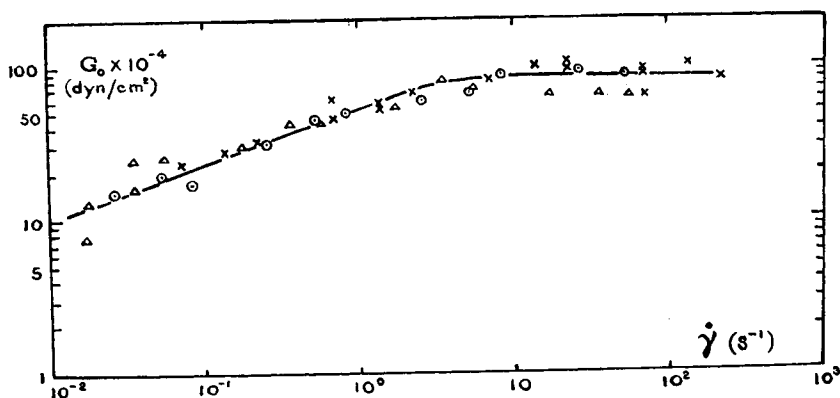


Fig. 7. Polymer A. Reduced initial shear modulus/shear rate relationship: reference temperature 200°C. (X), 156°C; (O), 180°C; ( $\Delta$ ), 200°C.

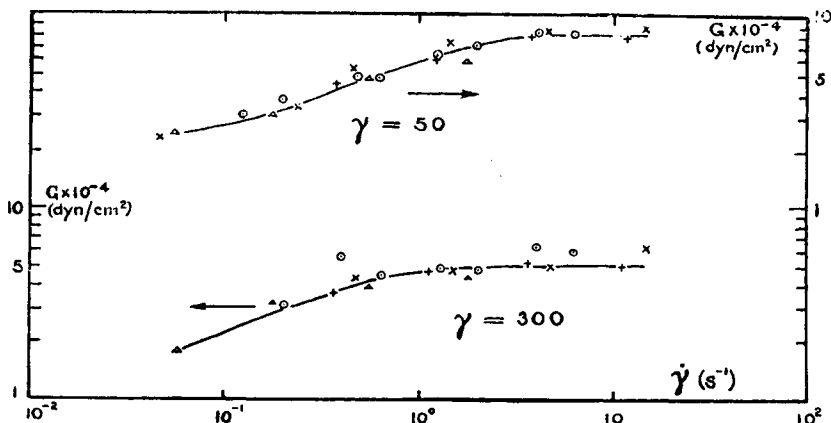


Fig. 8. Polymer A. Reduced shear modulus/shear rate relationship at shears of 50 and 300: reference temperature 200°C. (X), 156°C; (+), 165°C; (O), 180°C; ( $\Delta$ ), 200°C.

in good agreement with the values found by Dexter et al.<sup>12</sup> by a birefringence method, and by Bagley<sup>13</sup> from capillary end corrections. There is no longer any clear indication that the equilibrium modulus changes with temperature. Polymer B gives a similar curve. Polymer C on the other hand shows no definite signs of  $G$ , at the lower shear, reaching a plateau even at the highest shear rates at which measurements were possible.

At the higher shear of 300 there appears to be some fall in the plateau modulus of polymer A and, to a less extent, of polymer B, but there is an increase in the scatter as would be expected in view of the tendency for melt to leave the test space before this shear is reached. If loss of sample can be regarded as a uniform reduction in its effective radius this would have to drop by 0.14 cm to explain the fall in plateau level of polyethylene A. Although the quantity of sample lost was small, recession of the free surface



