Dynamics of a Polymer Solution in a Rigid Matrix

Carmen Kloster,[†,‡] Clara Bica,[‡] Colette Lartigue,[†] Cyrille Rochas,[†] Dimitrios Samios,[‡] and Erik Geissler*[,†]

Laboratoire de Spectrométrie Physique, CNRS UMR 5588, B.P. 87, 38402 St. Martin d'Hères Cedex, France, and Laboratorio de Instrumentação e Dinâmica molecular, Instituto de Quimica, Universidade Federal do Rio Grande do Sul, Porto Alegre, Rio Grande do Sul, Brazil

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ABSTRACT: We report dynamic light scattering measurements of solutions of a low molecular weight polymer (dextran M_w = 70 000), both in the free state and inside agarose hydrogels of varying concentrations. The light scattered from the rigid agarose matrix strongly heterodynes the signal from the mobile component, thereby allowing measurements both of the diffusion coefficient D_c and of the Rayleigh ratio R_θ of the dextran. For dextran concentrations c less than or equal to the overlap concentration c^*, D_c decreases as the concentration of the gel matrix c_g increases. The product D_cR_θ, which depends only on hydrodynamic factors, is, however, independent of the agarose concentration. It is concluded that the principal influence of the static gel matrix is to reduce the entropy and hence the osmotic pressure of the dextran solution. For concentrations of dextran greater than c^*, the gel structure undergoes a phase separation.

Introduction

Over the past few years, several investigations have been reported into the behavior of free polymer chains inside swollen networks. Measurements of swelling pressure and small-angle X-ray scattering show that free chains inside a gel of the same polymer do not behave like a polymer solution but instead as if they were additional network chains.[1−3] Small angle neutron scattering has shown that free chains in a swollen network adopt a collapsed configuration that is smaller than the unperturbed size of the molecule.[4,5] As predicted by theory,[6] the reduction in available configuration space in the random network causes the individual polymer coils to shrink as if they were in poor solvent conditions. Apart from swelling pressure measurements,[1,2] however, little is known about the effect of a gel matrix on the osmotic susceptibility of polymer solutions.

Ternary systems in general have recently become the subject of increased attention. The influence of a dissolved polymer on the formation of polyacrylamide hydrogels has been examined by static light scattering.[7] In dynamic light scattering investigations into ternary systems, emphasis has in the past been placed more on the measurement of the diffusion coefficient than on the intensity of the scattered light. Particular interest has been paid to cases in which the host matrix has the same refractive index as the solvent,[8] since this condition allows the movement of the guest polymer to be detected alone. Measurements have also been reported on the dynamics of free chains trapped inside biopolymer hydrogels;[9,10] here, because of the large difference in refractive index between the solvent and the matrix, index matching techniques are difficult to implement. It is generally found that the diffusion coefficient of the guest polymer is smaller than that in the free solution. To gain access to the thermodynamics of the solution, however, the intensity of the dynamically scattered light must also be measured.

In this article we use quasi-elastic light scattering to investigate the motion of flexible polymer molecules in a rigid gel matrix composed of a different polymer. Unlike gels made of flexible chains, the amplitude of the movements of a rigid-rod network is extremely small. The overwhelming majority of the light scattered by these systems is elastic: the pattern of light scattered by the network alone thus consists of a static array of speckles. This pattern may, however, evolve slowly under the influence of thermal stresses in the gel generated by the laser beam or by overall temperature fluctuations in the system. In principle, therefore, if such gels host a solution containing free polymer molecules, any quasi-elastic component in the scattered light is almost entirely attributable to the movement of the free chains in the network. This consideration enables us in principle to measure both the diffusion coefficient and the osmotic susceptibility of the polymer solution inside the matrix. In the situations described here, however, the static scattering can be as much as 3 orders of magnitude more intense than the fluctuating component of the guest solution. This condition sets a severe experimental challenge in the determination of the diffusion coefficient and the Rayleigh ratio of the solution. As the interpretation of such scattering spectra relies on proper separation between these two components, the theoretical section contains a summary description of the procedure and its underlying assumptions.

