The Present-Day Aspects of the Structural Approach to the Theory of Viscoelasticity of Linear Polymers

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The general principles of the construction of a theory of the viscoelasticity of polymer melts, solutions and blends are considered from the standpoint of a structural approach. The main problems are outlined, the difference in the solution of which is responsible for numerous currently existing structural theories. Methods are discussed, by means of which it is possible to take into account the effect of topological restraints on the dynamics of macromolecules which are imposed by the polymer environment. The self-consistent concept of microviscoelasticity is considered in detail.

1. INTRODUCTION

The key problem in polymer rheology is the construction of a consistent theory of the viscoelasticity of concentrated solutions and melts of linear polymers on the basis of certain structural concepts that reflect the specificity of the structure of these systems.

The existing structural theories of the dynamic properties of polymers rely on the theory of the dynamic properties of a single polymer molecule. The relaxation properties of flexible-chain polymers are successfully described by means of the subchain model which was first proposed by Kargin and Slonimsky[1] and later developed by Rouse.[2]

The main difficulty encountered in constructing such a theory lies in the consideration of intermolecular interaction. The dynamic effect of intermolecular interaction can be described in an effective way. Indeed, in

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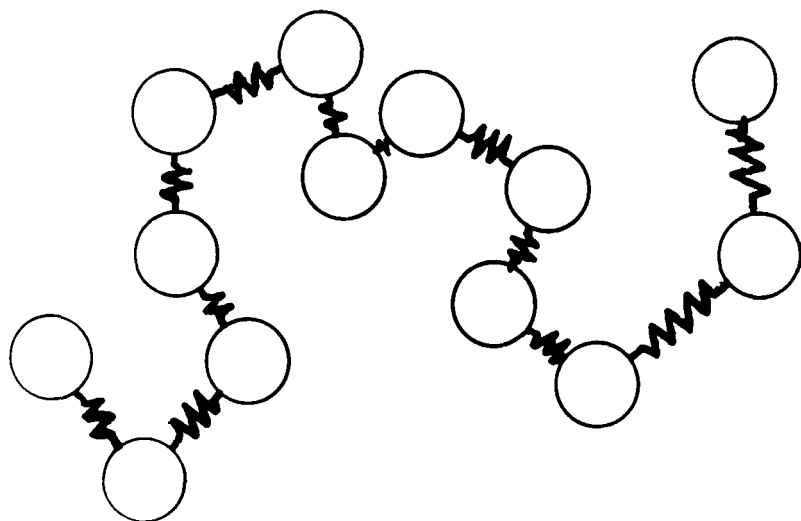
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FIGURE 1   The subchain model.

accordance with the concepts of the mechanics of constrained systems, one can pass over from the consideration of the motion of an assembly of coupled chains, of which a real polymer is composed, to the analysis of the motion of an equivalent system of free chains. In such an approach the equations of motion of individual macromolecules are set up with the dynamic effect of the surroundings being taken into account by introducing additional forces, whose action is equivalent to the action of a real environment. These forces are unknown and therefore additional assumptions are required for a more detailed determination of macromolecular motion. The above scheme of treatment is general for all the existing structural theories of the viscoelasticity of molten polymers and concentrated polymer solutions. The difference between the theories is in the manner in which the main problem in such a treatment — the modelling of the effect of the surroundings on macromolecular motion — is solved.

An attempt to take into account this effect in a simple manner, by introducing a viscous liquid instead of surrounding macromolecules, has proved successful only for polymers having moderate molecular masses. For high polymers the concept of a "purely viscous" environment which was first proposed by Kargin and Slonimsky[1] is found to be insufficient.

