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Aggregation Behavior in the Semidilute Poly(*N*-vinyl-2-pyrrolidone)/Water System

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ABSTRACT: Dynamic and static light scattering experiments were performed on aqueous solutions of poly(*N*-vinyl-2-pyrrolidone) in the dilute and semidilute regime. In the dilute regime, typical good solvent behavior is found. In the semidilute regime, we observe two relaxation times in the autocorrelation functions and intense forward scattering. The short time relaxation has a typical q^2 dependence, characteristic of diffusion, and the long time relaxation an approximately q^3 dependence, characteristic of intraparticle dynamics. This behavior is not consistent with predicted semidilute, good solvent system behavior but instead indicates the presence of aggregates. Using combined static and dynamic scattering, we show these aggregates to be approximately 2−3 times the size of the dilute-solution radius of gyration. We attribute this anomalous behavior to the unique, tetrahedral hydrogen bond network of water and show that denaturing the water through the addition of denaturing agents known to disrupt the water structure significantly diminishes the aggregate size. We also show through pressure denaturation that the aggregation process is reversible.

1. Introduction

Water-soluble polymers have been extensively studied for reasons of both scientific interest and commercial applications. In general, water solubility for a nonionic water-soluble polymer is conferred through a balance between the hydrophilic nature of some polar portion, responsible for the polymer's solubility in water, and a nonpolar portion, typically the backbone, which gives rise to hydrophobic interactions. The polymer's solution properties are determined to a large degree by the balance between hydrophilic and hydrophobic interactions.

Poly(*N*-vinyl-2-pyrrolidone), hereafter denoted as PVP, can be considered a typical water-soluble polymer. It contains a strong hydrophilic component (the amide group) and a significant hydrophobic moiety (six carbons per monomer unit). PVP has a wide variety of commercial applications, finding use in the medical, food, and pharmaceutical industries for such diverse uses as a blood plasma substitute, binding agent for drug delivery, and food thickener.[1,2] Because of its many uses and its structural similarity to biopolymers, PVP has been extensively studied through nearly every technique used in the characterization of macromolecules including viscometry, osmometry, NMR, and light scattering.[3−9] Past light scattering experiments have been somewhat limited. The molecular weight scaling behavior has been not quantified for the dilute concentration regime, nor has there been a complete investigation of the slow mode, discovered in the autocorrelation function in the semidilute region.[10] Of particular interest is the origin of this slow mode.

Slow modes have been predicted and observed for semidilute, θ-solvent systems. In such systems the absence of excluded volume effects leads to entanglements, which gives rise to a gel modulus[11−14] and a resulting slow relaxation. This slow relaxation time has been predicted and observed to be q-independent. Good solvent, semidilute systems are not expected to display slow mode behavior, and this has been found to be generally true for hydrocarbon systems.[14,15] However, various aqueous, good solvent systems have been found to display slow mode behavior in the semidilute region.[10,16−18] To our knowledge, the physical cause of this anomalous behavior has not been explained. In this paper we present some experimental results on PVP in water and denatured water in an attempt to elucidate the origin of this slow mode.

This paper is organized in the following manner. We start by presenting experimental results obtained from static and dynamic light scattering experiments in the dilute regime. These confirm the essentially ideal good solvent behavior of PVP in water. We then present experimental results obtained from aqueous, semidilute solutions. We show that the fast mode behavior is characteristic of typical, good solvent, semidilute behavior and that the slow mode behavior is most likely due to polymer aggregation. By combining the dynamic and static light scattering results, we extract a form factor and a size estimate for the aggregates. We then present results obtained from dilute and semidilute solutions of PVP in chemically denatured water. The purpose of these experiments is to determine if the anomalous slow mode behavior is reduced when the water structure is disrupted. We find that this is indeed the case. Finally, we show through the use of pressure-denaturation experiments that the aggregation is completely reversible.

2. Sample Preparation and Experimental Conditions

Commercial samples of PVP of varying molecular weights were purchased from Aldrich and dialyzed. The $M_w = 592$ kg/mol sample was synthesized in-house. The molecular weights (determined by static light scattering) and polydispersities (determined by GPC) are tabulated in Table 1. Although the polydispersitites of these samples are large, our values are similar to those used in other studies of this polymer.[1] Distilled, deionized water was obtained from a Millipore Continental Water Systems unit. The level of impurities from such a system is stated to be 20 ppb. Stock solutions were prepared gravimetrically and allowed to stir overnight. Varying amounts of stock solution were syringe filtered directly into light scattering cells, and then diluted to the desired concentrations with syringe filtered water. The filters used were either 0.22 or 0.45 μm Millipore filters, depending on the molecular weight of the polymer. The solutions were then centrifuged to remove any residual dust.

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Table 1. Tabulation of Results from Static and Dynamic Light Scattering Experiments in Dilute, Aqueous Solutions of PVP at $T = 25$ °C

M_w (g/mol)	M_w/M_n	A_2 (10^{-4} mol·mL/g^2)	$\langle R_g^2\rangle_z^{1/2}$ (nm)	R_H (nm)
10 000 ± 200	1.85	15.4 ± 1.1		2.8 ± 0.1
49 000 ± 300	3.24	8.4 ± 1.0		7.7 ± 0.1
389 000 ± 3 000	3.56	4.7 ± 0.2	40.7 ± 1.1	21.0 ± 0.1
592 000 ± 15 000	2.14	4.4 ± 0.8	48.5 ± 1.1	32.1 ± 0.3
815 000 ± 13 000	2.70	3.7 ± 0.5	71.7 ± 0.6	38.1 ± 0.4

Static light scattering measurements were done with a Brookhaven 2030 goniometer with the accompanying Zimm plot software. The polarized light source was either the 530.9 nm line of a krypton laser, or the 488 nm line of an argon ion laser. The value of dn/dc for PVP in water for both wavelengths is stated to be 0.18 mL/g.[19] Dynamic light scattering measurements were done with an ALV5000 correlator from ALV. The angular range of measurements was 30−150°. The viscosity of aqueous 1 M thiourea at 25 °C was measured to be 0.89 cP by a Contraves Low Shear 30 viscometer. The refractive index was measured by a Chromatix KMX-16 laser differential refractometer to be 1.35.

