DWS Microrheology of a Linear Polysaccharide

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Received August 8, 2005; Revised Manuscript Received December 22, 2005

Diffusing wave spectroscopy has been used to measure the rheological behavior of pullulan ($M_w = 1 \times 10^5$) aqueous solutions up to concentration of 40 g/dL. It was found that these solutions were mainly viscous, with the loss modulus G'' higher than the elastic modulus G'. The plot of the specific viscosity η_{sp} as a function of pullulan concentration showed two critical concentrations $c^* = 4$ g/dL and $c^{**} = 15$ g/dL. For $c < c^*$, $\eta_{sp} \approx c^{1.25\pm0.05}$; for $c^* < c < c^{**}$, $\eta_{sp} \approx c^{2\pm0.05}$; and for $c > c^{**}$, $\eta_{sp} \approx c^{4.5\pm0.5}$. These results are in very good agreement with those reported in the literature.

1. Introduction

Since its introduction as a microrheological technique by Mason and co-workers,[1,2] diffusing wave spectroscopy (DWS) has been widely used to probe the rheological behavior of complex fluid systems. An advantage of DWS over conventional rheological methods is that it gives access to high-frequency rheological behavior of soft-material systems. These systems include, to cite but a few, concentrated emulsions,[1] water-soluble synthetic polymers,[3] concentrated surfactant solutions,[4] and gels.[5]

The DWS determination of the rheological properties of a medium is accomplished by measuring the temporal behavior of the mean-square displacement (MSD), $\langle \Delta r^2 \rangle$, of probe particles embedded in the medium. If the medium was a purely viscous liquid, the probe particle would undergo Brownian motion, and the MSD would vary linearly with time, $\langle \Delta r^2 \rangle \sim t$. If the medium was a solid, the probe particle would oscillate about a fixed position, and the MSD would be independent of time, $\langle \Delta r^2 \rangle \sim t^0$. The MSD of a probe particle embedded in a general viscoelastic medium would vary as $\langle \Delta x^2 \rangle \sim t^{\alpha}$, where α varies between zero and unity depending on the nature of the medium. DWS is used to determine $\langle \Delta r^2 \rangle$ and α and hence the elastic (G') and loss (G'') moduli of the medium. It is essential to use neutrally buoyant, inert probe particles of a size and to a concentration such that the light is multiply scattered. Each photon must suffer so many collisions with probe particles that its path is completely randomized as it diffuses through the medium.

Mason and co-workers[1,2] and also Dasgupta and co-workers[3] have detailed the theory of DWS microrheology. They have shown that the viscoelastic moduli are given as functions of frequency ω as[3]

$$G(\omega) = \frac{k_B T}{\pi a \langle \Delta r^2(1/\omega) \rangle \Gamma[1 + \alpha(\omega)]} \tag{1}$$

$$\begin{aligned} G'(\omega) &= G(\omega) \cos[\pi\alpha(\omega)/2] \\ G''(\omega) &= G(\omega) \sin[\pi\alpha(\omega)/2] \end{aligned} \tag{2}$$

These equations are used to calculate G' and G''. $\langle \Delta r^2(1/\omega) \rangle$ is the value of the MSD at time t, which is equal to $^1/_{\omega}$, and $\alpha(\omega) = \partial \ln\langle \Delta r^2(\tau) \rangle / \partial \ln t$ is the slope of the graph of MSD plotted against time to logarithmic scales evaluated at t. The Γ function is the result of Fourier transform.

Pullulan is an exocellular microbial polysaccharide typically obtained by cultivation of strains of the fungus *Aureobasidium pullulans* on glucose.[6] It is a linear random coil polysaccharide composed of maltotriose units linked by α-D-(1,6) glycosidic bonds. Although pullulan is a very good candidate as a model linear biopolymer, little is reported in the literature about its rheological behavior. Pullulan does not form gels, and its aqueous solutions have relatively low viscosity exhibiting Newtonian or near-Newtonian flow behavior at low polymer concentrations. Lazaridou and co-workers[7] have used capillary and rotational viscometers to measure the viscosity of aqueous solutions of three pullulan samples of different molar masses ranging between 100 and 560 × 10^3 daltons to concentrations of 12 g/dL. Their measurements showed that the intrinsic viscosity [η] values ranged from 0.38 to 0.70 dL/g, which are low when compared to other polysaccharides, and attributed this to the low molecular weight and to the relatively high chain flexibility of pullulan. Although Nordmeier[8] found that pullulans did not form spherical random coils in dilute solution, indicating that they were less flexible than dextran and synthetic random coil polymers, with a Flory constant of 0.556.

