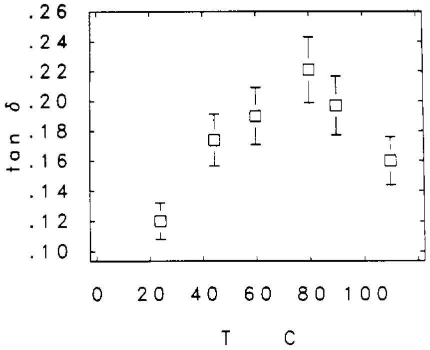

Figure 5. Mechanical loss tan δ plotted vs. temperature for the 65% gel. A loss maximum is observed at approximately 80 °C. The Brillouin frequency at this temperature was 5.9 GHz.

over the past few years. The primary variable which affects the hypersonic properties of polymeric systems is the local structural relaxation of the fluid. Long-range or other slow processes which may have dramatic effects on the low-frequency properties are often not observable at hypersonic frequencies.

References and Notes

(1) Montrose, C. J.; Solovyev, V. A.; Litovitz, T. A. *J. Acoust. Soc. Am.* **1968**, *43*, 117.
(2) Patterson, G. D. *CRC Crit. Rev. Solid State Mater. Sci.* **1980**, *9*, 373.
(3) Ferry, J. D. "Viscoelastic Properties of Polymers"; Wiley: New York, 1970.
(4) Herzfeld, K. F.; Litovitz, T. A. "Absorption and Dispersion of Ultrasonic Waves"; Academic Press: New York, 1959.
(5) Fabelinskii, I. L. "Molecular Scattering of Light"; Plenum Press: New York, 1968.
(6) Patterson, G. D. *J. Macromol. Sci., Phys.* **1977**, *B13*, 647.
(7) Patterson, G. D.; Latham, J. P. *J. Polym. Sci., Macromol. Rev.* **1980**, *15*, 1.
(8) Patterson, G. D.; Lindsey, C. P.; Alms, G. R. *Macromolecules* **1978**, *11*, 1242.
(9) McCrum, N. G.; Read, B. E.; Williams, G. "Anelastic and Dielectric Effects in Polymeric Solids"; Wiley: London, 1967.

Depolarized Light Scattering from Macromolecules: Effects of Torsional Oscillations, Conformational Transitions, and Overall Rotations

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ABSTRACT: Depolarized dynamic light scattering spectra of dilute polymer solutions can be interpreted as due to the unequally weighted contributions of two processes: (1) a slow, molecular weight dependent contribution arising from the overall rotation of the molecule and (2) a fast, molecular weight independent process arising from some sort of local chain motions. To account for these observations we have derived an expression for the depolarized spectrum $I(\omega)$ of a schematic model consisting of a linear sequence of optically anisotropic segments, each of which is able to rotate about the chain axis. By coupling the rotations of adjacent segments harmonically, we mimic torsional oscillations of bonds about equilibrium rotation angles γ_i. Conformational transitions are mimicked by allowing the γ_i to be time dependent. Our results allow the assessment of the relative contributions to $I(\omega)$ of torsional oscillations, conformational transitions, and overall rotation; e.g., for the limiting case of a long rod with a large torsional potential, two unequally weighted Lorentzians occur only if conformational transitions are permitted.

Introduction

In addition to the now standard use of dynamic light scattering to obtain translational and overall rotational diffusion constants of macromolecules,[1] there is the additional possibility of obtaining rate constants for internal motions within the macromolecule. Although the customary polarized measurements can yield information about very slow intramolecular motions provided that the molecular weight is sufficiently high,[2] it is depolarized dynamic light scattering which is more promising for studying internal motions, irrespective of their time scale.[3-5]

The most suggestive study so far is that of Bauer, Brauman, and Pecora[3] (BBP) on dilute polystyrene fractions in CCl_4. Their spectra are reported in terms of the contribution of two unequally weighted Lorentzians. One of these is a slowly relaxing molecular weight dependent contribution which BBP identify with the overall rotation of the molecule. The other is a rapidly relaxing molecular weight independent contribution which they attribute to a local motion, viz., the rotation of phenyl groups about the main-chain axis. It is unclear wheather these features will be characteristic of the spectra of other polymer-solvent systems where the particular mechanism favored by BBP is less likely (or impossible).

Here we consider whether some simple idealized molecular model may, under certain conditions, exhibit the type of behavior observed by BBP. Evans[6] has used a dynamic theory of Fixman's[7] to treat interacting bond polarizabilities and has concluded that dipole-induced dipole interactions involving the substituents perpendicular to the main chain are responsible for the fast relaxation observed by BBP. We use a simpler model, which is of interest precisely because it is able to account for essentially those features which are experimentally observed, but without invoking either the mechanism suggested by BBP or that by Evans.

The model is similar to that employed by Shore and Zwanzig[8] in treating dielectric relaxation by means of a linear sequence of spins and to the linear elastic model employed both by Barkley and Zimm[9] and by Allison and Schurr[10] in their treatments of fluorescent depolarization

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by DNA. Our version of the model is a rodlike arrangement of cylindrically anisotropic segments which interact with adjacent neighbors harmonically.[11] Fluctuations of the polarizability, as viewed in a laboratory coordinate system, arise both from overall rotations of the molecule and from rotational motions of the segments about the molecular axis. The rodlike character of the model not only simplifies the dynamics by disallowing kinks to occur along the chain, but the common, though questionable,[12] assumption of the independence of local and overall motions is more legitimate. Although the rodlike model is physically unrealistic for a flexible chain molecule, it is instructive because it allows us to show that neither specific polarizability mechanisms nor chain flexibility is necessary as such to account for the salient features of the experimental observations.

Theory

Consider a collinear sequence of cylindrically optically anisotropic segments which can rotate about the molecular axis. Such rotations generate an observable change in the molecular polarizability. Each segment interacts with its adjacent neighbors by a harmonic torsional potential. This is the means by which torsional interactions in a real molecule are mimicked, whereas the cylindrical anisotropy of the segments plays a corresponding role for those motions in the side chains of real chains which generate fluctuations in the polarizability. The polarizability measured in a laboratory frame consists of contributions from both overall molecular rotation and segmental rotations.

