Polymer solutions and melts which are polydisperse with respect to molecular weight behave differently in various ways than monodisperse ones under conditions of unidirectional longitudinal flow. Inasmuch as polydispersions are mixtures of monodisperse fractions, each of a different molecular weight, the differences in the mechanical properties are due to causes which ought to be sought in the dependence of the mechanical properties of monodisperse polymers on their molecular weight. When monodisperse polymers are deformed longitudinally at a constant rate until a certain stress level \( \sigma_{cr} \) has been reached, it is possible that a condition of steady longitudinal flow will be reached with both the axial tension and the axial strain rate remaining constant in time. When the stress exceeds \( \sigma_{cr} \), the material responds to uniaxial tension as one of high elasticity, i.e., loses its ability to flow [1-4]. The magnitude of \( \sigma_{cr} \) is somewhat above \( 10^5 \) dyne/cm\(^2\) and is almost independent of the molecular weight of the monodisperse polymer, depending only on the macromolecular structure. The flow of melts of monodisperse polymers is characterized by a constant longitudinal viscosity until rupture occurs. In the case of polydisperse polymers, on the other hand, the longitudinal viscosity has been found to increase with the strain rate [5, 6].

For polymers with a narrow molecular weight spectrum, the trend of the stress-strain curves at constant strain rates resembles that of creep attenuation curves. The stress-strain curves for materials with a wide molecular weight spectrum, such as low-density polyethylene [7, 8] and polypropylene [9], follow a similar trend at low longitudinal strain rates. After polymers with either a narrow or wide molecular weight spectrum have been elongated for some time, anomalies in their stress-strain relations appear. In the first case the stress increment increases sharply, indicating that the melt has hardened. No such kinks appear on the stress-strain curves for monodisperse specimens. This anomaly can be hypothetically regarded as being a result of relaxation transitions concurrent with an increasing orientation of macromolecules.

It is expedient to use the process of linear periodic deformation for studying relaxation processes. It has been proposed earlier [10] that elastic and viscous properties of an extensible fluid be evaluated on the basis of the viscoelastic characteristics of the given material, these characteristics being measurable directly during the elongation process, and that linear periodic longitudinal deformation be superposed on the longitudinal flow for this purpose.

This method yields estimates of the elasticity and the viscosity of a material within a single test, while previous methods of separating reversible strains from irreversible ones on the basis of measurements of the elastic recoil after unloading of the specimen requires several tests to be performed on various different specimens [5, 11-13].

It has also been shown in an earlier study [14] that the total resistance of certain liquid polymers to elongation can be determined from their characteristics of linear viscoelasticity, these characteristics having been measured under conditions of linear periodic shearing.

For the purpose of describing the linear periodic deformation superposed on nonsteady longitudinal elongation at a constant strain rate, the one-element Maxwell model was extended [10] to the case of finite strains and written in terms of contravariant components of the stress deviator:
\[ \sigma^{ij} + \tau \frac{D\sigma^{ij}}{Dt} = 2\eta \varepsilon^{ij}, \]  

(1) 

where \( \tau \) denotes the relaxation time, \( \eta \) denotes the viscosity, and the components \( \varepsilon^{ij} \) of the strain rate tensor are defined according to the relation

\[ \varepsilon^{ij} = \frac{1}{2} \left( \frac{\partial u_i}{\partial x_k} g^{kj} + \frac{\partial u_j}{\partial x_k} g^{ik} \right) \]

(\( g^{ik} \) being the components of the inverse metric tensor).

The derivative of the stress is [15]

\[ \frac{D\sigma^{ij}}{Dt} = \frac{\partial \sigma^{ij}}{\partial t} - \frac{\partial \sigma^{ik}}{\partial x_k} g^{jk} - \frac{\partial \sigma^{jk}}{\partial x_k} g^{ik}. \]

The problem of uniaxial elongation is solved for the case where the axial velocity \( v_Z \) in a system of \( R, \phi, Z \) coordinates is not a function of the \( R \) coordinate and the radial velocity \( v_R \) is uniform along the specimen, i.e., not a function of the \( Z \) coordinate. Under these conditions we have

\[ \frac{\partial \sigma_z}{\partial Z} = \dot{\varepsilon} + \varepsilon_0 \cos \omega t; \quad \frac{\partial \sigma_R}{\partial R} = \frac{-\dot{\varepsilon} + \varepsilon_0 \cos \omega t}{2}, \]

where \( \dot{\varepsilon} \) is the rate of steady axial strain, \( \varepsilon_0 \) is the amplitude of periodic strain, and \( \omega \) is the angular frequency of periodic strain.

In this study we use the term "steady flow" to denote longitudinal flow at a constant strain rate, regardless of whether or not the stress remains constant. The flow is defined as steady after the stress has become constant and independent of the strain.

The solution of Eq. (1) for unidirectional flow at a strain rate \( \dot{\varepsilon} + \varepsilon_0 \cos \omega t \) is given in [10]. Solutions extended to continuous distributions of the relaxation frequency lead to the following expressions for the components \( E' \) and \( E'' \) of the longitudinal complex modulus of elasticity:

\[ E' = \varepsilon_0 \int_0^\infty \left[ \frac{2}{(s - 2\dot{\varepsilon})^2 + \omega^2} + \frac{\omega^2 + \dot{\varepsilon} (s + \dot{\varepsilon})}{(s + \dot{\varepsilon})^2 + \omega^2} + \right. \]

\[ \left. + 4\dot{\varepsilon} \frac{1 - e^{-(s - 2\dot{\varepsilon})t}}{s - 2\dot{\varepsilon}} + \frac{1 - e^{-(s + \dot{\varepsilon})t}}{s + \dot{\varepsilon}} \right] N(s) ds; \]

(2)

\[ E'' = \varepsilon_0 \int_0^\infty \left[ \frac{2}{(s - 2\dot{\varepsilon})^2 + \omega^2} + \frac{1}{(s + \dot{\varepsilon})^2 + \omega^2} - \right. \]

\[ \left. \frac{1}{s + \dot{\varepsilon}} \right] N(s) ds; \]

(3)

where \( N(s) \) represents the relaxation frequency spectrum and \( s \) is the relaxation frequency.

According to expressions (2) and (3), component \( E' \) of the modulus is a function of and component \( E'' \) is independent of the duration of the deformation process, i.e., of the total elongation. Both components depend on the angular frequency of periodic deformation and on the velocity of steady longitudinal flow.

Calculations according to expressions (2) and (3) have been compared with test results for grade P-20 polyisobutylene. Those tests were performed on cylindrical specimens with a gage length \( L_0 = 10 \) cm and an initial diameter \( D_0 = 0.38 \) cm. In order to produce specimens of length \( L_0 \) and diameter \( D_0 \), a volume \( v = \pi D_0^2 L_0 / 4 \) of raw material was placed between two plates of acrylic glass, together with three calibrated identical balls of diameter \( d \) which would ensure the correct diameter of those specimens as well as plane-parallelism of the plates. The upper plate was then rolled relative to the lower plate by reciprocating action. In the process a specimen was shaped to its proper initial diameter. The rolling was continued until stresses produced in a specimen by this forming operation began to relax. A finished specimen had a smooth surface and a uniform diameter throughout its length.