Quantitative Experimental Confirmation of the Chain Contraction Assumption of the Hydrodynamic Scaling Model[†]

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For *cis*-polyisoprene in a variety of solvents, published dielectric relaxation measurements[1] have determined the concentration dependence of the magnitude $\langle R^2 \rangle$ and collective relaxation time τ_n of the polymer end-to-end vectors. It is here shown for the first time that the measured concentration dependence of $\langle R^2 \rangle$ accounts *quantitatively* for the transformation of a formal simple-exponential concentration dependence of a polymer transport coefficient into the observed stretched-exponential concentration dependence of that coefficient, as seen in the hydrodynamic scaling model of polymer dynamics.[2] Specifically, it is here shown that R and τ_n are correlated by $\tau_n = \tau_{n_0} \exp(ac^1 \langle R^2 \rangle^{3/2})$, a being a constant independent of c and R, the nonexponential concentration dependence of τ_n arising from the concentration dependence of R in accord with expectations based on the ansatz of ref 2.

Introduction

The nature of the dynamics of polymer chains in nondilute solutions remains a major challenge for physical chemistry. While at one time it appeared that the tube model for polymer melts[3] also could be applied to solutions, more recent reviews[4,5,6] conclude that tube/reptation models are not applicable to polymer solutions, at least for polymers in the molecular weight and concentration ranges heretofore commonly studied. For example, Lodge et al.[4] remark "it is unlikely that reptation is significant in the semidilute regime", in essence because in a typical (say, volume fraction $\phi \approx 0.1$) semidilute solution the diameter ξ of the hypothesized tube would be larger than the radius of gyration R_g of the polymer, except for the very highest molecular weight polymers. Skolnick and Kolinski[5] conclude that "the precise mechanism of (polymer) motion is not in fact resolved", because "A number of theories having quite a different physical basis can reproduce the experimental results ...". Similarly, on the basis of a demonstration of non-power-law behavior for the concentration and molecular weight dependences of polymer self-diffusion in almost all systems, Phillies[6] concluded that "Reptation is probably not important for polymer self-diffusion in solution."

The above reviews treat a long series of papers using many different physical methods. An experimental technique that has not received as quite as prominent a level of attention is dielectric relaxation, which was recently reviewed by Adachi and Kotaka.[1] Adachi and Kotaka base their analysis on the results of Stockmayer,[7] who divided dielectric responses of polymers into three classes determined by the nature of the polymer dipoles. Stockmayer's classes involved: (i) dipoles associated with pendant sidegroups, which in general can relax via rapid side chain motion, (ii) dipoles associated with the chain contour, oriented perpendicular to the contour, which in general can relax via local segmental motions, and (iii) dipoles associated with and aligned parallel to the chain contour (classified "type-A" by Stockmayer) for which the magnitude of the total dipole moment is proportional to the average magnitude of the

end-to-end vector. The dielectric relaxation of these type-A dipoles is governed by rotational and other relaxations of the end-to-end vector, i.e., by whole-chain rotational diffusion. The focus of Adachi and Kotaka's review is dielectric response and relaxation of type-A polymers.

In a careful series of experiments, Adachi et al.[8−10] examined dielectric relaxation of short and long *cis*-polyisoprene chains in good and theta solvents. *cis*-Polyisoprene has predominantly type-A dielectric properties; its slow dielectric relaxation reflects the motions of the polymer's end-to-end vector. Adachi et al. measured the dielectric relaxation strength $\Delta\epsilon$, the characteristic relaxation time τ_n of the slowest normal mode process, and the width of the loss curve, which gives the width of the distribution of relaxation times. $\Delta\epsilon/c$ is proportional to the mean-square end-to-end vector $\langle R^2 \rangle$; τ_n is the time constant for the autocorrelation function of the polymer end-to-end vector.

On a fundamental level,[1,8,10] dielectric relaxation experiments study the total dipole moment $\vec{M}$ of all of the polymer chains in solution. A single type-A polymer chain may be envisioned as a series of short segments, each having a dipole moment $\vec{d}_i^a$ along the segment, the total dipole moment $\vec{m}^a$ of all M segments of a chain being

$$\vec{m}^a = \sum_{i=1}^{M} \vec{d}_i^a \tag{1}$$

where i and a label the segment and the chain, respectively. The total dipole moment of the chains, parallel to their contour, is $\vec{M} = \sum_{a=1}^{N} \vec{m}^a$, while the dielectric relaxation strength and relaxation time follow from the normalized temporal autocorrelation function

$$\Phi(t) = \frac{\langle \vec{M}(0) \cdot \vec{M}(t) \rangle}{\langle \vec{M}(0) \cdot \vec{M}(0) \rangle} \tag{2}$$

In addition to the dipoles parallel to the polymer contour, the system also includes rapidly-relaxing solvent dipoles and rapidly-relaxing dipoles of the chain perpendicular to its contour. The rapidly-relaxing dipoles do not appear in eq 2 and instead contribute to the local field.

