Dielectric and mechanical relaxation times of a polymer using intermolecular forces

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Expressions are derived for the dielectric and mechanical base relaxation times of a polymer above its glass transition temperature. Coupled oscillator theory is invoked to show that a low-frequency dielectric relaxation should have a relaxation time proportional to the degree of polymerization, N. A damped linear array is used to calculate the base mechanical relaxation time, τ_p. The principles of intermolecular forces and dielectric energy dissipation are taken from previous work of the author in order to model the frictional drag and elastic constants required by the equation of motion of the damped linear array. The relaxation time τ_p is shown to be proportional to $N^{3.33}$. Finally, τ_p is used to develop the relation between zero-shear viscosity and molecular weight for a polymer melt, with polystyrene used as an example.

(Keywords: relaxation time; viscosity; elastic modulus; intermolecular forces; dielectrics; entanglement)

INTRODUCTION

A series of recent papers[1-3] have proposed two fundamental mechanisms that can be used to explain and predict the viscoelastic properties of a polymer. The first proposal is that all the physical properties of a polymer are a direct consequence of intermolecular forces between monomeric units or between polymer macromolecules, with particular emphasis upon the replacement of statistical concepts to explain the elastic modulus of a polymer above its T_g. The second proposal is that mechanical energy is dissipated dielectrically during the relative motion of polymer molecules.

The author has suggested[3] that the above two mechanisms could be applied to the equations of motion of the monomeric units within a damped lattice of a polymer macromolecule. This suggestion will be developed in this paper, but first a more advanced model for the dielectric relaxation times of a polymer at high temperatures and low frequencies must be found in order to apply the dielectric dissipation hypothesis.

DIELECTRIC RELAXATION TIME

A suggestion of Frölich has been developed[2] into a relation between the dielectric relaxation time, τ_m, of the monomer units in a polymer chain and the relaxation time of a free monomer unit, τ_0, in terms of the depth of the potential well of interaction between two monomer units, ϕ_0, a temperature characteristic of the backbone chemical bond, T_α, and Boltzmann's constant, k:

$$\tau_m = \tau_0 \exp\left(\frac{\phi_0}{k(T-T_\alpha)}\right) \qquad (1)$$

As more mer units are added to the backbone chain, it would seem appropriate to assume that the sum of these strong interactions down the length of the chain should follow the theories for coupled electrical oscillators[4]. Thus the base relaxation time, τ_N, of a chain of N units with $N \gg 1$ becomes:

$$\tau_N = (N\tau_m/\pi) \qquad (2)$$

Coupled oscillation theory indicates that the full dielectric power of each mer-unit dipole will only be visible at low frequencies, $\nu \simeq 1/\tau_N$, and that the monomeric peak of dielectric loss constant, ε'', should increase with decreased interaction energy coupling at higher temperatures above T_α. Both these trends are seen in the work of Ishida and coworkers[5] on the dielectric response of poly(acrylonitrile): *Figure 1* shows their data for ε'' at two temperatures for a molecular weight of 99 000. The broken curves are the predictions of equation (2) for the low-frequency relaxation relative to the observed values of τ_m. The peak height of the predicted curves uses the full dipole moment of acrylonitrile (1.3×10^{-29} C m) in the Onsager equation for dielectric constants[6], which gives an expected peak height of $\varepsilon'' = 14$.

Low-frequency tails in ε'' at high temperatures, of the kind shown in *Figure 1*, have been observed consistently in these laboratories, but attempts to extend the lower-frequency range into a region around the peak at $1/\tau_N$ have so far been unsuccessful.

MECHANICAL RELAXATION

The distribution of mechanical relaxation times in a polymer above its glass transition temperature, T_g, can be derived from damped lattice theories, as discussed by Tobolsky[7]. The simplest of such theories is that of a damped linear array of N mer units in the x direction:

$$m\ddot{x} + f\dot{x} + C_m \Delta x = 0 \qquad (3)$$

where each mer unit has a mass, m, a frictional drag force per unit velocity, f, and a linear spring constant, C_m, between adjacent mer units that move by a distance, Δx, from their equilibrium position.

