Role of Sucrose in Pectin Gelation: Static and Dynamic Light Scattering Experiments

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Received April 1, 2002; Revised Manuscript Received July 25, 2002

ABSTRACT: We report data on static and dynamic light scattering of semidilute solutions of high methoxyl pectin in the presence of different amounts of sucrose, ranging from few % (w/w) up to a value just below the threshold required for gel formation. The apparent gyration radius of the pectin is found to slightly increase with sucrose concentration while the mean relaxation time displays a diverging behavior, strongly correlated with the increase of the solvent bulk viscosity. The dynamic behavior on approaching the condition required for gelation exhibits features typical of a glass transition, providing new insight into the role of sucrose in promoting the gelation of pectin.

Introduction

Pectin is a natural polysaccharide obtained from citrus peel or apple pomace and used primarily as gelling agent in the food industry. The major constituent is a linear sequence of 1,4-linked α-D-galactopyranosyluronic acid with some of the carboxyl groups esterified with methanol. Interruptions with L-rhamnose residues 1,2-linked make the backbone irregular and provide kinks responsible for flexibility increase.[1] Some neutral sugars are also present in minor proportions as side chains. Depending on the amount of methyl ester groups, pectin is classified as high methoxyl (HM) having 50% or higher esterification degree and low methoxyl (LM) pectin. Both types of pectin form gel at concentration of few g/L, but in different conditions: gelation of LM pectin requires the presence of calcium,[2,3] and it is observed over a wide range of pH, whereas HM pectin may form gel at acid pH (lower than 3.5) only in the presence of a large amount of sugars or similar cosolutes[2−4] which are known to reduce water activity.[4−6]

The role of calcium in promoting the gelation of LM pectin is well understood in terms of the "egg-box" model[7] where calcium ions provide intermolecular bridges between the carboxyl groups of the pectin chains.[8] In contrast, the role of sugars in promoting the gelation of HM pectin is still not clear. It is well accepted that HM pectin gels are stabilized by both hydrogen-bonding and hydrophobic interactions.[4] The latter primarily involve the methyl ester groups, as inferred by X-ray diffraction data,[9] and are enhanced by the presence of sugars in solution. This type of cosolute is known to increase the thermal stability of protein structure[5,6] by increasing the thermodynamic cost of keeping hydrophobic groups exposed to the solvent. The consistency between the stabilizing effects of sugars on the protein structure and the efficiency in promoting the pectin gelation has been taken as grounds for assessing the relevance of the hydrophobic interactions in the gelation mechanism of HM pectin.[4] On the other hand, computational studies[10,11] suggested that the solvent composition may have more specific effects on chain dimension and stiffness by modulating the repulsive electrostatic interactions between charged groups. More in general, the presence of cosolutes is known to have pronounced effects on the properties and stability of supramolecular structures.[12−14]

In the present work we perform static and dynamic light scattering experiments on pectin solution with different amounts of sucrose, ranging from few % (w/w) up to a value just below the threshold required for gel formation. The aim is to relate the sucrose effects on pectin properties in solution with the occurrence of gelation observed only in the presence of a very large amount of such cosolute. In applying light scattering techniques to the study of natural polysaccharides such as pectin, the major difficulty is caused by the presence of large aggregates even in very dilute solution.[15−18] This, along with the heterogeneity of pectin molecular structure and its dependence on the extraction techniques,[16] makes arduous to obtain accurate determination of molecular weight and mean-square gyration radius.[15−18] Extensive work[17,19,20] on the effects of different techniques of solution clarification had shown that a too hard procedure causes the loss of pectaceous material; the high molecular weight species observed in pectin solution are not fragments of extraneous materials but indeed pectin aggregates which may have a role in gelation. For these reasons, we work on mildly clarified, semidilute (0.2% w/w) pectin solutions containing from 0 to 50% (w/w) of sucrose. At the pectin concentration here studied, gelation occurs at ∼55−60% of sucrose, as shown by rheological measurements.[21] Results, although concerning pectin in solution, provide new insight into the role of sucrose in pectin gelation, suggesting that it could be analogous to a glass transition promoted by the strong increase of solvent viscosity.