Our object is to derive a formula for $I(\omega)$, the dynamic light scattering spectrum. This quantity is the Fourier transform of the autocorrelation function of the molecular polarizability, $\langle \alpha_{yz}(0)\alpha_{yz}^*(t) \rangle$.

Let there be N identical segments, each of which has a segmental anisotropy (S) expressed in a local segmental frame given by

$$\alpha(S) = \begin{bmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_3 \end{bmatrix} \tag{1}$$

It is convenient to use spherical components when treating the polarizability of both the segments and the molecule. For the segmental anisotropy it is convenient to define the quantities $\Delta\alpha$ and $\Delta\beta$ as follows:

$$\Delta\alpha = (2/6^{1/2})[\alpha_3 - (\alpha_1 + \alpha_2)/2]$$
$$\Delta\beta = (\alpha_1 - \alpha_2)/2 \tag{2}$$

In terms of these quantities, the spherical components in the segmental frame are

$$\alpha_0^{(2)}(S) = \Delta\alpha$$
$$\alpha_{\pm1}^{(2)}(S) = 0 \tag{3}$$
$$\alpha_{\pm2}^{(2)}(S) = \Delta\beta$$

These components are related to the laboratory-based segmental quantities as follows. Let α_{yz} be the yz component of α for the molecule in laboratory coordinates. For incident light polarized in the z direction, the appropriate function which measures the dynamics of fluctuations in the polarizability in the depolarized type of measurement is $\langle \alpha_{yz}(0)\alpha_{yz}^*(t) \rangle$. To evaluate this we need $\alpha_1^{(2)}$ and $\alpha_{-1}^{(2)}$, the spherical components of the molecule expressed in laboratory coordinates. The connection is

$$\alpha_{yz} = (-i/2)(\alpha_1^{(2)} + \alpha_{-1}^{(2)}) \tag{4}$$

where the $\alpha_{\pm1}^{(2)}$ are given by

$$\alpha_1^{(2)} = \sum_{m'=-2}^{+2} \alpha_{m'}^{(2)}(M) D_{m'+1}^{(2)}(\Omega) \tag{5}$$

and

$$\alpha_{-1}^{(2)} = \sum_{m'=-2}^{+2} \alpha_{m'}^{(2)}(M) D_{m'-1}^{(2)}(\Omega) \tag{6}$$

Here $\alpha_{m'}^{(2)}$ are the spherical components of the molecular polarizability in the molecule-based coordinate system, $D_{m'\pm1}^{(2)}(\Omega)$ are the Wigner rotation matrices,[13] and Ω represents the orientation of the molecular frame in the laboratory frame. The molecular spherical components $\alpha_{m'}^{(2)}(M)$ can be expressed in terms of the spherical segmental components $\alpha_k^{(2)}(S)$ by the equation

$$\alpha_{m'}^{(2)}(M) = \sum_{k_1} \alpha_{k_1}^{(2)}(S) D_{k_1 m'}^{(2)}(\xi_1) + \sum_{k_2} \alpha_{k_2}^{(2)}(S) D_{k_2 m'}^{(2)}(\xi_2) + \ldots + \sum_{k_N} \alpha_{k_N}^{(2)}(S) D_{k_N m'}^{(2)}(\xi_N) \tag{7}$$

where each sum represents in turn the contribution to $\alpha(M)$ of a given segment. The angular sets $\{\xi_j\}$ give the orientations of the successive segments in the molecular frame. If we take the z axis of the molecular frame to be the molecular axis, then since[13,14]

$$D_{qm'}^{(2)}(\xi_j) = e^{-iq\alpha_j} d_{qm'}^{(2)}(\beta_j) e^{-im'\gamma_j} \tag{8}$$

we have for our model $\beta_j = 0$ for all segments since β_j is the angle between successive z axes of the segments, $\alpha_j = 0$ for all segments, and the γ_j are the orientation angles of the segments; viz., γ_j is the angle between the x axis of the jth segment and that of the molecular frame. Since[14]

$$d_{qm'}^{(2)}(0) = \delta_{qm'} \tag{9}$$

then

$$\sum_{k_j} \alpha_{k_j}^{(2)}(S) D_{k_j m'}^{(2)}(\xi_j) = \alpha_{m'}^{(2)}(S) e^{-im'\gamma_j} \tag{10}$$

and thus from eq 7 and 10 we have

$$\alpha_{m'}^{(2)}(M) = \alpha_{m'}^{(2)}(S) \sum_{j=1} e^{-im'\gamma_j} \tag{11}$$

From eq 3 this then gives for the spherical components of the molecular polarizability in the molecular frame the following results:

$$\alpha_0^{(2)}(M) = N\Delta\alpha$$
$$\alpha_1^{(2)}(M) = \Delta\beta \sum_{j=1}^{N} e^{-2i\gamma_j} \tag{12}$$
$$\alpha_{-1}^{(2)}(M) = \Delta\beta \sum_{j=1}^{N} e^{2i\gamma_j}$$

Combining eq 4, 5, 6, and 12 gives for α_{yz}, as observed in the laboratory, the result

$$\alpha_{yz} = (-i/2)\{N\Delta\alpha(D_{01}^{(2)}(\Omega) + D_{0-1}^{(2)}(\Omega)) + \Delta\beta(D_{21}^{(2)}(\Omega) + D_{2-1}^{(2)}(\Omega))(\sum_j e^{-2i\gamma_j} + \sum_j e^{2i\gamma_j})\} \tag{13}$$