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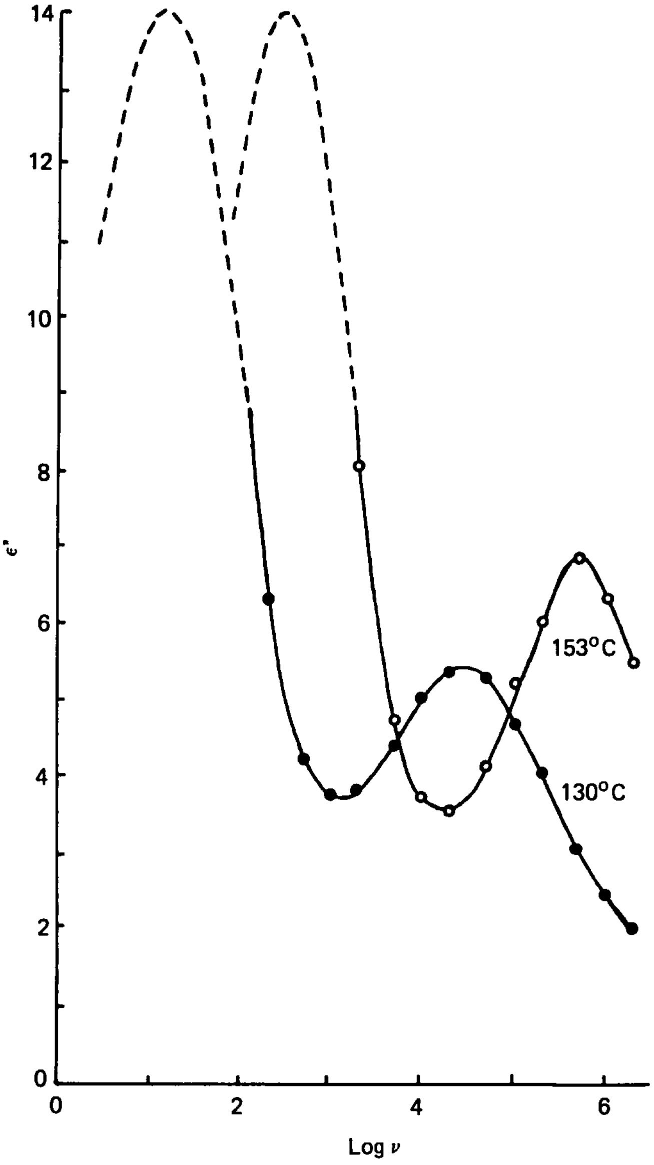

Figure 1 Dielectric loss constant, ε'', for poly(acrylonitrile) as a function of frequency, ν, at two temperatures, 130 and 153°C. Full curves and points are from the data of Ishida and coworkers[5]. Broken curves are predicted by equation (2)

The solution of equation (3) under non-inertial conditions gives a base relaxation time, τ_p:

$$\tau_p = \frac{f}{2\pi^2 C_m} N^2 \qquad (4)$$

The terms f and C_m for the monomer units must now be calculated.

Unit frictional drag

In a linear shear field, the author suggests an appropriate expression for the frictional drag force, f, between adjacent non-chemically bonded mer-units:

$$f = \eta_m (\pi/2) R_m \qquad (5)$$

Here, η_m is the intrinsic viscosity of each mer unit in its own environment and R_m is the radius of a mer unit.

By combining equations (5) and (2) with the viscosity expressions derived previously[1] in terms of the surface free energy of a polymer melt, S_p, and the static and high-frequency values of the dielectric constant, ε_s and ε_i, respectively, we obtain:

$$f = \frac{\pi}{2} S_p \frac{\varepsilon_s - \varepsilon_i}{(\varepsilon_s \varepsilon_i)^{1/2}} \tau_m N \qquad (6)$$

Spring constant

An expression can be derived[3] for the spring constant, C_p, of a macromolecule in terms of its radius, R_p, and the energy of interaction between two macromolecules, ϕ:

$$C_p = \partial^2 \phi / \partial R_p^2 \qquad (7)$$

The tension in the macromolecular spring must be the product of this spring constant and the sum of all the monomeric unit deformations. For spherical macromolecules with a radius proportional to $N^{1/3}$ this gives:

$$C_m = C_p N^{1/3} \qquad (8)$$

Combining equations (7) and (8) and using a Lennard-Jones potential function for ϕ in terms of R_p, the radius at absolute zero of temperature, R_0, and the depth of the interaction potential well, ϕ_0, we obtain:

$$C_m = \frac{12\phi_0}{N^{1/3} R_m^2} \left[7\left(\frac{R_0}{R_p}\right)^6 - 13\left(\frac{R_0}{R_p}\right)^{12} \right] \qquad (9)$$

Base relaxation time, τ_p

Equations (6) and (9) can be substituted into equation (4) to yield an expression for τ_p, which shows a dependence of τ_p upon N to the power 3.33.