Materials and Methods

Pectin Samples. Slow-set high methoxyl pectin with a degree of esterification of 64.5% was a kind gift from Hercules Inc. (Wilmington, DE). Water was Millipore Super Q filtered with 0.22 μm filters. All other chemical compounds used were from Merk Co. A stock solution at pectin concentration of 2% w/w was preliminarily prepared by dissolving the powder in pure water at 100 °C for few minutes in a high-speed mixer. The solution was then cooled at room temperature overnight,

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10.1021/ma0205109 CCC: $22.00
Published on Web 08/23/2002

stored at 4 °C, and used up to 2 or 3 days. Samples for experiments were prepared by heating to 100 °C the potassium citrate buffer (pH 3.4) with the appropriate amount of water and sucrose. The pectin solution was then added and boiled for few minutes. The final buffer concentration was 12 mM. The final pectin concentration was 0.2% w/w. While heating and stirring, a few microliters of 50% acid citric solution was added to adjust the pH value to 3.1. Samples were finally filtered at 80 °C through 0.45 μm Corning filters directly into cuvettes. For each sucrose concentration, the same procedure was followed in preparing a sample without pectin to be used for measuring the solvent scattering.

Static and Dynamic Light Scattering Experiments. The sample was allowed to equilibrate at 20 °C for 1 h into a thermostated cell compartment of a Brookhaven Instruments BI200-SM goniometer. The temperature was controlled to within 0.1 °C using a thermostated recirculating bath. The light scattered intensity and time autocorrelation function were measured by using a Brookhaven BI-9000 correlator and a 100 mW Ar laser (Melles Griot) tuned at $\lambda = 514.5$ nm. Measurements were taken at different scattering vector $q = 4\pi n\lambda_0^{-1} \sin(\theta/2)$ where n is the refraction index of the solution, λ_0 is the wavelength of the incident light, and θ is the scattering angle. Values of the refraction index at different sucrose concentration were taken from the literature.[22]

Samples containing up to 50% sucrose do not form gel even after some days, and scattered light intensity and relaxation time do not show time dependence. The sample with 60% of sucrose takes a few hours to form a fully transparent gel. In this case, the scattered intensity was collected on different regions of the specimen by using a motor-driven cell holder. Comparison between time- and ensemble-averaged scattering intensity was also performed on a sample with 50% of sucrose, a value very close to that required for observing macroscopic gelation. Even in these conditions, no difference was observed, as expected for an ergodic system.[22−24]

Static light scattering data were corrected for the background scattering of the solvent and normalized by using toluene as calibration liquid. In dynamic light scattering experiments the correlator was operated in the multi-τ mode; the experimental duration was set in order to have 10 000 counting on the last channel of the correlation function.

Data Analysis. The first cumulant $\Gamma(q)$ was determined by a three-cumulant fit of the field time correlation function $g^{(1)}(q,t)$. Only the last 50 points of the total 200 channels are excluded in the fit at all angles and sucrose concentrations. The polydispersity is found to increase from about 0.3 at zero sucrose concentration up to 1 for the 50% sucrose concentration.

Results and Discussion

Static Light Scattering Experiments. The left panel of Figure 1 shows the excess scattering intensity at $T = 20$ °C of 0.2% (w/w) pectin solutions with different amounts of sucrose. Data are plotted vs q-vector on a double-logarithmic scale. The main visible effect of increasing sucrose concentration is the intensity decrease. This can be expected as due to the increase of the refraction index of the solvent, which reduces the specific refractive index increment (dn/dc) of the solute.[25] Quantitative comparison of data at different solvent composition requires accurate dn/dc measurements, which in our case are made not feasible with the standard differential diffractometers due to the high viscosity of the solvent. On the other hand, information that can be derived at the molecular level from this quantity such as solvent preferential hydration or exclusion[25] has a clear meaning at very dilute polymer concentrations, well below the value of the pectin concentration here studied.[15,16] To the purpose of the present work it is sufficient to recall that the dn/dc change does not affect the q dependence of the structure factor $P(q)$, that is, the shape of the q dependence of scattered intensity on a logarithmic scale. In the right panel of Figure 1 data at different sucrose concentrations have been arbitrarily shifted along the y-axis to evidence that visibly distinct curves at low q value show an identical power-law behavior at larger q. The power-law exponent is also equal to that found in the gel formed in the presence of higher sucrose concentration (60% w/w). The q dependence of the structure factor can be described by the empirical approximation often used for describing the q dependence of the static light scattered from fractal clusters:[26,27]

