Dynamic Light Scattering and Viscoelasticity of a Binary Polymer Solution

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Received September 9, 1991; Revised Manuscript Received November 12, 1991

ABSTRACT: The effect of viscoelasticity on the dynamic light scattering spectrum of a binary polymer solution is examined using a hydrodynamic theory. It is shown that when the coupling of the concentration fluctuation to the viscoelasticity is present, the time correlation function of the concentration fluctuation is bimodal, consisting of a single-exponential decay and a group of relaxation modes, characterizing the relaxation of the longitudinal stress tensor of the binary solution. The rate constant of the single-exponential decay is equal to q^2D_c, where q is the amplitude of the scattering vector and D_c is the cooperative diffusion coefficient. The viscoelastic modes have rate constants spanning a wide dynamic range from the fast cooperative diffusion modes to the slowest stress relaxation modes. In appropriate limits, the present theory reduces to the result previously obtained by Brochard and de Gennes and that by Adam and Delsanti for the semidilute binary polymer solution using a transient gel model. In addition to binary solutions consisting of polymers of high molecular weight, the present result is also expected to apply to viscoelastic nonpolymeric liquids as well.

I. Introduction

Dynamic light scattering from a dilute polymer solution with a monodisperse molecular weight polymer is essentially characterized by a single exponentially decaying time autocorrelation function of the intensity of the scattered light. If the amplitude of the scattering vector q is sufficiently small such that $qR_g < 1$, where R_g is the mean radius of gyration of macromolecules in solution, then the exponential decay is due to translational diffusion of polymer in the solvent. Thus, by measuring the decay rate constant, one can obtain the translational diffusion coefficient, which is then related to the hydrodynamic radius of the macromolecule in solution.[1,2] For values of q where $qR_g > 1$, the intramolecular modes of the polymer also contribute to the scattering spectrum. The intramolecular motions do not bring about significant deviations from the exponential decay. Effects of the intramolecular motions on the dynamic light scattering spectrum in the dilute polymer solution have been the subject of earlier investigations and have been reviewed by Han and Schaefer.[3]

Increasing the polymer concentration slightly causes the diffusing coefficient to either decrease or increase with increasing polymer concentration, depending on the solvent quality. For good solvents, the diffusion coefficient increases with increasing concentration, but it decreases for poor solvents. In the dilute concentration regime, there is no significant change in the shape of the autocorrelation function when the polymer concentration is changed. However, a further increase in the polymer concentration beyond the overlap concentration, defined by $C^* = M/[(4/3)\pi Rg^3]N_A$, results in major deviations from the single-exponential decay in the time autocorrelation function of the scattered light.[4-16] Here N_A is Avogadro's number; M is the molecular weight. The overlap concentration C^* separates the dilute from the semidilute regime. Above C^*, neighboring polymer chains begin to overlap, and the hydrodynamic interaction is screened. The effect results in a complex concentration dependence for the diffusion coefficient. Using a transient gel model, de Gennes developed a scaling theory for the semidilute solution in thermodynamically good solvents.[17-19] The central prediction of the theory is that a single characteristic length exists in such a system and, consequently, only one dynamic process, characterized by a cooperative diffusion coefficient (D_c), is expected. He has related the cooperative diffusion coefficient D_c to the osmotic modulus M_π and gel modulus M_0 by $D_c = (M_\pi + M_0)/\xi\rho_2^0$. Here ξ is the friction coefficient due to solvent molecules and ρ_2^0 is the concentration of the polymer in solution (g/mL). At low frequency the gel modulus contribution is negligible, and the cooperative diffusion coefficient is determined only by the osmotic modulus M_π ($D_\pi = M_\pi/\xi\rho_2^0$), whereas at very high frequency the cooperative diffusion coefficient is determined by the gel modulus M_0 ($D_g = M_0/\xi\rho_2^0$). The hydrodynamic correlation length ζ_h is defined by $\zeta_h = kT/6\pi\eta D_c$. The variation of ζ_h with concentration is rather complex, depending on the solvent quality. The complex concentration dependence of D_c or ζ_h has been discussed by Han and Schaefer in terms of scaling theory.[3]

Experimentally it is found, however, that although the cooperative diffusion process dominates in semidilute solutions, other modes are also present, and they lead to deviation from a single-exponential decay of the autocorrelation function, becoming more pronounced as the solvent quality is decreased. Adam and Delsanti have modified de Gennes' theory by allowing the transient gel to relax. They obtained a q^2-dependent collective diffusion mode and a single q-independent relaxation viscoelastic mode as the result.[5] The q^2-dependent collective diffusion mode was referred to as the fast mode and the q-independent relaxation viscoelastic mode as the slow mode associated with the chain disengagement relaxation.

