Effect of Denaturant and Polymer Concentration on the Structural and Dynamical Properties of Aqueous Solutions of Poly(*N*-acetamido acrylamide)

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ABSTRACT: Poly(*N*-acetamido acrylamide), PAAA, associates in aqueous solution. Dynamic and static light scattering and viscometry are employed to study this association in aqueous solution. The initial relaxation rate Ω_0 shows a q^3 dependence for PAAA in water (q is the magnitude of the scattering vector) even at concentrations as low as 0.03%. When this polymer is dissolved in 2 M aqueous sodium thiocyanate, only a diffusive (q^2-dependent) relaxation mode is observed. The results of the reduced viscosity of very dilute PAAA−water solutions suggest the formation of clusters. Addition of sodium thiocyanate breaks up the clusters. From static light scattering of PAAA-water solutions, it is found that the fractal dimension increases with increasing polymer concentration. This indicates that the clusters become more compact at higher concentrations. This conjecture is supported by the viscosity results, where the reduced viscosity shows a large increase with concentration and passes through a well-pronounced maximum at c ≈ 0.05%.

Introduction

In recent years, much effort has been devoted to the study of associating polymer systems due to their wide range of applications.[1,2] In these investigations, both the viscoelastic properties[3−6] and dynamics[7,8] of the systems have been examined. However, all these systems are amphiphilic, hydrophobically modified water-soluble polymers. The driving force behind the association process is the interaction between the hydrophobic segments in order to minimize their exposure to water. Above a certain concentration, individual polymer molecules start to associate. In this process, clusters are formed, and as the concentration increases, these clusters grow both in size and in number. At a sufficiently high concentration, a network composed of interpenetrating clusters is created. This network is temporary in the sense that junctions that hold the network together will break and form frequently on the time scale of the experiments.

In a number of papers, Haas et al.[9−12] has described the synthesis and some of the physical properties of poly(*N*-acetamido acrylamide), PAAA, a homopolymer that, in the semidilute regime, forms a thermoreversible gel in water. The gel dissolves when hydrogen bond breaking agents such as urea or sodium thiocyanate are added. These authors were mostly interested in the kinetics of polymerization, and little attention was paid to the dynamic features of the solutions. With the aim to gain more insight into the solution properties of this polymer, both dynamic and intensity light scattering experiments as well as viscometry were employed in this investigation. The preliminary results show that this polymer associates in water well below the gel concentration. In view of this, we have chosen to study the solution behavior of PAAA at concentrations well below the gel concentration. This polymer may be visualized as a hydrophilic associating homopolymer. There are no specific sites on the polymer chain available for the formation of intermolecular hydrophobic associations (see Figure 1).

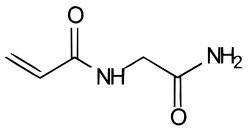

Figure 1. Structure of the monomer *N*-acetamido acrylamide.

In the study of associating polymer systems, the properties of hydrophobically modified polymers are usually considered, and the behavior of this polymer is often compared with that of an unmodified analogue. In addition, the effect of hydrophobicity is usually also addressed. To gain a deeper understanding of the type and strength of the associations encountered here, we have chosen to study the properties of PAAA in pure water and with different concentrations of the denaturing agent sodium thiocyanate. This salt and other denaturing agents,[13,14] such as urea, may disrupt both the water structure and the interactions between and within the polymer chains.

Much attention[15−17] has been focused on the gelation of aqueous polymer systems. Several different thermoreversible gelling systems have been studied, such as Pluronic, which is a triblock copolymer consisting of poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide),[18−20] poly(vinyl alcohol),[21−23] and systems of ethyl(hydroxyethyl)cellulose in the presence of ionic surfactants.[24,25] In addition, studies on other types of systems have also been reported.[26−29] The mechanism of gelation is not the same in these systems. As a first step to understand gelation of aqueous solutions of PAAA, it seems to be essential to gain insight into the cluster formation process operating in dilute and moderately concentrated solutions of PAAA.

The current understanding[30−33] of networks and clusters formed during gelation or association is based on concepts such as size distribution statistics, fractal dimension, and self-similarity properties.