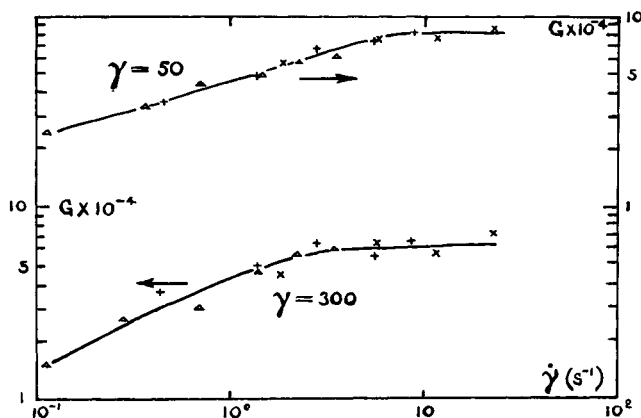


Fig. 9. Polymer B. Reduced shear modulus/shear rate relationship at shears of 50 and 300: reference temperature 200°C. (x), 151°C; (+), 180°C; ( $\Delta$ ), 210°C.

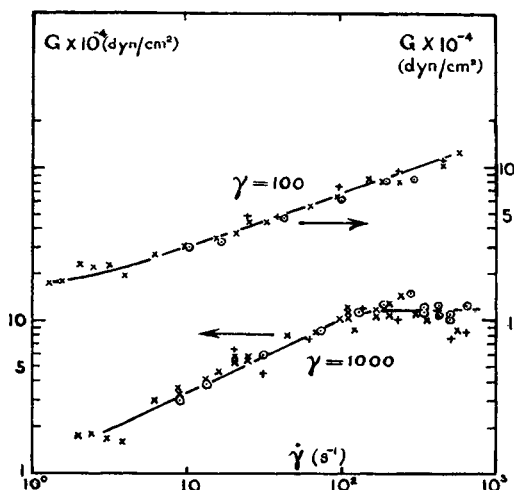


Fig. 10. Polymer C. Reduced shear modulus/shear rate relationship at shears of 100 and 1000: reference temperature 200°C: (+), 120°C; (x), 135°C; ( $\odot$ ), 150°C.

in the region of the middle shear plane could possibly account for this. Accordingly no great significance can be attached to the apparent fall in equilibrium modulus.

Isothermal boundary conditions are likely to have been approximated at the low shear rates applied to polymers A and B, in which case the temperature rise would be negligible. At intermediate shear rates with polymer C significant temperature gradients could develop in the melt, but would probably become pronounced only at fairly high shears. Shearing would then cease to be uniform and results would become difficult to interpret. No doubt this contributed to the greater scatter of points about the curve for a shear of 1000 in Figure 10. At the highest shear rates used with poly-

mer  $C$  adiabatic conditions would have been approached. In these circumstances the temperature rise at a shear  $\gamma$  is

$$\Delta T = \frac{\bar{P}_{12}\gamma}{J\rho c} \quad (4)$$

where  $P_{12}$  is the mean value of  $P_{12}$  up to this shear,  $J$  is the mechanical equivalent of heat,  $\rho$  the polymer density and  $c$  its specific heat. This can be quite high (e.g., 30°C at a shear of 1000 for polyethylene  $C$  at a nominal temperature of 120°C and shear rate of 178 s<sup>-1</sup>). While one can allow for this temperature rise in reducing the results to a standard temperature (and this has been done in Fig. 10), it is much more difficult to allow for the changed rheological breakdown attributable to the varying temperature. Nevertheless, if it could be shown that the modulus in the plateau region, after taking account of the calculated temperature rise in the reduction operation, was materially different at high, as compared with low shears, it would provide useful evidence concerning the nature of rheological breakdown. Unfortunately, as we have seen, polymer  $C$  gave no indication of a plateau at low shears. This may have been because, for reasons already discussed, there was a limit to the shear rates at which reliable determinations of  $G$  could be made at low shears. At a shear of 1000, however, there appeared to be a plateau at about  $1.3 \times 10^5$  dyn/cm<sup>2</sup> for shear rates above 100 s<sup>-1</sup> at 200°C. At an intermediate shear of 300 there also seemed to be a plateau at about the same level, but not until shear rates exceeded 300 s<sup>-1</sup> at about 200°C.

