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Dynamics of Cellulose Whiskers in Agarose Gels. 1. Polarized Dynamic Light Scattering

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ABSTRACT: The dynamics of cotton cellulose microcrystals ("whiskers") trapped in agarose hydrogels of varying concentrations was studied by polarized dynamic light scattering. The rigid agarose network strongly heterodynes the signal of the mobile whiskers, thereby enabling the measurement of their diffusion coefficient D and their fluctuating scattered intensity R_θ. For low agarose gel concentrations, i.e., when the mesh size of the agarose network is larger than the length of the whiskers, the dynamics does not depend on the whisker content. The product of D and R_θ, which is inversely proportional to the friction coefficient, is independent of the gel concentration, indicating that the network does not hinder the whiskers. When the mesh size of the network is smaller than the length of the whiskers, the whisker content influences the dynamics and the product $R_\theta D$ becomes dependent on the gel concentration; i.e., frictional effects arise. Also in this condition domains with different whisker contents may develop in the gel.

Introduction

Cellulose microcrystals, called "whiskers", have increasingly attracted attention due to their interesting physical properties related to their aspect ratio. By the addition of sulfate groups to the microcrystal surface, aqueous suspensions of cellulose whiskers may be stabilized via attraction/repulsion forces of electrical double layers[1] and yield chiral nematic phases at concentrations as low as 5% (w/w) for cotton microcrystals.[2] Cellulose whiskers are colloidal particles that have the form of rigid rods. In contrast to the dynamics of flexible coil polymers in solution, the dynamics of rigid rods is not yet completely understood. The dynamics of these whisker suspensions in water and in dextran solutions has been studied using dynamic light scattering (DLS) and will be published in a forthcoming paper.[3]

Agarose gels are widely used in the food and in the pharmaceutical industries. In recent years their importance in gel chromatography has led to many studies into their structure and properties but a full understanding is still lacking.[4] In previous studies[5,6] the dynamics of a flexible polymer (dextran), trapped in agarose gels of varying concentrations, was probed by dynamic light scattering. It was found that, for low molar mass dextran (M = 70 000 g/mol), the diffusion coefficient decreases in the gel, but the intensity of the dynamically scattered light increases, with the result that the friction coefficient is the same whether it is in the free solution or in the gel.[5] The decrease in translational diffusion coefficient is caused by a reduction of the osmotic pressure of the dextran confined in the agarose network.[6] For higher molar mass dextran (M = 500 000 and 2×10^6 g/mol), the friction coefficient was found to be higher in the gel than in the free solution as far as the dilute regime of dextran is concerned.[6] This effect was attributed to entanglements between the free polymer and the network.

To study the dynamics of rigid particles inside agarose hydrogels, in this work we used cellulose whiskers as a guest component in the host agarose matrix. Their diffusional behavior was investigated by polarized dynamic light scattering (VV configuration, i.e., both incident and scattered light vertically polarized). Because of their anisotropy, these whiskers strongly depolarize light, and in a second part of this study using depolarized dynamic light scattering (VH configuration), results will be reported in a forthcoming paper. The whiskers originate from cotton and have an average length of 170 nm with an aspect ratio of about 10.[2]

To investigate the role of the agarose network on the dynamics of trapped particles, the dynamics of whiskers was studied vs different agarose gel concentrations (Table 1).

Theoretical Background

At room-temperature agarose hydrogels are rigid, and the amplitude of their dynamics is therefore extremely small. Most of the light scattered by agarose is elastic. When this gel contains free particles, any quasi-elastic component in the scattered light may therefore be almost entirely attributed to the mobility of the free particles. The static component of the light scattered by the matrix is much stronger than the fluctuating one of the guest particles. As a consequence, the signal of the guest particles is strongly heterodyned.[5−8] For the whiskers trapped in the gel, the total average scattering intensity $\langle I \rangle$ is therefore

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Table 1. Relation of the Average Whisker Length (L_w = 170 nm) to the Maximum Size L_{mesh} of the Agarose Network Mesh Estimated from the Position q_m of the Intensity Maximum in Small Angle Light Scattering[4]

agarose concn (g/L)	$L_{mesh} = 2\pi/q_m$(nm)
2	435
6	200
10	140
16	100

$$\langle I \rangle = \langle I_f + I_s \rangle \quad (1)$$

where

I_f is the fluctuating component of the scattered light (due to whiskers) and I_s is static component (due to the agarose matrix).