Equation 2 implicitly contains self (single-chain) terms (terms in $\vec{d}_i^a \cdot \vec{d}_j^a$, for $i \neq j$) and distinct (two-chain) terms (terms in

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$\vec{d}_i^a \cdot \vec{d}_j^b$ for $i \neq j$ and $a \neq b$). In dilute solutions, only the self terms are significant. Adachi et al.[8-10] give substantial arguments that the distinct terms of $\Phi(t)$ remain unimportant in concentrated solutions of nonrigid polymers. In particular, Adachi et al. note that $\vec{m}^a$ for the polymers that they studied is not large, so dipole−dipole interactions will not significantly align nearby chains. One also notes that while excluded volume forces may tend to align adjoining chain segments to run parallel rather than perpendicular to each other so as to minimize overlaps, there does not appear to be a substantial reason for those segments to align parallel rather than antiparallel to each other, so that $\langle \vec{d}_i^a \cdot \vec{d}_j^b \rangle = 0$ by symmetry, for neighboring segments of two different chains a and b. By these arguments, the distinct terms of eq 2 will be small at all concentrations; $\Phi(t)$ will always be dominated by its single-chain terms. So long as $\Phi(t)$ is dominated by single-chain terms, Adachi et al.'s[1] interpretation of the strength of the dielectric relaxation in terms of the mean-square radius of gyration of the polymer chains (via a relation shown by Adachi et al.[9] to be analogous to the better-known relationship between the intrinsic viscosity and R_g^2) remains valid.

Adachi et al.[8-10] determined $\Delta\epsilon$ and τ_n as functions of *cis*-polyisoprene concentration for c from extreme dilution up (in some cases) to the bulk, in solvents including benzene (good solvent), dioxane (theta solvent), hexadecane, and eicosane, with chains of molecular weight M of 8.6, 102, and 164 kDa. For *cis*-polyisoprene in either good or theta solvents τ_n increases markedly—in some cases by several hundredfold—as c is increased from 0 to ca. 0.5 g/mL. Adachi et al.[8-10] found that $\Delta\epsilon/c$, and by inference the length R of the end-to-end vector, of *cis*-polyisoprene in good solvents decreases with increasing polymer concentration.

The shrinkage of R at large c was expected theoretically. R is closely related to the radius of gyration R_g of a polymer. In good solvents R_g was predicted by Daoud et al.[11] to shrink with increasing c, as was confirmed experimentally by Daoud et al.[11] for polystyrene in carbon disulfide and by King et al.[12] In contrast, $\langle R^2 \rangle$ of *cis*-polyisoprene in the theta solvent dioxane is found by Adachi et al.[9] to be independent of c, in agreement with the model of Daoud et al.[11] In some cases, Adachi and collaborators were able to convert $\Delta\epsilon/c$ into quantitative values for $\langle R^2 \rangle$.

Some time ago, I proposed[6] a physical picture—the hydrodynamic scaling model—for polymer solution dynamics. The model makes quantitative predictions[2] for the behavior of the polymer self-diffusion coefficient. A review article on the model[13] and explorations of limits of the model[14,15,16] have been published.

The hydrodynamic scaling model is based on three major physical assumptions. The following summary of these assumptions and their application is phrased in terms of the polymer self-diffusion coefficient D_s, for which complete calculations were done. For full derivations see ref 2. However, the same ansatz with different numerical factors applies to other mechanical transport coefficients including dielectric relaxation. In particular:

(i) The dominant interaction between polymer chains in solution is assumed to be hydrodynamic in nature and described by generalizations of the low-Reynolds-number hydrodynamic treatment seen, if only for intrachain interactions, in the Kirkwood−Risemann model.[17] Topological interactions are assumed to provide at most secondary corrections. In contrast to this assumption, in the tube model of ref 3 topological interactions dominate hydrodynamic forces.

As a consequence, at low concentrations the concentration dependence of the self-diffusion coefficient D_s may be approximately written

$$D_s = D_{so}(1 + ac) \quad (3)$$

and similarly for other polymer transport coefficients. Here D_{so} is the bare self-diffusion coefficient of an isolated polymer chain, and a is obtained from an ensemble average over hydrodynamic interactions between beads on two neighboring polymer chains. For polymer self-diffusion, a has been calculated (to lead order in a series expansion) quantitatively with no adjustable free parameters.[2]

(ii) Equation 3 is taken from low to high concentration via a self-similarity assumption, whose rigorous mathematical consequence it is to replace eq 3 with an exponentiated form

$$D_s = D_{so} \exp(ac) \quad (4)$$

(iii) As found by Daoud et al.[11] and King et al.,[12] polymer chains in good solvents contract with increasing polymer concentration, the scaling approximation for semidilute solutions being

$$R_g^2 \sim c^{-x} \quad (5)$$

The exponent x is $1/4$ for a large polymer in a good solvent; clearly eq 5 cannot persist all the way to zero concentration. Polymer chains in theta solvents, and short chains in all solvents, are expected to have a mean-square radius of gyration and an end-to-end vector that are independent of c.