Typical values of the equation parameters are illustrated by the example[1-3] of polystyrene at $T = 490$ K: $S_p = 0.024\ \mathrm{J\,m^{-2}}$, $\phi_0 = 1.75 \times 10^{-20}$ J, $T_\alpha = 323$ K, $\tau_0 = 3.4 \times 10^{-11}$ s, $R_m = 3.1 \times 10^{-10}$ m and $(\varepsilon_s - \varepsilon_i)/(\varepsilon_s \varepsilon_i)^{1/2} = 0.013$. These values give:

$$f = 3.5 \times 10^{-11} N$$
$$C_m = 1.1 N^{-1/3}$$
$$\tau_p = 1.6 \times 10^{-12} N^{3.33}$$

A general expression for τ_p in a polystyrene melt is in agreement with the empirical expression quoted previously[3] from stress–relaxation modulus experiments:

$$\tau_p \approx 10^{-15} N^{3.33} \exp\left(\frac{1236}{T - T_\alpha}\right) \qquad (10)$$

Equation (10) uses the parameter values for a typical melt temperature of 490 K given above, and assumes that the main temperature dependence comes from the exponential term in τ_m, given in equation (1).

VISCOSITY

The deformation of a polymer macromolecule under shear must be dominated by the relative magnitude of the frictional drag forces and the elastic reaction forces on each mer unit of the damped lattice.

Equations (6) and (9) show that frictional drag increases and elastic reaction decreases with increasing value of N. Let a value N_c be defined as a value of N below

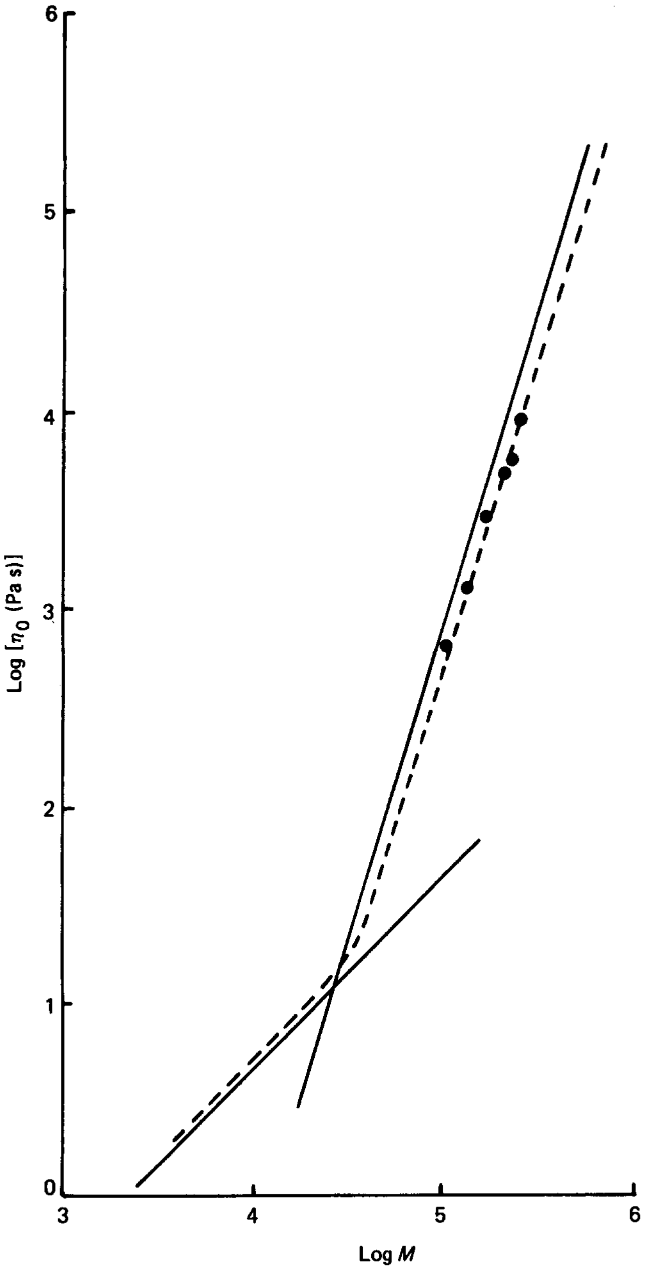

Figure 2 Viscosity, η_0, as a function of molecular weight, *M* for polystyrene at $T = 490$ K. Full lines are predicted by equations (12) and (14). Broken lines are from experimental data of Fox and coworkers[8]. Points are experimental reference points generated internally

