Macromolecules

Volume 11, Number 5 September–October 1978

Theory of Concentration Dependence of Polymer Relaxation Times in Dilute Solutions

M. Muthukumar and Karl F. Freed*

The James Franck Institute and The Department of Chemistry,
The University of Chicago, Chicago, Illinois 60637. *Received March 3, 1978*

ABSTRACT: The Freed–Edwards theory of the concentration dependence of the hydrodynamics of polymer solutions is generalized to consider the concentration dependencies of the Rouse mode relaxation times at low frequencies and at low, but finite, concentrations in both good and Θ solutions. It is shown that the concentration dependencies of the Rouse mode relaxation times are of the form $\tau_p = \tau_p{}^0(1 + c\mathcal{A}p^{-\kappa} + \ldots)$, to lowest order in the concentration, c, where p is the Rouse mode index and $\tau_p{}^0$ is the infinite dilution lifetime. κ is 0.5 for Θ solutions and 0.65–0.8 for good solutions. An explicit expression for the positive constant $\mathcal{A}$ is given and its dependence on the extent of excluded volume effect is discussed. An expression for the frequency dependent Huggins coefficient is derived. The dimensionless ratio, γ, used to characterize the experimental limiting concentration dependence of the viscoelastic properties of polymer solutions, is calculated in the framework of our theory. γ is obtained as 2.4366 for Θ solutions and in the range of 2.7394 to 2.8445 for good solvents in reasonable agreement with data on polystyrene.

I. Introduction

Theories are available to describe the dynamic viscoelastic properties for polymer solutions at infinite dilution.[1,2] Extensive measurements of dynamic viscoelastic properties of several polymers at very low concentrations show that the infinite dilution behavior in Θ solvent corresponds to the theory of Zimm[3] at sufficiently low frequencies. In good solvents the results can be described in the theory of Tschoegl[4] with intermediate hydrodynamic interaction.

At finite concentrations, all the Rouse modes, in principle, must develop concentration dependencies. In order to interpret their experimental data, Johnson et al.[5] consider simple models because of the lack of theories of the concentration dependence of viscoelastic properties of polymer solutions. Their models involve two extreme cases as follows: (i) The relaxation frequencies of all the Rouse modes are shifted equally due to the finite concentration; (ii) Only the relaxation frequency of the lowest mode is affected by concentration, and the rest of the Rouse modes behave as if in infinite dilution. Comparing the simple model prediction with their experimental measurements, they conclude that case (ii) is closer to the reality, but that the deviation from experimental values is due to the omission of the smaller concentration dependence of the lifetimes of higher modes.

Thus, it is of interest to consider a theory of the concentration dependence of polymer dynamics at finite, but low, concentrations in which all of the Rouse mode lifetimes may be affected. Recently, a theory of polymer viscosity in concentrated solutions has been presented by Freed and Edwards.[6-8] Hence, we generalize the Freed–Edwards theory to consider the frequency dependence of the viscosity at low, but finite, concentration of the polymer solution in both good solvents and Θ solvents.

In this paper, we ignore the presence of internal viscosity because the experiments of interest involve sufficiently low frequencies that this extra loss mechanism is not required. However, either the phenomenological form of Peterlin or any other form, that would result out of the major efforts pursued by different research groups at present, can readily be incorporated into the general theory presented here without any difficulty.

In order to consider the frequency dependence of the viscosity at low, but finite, concentrations of the polymer solution a Rouse–Zimm model is utilized for systems under Θ conditions. A concentration dependence of the Rouse-mode relaxation rates arises because of the following physical processes: Interpolymer hydrodynamic interactions imply that, say, monomer i or chain α has hydrodynamic interactions with other chains β which, in turn, have hydrodynamic interactions with monomers $j \neq i$ on α. This leads to a concentration dependent indirect (i.e., via other chains) hydrodynamic interaction between all pairs of monomers i and j on each chain α. Just as the direct (zero concentration, Oseen) hydrodynamic interactions change all of the Rouse relaxation rates into the Rouse–Zimm values, the indirect hydrodynamic interactions provide an additional *concentration-dependent* portion to these rates at finite concentrations. The indirect hydrodynamic interactions occur in the static limit, but they also acquire a frequency dependence by virtue of the

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dynamics of the polymers. This frequency dependence, however, is found to only affect numerical coefficients.

In good solvents a Rouse model for the chain backbone is untenable, so we utilize a Tschoegl type model which contains a nonuniform scaling of the bead spring force constants by factors of $|i-j|^{1-\nu}$. In addition, the effects of interchain excluded volume are modeled by the inclusion of a concentration dependence to these non-Rouse backbone force constants. Again the concentration dependent indirect hydrodynamic interactions provide a concentration dependent contribution to the relaxation rates of the chain modes (which we term "Rouse modes").

Before presenting the outline of this paper, we briefly summarize the important results derived in this paper for the benefit of experimentalists who are uninterested in the mathematical details.

(i) First, all the Rouse mode relaxation times, τ_p, develop concentration dependencies of the form

$$\tau_p = \tau_p{}^0(1 + c\mathcal{A}p^{-\kappa} + ..) \tag{I.1}$$

to lowest order in the concentration, c. Here p is the Rouse mode index, $\tau_p{}^0$ is the infinite dilution lifetime, and $\mathcal{A}$ and κ are positive constants, both depending on the extent of the presence of excluded volume effect [see eq V.3]. κ is $^1/_2$ for Θ solvent systems in the range of 0.65 to 0.80 and for good solvent systems. Thus, all the Rouse mode relaxation times are lengthened by an increase in concentration of the polymer solution, the lowest mode being affected the most and the higher ones being affected progressively less.

(ii) From the values of κ, it is shown that the concentration dependence of the Rouse mode relaxation times is more pronounced in a Θ solvent than in a good solvent. However, the decreasing importance of the concentration dependent shift of the lifetimes of the higher Rouse modes becomes more pronounced in a good solvent.

(iii) A dimensionless ratio, γ, has been defined in the literature[5] as a very useful experimental measure of the development of the limiting concentration dependence of the viscoelastic properties of polymer solutions. We have calculated this quantity in the framework of our theoretical derivation. It is found to be independent of $\mathcal{A}$ for $\omega\tau_1 << 1$, and for this low frequency range we calculate the values

$$\gamma = 2.4366 \text{ for a } \Theta \text{ solvent}$$

$$\gamma = 2.7394\text{–}2.8445 \text{ for a good solvent} \tag{I.2}$$

(iv) A discussion of the frequency dependent Huggins coefficient shows that the Huggins coefficient is directly proportional to $\mathcal{A}$. Hence, the experimental determination of the Huggins coefficient can be utilized to obtain an experimental value of $\mathcal{A}$ and consequently the magnitude of the leading concentration dependence of the various Rouse mode relaxation times under any given extent of excluded volume effect.

The organization of the paper is as follows. In section II, we review the basic physical content of the Freed–Edwards theory and generalize the important results for good solvents and for finite frequencies of the experimental probe. The dynamic mean-square segment-to-segment distance and the effective concentration dependent hydrodynamic interaction tensor are the basic ingredients of the theory for the description of the concentration dependent mode lifetimes and dynamic viscosity. In section III, we discuss the concentration dependence of the random thermal forces in the fluid, which drive the Brownian motion of the polymer chains, to derive the concentration dependent dynamical mean-square bead-to-bead distance. In section IV, we discuss the frequency dependent hydrodynamic interaction tensor, the mathematical difficulties involved in its evaluation, and the approximations that have been invoked. In section V, the leading concentration dependence of all the Rouse mode relaxation times is obtained in the form of (I.1) above. In section V, a derivation is given for the dynamic specific viscosity in terms of the relaxation times for the individual Rouse modes. An expression for the frequency dependent Huggins coefficient is also presented. In the final section, we review the assumptions invoked and the major results derived in this paper.

II. Review of Freed–Edwards Theory

As the detailed derivations of the equations, involved in the theory of the concentration dependent polymer dynamics in solution, are discussed in the earlier papers,[6–11] only the final results, necessary to display the physical concepts and to proceed with the analysis herein, are given.