It was therefore necessary to refine the theory. An important stage in the subsequent development of the theory was the publication of the works by Bueche[3] and Ferry, Landel and Williams,[4] which laid the foundation for the so-called entanglement concept. According to the main assumption of this

concept, the interaction of macromolecules with their immediate surroundings is localized at isolated, rather sparsely spaced points—at points of entanglement with other macromolecules. It is assumed that the entanglement effect may be taken into consideration with the aid of an increased value of the friction factor at points of contact between the entangled macromolecules. The main result of the investigations carried out by these authors is that they explain the appearance of a plateau on the frequency dependence of the elastic modulus $G'(\omega)$, which is associated with the resolution of the relaxation spectrum of a high polymer into two groups of relaxation times differing strongly in magnitude. The predicted distribution of long relaxation times does not, however, correspond to the experimentally observed distribution. It has been shown[5,6] that this shortcoming cannot be eliminated through the possible variations of the friction factors of slow beads which reflect the nonequivalence of entanglements. Figure 2 shows the characteristic frequency dependences of the storage modulus, $G'(\omega)$, and the loss modulus, $G''(\omega)$, which are obtained in this case and which reflect the distribution of the relaxation times of the system. As can be seen, in the frequency region corresponding to the appearance of a plateau on the curve of G', where the distribution of high relaxation times is manifested, a wedge-type shift to the plateau region is observed in contrast to experiment.

It was found later that this is associated with the neglect of an important circumstance—the elastic effect of entanglements on the motion of the entangled polymer chain. The elastic forces operating at points where polymeric chains are entangled with surrounding molecules were first taken into account by Graessley.[7] This was done with the aid of a model, in which all large beads are bound with each other through the centre of gravity by elastic springs. The most consistent model in this respect has recently been advanced by Shen and his colleagues,[8,9] who introduced additional extra elastic constraints between various pairs of slow beads.
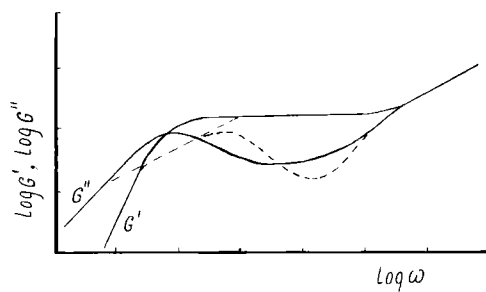

FIGURE 2   A comparison of the characteristic frequency dependences of the components of the dynamic modulus calculated for the model of nonequivalent entanglements (the dashed line) with experiment (the full line).

Despite the attractiveness of the entanglement concept, which takes account of the polymeric nature of the medium surrounding the macromolecule, the key proposition of this concept concerning the localized character of the dynamic interaction of the polymer macromolecule with its surroundings is far from obvious. Attempts have therefore been made lately to build up a theory by imposing kinematic restraints on the motion of macromolecules. Mention should first of all be made of the model of constraints in the form of a tube, which has been intensively developed in recent years,[10][13] This model, however, leads to a wider, wedge-type distribution of high relaxation times than that observed in experiments.[14]

2. THE CONCEPT OF MICROVISCOELASTICITY

The dynamic interaction of macromolecules with the polymer environment is described more consistently by the concept of microviscoelasticity.[15][18] Taking into account that single molecules exhibit relaxation properties, it is natural to presume that their environment, which is composed of macromolecules of the same species, also displays relaxation properties, i.e. is viscoelastic. In other words, it is assumed that the polymer macromolecule is moving among macromolecules of the same species as if in a certain viscoelastic liquid characterized by the nature of the polymer. According to the concept of microviscoelasticity, the fundamental equations for the dynamics of a single macromolecule may be written as follows:

$$\frac{\mathrm{d}}{\mathrm{d}t}\tau_i^\alpha = u_i^\alpha \tag{1}$$

$$m\frac{\mathrm{d}u_i^\alpha}{\mathrm{d}t} = -\int_0^\infty B^{\alpha\gamma}(s)(u_i^\gamma - v_{ij}\tau_j^\gamma)_{t-s}\,\mathrm{d}s - \int_0^\infty G^{\alpha\gamma}(s)(u_i^\gamma - \omega_{ij}\tau_j^\gamma)_{t-s}\,\mathrm{d}s - 2I\mu A^{\alpha\gamma}\tau_i^\gamma \\ + \Phi_i^\alpha(t), \quad \alpha = 0,\ldots,N$$

Here τ^α and $\mathbf{u}^\alpha$ are, respectively, the radius-vector and the velocity of the α-th particle of the chain which simulates the macromolecule (see Figure 1).