Theoretical Section

The question of optical heterodyning in gels has been abundantly treated in the past.[11−16] At the temperature of measurement (25 °C), the agarose matrix is practically rigid, generating a static speckle pattern whose intensity $I_s(q)$ and phase depend on the particular speckle observed. The total electric field at the detector is then the sum of the static field and the field $E_f(t)$ from the mobile polymers in the network. The resulting intensity fluctuations yield the field correlation function, $g(t)$, and also the fluctuating intensity, $I_f(t) = |E_f(t)|^2$.

[†] Laboratoire de Spectrométrie Physique.
[‡] Universidade Federal do Rio Grande do Sul.

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For a mobile polymer obeying Fick's equation, the correlation function $g(t)$ is

$$g(t) = \exp(-D_c q^2 t) \quad (1)$$

where D_c is the diffusion coefficient and q (=$(4\pi n/\lambda)$ sin$(\theta/2)$) is the transfer wave vector. At low polymer concentrations, D_c describes the translational diffusion of the individual polymer molecules. Equation 1 involves time fluctuations of the concentration only; permanent spatial fluctuations in the system contribute to the static scattering, but not to the dynamics. The correlation spectrum of the intensity $I(t)$ is then

$$(1/t_E)\int I(t)\, I(t+\tau)\, dt = I_s^2 + 2I_s\langle I_f\rangle + \langle I_f\rangle^2\,[1 + \beta g^2(\tau)] + 2I_s\langle I_f\rangle\beta g(\tau) \quad (2)$$

where the angular brackets are averages over the experimental accumulation time t_E, and β ($\leq$1) is the optical coherence factor. Normalizing (2) by the square of the average intensity (computer baseline), i.e.

$$\langle I\rangle^2 = \langle I_s + I_f\rangle^2 = \langle I_s\rangle^2 + 2\langle I_s\rangle\langle I_f\rangle + \langle I_f\rangle^2 \quad (3)$$

yields the total intensity correlation function

$$G(\tau) = \frac{\int I(t)\, I(t+\tau)\, dt}{\langle I\rangle^2 t_E} \quad (4)$$

As stated above, however, in most gels the speckle pattern evolves slowly with time, and I_s is not a true constant. This consideration has stimulated investigations into the notion of ensemble averaging and nonergodicity.[14,15] In the present case, the dissolved polymer molecules are free to overlap and are therefore fully ergodic. Any time dependence of I_s is assumed to be sufficiently slow for it to be distinct from the fast fluctuations in I_f due to the motion of the free polymer. The time average of I_s^2, namely $\langle I_s^2\rangle$, determines the effective constant baseline ("far point") to which the correlation spectrum decays, i.e.

$$\text{far point} = (1/t_E)\int I(t)\, I(t+\tau_\infty)\, dt = \langle I_s^2\rangle + 2\langle I_s\rangle\langle I_f\rangle + \langle I_f\rangle^2 \quad (5)$$

where τ_∞ is the extended channel delay. Here we are concerned only with the quantities $\langle I_f\rangle$ and $g(t)$. To obtain these, the far point is subtracted from eq 2, and the result is normalized by the computer baseline. This yields for the dynamic component of the intensity correlation function

$$H(\tau) = G(\tau) - \frac{\langle I_s^2\rangle + 2\langle I_s\rangle\langle I_f\rangle + \langle I_f\rangle 2}{\langle I\rangle^2} = \beta[2X(1-X)g(\tau) + X^2 g^2(\tau)] \quad (6)$$

where $X = \langle I_f\rangle/\langle I_f + I_s\rangle$ and $H(\tau)$ tends to zero as τ tends to ∞. β is found by extrapolating $G(\tau)$ to $\tau = 0$ for a dilute suspension of latex beads (for which $X = 1$). In the present optical arrangement, $\beta = 0.96$. Hence, for the heterodyne case eq 5 is soluble[15] for X and for $g(\tau)$. The required intensity is thus

$$I_f = X\langle I\rangle \quad (7)$$

where $\langle I\rangle = \langle I_f + I_s\rangle$ is the total intensity averaged over the experimental observation time t_E.