The hydrodynamic interaction whose average yields a depends on the size of the polymer chains, so that $a \sim R^n$ and therefore $a \sim c^{-xn/2}$. In eq 4, a can be separated into a factor that is independent of polymer size and a factor that is a power of R, so eq 5 can be rewritten

$$D_s = D_{so} \exp(a'R^n c^1) \quad (6)$$

or

$$D_s = D_{so} \exp(\alpha c^{1-xn/2}) \quad (7)$$

where α incorporates the proportionality factor linking R with c. Reasonable (factor-of-three) agreement between measured and computed values for α was obtained.

From eq 7 the hydrodynamic scaling model predicts that $D_s(c)$ follows a stretched exponential in c, in complete agreement with virtually the entire literature on polymer self-diffusion in solution.[6,13] For polymer self-diffusion, $n = 4$, so for large polymers in good solvents $1 - nx/2 \cong 0.5$ as found experimentally at large M.[6,2] Equation 6 and the calculated[2] values for a and $1 - xn/2$ are quantitatively consistent with experiment, even though there are no free parameters available for adjusting either a or $1 - xn/2$.

A fundamental criticism of the hydrodynamic scaling model has been that chain contraction is a relatively weak effect that has only a very modest influence on R. For polystyrene[11,12] or for *cis*-polyisoprene in benzene,[9] between extreme dilution and the melt R_g and R change by perhaps 50%. It might appear that this limited variation in R or R_g would not readily account for the replacement of exponential with stretched-exponential behavior. Furthermore, eq 7 is based on the theoretical[11] scaling-law form for $R_g(c)$, eq 5, which is obviously not valid as $c \rightarrow 0$. It is thus not clear that chain contraction and the hydrodynamic scaling model actually account for the nonex-

ponential concentration dependence of polymer transport properties, especially at a precision beyond that afforded by eq 5.

The objective of this article is to demonstrate that the hydrodynamic scaling model of polymer solution dynamics correctly describes dielectric relaxation in polymer solutions. It is demonstrated below for the first time that the *measured* concentration dependence of R for *cis*-polyisoprene in a variety of solvents accounts *quantitatively* for the nonexponentiality of the concentration dependence of τ_n for all systems studied by Adachi et al.,[8–10] in accord with the ansatz supplied by the hydrodynamic scaling model.

Polymer Radii

Adachi et al. report measurements of $\Delta\epsilon/c$ and τ_n for 8.6 kDa and 164 kDa *cis*-polyisoprene in dioxane and benzene,[9] 101 kDa *cis*-polyisoprene in hexadecane and eicosane,[10] and 102 kDa *cis*-polyisoprene in benzene.[8] This section treats the concentration dependence of $\Delta\epsilon/c$, which from the studies of Adachi et al.[8] is linearly proportional to $\langle R^2 \rangle$. In some cases, refs 8–10 determined absolute values for $\langle R^2 \rangle$; in other cases they only report $\langle R^2(c) \rangle$ in arbitrary units.

Dioxane is a theta solvent for *cis*-polyisoprene; as confirmed experimentally,[9] in this solvent $\langle R^2 \rangle$ is independent of c. For the other polymer–solvent pairs, $\langle R^2 \rangle$ as a function of c appears in Figure 1. In each case, $\langle R^2 \rangle$ declines with increasing c, the slope being steeper at small c. The analysis in the following section requires a smooth analytic form that fits and interpolates each data set. We tried several forms, choosing one that went through data points with a minimum of systematic error. There is no claim here that these mathematical forms have fundamental physical significance. However, power laws have frequently been applied to polymer properties,[3] while a stretched-exponential approximant has previously been found to be effective for describing another equilibrium property, namely the pressure of concentrated hard spheres,[18] so our selection of forms is not particularly outre. Figure 1 allows the reader to examine the utility of our interpolating functions.

The hydrodynamic scaling model refers to polymer molecules imbedded in a solvent that is responsible for the momentum transfer. This model ceases to be applicable when the solution contains substantially more polymer than solvent, so we restrict ourselves not to include measurements made at extremely high c. Corresponding to this restriction, we truncated Adachi et al.'s[8–10] high-concentration data, as seen in Figure 1.