The pure fluid is taken to obey the linearized Navier–Stokes equation with force terms describing the friction forces exerted on the fluid by the polymers in solution. The polymers experience these friction forces as well as random forces which are responsible for driving the chain Brownian motion. The equations for the coupled dynamics of the polymer and fluid, respectively, are then given by[6–8]

$$\rho_0\frac{\partial}{\partial t}\mathbf{u}(\mathbf{r},t) - \eta_0\nabla^2\mathbf{u}(\mathbf{r},t) + \nabla P(\mathbf{r},t) = \mathbf{F}(\mathbf{r},t) + \sum_{\alpha=1}^{N}\sum_{i=1}^{n}\delta[\mathbf{r} - \mathbf{R}_{\alpha i}(t)]\sigma_{\alpha i}(t) \tag{II.1}$$

$$\boldsymbol{\Delta}_{\alpha i}(t)\mathbf{R}_{\alpha i}(t) = -\boldsymbol{\sigma}_{\alpha i}(t) + \mathbf{f}_{\alpha i}(t) \tag{II.2}$$

In (II.1), $\mathbf{u}(\mathbf{r},t)$ is the fluid velocity at the space–time point $\mathbf{r}$, t; ρ_0 and η_0 are the pure fluid density and shear viscosity, respectively; $P(\mathbf{r},t)$ is the fluid pressure which is determined by the condition of fluid incompressibility,

$$\nabla\cdot\mathbf{u}(\mathbf{r},t) = 0 \tag{II.3}$$

$\mathbf{F}(\mathbf{r},t)$ is the sum of the random thermal forces in the fluid, responsible for driving the Brownian motion of the polymer chains, as well as those external forces which drive the fluid flow; and $\sigma_{\alpha i}(t)$ is the force exerted on the fluid by the i^{th} segment of chain α. The operator $\Delta_{\alpha i}$ in the polymer eq II.2 includes any desired model dynamics of the free chain, e.g., for the simplest case of the bead-spring model,[1,3,12] it is

$$\Delta_{\alpha i}(t)\mathbf{R}_{\alpha i}(t) = \sum_j \frac{3k_{\mathrm{B}}T}{l^2}A_{ij}\mathbf{R}_{\alpha j}(t) \tag{II.4}$$

with the usual nearest-neighbor Rouse matrix as

$$A_{ij} = 2\delta_{ij} - \delta_{i,j+1} - \delta_{i,j-1} \tag{II.5}$$

Here k_{B} is the Boltzmann constant, T is the temperature, and l is the Kuhn effective step length. The forces $\mathbf{f}_{\alpha i}(t)$ include all the polymer–polymer interactions.

A. Scaling of Rouse Frequencies at Finite Concentration. As mentioned in the Introduction, the internal viscosity and its microscopic origins are not discussed in this paper. Hence, $\mathbf{f}_{\alpha i}$ involves only the excluded volume interactions. As in the treatments of Tschoegl,[4] Bloomfield and Zimm,[13] and Ptitsyn and Eizner,[14] we assume that the excluded volume interactions are manifested only as a change[15] in the effective force constant matrix by an overall scaling of $\langle|\mathbf{R}_i - \mathbf{R}_j|^{-1}\rangle^2/\langle|\mathbf{R}_i - \mathbf{R}_j|^{-1}\rangle_0{}^2$. Thus, in good solvents the polymer equation contains the term

$$\Delta_{\alpha i}\mathbf{R}_{\alpha i}(t) = \sum_j \frac{3k_{\mathrm{B}}T}{l^2}\,\alpha_{\mathrm{s}}{}^{-2}A_{ij}\mathbf{R}_{\alpha j}(t) \tag{II.6}$$

$$\alpha_s{}^{-1} = \frac{\langle |\mathbf{R}_i - \mathbf{R}_j|^{-1} \rangle}{\langle |\mathbf{R}_i - \mathbf{R}_j|^{-1} \rangle_0} \tag{II.7}$$

with $\alpha_s{}^{-1}(i,j)$ the nonuniform expansion parameter. In obtaining $\alpha_s{}^{-2}$, we use the static mean-square segment-to-segment distance through first order in concentration, c, in the general form[16]

$$\langle [\mathbf{R}_i - \mathbf{R}_j]^2 \rangle = l^{1+\nu} A|i - j|^{\nu}(1 - Bl^{\mu}c|i - j|^{\mu} + o(c^2)) \tag{II.8}$$

The first term in the right-hand side of (II.8) describes the fully developed intramolecular excluded volume effect, and the second term describes that due to the intermolecular excluded volume effect. Its form arises from the result of lattice calculations.[17] The coefficients A and B have the dimensions of (length)$^{1-\nu}$ and (length)$^{-\mu}$/concentration, respectively. The derivations given below and the final results can readily be adapted to Θ solvent systems by simply setting

$$\nu = 1, \qquad A = 1, \qquad B = 0 \tag{II.9}$$

Substituting (II.8) into (II.7), we get through $o(c)$

$$\alpha_s{}^{-2} = A^{-1} l^{1-\nu}|i - j|^{1-\nu}(1 + \beta Bcl^{\mu}|i - j|^{\mu} + \ldots) \tag{II.10}$$

where the constant β is introduced to enable the imposition of the requirement that the equilibrium limit of (II.2) with (II.6) and (II.10) reproduce the correct value of (II.8). The constant β is to be determined below using the fluctuation–dissipation theorem.

B. Effectivie Medium Theory of Hydrodynamics of Polymer Solutions. We now present the salient features of the effective medium theory of the hydrodynamics of polymer solutions at finite concentration[10] which provides our approximate solutions of (II.1) and (II.2). We are only interested in the average properties of the polymer solution where the average is over the distribution of all possible internal polymer configurations and the spatial centers of mass for the various chains at some initial instant of time. This averaged solution is described hydrodynamically by a stress tensor involving the summation of a portion due to the pure solvent alone plus the as yet unknown part due to the average effects of all the polymers. Since only the divergence of the stress tensor occurs in the (momentum flux) hydrodynamic equation, it is the principal object of concern. The divergence of this polymer contribution to the stress tensor is expressed as $\int \mathrm{d}\mathbf{r}' \, \mathrm{d}t' \boldsymbol{\Sigma}(\mathbf{r}-\mathbf{r}';t-t')\cdot\mathbf{u}(\mathbf{r}',t')$ where $\boldsymbol{\Sigma}$ is a tensor. Therefore, the effective Navier–Stokes equation for the averaged solution is represented as

$$\rho \frac{\partial}{\partial t}\mathbf{u}(\mathbf{r},t) - \eta\nabla^2\mathbf{u}(\mathbf{r},t) - \int \mathrm{d}\mathbf{r}'\mathrm{d}t'\boldsymbol{\Sigma}(\mathbf{r}-\mathbf{r}',t-t')\cdot\mathbf{u}(r',t') = \mathbf{F}(r,t) \tag{II.11}$$

Suppose the averaging were initially carried out over all chains but one particular chain α. If there were no statistical correlations between α and the other chains in solution, lasting for times on the order of or longer than ω^{-1} (where ω is the frequency of the experimental probe), we could view chain α as moving in the averaged polymer solution rather than in the pure solvent. Thus, the intrachain hydrodynamic interactions within the test chain α are determined by the averaged fluid with stress tensor equal to that of the pure solvent plus the as yet unknown part due to the remaining averaged polymer chains. The problem of the chain dynamics of the test polymer α in the averaged fluid now is analogous to that considered at infinite dilution except that $\boldsymbol{\Sigma}$ is still unknown. Nevertheless, given $\boldsymbol{\Sigma}$ it is possible to evaluate the net increment, $\delta\boldsymbol{\Sigma} = \delta\boldsymbol{\Sigma}(\boldsymbol{\Sigma})$, due to the test chain α. However, since the chain α is identical to all the previously averaged chains, the net increment, $\delta\boldsymbol{\Sigma}$, is identical to that contributed by each of the other averaged chains. Hence $\boldsymbol{\Sigma}$ is just N times the contribution from α, i.e.,

$$\boldsymbol{\Sigma} = N\delta\boldsymbol{\Sigma}(\boldsymbol{\Sigma}) \tag{II.12}$$

This procedure leads to a self-consistent set of equations for the desired $\boldsymbol{\Sigma}$.

When a single chain is present in a pure solvent, the hydrodynamic interaction between any two beads i and j on the chain is described by the dynamic Oseen tensor which may be written in integral representation as

$$\mathbf{K}_0(\mathbf{R}_i(t) - \mathbf{R}_j(t')) = \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \int \frac{\mathrm{d}\omega}{2\pi} \frac{(\mathbf{1} - k^{-2}\mathbf{kk})}{(i\omega\rho_0 + \eta_0 k^2)} \times \exp\{-i\omega(t - t') + i\mathbf{k}\cdot[\mathbf{R}_i(t) - \mathbf{R}_j(t')]\} \tag{II.13}$$

In (II.13) the time dependence becomes important when $\omega\rho_0$ becomes comparable to $\eta_0 k^2$, where k is proportional to the reciprocal of some relevant length of interest.[6] The minimum value of $\omega\rho_0$ is obtained by choosing this length to correspond to the mean radius of the chain, $n^{1/2}l$. This implies that the fluid dynamics (the $\omega\rho_0$ term) can be ignored for

$$\omega < \frac{\eta_0}{\rho_0 n l^2} \sim 10^9 \text{ Hz} \tag{II.14}$$

where the values $(\eta_0/\rho_0) = 0.01$ cm^2 s^{-1}, $l \sim 7$ Å, and $n = 10^4$ have been used to obtain the numerical estimates. As current experiments on dynamical viscosities, and the ones with which our theoretical predictions are compared, involve considerably lower frequencies the $\omega\rho_0$ term may be dropped. Neglecting $\omega\rho_0$ and evaluating the ω integral yields the static limit

$$\mathbf{K}_0(\mathbf{R}_i(t) - \mathbf{R}_j(t')) = \delta(t - t') \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} (\eta_0 k^2)^{-1} \times (\mathbf{1} - k^{-2}\mathbf{kk}) \exp\{i\mathbf{k}\cdot[\mathbf{R}_i - \mathbf{R}_j]\} \tag{II.15}$$

which, apart from the $\delta(t - t')$, can be shown to be identical to the familiar Oseen tensor.