To obtain $\langle \alpha_{yz}(0)\alpha_{yz}^*(t) \rangle$, we use eq 13 to construct the ensemble average. In our model, the rotations of segments about the molecular axis cause negligible effects on the overall rotational motion of the molecule since the rodlike character of the molecule is unaffected by such motions. Interactions between segmental rotations and overall rotation will be significant only for the unlikely case where these processes occur at comparable rates. For all cases of practical interest, Ω and the γ_j relax at greatly different rates, and terms in $\langle \alpha_{yz}(0)\alpha_{yz}^*(t) \rangle$ which involve them can be averaged independently. Thus we have

$$\langle \alpha_{yz}(0)\alpha_{yz}{}^*(t)\rangle = [N^2(\Delta\alpha)^2R_0(t)/2] + (\Delta\beta)^2R_2(t)\sum_j\sum_k\langle e^{2i(\gamma_j(t)-\gamma_k(0))}\rangle \quad (14)$$

In eq 14 we have made use of the relation[15]

$$\langle D_{qr}{}^{(2)}(\Omega(t))D_{q'r'}{}^{*(2)}(\Omega(0))\rangle = R_q(t)\delta_{qq'}\delta_{rr'} \quad (15)$$

where $R(t)$ is the autocorrelation function for a cylindrically symmetrical rod:[14]

$$R_q(t) = (1/5)\exp\{-[6\theta_\perp + q^2(\theta_\parallel - \theta_\perp)]t\} \quad (16)$$

Here $\theta_\parallel$ and $\theta_\perp$ are the rotational diffusion constants for rotation about, and perpendicular to, respectively, the molecular axis.

If the segments have cylindrical symmetry, then $\Delta\beta = 0$, and we recover Pecora's result[16] for a cylindrically isotropic rod. When the segments are cylindrically anisotropic, $\Delta\beta \neq 0$ and contributions to the autocorrelation function arise both from overall rotation via $R_2(t)$ and from segmental orientations via the sum $S(t)$ defined by

$$S(t) = \sum_{j,k=1}^{N}\sum\langle e^{2i(\gamma_j(t)-\gamma_k(0))}\rangle \quad (17)$$

The time scale of $R_2(t)$ and of $R_0(t)$ are both determined by overall molecular rotation, although the relaxation time in $R_2(t)$ involves both $\theta_\parallel$ and $\theta_\perp$, where $R_0(t)$ involves only the latter. The sum $S(t)$, on the other hand, contributes a time dependence to the autocorrelation function arising from local orientations and oscillations about the molecular axis, both processes being considerably faster than the overall rotation of the molecule.

We now examine $S(t)$ for the case where adjacent segments interact via a harmonic potential. To evaluate $S(t)$, we make use of the discovery[9,10] that a model of successive elements which interact harmonically when twisting motions occur is equivalent to the Rouse–Zimm spring-and-bead model of translational motions, provided that the twisting motions are overdamped viscous motions about equilibrium rotation angles $\{\gamma_j'\}$. The force constant κ (actually a torque constant) and the segmental diffusion constant D_b which occur below refer to rotational motion of a segment about the molecular axis. The angular coordinates of the segments $\{\gamma_j\}$ can be related to normal coordinates $\{\eta_k\}$ by the relationships

$$\gamma = \mathbf{Q}\eta + \gamma' \quad (18)$$

$$Q_{jk} = (2/N)^{1/2}(1/2^{1/2}); \qquad k = 0$$

$$Q_{jk} = (2/N)^{1/2}\{\cos[k\pi(j + \tfrac{1}{2})/N]\}; \qquad 1 \le k \le N - 1 \quad (19)$$

In terms of these normal coordinates eq 17 can be written

$$S(t) = \sum_j\sum_k\langle e^{2i[\sum_m(Q_{jm}\eta_m(t)-Q_{km}\eta_m(0)]}\rangle\langle e^{2i(\gamma_j'(t)-\gamma_k'(0)}\rangle \quad (20)$$

To evaluate the averages over the normal coordinates in eq 20 we proceed similarly to Pecora,[17] who evaluated an analogous equation while treating the Rouse–Zimm model. In our case, since the motions are rotations and not translations, proper attention must be given to the limits of integration and to normalization constants in the appropriate probability functions. Also, we must distinguish the zeroth normal mode, which corresponds to a free rotation of all segments in concert about the molecular axis, from the other $N - 1$ modes which correspond to cooperative relative motions of the segments. For the probability $\Phi_m(0)$ of observing $\eta_m(0)$ at time zero we have

$$\Phi_0 = 1/2\pi; \qquad m = 0 \quad (21)$$

and

$$\Phi_m = (1/2\pi\langle\eta_m{}^2\rangle)^{1/2}\exp\{-\eta_m{}^2(0)/\langle\eta_m{}^2\rangle\}; \qquad m \ge 1 \quad (22)$$

where the equilibrium value of $\eta_m{}^2$ can be written in terms of the torsional force constant κ and the eigenvalue $\lambda_m{}^2 = 4\sin^2(m\pi/2N)$ and the relaxation time τ_m of the mode as follows:

$$\frac{1}{\langle\eta_m{}^2\rangle} = \frac{\kappa\lambda_m{}^2}{kT} = \frac{1}{\tau_mD_b} \quad (23)$$

where k is Boltzmann's constant and T is the absolute temperature. For the conditional probability $\psi_m(t)$ of finding a value $\eta_m(t)$, given an earlier value $\eta_m(0)$, we have

$$\psi_0(t) = (1/4\pi D_bt)^{1/2}\exp\left\{-\frac{[\eta_0(t) - \eta_0(0)]^2}{4D_bt}\right\}; \qquad m = 0 \quad (24a)$$

$$\psi_m(t) = \frac{1}{[2\pi\langle\eta_m{}^2\rangle(1 - \exp(-2t/\tau_m))]^{1/2}} \times \exp\left\{-\frac{[\eta_m(t) - \eta_m(0)e^{-t/\tau_m}]}{2\langle\eta_m{}^2\rangle(1 - \exp(-2t/\tau_m))}\right\}; \qquad m \ge 1 \quad (24b)$$

where the relaxation time τ_m can be expressed in terms of λ_m,κ and the segmental rotational friction constant ζ_b by the equation

$$\tau_m = \zeta_b/\kappa\lambda_m{}^2 \quad (25)$$

The contribution of segmental motions can now be evaluated by using eq 20–25:

$$S(t) = \sum_j\sum_k\langle e^{2i(\gamma_j'(t)-\gamma_k'(0))}\rangle\prod_{m=0}^{N-1}\int\int e^{2i[\sum_m(Q_{jm}\eta_m(t)-Q_{km}\eta_m(0))]}\Phi_m(0) \times \psi_m(t)\,\mathrm{d}\eta_m(t)\,\mathrm{d}\eta_m(0) \quad (26)$$