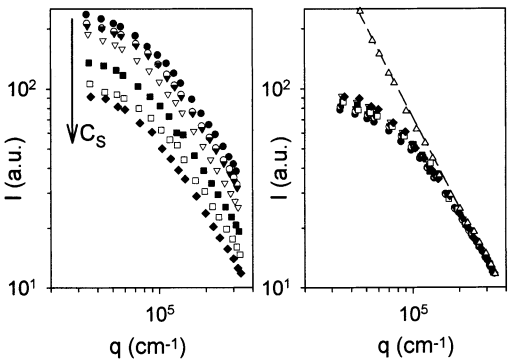

Figure 1. Left: excess scattering intensity of 0.2% (w/w) pectin solutions for different sucrose concentrations: (●) 0%; (○) 5%; (▼) 10%; (▽) 20%; (■) 30%; (□) 40%; (◆) 50%; $T = 20$ °C. Right: same data shifted along the y-scale to make coincident the points at higher q values. Data relative to a gelled sample formed in the presence of 60% sucrose are also shown (△).

$$P(q) = \frac{I(q)}{I(q=0)} = (1 + a(qR_g)^2)^{-d_f/2} \quad \text{with } a = \frac{2}{3d_f} \qquad (1)$$

where d_f is the fractal dimension and R_g the gyration radius. In the case of semidilute solutions, the same expression can be used with R_g being the apparent gyration radius proportional, with a factor of order one,[28] to the static screening length ξ. The latter represents the monomer−monomer correlation length beyond which excluded-volume interactions are screened by the presence of monomers of other chains.[28]

Fitting of each set of data to eq 1 was performed including $I(q=0)$ as fit parameter. In a first run R_g, d_f, and $I(q=0)$ were left as free parameters. Since the spreading of the d_f values over all sucrose concentration was found very small, we repeated the fitting procedure by keeping d_f constant and equal to the found average value ($d_f = 1.55 \pm 0.1$). We recall that the same value is found in a gelled sample formed at 60% sucrose concentration, as shown in Figure 1. Although rather low, it is consistent with that observed in other gels, in which a low packing of polymers allows a cross-link percolation even at very low concentration.[29,30] Results for R_g at different sucrose concentration are plotted in Figure 2. A steady, although small, increase of R_g is observed at increasing sucrose concentration. Scattered intensity data, normalized for $I(q=0)$, are plotted as a function of qR_g in Figure 3. All data collapse to one common master curve, highlighting the reliability of the sucrose effect on the increase of screening length. In the frame of the "blob" model[31] this effect can be visualized as an increase of the "blob" size, reflecting an increased local stiffness of the chain. The latter must be traced to the repulsive electrostatic interaction between charged

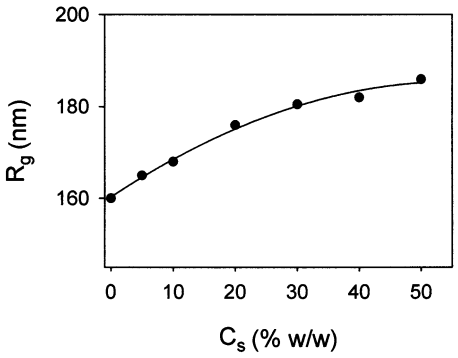

Figure 2. Apparent gyration radius of pectin at different sucrose concentrations obtained by fitting data to eq 1.

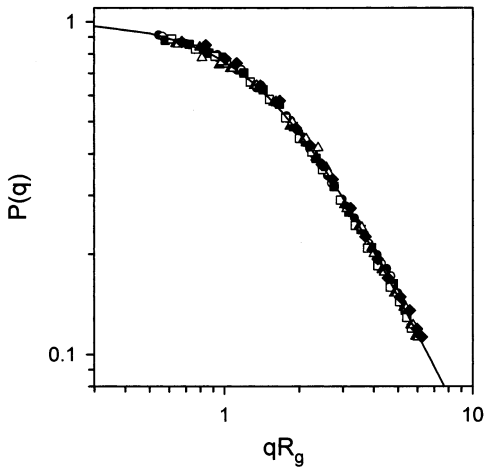

Figure 3. $P(q)$ vs qR_g. Symbols as in Figure 1. R_g values at different sucrose concentrations are given in Figure 2. The continuous line is the fit to eq 1 with $d_f = 1.55$.