When a single test chain undergoes dynamical motion in the effective averaged medium containing the solvent and the remaining $N - 1$ chains, the intrachain hydrodynamic interactions are described by the renormalized concentration dependent effective "Oseen" tensor (spherically averaged)

$$\mathbf{1}K(\mathbf{R}_i(t) - \mathbf{R}_j(t')) = \frac{2}{3} \int \frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \int \frac{\mathrm{d}\omega}{2\pi} \times \exp[-i\omega(t - t')] \frac{\langle \exp\{-i\mathbf{k}\cdot[\mathbf{R}_i(t) - \mathbf{R}_j(t')]\}\rangle}{\{i\omega\rho_0 + \eta_0 k^2 - \Sigma(k,\omega)\}} \tag{II.16}$$

The presence of Σ in the denominator simply implies that the hydrodynamic disturbance propagates through the averaged solution rather than the pure solvent in (II.13) and (II.15). At low frequencies, when $i\omega\rho_0$ may be neglected, the frequency dependence of Σ generally implies a frequency dependence for $\mathbf{K}_{ij}$. Physically, the origins of this effect are clear. The term in Σ in (II.16) arises because a hydrodynamic disturbance, initially created at time t' by bead j on chain α, propagates to chains β, γ, ..., before returning to bead i on α at time t. Because of the relaxation of chains, β, γ, ..., this introduces a dynamical character to this returning disturbance. As shown below in section IV the important frequencies in $\Sigma(k,\omega)$ correspond to the spectrum of relaxation frequencies of the chains.

When a detailed analysis is performed, $\boldsymbol{\Sigma}(k,\omega)$ is found in the limit of zero shear rate to be of the form,

$$\mathbf{1}\Sigma(k,\omega) = -\frac{N}{V}\int_{-\infty}^{\infty}\mathrm{d}(t - t') \exp[-i\omega(t\ t')] \times \sum_{i,j}^{n}\langle \exp\{-i\mathbf{k}\cdot[\mathbf{R}_i(t) - \mathbf{R}_j(t')]\}\Delta_i(t)\mathbf{Y}_{ij}(tt')\rangle \quad \text{(II.17)}$$

where the polymer operator $\mathbf{Y}$ is given by

$$\left[\frac{\partial}{\partial t}\mathbf{1} + \mathbf{K}(k,t-t',c)\Delta\right]\mathbf{Y} = \mathbf{1} \quad \text{(II.18)}$$

and the angular brackets in (II.17) and below denote that an average is taken over an equilibrium distribution of chain conformation and a uniform distribution of the center of mass position at the initial time t'. For explicit values of the various matrices in (II.18) see Appendix A. It is thus seen from eq II.16–II.18 that the equations for $K_{ij}(t-t',c)$ and Σ are coupled. A continuous limit is employed where $\mathbf{R}(s',t)$ denotes the position of the segment at position s' along the chain $[\mathbf{R}_j(t') = \mathbf{R}\ (s' = jl, t')]$. This approach and the use of Fourier integrals are equivalent to the introduction of Kirkwood–Riseman type approximations for the Rouse and Rouse–Zimm infinite dilution relaxation times.[8] Utilizing these approximations, the coupled equations for $\boldsymbol{\Sigma}$ and $\mathbf{K}$ are (see Appendix A) as follows:

$$\Sigma(k,\omega) = -\frac{clN_{\mathrm{A}}}{\pi M_{\mathrm{A}}}\int_0^{\infty}\mathrm{d}q\int_{-\infty}^{\infty}\mathrm{d}(t - t') \times \exp[-i\omega(t - t')]\Gamma(k,q,t-t')Z^{-1}(q,t-t') \quad \text{(II.19)}$$

$$Z^{-1}(q,t-t') = \int_{-\infty}^{\infty}\frac{\mathrm{d}\omega}{2\pi} \exp[i\omega(t - t')]\frac{\Lambda(q)}{[i\omega + \Lambda(q)K(q,\omega)]} \quad \text{(II.20)}$$

$$K(q,\omega) = \int_{-\infty}^{\infty}\mathrm{d}(s - s')e^{iq(s-s')}\int_{-\infty}^{\infty}\mathrm{d}(t - t')K(s-s',t-t') \times \exp[-i\omega(t - t')] \quad \text{(II.21)}$$

$$\Gamma(k,q,t-t') = \int_{-\infty}^{\infty}\mathrm{d}(s - s') \exp[iq(s - s')]S(s-s',k,t-t') \quad \text{(II.22)}$$

$$S(s-s',t-t',k) = \langle \exp\{i\mathbf{k}\cdot[\mathbf{R}(s,t) - \mathbf{R}(s',t')]\}\rangle \quad \text{(II.23)}$$

$$S(s-s',t-t',k) \simeq \exp\{-(k_2/6)\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle \quad \text{(II.24)}$$

$K(q,\omega)$ is the bead space–time Fourier transform of the renormalized effective concentration and time-dependent hydrodynamic interaction tensor for the Rouse mode with wave vector $q = 2\pi p/nl$ (p, the Rouse mode index, is an integer). $S(s-s',t-t',k)$ is the dynamic concentration dependent segment pair correlation function. M_{A} is the "monomer" molecular weight, N_{A} is the Avogadro's number, and n is the number of effective Kuhn step lengths per chain. $\Lambda(q)$ is defined in (A3).

As dictated by the structure of the effective Navier–Stokes equation, eq II.6, the solution viscosity is given by

$$[\eta_{\mathrm{sol}}(\omega) - \eta_0(\omega)]\mathbf{1} = -\lim_{k\to 0}\frac{1}{k^2}[\boldsymbol{\Sigma}(k,\omega) - \boldsymbol{\Sigma}(0,\omega)] \quad \text{(II.25)}$$

III. Determination of $\langle[\mathbf{R}_i(t) - \mathbf{R}_j(t')]^2\rangle$ at Finite Concentration

The coupled equations for $\Sigma(k,\omega)$ and $K(q,\omega)$, given in the previous section, depend on the nature of the chain dynamics through the appearance of $\langle[\mathbf{R}_i(t) - \mathbf{R}_j(t')]^2\rangle$ in II.16 (see (II.23) and (II.24)). This is quite natural in view of the fact that at low frequencies all the frequency dependence of $\Sigma(k,\omega)$ derives from the chain dynamics and that the correlation function $\langle[\mathbf{R}_i(t) - \mathbf{R}_j(t')]^2\rangle$ contains the relevant information concerning the chain relaxation frequencies. [As demonstrated in section IV, this frequency dependence also imposes upon the concentration dependent effective hydrodynamic interactions $K(q,\omega)$.] It is therefore clear that it is necessary to determine the nature of the concentration dependence of $\langle[\mathbf{R}_i(t) - \mathbf{R}_j(t')]^2\rangle$ before being able to attempt approximate solutions of eq II.17–II.21 at finite frequencies and finite concentrations.

The relevant information required to evaluate $\langle[\mathbf{R}_i(t) - \mathbf{R}_j(t')]^2\rangle$ can be obtained from the Langevin equation for the dynamics of the test chain in the effective averaged solution under the influence of the random forces which drive the Brownian motion of the chain. Theories of chain dynamics at infinite dilution are generally presented within the diffusion equation formulation. The Freed–Edwards theory of the hydrodynamics of polymer solutions at finite concentration, on the other hand, is naturally approached within the Langevin framework.[6-8] Given the Langevin equations and special conditions on the properties of the random forces, driving the chain Brownian motion, it is then possible to pass to the appropriate diffusion equation. In this section $\langle[\mathbf{R}_i(t) - \mathbf{R}_j(t')]^2\rangle$ is evaluated from the test chain Langevin equation. This procedure involves an analysis of the physical origins of the random forces responsible for the chain Brownian motion. At infinite dilution (and no "internal viscosity") Edwards and Freed[6] show that these forces arise from the random thermal velocity fluctuations in the fluid which are transmitted to the polymer chain by the hydrodynamic boundary conditions (and then are propagated by hydrodynamic interactions). The same result naturally emerges for finite concentrations by use of the fluctuation–dissipation theorem, a condition requiring that $\langle[\mathbf{R}_i(t) - \mathbf{R}_i(t')]^2\rangle$ must approach its equilibrium limit (II.8) as $t \to t'$.