The aim of this paper is to investigate the rheological behavior of pullulan aqueous solutions over a wide concentration range (up to 40 g/dL) using diffusing wave spectroscopy (DWS).

2. Materials and Methods

2.1. Materials and Sample Preparation. Pullulan was purchased from Fluka (product number 70074), with weight average molar mass of 100 000 daltons and ratio of weight averaged to number averaged molar mass of 1.9. Latex particles of diameter 1.053 μm in a stock solution of 2.67% were obtained from Polysciences Inc. (Warrington, PA).

A mere aqueous solution of 50% pullulan in Milli-Q water (water purified using a Milli-Q apparatus, Millipore Corp., Bedford, MA)

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10.1021/bm050566l CCC: $33.50

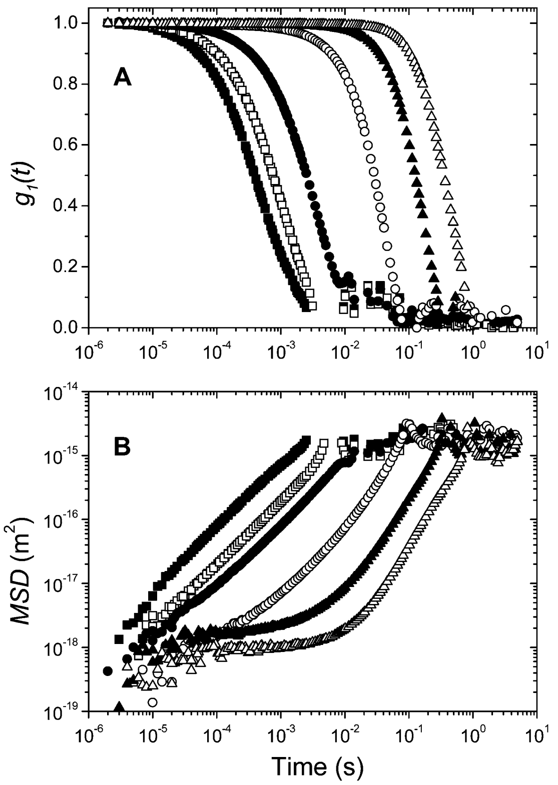

Figure 1. (A) Field autocorrelation function $g_{(1)}(t)$ and (B) mean-square displacement MSD as a function of correlation time for different pullulan solutions. Pullulan concentrations were 2% (■), 6% (□), 10% (●), 20% (○), 30% (▲), and 40% (△).

containing 0.02% sodium azide was prepared. This mere solution was stirred at room temperature overnight using a magnetic stirrer. Samples containing different pullulan solutions and 0.5% latex particles were obtained by mixing appropriate amounts of pullulan mere solution, Milli-Q water, and latex particles and were stirred overnight to ensure complete mixing.

2.2. DWS Experimental Setup. The DWS experimental arrangement used in this study has been fully described previously.[9] The samples were contained in glass cells of width 10 mm, height 50 mm, and path length L of 4 mm, and were illuminated with a 35 mW HeNe Melles-Griot laser operating at wavelength $\lambda = 633$ nm. The laser beam was expanded to approximately 8 mm on the surface of the cell, and the light scattered both forward (transmitted) and backward (backscattered) was separately detected using single-mode optical fibers (P1-3224-PC-5, Thorlabs Inc., Germany) fitted with GRIN lenses (F230FC-B FC, Thorlabs Inc., Germany). The optical fibers were connected to a Hamamatsu HC120-08 PMT photomultiplier tube module, and the intensity autocorrelation functions of the scattered light were obtained using a Malvern 7132 correlator.