The normalized intensity correlation function $G(\tau)$ is then expressed as:

$$G(\tau) = (\langle I_s^2 \rangle + 2\langle I_s \rangle \langle I_f \rangle + \langle I_f \rangle^2)/\langle I \rangle^2 + \beta[2X(1 - X)g(\tau) + X^2 g(\tau)^2] \quad (2)$$

where X is the fluctuating fraction of the scattered light ($X = \langle I_f \rangle/\langle I \rangle$), β the optical coherence factor of the detection system and $g(\tau)$ the electric field correlation function of the dynamic component.

The absolute intensity R_θ of the fluctuating component is given by

$$R_\theta = (R_v X \langle I \rangle \sin \theta)/(I_{stand} \mathrm{Tr}) \quad (3)$$

where R_v is the Rayleigh ratio of the standard (toluene), I_{stand} the intensity scattered by the standard, θ the scattering angle, and Tr the transmittance of the sample.

It is known[9] that the diffusion coefficient D depends on the osmotic pressure π as

$$D = (\partial \pi/\partial \mathrm{c})/f \quad (4)$$

where f is a friction coefficient that contains the hydrodynamic interactions and c is the concentration of particles. The Rayleigh ratio R_θ is given by

$$R_\theta = (\mathrm{K}ckT)/(\partial \pi/\partial \mathrm{c}) \quad (5)$$

where K is the contrast factor for light scattering and kT is the Boltzmann factor.

From eqs 4 and 5, it follows that the product $R_\theta D$ is independent of the osmotic pressure:

$$R_\theta D = KkT_c/f \quad (6)$$

At constant temperature and particle concentration, this product depends only on the friction coefficient, and physically it represents the mobility of the particles in the medium.

Experimental Section

The whisker sample was supplied by Dr. T. Ebeling and Dr. M. Paillet (CERMAV-CNRS) and prepared as described by Dong et al.[10]

The whisker/agarose hydrogels were prepared in the desired proportions by adding deionized water and the whisker stock suspension to the appropriate weight of agarose (Hispanagar, Spain). The mixtures were boiled under stirring. After complete dissolution, the samples were transferred to cylindrical glass tubes, which were subsequently sealed. The tubes were then heated to 100 °C and allowed to cool. The whisker concentration was varied in the range $0.01 < c_w < 0.325\%$ w/v. The agarose gel concentration was studied in the range $2 < c_{agarose} < 16$ g/L. Polarized dynamic light scattering measurements were performed at 25 °C with a Malvern Instruments 7032 correlator and a Spectra Physics SP1161 laser working at 488 nm. The laser and the goniometer were fixed to an optical antivibration table. All free whisker suspensions and gels were measured at angles 60, 90, and 120°. Transmittance of the samples was measured in the same tubes using a Beckmann DU-640 spectrophotometer at 488 nm. The cylindrical tubes were placed in rectangular cuvettes containing water in the intervening space in order to counter any lens effect.

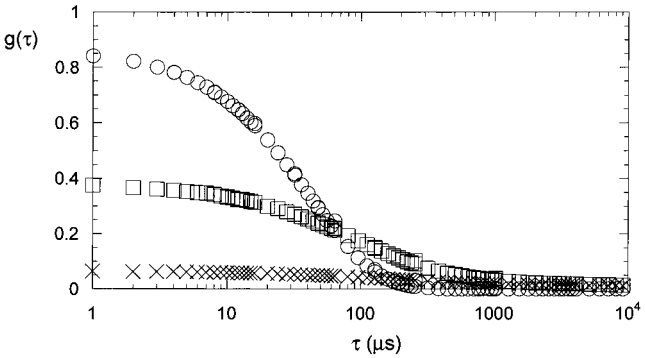

Figure 1. Reduced intensity correlation functions ($G(\tau) - 1$) for a free whisker suspension (○) and for whiskers in agarose gels with $c_{agarose} = 6$ g/L (□) and $c_{agarose} = 10$ g/L (×) at the same whisker content $c_w = 0.04\%$ (w/v). Scattering angle: 90°.