Here and throughout the paper, our method for obtaining parameters was a nonlinear least-squares fit using the simplex algorithm. The quantity being minimized was the fractional error in the fit. In Figure 1a, for the 9 kDa polymer $\langle R^2(c) \rangle$ was fit to a power law $\langle R^2 \rangle = ac^{-x}$. In the remainder of parts a–c of Figure 1, $\langle R^2(c) \rangle$ was fit to a stretched exponential $\langle R^2(c) \rangle = R_0^2 \exp(-ac^\nu)$. Because $-x < 0$, the power law form for $\langle R^2 \rangle$ diverges as $c \to 0$. However, we only used the power-law form as an interpolant within the concentration regime in which $\langle R^2 \rangle$ was actually measured; in this regime, the power law describes the data well.

From Figure 1a, the measured extent of chain shrinkage was much less for 9 kDa polyisoprene than for 164 kDa polyisoprene in the same solvent. From Figure 1b, the degree of chain shrinkage for 101 kDa polyisoprene was substantially greater in hexadecane than in eicosane.

Hydrodynamic Scaling and Dielectric Relaxation

Here we apply the ansatz of the hydrodynamic scaling model to treat dielectric relaxation. We then test the treatment against the aforementioned dielectric relaxation data. In order to obtain
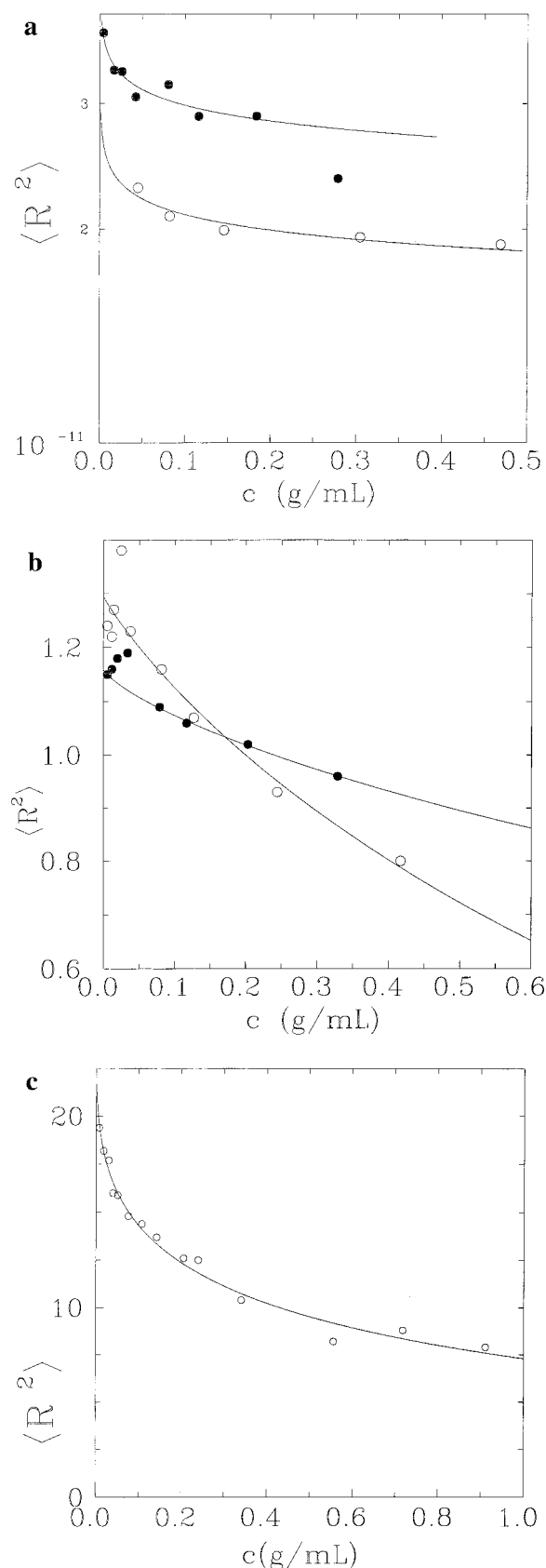

Figure 1. Mean-square end-to-end vector of polyisoprene against concentration, from data of Adachi et al.,[8–10] showing chain contraction with increasing c, for various molecular weights and solvents: (a) 9 kDa (open points, power-law fit, arbitrary units for R) and 164 kDa (filled points, stretched-exponential fit, R in cm) in benzene;[10] (b) 101 kDa in hexadecane (open points) and eicosane (filled points)[10] (arbitrary units, stretched-exponential fits); (c) 102 kDa in benzene[8] (stretched-exponential fit).

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the concentration and chain radius dependences of τ_n, we follow the ansatz used in ref 2 (in particular ref 2c, eqs 1−42) where the model is used to treat D_s. Following eq 6, if the model were applicable to dielectric relaxations, τ_n would be parameterized as

$$\tau_n = \tau_{n_0} \exp(ac^{\nu}R^{2\psi}) \qquad (8)$$

Here τ_{n_0} and ψ are a bare relaxation time and a scaling exponent; other symbols are defined above.