For the present system, therefore, it is seen that spatial averaging of the speckle pattern is not necessary to determine I_f. This assumption was confirmed by comparing intensity measurements from several different positions in the sample and for different values of the incident beam attenuator; the resulting variation in I_f was less than 10%. To obtain the absolute value of the fluctuating intensity, R_θ, however, the transmission Tr of the sample must be measured, as well as the intensity $I_{stand} = R_v I_0$ from a standard sample (toluene), where R_v is the Rayleigh ratio of the standard and I_0 is the intensity of the incident beam. Thus, finally,

$$R_\theta = \frac{R_v X\langle I\rangle \sin\theta}{I_{stand}\,\mathrm{Tr}} \quad (8)$$

where θ is the scattering angle and where we assume that the incident laser intensity I_0 is the same for the measurements of the sample and of the standard. In the agarose–water gels used for the present measurements, Tr can be appreciably smaller than unity (0.25 $\leq$ Tr $\leq$ 1).

Sample Preparation

The dextran, of molecular weight M_w = 70 000, was used as supplied by Sigma. The agarose was graciously provided by R. Armisen (Hispanagar, Spain). Its molecular weight, determined by viscometry,[17] is $M_w = 1.2 \times 10^5$. The sulfate content specified by the manufacturer is 0.1%. The methyl content was found by ^{1}H NMR to be 0.6%. Dextran solutions were investigated in the concentration range 2 g L^{-1} $\leq c \leq$ 100 g L^{-1}; the agarose concentration of the host gel was in the range $0 \leq c_g \leq 40$ g L^{-1}.

The samples were prepared by mixing the appropriate weights of agarose and dextran in deionized water and heating the mixture to 100 °C. The resulting solutions were stirred until complete dissolution and then transferred to cylindrical glass tubes of 10 mm outer diameter and sealed. The samples were melted again at 100 °C and allowed to cool to room temperature; gelation of the agarose occurred as the temperature fell below 45 °C.

Dynamic light scattering measurements were made with a Spectra Physics SP162 laser working at 488 nm, and a Malvern Instruments 7032 multibit correlator. All measurements were made in a temperature-controlled bath at 25 °C. The laser and goniometer were fixed to an optical table that was isolated from the building by pneumatic supports. Care was taken to eliminate any source of mechanical vibrations from the optical table, since any excitation of the fundamental frequency either of the sample or of the table is detected in the scattered signal.

Measurements of the transmission of the samples were made in the same cells, using a Kontron Uvikon 810 spectrophotometer working at 488 nm. To counter the lens effect of the cylindrical light scattering cells, these were placed in rectangular glass cuvettes containing water in the intervening space. A mask was applied to ensure that only light traversing the cylinder diameter was detected by the spectrophotometer.

Results and Discussion

All the polymer solutions and gels were measured at 60°, 90°, and 150°. This angular range was selected to

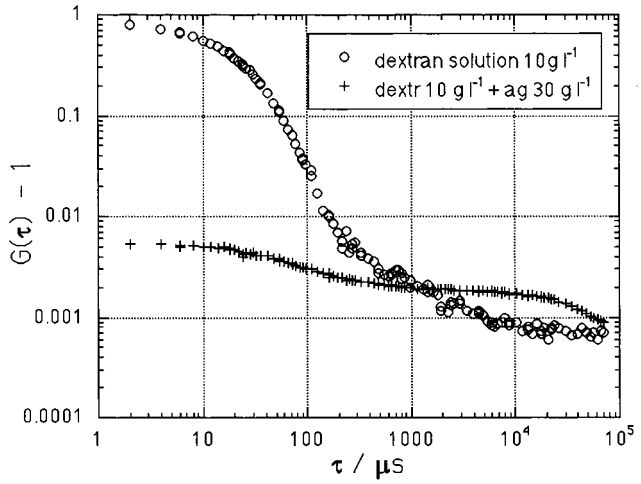

Figure 1. Intensity correlation function of a 10 g/L dextran solution (M_w = 70 000) at 25 °C in the free solution (circles) and in an agarose gel of concentration 30 g L. Scattering angle 90°.