Results and Discussion

For all free whisker suspensions the correlation function is homodyne, since the intercept of the reduced intensity correlation function ($G(\tau) - 1$) at $\tau = 0$ is close to the coherence factor β of the optical arrangement ($\beta = 0.90$). For the whiskers trapped in the gel, however, the values of ($G(0) - 1$) are much smaller (Figure 1). As found previously,[5,6] this fact is due to heterodyning of the fluctuating scattered light component by the static light scattered by the agarose gel.

It is known[11] that for long rodlike macromolecules the polarized light scattering spectrum contains contributions from translational and rotational diffusion modes according to eq 7

$$I_{vv}(\mathbf{q},t) = \langle N \rangle \alpha_{iso}^2 \exp^{-q^2Dt} + \frac{4}{45} \langle N \rangle \alpha_{aniso}^2 \exp^{-(6\Theta t + q^2 Dt)} \quad (7)$$

where $\langle N \rangle$ = number of particles in the scattering volume, α_{iso} = isotropic part of the polarizability tensor, α_{aniso} = anisotropic part of the polarizability tensor, Θ = rotational diffusion coefficient, D = translational diffusion coefficient, and $\mathbf{q}$ = scattering vector of modulus

$$q = \frac{4\pi n}{\lambda_0} \sin\left(\frac{\theta}{2}\right) \quad (35)$$

where n is the refractive index of the medium, θ is the scattering angle, and λ_0 the wavelength of the radiation in vacuo.

The product of the scattering vector q and the polymer length L determines the relative contribution of each mode. For small qL translational diffusion dominates the dynamics.[12] In this case, the time correlation function should not depend on the scattering angle when

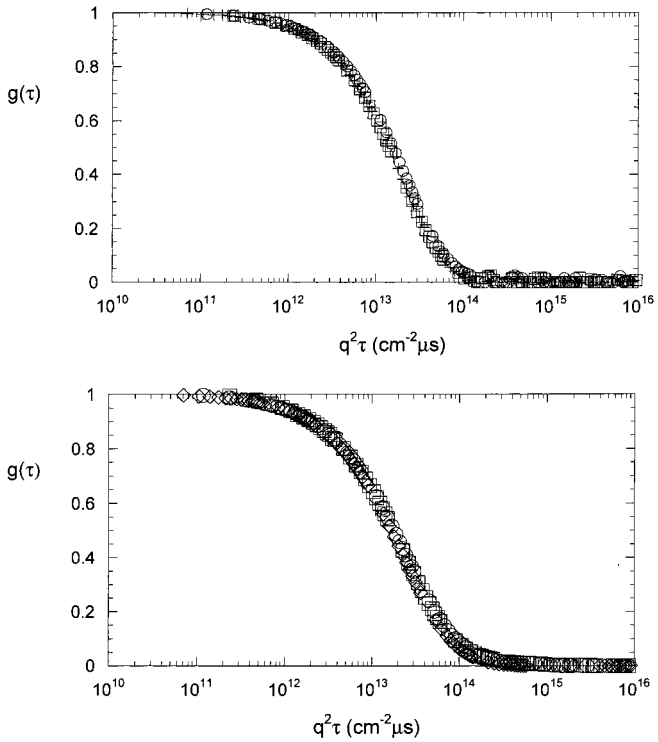

Figure 2. Field correlation functions $g(\tau)$ vs $q^2\tau$ (cm^{-2} μs) for angles 60, 90, and 120° and whisker content $c_w = 0.02\%$ (w/v): (A) free whisker suspension; (B) agarose concentration of 2 g/L.