Until 1988, the line-shape deviation from the single-exponential decay was analyzed mostly by the cumulant method.[6] But the cumulant method is only applicable for the correlation function at short times and does not provide clear information about the global nature of the line-shape deviation. Following the work of Wang et al.,[20,21] who first used the CONTIN program[22] to extract the continuous retardation time spectrum of the bulk polymer melt from the DLS spectrum,[23] Brown, Stepanek, and co-workers have analyzed the shape of the autocorrelation function of the semidilute polymer solution using the same technique.[24-27] Their CONTIN analysis of the semidilute polymer solution shows a bimodal distribution in the relaxation time spectrum, with one mode having the relaxation rate proportional to q^2 and the other consisting of a group of closely spaced q-independent modes having relaxation times stretching from the fast to the slowest

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viscoelastic mode. The diffusion coefficient associated with the q^2-dependent mode in the semidilute solution is associated with the cooperative diffusion coefficient, D_c. While the cooperative diffusion coefficient is found to increase with increasing polymer concentration, above some limiting molecular weight, it does not change with the molecular weight. The molecular weight independence suggests that concentration fluctuations in the semidilute polymer solution relax without overall chain motion. On the other hand, the relaxation times of the q-independent modes were found to increase strongly with increasing molecular weight, thereby suggesting that overall chain motion is involved in this case.

Brown, Stepanek, and co-workers further examined similarities between the relaxation time distributions for polystyrene in semidilute solutions in the θ solvent, bis(2-ethylhexyl)phthalate (dioctyl phthalate, DOP), obtained from dynamic light scattering and dynamic mechanical (shear) measurements.[4,28,29] They found that the dynamic processes probed at long times for both techniques are characterized by a similar dynamic range of relaxation; however, as the solvent quality changes, the distribution of relaxation times from dynamic light scattering appears to be more sensitive in the slow part of the spectrum.[28,29] The empirical approach ventured by Brown, Stepanek, and co-workers has motivated this author to undertake a theoretical analysis to clarify the effect of viscoelasticity on the DLS spectrum.[30] In this paper, we extend the previous result by performing a perturbation calculation to simplify the dispersion equation previously derived in ref 30. We present the result explicitly in terms of the time autocorrelation function. The result should facilitate a direct comparison with the experiment using an electronic correlator.

The outline of this paper is as follows. In section II, we review the technique previously used to relate the concentration fluctuations with the viscoelasticity of a binary solution. In section III, we discuss the effect of viscoelastic relaxation on the time correlation function of concentration fluctuations. The perturbation calculation and comparison with previous theories are also made in this section. A conclusion is given in section IV.

II. Concentration Fluctuations and Viscoelasticity

For the polymer solution in the dilute and semidilute region, the refractive index is modulated more strongly by concentration than by density fluctuations. As a result, the dynamics of concentration fluctuations determines the light scattering spectrum. To give the continuity of the present paper and obtain equations needed for this paper, we review in this section how the equations well-known in linear viscoelasticity theory can be used to describe the coupling of the viscoelastic property of the polymer solution to the concentration fluctuation spectrum. We start with the linearized hydrodynamic equation[31]

$$\frac{\partial}{\partial t}(\delta\rho) = -\nabla\cdot(\rho\mathbf{v}) \approx -\rho_0\nabla\cdot\mathbf{v} \tag{1}$$

supplemented with the constitutive equation for the linear viscoelastic liquid[1]

$$\rho_0\frac{\partial}{\partial t}\mathbf{v} = -\nabla p + \int_0^t \mathrm{d}t'\,[\{K(t-t') + {}^1/_3G(t-t')\}\,\nabla(\nabla\cdot\mathbf{v}(t')) + G(t-t')\nabla^2\mathbf{v}(t')] \tag{2}$$

where ρ_0 is the equilibrium mass density, $\mathbf{v}$ is the fluid velocity, K is the compressional modulus, and G is the shear modulus. $\delta\rho$ is the fluctuation from the equilibrium density.