Within the model, the nonexponential aspect of the dependence of D_s or τ_n on c arises exclusively from the concentration dependence of R; the model predicts $\nu = 1$ for eq 8. D_s and τ_n depend on chain radius R because the hydrodynamic coupling between two chains depends on their R. D_s is described by translational diffusion, but τ_n as treated here is primarily controlled by rotational motion. Just as eq 42 of ref 2c for translational motion invokes the hydrodynamic interaction tensor $\mathbf{b}_{ch,il}$ describing the coupled translational motions of two chains, so also will the corresponding equation here for dielectric relaxation invoke the hydrodynamic interaction tensor $b_{ch,il}^{RR}$ that describes the coupled rotational motion of two chains. The dimensional dependence of $\mathbf{b}_{ch,il}^{RR}$ on chain radius R and interchain distance r is apparent from the work of Mazur and van Saarloos,[19] who treat the corresponding tensor for two hard spheres. In ref 19 it is shown that the self-part of the rotational coupling tensor scales as R^6/r^3, r being the sphere–sphere separation. Noting that the dimensionalities are the same for spheres and chains, and integrating r over allowed chain–chain distances with a lower cutoff $r \approx R$, the rotational equivalent of eq 43 of ref 2 depends on R as R^3. One therefore predicts $\psi = {}^3/_2$ in eq 8 as the expectation for dielectric relaxation from the hydrodynamic scaling ansatz. The remainder of this section tests the predictions $\nu = 1$ and $\psi = {}^3/_2$.

First, Figure 2 shows τ_n of Adachi et al.[9] for *cis*-polyisoprene in dioxane. Dioxane is a theta solvent for *cis*-polyisoprene, so R is independent of c. The exponential in eq 8 then depends on c only through c^{ν} with $\nu = 1$. Therefore, τ_n for *cis*-polyisoprene:dioxane is predicted to be a simple exponential in c. We made nonlinear least-square fits of the data in Figure 2 to eq 8, both with $\nu = 1.00$ forced and with ν as a free parameter. For parts a and b of Figure 2, the free-floated values of ν were 1.04 and 1.16, respectively. Relative to the error in the fit obtained while forcing $\nu = 1.00$, there is less than a one percentage point improvement in the fractional root mean square (RMS) error in the fit attendant to floating ν. In parts a and b of Figure 2, the best-fit lines generated with ν forced to unity and the best-fit lines with ν used as a a free parameter differ by much less than the visible scatter in the data points. Experimentally (neglecting the one outlier point in Figure 2b), the hydrodynamic scaling prediction $\nu = 1$ for τ_n of polymers in theta solvents is confirmed to good accuracy.

Second, Figure 3 shows τ_n for *cis*-polyisoprene of molecular weights 8.6, 102, and 164 kDa in benzene. Parts a and c of Figure 3, use data from ref 9; Figure 3b uses data from ref 8. Each data set for τ_n was fit via nonlinear least-squares to eq 8, taking R from Figure 1, with a and τ_{n_0} as free parameters. Benzene is a good solvent for *cis*-polyisoprene. Over the concentration range under consideration, $\langle R^2 \rangle$ of the higher molecular weight polymers declines 50% with increasing c, as seen in Figure 1. Separate fits were made with $(\nu,\psi) = (1,{}^3/_2)$ and with either ν or ψ as a floated free parameter. For each molecular weight, the fit included all displayed points except the largest c point of Figure 3c, which is displayed but not used in the analysis. The data here were truncated at larger c to avoid the meltlike regime in which the model is not applicable.
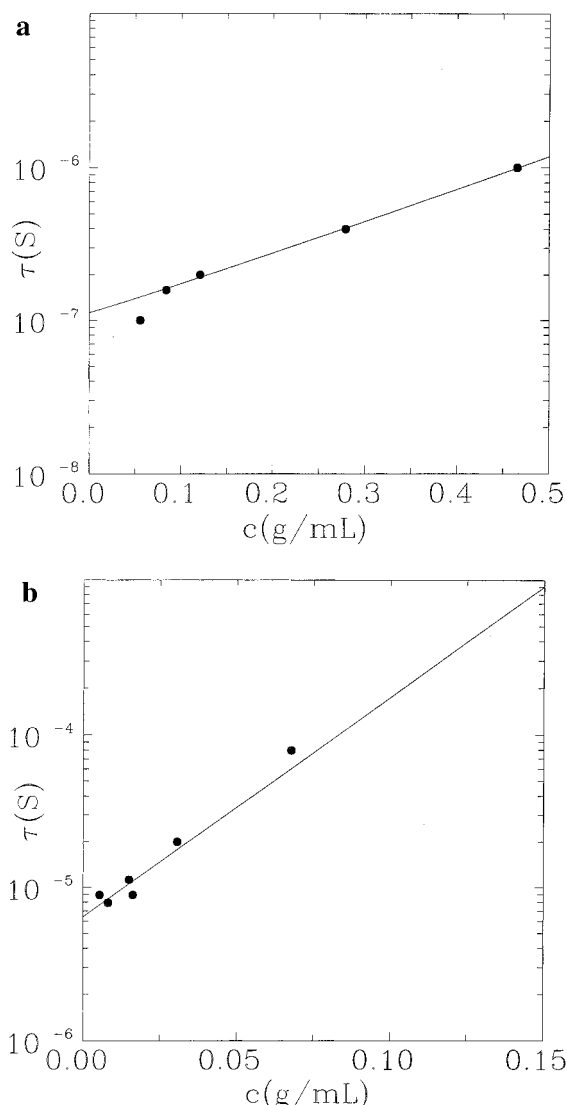