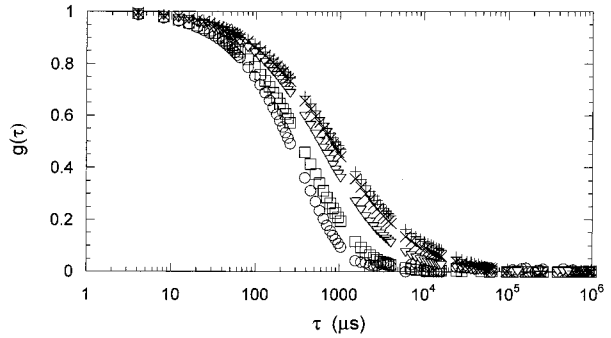

Figure 3. Field correlation functions $g(\tau)$ at $c_w = 0.08\%$ (w/v) and various gel concentrations: (○) free whisker suspension, (□) 2 g/L, (▽) 6 g/L, (×) 10 g/L, and (+) 16 g/L.

plotted against $q^2\tau$, where τ is the delay time. Indeed, the polarized electric field time correlation functions measured for each whisker concentration at different angles superimpose when plotted against the product $q^2\tau$ (Figure 2, parts A and B). In the systems studied, the inverse relaxation time was observed to consist of two modes, one fast and one slow, both of which were proportional to q^2. These two modes are therefore purely diffusive.

Figure 3 shows field correlation functions (calculated according to eq 2) at the same whisker content (c_w = 0.08% w/v) for various agarose concentrations at θ = 90°. Bearing in mind that cotton whiskers have a tendency to aggregate[2,3] the fast mode can be attributed to the single rods and the slow one to clusters. It can also be seen that the motion of the whiskers becomes slower as the agarose concentration increases. This is consistent with previous studies.[5,6,13] A two-exponential fit to the correlation functions $g(\tau)$ according to eq 8 gives a good description of the dynamics

$$g(\tau) = a_1 \exp(-D_1 q^2 \tau) + a_2 \exp(-D_2 q^2 \tau) \qquad (8)$$

where a_1, a_2 are the relative intensities of each mode and D_1, D_2 the corresponding diffusion coefficients.

The dependence upon whisker content of the translational diffusion coefficient corresponding to the fast mode (D_{fast}) is shown in Figure 4. For the whisker suspensions and for the gel concentration at 2 g/L, it was verified that D_{fast} does not depend on the whisker concentration. Also, within the experimental error, the same values for D_{fast} were obtained whether in the free suspension or in the gel up to $c_{agarose}$ = 2 g/L. Above $c_{agarose}$ = 6 g/L a decrease of D_{fast} with the whisker concentration can be observed. At the same whisker concentration, a slight decrease of D_{fast} with the gel concentration can be seen beyond $c_{agarose}$ = 6 g/L. Higher gel concentrations and lower whisker contents could not be further analyzed owing to the low signal-to-noise ratio.

In the case of the slow mode (Figure 5), the diffusion coefficient D_{slow} decreases by as much as 1 order of magnitude when the gel concentration increases. In contrast to D_{fast}, D_{slow} for $c_{agarose}$ = 2 g/L is already lower than for the free suspension. For $c_{agarose}$ = 2 g/L and for the free suspension, D_{slow} does not depend on the whisker concentration. As in the case of D_{fast}, only above $c_{agarose}$ = 6 g/*L* is a decrease of D_{slow} observed upon increasing the whisker concentration. This decrease in D_{slow} becomes markedly more pronounced for gel concentrations 10 and 16 g/L. It is interesting to recall that for these gel concentrations the pore size of the agarose network is smaller than the length of the whisker rods (see Table 1). So the accentuated decrease in D_{slow} is certainly related to hindering of the rod clusters by the gel matrix. The influence of the matrix on the fast and the slow relaxation of the guest particles can be seen more easily in Figure 6 where the ratio of the diffusion coefficient in the gel to that in the free suspension (D_{gel}/D_{free}) is plotted against the gel concentration for all whisker contents. One can see in this double logarithmic representation that the ratio D_{gel}/D_{free} decreases linearly with the gel concentration and practically does not depend on the whisker content. It can also be seen that again the slow mode decreases more rapidly (exponent = −1.08) than the fast mode (exponent = −0.46) with the gel concentration.