3. Experimental Results

3.1a. Static Light Scattering in the Dilute Regime. For a dilute polymer solution the scattering intensity is given by the well-known Zimm equation:[20,21]

$$\frac{KC}{\Delta R(\theta)} = \frac{1 + q^2\langle R_g^{\,2}\rangle_z/3}{M_w} + 2A_2C \tag{1}$$

which applies when $2A_2C < 1/M_w$ and $q^{-1} \gg R_g$. Here, $K = 4\pi^2 n^2(\partial n/\partial c)^2/(N_A\lambda^4)$, n is the solvent refractive index, N_A is Avogadro's number, C is the polymer concentration, $\Delta R(\theta)$ is the excess Rayleigh scattering, M_w is the weight average polymer molecular weight, A_2 is the second virial coefficient, and $\langle R_g^2\rangle_z$ is defined as the z-average square of the radius of gyration. Figure 1a shows the molecular weight dependence of A_2. The inset is the Zimm plot for M_w = 815 kg/mol. The power law dependence of A_2 on M_w is found to be

$$A_2 = [(2.87 \pm 0.83) \times 10^{-2}]M_w^{\;-0.32\pm0.02}\ \mathrm{mL{\cdot}mol/g^2} \tag{2}$$

The theoretical[22] power law dependence for monodisperse, random coil polymers in a good solvent is $A_2 \propto M_w^{\;-0.20}$. Fetters et al.[23] tabulated the measured power law dependence of A_2 of numerous hydrocarbon systems with $M_w/M_n \le 1.1$ and find that the molecular weight scaling of A_2 ranges from −0.188 to −0.285. The molecular weight scaling of A_2 for polydisperse polymer samples such as ours is dependent upon both the molecular weight distribution for each sample and the molecular weight dependence of the scattering cross section. Within a sample the higher molecular weight chains scatter light more strongly, which tends to lower the measured A_2 value. Hence if the higher molecular weight samples are more polydisperse, the power law dependence will tend to be lower, as observed here. Thus the observed scaling behavior is consistent with a good solvent system. The actual magnitudes of the A_2 values are approximately 30% larger than those for a prototypic good solvent system such as polystyrene in toluene.[23] Unlike hydrocarbon systems where the weak van der Waals interactions ensure a positive Flory interaction parameter,[22] aqueous systems have strong hydrogen-bond interactions which can lead to large negative Flory interaction parameters. If the hydrocarbon moiety is small, the A_2 values can be appreciably larger.[24]

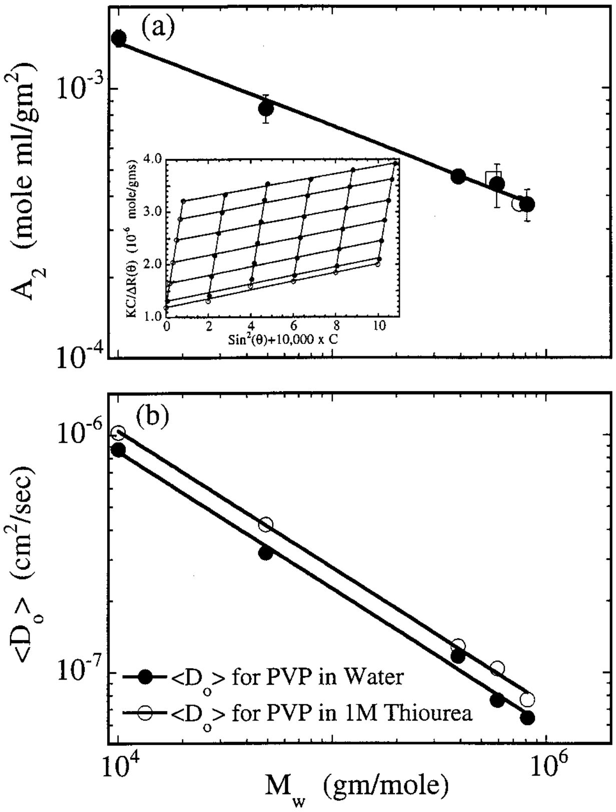

Figure 1. (a) Measured A_2 values (filled circles) for PVP in water at $T = 25$ °C. The open symbols are A_2 values found by Nordmeier and Lechner (open circle)[9] and Eisele and Burchard (open square).[10] The inset is a Zimm plot for the M_w = 815 kg/mol sample. (b) $\langle D_0\rangle$ as a function of M_w for PVP in water (closed circles) and PVP in aqueous 1 M thiourea (open circles). The molecular weight scaling for A_2 and $\langle D_0\rangle$ are consistent with good solvent behavior.

Utilizing the three molecular weights for which we could measure $\langle R_g^2\rangle_z^{1/2}$, we obtain a molecular weight dependence of $M_w^{\;0.82}$. This is larger than the Flory prediction of $^3/_5$, but considering the paucity of our data as well as the above-mentioned polydispersity, it seems reasonable to conclude that our values are consistent with good solvent behavior.