Figure 2. τ_n against polymer concentration for (a) 8.3 kDa and (b) 164 kDa *cis*-polyisoprene in the theta solvent dioxane. Solid lines are nonlinear least-squares fits to eq 8. The hydrodynamic scaling ansatz correctly predicts the indicated simple-exponential concentration dependence.

For Figure 3a, floating either ν or ψ gives values for these parameters (1.001 instead of 1 for ν, 1.27 instead of 1.5 for ψ) that do not quite match the expectation from the ansatz. However, there is less than a 0.1 percentage point improvement in the RMS error of the nonlinear least-squares fit associated with floating ν or ψ rather than keeping them fixed. For Figure 3b, floating ν and/or ψ, rather than fixing them at 1 and 1.5, respectively, does not improve the quality of the fit appreciably. For Figure 3c, floating ψ has almost no effect on the fit. Floating ν reduces ν from 1 to 0.84 and substantially reduces the RMS error in the fit. On the scale of the Figure, the fit with ν floated is slightly more concave downward than is the displayed curve. For all three polymers, to within experimental error the experimental measurements are consistent with the theoretical values $\nu = 1$ and $\psi = {}^3/_2$.

In parts a–c, of Figure 3, the smooth curves represent eq 8 with ν and ψ at their ideal values and R from the smooth curves in Figure 1. The fitting parameters in eq 8 were the bare relaxation time τ_{n_0} and the prefactor a. Observe that a is a simple constant that can change the abscissa scale but cannot change the shape of the smooth curves. In each case, the fitted curves are in excellent agreement with experiment.
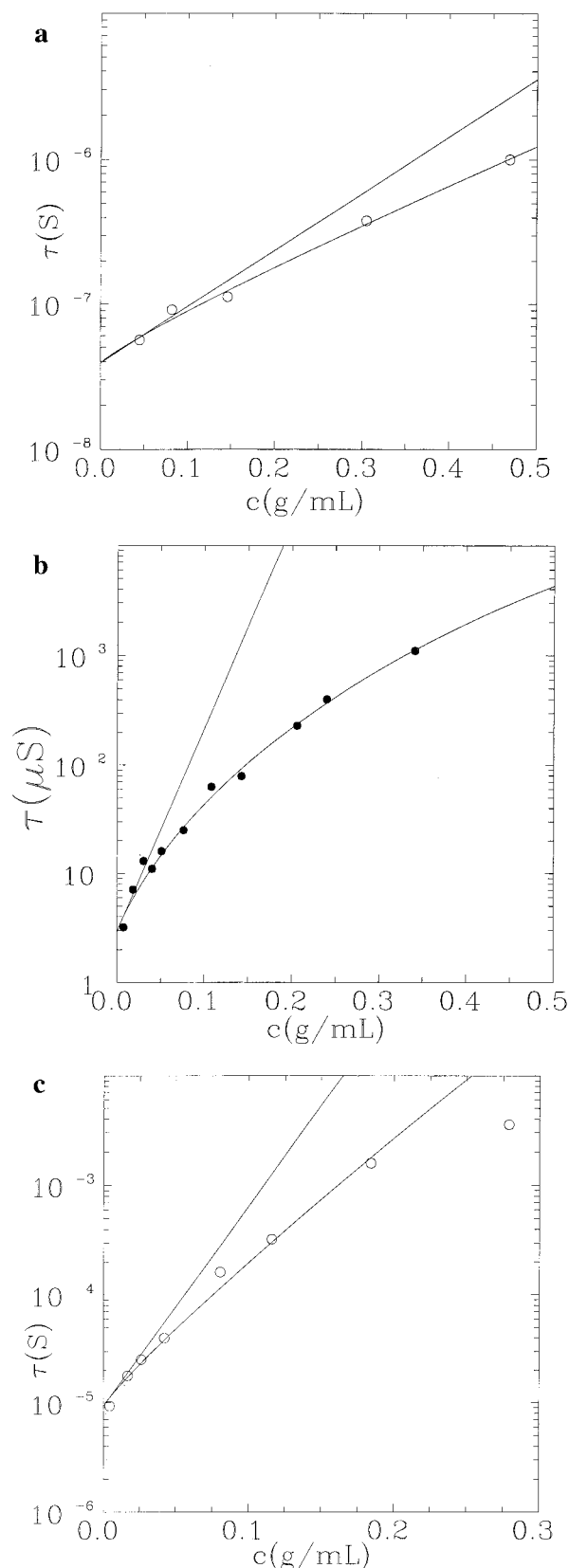
Figure 3. τ_n against polymer concentration for (a) 8.3 kDa, (b) 101 kDa, and (c) 164 kDa *cis*-polyisoprene in the good solvent benzene. Curved lines are fits to eq 8 with τ_{n_0} and a as free parameters, and $(\nu,\psi) = (1,^3/_2)$. $R(c)$ was taken to be the appropriate smooth curve in Figure 1. Solid lines are simple exponentials (eq 8) using the same parameters a, τ_{n_0} as for the smooth curves, but with R fixed at its lowest-measured-concentration value.