The result is

$$S(t) = e^{-4\theta_\parallel t}\sum_j\sum_k\langle\epsilon^{2i(\gamma_j'(t)-\gamma_k'(0))}\rangle\prod_{m=0}^{N-1}e^{-2\langle\eta_m{}^2\rangle[Q_{jm}{}^2+Q_{km}{}^2-2Q_{jm}Q_{km}e^{-t/\tau_m}]} \quad (27)$$

A result essentially equivalent to eq 27 was obtained by Allison and Schurr.[10] Their eq 9, however, contains only the $j = k$ terms, as is appropriate for the fluorescence depolarization which they treated. Depolarized light scattering, however, requires also the terms for which $j \neq k$.

In Appendix A a formal result is given for eq 27. This result, which is given in terms of integrals of Bessel functions, is not as useful for obtaining insight into the conditions which correspond to observing the experimental results of BBP as is an approximate solution. Accordingly, we examine a short-time solution of eq 27, i.e., for times long enough for inertial effects to be negligible but short in the sense that $e^{-t/\tau_m} \simeq 1 - t/\tau_m$. For the product in eq 27 we thus have $\prod_m e^{-2\langle\eta_m{}^2\rangle(Q_{jm}-Q_{km})^2}e^{-4D_btQ_{jmm}Q_{km}}$, which gives, since $\sum_m Q_{jm}Q_{km} = (1 - 1/N)\delta_{jk}$ and $D_b = N\theta_\parallel$,

$$S(t) = e^{-4D_bt}\sum_j\sum_k\langle e^{2i(\gamma_j'(k)-\gamma_k'(0))}\rangle\prod_m e^{-2\langle\eta_m{}^2\rangle(Q_{jm}-Q_{km})^2} \quad (28)$$

For the $j = k$ terms, this gives

$$S(t) = e^{-4D_bt}\sum_j\langle e^{2i(\gamma_j'(t)-\gamma_k'(0))}\rangle \quad (29)$$

We show in Appendix B that for the $j \neq k$ terms

$$\prod_m e^{-2\langle\eta_m{}^2\rangle(Q_{jm}-Q_{km})^2} = e^{(-2kT/\kappa)|j-k|} \quad (30)$$

The short-time solution for $S(t)$ is thus

$$S(t) = e^{-4D_bt}\sum_j \langle e^{2i(\gamma_j'(t)-\gamma_j'(0))}\rangle + e^{-4\theta_{\|}t}\sum_j\sum_k \langle e^{2i(\gamma_j'(t)-\gamma_k'(0))}\rangle e^{(-2kT/\kappa)|j-k|}; \qquad j \neq k \quad (31)$$

and substituting this result in eq 14 gives

$$\langle \alpha_{yz}(0)\alpha_{yz}{}^*(t)\rangle = [N^2(\Delta\alpha)^2R_0(t)/2] + (\Delta\beta)^2R_2(t)\{e^{-4D_bt}\sum_j \langle e^{2i(\gamma_j'(t)-\gamma_j'(0))}\rangle + e^{-4\theta_{\|}t}\sum_j\sum_k \langle e^{2i(\gamma_j'(t)-\gamma_k'(0))}\rangle e^{(-2kT/\kappa)|j-k|}\}; \qquad j \neq k \quad (32)$$

The time dependence of the polarizability autocorrelation function for this model has contributions arising from the following three sources: (1) Overall rotation of the molecule via terms involving $R_0(t)$, $R_2(t)$, and $\theta_{\|}$. These occur on a time scale of ca. 10^{-4} s. (2) Conformational transitions. In eq 32, these give changes in the population of the equilibrium states, $\{\gamma_j'\}$. Such changes occur on a time scale of ca. 10^{-9} s. (3) Torsional oscillations about equilibrium states. These are reflected in eq 32 by the segmental rotational diffusion constant D_b and the force constant κ. These changes occur on a time scale of ca. 10^{-12} s.

Discussion

We consider first the molecular weight dependence of the various terms in eq 31. The first term is proportional to N^2, and as has been indicated above, is identical with Pecora's result for a cylindrically symmetrical rod. The term involving $\exp(-4D_bt)$, which arises from independent rotations of segments, is proportional to N. This contribution will be unobservable for large macromolecules: not only is the weighting by N negligible compared to weighting by N^2 but, in addition, this relaxation occurs too rapidly to be observed.

The situation is different for the contributions arising from interactions between the segments, where $j \neq k$. If the value of $\langle \exp(2i(\gamma_j'(t) - \gamma_k'(0)))\rangle$ does not depend on the locations of segments j or k, then the weighting of the term in question becomes proportional to the quantity $\sum_j\sum_k \exp[-(2kT/\kappa)|j-k|]$. If $2kT/\kappa \rightarrow \infty$, then this term vanishes irrespective of the value of N; this is because this case corresponds to independent (and therefore noninteracting) segments. If $2kT/\kappa \rightarrow 0$, however, this term is weighted by a factor of N^2. This limit corresponds to a long stiff rod, i.e., to strongly interacting segments. For large N, a pair of segments can be chosen in N^2 ways. Rewriting eq 32 for the case of large N and small kT/κ we obtain

$$\langle \alpha_{yz}(0)\alpha_{yz}{}^*(t)\rangle = [N^2(\Delta\alpha)^2R_0(t)/2] + N^2(\Delta\beta)^2R_2(t)e^{-4\theta_{\|}t}C(t) \quad (33)$$

where

$$C(t) = \sum_j\sum_k \langle {}^{2i(\gamma_j'(t)-\gamma_k'(0))}\rangle \quad (34)$$

Examination of eq 33 shows that if $\langle \alpha_{yz}(0)\alpha_{yz}{}^*(t)\rangle$ is to have a time dependence different from that of the overall molecular rotation, then it must arise from $C(t)$; i.e., conformational transitions between equilibrium states must occur.