Figure 7 shows the dependence of the dynamically scattered intensity (calculated from eq 3) upon the scattering vector for the free whisker suspension of c_w = 0.08% (w/v) and for gels at the same whisker content. At a gel concentration of 2 g/L the intensity is higher than that of the free suspension, but at $c_{agarose}$ = 6 g/L it becomes equal, while for yet higher gel concentrations it is smaller. Although an angular dependence can be observed in the case of the free whisker suspension and the lower gel concentrations, for our further analysis we take an average of the intensity values over the measured angles. This procedure is adopted in order to reduce random errors, since the precision in the measurement of the dynamically scattered intensity is smaller than in standard light scattering, being limited to about 20%.[5]

The intensity R_θ displays a linear dependence on the whisker content for all gel concentrations studied (Figure 8). For $c_{agarose}$ = 2 g/L, R_θ is higher than in the free suspension. Up to c_w = 0.08% w/v, R_θ is the same for the free suspension as for $c_{agarose}$ = 6 g/L, while

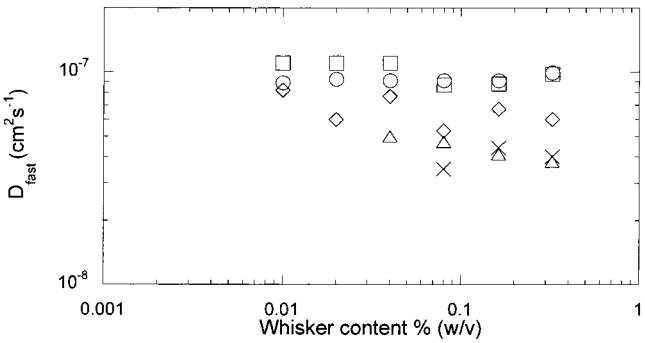

Figure 4. Diffusion coefficient of the fast mode (cm^2/s) as a function of whisker content (%, w/v) at various gel concentrations: (○) free whisker suspension, (□) 2 g/L, (◇) 6 g/L, (△) 10 g/L, and (×) 16 g/L.

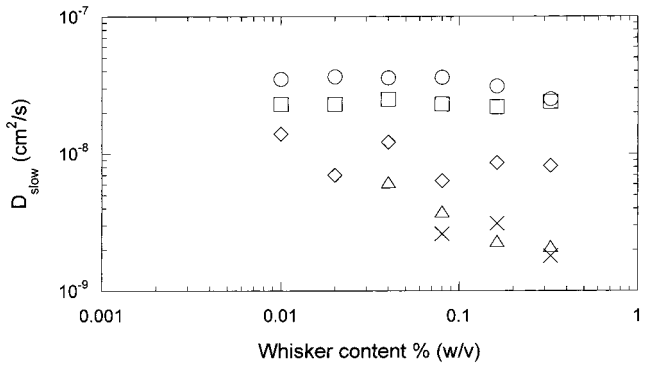

Figure 5. Diffusion coefficient of the slow mode (cm^2/s) as a function of whisker content (%, w/v) at various gel concentrations. Symbols as in Figure 4.

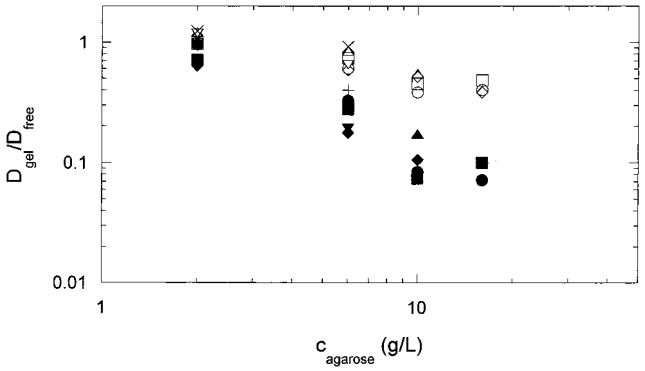

Figure 6. Ratio of the diffusion coefficient of the whiskers in the gel to that in the free suspension (D_{gel}/D_{free}) at various whisker contents as a function of gel concentration. Open symbols correspond to the fast mode and filled ones to the slow mode: (○) c_w = 0.325% (w/v), (□) c_w = 0.163% (w/v), (◇) c_w = 0.08% (w/v), (△) c_w = 0.04% (w/v), (▽) c_w = 0.02% (w/v), (×, +) c_w = 0.01% (w/v).