The Langevin equation for the dynamical motion of the single test chain in the averaged fluid of the solvent and the remaining (configurationally averaged) chains is given by[9]

$$\frac{\partial}{\partial t}\mathbf{R}_i(t) + \sum_{m,j}\int \mathrm{d}t'\, K_{ij}(t-t',c)\Delta_{jm}(t')\mathbf{R}_m(t') = \int \mathrm{d}t'\,\mathrm{d}\mathbf{r}\,\mathrm{d}\mathbf{r}'\ \delta[\mathbf{r} - \mathbf{R}_i(t)]\mathbf{G}(\mathbf{r}-\mathbf{r}';t-t')\cdot\mathbf{F}(\mathbf{r}',t') \quad \text{(III.1)}$$

where $K_{ij}(t-t',c)$ is the above mentioned renormalized, concentration dependent, hydrodynamic interaction between any two beads of a chain, and $\mathbf{G}(\mathbf{r}-\mathbf{r}';t-t')$ describes the dynamical propagation of hydrodynamic disturbances between two space points $\mathbf{r}$ and $\mathbf{r}'$ in the averaged solution. $\mathbf{G}$ may be obtained from the solution of (II.11) as

$$\mathbf{U}(\mathbf{r},t) = \int \mathrm{d}\mathbf{r}'\,\mathrm{d}t'\,\mathbf{G}(\mathbf{r}-\mathbf{r}';t-t')\cdot\mathbf{F}(\mathbf{r}',t') \quad \text{(III.2)}$$

for any aribitrary $\mathbf{F}$. In (III.1), $\mathbf{F}$ is the sum of the external forces, $\mathbf{F}_0$, driving the fluid flow and the random thermal forces, $\mathbf{F}^*$, in the fluid which drive the Brownian motion of the polymer chain.[18] Considering a fluid which is at rest in the absence of polymers, $\mathbf{F}$ involves only the random thermal forces,

$$\mathbf{F} = \mathbf{F}^* \quad \text{(III.3)}$$

Equation III.1 merely states (i) that the chain dynamics is governed by an effective Rouse–Zimm like equation where the hydrodynamic interactions are determined by concentration dependent effective values,[6-10,19] (ii) that the Rouse frequencies may become concentration dependent, and (iii) that the Brownian motion is driven by the thermal velocity fluctuations,

$$V^*(\mathbf{R}_i(t),t) = \int \mathrm{d}\mathbf{r}'\,\mathrm{d}t'\,\mathbf{G}(\mathbf{R}_i(t)-\mathbf{r}';t-t')\cdot\mathbf{F}^*(\mathbf{r}',t') \quad \text{(III.4)}$$

occurring in the averaged fluid.

Using (III.4) and taking the Fourier transforms of (III.1) with respect to both time and position variables, the chain Langevin equation becomes

$$\mathbf{R}(q,\omega) = Y(q,\omega,c)V^*(q,\omega) \quad \text{(III.5)}$$

where Y is given by

$$[i\omega + \Lambda(q)K(q,c,\omega)]Y = 1 \quad \text{(III.6)}$$

in accordance with (II.18).

Before proceeding further, we note the simple fact that the Rouse mode relaxation rates, $2\omega(q)$, are the solutions to the equation

$$i\omega(q) + \Lambda(q)K(q,c,\omega(q)) = 0 \quad \text{(III.7)}$$

Therefore, assuming that a single relaxation rate is relevant (as shown to be the case in section V) the Rouse relaxation times are given by

$$\tau(q) = \frac{1}{2\omega(q)} = [2\Lambda(q)K(q,c,\omega(q))]^{-1} \quad \text{(III.8)}$$

This important result requires only the knowledge of the renormalized, concentration and frequency dependent hydrodynamic interaction tensor and the effective concentration dependent relaxation times, proportional to $\Lambda^{-1}(q)$, of the various Rouse modes of the polymer chain in the free draining limit. The $\tau(q)$ are analyzed in greater detail in the following section.

We now return to (III.5). Multiplying (III.5) with $\mathbf{R}(q',\omega')$ and taking an equilibrium configurational average gives the dynamic correlation function between two modes of the chain as

$$\langle \mathbf{R}(q,\omega)\mathbf{R}(q',\omega')\rangle = Y(q,\omega,c)Y(q',\omega',c)\langle \mathbf{V}^*(q,\omega)\mathbf{V}^*(q',\omega')\rangle \quad \text{(III.9)}$$

Since $\mathbf{V}^*(q,\omega)$ is the velocity field arising from the transmission of the random thermal forces from the fluid to the polymer by the hydrodynamic boundary conditions, the fluctuation-dissipation theorem may be utilized to obtain the correlation function of these random velocity fields. Defining $\Theta(q)$ (to be determined below) such that

$$\langle \mathbf{V}^*(q,\omega)\mathbf{V}^*(q',\omega')\rangle = \Theta(q,c)\delta(\omega + \omega')\delta(q - q') \quad \text{(III.10)}$$

and effecting two double Fourier transforms of (III.9) we obtain the expression[6,8] for the dynamic mean-square bead-to-bead distance

$$\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle = 2\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega}{2\pi}\int_{-\infty}^{\infty}\frac{\mathrm{d}q}{2\pi}\,Y(q,\omega,c)Y(q,-\omega,c) \otimes \Theta(q,c)\{1 - \cos[q|s - s'| + \omega(t - t')]\} \quad \text{(III.11)}$$

The value of $\Theta(q,c)$ can be determined by specializing (III.11) for a polymer chain under static equilibrium conditions, $t = t'$, and by requiring that the correct equilibrium value in (II.8) is obtained. Substituting (II.6) into (III.11) and using (II.8) for the left-hand side of (II.11) yields

$$lA|s - s'|^{\nu}(1 + Bc|s - s'|^{\mu} + \ldots) = 2\int_{-\infty}^{\infty}\frac{\mathrm{d}q\,\mathrm{d}\omega}{(2\pi)^2} \times \frac{\Theta(q,c)[1 - \cos(q|s - s'|)]}{[i\omega + \Lambda(q)K(q,c,\omega)][-i\omega + \Lambda(q)K(q,c-\omega)]} = \int_{-\infty}^{\infty}\frac{\mathrm{d}q}{2\pi}\,\frac{\Theta(q,c)[1 - \cos(q|s - s'|)]}{\Lambda(q)K(q,c,\omega_q)[1 + i\Lambda(q)|\partial K(q,c-\omega)/\partial\omega|_{\omega_q} + \ldots)} \quad \text{(III.12)}$$

where ω_q is the solution of (III.7). Substituting (A3) into (III.12) gives

$$\Theta(q,c) = \frac{\lambda l c_1}{c'(\nu)}K(q,c,\omega_q)\left[1 + i\Lambda(q)\left|\frac{\partial K(q,c,-\omega)}{\partial\omega}\right|_{\omega_q} + \ldots\right] \quad \text{(III.13)}$$

$$\beta = \frac{c_1}{c_2}\,\frac{c'(\nu)}{c'(\nu + \mu)} \quad \text{(III.14)}$$

$$c'(x) = \int_{-\infty}^{\infty}\frac{\mathrm{d}y}{2\pi}\,\frac{(1 - \cos y)}{(y)^{1+x}} \quad \text{(III.15)}$$

where c_1 and c_2 are given in Appendix A. Combining (III.6), (III.10), and (III.13) gives the dynamic mean-square bead-to-bead distance,

$$\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle = 2\int_{-\infty}^{\infty}\frac{\mathrm{d}q\,\mathrm{d}\omega}{(2\pi)^2}\,\frac{\lambda l c_1}{c'(\nu)} \times \frac{K(q,c,\omega_q)[1 + i\Lambda(q)|\partial K(q,c,-\omega)/\partial\omega|_{\omega_q} + \ldots]}{\{i\omega + \Lambda(q)K(q,c,\omega)\}\{-i\omega + \Lambda(q)K(q,c,-\omega)\}} \otimes \{1 - \cos[q|s - s'| + \omega(t - t')]\} \quad \text{(III.16)}$$

IV. Frequency Dependent Hydrodynamic Interaction

Using the continuous notation for bead position variable and (II.24), eq II.16 becomes

$$K(s-s',t-t',c) = \frac{2}{3}\int\frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3}\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega}{2\pi} \times \frac{\exp\{i\omega(t - t') - (k^2/6)\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle\}}{[\eta_0 k_2 - \Sigma(k,\omega)]} \quad \text{(IV.1)}$$

where the condition $\omega \ll \eta_0 k^2/\rho_0$ has been used. Expanding $K(s-s',t-t',c)$, $\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle$, and $\Sigma(k,\omega)$ in a Taylor series in powers of concentration, retaining terms in the lowest two orders in each case, yields

$$K(s-s',t-t',c) = K^{(0)}(s-s',t-t') + cK^{(1)}(s-s',t-t') + \ldots \quad \text{(IV.2)}$$

$$\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle = \langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle_0 + c\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle_1 + \ldots \quad \text{(IV.3)}$$

$$\Sigma(k,\omega) = c\Sigma^{(1)}(k,\omega) + c^2\Sigma^{(2)}(k,\omega) + \ldots \quad \text{(IV.4)}$$

Combining eq IV.2–IV.4 with eq IV.1 produces

$$K^{(0)}(s-s',t-t') = \frac{2}{3}\int\frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \times \exp\left\{-\frac{k^2}{6}\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle_0\right\}\delta(t - t') \quad \text{(IV.5)}$$

$$K^{(1)}(s-s',t-t') \equiv K_1^{(1)}(s-s',t-t') + K_2^{(1)}(s-s',t-t') = -\frac{1}{9\eta_0}\int\frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3}\,\delta(t - t')\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle_1 \times \exp\left\{-\frac{k^2}{6}\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle_0\right\} + \frac{2}{3}\int\frac{\mathrm{d}^3\mathbf{k}}{(2\pi)^3} \times (\eta_0 k^2)^{-2}\exp\left\{-\frac{k^2}{6}\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle_0\right\}\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega}{2\pi}\exp\{i\omega(t - t')\}\Sigma^{(1)}(k,\omega) \quad \text{(IV.6)}$$

Thus, $K^{(0)}(s-s',t-t')$ and $K_1^{(1)}(s-s',t-t')$ are frequency independent quantities $[\alpha\delta(t - t')]$. The frequency dependence of K enters to order c only through $K_2^{(1)}(s-s',t-t')$, and this is now discussed in some detail.