Third, the consequences of chain contraction are demonstrated by the straight lines in parts a–c of Figure 3. Each straight
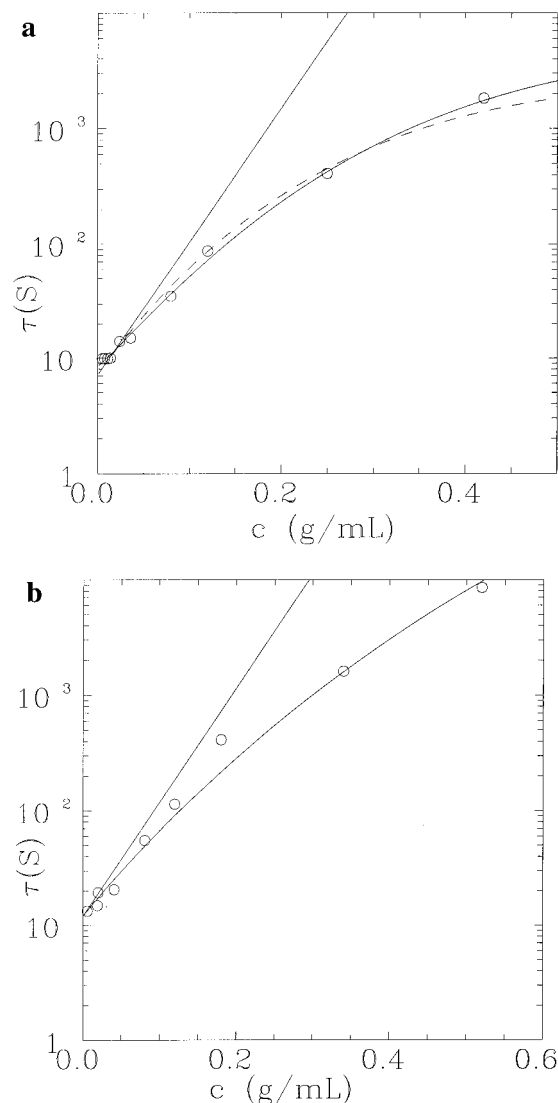

Figure 4. τ_n against polymer concentration for 101 kDa *cis*-polyiso-prene in (a) hexadecane and (b) eicosane, which are moderately good solvents for this polymer. Curved lines are fits to eq 8 with R from Figure 1 and with $\nu = 1$ or (4a, solid line) ν as a free parameter. Straight lines were computed using eq 8 and the same parameters τ_{n_0} and a as for the curves, but with R fixed at its lowest-measured-concentration value.

line was generated by fixing ν and ψ at the theoretical values and taking a and τ_{n_0} from the nonlinear fits described above. Chain contraction was suppressed by fixing $\langle R^2 \rangle$ at a single value, namely the value attained by $\langle R^2 \rangle$ at the lowest-concentration point in each figure. The resulting straight lines are in reasonable agreement with the initial slope d log τ_n/dc of the data, but clearly fail to represent well the behavior of τ_n at elevated concentration. In contrast, when chain contraction is included in the calculation by taking R from the functions of c of Figure 1, one obtains the curved lines, which agree well with the measured τ_n at all concentrations. Including chain contraction in eq 8 thus transforms eq 8 from a function that does not match the measured $\tau_n(c)$ well into a function that does agree with $\tau_n(c)$.

Furthermore, chain contraction is expected[11] to be markedly less prominent for small than for large chains, so the deviation of $\tau_n(c)$ from simple-exponential behavior should be smaller for low than for high molecular weight polymers. Comparison of parts a–c of Figure 3 confirms this expectation.