beyond this value of c_w the intensity becomes higher in the gel. For high gel concentrations ($c_{agarose}$ = 10 and 16 g/L) the scattered intensity R_θ is smaller in the gel than in the free suspension. No plateau typical of the semidilute regime is visible in the dependence of the intensity upon c_w: this implies that the range of whisker concentration studied still corresponds to the dilute regime. This means that interactions between the whisker rods must be weak. It is therefore reasonable to decompose the total intensity into a fast and a slow part proportionally to the relative intensity of each mode (Table 2).

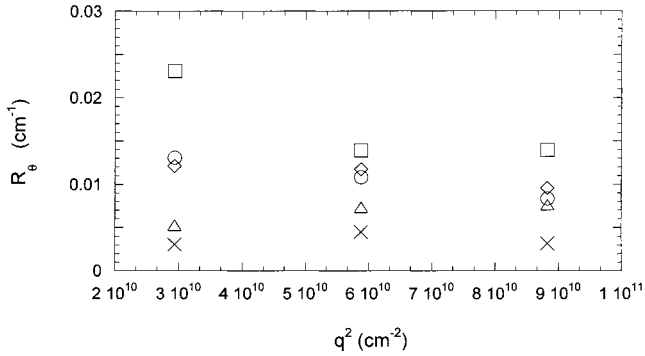

Figure 7. Dynamically scattered intensity R_θ (cm^{-1}) as a function of q^2 (cm^{-2}) at various gel concentrations (symbols as in Figure 4). Whisker content: 0.08% (w/v).

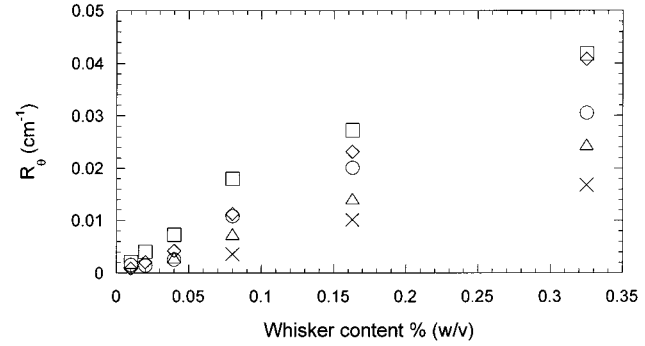

Figure 8. Dynamically scattered intensity R_θ (cm^{-1}) as a function of the whisker content at various gel concentrations (symbols as in Figure 4).

Table 2. Relative Intensities of the Fast and of the Slow Modes as a Function of the Gel Concentration

gel concn (g/L)	rel intens of the fast mode (a_1)	rel intens of the slow mode (a_2)
0	0.35	0.65
2	0.40	0.60
6	0.55	0.45
10	0.55	0.45
16	0.60	0.40

As can be seen in Table 1, at high gel concentrations, the length of the whisker rods is greater than the largest mesh size of the agarose network. In this situation frictional effects may become significant. From eq 6, the product $R_\theta D$ is expected to be independent of the osmotic pressure, being inversely proportional to the friction coefficient. For a given whisker content a decrease of the quantity $R_{\theta slow}D_{slow}$ (Figure 9) is indeed observed at high gel concentrations compared to the free suspension. When the average rod length (L_w) exceeds the mesh size (L_{mesh}) of the agarose network the friction coefficient is thus higher in the gel than in the free suspension and the mobility of the rod is smaller. When $L_w < L_{mesh}$ the friction coefficient in the gel is the same as in the free suspension, as can be seen in Figure 9 for $c_{agarose}$ = 2 g/L. In the last case, also, the mobility is the same. Figure 9 also confirms the linear concentration dependence of the product $R_{\theta slow}D_{slow}$ predicted by eq 6.