To evaluate $C(t)$ in a way which is both simple and illustrative, we employ a two-state jump model. Let γ_a and γ_b be the two equilibrium states, let σ be the statistical weight of state b relative to state a, and let λ_a and λ_b be the probabilities per unit time of a jump from the subscripted state to the other state, respectively. The a priori probabilities that a bond be found in a given state are

$$p_a = 1/(1 + \sigma)$$
$$p_b = \sigma/(1 + \sigma) \quad (35)$$

The conditional probabilities $P(m_t|l_0)$ of finding any one bond in state m at time t, given that any bond is known to be in state l at time zero (m and l each are either a or b) are easily found by recognizing that the interconversion between states a and b is equivalent to the standard problem of two reversible first-order reactions. The results are

$$P(a_t|a_0) = 1 - \left(\frac{\lambda_a}{\lambda_a + \lambda_b}\right)[1 - \exp(-[\lambda_a + \lambda_b]t)]$$
$$P(a_t|b_0) = \left(\frac{\lambda_b}{\lambda_a + \lambda_b}\right)[1 - \exp(-[\lambda_a + \lambda_b]t)]$$
$$P(b_t|b_0) = 1 - \left(\frac{\lambda_b}{\lambda_a + \lambda_b}\right)[1 - \exp(-[\lambda_a + \lambda_b]t)]$$
$$P(b_t|a_0) = \left(\frac{\lambda_a}{\lambda_a + \lambda_b}\right)[1 - \exp(-[\lambda_a + \lambda_b]t)] \quad (36)$$

Since for the two-state jump model $C(t)$ can be written

$$C(t) = \sum_l \sum_{m=a,b} e^{-2i\gamma_l}P(m_t|l_0)e^{2i\gamma_m} \quad (37)$$

we obtain, using eq 35, 36, and 37 and the relation $\lambda_a/\lambda_b = \sigma$

$$C(t) = 1 - \frac{2\lambda_a\lambda_b}{(\lambda_a + \lambda_b)^2}(1 - \cos 2|\gamma_a - \gamma_b|)[1 - \exp(-[\lambda_a + \lambda_b]t)] \quad (38)$$

This can also be written in the following way to display the effect of the energy difference between the states (via σ):

$$C(t) = 1 - \frac{2\sigma}{(1 + \sigma)^2}(1 - \cos 2|\gamma_a - \gamma_b|)[1 - \exp(-[1 + \sigma]\lambda_bt)] \quad (39)$$

Equations 38 and 39 show that torsional jumps between the equilibrium states produce no observable effect if $|\lambda_a - \lambda_b| = \pi$; i.e., $C(t) = 1$ for all values of t for this case. This is because a rotation of π does not produce a detectable change in polarizability. The maximum effect on relaxation occurs when $|\lambda_a - \lambda_b| = \pi/2$ and $\sigma = 1$.

Skolnick and Helfand[18] have applied Kramers' reaction rate theory[19] to the conformational transitions experienced by a bond attached to tails of varying lengths and consisting of various sequences of bond states. Using reasonable values for the molecular parameters required to calculate the rate of a t $\rightarrow$ g$^+$ transition for polymethylene, they find values at 100 °C which are typically ca. 2 ns^{-1}, with no dependence on total chain length. By correcting this result for (a) the friction constant of a polystyrene monomer compared to that of a polymethylene monomer and (b) the effect of temperature, we obtain a value of ca. 0.4 ns^{-1} for polystyrene at 25 °C (using still, however, the force constants and activation energy appropriate to polymethylene). A crude, but representative, estimate of the relaxation time of conformational transitions of this type should therefore be ca. 2 or 3 ns^{-1} for polystyrene. This is only 30–50% lower than the relaxation rate observed by BBP for the broad, molecular weight independent contribution to their spectra.

Having established the plausibility of the jump model which leads to eq 39 for $C(t)$, we can write eq 33 as follows:

$$\langle \alpha_{yz}(0)\alpha_{yz}{}^*(t)\rangle = \frac{N^2(\Delta\alpha)^2 \exp(-6\theta_\perp t)}{10} + \frac{N^2(\Delta\beta)^2}{5} \exp[-(2\theta_\perp + 8\theta_\|)t] \times \left\{1 - \frac{2\sigma}{(1+\sigma)^2}(1 - \cos 2|\gamma_a - \gamma_b|)[1 - \exp(-[1+\sigma]\lambda_b t)]\right\} \tag{40}$$

The spectrum $I(\omega)$ corresponding to eq 40 is

$$I(\omega) = \frac{N^2(\Delta\alpha)^2}{20\pi} \frac{6\theta_\perp}{\omega^2 + (6\theta_\perp)^2} + \frac{N^2(\Delta\beta)^2}{10\pi}\left[1 - \frac{2\sigma}{(1+\sigma)^2}(1 - \cos 2|\gamma_a - \gamma_b|)\right] \times \frac{2\theta_\perp + 8\theta_\|}{\omega^2 + (2\theta_\perp + 8\theta_\|)^2} + \frac{N^2(\Delta\beta)^2}{10\pi} \frac{2\sigma}{(1+\sigma)^2} \times (1 - \cos 2|\gamma_a - \gamma_b|)\frac{2\theta_\perp + 8\theta_\| + (1+\sigma)\lambda_b}{\omega^2 + (2\theta_\perp + 8\theta_\| + (1+\sigma)\lambda_b)^2} \tag{41}$$