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Computer simulations have played an essential role in our understanding of these features. Several theoretical models have been introduced, and the fractal dimension has been calculated through simulations. In many real associating systems involving diffusion-limited growth, a large number of diffusion clusters will exist at any given time, and these clusters can grow by sticking to each other as well as from single particle addition. In the formation of cluster−cluster aggregates it has been shown that these structures are very open with a mass fractal dimension $d_f = 1.75-1.80$. The low fractal dimensions of this diffusion-limited cluster−cluster aggregation (DLCA) model reflects the loose, open structure of the aggregates formed. This simple model is based upon the assumption that diffusion is the rate-limiting step in the formation of clusters. However, it is also possible for the cluster association rate to be limited by the probability that particles will stick upon contact. If the sticking probability is small, the clusters will need to collide many times before they stick, and the net effect of this behavior is that the diffusing clusters are allowed to penetrate further into each other before sticking. This type of aggregation process is frequently referred to as reaction-limited cluster−cluster aggregation (RLCA). In this case, simulations have shown an increase in the fractal dimension over the diffusion-limited model with $d_f = 2.1$; i.e., the aggregate structures are more compact. If we now consider the cluster sizes distribution in the framework of the percolation theory, the polydispersity exponent τ has a universal value of 2.2 and is related to the fractal dimension by the hyperscaling relationship $d_f(\tau - 1) = d$, yielding a fractal dimension of $d_f = 2.5$ in three dimensions ($d = 3$).

The results from this work will show that PAAA forms aggregates even in dilute solution. The initial relaxation process of PAAA in water, probed in dynamic light scattering experiments, is associated with the relaxation of the internal modes from the polymer clusters. Addition of thiocyanate to the system breaks up the clusters. When the concentration of thiocyanate is 2 M, only a single relaxation mode, associated with the translational diffusion of the molecularly dispersed entities, is observed.

From static light scattering experiments, the fractal dimension of the clusters is determined. The results suggest that the fractal dimension rises as the polymer concentration is increased. The aggregates of PAAA in water can be visualized as clusters that gradually buildup a three-dimensional network.

General Considerations

Dynamic Light Scattering (DLS). The technique of photon correlation spectroscopy[34,35] probes the dynamics of the concentration or density fluctuations directly. The intensity fluctuations of the scattered light are probed. From these measurements, the normalized intensity autocorrelation function $g_2(t,q)$ is determined as a function of time t and a scattering vector q. The magnitude of the scattering vector at a scattering angle θ is $q = (4n\pi/\lambda)\sin(\theta/2)$, where n is the refractive index of the solution and λ is the wavelength of the incident light in a vacuum. If the scattered light obeys Gaussian statistics, $g_2(t,q)$ is related to the theoretically tractable first-order field autocorrelation function $g_1(t,q)$ through the Siegert relation, $g_2(t,q) = 1 + B|g_1(t,q)|^2$, where $B \leq 1$ is a coherence factor that depends on the experimental geometry.

The correlation function describes how the concentration fluctuations relax toward equilibrium at a length scale of $1/q$. In dilute solutions there are two different dynamical regimes, that can be probed. It is instructive to introduce the quantity qL, where L is a characteristic length, e.g., the mean hydrodynamic radius R_h in dilute solution. When $qL < 1$, the global dynamics is probed and the translational diffusion coefficient of individual molecules can be determined. In the case of a monodisperse polymer, $g_1(t,q)$ decays in the form of a single exponential, $g_1(t,q) = \exp(t/\tau)$, where $1/\tau = Dq^2$. Here τ is the relaxation time and D is the mutual diffusion coefficient. If the scattering objects are larger so that $qL > 1$, the various internal modes begin, in addition to the translational diffusion mode, to contribute significantly to the correlation function, giving rise to multiexponential time correlation functions. In this domain, the contribution from the translation is small, and the resulting time correlation function is dominated by the internal motions of the polymer chains. The fundamental relaxation rate is found to be independent of the molecular weight of the polymer,[36] and hence the polydispersity effects should not be important. If hydrodynamic interactions are taken into account (Zimm behavior), the characteristic frequency $\omega_c(q)$ for a Gaussian chain[36] is proportional to $(k_bT/\eta_0)q^3$, where T is the temperature, η_0 is the viscosity of the solvent, and k_b is Boltzmann's constant. It has been shown[37] that the characteristic frequency $\omega_c(q)$ coincides with the initial relaxation rate Ω_0, calculated from the initial decay of the correlation function. If the hydrodynamic interactions are screened[38] (Rouse behavior), the characteristic frequency will be proportional to q^4.