For the bulk polymer the local pressure fluctuation is proportional to the density fluctuation, neglecting the temperature fluctuation contribution which does not fall in the time window of 10–10^{-6} s considered in this paper. Equations 1 and 2 complete the description of the bulk polymer system.[23] But for the polymer solution, in addition to the density fluctuation, the local pressure fluctuation is also affected by the polymer concentration due to the osmotic pressure. Thus, the ∇p term in eq 1 consists of two contributions

$$\nabla p = \frac{1}{\rho_0\chi_T}\nabla\rho + \left(\frac{\partial p}{\partial\rho_2}\right)_{T,\rho}\nabla\rho_2 \tag{3}$$

where χ_T is the isothermal compressibility of the polymer solution. The isothermal sound velocity v_T is equal to $1/(\rho_0\chi_T)^{1/2}$. Because of the presence of the $\nabla\rho_2$ term, which is related to the osmotic pressure, the viscoelastic property and concentration fluctuations are mixed in the polymer solution. Here ρ_2 is in terms of the number of grams of polymer per unit volume.

Equations 1–3 can be combined to yield

$$\frac{\partial^2\rho}{\partial t^2} = \frac{1}{\rho_0\chi_T}\nabla^2\rho + \left(\frac{\partial p}{\partial\rho_2}\right)_{T,\rho}\nabla{\rho_2}^2 + \frac{1}{\rho_0}\int_0^t\mathrm{d}t'\left[K(t-t') + \frac{4}{3}G(t-t')\right]\nabla^2\left(\frac{\partial\rho(t')}{\partial t'}\right) \tag{4}$$

Equation 4 is a differential integral equation containing both density and concentration variables. To complete the description of the dynamics of the concentration fluctuation, we need another hydrodynamic equation to describe the concentration variable. For this we followed the work of Bearman and Kirkwood (BK)[32] and found that the equation of motion for the concentration variable of the solute (polymer) is given by (neglecting the convection terms, which contribute to second order)

$$\frac{\partial}{\partial t}(\rho_2\mathbf{v}_2) = \nabla\cdot\sigma_2 - \rho_2\nabla\mu_2 + \rho_2\mathbf{F}_2 \tag{5}$$

where σ_2 is the partial stress tensor acting on the polymer component 2. $\mathbf{v}_2$ is the local center of mass velocity of component 2; ρ_2 is its concentration, and μ_2 is the chemical potential (the Gibbs free energy per unit mass). $\mathbf{F}_2$ is the average frictional force per unit mass exerted on molecules of species 2.

For the binary system, consisting of a polymer component and a small molecular solvent, we assume that the total stress tensor is the sum of contributions from the solvent and from the polymer molecules. Thus, the stress tensor for the polymer component is the total stress tensor minus that from the solvent contribution. However, for light scattering, the solvent viscosity terms contribute only to the damping of the sound wave at high frequency (10^9 Hz), and these terms make no contribution to the spectrum of the concentration fluctuations in the polymer solution at a frequency less than 10^6 Hz.

To proceed, we eliminate $\mathbf{v}$ and $\mathbf{v}_2$ by using eq 1 and the continuity equation for component 2 and obtain

$$\frac{\partial^2}{\partial t^2}(\delta\rho_2) = \frac{1}{\rho_0}\int_0^t\mathrm{d}t'\,M(t-t')\,\frac{\partial}{\partial t'}(\nabla^2\delta\rho) - \frac{\eta_l}{\rho_0}\frac{\partial}{\partial t}(\nabla^2\delta\rho) + \rho_2\nabla^2\mu_2 - \rho_2\nabla\cdot\mathbf{F}_2 \tag{6}$$

where $M(t)$ is the longitudinal modulus of the solution equal to $\{K(t) + (4/3)G(t)\}$, and η_l is the longitudinal viscosity of the solvent equal to $[\kappa_1 + (4/3)\eta_1]$.