The first term on the right-hand side of the second equation in (1) describes the viscoelastic resistance experienced by the macromolecule moving in its polymer environment.

The second term represents the viscoelastic internal friction, i.e. the kinetic rigidity of the macromolecule caused by both the intramolecular and intermolecular interactions.

The third term describes the elastic force acting on the chain particles from the side of the nearest neighbours.

The Brownian motion of the macromolecule is taken into account with the aid of a Gaussian fluctuating force $\mathbf{\Phi}^\alpha$ with an averaged value equal to zero.

Thus, the problem of the viscoelasticity of molten polymers and concentrated polymer solutions reduces to the description of a non-Markovian stochastic process defined by a system of generalized Langevin equations.

The Langevin equations in the form indicated includes the inertial effects of the particles and the medium and the effects of viscoelasticity, hydrodynamic interactions, internal viscosity and long-range interactions.

The rheological (constitutive) equations of the systems considered are constructed directly from the equations of motion for single macromolecules without recourse to the differential equation for the distribution function usually employed in the traditional method. The state of the medium is characterized by the velocity of motion $\mathbf{v}(\mathbf{x}, t)$ and the densities $\rho(\mathbf{x}, t)$ of the volume elements, into which the assembly of particles of all the chains are split when the continuum approximation is used. They are defined in terms of the coordinates and the velocities of the particles in an ordinary way:

$$\rho(\mathbf{x}, t) = \left\langle \sum_{a,v} m\delta(\mathbf{x} - \tau^{\alpha v}(t)) \right\rangle,$$

$$\rho v_k(\mathbf{x}, t) = \left\langle \sum_{a,v} m u_k^{av}(t) \cdot \delta(\mathbf{x} - \tau^{\alpha v}(t)) \right\rangle \tag{2}$$

Here $\mathbf{x}$ is the radius-vector of the element which is considered to be a point in the continuum: a and v are, respectively, the numbers of macromolecules and particles in them. The angular brackets signify ensemble averaging of realizations of random forces acting on particles. The hydrodynamic equations and the stress tensor of the medium are determined by means of differentiation of Eq. (2) with respect to time with subsequent use of the equations of motion of the particles. With suitable detailing of the functions involved these equations are found to be applicable to polymer solutions, melts and blends. In the normal coordinates $\rho_i^v = R_{\beta v}\tau_i^v$, which diagonalize the force matrices contained in the equations for the dynamics of macromolecules, the stress tensor has the form

$$\sigma_{ik} = -p\delta_{ik} + nT \sum_{v=1}^{N} \left[2\mu\alpha_v \langle \rho_i^v(t)\rho_k^v(t) \rangle - \delta_{ik} \right.$$

$$= +\frac{1}{T} \int_0^\alpha \varphi_v(s)(\langle \rho_i^v(t)\dot{\rho}_k^v(t-s) \rangle - \omega_{ke}(t-s)\langle \rho_e^v(t-s)\rho_i^v(t) \rangle) \, ds \left. \right] \tag{3}$$

Here n is the number of macromolecules in unit volume; T is the temperature in energy units; α_v and $\varphi_v(s)$ are the eigenvalues of the force matrices A and G;

ω_{ke} is the antisymmetric part of the velocity-gradient tensor for the system. The law of variation of the statistical characteristics of macromolecular motion contained in the stress tensor given by the formal solution of the system of equations (1).