3.1b. Dynamic Light Scattering in the Dilute Regime. In the limit of $qR_g \ll 1$ the dynamic structure factor of a polymer molecule in a dilute solution is an exponential with a decay time $\tau = 1/D_0q^2$, where D_0 is the self-diffusion coefficient, related to the hydrodynamic radius through the familiar Stokes−Einstein relation $D_0 = K_BT/6\pi\eta_0R_H$. Experimentally, the diffusion coefficients were obtained by measuring the intensity autocorrelation function. We follow the standard method of data reduction[25] to obtain the normalized, electric field autocorrelation function, $g_1(q,t)$. Polydispersities are accommodated through the cumulant form used here[26]

$$\ln|g_1(q,t)| = -\langle D_0q^2\rangle t + \frac{\mu_2t^2}{2} \tag{3}$$

where μ_2 is the second cumulant defined as $\langle(D_0q^2 - \langle D_0q^2\rangle)^2\rangle$. The measured polydispersity factors, given by $\mu_2/\langle D_0q^2\rangle^2$, are ≈0.25, confirming that the samples are polydisperse. [For polymer samples with $(M_w/M_n) < 2$ μ_2 is related to the polydispersity index by $\mu_2/\langle D_0q^2\rangle^2 =$

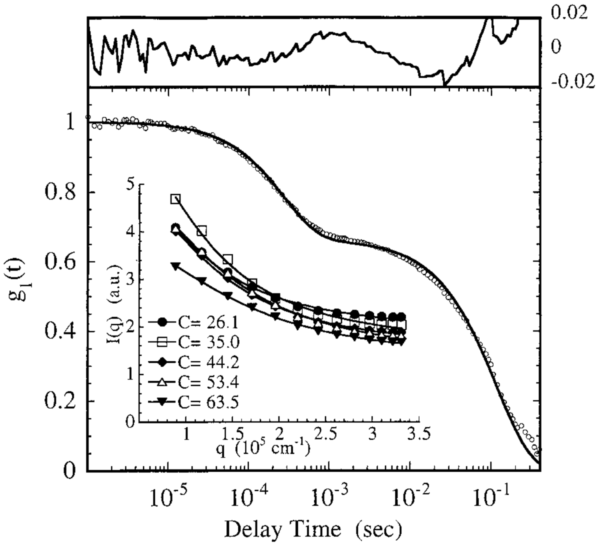

Figure 2. Autocorrelation function obtained at $\theta = 30°$ for a semidilute solution of PVP in water at $T = 25$ °C ($M_w = 389$ kg/mL, $C = 53.4$ mg/mL). The line is a fit to a double exponential relaxation, with the upper plot showing the residuals. The inset shows the scattering intensities for different semidilute concentrations.

$\nu^2(M_w/M_n - 1)$, where ν is the molecular weight scaling relation for diffusion.[27]] To determine $\langle D_0\rangle$, autocorrelation functions were obtained at multiple concentrations and q values. The fitted $\langle D(q,C)\rangle$ values were then extrapolated to zero concentration and zero q to obtain $\langle D_0\rangle$. Through use of the known solvent viscosity, these results are tabulated as R_H in Table 1. The molecular weight dependence of $\langle D_0\rangle$ is shown in Figure 1b. The power law dependence of $\langle D_0\rangle$ on M_w is found to be

$$\langle D_0\rangle = [(1.66 \pm 0.10) \times 10^{-4}]M_w^{-0.57\pm0.01}\ \mathrm{cm^2/s} \quad (4)$$

This power law scaling is consistent with many good solvent systems[23] and is equal to that obtained[24] for PEO in water, −0.571 ± 0.009.

3.2. Static and Dynamic Scattering in the Semidilute Region. The experimental results shown above indicate that dilute, aqueous solutions of PVP exhibit typical good solvent behavior. Therefore, one might expect continued good solvent behavior in the semidilute region. The static and dynamic properties of a polymer in a good solvent in the semidilute region are determined by a correlation length of concentration fluctuations (often described as a mesh size), ξ, which is predicted[22] to be molecular weight independent, and to follow a $C^{-0.75}$ scaling law. By measuring the cooperative diffusion coefficient, where $D_{coop} = K_BT/6\pi\eta_0\xi$, this scaling law has been observed in good solvent, semidilute, hydrocarbon systems.[15,28] Hence, if PVP in water follows the behavior typical of a good solvent, semidilute polymer system, then the autocorrelation function obtained from dynamic light scattering should be a single exponential, with a decay time which decreases with increasing concentration. Similarly, the angular distribution of scattering should become more isotropic as ξ decreases with increasing concentration. This behavior is not observed. Figure 2 shows a typical correlation function obtained for semidilute, aqueous solutions of PVP. It shows a double exponential decay, not the single one predicted by theory. The inset shows the structure factors at different concentrations. The scattering distribution is clearly not isotropic. These are scattering features typical of polymer aggregates. We have found that this behavior is strongly characteristic of all the $M_w \geq 389$ kg/mol samples, but very weak in the low M_w samples.

Polymer aggregation can, of course, occur due to some sort of sample degradation, but that is unlikely here. First, PVP is remarkably stable. The polymer conformation and properties are insensitive to wide variations in water properties such as pH or salt content.[1,2] In addition, the aggregation we report here is entirely reversible. To test this, a moiety of a concentrated solution which exhibits slow mode behavior was diluted, stirred, and placed in a separate scattering cell. It exhibited normal good-solvent behavior. More convincingly, in high pressure experiments which are described at the end of this paper, the slow mode was observed to decrease reversibly with application of pressure. This clearly indicates that the slow mode is a thermodynamically stable state, and not due to dust or other contaminants.