From (II.19) we obtain $\Sigma^{(1)}(k,\omega)$as

$$\Sigma^{(1)}(k,\omega) = -\frac{lN_A}{\pi M_A}\int_0^\infty dq \int_{-\infty}^\infty d(t-t') \times \exp[-i\omega(t-t')]\Gamma(k,q,t-t',c=0)Z^{(0),-1}(q,t-t') \quad \text{(IV.7)}$$

with

$$Z^{(0),-1}(q,t-t') = \int_{-\infty}^\infty \frac{d\omega}{2\pi} \exp[i\omega(t-t')]\frac{\Lambda^{(0)}(q)}{[i\omega + \Lambda^{(0)}(q)K^{(0)}(q,\omega=0)]} = \Lambda^{(0)}(q) \exp[-\Lambda^{(0)}(q)K^{(0)}(q,0)|t-t'|] \quad \text{(IV.8)}$$

Substituting (IV.8) and (II.22) into (IV.7) yields

$$\Sigma^{(1)}(k,\omega) = -\frac{lN_A}{\pi M_A}\int_0^\infty dq \int_{-\infty}^\infty d(t-t') \int_{-\infty}^\infty d(s-s') \times \exp\{-i\omega(t-t') + iq(s-s') - (k_2/6)\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle_0 - \Lambda^{(0)}(q)K^{(0)}(q,0)|t-t'|\}\Lambda^{(0)}(q) \quad \text{(IV.9)}$$

When (III.16) is substituted into (IV.9), we get the explicit expression for $\Sigma^{(1)}(k,\omega)$,

$$\Sigma^{(1)}(k,\omega) = -\frac{lN_A}{\pi M_A}\frac{\lambda c_1}{A}\int_0^\infty dq \int_{-\infty}^\infty d(t-t') \times \int_{-\infty}^\infty d(s-s')(q)^{1+\nu} \exp\left\{-i\omega(t-t') + iq(s-s') - \frac{\lambda c_1}{A}q^{1+\nu}K^{(0)}(q)|t-t'| - \frac{k_2}{3}\frac{\lambda l c_1}{c'(\nu)}\int_{-\infty}^\infty \frac{dq'\,d\omega'}{(2\pi)^2} \times \frac{K^{(0)}(q')[1-\cos(q|s-s'| + \omega'(t-t'))]}{\omega'^2 + \left[\frac{\lambda c_1}{A}(q')^{1+\nu}K^{(0)}(q')\right]^2}\right\} \quad \text{(IV.10)}$$

The q' integral in the exponential may be evaluated analytically, but the ω' one cannot (*even* under Θ conditions). Thus, despite the fact that all quantities on the right-hand side of (IV.10) are known, a four-dimensional integral is required, and this would even be difficult to perform numerically. (Note that the result is required in (IV.6) with two additional integrations which cannot be done analytically.) It is, therefore, evident that some approximations are required at this stage of the calculation. Here we use the approximation that $\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle_0$ is replaced by its equilibrium value $\langle[\mathbf{R}(s) - \mathbf{R}(s')]^2\rangle_0$ as this then enables the analytical evaluation of $\Sigma^{(1)}(k,\omega)$ for Θ-solvent systems. In this approximation the frequency dependence of $\Sigma^{(1)}(k,\omega)$ arises only through the time dependence of $Z^{(0),-1}(t-t')$. This does correctly exhibit the dependence of $\Sigma^{(1)}(k,\omega)$ on the relaxation frequencies, $2\omega_q$. The calculation of $\Sigma^{(1)}(k,\omega)$ is presented in Appendix B and is shown to result under Θ conditions in

$$\Sigma^{(1)}(k,\omega = -\frac{k_2 N_A \eta_0 l^{5/2}}{3^{1/2}M_A}\frac{1}{(F^2+E^3)}\left[\frac{\pi}{2(2)^{1/2}}E^{11/4} + \frac{\pi}{2(2)^{1/2}}E^{5/4}F + \frac{\pi}{3}F^{11/6} - \frac{\pi}{6}E^2F^{1/2} - \frac{\pi}{3}EF^{7/6}\right] \quad \text{(IV.11)}$$

where

$$E = \frac{k^4 l^2}{36} \quad \text{(IV.12)}$$

and

$$F = 3\pi^2\eta_0^2 l\omega^2/\lambda^2 \quad \text{(IV.13)}$$

Substituting (IV.11) into (IV.6) and again using the static mean-square bead-to-bead distance for $\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle_0$ we get

$$K_2^{(1)}(q,\omega) = \frac{l^2 N_A}{3\eta_0 M_A}I(q,\omega) \quad \text{(IV.14)}$$

where $I(q,\omega)$ is given in Appendix B.

As discussed in Appendix B, the use of the frequency dependent $\Sigma^{(1)}(k,\omega)$ in (IV.6) yields the same functional dependence of $\tau(q)$ on the Rouse modes, q, as is given by the use of $\Sigma^{(1)}(k,0)$ in (IV.6). The only change is in the numerical coefficient $\mathcal{A}$ of (I.1). Consequently, in the following sections we use only $K_2^{(1)}(q,\omega=0)$ and the resultant static concentration-dependent $K(q,c)$ to describe the concentration dependence of Rouse mode relaxation times and the frequency dependence of the Huggins coefficient.

V. Concentration Dependent Relaxation Times

The concentration dependent Rouse mode relaxation times are given by (III.8). In this section we analyze in detail the relaxation rates within the simple static limit [using $K_2^{(1)}(q,\omega=0)$] where the results may be obtained analytically. The more general treatment with $K_2^{(1)}(q,\omega)$ of (IV.14) for Θ conditions is shown in Appendix B to merely alter numerical factors. Given the static approximation the Rouse mode relaxation times follow from (III.8) as

$$\tau(q,c) = [2\Lambda(q)K(q,c,\omega=0)]^{-1} = \frac{A}{2\lambda c_1}\frac{q^{-(1+\nu)}}{K(q,c)}\left(1 - c\beta\frac{Bc_2}{c_1}q^{-\mu} + ...\right) \quad \text{(V.1)}$$

$K(q,c)$ has been evaluated in a previous paper[11] as a function of the exponents ν and μ. To first order in concentration it is given as

$$K(q,c) = K^{(0)}(q)\left[1 - c\left\{\xi_1\frac{q^{-\nu}}{K^{(0)}(q)} - \xi_2\frac{q^{((\nu/2)-\mu-1)}}{K^{(0)}(q)}\right\} + ...\right]$$

$$K^{(0)}(q) = \xi_3 q^{((\nu/2)-1)}$$

$$\xi_1 = \frac{1}{3\pi^2\eta_0}\frac{\pi^{1/2}l^2AN_A}{M_A\nu} \times \frac{\Gamma(2-(\nu/2))\Gamma((\nu-2)/2\nu)\Gamma((1-\nu)/\nu)\Gamma(\nu)}{\Gamma(1-(\nu/2))} \times \frac{\cos[(2-(\nu/2))\pi/2]\cos(\nu\pi/2)}{\cos[(1-(\nu/2))\pi/2]}$$

$$\xi_2 = \frac{B\pi^{1/2}}{2}\left(\frac{6}{lA}\right)^{1/2}\frac{\Gamma(\mu-(\nu/2)+1)}{3\pi^2\eta_0}\cos\left[\left(\mu - \frac{\nu}{2} + 1\right)\frac{\pi}{2}\right]$$

$$\xi_3 = \frac{1}{\eta_0\pi^{3/2}}\left(\frac{2}{3lA}\right)^{1/2}\Gamma\left(1-\frac{\nu}{2}\right)\cos\left[\left(1-\frac{\nu}{2}\right)\frac{\pi}{2}\right] \quad \text{(V.2)}$$

Substitution of (V.2) into (V.1) and use of $q = 2\pi p/nl$ gives

$$\tau_p = \tau_p^0[1 + c\mathcal{A}p^{-\kappa}] \quad \text{(V.3a)}$$

$$\kappa = ((3\nu/2) - 1) \quad \text{(V.3b)}$$

$$\mathcal{A} = \left(\frac{\xi_1}{\xi_3} - \frac{\xi_2}{\xi_3} - \frac{\beta Bc_2}{c_1}\right)\left(\frac{2\pi}{nl}\right)^{(1-(3\nu/2))} \quad \text{(V.3c)}$$

$$\tau_p^0 = \frac{A}{2\lambda c_1\xi_3}\left(\frac{2\pi}{nl}\right)^{-3\nu/2}p^{-3\nu/2} \quad \text{(V.3d)}$$

In the derivation of (V.3), the condition of $\mu = (3\nu/2) - 1$ has been imposed in order to generate a molecular weight independent Huggins coefficient. A small value of $|\mu - (3\nu/2) + 1|$ may be permissible, and the theoretical expressions can readily be obtained in this case. The result, $\mu = (3\nu/2) - 1$, has recently been obtained by the scaling theory.[16]