For eq 6 to be useful we also need to further express $\nabla^2\mu_2$ and $\nabla\cdot\mathbf{F}_2$ in terms of concentration ρ_2 and pressure p (or density ρ). By connecting the frictional force with the diffusion mass current, and from the Gibbs–Duhem equation, we show in ref 30 that

$$\nabla\cdot(\rho_2\mathbf{F}_2) = \xi\frac{\partial}{\partial t}(\delta\rho_2) \tag{7}$$

and

$$\rho_2\nabla^2\mu_2 = \phi_2 {\upsilon_{\mathrm{T}}}^2\nabla^2\rho + \left[\phi_1\left(\frac{\partial\pi}{\partial\rho_2}\right)_{p,T} - {\upsilon_{\mathrm{T}}}^2\phi_2\left(\frac{\partial\rho}{\partial\rho_2}\right)_{p,T}\right]\nabla^2(\delta\rho_2) \tag{8}$$

where $\xi = (\rho_0/M_1M_2)\xi_{12}$, ξ_{12} is the frictional coefficient and is given in terms of the intermolecular potential;[33] π is the osmotic pressure, and ϕ_1 and ϕ_2 are the volume fractions of the solvent and polymer, respectively. The friction coefficient ξ, due to solvent molecules in the semidilute polymer solution, is higher than 10^7 Hz.[34]

Equations 4 and 6, together with the auxiliary equations, eqs 7 and 8, are the coupled equations needed for the calculation of the quasielastic light scattering spectrum of a binary polymer solution.

Although the coupled equations, eqs 4 and 6, can be converted into an initial value problem and solved exactly to obtain the light scattering spectrum, here we are interested in an approximate solution suitable for describing the effect of the viscoelasticity of the polymer solution on the quasielastic light scattering spectrum arising from the concentration fluctuations. As an approximation, we neglect the pressure fluctuation term ∇p. This term contributes to the spectrum at the hypersonic frequency and can be neglected in the description of the quasielastic light scattering spectrum.[30] By neglecting the pressure fluctuation term, the concentration fluctuation becomes proportional to the density fluctuation (cf. eq 3) and the concentration equation, eq 6, is decoupled from the density equation, eq 4. The decoupled equation can be solved by standard techniques. The result gives

$$\delta\hat{\rho}_2(q,\omega) = \frac{1}{\Delta(\omega)}(\hat{m}(\omega) + \xi)\,\delta\rho_2(q) \tag{9}$$

where $\delta\hat{\rho}_2(q,\omega)$ is the Fourier transform in space and the Laplace transform in time of $\delta\rho_2(r,t)$, and

$$\Delta(\omega) = i\omega\hat{m}(\omega) + \phi_1 q^2\left(\frac{\partial\pi}{\partial\rho_2}\right)_{p,T} + i\omega\xi \tag{10}$$

The spectral power density of the scattered light can be obtained by first multiplying $\delta\hat{\rho}_2(q,\omega)$ with $\delta\rho_2{}^*(q)$ and then taking the real part after carrying out an ensemble average. As a result, we obtain

$$I(q,\omega) = \left(\frac{\partial\epsilon}{\partial\rho_2}\right)^2\langle|\delta\rho_2(q)|^2\rangle S(q,\omega) \tag{11}$$

where $S(q,\omega)$ determines the spectrum of the scattered light and is given by

$$S(q,\omega) = \mathrm{Re}\left(\frac{\hat{m}(\omega) + \xi}{\Delta(\omega)}\right) \tag{12}$$

The quantity $\hat{m}(\omega)$ that appears in eqs 10 and 12 is given by

$$\hat{m}(\omega) = \frac{q^2}{{\rho_2}^0}\beta\int_0^\infty \mathrm{d}t\, e^{-i\omega t}M(t) \tag{13}$$

We note in eq 13 that the longitudinal modulus $M(t)$ entering the concentration fluctuation equation is modified by the factor proportional to $(\partial\rho/\partial\rho_2)_{T,p}$. It is easy to show that this factor is equal to $(\bar{V}_1 - \bar{V}_2)/\bar{V}_1$, where $\bar{V}_1$ and $\bar{V}_2$ are the partial specific volumes of solvent and solute, respectively. Here we introduce the coupling parameter β which is equal to $(\rho_2{}^0/\rho_0)(\partial\rho/\partial\rho_2)_{T,p}$. It determines the effectiveness of the coupling of the concentration fluctuation to the viscoelasticity of the polymer solution. The coupling is important if there is a large difference in the partial specific volumes of the polymer and solvent components in the solution.