minimize possible effects of multiple scattering that can arise at small angles in turbid gels; the observed absence of depolarized scattering in the primary beam, however, shows that this condition was in fact unnecessarily strict. Measurements were made as a function of dextran concentration c between the dilute and the semidilute region, and also for various concentrations c_g of the agarose gel. The overlap concentration c^* in aqueous solution for the M_w = 70 000 sample is, from intrinsic viscosity measurements,[17] known to be c^* = 35 g/L.

For the pure dextran solutions, the correlation spectra were all found to be purely homodyne, the intercept of the reduced intensity correlation function $G(\tau) - 1$ at $\tau = 0$ being close to the measured value of β for our optical arrangement (Figure 1, circles). Effects of molecular association become visible, however, as the concentration increases, giving rise to a small quasi-static component in the scattered light. In contrast, for the spectra obtained from the dextran solutions in the agarose gels, the value of $G(0) - 1$ is about 2 orders of magnitude smaller (Figure 1, crosses). As changing the sample does not modify the optics, this reduction can be attributed to strong heterodyning by the light scattered from the agarose gel. The degree of heterodyning is found from eq 6; the resulting values of X lie in the range 10^{-2}–10^{-3}.

In Figure 2 the field correlation functions $g(\tau)$ calculated from the spectra measured at $\theta = 90°$ are shown for samples containing c = 10 g/L dextran, both in the free solution (circles) and in agarose gels of two different compositions. As found by Burne and Sellen[10] for dextran in gellan gels, the motion of the polymer inside the gel becomes slower as the gel concentration is increased. It can also be seen that with increasing gel concentration c_g, a second much slower motion appears, whose amplitude becomes increasingly large. The continuous lines shown in this figure are the least-squares fit to a double exponential function. While this fitting function is acceptable for the c_g= 0 and 5 g/L samples, a broader distribution of relaxation times is clearly necessary to describe fully the slow motion in the more concentrated gel, c_g = 30 g/L.

Figure 3 shows the angular dependence of the fast relaxation component in the dextran spectra found for the three samples of Figure 2. Bearing in mind the

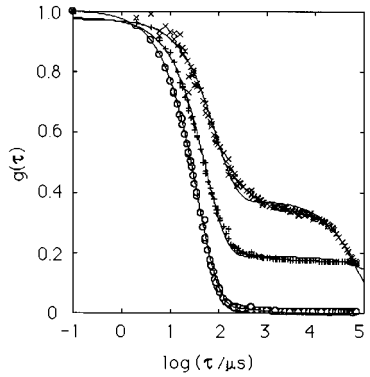

Figure 2. Field correlation function $g(\tau)$ calculated from eq 6 for dextran solutions at c = 10 g L^{-1}: (○) c_g = 0 (free solution); (+) in agarose gel with c_g = 5 g L^{-1}; (×) in agarose gel at c_g = 30 g L^{-1}. Scattering angle 90°. The continuous curves are least-squares fits to a two-exponential decay.