Equations V.3 are general, and the leading concentration dependence of Rouse mode relaxation times can readily be calculated for any value of the exponent ν. For Θ-solvent systems, use of (II.9) reduces to

$$\tau_p = \tau_p{}^0[1 + c\mathcal{A}p^{-\kappa}]$$

$$\tau_p{}^0 = \frac{\pi\eta_0(3l)^{1/2}}{2\lambda}\left(\frac{nl}{2\pi}\right)^{3/2}p^{-3/2}$$

$$\kappa = \tfrac{1}{2}$$

$$\mathcal{A} = \frac{\pi N_A l^2}{2M_A}\left(\frac{l}{3}\right)^{1/2}\left(\frac{nl}{2\pi}\right)^{1/2} \qquad \text{(V.4)}$$

Note that all the Rouse mode relaxation times are lengthened by an increase in concentration, in agreement with the experimental data. The structure of (V.3) shows that all the Rouse mode lifetimes, $\tau_p/\tau_p{}^0$, have a leading concentration dependence varying as $\sim p^{-\kappa}$. Hence, the lowest mode is shifted the most by an increase in concentration. Johnson et al.[5] consider two extreme models as follows: (i) All Rouse mode relaxation times are equally affected by concentration, $\tau_p = \tau_p{}^0(1 + ac)$, where a is a constant. (ii) Only the lowest mode lifetime is affected by concentration, $\tau_1 = \tau_1{}^0(1 + ac)$; all other $\tau_p = \tau_p{}^0$. They conclude, based on their experimental data, that the second model is closer to reality than the first, but that the actual situation corresponds to an intermediate case where the longest relaxation time is the first to be affected by increasing concentration and the others are affected to successively lesser degrees. Our derived result, (V.3), gives a quantitative portrayal of the same suggestions of Johnson et al., since it is the longest relaxation time that is theoretically found to be shifted the most as a function of (low) concentration.

The experimental analyses of Johnson et al. focus on a dimensionless quantity γ which is related to the concentration dependence of the viscoelastic properties. After defining γ, we evaluate it from our theoretical expressions in order to make comparisons with the experimental data. The comparison between theory and experiment provides a partial check on the uncontrollable approximation introduced by use of equilibrium values of $\langle[\mathbf{R}_i - \mathbf{R}_j]^2\rangle$ instead of $\langle[\mathbf{R}_i(t) - \mathbf{R}_j(t')]^2\rangle$ in (IV.6) and (IV.7).

The storage shear modulus, G', and the loss shear modulus, G'', are given by[1,2]

$$G' = -c\omega\eta_0 \mathrm{Im}\frac{1}{c}\eta_{\mathrm{sp}}(\omega,c) = \frac{cRTc_1}{Mc'(\nu)}\sum_p \frac{\omega^2\tau_p{}^2}{(1 + \omega^2\tau_p{}^2)}$$

$$G'' - \omega\eta_0 = c\omega\eta_0 \mathrm{Re}\frac{1}{c}\eta_{\mathrm{sp}}(\omega,c) = \frac{cRTc_1}{Mc'(\nu)}\sum_p \frac{\omega\tau_p}{(1 + \omega^2\tau_p{}^2)} \qquad \text{(V.5)}$$

where (VI.5) has been utilized [see the next section for the expression for $\eta_{\mathrm{sp}}(\omega,c)$ that has been quoted here.] Define γ' to be the ratio between the slope and the intercept when G'/c is plotted against c and γ'' to be the corresponding ratio when $(G'' - \omega\eta_0)/c$ is plotted against c. Further, let γ be equal to γ'/γ''. Substituting (V.3a) into (V.5) and assuming that the frequencies are low enough that $\omega\tau_p{}^0 << 1$, for all p, we obtain

$$\gamma' = 2\mathcal{A}\left(\sum_p p^{-\kappa}\tau_p{}^{0^2}\Big/\sum_p \tau_p{}^{0^2}\right), \quad \omega\tau_1{}^0 << 1 \qquad \text{(V.6a)}$$

$$\gamma'' = \mathcal{A}\left(\sum_p p^{-\kappa}\tau_p{}^0\Big/\sum_p \tau_p{}^0\right), \quad \omega\tau_1 << 1 \qquad \text{(V.6b)}$$

Use of (V.3b) and (V.3d) in (V.6) yields

$$\gamma = 2\frac{\zeta((9\nu/2) - 1)}{\zeta(3\nu - 1)}\,\frac{\zeta(3\nu/2)}{\zeta(3\nu)} = 2.4366 \text{ for a } \Theta \text{ solvent}$$

$$\gamma = 2.8445\text{–}2.7394 \text{ for a good solvent } (\nu = 1.1\text{–}1.2) \qquad \text{(V.7)}$$

where $\zeta(t)$ is Reimann's ζ function. Johnson et al.[5] experimentally obtain γ in the range of 2.3–3.7 for a Θ solvent and 2.4–3.4 for a good solvent. Thus, the agreement between our theoretical values and the experimental ones is reasonably good. A more stringent test may be obtainable from light scattering experiments.[22]

VI. Dynamical Shear Viscosity of Polymer Solutions and Huggins Coefficient

Expanding the exponential in (A6) and combining with (II.25) gives (see Appendix C)

$$\frac{1}{c}\eta_{\mathrm{sp}}(\omega,c) = -\frac{2N_A l}{3\eta_0 M_A}\int_{-\infty}^{\infty}\mathrm{d}(s - s')\int_{-\infty}^{\infty}\frac{\mathrm{d}\omega'}{2\pi}\times |\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle|_{\omega-\omega'}\Delta(s)Y(ss',\omega') \qquad \text{(VI.1)}$$

where we define the quantity

$$|\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle|_{\omega-\omega'} = \int_{-\infty}^{\infty}\mathrm{d}(t - t')\langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle \exp[-i(\omega - \omega')(t - t')]$$

Its frequency dependence may be retained in (VI.1) because this term enters only as a linear factor in (VI.1) as opposed to the intractable exponential dependence in (IV.10). Substitution of (III.16) and (A2) into (VI.1) yields

$$\frac{1}{c}\eta_{\mathrm{sp}}(\omega,c) = -\frac{2N_A\lambda l^2 c_1}{3\eta_0 M_A c'(\nu)}\int_{-\infty}^{\infty}\mathrm{d}(s - s')\int_{-\infty}^{\infty}\mathrm{d}(t - t')\times \int_{-\infty}^{\infty}\frac{\mathrm{d}q\,\mathrm{d}q'\,\mathrm{d}\omega'\,\mathrm{d}\omega''}{(2\pi)^4}\otimes\exp\{iq'|s - s'| - i(\omega - \omega')(t - t')\}\frac{\Lambda(q')}{[i\omega' + \Lambda(q')K(q',c,\omega')]}\otimes$$
$$[(K(q,c,\omega_q)[1 + i\Lambda(q)|[\partial K(q,c,-\omega)/\partial\omega]|_{\omega_q} + \ldots]\times \{1 - \cos[q|s - s'| + \omega''(t - ')]\})/(\{i\omega'' + \Lambda(q)K(q,c,\omega'')\}\{-i\omega'' + \Lambda(q)K(q,c,-\omega'')\})] \qquad \text{(VI.2)}$$

$$\frac{1}{c}\eta_{\mathrm{sp}}(\omega,c) = \frac{N_A\lambda l^2 c_1}{3\eta_0 M_A c'(\nu)}\int_0^{\infty}\frac{\mathrm{d}q}{\pi}\times \frac{1}{[i\omega + \Lambda(q)K(q,c,\omega_q) + \Lambda(q)K(q,c,\omega-\omega_q)]} \qquad \text{(VI.3)}$$

If we approximate (VI.3) by neglecting the ω_q and ω dependences in K, eq VI.3 becomes

$$\frac{1}{c}\eta_{\mathrm{sp}}(\omega,c) = \frac{N_A\lambda l^2 c_1}{3\eta_0 M_A c'(\nu)}\int_0^{\infty}\frac{\mathrm{d}q}{\pi}\,\frac{1}{[i\omega + 2\Lambda(q)K(q,c,0)]} \qquad \text{(VI.4)}$$

Use of (V.1) gives

$$\frac{1}{c}\eta_{\mathrm{sp}}(\omega,c) = \frac{2k_B T N_A c_1}{\eta_0 M c'(\nu)}\sum_p \frac{\tau_p}{(1 + i\omega\tau_p)} \qquad \text{(VI.5)}$$

Using the definition of the Huggins coefficient

$$\eta = \eta_0(1 + [\eta]c + k_H[\eta]^2c^2 + \ldots)$$

(VI.5) gives an expression for the Huggins coefficient

$$k_H(\omega) = \left(\frac{k_BTN_Ac_1}{\eta_0Mc'(\nu)}\right)^{-1}\mathcal{A}\frac{\sum_p p^{-\kappa}\tau_p{}^0/(1 + i\omega\tau_p{}^0)^2}{[\sum_p \tau_p{}^0/(1 + i\omega\tau_p{}^0)]^2} \quad \text{(VI.6)}$$

Thus, this derivation shows that the knowledge of Huggins coefficient can be utilized to obtain the values of $\mathcal{A}$ which determine the relative magnitude of the concentration dependence of the Rouse mode relaxation times. In general the frequency dependence of the Huggins coefficient is rather complicated, as is seen from (VI.6). However, if $\omega\tau_p{}^0 << 1$, then the above expression reduces to the static values of k_H obtained in ref 11. This implies then that for low enough frequencies, the Huggins coefficient is independent of the frequency, which is borne out by the experimental results of Johnson et al.

