Loss Moduli Under Steady Shearing of Concentrated Polystyrene Solutions

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ABSTRACT: Loss moduli were determined for concentrated solutions of (nearly) monodisperse polystyrene under steady shearing in the non-Newtonian regime. Whereas unentangled normal modes of chain motion were unaffected by shearing, the relaxation times of the entangled normal modes were shifted toward their unentangled values predicted by the Rouse theory. This result offers good evidence that disentanglement explains the non-Newtonian behavior of the polymer solutions studied in this research.

Polymer melts and solutions above their critical molecular weights for chain entanglement demonstrate dramatic decrease in viscosity with increasing shear rate. Although this striking non-Newtonian behavior is most often attributed to disentanglement of the chain-like molecules with increasing shear rate,[1,2] other explanations have been proposed.[3–9] There is, however, an experimental scheme which will establish whether or not the most important contribution to the non-Newtonian behavior of entangled polymer systems is indeed chain disentanglement. That scheme is to measure small-amplitude dynamic behavior of polymer fluids superimposed upon steady shearing.[10,11]

The complex dynamic modulus, $G^* = G' + iG''$, can be interpreted in terms of the various structural features of the polymer solution or melt in terms of the Rouse theory[12] and its extensions to entangled systems.[13–15] For example, in the transition zone, where $G' = G''$ and log–log plots of both moduli *vs.* angular frequency ω have slopes of $^1/_2$, G^* is a function only of temperature, local mobility of the repeat units (monomeric friction factor), molecular weight of a repeat unit, and the ratio of the mean-square end-to-end distance to molecular weight of an assembly of the unperturbed polymer molecules. It is not a function of degree of entanglement. Indeed it has been established that behavior in the transition zone is due to response of unentangled normal modes of chain motion. We should add that it is, however, true that the distribution of chain dimensions of an assembly of polymer molecules changes with increasing shear rate. It can nevertheless be shown that such coil distortion has no effect on the results of the Rouse theory or its extensions.[16] Indeed a major criticism of the Rouse model is that it predicts that there should be no affect of shear rate (and concomitant coil distortion) on steady-flow viscosity or any of the relaxation times.[17] It follows, therefore, that if the Rouse model is an adequate description of the behavior of an assembly of flexible polymer molecules, and if disentanglement is the primary cause of non-Newtonian flow, the transition region should be independent of shear rate even well into the non-Newtonian regime.

In the rubbery and terminal zones, however, G^* is greatly influenced by the presence of entanglements.[13–15] It has been established that chain entanglements extend the longest several relaxation times to even longer times.[13,14,18] Phenomenological considerations alone indicate that superimposing steady shearing in the non-Newtonian regime upon dynamic measurements would shift the terminal region to higher frequencies.[11] In the superposition of the two types of straining, the dynamic behavior is determined by measuring $\Delta\tau$ and $\Delta\dot{\gamma}$, the deviations of shear stress and shear rate from their steady-flow values. Since the loss modulus in the terminal zone is defined by the limit of the relationship

$$G'' = \omega(\Delta\tau/\Delta\dot{\gamma})$$

as ω, $\Delta\tau$, and $\Delta\dot{\gamma}$ all approach zero, one can write $G'' = \eta_c\omega$, where η_c is the consistency of the polymer fluid (slope of the stress–shear rate curve). It has been observed that for concentrated polymer solutions and polymer melts η_c decreases with increasing shear rate. Indeed, this behavior in the terminal zone has been observed experimentally,[19–22] but since it would be the expected result regardless of the mechanism of non-Newtonian flow, superposition of dynamic and steady-flow shearing offers no information about flow mechanisms unless they are carried out well into the transition region. No such experiments have been reported.

We have thus designed and constructed an instrument for superimposing dynamic and steady-flow measurements and examined concentrated polystyrene solutions to frequencies of about 1 decade into the transition zone.

Experimental Section

The instrument used in this research was a dynamic viscometer driven by a torsional pendulum. Details of construction and the analysis of its operation have been reported before.[14,23] Minor modifications were made to extend its frequency range and decrease instrument damping. We used a cone-and-plate geometry

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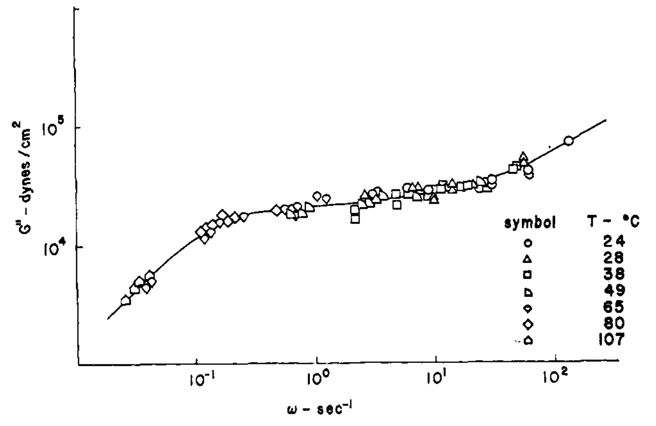

Figure 1. Master curve of G'' *vs.* ω at 25° for solution of 0.40 volume fraction polymer.