The dynamic modulus and relaxation times of the media considered are determined by using their expressions for the stress tensor. For linear polymers and their concentrated solutions it is assumed that the viscoelastic characteristics (microviscoelasticity) of the medium that surrounds the given macromolecule are determined by simple expressions for the external, $\beta_v[\omega]$, and internal, $\varphi_v[\omega]$, friction factors of the vth mode of the macromolecule:

$$\beta_v[\omega] = \zeta + \frac{\beta_v\zeta}{1 - i\omega\tau}, \qquad \beta_v = B \cdot v^{-e}$$

$$\varphi_v[\omega] = \frac{\varepsilon_v\zeta}{1 - i\omega\tau}, \qquad \varepsilon_v = E \cdot v^{-m} \tag{4}$$

which depend on frequency, since the medium is viscoelastic. τ is the relaxation time of the medium; ζ is a constant which has the meaning of the friction factor of the particle in a viscous liquid. The square brackets in Eq. (4) indicate a one-sided Fourier transform $a[\omega] = \int_0^\infty a(s)e^{i\omega s}\,ds$; β_v and ε_v are the weight factors. This leads to the following expression for the dynamic modulus:

$$G(\omega) = nT \sum_{v=1}^{N} \sum_{i,j}^{3} \left[A_i^v B_j^v \left(1 - \frac{\tau_v' - \tau_v^z}{2\tau_v^i - \tau} - \frac{\tau_v' - \tau_v^z}{2\tau_v^j - \tau} \right) \cdot \frac{-i\omega\tau_v^{ij}}{1 - i\omega\tau_v^{ij}} \right.$$
$$\left. + \left(A_i^v B_j^v \frac{2\tau_v^j}{\tau} + A_j^v B_i^v \right) \frac{\tau_v' - \tau_v^z}{2\tau_v^j - \tau} \frac{-i\omega\tau_v^{Bi}}{1 - i\omega\tau_v^{Bi}} \right] \tag{5}$$

where the following notations are used:

$$A_i^v = \frac{(\tau_v^i - \tau/2)^2}{(\tau_v^i - \tau_v^e)(\tau_v^i - \tau_v^m)}, \qquad \tau_v' = \tau_v^z(1 + \varepsilon_v)$$

$$B_i^v = \frac{(\tau_v^i - \tau/2)(\tau_v^i - \tau/2 - (\tau_v' - \tau_v^z))}{(\tau_v^i - \tau_v^e)(\tau_v^i - \tau_v^m)}, \qquad i \neq e, i \neq m$$

The dynamic modulus is defined by two sets of relaxation times:

$$\tau_v^{ij} = \frac{2\tau_v^i\tau_v^j}{\tau_v^i + \tau_v^j}, \qquad \tau_v^{Bi} = \frac{2\tau\tau_v^i}{2\tau_v^i + \tau} \tag{6}$$

The relaxation times τ_v^i are the solutions of the cubic equation:

$$\tau^3 - a_1^v\tau^2 + a_2^v\tau - a_3^v = 0 \tag{7}$$

with the coefficients

$$a_1^v = \tau + \tau_v' + B\tau_v^z,$$

$$a_2^v = (\tau/2)^2 + \tau(\tau_v' + \tau_v^z(1 + B))/2,$$

$$a_3^v = (\tau/2)^2 \tau_v^z$$

and are given by the following expressions:

$$\tau_v^1 = a_1^v/3 - 2 \, \text{sign}(q^v)\sqrt{-p^v/3} \, \cos\frac{\alpha^v}{3},$$

$$\tau_v^{2,3} = a_1^v/3 + 2 \, \text{sign}(q^v)\sqrt{-p^v/3} \, \cos\left(\frac{\alpha^v}{3} \pm \frac{\pi}{3}\right) \qquad (8)$$

Here the following notations are used:

$$p^v = -(a_1^v)^2/3 + a_2^v,$$

$$q^v = -2(a_1^v/3)^3 + a_1^v a_2^v/3 - a_3^v,$$

$$\cos \alpha^v = q^v/[2 \cdot (\text{sign } q^v \cdot (-p^v/3)^{1/2})^3]$$

The frequency dependence of the dimensionless dynamic modulus is determined by the following parameters of the model B, E, and τ_1^z. The last parameter is the maximum relaxation time of the macromolecule in a purely viscous segmental liquid. The effect of the parameters m and e, which are defined by Eq. (4), is insignificant.