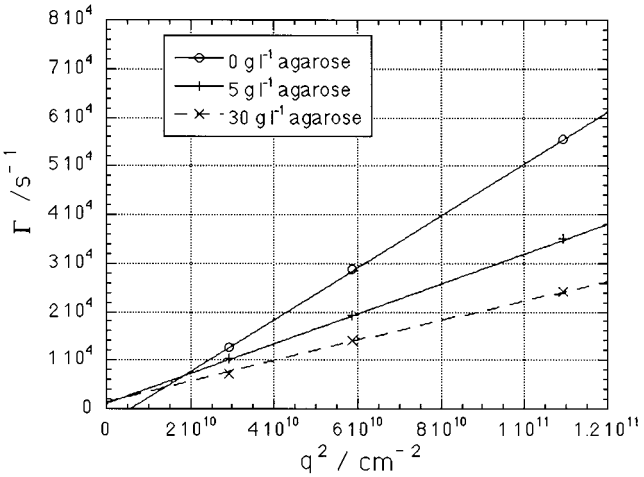

Figure 3. Relaxation rate Γ of the fast component of $g(\tau)$ for the same samples as in Figure 2, plotted as a function of q^2: (○) c_g = 0 (free solution); (+) c_g = 5 g L^{-1}; (×) c_g = 30 g L^{-1}.

error inherent in decomposing a multiexponential decay, the data in Figure 3 indicate that the fast relaxation rate is proportional to q^2. This is therefore a diffusive mode, the corresponding diffusion coefficient being denoted D_c. At low concentrations D_c describes the translational diffusion coefficient of the individual polymer coils, while above the overlap concentration c^*, it is a collective mode involving fluctuations of the local swelling of the polymer in the solvent.[18] The slow relaxation mode is less reproducible, making its angular dependence more difficult to determine; within the experimental error, however, the longer relaxation rate also varies as q^2.

The dependence of D_c upon the dextran concentration c is shown in Figure 4, for agarose concentrations lying between 0 and 40 g/L. In the free solution (circles), D_c increases monotonically, with no noticeable effect occurring at c^*. As the agarose concentration increases, however, the value of D_c for the dilute dextran solutions decreases significantly, but, with increasing dextran concentration, D_c approaches the values of the free solution. Thus, as the overlap concentration c^* is approached, the dextran solution in the gel appears to resemble that in the free state.

As the dextran concentration is further increased, another effect appears: for samples prepared above c^*, phase separation occurs during gelation. The resulting agarose gels become visibly turbid, and the measured

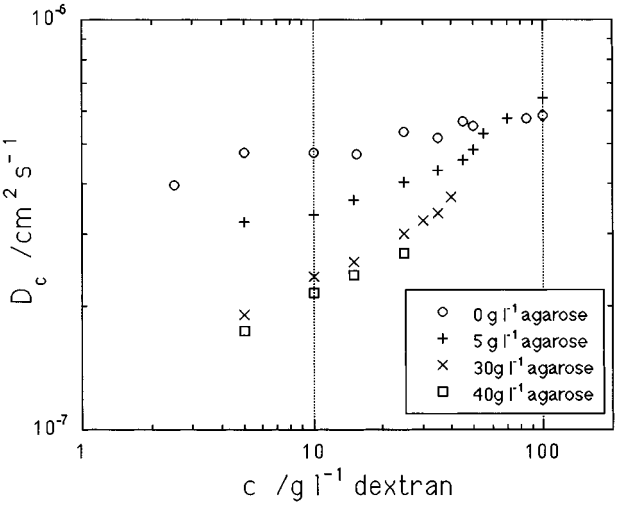

Figure 4. Diffusion coefficient D_c as a function of dextran concentration c in agarose gels of various concentrations c_g; (○) $c_g = 0$ (free solution); (+) $c_g = 5$ g L^{-1}; (×) $c_g = 30$ g L^{-1}; (□) $c_g = 40$ g L^{-1}.