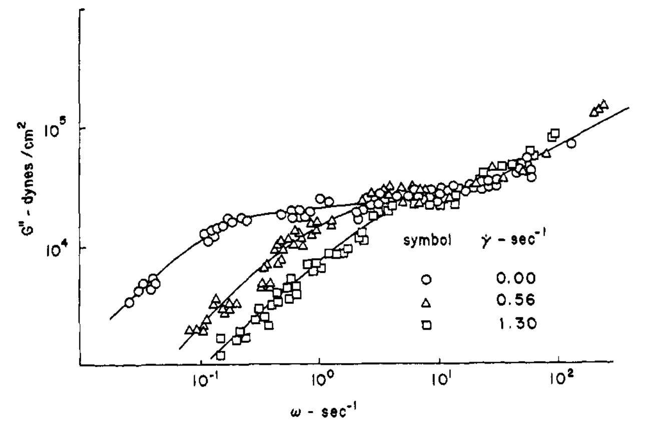

Figure 2. Master curves of G'' *vs.* ω at 25° for solution of 0.40 volume fraction polymer at various superimposed shear rates.

with the pendulum driving the cone. The plate was rotated through a variable-speed gear system by a synchronous motor and positioned vertically with a micrometer. The cone and plate were enclosed by a brass sleeve and kept in a nitrogen atmosphere. Temperatures above ambient were controlled by heating the sleeve with an electrical heating tape, and below ambient by cooling the nitrogen before it entered the sleeve.

The polystyrene was bought from Pressure Chemical Co. and had a weight-average molecular weight of 4.98×10^5. The polymer had a weight-average to number-average molecular weight ratio of 1.20. Selection of solvent, di-2-ethylhexyl phthalate, and preparation of the solutions were discussed previously.[14] Dynamic loss moduli were determined for frequencies from 6 to 120 radians/sec over a temperature range from 10 to 120°, and time-temperature superposition was used to obtain master curves at 25°.

Since the effect of steady shearing on the transition region was of prime importance, concentrations were used that placed the transition zone within the experimental frequency range of the instrument near 25°.

Results and Discussion

Figure 1 gives the master curve of G'' *vs.* ω reduced to 25° for the solution with 0.40 volume fraction of polymer without the superposition of steady shearing. Similar master curves for the same solution with superimposed steady shearing are shown in Figure 2, and the shift factors are shown in Figure 3. Only the master curves are reported for the solution with 0.60 volume fraction of polymer, and they are given in Figure 4.

We conclude that, to within experimental error of about $\pm 10\%$, transition behavior is independent of shear rate up to about 1.3 sec^{-1}, which is well within the non-Newtonian regime. Although the results of the experiments indicated that viscosities of both solutions are decreasing rapidly with increasing shear rate, we found that they could not be found with any confidence from the apparent terminal zones illustrated in Figures 2 and 4. Indeed we found, as before,[14] that time-temperature superposition for systems with rubbery plateaus that extend over a decade or more in frequency are totally unreliable. Consequently, we view the terminal zones in Figures 2 and 4 as being only of qualitative significance, but nevertheless of sufficient accuracy to establish that the measurements were made in the non-Newtonian regime.

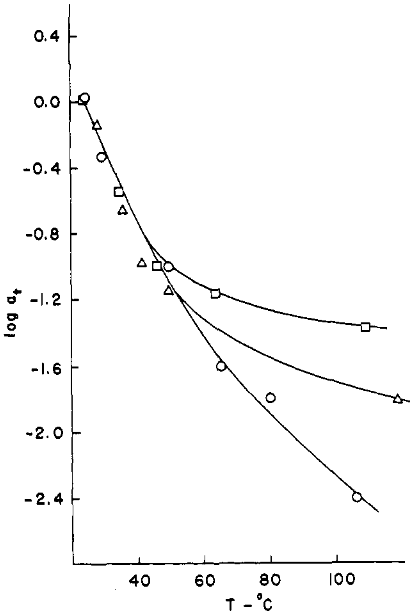

Figure 3. Shift factors for solutions of 0.40 volume fraction polymer at various superimposed shear rates.

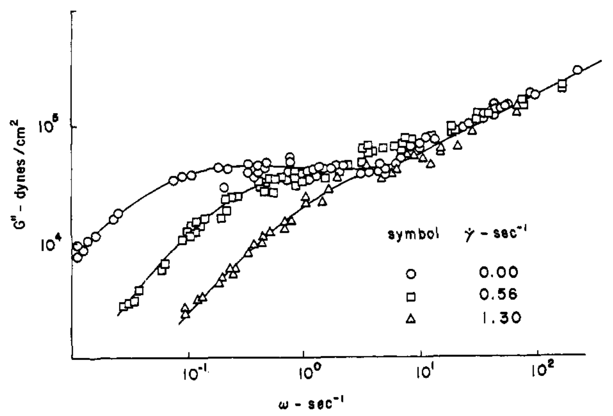

Figure 4. Master curves of G'' *vs.* ω at 25° for solutions of 0.60 volume fraction polymer at various superimposed shear rates.

For the solutions and shear-rate range considered in this research, we found that whereas the unentangled normal modes of chain motion were unaffected by steady shearing, the relaxation times of the entangled normal modes were shifted toward their unentangled values predicted by the Rouse theory. This result offers good evidence that the non-Newtonian behavior of these solutions is fully explained by disentanglement of polymer chains.

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