To investigate this anomalous behavior, we performed both dynamic and static light scattering experiments on semidilute solutions of PVP for $M_w = 389$, 592, and 815 kg/mol samples at different concentrations. All three samples show similar behavior. The overlap concentrations, as defined by $C^* = 1/[\eta]$, for PVP in water were determined from the recommended[1] scaling relation $[\eta] = 3.0 \times 10^{-2}\ \mathrm{M}^{0.63}$ mL/g. For the DLS data, the normalized, field autocorrelation functions (ACF) were fit to the double exponential form

$$g_1(t,q) = A_s(q)e^{-\Gamma_s t} + A_f(q)e^{-\Gamma_f t} \quad (5)$$

where Γ_s and Γ_f are the inverse relaxation times of the slow and fast components of the correlation functions, respectively, and $A_s(q)$ and $A_f(q)$ are the relative amplitudes ($A_s(q) + A_f(q) = 1$). Consideration of various functional forms, including the use of CONTIN, leads us to use this simple function, which was found to give good fits to the data and has a minimum number of fitting parameters (the solid line in Figure 2 is an example of a fit to the data using a double exponential form). Brown[17] found this to be true for semidilute solutions of poly(ethylene oxide) in water as well. The results of these fits for the $M_w = 389$ kg/mol sample at the highest concentrations are shown in Figure 3. Figure 3a shows that the amplitude ratio A_s/A_f rises with decreasing q. This indicates scattering from an object which is large relative to ξ. Figure 3c plots Γ_s versus q^3, where the solid lines are straight line fits. Power law fits of the q dependence of the slow components of the ACF for all molecular weights and concentrations give values ranging from 2.4 to 3.3, with an average value of 2.8. We see from these data that we have the unusual situation that the dominant low q relaxation has an approximate q^3 dependence. Clearly, this is not the q-independent scattering arising from viscoelastic effects found in semidilute θ-solvent systems.[11−14] This approximate q^3 behavior is typical of the well-known scattering dependence found for extremely large molecular weight polymer coils[29,30] and for different types of loose polymer aggregates.[31,32] In this regime the particles probed can no longer be considered point scatterers, and internal particle motions of length scale q^{-1} are seen.[22] Typically, this leads to a crossover to $\Gamma \propto q^2$ at lower q, but in our experiment, the large aggregate size ensures that $qR_{agg} \geq 1$; thus we do not observe this crossover. Figure 3b shows the

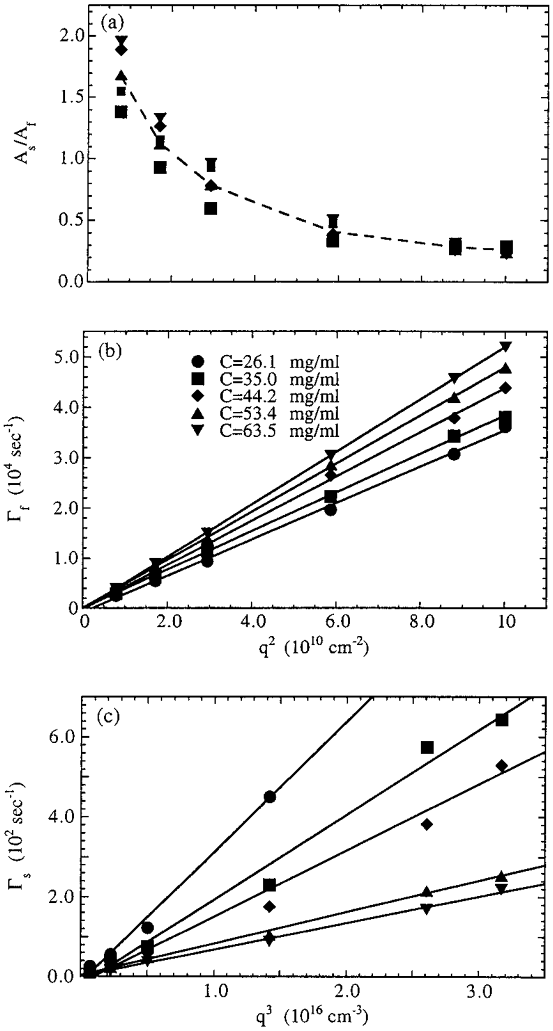

Figure 3. Shown above for M_w = 389 kg/mol at different semidilute concentrations: (a) A_s/A_f as a function of q^2, showing that A_s increases as q decreases, (b) Γ_f, as a function of q^2, indicating a q^2 dependence, and (c) Γ_s, as a function of q^3, indicating an approximate q^3 dependence The same legend applies to all plots. Similar behavior is found for the M_w = 592 and 815 kg/mol samples.

fast relaxation as a function of q^2, where the solid lines are straight line fits. This figure indicates that this fast component exhibits the typical q^2 dependence for the cooperative diffusion of a polymer in a good solvent in the semidilute region indicating, as expected, that $q\xi \leq 1$.

The concentration dependence of Γ_f and Γ_s (normalized to the dilute solution Γ_0) are plotted in Figure 4 for all molecular weights. The fast component at concentrations above C^* shows a concentration dependence consistent with the $C^{0.75}$ predicted by theory. The slow component exhibits a scaling which is approximately $C^{-1.25}$. This value is comparable to values found in other aqueous, semidilute systems.[10,16]

The inset of Figure 2 shows the scattering intensities for different semidilute, polymer concentrations. The excess scattering at low q is evident, but also one notes that the scattering intensities initially decrease with increasing q values, but then seem to plateau to nonzero values which are well above the background. The nonzero plateaus are due to isotropic scattering (in this q range) from the concentration fluctuations which produce the fast component of the ACF's. In support of this conclusion, the scattering intensities at the