In order to detail the viscoelastic characteristics of the medium that surrounds the isolated polymer chain, a consistent co-ordination of relaxation times is introduced. Considering that each macromolecule is surrounded by macromolecules of the same species, it is required that the characteristic relaxation time coincide with the characteristic relaxation time of the environment:

$$\tau_{\text{max}} = \tau$$

In other words, it is taken into account that the macromolecules and their environment relax in the same way. The self-consistent condition singles out a self-consistent solution from a set of possible solutions. A computer-assisted experiment has shown that it is precisely this solution that reflects most correctly the experimental situation. After the self-consistent test is carried out the dependence of the dimensionless dynamic modulus of the systems under consideration on the dimensionless frequency is determined by two parameters only, B and $\chi = \tau/2B\tau_1^z$, whose values depend on the molecular mass and concentration of the polymer. The parameter B is a measure of the viscoelasticity of the environment around the macromolecule. The parameter χ serves to compare the relaxation time of the macromolecular environment

with the characteristic relaxation time of the macromolecule in a viscous liquid, i.e. in a liquid with zero relaxation time. The values of B and χ can be calculated by means of the formulas for the initial shear viscosity η_0 and the plateau modulus G'_p which are predicted by theory:

$$\eta_0 = 1.46 n T B \tau_1^z$$

$$G'_p = 0.72 n T \chi^{-1} \tag{9}$$

Proceeding from the dimensional analysis we can show that B and χ are universal functions of the dimensionless parameter S and are independent of the chemical structure of polymers:

$$B \sim S^{2\delta}, \qquad \chi \sim S^{-2},$$

$$S \equiv n(\bar{S}^2)^{3/2} = \frac{N_A K}{\Phi} c M^{1/2} \tag{10}$$

Here N_A is Avogadro's number; K is a measure of the thermodynamic flexibility of macromolecules; Φ is the Flory constant ($\Phi = 2.6 \times 10^{21}$ $dl/g \cdot cm^3 \cdot mole$); c is the concentration. The parameter δ which appears in this equation is determined from the dependence of viscosity on molecular mass, $\eta_0 \sim M^{\delta+1}$. According to experimental data in the region of high molecular masses $\delta = 2.4$.

A comparison of the frequency dependences (predicted by theory) of the components of the dynamic modulus—the storage modulus G' and the loss modulus G''—with experimental findings[19] for molten polystyrene of molecular mass 2.15×10^5 at 160°C has shown (see Figure 3) that the theory describes all the specific features of the viscoelastic functions found by experiment—the presence of a plateau on the curve of G' and of a local maximum and a local minimum on the curve of G''. Apart from this, the theory predicts a new regularity for the manifestation of the viscoelastic properties of
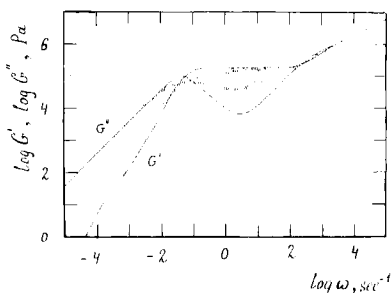

FIGURE 3 The theoretical (the solid lines) and experimental (the points) frequency dependences of the real (G') and imaginary (G'') components of the dynamic modulus of polystyrene of narrow MMD. The theoretical curves have been calculated for the following values of the parameters: $B = 145$ and $\chi = 0.06$.

polymers—the appearance of a point of inflection on the frequency dependence of G' in the frequency region that precede the appearance of the plateau. It should also be noted that there is observed a very sharp shift to the plateau on the theoretical curve of G', which is evidence of a very narrow distribution of long relaxation times for ideally monodispersed polymers.