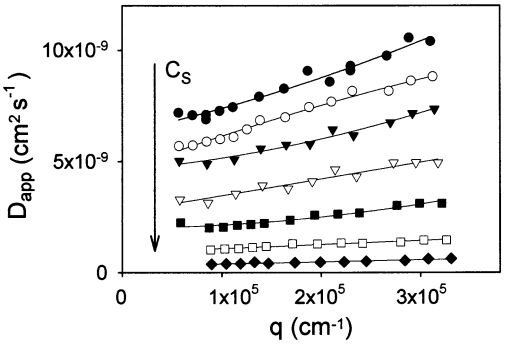

Figure 4. Apparent diffusion coefficient of pectin vs q at different sucrose concentrations. Symbols as in Figure 1.

groups of pectin enhanced by the decrease of dielectric constant of solution. We note that an opposite result should be expected on the basis of the decreased solvent quality.[28] Indeed, the sucrose is well-known to stabilize the native structure of proteins, and this effect is currently ascribed to the increased cost of keeping hydrophobic surfaces exposed to the solvent. In the case of semidilute solution of hydrophobic polymers, crowding of chains should be observed. In the pectin case, this type of effect appears hidden by the prevailing electrostatic contribution.

Dynamic light scattering experiments were performed on the same samples. The apparent diffusion coefficient, $D_{app} = \Gamma(q)/q^2$, obtained from cumulant analysis is shown in Figure 4 as a function of q at different sucrose concentrations. The main effect of

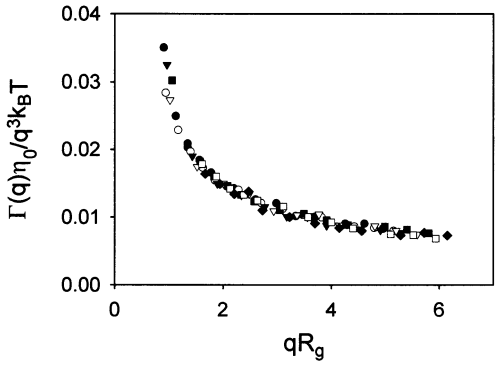

Figure 5. Dependence of $\Gamma^*(q)$ as defined in eq 2 on qR_g. Symbols as in Figure 1.

increasing sucrose concentration is the decrease of the apparent diffusion coefficient that can be related to the bulk viscosity increase. The q dependence is similar to that observed in the case of linear, flexible chains or branched polymers[27,28,31,32] when the dynamics of concentration fluctuations is probed on a length scale smaller than ξ.[33] In this case the main contribution to fluctuations is due to the internal modes and D_{app} increases proportionally to q.

It should be noted that this type of q dependence can also be obtained in largely polydisperse systems, where the contribution of particles of different size to the correlation function is strongly dependent on the scattering angle. To check this possibility, correlation functions were analyzed in terms of a distribution of relaxation times using CONTIN.[33] At all q values and sucrose concentration, a well-defined, moderately broad peak was found in the long time scale, with a mean relaxation time coincident within few percent with that calculated from cumulant analysis. On increasing sucrose concentration, it was also observed a small peak at a shorter time, corresponding to a fast decay already visible in the raw data and discussed below. In any case, its contribution to the scattered intensity was found negligible. The size distribution appears essentially monomodal at each scattering angle. Therefore, the diffusion coefficient obtained from cumulant analysis can be taken as the average value of this distribution.

The q dependence of the apparent diffusion coefficient can be more closely analyzed by plotting the data as $\Gamma^*(q)$ vs qR_g, with $\Gamma^*(q)$ defined as

$$\Gamma^*(q) = \left(\frac{\Gamma(q)}{q^3}\right)\left(\frac{\eta}{k_B T}\right) \qquad (2)$$

where η is the solvent bulk viscosity. The decay rate $\Gamma(q)$ at $qR_g \geq 1$ is predicted to scale as q^3 for chains with hydrodynamic interactions;[31] as a consequence, $\Gamma^*(q)$ should reach an asymptotic value that depends on polydispersity, branching, and solvent goodness. When data of Figure 4 are plotted in this way, a master curve is obtained as shown in Figure 5. The remarkable collapse of data relative to different sucrose concentration is obtained by taking into account the small change of R_g and the large increase of bulk viscosity (data from the literature[22]). The overall behavior is similar to that found for branched macromolecules:[28,32] for intermediate qR_g values, $\Gamma^*(q)$ displays a mixture of translational diffusional and internal motion, and the plateau is reached at very large qR_g values; also, it is much lower that that observed in the case of linear flexible chains.