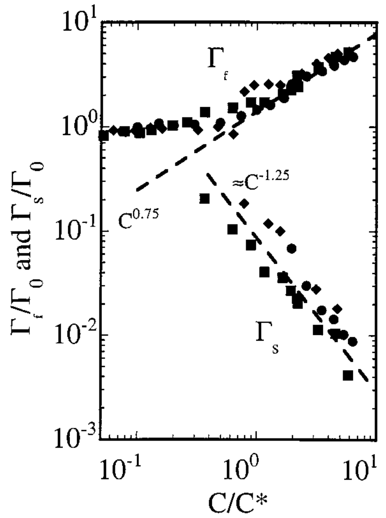

Figure 4. Normalized Γ_f and Γ_s as a function of C/C^* (C^* is defined as $1/[\eta]$) for M_w = 389 (circles), 592 (squares), and 815 (diamonds) kg/mol. The semidilute concentration scaling for Γ_f is consistent with that predicted by theory, as indicated by the dashed line. The concentration scaling for Γ_s is approximately $C^{-1.25}$, which is similar to results found in other aqueous systems.

plateaus have been found to decrease with increasing concentration; i.e., ξ decreases with increasing concentration, which leads to a decrease in scattering intensity. To analyze this intensity data, and thereby get an estimate of the aggregate size, we use the formalism used by Raspaud et al.[32] in which the quasi-elastic scattering is coupled with the static scattering to separate the scattering from the two components:

$$I(q) = I_{\text{slow}}(q) + I_{\text{fast}}(q) = I_0\{[A_s]_{q\to 0}P_s(q) + [A_f]_{q\to 0}P_f(q)\} \qquad (6)$$

where $[A_s]_{q\to 0}$ and $[A_f]_{q\to 0}$ are the relative amplitudes of the slow and fast components of the autocorrelation function at q = 0, and $P_s(q)$ and $P_f(q)$ are the form factors. For the experimental q range used we can consider $P_f(q)$ to be unity. With this assumption we get:

$$P_s(q) = \frac{I(q) - I_0|A_f|_{q\to 0}}{I_0|A_s|_{q\to 0}} \qquad (7)$$

for the form factor of the slow component. We apply this formalism to the highest concentration solutions ($C/C^* \geq 2.0$), where the slow modes are most distinct. Figure 5 shows the form factors obtained from eq 7 for the M_w = 389 kg/mol sample. The solid lines are Lorentzian fits.

In principle, the aggregate structure can be determined from the form factors. The q^3 dependence of Γ_s obtained from DLS indicates that these aggregates are loosely-bound particles with internal motions; a large particle with no internal motions would display only the q^2 dependence characteristic of diffusive behavior. Furthermore, this q^3 scaling indicates some sort of self similarity over these length scales, analogous to that for high molecular weight polymer where the same q^3 scaling is observed. The mass within the aggregates is clearly not confined to a few local centers but must be more uniform over the length scales under investigation (30−120 nm). To approximate this unknown density distribution, the form factors were fit to various polymer forms known to display internal motions, such as a

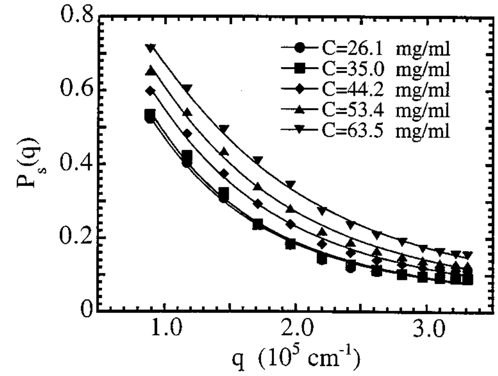

Figure 5. $P_s(q)$ for different semidilute concentrations. The solid lines are Lorentzian fits to the data. Fits to various form factors indicate aggregate radii on the order of 80–150 nm for all $C/C^* \geq 2.0$.

Gaussian coil, different types of branched forms, and a Lorentzian. The fits to all forms at all concentrations are quite good, with correlation coefficients ≥0.990. These fits to the different forms for all concentrations indicate aggregate radii on the order of 80–150 nm. Note, however, that the experimental q-range does not include the characteristic low q plateau, which is necessary to give a reliable indication of the size. The form factors were also fit to a uniform-density-sphere model. Here, the fits were appreciably worse, with correlation coefficients ≈0.950–0.960 for all fits, indicating that the aggregates do not have sharp boundaries.[33]

3.3. Polymer Properties in Denatured Water. Given the presence of aggregates, we now address the question of what interactions might lead to their formation. As is well-known, water has a tetrahedral, hydrogen bond network which is unique, and which gives rise to its many unusual physical properties.[34] An important feature of PVP is the strongly electronegative oxygen adjacent to the nitrogen atom in the carbonyl group. (It is this strongly electronegative oxygen which is responsible for dimer formation of 2-pyrrolidone molecules in chloroform.[35]) There is strong hydrogen bonding between these oxygens and the surrounding water molecules in solution. Evidence for this comes from various sources including IR measurements[36] and calorimetry experiments.[37] In a past viscometric study[38] it was suggested that this hydrogen bonding in conjunction with the tetrahedral hydrogen bond network of water can lead to interchain associations which would be an effective means for forming aggregates (see Figure 6). In support of this hypothesis, the addition of denaturing agents, small molecules known to disrupt water structure, causes a decrease in the specific viscosity. The authors suggest that this effect comes from the breakdown of water-mediated polymer–polymer associations. It is also possible, given the amphiphilic character of PVP, that the aggregates are due to hydrophobic interactions. In both explanations the tetrahedral hydrogen bond network of water is essential to aggregate formation. For this reason, we examined the effects of adding thiourea (CSN_2H_4) to the solution, a denaturing agent known to disrupt the water structure.[38–40] Güven and Eltan[38] have found that the specific viscosity of PVP in water decreases significantly from the addition of this agent.