3. Results and Discussion

Eleven aqueous pullulan solutions were prepared with concentrations ranging from 0 to 40 g/dL; all eleven transmitted autocorrelation functions were re-expressed in terms of MSD. Field autocorrelation functions of selected concentrations are shown in Figure 1A. These autocorrelation functions are asymptotic to unity at short times and asymptotic to zero at long times. The rheological properties of the sample determine the time scale over which the autocorrelation function falls from unity to zero; clearly dilute solutions can be investigated only at short times, whereas concentrated solutions can be investigated at long times. The corresponding MSDs of the probe particles are plotted against time to logarithmic scales in Figure 1B, where it is apparent that DWS measures the MSD over wide time ranges and that the time range is solution concentration dependent. For dilute solutions, the curves are linear with slopes close to unity, indicating purely viscous behavior over all times accessible to measurement. The variation of the MSD with time for the concentrated solutions is far more complex. At the longest times, the solutions act as viscous liquids, but as the time is reduced, the MSD becomes almost independent of time, indicating elastic behavior.

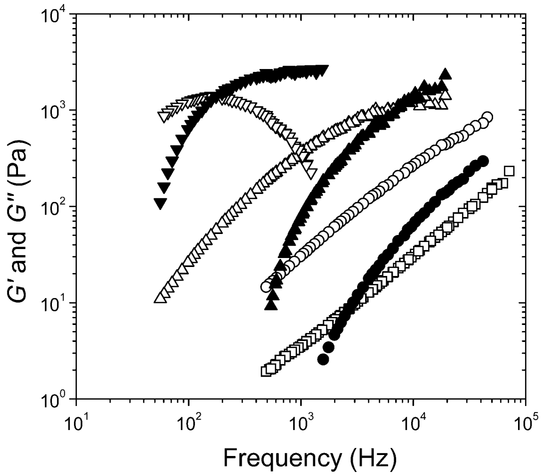

Figure 2. Elastic modulus G' (open symbols) and loss modulus G'' (solid symbols) as a function of frequency for different pullulan solutions. Pullulan concentrations were 2% (■), 10% (●), 20% (▲), and 40% (▼).

Notice in this experiment that the probe particle root-mean-square displacements range from 1 to 200 nm; these are the resolution limits imposed by the autocorrelation functions approaching unity or zero, respectively. The upper limit can be extended using dynamic light scattering.[3]

The rheological moduli obtained using eqs 1 and 2 are plotted against frequency to logarithmic scales in Figure 2. For all samples, G'' was larger than G' at low frequencies; indeed for dilute solutions (concentration less than 6 g/dL), only G'' was observed, for intermediate concentration solutions (6 g/dL to 10 g/dL), G'' was greater than G' with G' increasing more rapidly with frequency, and for large concentration solutions (15 g/dL to 40 g/dL), a crossover frequency, ω_c, was observed above which G' exceeded G''. The variation of crossover frequency with solution concentration c is shown in Figure 3; the linear least-squares fit implies $1/\omega_c \sim c^{5.45\pm0.51}$.

The complex viscosity η^* ($\eta^* = [(G'^2 + G''^2)^{1/2}]/\omega$) of each solution was obtained, and the specific viscosity is plotted against concentration to logarithmic scales in Figure 4, which also includes the values obtained by Lazaridou et al. using capillary and rotational viscometers for aqueous solutions of pullulan of three different molecular weights. The results obtained in this work are compatible with those of Lazaridou et al.[7] over the common concentration range, but this current work extends the range threefold from 12 g/dL to 40 g/dL. The good agreement with previous work is an important verification of the efficacy of the DWS technique. The graph shown in Figure 4 is a smooth curve; however, following previous authors,[10,11] we have approximated the curve using three straight lines, thereby dividing the data into three regions, bounded by the two critical concentrations c^* and c^{**}, with the dilute region ($c < c^*$), the semidilute region ($c^* < c < c^{**}$), and the concentrated region ($c > c^{**}$). We found that the viscosity varied as $\eta \sim c^{1.25\pm0.05}$ in the dilute region, Doublier et al.[12] and Morris[13] have found that for many polysaccharides this