The dispersion relationship of the concentration fluctuation dynamics is determined by the function $\Delta(\omega)$, which in turn, is determined by the osmotic modulus, given by $\rho_2(\partial\pi/\partial\rho_2)_{T,p}$, and by the dynamic longitudinal modulus of the polymer solution, given by

$$M^*(\omega) = i\omega\int_0^\infty \mathrm{d}t\, e^{-i\omega t}M(t) = M'(\omega) + iM''(\omega) \tag{14}$$

where $M'(\omega)$ and $M''(\omega)$ are the real and imaginary parts of the longitudinal modulus, respectively.

III. Effect of Viscoelastic Relaxation

Equation 12 is an important result. It describes the effect of the viscoelasticity of the polymer solution on the concentration fluctuation spectrum. Clearly, in addition to the osmotic pressure fluctuation, the dynamic longitudinal modulus also plays an important role. However, it should be emphasized that only for the polymer solution with a nonvanishing β parameter can the relaxation behavior of the longitudinal stress modulus affect the dynamic light scattering spectrum. The longitudinal stress modulus has a wide distribution of relaxation times, and we expect for the coupled system an extensive mixing between the viscoelastic relaxational process and the osmotic pressure fluctuation in the 10^{-1}–10^6 Hz frequency range. As a result, we anticipate observing a rather complex photon correlation spectrum in the semidilute polymer solution.

In passing, one should note that only the viscoelastic process, and not the osmotic effect, is probed by the dynamic mechanical relaxation technique.[1] Thus, the combination of dynamic light scattering and dynamic mechanical relaxation techniques will provide a powerful method to characterize the relaxation process in the semidilute polymer solution.

The stress relaxation modulus in general displays a broad distribution of relaxation times; thus we write

$$M(t) = \sum_i M_i e^{-t/\tau_i} \tag{15}$$

where M_i is the amplitude of the longitudinal modulus associated with the relaxation time τ_i. Using eqs 14 and 15, we can write the dynamic modulus as

$$M^*(\omega) = \sum_i\left(M_i - M_i\frac{1}{1 + i\omega\tau_i}\right) \tag{16}$$

It is easy to see that, at low frequency, the viscoelastic relaxation will not affect the concentration fluctuation spectrum. If τ_l is the longest relaxation time (or the terminal relaxation time) of the stress modulus, then, at frequency ω such that $\omega < \tau_l{}^{-1}$, the second term will cancel the first term on the right-hand side of eq 16, and the effect due to the dynamic modulus of the polymer solution is negligible. In this case, the concentration fluctuation spectrum has a Lorentzian line shape (or a single-exponential time correlation function), with the half-width at half-height equal to q^2D_π, where D_π is the mutual diffusion coefficient owing to the osmotic pressure fluctuation and is given by

$$D_\pi = \phi_1\left(\frac{\partial\pi}{\partial\rho_2}\right)_{p,T}\frac{1}{\xi} \tag{17}$$

The expression for the mutual diffusion coefficient is, with respect to the center of mass reference frame, identical to that obtained previously.[34]

While for $\omega < \tau_1^{-1}$ the expression for $S(q,\omega)$ is determined only by q^2D_π, the situation is more complex at higher frequencies, due to the mixing of the viscoelastic process. If the elastic part of the relaxation modulus is much greater than the relaxed part, i.e., when the condition $\omega\tau_i \gg 1$ is satisfied for all viscoelastic modes, the second term on the right-hand side of eq 16 is negligible. In this case, the light scattering spectrum is also a Lorentzian, with the half-width at half-height equal to D_c. Here D_c is the cooperative diffusion coefficient, given by

$$D_c = D_\pi + \beta\frac{M_0}{\xi\rho_2^{\,0}} \tag{18}$$

where $M_0 = \sum_i M_i$, the amplitude of the longitudinal stress modulus, which is identical to de Gennes' result, provided that $\beta = 1$.[17]