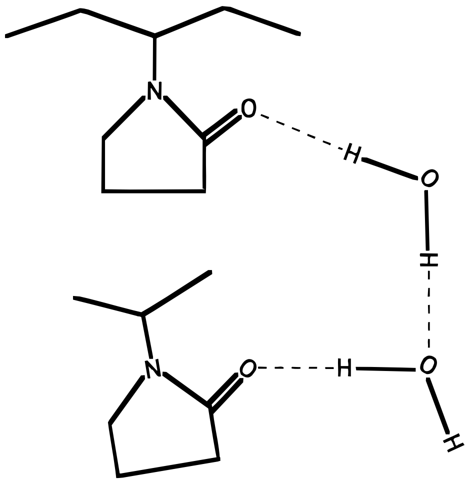

Figure 6. A suggested mechanism by which polymer aggregates are formed.[38] The tetrahedral hydrogen bond network of water effectively links the polymer molecules together.

3.3a. Chemical Denaturation. In a mixed solvent polymer system the measured values of M_w and A_2 are sensitive to cosolvency effects. Therefore, a full analysis of the dilute solution static scattering of PVP in aqueous 1 M thiourea is more complex [41] than in the neat water situation. The $\langle R_g^2\rangle_z^{1/2}$ can still be measured from the angular dependence; we find that the values decrease in magnitude by an average of 10% over those in pure water. This indicates a decline in solvent quality. Dynamic light scattering is not as sensitive to cosolvency effects. Figure 1b plots the diffusion coefficient of PVP in aqueous 1 M thiourea. We find that the diffusion coefficients increase by about 25%, although the molecular weight dependence is unaltered:

$$\langle D_0\rangle = [(2.10 \pm 0.28) \times 10^{-4}]M_w^{-0.58\pm0.01}\ \mathrm{cm^2/s} \quad (8)$$

This also indicates a decline in solvent quality. However, the solvent quality is still higher than that of a θ solvent. First, from static light scattering we find that the polymer coils expand as the polymer concentration decreases, indicating that $A_2 > 0$. Also, the scaling law (eq 8) for $\langle D_0\rangle$ is consistent with that of a good solvent system.

Upon the addition of thiourea to semidilute concentrations of PVP in water there is a significant reduction in the slow mode amplitude. In the prototypical semidilute polymer system the slow mode amplitude increases with declining solvent quality.[14] This further indicates that the slow mode seen in PVP/water is different from the typical slow mode behavior. Figure 7 compares the autocorrelation functions obtained for PVP (M_w = 389 kg/mol, C = 53.4 mg/mL) in neat water and in aqueous 1 M thiourea. Figure 8 plots A_s/A_f as a function of C/C^* for semidilute solutions of PVP in water (solid symbols) and aqueous 1 M thiourea (open symbols). It shows that at the highest polymer concentrations A_s/A_f decreases from ≈1.90 to ≈0.45 upon addition of thiourea (θ = 30°). Also, the average decay times of the thiourea solutions are a factor of 3 lower. The inset of Figure 7 shows that the angular scattering intensity for the thiourea solution is more isotropic. All these results are consistent with a decrease in polymer aggregation. The faster relaxation time increases about 20%, which is consistent with declining solvent quality. The Γ_f maintains its q^2 dependence. Γ_s has a q dependence clearly greater than 2; however, due to the small A_s and the increase in Γ_s the two components are not clearly distinguishable at higher q values, making the power law dependence difficult to quantify (in the neat water situation the slow component was distinct for all

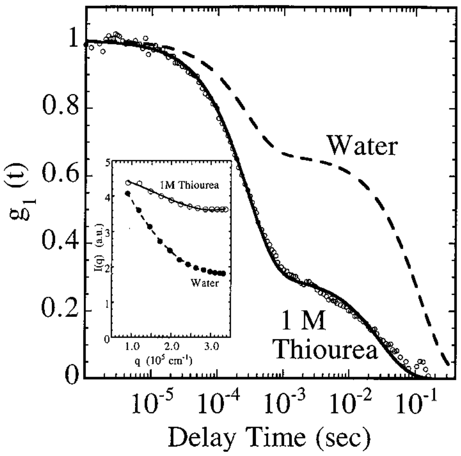

Figure 7. Comparison of autocorrelation functions obtained at $\theta = 30°$ from semidilute solutions of PVP ($C = 53.2$ mg/mL) in aqueous 1 M thiourea (solid line with filled squares) and in water (dashed line). The solid line is a fit to a double exponential form (see Figure 2). The inset compares the angular scattering intensities at the same concentration; the forward scattering is greatly reduced with the addition of thiourea.

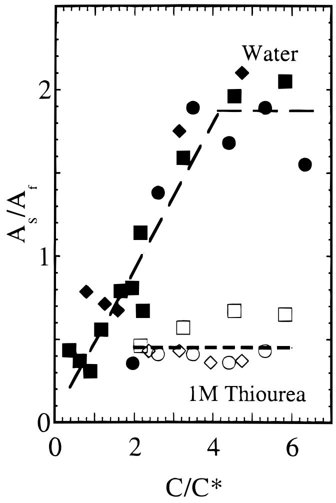

Figure 8. A_s/A_f as a function of normalized concentration. The solid symbols are in water, and the open symbols are in aqueous 1 M thiourea. The addition of thiourea causes a large decline in the ratio of the slow and fast amplitudes. The M_w = 389, 592, and 815 kg/mol samples are represented by circles, squares, and diamonds, respectively.

q values). Addition of more thiourea does not seem to further decrease the slow mode amplitude. We have also investigated the effect of a second denaturating agent, guanidine sulfate ($[H_2NC(=NH)NH_2]_2{\cdot}H_2SO_4$). The results are similar to those for thiourea.