This result, valid for large N and for the case of strongly interacting segments, shows that the spectrum $I(\omega)$ consists of three Lorentzians. The first two of these have line widths which depend strongly on molecular weight since overall molecular rotation is the only process responsible for the broadening. The line width of the third Lorentzian is dominated by the rate of conformational transitions and is essentially equal to $(1 + \sigma)\lambda_b$, a quantity which is independent of molecular weight. The ratio of weighting factors of the second and third Lorentzians is $(1 - A)/A$, where

$$A = \frac{2\sigma}{(1+\sigma)^2}(1 - \cos 2|\gamma_a - \gamma_b|) \tag{42}$$

The quantity A vanishes if $|\gamma_a - \gamma_b| = 0$ or π and is a maximum when $|\gamma_a - \gamma_b| = \pi/2$. For this case, and assuming as a typical value $\sigma = 0.414$, we find that $A = 0.88$, so $(1 - A)/A = 0.13$. For equal probabilities of the two states γ_a and γ_b, $\sigma = 1.0$, and then $A = 1.0$ and $(1 - A)/A = 0$. Thus, to a good approximation we may regard eq 41 to be dominated by *two* Lorentzians, the first and the third, so that $I(\omega)$ can be written

$$I(\omega) \cong \frac{N^2(\Delta\alpha)^2}{20\pi} \frac{6\theta_\perp}{\omega^2 + (6\theta_\perp)^2} + \frac{N^2(\Delta\beta)^2}{10\pi} A \frac{(1+\sigma)\lambda_b}{\omega^2 + [(1+\sigma)\lambda_b]^2} \tag{43}$$

This equation exhibits the main features observed by BBP: two Lorentzians which have unequal weights, one of which has a narrow line width which is molecular weight dependent (via $\theta_\perp$) and the other of which is broad and molecular weight independent (via $(1 + \sigma)\lambda_b$). In order for the ratio of the weighting factors in eq 43 to have the 1:4 value observed by BBP at high molecular weights, we find, using $A = 0.88$, that $\alpha_1 - \alpha_2 \simeq [\alpha_3 - (\alpha_1 + \alpha_2)/2](0.18)$. This result means that the segmental deviation from cylindrical isotropy is ca. 18% of that of the "main" deviation, i.e., of the difference between the polarizability along the segmental z axis and the average of the values perpendicular to that axis. This appears to be a reasonable value.

The spectrum predicted by our model differs significantly from that predicted by Ono and Okano,[5] who explicitly adopted the Rouse dynamical model, and by Norisuye and Yu,[20] who, in effect, use the same model by assuming a normal coordinate transformation of *position* coordinates. In either case, the predicted spectrum consists of a set of N *equally weighted* Lorentzians. The crucial factor omitted in these treatments is the presence of an interaction between segments which affects their mutual orientations.

Lin and Wang[21] have considered the role played by torsional oscillations in depolarized scattering but they conclude that these oscillations make a direct contribution to the observed spectrum whereas our model utilizes such oscillations only as a device to introduce orientational correlations. Torsional oscillations occur too rapidly to be observed directly and, at least in our model, with a very low intensity; cf. the remarks following eq 32 above. Furthermore, the segmental angular displacements treated by Lin and Wang are actually only indirectly related to torsional oscillations. These displacements are expressed not as rotations about chain bonds but as rotations with respect to an axis defined in terms of some average configuration of the molecule.

The artificiality of our model does not justify either a more systematic application to experimental data or a more elaborate treatment of the conformational transitions than the simple-jump model presented above. The significant point which this model does allow us to make is that intersegmental interactions of some sort are necessary in order to account for the observations of BBP. We do not here favor or reject any particular mechanism of intersegmental interaction. The harmonic potential was employed not because we insist that torsional oscillations must play a major role in the depolarized scattering from real chains but because of the mathematical simplications which are thereby introduced. We conjecture, however, that any satisfactory explanation of the observations of BBP will require the introduction of some type of intersegmental interactions.

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Appendix A

We present here a formal result for eq 27. Consider the m factors in F, where

$$F = \prod_m e^{-2\langle\eta_m{}^2\rangle[Q_{jm}{}^2 + Q_{km}{}^2 - 2Q_{jm}Q_{km}e^{-t/\tau_m}]} \tag{A1}$$

This can be written

$$F = G \times H \tag{A2}$$

where

$$G = \prod_m e^{-2\langle\eta_m{}^2\rangle(Q_{jm} - Q_{km})^2} = e^{(-2kT/\kappa)|j-k|} \tag{A3}$$

$$H = \prod_m e^{-4\langle\eta_m{}^2\rangle[Q_{jm}Q_{km}(1 - e^{-t/\tau_m})]} \tag{A4}$$

The second equality in eq A3 is proven in Appendix B.

Using eq 18, 23, and 35, we can write H as

$$H = e^{(-kT/\kappa)S} \tag{A5}$$

where

$$S = \frac{1}{N}\sum_{m=1}^{N} \frac{\cos[(m\pi/N)(k - j)] + \cos[(m\pi/N)(k + j + 1)]}{\sin^2(m\pi/2N)} \times (1 - e^{-A\sin^2(m\pi/2N)}) \tag{A6}$$

where $A \equiv 4\kappa/\zeta$. For large N, this can be written

$$S = \frac{1}{\pi}\int_0^{\pi} \cos\,[(k-j)x]\frac{1-e^{-A\sin^2(x/2)}}{\sin^2(x/2)}\,\mathrm{d}x + \frac{1}{\pi}\int_0^{\pi} \cos\,[(k+j+1)x]\frac{1-e^{-A\sin^2(x/2)}}{\sin^2(x/2)}\,\mathrm{d}x \quad \text{(A7)}$$

To evaluate these integrals, consider the integral

$$M_m(\alpha) = \int_0^{\pi} (\cos mx)e^{-\alpha\sin^2(x/2)}\,\mathrm{d}x \quad \text{(A8)}$$

In terms of $M_m(\alpha)$

$$\int_0^{\pi} (\cos mx)\frac{1-e^{-A\sin^2(x/2)}}{\sin^2(x/2)}\,\mathrm{d}x = \int_0^{A} M_m(\alpha)\,\mathrm{d}\alpha \quad \text{(A9)}$$