However, de Gennes' result was obtained by a very different method, using a pseudogel model to describe the dynamics of the semidilute solution consisting of high molecular weight polymers.[17-19] In the semidilute concentration region, neighboring chains are overlapped and the semidilute solution is considered as a transient gel with a mesh size of length l (the correlation length), where the light scattering probing wavelength q^{-1} is larger than the correlation length l (i.e., $ql \ll 1$). At the frequency ω greater than τ_R^{-1}, where τ_R is a relaxation time for complete disentanglement of one chain from the others, de Gennes argued that the equation of motion for the longitudinal displacement of the polymer will be governed by both frictional and restoring forces. The restoring force arises from the osmotic pressure and the elastic modulus of the polymer chains. From the equation of motion, de Gennes obtained a collective diffusion coefficient D_c equal to $[M_0 + \rho_2^{\,0}(\partial\pi/\partial\rho_2)_{p,T}]/(\xi\rho_2^{\,0})$. If the osmotic force is neglected, de Gennes' theory reduces to the result of Tanaka, Hocker, and Bennedek (THB),[35] who pioneered the measurement and interpretation of the dynamic light scattering spectrum from thermally excited displacement fluctuations in polyacrylamide gels.

We have obtained eq 18 without assuming the transient gel model. What is needed is the assumption of a time-independent longitudinal modulus; i.e., only the elastic part of the relaxation modulus makes the contribution to the dynamics of the concentration fluctuations. Thus, de Gennes' result corresponds to a "frozen" gel for which the stress modulus is not allowed to relax. For the solution containing high molecular weight polymers, there will be a plateau region in which the stress modulus is nearly constant.[1] In this region, we expect de Gennes' theory to be valid, provided that β does not vanish. However, for a solution consisting of polymers of low molecular weight or for nonpolymeric viscoelastic fluids, the stress plateau may be very narrow or nonexistent.[1] In such situations, de Gennes' result will not apply.

To describe such systems, we consider the case in which the condition $\omega\tau_i > 1$ is satisfied for all viscoelastic modes, and the $M_i/(1 + \omega\tau_i)$ terms; i.e., all of the second terms on the right-hand side of eq 16 are small compared with the first (elastic) term so that we can treat them as a perturbation. By considering the second terms as first order, we can show by a straightforward calculation that eq 9 is reduced to

$$\delta\hat{\rho}_2(q,\omega) = \frac{\delta\rho_2(q)}{i\omega + D_cq^2}\{(1 + (\beta q^2M_0/\rho_2^{\,0}\xi)/(i\omega + q^2D_c) + (q^2D_c/\xi)\hat{m}(\omega)/(i\omega + q^2D_c) + O(\hat{m}^2)\} \tag{19}$$

With some additional algebra, eq 19 can be converted into an equation in the time domain as

$$\delta\rho_2(q,t) = \left\{[1 + (q^2\beta M_0/\xi\rho_2^{\,0})t]e^{-q^2D_ct} + \left(\frac{D_cq^4}{\xi\rho_2^{\,0}}\right)\beta\int_0^t se^{-D_cq^2s}M(t-s)\,\mathrm{d}s + ...\right\}\delta\rho_2(q) \tag{20}$$

The normalized autocorrelation function of concentration fluctuations, which is experimentally measured by using an electronic correlator, can be obtained by inserting eq 15 for $M(t)$ into eq 20 and then carrying out the time integration.

After this is accomplished, we obtain

$$g(q,t) \equiv \frac{\langle\delta\rho_2(q,t)\ \delta\rho_2{}^*(q)\rangle}{\langle|\delta\rho_2(q)|^2\rangle} = Ae^{-D_cq^2t} + \sum_i B_ie^{-t/\tau_i} \tag{21}$$

where

$$A = 1 + (\beta q^2M_0/\xi\rho_2^{\,0})t - \frac{D_cq^4}{\xi\rho_2^{\,0}}\beta\sum_i\left[\frac{M_it}{D_cq^2 - \tau_i^{-1}} + \frac{M_i}{(D_cq^2 - \tau_i^{-1})^2}\right] \tag{22a}$$

$$B_i = \frac{D_cq^4}{\xi\rho_2^{\,0}}(\beta M_i)/(D_cq^2 - \tau_i^{-1})^2 \tag{22b}$$