We now apply the analysis presented above to extract the effective size of the remaining aggregates through combining the static and dynamic scattering. The isotropic scattering due to the expected concentration fluctuations of length ξ (the fast component in the correlation function) dominates the resulting scattering. Applying the formalism of Raspaud et al. to find the form factors, and then fitting to the same forms as previously, we find the aggregate radii for all concentrations ($C/C^* \geq 2.0$) to be from 50 to 96 nm. This is an average decrease in the aggregate radii of gyration of roughly 33% from the neat water case, and a factor of 3 decrease in aggregate volume. We find that, in the semidilute concentration range examined, there is no noticeable correlation between aggregate size and polymer concentration for the 1 M thiourea solutions.

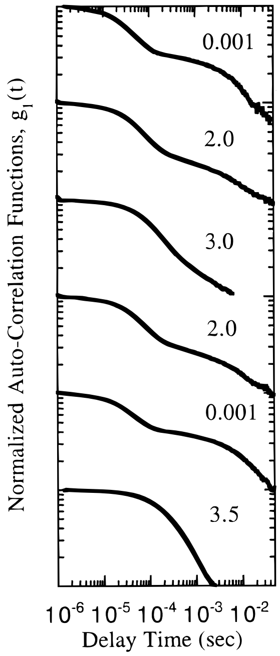

Figure 9. Normalized, field autocorrelation functions obtained from a semidilute, aqueous PVP sample (M_w = 389 kg/mol, $C/C^* = 6.0$) at different pressures. Application of pressure reduces the slow mode amplitude and decay rate, similar to the effect of thiourea. The process is clearly reversible, as shown in the sequence of pressurization and depressurization (from top to bottom). The number by each ACF indicates the pressure in kbar; phase separation occurs at 3.75 kbar.

3.3b. Pressure Denaturation. We have also examined the semidilute, solution properties of PVP in water under high pressure.[42] Unlike van der Waals bonds, hydrogen bonds are highly directional; bending the bond by as little as 10° from its optimum orientation typically breaks the bond.[43] A certain volume is therefore needed to form strong hydrogen bonds. Application of pressure decreases the volume, thereby bending the bonds and disrupting the water structure.[44] Thus, the physical properties of aqueous systems are highly pressure sensitive, in complete contrast to hydrocarbon systems.[45] One important advantage of this over chemical denaturation is its reversibility. Studies of dilute solution behavior show that application of pressure to this system causes a continuous decline in solvent quality, resulting in phase separation at 3.75 kbar for M_w = 389 kg/mol. Figure 9 shows the autocorrelation functions obtained from an aqueous, semidilute solution of PVP (M_w = 389 kg/mol, C = 60 mg/mL, C/C^* = 6.0, $\theta = 90°$). As expected, the ACF obtained at ambient pressure inside the pressure cell clearly shows a slow component. As pressure is applied, the slow component decreases, and as shown in the figure, the effects are fully reversible. We fit these ACF's to the double exponential form (eq 5), and, as shown in Figure 4 of Sun and King,[42] Γ_f and Γ_s smoothly and reversibly change as a function of pressure. At 3.5 kbar pressure, Γ_f is almost an order of magnitude smaller than its ambient-pressure value and Γ_s an order of magnitude larger, making them comparable in magnitude, within a factor of 5. This decrease in Γ_f is consistent with the effect of going from good to Θ-solvent conditions in a typical semidilute solution (see Figure 6.24 of Brown and Nicolai[14]). The strong increase in Γ_s is similar to that observed upon addition of thiourea. These changes in relaxation time are accompanied by a significant decline in A_s; between ambient and 3.0 kbar pressure A_s decreases about 45% (from 0.29 to 0.16). Clearly, the aggregate formation is disrupted, similar to the case of chemical denaturation. Lacking the angular dependence of the scattering (both static and dynamic), we are unable to extract aggregate radii as we did above. However, at the highest pressures, 3.0−3.5 kbar, direct comparison with the scattering from the thiourea solution at $\theta = 90°$ shows that the relative slow mode amplitudes are comparable. This suggests that the aggregates may be similar in the two cases.

4. Conclusion

In conclusion, through dynamic and static light scattering in the dilute region we have shown that PVP in water at $T = 25$ °C is a typical good solvent system. Through further experiments in the semidilute region, we have shown that the fast relaxation in the autocorrelation functions of aqueous, semidilute solutions of PVP is due to the usual concentration fluctuations of length ξ expected in a good solvent system and that the slow component is caused by the formation of aggregates. We analyze the combined static and dynamic scattering to obtain an estimate of the size of the aggregates. They are 2−3 times the size of the dilute-solution radius of gyration. Upon addition of thiourea, a denaturing agent known to disrupt the water structure, there is a significant decrease in the amplitude and decay time of the slow component, as well as in the low q static scattering. Analysis of the scattering in this case suggests that the remaining aggregates are significantly reduced in size. Experiments done with pressure-induced water denaturation show that the aggregation is reversible.