Furthermore

$$M_m(\alpha) = e^{-\alpha/2}\int_0^{\pi} (\cos mx)e^{(\alpha/2)\cos x}\,\mathrm{d}x \quad \text{(A10)}$$

and therefore

$$M_m(\alpha) = e^{-\alpha/2}\pi I_m(\alpha/2) \quad \text{(A11)}$$

where $I_m(\alpha/2)$ is a modified Bessel function and the integral in (A10) is given by (9.6.19) in Abromowitz and Stegun.[22]

This gives

$$\int_0^{A} M_m(\alpha)\,\mathrm{d}\alpha = 2\pi\int_0^{A/2} e^{-w}I_m(w)\,\mathrm{d}w \quad \text{(A12)}$$

so

$$\int_0^{\pi} (\cos mx)\frac{1-e^{-A\sin^2(x/2)}}{\sin^2(x/2)}\,\mathrm{d}x = 2\pi\left\{\frac{A}{2}e^{-A/2}[I_0(A/2) + I_1(A/2)] + m[e^{-A/2}I_0(A/2) - 1] + 2e^{-A/2}\sum_{l=1}^{m-1}(m-l)I_l(A/2)\right\} \quad \text{(A13)}$$

Substituting (A13) in (A7) gives

$$S = 2\{Ae^{-A/2}[I_0(A/2) + I_1(A/2)] + [e^{-A/2}I_0(A/2) - 1] \times (2k+1) + 2e^{-A/2}[\sum_{l=1}^{k-j-1}(k-j-l)I_l(A/2) + \sum_{l=1}^{k+j}(k+j-l)I_l(A/2)]\} \quad \text{(A14)}$$

The formal solution, for large N, for eq 27 is thus

$$S(t) = e^{-4\theta_{\parallel}t}\sum_j\sum_k \langle e^{2i(\gamma_j'(t)-\gamma_k'(0))}\rangle e^{(-2kT/\kappa)|j-k|}e^{-(kT/\kappa)S} \quad \text{(A15)}$$

with $A = 4\kappa/\zeta$ and S given by (A14).

Appendix B

In order to show that eq 30 holds

$$\prod_m e^{-2\langle\eta_m^2\rangle(Q_{jm}-Q_{km})^2} = e^{(-2kT/\kappa)|j-k|} \quad (30)$$

where

$$Q_{jm} = (2/N)^{1/2}[\cos\,(m\pi/N)](j + \tfrac{1}{2})$$

$$Q_{km} = (2/N)^{1/2}[\cos\,(m\pi/N)](k + \tfrac{1}{2})$$

$$\langle\eta_m^2\rangle = (kT/\kappa)[1/4\sin^2(m\pi/2N)]$$

we write

$$2\langle\eta_m^2\rangle(Q_{jm}-Q_{km})^2 = \frac{4kT}{\kappa}\frac{1}{N}\frac{\sin^2[m\pi(j+k+1)/2N]\sin^2[m\pi(j-k)/2N]}{\sin^2(m\pi/2N)} \quad \text{(B1)}$$

where we have used $\cos A - \cos B = -2\sin[(A+B)/2]\sin[(A-B)/2]$. Thus

$$\prod_m e^{-2\langle\eta_m^2\rangle(Q_{jm}-Q_{km})^2} = e^{(-4kT/\kappa)I_1} \quad \text{(B2)}$$

where

$$I_1 = \frac{1}{N}\sum_{m=1}^{N-1}\frac{\sin^2[m\pi(j+k+1)/2N]\sin^2[m\pi(j-k)/2N]}{\sin^2(m\pi/2N)} \quad \text{(B3)}$$

When N is large, this can be written

$$I_1 = \frac{2}{\pi}\int_0^{\pi/2}\frac{\sin^2[t(j+k+1)]\sin^2[t(j-k)]}{\sin^2 t}\,\mathrm{d}t \quad \text{(B4)}$$

Futhermore

$$\sin^2[t(j-k)] = \frac{1-\cos[2t(j-k)]}{2} \quad \text{(B5)}$$

and

$$\frac{\sin^2[t(j+k+1)]}{\sin^2 t} = (j+k+1) + 2\sum_{p=1}^{j+k}(j+k+1-p)\cos(2pt) \quad \text{(B6)}$$

where (B6) makes use of the relationship[23]

$$\sin^2(m\theta)/\sin^2\theta = m + \sum_{p=1}^{m-1}(m-p)\cos(2p\theta) \quad \text{(B7)}$$

Combining (B4), (B5), and (B6) gives

$$I_1 = I_2 - I_3 \quad \text{(B8)}$$

where

$$I_2 = \frac{1}{\pi}\int_0^{\pi/2}[(j+k+1) + 2\sum_{p=1}^{j+k}(j+k+1-p)\cos(2pt)]\,\mathrm{d}t \quad \text{(B9)}$$

and

$$I_3 = \frac{1}{\pi}\int_0^{\pi/2}\cos[2t(j-k)]\{(j+k+1) + 2\sum_{p=1}^{j+k}(j+k+1-p)\cos(2pt)\}\,\mathrm{d}t \quad \text{(B10)}$$

Since $I_2 = (j+k+1)/2$ and $I_3 = (j+k+1)/2 - |j-k|/2$

$$I_1 = |j-k|/2 \quad \text{(B11)}$$

and

$$\prod_m e^{-2\langle\eta_m^2\rangle(Q_{jm}-Q_{km})^2} = e^{(-2kT/\kappa)|j-k|} \quad \text{(B12)}$$

which is eq 30.

References and Notes

(1) Berne, B.; Pecora, R. "Dynamic Light Scattering"; Wiley-Interscience: New York, 1976.
(2) Huang, W. N.; Frederick, J. E. *Macromolecules* **1974**, *7*, 34.
(3) Bauer, D. R.; Brauman, J. I.; Pecora, R. *Macromolecules* **1975**, *8*, 443.
(4) Han, C. C.; Yu, H. *J. Chem. Phys.* **1974**, *61*, 2650.