Equation 21 shows that of the correlation function $g(q,t)$ is divided into two groups (bimodal), consisting of one single-exponential decay with amplitude A which depends linearly on time, and a group of relaxation modes consisting of time-independent amplitudes B_i, characterizing the structural (longitudinal stress) relaxation of the binary solution. The time constant of the single-exponential decay term depends on q^2, and the time constant of each of the structural relaxation modes is q-independent. The amplitude factors A and B_i are, in general, wave vector dependent. In the small q region such that $D_cq^2 \ll \tau_i^{-1}$, both A and B_i have a q^4 dependence; however, in the large wave vector regime so that $D_cq^2 \gg \tau_i^{-1}$ for all structural modes, both A and B_i become q-independent, and they are given by

$$A = 1 - \frac{\beta M_0}{\xi\rho_2^{\,0}D_c} = 1 - \beta M_0/(M_0 + M_\pi) \tag{23a}$$

and

$$B_i = \beta M_i/(M_0 + M_\pi) \tag{23b}$$

where $M_\pi = \phi_1\rho_2^{\,0}(\partial\pi/\partial\rho_2)_{p,T}$ is the osmotic modulus. Equations 21 and 23 show that, as the intensity of the stress relaxation (viscoelastic) mode increases, the intensity of the cooperative diffusion mode decreases. In other words, the viscoelastic mode intensity grows at the expense of the collective diffusion mode. Because of the presence of the quantity osmotic modulus M_π in the denominator of the B_i expression, the amplitude of the viscoelastic mode is considerably reduced for the solutions with a large osmotic modulus. For polymers in good solvents, polymer chains are extended and the solvent molecules strongly solvate the polymer chains. Thus, at a polymer concentration the osmotic pressure in good solvents is considerably larger than that in Θ solvents. As a result, the amplitude of the viscoelastic mode B_i is smaller in the good solvents. Thus, due to the presence of M_π in the denominator, the viscoelastic relaxation spectrum deduced from dynamic light scattering may differ from that deduced from the mechanical relaxation measurement. In the $D_c q^2 \gg \tau_i$ regime, the time dependence terms in A also cancel out, and the amplitude factor A becomes independent of both q and t. However, in the $D_c q^2 \ll \tau_i$ regime, the time dependence does not cancel out, and the diffusion mode is not a simple single-exponential but rather of the type $(a + bt)\exp(-D_c q^2)$. However, the experimental data so far obtained have not been analyzed in this manner.

It is interesting to consider the case of one single stress relaxation mode, as was assumed in de Gennes' transient network model. In the literature of semidilute polymer solutions, the structural relaxation mode has been called the slow mode, and the collective diffusion mode is known as the fast mode, due originally to Adam and Delsanti.[5] According to eq 23a,b, the ratio of the amplitudes of the collective diffusion and the structural relaxation modes is (assuming $\beta = 1$)

$$\frac{A}{B} = \frac{1 - M_0/(M_0 + M_\pi)}{M_0/(M_0 + M_\pi)} = \frac{M_\pi}{M_0} \tag{24}$$

This result is identical to the fast mode–slow mode amplitude ratio of Adam and Delsanti,[5] who modified de Gennes' frozen gel model to allow for structural relaxation. However, as pointed out above, the stress modulus has in general a wide distribution of relaxation times. Since their calculation only takes into account the chain disentanglement relaxation, the result will not be correct for describing the effect of linear viscoelastic properties of polymer solutions on the dynamic light scattering spectrum.

In order to properly describe the viscoelastic behavior of high molecular weight polymers in the semidilute solution, a distribution of structural relaxation modes covering the dynamic region of the fast collective diffusion to the slowest mode connected with the characteristic disentanglement time of the whole transient network has to be considered. We again emphasize, however, that the assumption of a transient network is not necessary in the present approach. Furthermore, the existence of the coupling parameter β is necessary to bring about the coupling of the osmotic pressure (or concentration) fluctuation and viscoelasticity. In the semidilute solution, the volume of the solution is larger than the sum of the individual components, β is positive but not equal to 1.