These results suggest that the polymer aggregation depends upon the tetrahedral hydrogen bond network, a characteristic feature of water. Recently de Gennes[46] proposed a Flory−Huggins model with a modified enthalpy of mixing in which two monomers repel one another (a good solvent system), but a cluster of monomers can form a stable complex. From this, he shows that at certain polymer concentrations and interaction potentials two separate phases can coexist. This model, developed for PEO in water, suggests that such interactions, for example, hydrophobic interactions, can be a driving force for aggregate formation. Assuming these aggregates are thermodynamically stable, our work raises several questions. First, what is the internal structure of these aggregates? For instance, given the amphiphilic character of typical nonionic water-soluble polymers, do they have a hydrophobic core with a hydrophilic surface, similar to micelles? An extended q range could give information on this, particularly if combined with the contrast matching techniques of neutron scattering. Also, what sets their characteristic size and concentration scaling of the relaxation time? It is also of interest that they seem to be only weakly present at low molecular weights ($M_w \leq 49$ kg/mol), a feature also observed for PEO in water.[16]

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References and Notes

(1) Molyneux, P. *Water-Soluble Synthetic Polymers: Properties and Behavior*; CRC Press: Boca Raton, FL, 1983; Vol. 1, pp 225.
(2) Bühler, V. *Kollidon: Polyvinylpyrrolidone for the Pharmaceutical Industry*; BASF: Ludwigshafen, Germany, 1992; p 285.
(3) Frank, H. P.; Levy, G. B. *J. Polym. Sci.* **1953**, *10*, 371−378.
(4) Levy, G. B. *J. Polym. Sci.* **1955**, *17*, 247−254.
(5) Krevelen, D. W. V.; Hoftyzer, P. J. *J. Appl. Polym. Sci.* **1967**, *11*, 1409−1418.
(6) Meza, R.; Gargallo, L. *Eur. Polym. J.* **1977**, *13*, 235−239.
(7) Burchard, W.; Eisele, M. *Pure Appl. Chem.* **1984**, *56*, 1379−1390.
(8) Rathbone, S. J.; Haynes, C. A.; Blanch, H. W.; Prausnitz, J. M. *Macromolecules* **1990**, *23*, 3944−3947.
(9) Nordmeier, E.; Lechner, M. D. *Macromolecules* **1991**, *24*, 2529−2537.
(10) Eisele, M.; Burchard, W. *Macromolecules* **1984**, *17*, 1636−1638.
(11) Brochard, F. *J. Physique* **1983**, *44*, 39−43.
(12) Adam, M.; Delsanti, M. *Macromolecules* **1985**, *18*, 1760−1770.
(13) Dixon, P. K.; Pine, D. J.; Wu, X. L. *Phys. Rev. Lett.* **1992**, *68*, 2239−2242.
(14) Brown, W.; Nicolai, T. In *Dynamic Light Scattering: The Method and Some Applications*; Brown, W., Ed.; Oxford University Press: New York, 1993; p 735.
(15) Wiltzius, P.; Haller, H. R.; Cannell, D. S.; Schaefer, D. W. *Phys. Rev. Lett.* **1983**, *51*, 1183−1186.
(16) Brown, W. *Macromolecules* **1984**, *17*, 66−72.
(17) Brown, W. *Polymer* **1985**, *26*, 1647−1650.
(18) Fang, L.; Brown, W. *Macromolecules* **1990**, *23*, 3284−3290.
(19) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975.
(20) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1093−1099.
(21) Zimm, B. H. *J. Chem. Phys.* **1948**, *16*, 1099−1116.
(22) de Gennes, P.-G. *Scaling Concepts in Polymer Physics*; Cornell University Press: Ithaca, 1979; p 324.
(23) Fetters, L. J.; Hadjichristidis, H.; Lindner, J. S.; Mays, J. W. *J. Phys. Chem. Ref. Data* **1994**, *23*, 619−640.
(24) Devanand, K.; Selser, J. C. *Macromolecules* **1991**, *24*, 5943−5947.
(25) Stepanek, P. In *Dynamic Light Scattering*; Brown, W., Ed.; Oxford University Press: New York, 1993.
(26) Koppel, D. *J. Chem. Phys.* **1972**, *57*, 4814−4820.
(27) Selser, J. C. *Macromolecules* **1979**, *12*, 909−916.
(28) Brown, W.; Nicolai, T. *Colloid Polym. Sci.* **1990**, *268*, 977−990.
(29) Adam, M.; Delsanti, M. *Macromolecules* **1977**, *10*, 1229−1237.
(30) Seery, T. A. P.; Shorter, J. A.; Amis, E. J. *Polymer* **1989**, *30*, 1197−1203.
(31) Layec, Y.; Layec-Raphalen, M. N. *J. Phys. Lett.* **1983**, *44*, 121−128.
(32) Raspaud, E.; Lairez, D.; Adam, M.; Carton, J. P. *Macromolecules* **1994**, *27*, 2956−2964.
(33) Polik, W. F.; Burchard, W. *Macromolecules* **1983**, *16*, 978−982.
(34) Stillinger, F. H. *Science* **1980**, *209*, 451−457.
(35) Luck, W. A. P. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1973; Vol. 2, pp 235−321.
(36) Klotz, I. M. *Science* **1959**, *128*, 815.
(37) Jellinek, H. H. G.; Fok, S. Y. *Kolloid Z. Z. Polym.* **1967**, *220*, 122−133.
(38) Güven, O.; Eltan, E. *Makromol. Chem.* **1981**, *182*, 3129−3134.
(39) Simpson, R. B.; Kauzmann, W. *J. Am. Chem. Soc.* **1953**, *75*, 5139−5154.
(40) Franks, F. In *Water: A Comprehensive Treatise*; Franks, F., Ed.; Plenum Press: New York, 1975; Vol. 4, pp 1−94.
(41) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971; p 419.
(42) Sun, T.; King, H. E., Jr. Submitted for publication. 1995.
(43) Walker, J. S.; Vause, C. A. *Sci. Am.* **1987**, *May*, 98−105.
(44) Jonas, J.; Defries, T.; Wilbur, D. J. *J. Chem. Phys.* **1976**, *65*, 582−588.
(45) Cook, R. L.; King, H. E., Jr.; Peiffer, D. G. *Macromolecules* **1992**, *25*, 2928−2934.
(46) de Gennes, P. G. *C. R. Acad. Sci., Ser. 2* **1991**, *313*, 1117−1122.

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