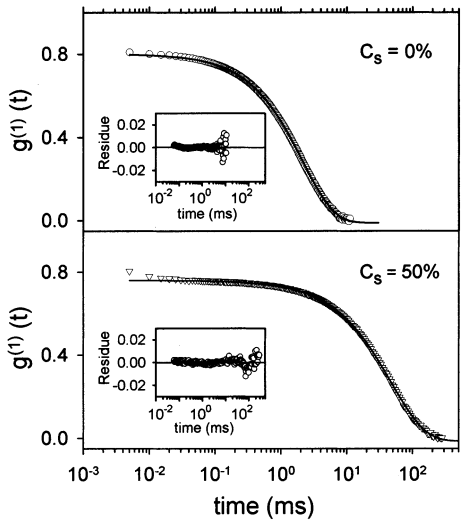

Figure 6. Field correlation functions $g^{(1)}(t)$ at 90° scattering angle for two pectin samples at 0% and 50% sucrose concentration. Continuous lines represent the fit to a stretched exponential function. Residue plots of fitting are shown in the insets.

It has been suggested that this can reflect a reduced internal flexibility of chains due to branching or to constraints imposed by the transient network.[32]

The field correlation functions, $g^{(1)}(t)$, of samples at 0% and 50% sucrose concentration and 90° scattering angle are shown in Figure 6. The fit of data with a single-exponential form was found very poor even in the case of 0% of sucrose where it is not clearly visible the contribution of the fast decay observed at 50% of sucrose. Indeed, the presence of this contribution is gradually appearing with increasing sucrose concentration, suggesting that it could be ascribed to solvent relaxation, as observed in other polymers in organic solvents when the size of the solvent molecules is large enough.[35] In our case, because of the small amplitude of the fast mode and the shortage of experimental points in this time scale, data fit with a bimodal exponential function or a function with two stretched exponentials cannot give reliable results. Thus, we have neglected the fast decay and considered the slow mode only; data were fitted with the stretched exponential function:

$$g^{(1)}(t) = A \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{3}$$

Fit residues are shown in the insets of Figure 6. The stretch parameter β is 0.92 and 0.82 for 0% and 50% sucrose concentration, respectively. A gradual decrease of β is observed on increasing sucrose concentration for large q values down to about 1.5×10^5 cm^{-1}. At lower q this dependence is not visible anymore, and β is about 0.95 ± 0.03. The mean relaxation time, $\langle\tau\rangle$, is calculated by

$$\langle\tau\rangle = \left(\frac{\tau}{\beta}\right)\Gamma(\beta^{-1}) \tag{4}$$

where $\Gamma(x)$ is the gamma function. Results at two different scattering angles vs sucrose concentration are shown in Figure 7. The smooth curves drawn in the figure are best fits to the diverging expression[36]

$$\langle\tau\rangle = \langle\tau_0\rangle(C_s^* - C_s)^{-\nu} \tag{5}$$

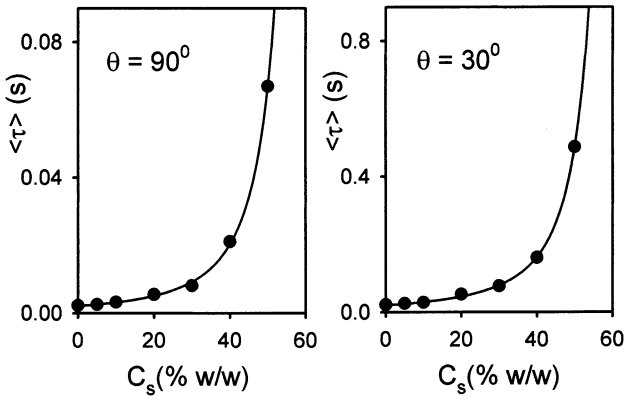

Figure 7. Mean relaxation time calculated by eq 4 vs sucrose concentration at two different scattering angles. Continuous lines represent the fit to eq 5 with $\nu = 2.2 \pm 0.2$ and $C_s^* = 65 \pm 3$ in both cases.