VII. Conclusion

A theory has been presented for the dynamic viscosity for polymer solutions at low, but finite, concentration. Apart from the basic assumptions in the Freed–Edwards theory, it is argued that for low enough frequencies, the frequency and concentration dependent hydrodynamic interaction can be replaced by the static concentration dependent hydrodynamic interaction. Corrections for Θ solvents merely alter some numerical coefficients.

The major results of our theory are the following:

(1) The relaxation times of all the Rouse modes are all lengthened as a function of the concentration of the polymer solution,

$$\tau_p = \tau_p{}^0(1 + c\mathcal{A}p^{-\kappa} + \ldots)$$

The lowest Rouse mode is the one that is shifted the most. The higher modes are progressively less affected.

(ii) The concentration dependence of the relaxation times depends on whether the solvent is a Θ solvent or a good one. All the relaxation times are less affected in good solvents than in Θ solvents. Moreover, the decreasing importance of the shift for higher Rouse modes becomes more pronounced in a good solvent.

(iii) The dimensionless ratio, γ, which is a useful experimentally utilized measure of the concentration dependence of the viscoelastic properties of polymer solutions,[5] is calculated to be 2.4366 and 2.7394–2.8445 for Θ solutions and good solutions, respectively. This is in agreement with the eperimental results of Johnson et al.[5]

(iv) For frequencies $\omega\tau_p{}^0 << 1$, the Huggins coefficient is independent of the frequency. For high frequencies, it behaves as

$$k_H(\omega) = \left(\frac{k_BTN_Ac_1}{\eta_0Mc'(\nu)}\right)^{-1}\mathcal{A}\frac{\sum_p p^{-\kappa}\tau_p{}^0/(1 + i\omega\tau_p{}^0)^2}{[\sum_p \tau_p{}^0/(1 + i\omega\tau_p{}^0)]^2}$$

when the frequency dependence of $K^{(1)}$ is neglected.

Acknowledgment. Research supported, in part, by NSF Grant DMR 76-82935 and MRL (NSF) facilities at the University of Chicago.

Appendix A

The polymer operator Y is defined as the solution to the equation

$$\sum_{p=1}^{n}\int \mathrm{d}t'\left[\frac{\partial}{\partial t}\delta_{ip}\delta(t - t')\mathbf{1} + \mathbf{K}_{ip}(t,t')\Delta_p(t')\right]Y_{pj}(t',t'') = \mathbf{1}\delta_{ij}\delta(t - t') \quad \text{(A1)}$$

Using the continuous notation for polymer bead positions and combining with (II.6) and (II.10) and Fourier transforming with respect to time and position variables converts (A1) to the explicit "solution"

$$\Delta(q)Y(q,\omega) = \Lambda(q)/[i\omega + \Lambda(q)K(q,c,\omega)] \quad \text{(A2)}$$

where

$$\Lambda(q) = \frac{\lambda}{A}c_1q^{1+\nu}\left(1 + c\frac{\beta Bc_2}{c_1}q^{-\mu}\right) \equiv \Lambda^{(0)}(q) + c\Lambda^{(1)}(q) \quad \text{(A3)}$$

$$\lambda = 3k_BT/l \quad \text{(A4)}$$

and c_1 and c_2 are constants which arise from the integration and depend on the variation of $K(s-s',c,\omega)$ with $s - s'$. For example, when $K(s-s',c,\omega) \propto |s - s'|^{-\nu/2}$ the constants are

$$c_1 = \frac{\Gamma(2 - (3\nu/2)) \cos [(\pi/2)[2 - (3\nu/2)]]}{\Gamma(1 - (\nu/2)) \cos [(\pi/2)[1 - (\nu/2)]]}$$

$$c_2 = \frac{\Gamma(2 + \mu - (3\nu/2)) \cos [(\pi/2)[2 + \mu - (3\nu/2)]]}{\Gamma(1 - (\nu/2)) \cos [(\pi/2)[1 - (\nu/2)]]} \quad \text{(A5)}$$

where $\Gamma(\xi)$ is the gamma function.

In the spirit of the preaveraging approximation, the average in (II.17) is approximated by a product of averages

$$\Sigma(k,\omega) = -\frac{N}{V}\int_{-\infty}^{\infty}\mathrm{d}(t - t') \exp[-i\omega(t - t')] \times \sum_{i,j}^{n}\langle\exp\{-i\mathbf{k}\cdot[\mathbf{R}_i(t) - \mathbf{R}_j(t')]\}\rangle\langle\Delta_i(t)\mathbf{Y}_{ij}(tt')\rangle \quad \text{(A6)}$$

This approximation is carried out with all the concentration dependences of $\langle[\mathbf{R}_i(t) - \mathbf{R}_j(t')]^2\rangle$, $\langle\Delta_iY_{ij}(t - t')\rangle$, and $K_{ij}(t - t')$ intact. It is thus assumed that in the low, but finite, concentration regime, which is discussed here, correlations between chains for time scales greater than ω^{-1} can safely be ignored. Substituting (A2) into (A6), changing to continuous variable notation for bead positions, and Fourier transforming then leads to

$$\Sigma(k,\omega) = -\frac{clN_A}{\pi M_A}\int_0^{\infty}\mathrm{d}q\int_{-\infty}^{\infty}\mathrm{d}(t - t') \exp[-i\omega(t - t')] \times \int_{-\infty}^{\infty}\frac{\mathrm{d}\omega'}{2\pi}\exp[i\omega'(t - t')] \otimes \frac{\Lambda(q)\Gamma(k,q,t-t')}{[i\omega' + \Lambda(q)K(q,c,\omega')]} \quad \text{(A7)}$$

where $\Gamma(k,q,t-t')$ is given by (II.22).

Appendix B

For Θ-solvent systems, (IV.10) reduces to

$$\Sigma^{(1)}(k,\omega) = -\frac{\lambda lN_A}{\pi M_A}\int_0^{\infty}\mathrm{d}q\ q^2\int_{-\infty}^{\infty}\mathrm{d}(t - t')\int_{-\infty}^{\infty}\mathrm{d}(s - s') \times \exp\{-i\omega(t - t') + iq(s - s') - (k^2/6) \times \langle[\mathbf{R}(s,t) - \mathbf{R}(s',t')]^2\rangle_0 - \lambda q^2K^{(0)}(q,0)|t - t'|\} \quad \text{(B1)}$$

When the equilibrium value $\langle[\mathbf{R}(s) - \mathbf{R}(s')]^2\rangle$ is used in the exponential of (B1), the latter is reduced to

$$\Sigma^{(1)}(k,\omega) \simeq -\frac{k^2l^2N_A}{6\pi M_A}\int_0^{\infty}\mathrm{d}q\frac{\lambda q^2}{[(k^2l/6)^2 + q^2]} \times \frac{\lambda q^2K^{(0)}(q,0)}{[\omega^2 + \lambda^2q^4K^{(0)}(q^2,0)]} \quad \text{(B2)}$$

$$\Sigma^{(1)}(k,\omega) = -\frac{k^2l^{5/2}N_A\eta_0}{2(3)^{1/2}M_A}\int_0^{\infty}\mathrm{d}q\frac{q^{7/2}}{(E + q^2)(F + q^3)} \quad \text{(B3)}$$

$$\Sigma^{(1)}(k,\omega) = -\frac{k^2 N_A \eta_0 l^{5/2}}{3^{1/2} M_A}\frac{1}{(F^2+E^3)}\times \left[\frac{\pi}{2(2)^{1/2}}(E^{11/4}+E^{5/4}F)+\frac{\pi}{3}(F^{11/6}-{}^1\!/\!_2E^2F^{1/2}-EF^{7/6})\right] \tag{IV.11}$$

where E and F are defined in (IV.12) and (IV.13).

Substitution of (IV.11) into (IV.6) gives

$$K_2^{(1)}(q,\omega) = -\frac{N_A l^{5/2}}{3(3)^{1/2}\pi^2\eta_0 M_A}\int_0^\infty \mathrm{d}k\frac{k^2 l/3}{[(k^2 l/6)^2+q^2]}\times \frac{1}{(F^2+E^3)}\left[\frac{\pi}{2(2)^{1/2}}(F^{11/4}+E^{5/4}F)+ \frac{\pi}{3}\left(F^{11/6}-\frac{1}{2}E^2F^{1/2}-EF^{7/6}\right)\right] \tag{B4}$$