which polymer macromolecules remain as undistorted spheres under shear, and above which the spheres are increasingly distorted to the shape of a prolate ellipsoid[1]. The non-inertial damped lattice model of this report can be applied only for $N > N_c$. Below N_c, each macromolecule must be considered as a discrete unit, and the viscosity equations for a simple fluid must be applied[1]:

$$\eta = \frac{S_p}{R_m}\frac{\varepsilon_s - \varepsilon_i}{(\varepsilon_s \varepsilon_i)^{1/2}}\tau_m N \tag{11}$$

For example, polystyrene at $T = 490$ K and below N_c gives:

$$\eta = 0.05N \tag{12}$$

Above N_c, the zero-shear viscosity, η_0, is related to the plateau modulus, G_0:

$$\eta_0 = G_0 \tau_p \tag{13}$$

Using polystyrene at 490 K again, with a value for the plateau modulus of $G_0 = 10^5\ \mathrm{N\ m^{-2}}$, we obtain:

$$\eta_0 = 1.5 \times 10^{-7} N^{3.33} \tag{14}$$

Equations (12) and (14) are plotted in *Figure 2* as zero-shear viscosity as a function of molecular weight for polystyrene at $T = 490$ K. The data of Fox and coworkers[8] are plotted as broken lines, and some experimental data points for a polystyrene of narrow molecular-weight distribution, generated within Dow Chemical, have been included for reference. Agreement between prediction and experiment is seen to be good.

The value of η_0 from equation (13) can now be used to predict the shear-dependent viscosity, η, at a shear rate $\dot{\gamma}$ for spherical macromolecules being deformed from a radius R_p to a prolate ellipsoid form with a long-axis radius of R_e (ref. 1), which was derived previously using empirical data for macromolecular interactions:

$$\eta = \eta_0 (R_p/R_e)^3 \tag{15}$$

and

$$\eta\dot{\gamma} = G_0[(R_e/R_p) - 1] \tag{16}$$

Applying equations (13) and (15) to equation (16), we obtain:

$$\tau_p \dot{\gamma} = \left(\frac{R_e}{R_p}\right)^3 \left(\frac{R_e}{R_p} - 1\right) \tag{17}$$

which can be used with equation (15) to predict η.

DISCUSSION

The damped linear array of this report should, perhaps, be replaced by a more general three-dimensional Debye lattice. However, the success of this simple model may be due to the physical model of a collapsed coil chain, of length proportional to N, being confined within a sphere of radius proportional to $N^{1/3}$. Thus, the direction x used in the equation of motion would always be parallel to the chain backbone, and the deformation in x would, in fact, be shear deformations of adjacent chains within a macromolecule.

The simplistic physical model given above reflects the conviction of the author that the entanglement hypothesis need not be invoked to explain the change in gradient of the viscosity curve, seen in *Figure 2*. Thus, the N_c of this model, which is due to a deformation of discrete macromolecules, can replace the entanglement molecular weight, M_c (ref. 9).

The next step in this work is to show that the deformation of discrete polymer macromolecules can predict the plateau value of elastic modulus, G_0, of a polymer above its T_g as a function of both molecular weight and rate of deformation. This will involve a balance between the reduced degree of interaction between macromolecules in their direction of extension and increased interaction normal to this direction, the balance being both molecular-weight and deformation-rate dependent.

CONCLUSIONS

Coupled electrical oscillator theory indicates that a low-frequency dielectric relaxation process can be expected in a polymer, with a relaxation time proportional to the degree of polymerization, N.

The N constituent mer units of a polymer macromolecule have been modelled as a damped linear array in order to calculate their base mechanical relaxation time, τ_p. The frictional drag factor of the equation of motion of a mer unit can be calculated from the principle of dielectric energy dissipation, and the elastic term by application of intermolecular force theory. For $N \gg 1, \tau_p$ is proportional to $N^{3.33}$, and the application of expressions for τ_p to calculate polymer melt viscosity are in good agreement with experimental data for polystyrene.

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