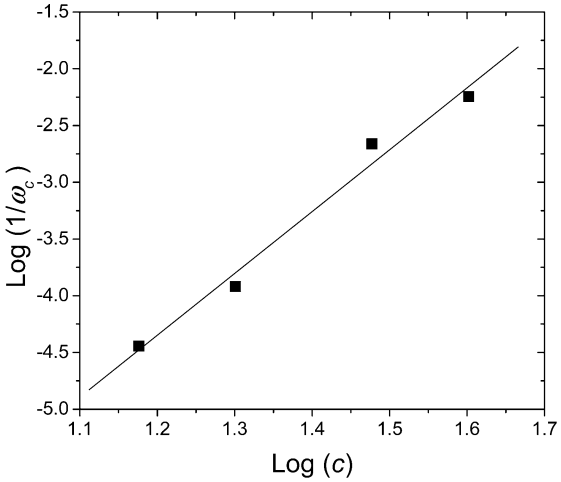

Figure 3. The crossover time $(1/\omega_c)$ as a function of pullulan concentration to logarithmic scales. The solid line is the linear fit yielding a slope of 5.45 ± 0.51.

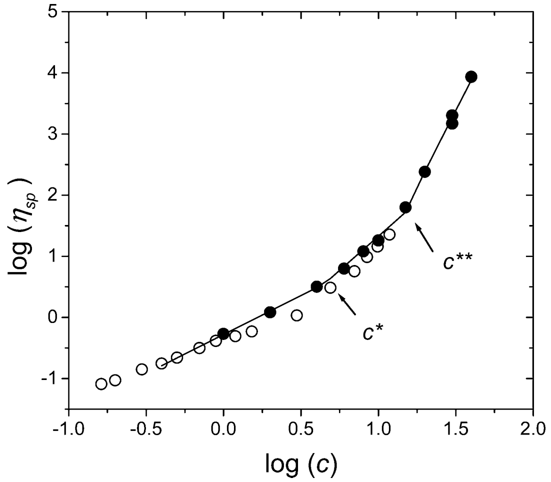

Figure 4. Specific viscosity as a function of the reduced concentration. Solid symbols are from present work, and open symbols are for solutions of pullulan ($M_w = 99 \times 10^3$) reported from Lazaridou et al.[7] Solid lines are the fits to results from present work (see text for values).

exponent lies between 1.1 and 1.4. In the semidilute region, the viscosity varied as $\eta \sim c^{2.0\pm0.05}$, in good agreement with theory and the values reported for other polysaccharides.[10] In the concentrated regime, we found, $\eta \sim c^{4.5\pm0.5}$, where the exponent is predicted by de Gennes[14] to be 4.5 for very large molar mass flexible polymers in good solvents, assuming the Flory constant is 0.556 as reported by Nordmeier.[8] This excellent agreement is probably more fortuitous than significant. The exponent is generally found experimentally to be between 3.3 and 5 for aqueous solutions of many random coil polysaccharides, although the exponent can be as high as 5.5 for xanthan.[15]

The reciprocal of the frequency at which G' is equal to G'' can be identified with the relaxation time; this can be identified for solutions with concentrations greater than 10 g/dL. The relaxation time is plotted against the concentration to logarithmic scales in Figure 3. We find the exponent to be 5.5, which is higher than that found in synthetic polymers, but studies of other polysaccharides have also found large exponents.[15]

This difference between synthetic polymers and polysaccharides probably has two causes: first, pullulan is insufficiently flexible; and second, the pullulan used in this work had too small a molar mass to achieve a reptation regime. Furthermore, the polydispersity of the pullulan sample and its tendency to aggregate at high concentration could be the cause for the discrepancy between the synthetic polymers and polysaccharides.

4. Conclusions

The DWS measures of viscosity presented here are in good agreement with a previous study of aqueous pullulan solutions undertaken with capillary and rotating viscometers. Good agreement has also been demonstrated between DWS and theory, but observations on the five most concentrated solutions do not support the entanglement theory of polymer viscosity. This may, in part, be due to stiffer conformation of pullulan, to the low molar mass and the polydispersity of the pullulan sample, and to the aggregation of pullulan molecules at high concentrations.

Acknowledgment. We thank Pascal Hebraud for fruitful discussions and Adam Swanson for his technical assistance. The financial support of the New Zealand Foundation for research and technology, through the ISAT linkage grant, is gratefully acknowledged. A.J. Swanson was supported by a Massey University MURF grant.

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BM050566L