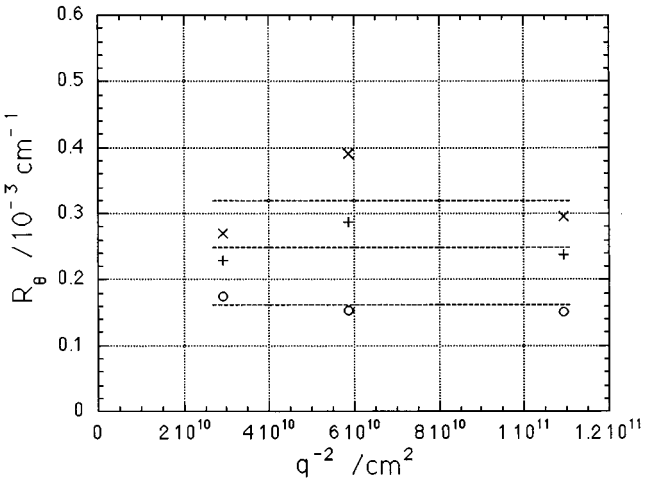

Figure 5. Rayleigh ratio R_θ as a function of q^2 for dextran solutions at $c = 10$ g L^{-1} in agarose gels of differing concentrations c_g: (○) $c_g = 0$ (free solution); (+) $c_g = 5$ g L^{-1}; (×) $c_g = 30$ g L^{-1}. The dashed horizontal lines are the resulting averaged intensities.

light scattering relaxation rates can depend on the region investigated in the sample.

The total intensity of the dynamically scattered intensity R_θ is shown in Figure 5 as a function of q^2 for dextran solutions at concentration $c = 10$ g/L, in gels of different agarose concentrations c_g. Owing to the more complex procedure, the inherent errors in this type of analysis are significantly greater than in standard light scattering: the precision of these measurements is limited to about 20%. It is therefore unjustified to deduce a structure factor from these data, but it is clear that R_θ in the gel is greater than that in the free solution. To reduce the random error in the intensity measurements, an average of the scattering intensity is taken over the measured angles. The results are shown in Figure 6 as a function of dextran concentration, for different gel compositions. Data from the phase-separated samples have been omitted in this figure. It can be seen in this double logarithmic scale that the scattered intensity increases practically linearly with dextran concentration up to c^*. Above this concentration the free solution exhibits a plateau, as

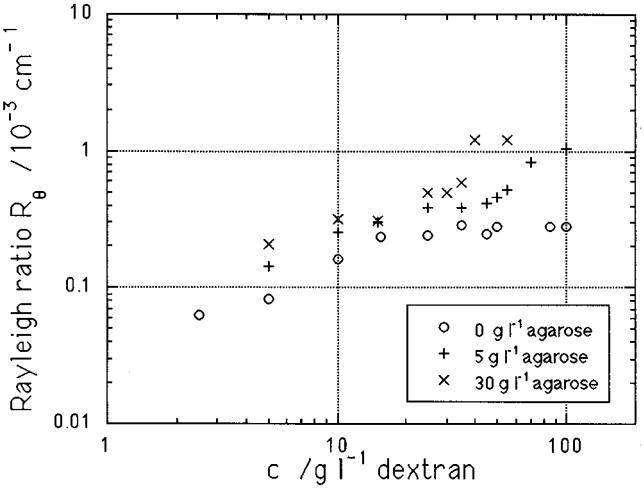

Figure 6. Rayleigh ratio R_θ as a function of dextran concentration c in agarose gels of differing concentrations c_g: (○) $c_g = 0$ (free solution); (+) $c_g = 5$ g L^{-1}; (×) $c_g = 30$ g L^{-1}.

expected in the vicinity of the maximum in semidilute solutions. For the gels, however, the intensity increases strongly in the semidilute region.

For the dextran sample used here, the radius of gyration R_G, measured by static light scattering, was found to be 9.6 nm. This result is consistent with previous measurements made on this system.[19] For the present observations therefore, $qR_G \ll 1$, and, as far as the individual dextran coils are concerned, the experimental condition is close to the thermodynamic limit $q = 0$. In this approximation, the scattered intensity is given by

$$R_\theta = Kc \frac{kT}{\partial\Pi/\partial c} \tag{9}$$

where Π is the osmotic pressure of the solution and K is the contrast factor for light scattering.