3. MICRO- AND MACROVISCOELASTICITY

In connection with the establishment of the relationship between microviscoelasticity taken up by an isolated macromolecule and the observed macroviscoelasticity it becomes necessary to study the viscoelasticity of dilute blends of two polymers, $A + B$, with a limiting low content of the higher-molecular-mass component B, so that molecules of species B do not interact with each other. In this case, it will be natural to assume at the outset that component A forms, for macromolecules of species B, a viscoelastic medium described by the storage and loss moduli of the original component A. Then, on the basis of the formula derived earlier:[16]

$$M(\omega) = M_A(\omega) + \sum_{\alpha=1}^{N} \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega' \frac{i\omega}{\omega'(\omega - \omega')}$$

$$\times \frac{M_A(\omega')}{\mu_\alpha/2\gamma + M_A(\omega')} \cdot \frac{M_A(\omega - \omega')}{\mu_\alpha/2\gamma + M_A(\omega - \omega')} \tag{11}$$

which relates the dimensionless dynamic moduli of a linear viscoelastic liquid of the general type $M_A = G_A/nT$ and of a dilute solution of a polymer in it, $M = G/nT$, it is possible to determine the frequency dependence of the storage and loss moduli of dilute mixtures. Equation (11) contains the dimensionless concentration γ, which is connected with the intrinsic viscosity by the relation $\gamma = 6c[\eta]$ if it is assumed that the macromolecules are draining: $\mu_\alpha = (\pi\alpha)^2$.

In a particular case where the medium is viscous, $M_A = -i\omega\bar{\eta}_s$, $\bar{\eta}_s = \eta_s/nT$. From Eq. (11) we obtain an integral form of the storage and loss moduli of dilute solutions of polymers in a viscous Newtonian liquid:

$$M'_\beta = \sum_{\alpha=1}^{N} \frac{1}{2\pi}$$
$$\times \int_{-\infty}^{\infty} d\omega' \frac{\omega\mu_\alpha/2\gamma}{\omega'(\omega - \omega')} \frac{M''_{A\omega'} M''_{A\omega-\omega'}[M''_{A\omega'} + M''_{A\omega-\omega'}]}{[(\mu_\alpha/2\gamma)^2 + M''^2_{A\omega'}] \cdot [(\mu_\alpha/2\gamma)^2 + M''^2_{A\omega-\omega'}]},$$

$$M''_\beta - \omega\eta_s = \sum_{\alpha=1}^{N} \frac{1}{2\pi}$$
$$\times \int_{-\infty}^{\infty} d\omega' \frac{\omega}{\omega'(\omega - \omega')} \frac{M''_{A\omega'} M''_{A\omega-\omega'}[(\mu_\alpha/2\gamma)^2 - M''_{A\omega'} M''_{A\omega-\omega'}]}{[(\mu_\alpha/2\gamma)^2 + M''^2_{A\omega'}] \cdot [(\mu_\alpha/2\gamma)^2 + M''^2_{A\omega-\omega'}]} \tag{12}$$

Using a Fourier transform, it is easy to show that the formulas derived, (Eq. (12), reduce to the well-known Rouse formulas.

4. CONCLUSION

The main difficulty in the theory of the viscoelasticity of molten polymers and concentrated polymer solutions was to explain slow relaxation processes. The appearance of a plateau was ascribed to the mechanical entanglement network formed by labile junctions or entangled portions of the chain. From the analysis made here it follows that it is precisely the account taken of the viscoelasticity of the medium surrounding the macromolecules of concentrated polymer systems that naturally leads to the experimentally observed distribution of long relaxation times.

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