As shown above, β is proportional to the change of the solvent density with respect to the polymer concentration. The quantity is usually positive, due to the fact that polymers in general have a larger density than most solvents. An exception is CCl_4, whose density (=1.52 g/cm^3) is larger than those of most polymers. Thus, adding a polymer to the CCl_4 solution generally decreases rather than increases the solution density. This gives rise to a negative β unless the polymer–CCl_4 interaction causes a large volume decrease. It would be interesting to study the concentration dependence of the dynamic light scattering spectrum of the polymer/CCl_4 system to examine the effect of negative β. In general, β is concentration dependent. In good solvents, the change in the solution density with concentration is not expected to be as large as that in Θ and poor solvents, due to the fact that polymer chains are greatly solvated by solvent molecules in good solvents. Thus, in good solvents, a smaller β is expected for polymers in the semidilute regime. In accordance with eq 23b a smaller β and larger osmotic modulus of the semidilute solution in the good solvent will render the viscoelastic modes weaker in the dynamic light scattering spectrum than in the Θ solvent. This prediction is qualitatively in agreement with the experiments.[4] However, a quantitative verification of the theoretical result would require an experimental determination of β and M_0. This work is presently in progress in our laboratory.

One may proceed to obtain the general result by expressing the spectral power density of the scattered light in terms of the whole frequency dependence in the longitudinal stress modulus. But the general case has been considered in our previous paper,[30] and we refer the interested reader to that reference.

IV. Summary and Conclusions

Mechanical relaxation and dynamic light scattering are techniques which are intimately related. Efforts have been made to find a correlation of dynamics data of polymer liquids obtained by dynamic light scattering and by mechanical relaxation techniques. Making the correlation not only helps in the understanding of the light scattering spectrum but also helps in bringing about the unification of the information that has been separately obtained by the two techniques. In the one-component bulk polymer melt, the density–density time correlation function is shown to be equivalent to the relaxational bulk longitudinal creep compliance.[23] In this paper, we extend the earlier work on bulk polymers and consider problems involved in correlating dynamic light scattering with mechanical relaxation for a binary solution. We analyze the effect of viscoelasticity on the dynamic light scattering spectrum of the binary solution. The result shows that when the coupling of the concentration fluctuation and the viscoelastic effect is present, the time dependence in the time autocorrelation function of concentration becomes bimodal, consisting of one single-exponential decay with an amplitude which in general depends linearly on time and a group of relaxation modes consisting of time-independent amplitudes, characterizing the structural (longitudinal stress) relaxation of the binary solution. The rate constant of the single-exponential decay term is equal to $q^2 D_c$, but the time rate constant of each of the structural relaxation modes is q-independent. The cooperative diffusion coefficient D_c derives contributions both from the osmotic pressure fluctuation and from the viscoelasticity affecting mechanical properties of the binary solution. For the semidilute polymer solution, in which chains are overlapped, the present result reduces to the result of Adam and Delsanti, provided that the coupling coefficient, β, is equal to 1 and there is only one stress relaxation mode. However, we have shown that the q-independent modes can have their positions anywhere in the dynamic viscoelastic spectrum and are not just restricted to slow modes. Since the present calculation is based on linear viscoelastic theory and does not require the transient gel model, our result should have a wide range of applicability. Description of the dynamic light scattering spectrum of binary solutions with a distribution of longitudinal stress relaxation times, or for solutions consisting of small molecular weight polymers, for which the theories of de Gennes or Adam and Delsanti will not apply, can be anticipated from the present theory.

However, although dynamic light scattering and mechanical relaxation measurement of polymer solutions yield closely related information, there exist significant differences in the relative contributions of the corresponding components in the distributions of the relaxation time spectra obtained by the two techniques. In addition, since only the longitudinal modulus $M(t)$ enters into the theory of DLS, unless the dynamics underlying $M(t)$ is similar to that of $G(t)$, there will not be a direct one to one comparison between the results of the mechanical shear modulus measurement and DLS. Experimental investigations are needed for the clarification.

Acknowledgment. This work is supported in part by a grant from the National Science Foundation and Exxon Chemical Co.

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