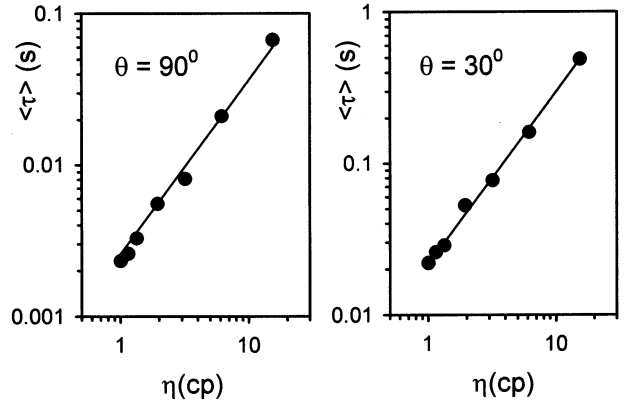

Figure 8. Double-logarithmic plot of the mean relaxation time vs the macroscopic viscosity of the solvent at two different scattering angles. The slope of the straight line is 1.1 ± 0.1 in both cases.

where C_s^* is the critical sucrose concentration at which the diffusivity goes to zero. We found $\nu = 2.2 \pm 0.2$ and $C_s^* = 65 \pm 3$. The latter is in good agreement with the sucrose amount required for obtaining a pectin gel, as experimentally observed.[21] The diverging behavior of mean relaxation time suggests taking into account the similar diverging increase of the bulk viscosity with increasing sucrose concentration. This is made in Figure 8, where $\langle\tau\rangle$ values of Figure 7 are reported vs the bulk viscosity of the solvent. A straight line of slope 1.1 ± 0.1 is obtained in both cases, so evidencing that the critical dynamic slowing down of the system reflects the huge increase of bulk viscosity, as usually observed in glass-forming liquids.[37] A failure of the system to structurally relax on the experimental time scale is predicted to occur at a value of sucrose concentration where gelation is in fact observed. These findings recall the similarity between the colloidal glass transition and gelation, recently discussed in the literature.[36,38] Indeed, both processes can be seen as "manifestations of a more general jamming transition"[38] induced by the kinetic arrest of the system. Considering the large amount of sucrose required for observing macroscopic gelation, this similarity should be equally applied if we look at our data in terms of pectin effects on the temperature of glass transition of aqueous sucrose solution. This point of view has been embraced in description of gelation of κ-carrageenan or galactomannan in glucose syrup.[39] As a matter of fact, the elongated larger size of the polysaccharide with respect to sucrose molecule provides

at moderate polymer concentration a transient network which evolves toward a frozen (glass) configuration when the viscosity diverges. Further, the increased stiffness and swelling of the chains induced by the presence of sucrose may promote interactions between larger clusters so contributing to establish the freezing conditions.

Conclusions

We have studied the effect of increasing sucrose concentration on static and dynamic light scattering of pectin solutions to the purpose of understanding the role of sucrose in pectin gelation. Angular dependence of data indicates that, under our experimental conditions, pectin in solution behaves like a system of branched clusters with strong hydrodynamic interactions. Two main effects are observed on increasing sucrose concentration: (i) the screening length increases while the fractal dimension remains constant and equal to that found in a gelled sample; (ii) the dynamics displays a stretched diffusional behavior with a diverging mean relaxation time, proportional to solvent bulk viscosity. The divergence of viscosity and associated structural relaxation time, a typical hallmark of a glass transition, is predicted to occur at a critical value of sucrose concentration where gelation is, in fact, observed.

The similarity between gelation of attractive colloidal systems and glass transition has been recently discussed in terms of a "jamming" transition.[36,38] In this frame, the liquid-to-solid transition of a polymeric system is seen as a kinetic arrest due to critical crowding of clusters occurring at increasing volume fraction and attractive energy. In the case of pectin, gelation at a given polymer concentration occurs on increasing sucrose concentration. The latter appears to play the role of a critical parameter of the freezing transition, since its presence increases the strength of both excluded-volume and hydrodynamic interactions.

Acknowledgment. We thank Dr. Sung Gun Chu for having stimulated our attention to the gelation mechanism of HM pectin and Hercules Inc., Wilmington, DE, for having kindly provided the pectin. We also thank Dr. M. Manno for discussions and a critical reading of the manuscript. Technical support from Mrs. F. Giambertone, G. Lapis, M. Lapis, and R. Megna is also acknowledged. The present work is part of a research project "Role of solute-solvent interactions in the gelation of biomolecules" inside the COST P1-WG1 "Soft Condensed Matter" European Program.

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MA0205109