Fourth, Figure 4 shows τ_n for *cis*-polyisoprene in its moderately good solvents hexadecane (Figure 4a) and eicosane

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(Figure 4b). The data analysis procedures here were fundamentally the same as those used to generate Figure 3. Each set of measurements was fit to eq 8, with (ν,ψ) fixed at their ideal values (1, 1.5) and with ν or ψ floated, while taking R as a function of c from Figure 1.

Figure 4a shows both the fit with (ν,ψ) fixed (dashed line) and with ν but not ψ floated (solid line). Increasing ν from 1 to 1.12 does slightly improve the fit, especially for the highest-concentration point, but it is apparent that leaving $\nu = 1.00$ (dashed line) is reasonably consistent with the data. In each plot, the effect of chain contraction is again demonstrated by evaluating eq 8 with the parameters from the abovementioned fits, while holding R constant at the value that R obtains at the lowest-concentration point. If R is a constant and $\nu = 1$, eq 8 predicts a simple-exponential concentration dependence for τ_n; this simple exponential is shown in parts and b of Figure 4 as a straight line. In each solvent, the straight line agrees reasonably well with the data and their slope at small c, but deviates badly from experiment at elevated polymer concentration.

The deviation of τ_n from a simple-exponential dependence of τ_n on c is again determined quantitatively by chain contraction. The correlation between $\tau_n(c)$ and $\langle R^2 \rangle$ is precisely as described by the hydrodynamic scaling model; $\langle R^2 \rangle$ enters the stretched-exponential form for τ_n as its $3/2$ power. The effect of chain contraction is to cause the predicted $\tau_n(c)$ to deviate from a simple exponential in c to precisely the extent required for the hydrodynamic scaling ansatz's prediction $\nu = 1$ and $\psi = 3/2$ to predict a $\tau_n(c)$ that agrees with experiment.

Fifth, in Figures 2−4, the effect of chain contraction on the exponential of eq 8 was examined. The prefactor τ_{n_0} was treated as a constant. It could, however, be argued that t_{n_0} should be interpreted, not as the value of τ_n at zero polymer concentration, but as the c-dependent hypothetical value that τ_n would have for a polymer chain that was transferred from a concentrated to a highly dilute solution without changing R. With the latter interpretation, τ_{n_0} would depend on $R(c)$ in the same way that the true zero-concentration $\lim_{c \to 0} \tau_n$ depends on $R(0)$; for rotational diffusion, $\tau_{n_0} \sim R^{-3}$.

Figure 2 treats chains in a theta solvent, for which R is independent of c, so this question of interpretation has no effect on the analysis in Figure 2. However, in Figures 3 and 4, replacing $\tau_{n_0} \to \bar{\tau}R(c)^{-3}$ will change the fit to the data. We therefore reanalyzed all measurements in Figures 3 and 4, while replacing τ_{n_0} with $\bar{\tau}R(c)^3$ and using $\bar{\tau}$ as the free parameter. Under this reanalysis, our fits to Adachi et al.'s data either did not change in their RMS error appreciably or modestly improved in their RMS error. We conclude that interpreting τ_{n_0} as a dressed rather than a true zero-concentration relaxation time at worst has no effect on our interpretation, but in other cases the reinterpretation modestly improves the quality of fits to the available data.

Discussion

This paper has examined the effect of chain contraction on polymer transport coefficients by applying the hydrodynamic scaling model.[2] The hydrodynamic scaling model includes chain contraction as a fundamental assumption. In this model, chain contraction is responsible for replacing a simple-exponential concentration dependence with a nonexponential concentration dependence. In the historical[2,6] development of the hydrodynamic scaling model, chain contraction was assumed to be described by the static scaling argument[11] seen in eq 5. This assumption leads to a stretched-exponential concentration dependence with a scaling exponent ν that is in reasonable agreement with experiment. In contrast, here an assumed static scaling of R was replaced by actual experimental values for R.

In a theta solvent, polymer chains should not contract if concentration is increased. The hydrodynamic scaling model then predicts that transport coefficients for theta systems should have a simple-exponential dependence on c. This prediction is confirmed by Figure 2. In a good solvent, polymer chains contract with increasing c, causing eq 8 to predict a nonexponential dependence of τ_n on c. The degree of nonexponentiality is of $\tau_n(c)$ is determined by the degree of chain contraction. Chains that contract less substantially (9 kDa polyisoprene in benzene, 101 kDa polyisoprene in eicosane) should show relatively weak deviations from simple-exponential behavior, as seen in Figures 3a and 4b. Chains that contract more substantially at large c should show a more pronounced nonexponentiality in their dependence of τ_n on c, also as seen experimentally. The curved lines in Figures 3 and 4 show for each system that chain contraction accounts quantitatively for the nonexponential behavior of $\tau_n(c)$, precisely as predicted by the hydrodynamic scaling ansatz and the analysis above that yields eq 8 with $\psi = 3/2$.

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