Furthermore, the diffusion coefficient can be expressed as

$$D_c = \frac{\partial\Pi/\partial c}{f} \tag{10}$$

where f is a friction coefficient that contains the hydrodynamic interactions. (Generally, f is understood to be the friction coefficient of the individual monomers, but, provided we restrict ourselves to the dilute regime, it is legitimate to consider f as being that of the whole molecule.) It follows from eqs 9 and 10 that the product

$$D_c R_\theta = KkTc/f \tag{11}$$

contains no thermodynamic information but reflects only the hydrodynamic interactions. In the present case, we make the explicit assumption that the dextran solution forms a single phase within the gel matrix and that R_θ therefore governs both the fast and the slow relaxation rates.

Figure 7 shows the variation of D_cR_θ as a function of c in different gel environments. Within experimental error, the points fall on a master curve below c^*: this result means that the friction coefficient f of the dextran molecule is the same whether it is in free solution or in the gel. It follows that the observed decrease in the diffusion coefficient of dextran in the gel with respect to the free solution is a result of a decrease in the

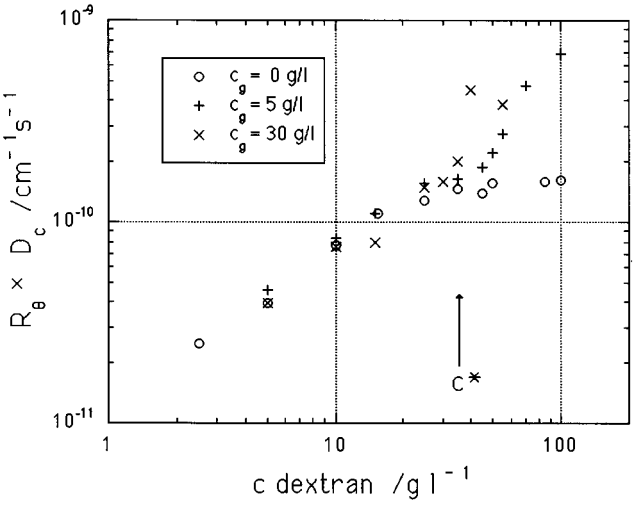

Figure 7. Product $R_\theta D_c$ as a function of dextran concentration c with various agarose gel concentrations c_g: (○) $c_g = 0$ (free solution); (+) $c_g = 5$ g L^{-1}; (×) $c_g = 30$ g L^{-1}.

osmotic modulus and is therefore unrelated to the friction of the surrounding matrix. The gel matrix is, however, purely static, and its configurational entropy is zero; under these conditions, its influence is confined to reducing the free space available to the dextran molecules, thereby decreasing their entropy. This situation is a corollary of the observed reduction in radius of gyration of polymers trapped in random networks, where the cross-links reduce the configuration entropy of the guest molecules.[4−6]

At concentrations beyond c^* the product D_cR_θ in the gel exceeds that of the free solution. The reason for this finding is unclear at present, but it may simply reflect the fact that, owing to the reduced osmotic pressure, the overlap concentration c^* of the dextran in the gel is greater than in the free solution.

Conclusions

Low molecular weight dextran ($M_w = 70\,000$), when dissolved inside agarose hydrogels, exhibits single phase behavior at concentrations $c \leq c^*$, where c^* is the overlap concentration of the dextran. Above c^*, phase separation occurs; this behavior contrasts with that of the free solution, which is continuously soluble in water. For dextran concentrations less than or equal to the overlap concentration, the diffusion coefficient D_c is reduced and the Rayleigh ratio R_θ is enhanced compared to the free solution. In this concentration range, however, the quantity D_cR_θ, which depends only on hydrodynamic factors, is found to be independent of the agarose concentration. It is concluded that the rigid gel matrix reduces the osmotic pressure of the dextran solution by reducing the configuration space available to the dextran.

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