Figure 10 shows the ratio of the friction coefficients in the gel and in the free suspension (f_{gel}/f_{free}) as a function of gel concentration both for the fast and slow modes. This quantity was obtained from $(R_\theta D)_{free}/(R_\theta D)_{gel}$. At $c_{agarose}$ = 2 g/L, the friction is practically the same as in the absence of gel. At $c_{agarose}$ = 6 g/L, it remains the same in the case of the fast mode, probably because L_w does not yet exceed the mesh size. For the

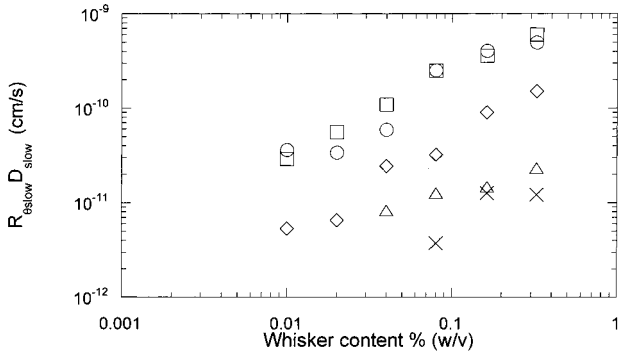

Figure 9. Product $R_{\theta slow}$ D_{slow} (cm/s) of the slow part of the dynamically scattered intensity and the diffusion coefficient corresponding to the slow mode as a function of whisker content at various gel concentrations (symbols as in Figure 4).

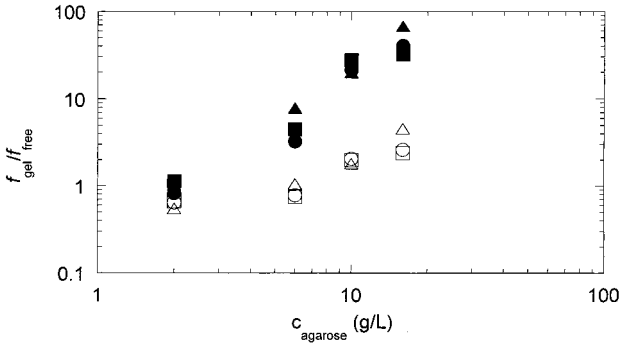

Figure 10. Ratio of friction coefficients in the gel to the free whisker suspension for some whisker contents as a function of the gel concentration. Open symbols correspond to the fast mode and filled ones to the slow mode: (○) $c_w = 0.325\%$ (w/v), (□) $c_w = 0.163\%$ (w/v), and (△) $c_w = 0.08\%$ (w/v).

slow mode, however, the friction in the gel clearly increases at $c_{agarose} = 6$ g/L with respect to the free suspension. This can be understood if we recall that the slow mode corresponds to clusters of rods: the average size of the clusters therefore already exceeds the pore size of the agarose network at this gel concentration. At $c_{agarose} = 10$ and 16 g/L, the ratio f_{gel}/f_{free} for the slow mode shows a very marked increase. The friction in the gel for the slow mode increases more steeply with the agarose concentration (exponent 1.9) than in the case of the fast mode (exponent 1.3). Considering that the agarose network displays a distribution of pore sizes,[4] we could easily assume that whiskers are excluded from regions of small pore size and concentrate into the large pores.

Conclusion

We have conducted a study of the dynamics of cellulose whiskers in agarose gels by polarized DLS. Such observations are of relevance to situations in which rigid anisotropic molecules are subjected to gel chromatography. No rotational modes were detected in the VV configuration, the observed fast and the slow modes being purely translational. In general, the results can be satisfactorily explained as a function of the relationship between the length of the whisker rod and the mesh size of the agarose network. For low agarose gel concentrations, i.e., when the mesh size of the agarose network is larger than the length of the whiskers, whisker rods are not hindered by the network. When the mesh size of the network is smaller than the whisker length, frictional effects arise that are very pronounced in the case of rod clusters. In this condition domains with different whisker contents may also develop in the gel since the rods may be excluded from regions of small pore size and concentrate into large ones.

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