Macromolecules 1981, *14*, 1290–1298

(5) Ono, K.; Okano, K. *Jpn. J. Appl. Phys.* **1970**, *9*, 1356.
(6) Evans, G. T. *J. Chem. Phys.* **1979**, *71*, 2263.
(7) Fixman, M.; Evans, G. T. *J. Chem. Phys.* **1978**, *68*, 195. Fixman, M. *Ibid.* **1978**, *69*, 1527, 1538.
(8) Shore, J. E.; Zwanzig, R. *J. Chem. Phys.* **1975**, *63*, 5445.
(9) Barkley, M. D.; Zimm, B. H. *J. Chem. Phys.* **1979**, *70*, 2991.
(10) Allison, S. A.; Schurr, J. M. *Chem. Phys.* **1979**, *41*, 35.
(11) An early attempt to account for damped torsional oscillations was made by Tobolsky and DuPre (Tobolsky, A. V.; DuPre, D. B. *Adv. Polym. Sci.* **1969**, *6*, 103). However, they did not treat angular coordinates explicitly and ascribed the damping to the velocity of a given segment rather than to the *relative* velocity of adjacent segments as done in ref 9 and 10.
(12) Reference 1, p 149.
(13) Reference 1, Chapter 7.
(14) Brink, D. M.; Satchler, G. R. "Angular Momentum"; Oxford University Press: New York, 1968.
(15) Aragon, S.; Pecora, R. *J. Chem. Phys.* **1977**, *66*, 2506.
(16) Pecora, R. *J. Chem. Phys.* **1968**, *48*, 4126.
(17) Pecora, R. *J. Chem. Phys.* **1968**, *49*, 1032.
(18) Skolnick, J.; Helfand, E. *J. Chem. Phys.* **1980**, *72*, 5489.
(19) Kramers, H. A. *Physica (Utrecht)* **1940**, *7*, 284.
(20) Norisuye, T.; Yu, H. *J. Chem. Phys.* **1978**, *68*, 4038.
(21) Lin, Y.-H.; Wang, C. H. *J. Chem. Phys.* **1977**, *66*, 5578.
(22) Abromowitz, M.; Stegun, I. A. *Natl. Bur. Stand. (U.S.) Appl. Math. Ser.* **1964**, *No. 55.*
(23) Whittaker, E. T.; Watson, G. N. "A Course of Modern Analysis"; Cambridge University Press: London, 1973; p 171.

Considerations on the Multiple Scattering Representation of the Concentration Dependence of the Viscoelastic Properties of Polymer Systems

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ABSTRACT: The multiple scattering theory for the concentration dependence of the viscoelastic properties of polymer solutions is rederived with a discrete bead-type model for the polymer chains and the familiar Rouse and Zimm matrices. The use of the discrete chain model is helpful to eliminate errors arising from considering the limits of long wavelength, low frequencies, and long (essentially continuous) chains in improper orders or in an approximate fashion. The discrete chain representation enables us to prove the following theorems for *phantom polymer chains*: (i) There is no hydrodynamic screening, i.e., no Darcy's law retarding forces on the polymers, for individual chains at infinite dilution. (ii) Theorem i enables us to convert the multiple scattering theory correlation function for the frequency-dependent intrinsic viscosity identically into the Rouse–Zimm expression within the preaveraging approximation. (iii) The hydrodynamic screening is shown to vanish term by term in the multiple scattering expansion and, hence, to all orders in concentration. From theorem iii and results on the concentration dependence of the viscosity of suspensions of spheres, it becomes clear that the origin of hydrodynamic screening lies in the presence of entanglements and interchain interactions. The mathematical complexity of the description of entanglements leads us to consider only a qualitative phenomenological model of the hydrodynamic screening and the transition it induces from low-concentration Rouse–Zimm-type behavior to high-concentration Rouse-like hydrodynamic properties.

1. Introduction

The Rouse–Zimm theory[1,2] has been widely successful in providing a molecular basis for the understanding of the viscoelastic and frictional properties of individual polymer chains in solution.[3] Despite its enormous utility, the theory is limited to the case of infinite dilution (one polymer molecule), very low frequencies ($\lesssim 10^4$–10^6 Hz), and zero shear rate (a stationary fluid). A treatment of the higher frequencies requires a molecular understanding of the phenomena which have been classified under the phenomenological heading of internal viscosity, while a description at nonzero shear rates necessitates a fully nonlinear theory.

We have provided a comprehensive theory of the concentration dependence of the viscoelastic properties of polymer solutions based upon a multiple scattering formulation.[4-11] In this representation the fluid velocity field is represented as a superposition of all possible processes in which the incident fluid velocity field has its flow patterns disturbed, or scattered, by no polymer chains, by one chain, by two chains, etc., with all possible sequences of scattering by many chains. The theory has been implemented in dilute and in concentrated solutions. In the latter case an effective medium theory[6-10] is utilized to provide a physically simple self-consistent formulation of the concentration-dependent hydrodynamics. The infinite-dilution limit is found to agree with the Rouse–Zimm predictions of the frequency-dependent intrinsic viscosity $[\eta(\omega)]$, although a detailed proof has not yet been given to demonstrate that the multiple scattering representation correlation function expression for $[\eta(\omega)]$ is indeed equivalent to the Rouse–Zimm theory. Here we show, in fact, within the popular preaveraging approximation the complete equivalence of the two theories at infinite dilution.

The multiple scattering theory of Freed and Edwards is, however, also applicable for nonzero polymer concentrations. The theory has shown the importance of "hydrodynamic screening" in producing a transition from a Rouse–Zimm-like viscosity function, depending on $cM^{1/2}$ (in Θ solvents), where c is the polymer mass concentration and M is the molecular weight, at lower concentrations to a cM-dependent viscosity for high concentrations but nonmacroscopically entangled solutions. This

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