### Conclusions

It may be questioned whether eq. (3) gives a correct value of the modulus, since it depends upon the assumption that the principal axes of stress and of recoverable strain are parallel. An alternative form of eq. (3) is

$$\gamma_R = (P_{11} - P_{22})/P_{12} \quad (3a)$$

where  $\gamma_R$  is the recoverable shear. It has previously been pointed out<sup>1</sup> that the experimentally determined value of shear recovery following shearing of a polymer melt cannot be expected to be as great as  $\gamma_R$  because stress relaxation occurs during recovery. Lodge's theory gives the ultimate recovery (constrained to a simple shear) as  $(P_{11} - P_{22})/2P_{12}$  and experimental determinations usually lie between this quantity and  $\gamma_R$  as given by eq. (3a).<sup>1,3,12,14</sup> It follows that the value of  $G$  given by eq. (3), even if not exact, is unlikely to be in error by a factor greater than 2.

The reduction in modulus, observed for polymer  $A$ , from about  $9 \times 10^5$  dyn/cm<sup>2</sup> at the initiation of shearing to a tenth of this value at a shear of 50 must therefore be regarded as a real effect, evidently reflecting a substantial decrease in the concentration of crosslinks, formed by secondary valency forces or entanglements. This confirms the view of Pollett<sup>15</sup> and other authors<sup>9,16</sup> that disruption of a network structure occurs.

The comparatively small drop in the plateau value of  $G$  for polymers  $A$  and  $B$  as the shear increased from 50 to 300 could be due to a further reduction in the number of cross-links operative at any instant, but the possibility that it is due to a small reduction in the effective sample radius cannot be excluded. In the case of polymer  $C$  the appearance of a plateau at high shears must be regarded with even greater suspicion, not only because it is impossible to see whether the melt is being uniformly sheared at rates of the order of  $100 \text{ s}^{-1}$ , but also because of the improbable reduction in the shear rate at which the plateau commences as the applied shear increases.

Over a considerable range of shear rates the modulus lies in the terminal zone, and it is then inappropriate to apply eq. (1) without further justification. The terminal zone is usually attributed to the occurrence of flow i.e. sliding of the molecules past one another. This is reasonable when applied to the initial modulus  $G_0$  obtained by the method of Vinogradov and Belkin. Equation (3a) on the other hand relates the stress components to the recoverable strain, regardless of any flow as such, which should therefore be no more relevant to eq. (3). Some additional explanation of the shear rate dependence of  $G$  at low rates is consequently needed. A possible interpretation is that as the available time in which entanglements can dissipate is increased, fewer of them act as effective crosslinks. This means that there is more slip and in this sense the terminal zone is still attributable to flow. If this explanation is correct, the modulus values in the terminal zone correspond to statistical thermodynamic equilibrium of the chain configurations, and the applicability of the theories of Lodge and Kaye is not affected. In that case it is difficult to see how the hypothesis that rheological breakdown is due to molecular disentanglement can be reconciled with the observed increase in  $G$  with applied shear unless Kaye's model is seriously at fault. If on the other hand, some alternative explanation of the terminal zone proves to be correct, it is possible that the increase in  $G$  with shear is a consequence of observed values not being plateau values. The present work cannot be regarded as providing very definite evidence that the plateau level falls during the later stages of shearing, but there seems little doubt that it does so in the early stages of shearing, and that this is due to rupture of the network initially present.

Conflicting views as to whether Hooke's law is obeyed in shear by polymer melts is seen to have a simple explanation. Experimenters working at comparatively low shear stresses<sup>1,14</sup> have obtained a variable shear modulus because their data corresponded to the terminal zone. Others,<sup>12,13</sup> working at higher shear stresses have obtained a constant modulus because it lay in the plateau region.

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