Performing this rather tedious integration results in

$$K_2^{(1)}(q,\omega) = -\frac{N_A l^2}{3\eta_0 M_A}I(q,\omega) \tag{IV.14}$$

where

$$I(q,\omega) = \frac{1}{(q^6-a^2\omega^4)}\left\{\frac{1}{4}q^5+\left[\frac{3^{1/2}-1}{18}-\frac{\Gamma(7/12)\Gamma(5/12)}{9(2)^{1/2}\pi}+ \frac{\Gamma(11/12)\Gamma(1/12)}{18(2)^{1/2}\pi}\right]\otimes q^4(a^{1/2}\omega)^{2/3}+\frac{1}{6}q^{7/2}(a^{1/2}\omega)+ \left[\frac{1}{36}-\frac{\Gamma(7/12)\Gamma(5/12)}{9(2)^{1/2}\pi}+\frac{\Gamma(11/12)\Gamma(1/12)}{9(2)^{1/2}\pi}\right]q^2(a^{1/2}\omega)^2- \frac{1}{3}q^{3/2}(a^{1/2}\omega)^{7/3}-\left[\frac{1+3^{1/2}}{18}-\frac{\Gamma(7/12)\Gamma(5/12)}{18(2)^{1/2}\pi}- \frac{\Gamma(11/12)\Gamma(1/12)}{q(2)^{1/2}\pi}\right](a^{1/2}\omega)^{10/3}-\frac{1}{3}q^{-1/2}(a^{1/2}\omega)^{11/3}\right\} \tag{B.5}$$

and $a \equiv 3\pi^2\eta_0^2 l/\lambda^2$. When $\omega = 0$, (B5) clearly shows that

$$I(q,0) = {}^1\!/\!_4 q^{-1} \tag{B6}$$

Substitution of (B6) into (IV.14) gives the same result given in ref 11 for $K_2^{(1)}(q,\omega)$. It is also seen from (B5) that $I(q,\omega)$ becomes important only for $\omega \sim a^{-2}q^{3/2}$. Under this approximation (B5) simply becomes

$$I(q,\omega) \sim \chi q^{-1}$$

where χ is independent of q. Thus, keeping the time-dependent $Z^{(0),-1}(q,t-t')$ in the derivation results only in a change in the numerical coefficient in (B6). The functional dependence of $K_2^{(1)}(q)$ on q remains the same in both cases.

Appendix C

The evaluation of the viscosity of polymer solutions at finite concentrations has been beset by a number of technical difficulties. Earlier work led to the appearance of improper integrals for the Huggins coefficient. On the other hand, the Freed-Edwards theory does not encounter divergent integrals. However, there still persist a number of very technical mathematical problems. In order to properly consider the concentration dependent solution viscosity, it is necessary to self-consistently evaluate the concentration dependent effective hydrodynamic interaction, K of (II.16), the polymer contribution to the divergence of the stress tensor [or equivalently Σ of (II.17)]. Both of these quantities, in turn, depend upon $\langle\exp\{-i\mathbf{k}\cdot[\mathbf{R}_i(t)-\mathbf{R}_j(t')]\}\rangle$ which can only be written, cf. (III.16), in terms of $\mathbf{K}$. The presence of factors of $\langle[\mathbf{R}_j(t)-\mathbf{R}_j(t')]^2\rangle$ in exponentials has proven, heretofore, to be mathematically intractable. Two approximations have therefore been invoked as follows:

(1) We employ a continuum limit which is in the spirit of the original Kirkwood-Riseman type approximation for K within the Rouse mode representation.

(2) When $\langle[\mathbf{R}_i(t)-\mathbf{R}_j(t')]^2\rangle$ appears in exponentials, it is replaced by the time-independent, equilibrium value $\langle[\mathbf{R}_i-\mathbf{R}_j]^2\rangle$ because of our inability to mathematically handle the former as explained in this paper.

Approximation (1) implicitly involves the use of the limit of long chains, $L \to \infty$, before considering the hydrodynamic limit, $k^2 \to 0$, to extract the polymer viscosity from (II.25). The correct order of the limits should be to consider $k^2 \to 0$ first, then to take $L \to \infty$. Thus, k^2Ll must be a small parameter in the hydrodynamic limit, while approximation (1) implicitly considers it to be large. This leads to an overall error of a factor of 0.5 in calculated static viscosities. Approximation (2), on the other hand, ignores the presence of exponentially decaying contributions to $\langle[\mathbf{R}_i(t)-\mathbf{R}_j(t')]^2\rangle$ which leads to an overall error of a factor of 2 in static viscosities when the equilibrium $\langle[\mathbf{R}_i-\mathbf{R}_j]^2\rangle$ is employed from the outset. The net effect of both approximations (1) and (2) is to offset each other for static viscosities.

However, in the present paper we are concerned with dynamical viscosities at finite concentration. Approximation (1) is still invoked to enable the evaluation of the required expressions, but the dynamical $\langle[\mathbf{R}_i(t)-\mathbf{R}_j(t')]^2\rangle$ is, of necessity, retained in the expression in (VI.1) for $\eta(\omega,c)$, so the offsetting of errors does not occur, and (VI.1) requires an extra overall factor of 2 to compensate for this fact. While the point is rather minor, it is a very subtle one, so an explanation of these factors of 2 is provided in this appendix.

The above noted errors can be illustrated simply by a consideration of the zero frequency intrinsic viscosity as calculated using the schemes of (a) approximations (1) and (2), (b) (1) only, (c) (2) only, (d) exact. In cases (a) and (d) the identical correct results are obtained. For calculation (b) the expression for the intrinsic viscosity is

$$[\eta] = -\frac{lN_A}{3L\eta_0 M_A c}\sum_{p=1}^{\infty}\int_{-\infty}^{\infty}\mathrm{d}(t-t')\times \int_{-\infty}^{\infty}\mathrm{d}(s-s')\langle[\mathbf{R}(s,t)-\mathbf{R}(s',t')]^2\rangle\otimes\Lambda^{(0)}\left(\frac{2\pi p}{L}\right)\times \exp\left[\frac{2\pi ip}{L}(s-s')-\Lambda^{(0)}\left(\frac{2\pi p}{L}\right)K^{(0)}\left(\frac{2\pi p}{L},0\right)|t-t'|\right] \tag{C1}$$

Utilizing (III.16) it is found that (dropping the $p = 0$ part which does not contribute to (C.1))

$$\int_{-\infty}^{\infty}\mathrm{d}(s-s')\langle[\mathbf{R}(s,t)-\mathbf{R}(s',t')]^2\rangle\exp\left[\frac{2\pi ip}{L}(s-s')\right] = -\frac{\lambda lc_1}{c'(\nu)}\frac{1}{\Lambda^{(0)}(2\pi p/L)}\exp\left[-\Lambda^{(0)}\left(\frac{2\pi p}{L},0\right)|t-t'|\right],\quad p \neq 0 \tag{C2}$$

The integral over $t - t'$ in (C1) results in a factor of $[2\Lambda^{(0)}(q)K^{(0)}(q,0)]^{-1}$. If the equilibrium value $\langle[\mathbf{R}(s) -$

$\mathbf{R}(s')]^2\rangle$ were used instead [calculation (a)], the $t = t'$ limit of (C2) would be utilized in (C1), resulting in a value twice as large. Hence, calculation (b) is too small by a factor of 2.

In order to consider calculation (c) it is necessary to employ a discrete notation as is done in ref 8 and 9. In these calculations the finite chain length corrections involve terms of the form $\exp(-k^2Ll/6) - 1$ which would yield a predicted viscosity twice too large if retained. Consequently, if approximations (1) and (2) are not simultaneously employed, the appropriate overall factors of 2 or 0.5 must be appended. At infinite dilution calculations may be done precisely, but at finite concentrations the approximations (1) and (2) become invaluable. Present understanding of the intricacies of the ordering of the limits, arising from approximation (1), may enable us to alleviate the necessity of applying these correction factors.

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The Onset of Entangled Behavior in Semidilute and Concentrated Polymer Solutions

J. Klein*

Physics and Chemistry of Solids, Cavendish Laboratory,
Cambridge CB3 OHE, England. *Received August 17, 1977*

ABSTRACT: It is proposed that the onset of entangled behavior with increasing N (degree of polymerization) in polymer solutions of concentration $c > c^*$ (overlap concentration) corresponds to the point where molecular diffusion becomes restricted to reptation alone. An internally self-consistent model for reptation in such solutions, based on a reptation and "tube"-reorganization concept, is developed. By treating the relaxation of molecules as a cooperative phenomenon the onset of reptation is identified as a second-order, ferromagnetic-like transition occurring at a critical N and entanglement density. It is possible to compare some predictions of our treatment with experiments on the variation of N_c (critical N for onset of entangled behavior) with c, by incorporating results of previous studies on static-correlation properties in semidilute polymer solutions. The agreement is surprisingly good.

I. Introduction

There is a well-known transition in the time-dependent properties of polymer solutions occurring at concentrations well above the overlap concentration[14] $c = c^*$ (indeed, in undiluted polymer) as a function of molecular weight M: this is the onset of "entangled" behavior,[1,2a] which manifests itself in a number of properties. The variation of steady-flow viscosity η for $c > c^*$ as a function of molecular weight M (or N, the degree of polymerization) shown in Figure 1 is an example.[1,2a] Experimentally, a rather sharp change in the slope of the log N vs. log η plot is observed to occur at some critical polymer length $N = N_c$. The value of N_c varies with the concentration c; for undiluted polymers N_c is the equivalent of around 300–600 backbone units, the value depending on the polymer. The experimental situation has been extensively reviewed.[1,2a]

The precise nature of entanglements and the role they play in modifying the dynamic properties of concentrated polymer systems are not well understood. It is customary to consider[3] the critical point at $N = N_c$ (or $M = M_c$) as that at which entanglement couplings between different molecules form; as molecules drag past each other there is enhanced friction at the coupling points, leading, for example, to the higher N dependence of η (Figure 1) as-

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* Address correspondence to this author at the Polymer Department, Weizmann Institute of Science, Rehovot, Israel.

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