Studies have been carried out[39−41] on polystyrene samples of different molecular weight in order to probe the different dynamical regimes. Ω_0 showed a q^3 dependence when $qL > 1$ and a q^2 dependence when $qL < 1$. In the former case, the correlation function is composed of two relaxation processes; one is caused by a translational diffusion and the other is related to the relaxation of internal modes. This mixture of modes obstructs a distinct separation of the relaxation modes. It is only possible to extract the relaxation of internal motions from the initial slope of the correlation function. Attempts have been made to separate the relaxation mode caused by the diffusive motion from the other internal relaxation modes. In the range of scattering angles available with the present experimental setup it is only possible to probe in the domain $qL > 1$ for the PAAA-water solutions at the considered concentrations. As a result, the measured correlation function is a complex decay representing the resultant decay of different superimposed modes of motion, where the contribution from the translational mode is small. Due to this overlap, the internal motion decay times cannot unambiguously be separated from the diffusion decay time. Therefore, we have determined the initial relaxation rate with the aid of the method of cumulants.[34]

The q dependence of the initial relaxation mode or the average decay rate in the range $qL > 1$ has been reported for various systems. Dynamic light scattering experiments on colloidal silica under slow aggregation conditions revealed[42] that the mean decay rate scales such as $q^{2.7}$. The discrepancy from the expected q^3 behavior was explained by the fact that the hydrodynamic radius has a different fractal dimension than the corresponding static quantity, the radius of gyration.

However, recent DLS studies[43] on aggregating polystyrene latex particles in solution and on percolating dense microemulsions reported a q^3 dependence of the initial relaxation rate. Furthermore, DLS experiments[44] on branched polymeric clusters in dilute solutions also revealed a q^3 dependency. It was argued that the q^3 dependence is a universal behavior in polymer dynamics whatever the structure is.

Static Light Scattering. An intensity light scattering experiment probes density correlations on a length scale q^{-1}. This method allows one to obtain the fractal dimension[30,31,45,46] of the scattering objects if $qL > 1$. The fractal geometry of a cluster can be expressed in terms of the fractal dimension d_f, where $M(r)$ is the amount of mass inside a sphere of radius r.

$$M(r) \propto r^{d_f} \tag{1}$$

From the definition of the Hausdorff dimension and eq 1 it is found that $d_f = \ln(M_{i+1}/M_i)/\ln(r_{i+1}/r_i)$ where i denotes the generation number. As the fractal dimension decreases, the structure appears sparser, until at $d_f = 1$ (the lowest possible physical value for a connected fractal), the object becomes essentially a line.

The scattered intensity $I(q)$ is proportional to the total mass, M contained in a volume of radius $r = 1/q$. Thus one obtains the following relation for the decay of the scattered intensity:

$$I(q) \propto q^{-d_m} \tag{2}$$

The fractal dimension may be found from a log−log plot of the scattered intensity versus the magnitude of the scattering vector q. However, this simple behavior is only observed if the clusters are uniform in size. The impact of the polydispersity effect is usually so strong[30] that the scattering exponents change. In that case, eq 2 can be rewritten in the form

$$I(q) \propto q^{-d_f(3-\tau)} \tag{3}$$

The mean field theory predicts that the polydispersity exponent $\tau = 2.5$ and the percolation theory gives $\tau = 2.2$.

Experimental Section

Synthesis of *N*-Acetamido Acrylamide. Acryloyl chloride (Fluka 97%, $M_r = 90.5$) and glycinamide hydrochloride (Fluka 99%, $M_r = 110.5$) were used as received. Water was distilled twice. Potassium persulfate was recrystallized from water prior to use. Other solvents and chemicals were used without further purification. The monomer N-acetamido acrylamide (**I**) was prepared as described elsewhere,[9] except that it was recrystallized twice from an acetone/methanol (1:1) mixture. Identification was confirmed with ^{1}H NMR. The structure of the monomer is displayed in Figure 1.

Polymerization of *N*-Acetamido Acrylamide. The monomer (I) (4.5 g) was dissolved in 450 mL of double-distilled degassed water. After the reaction was heated to 50 °C, the initiator, an aqueous solution of potassium persulfate (2.0 mL 0.50 wt %) and 2-propanol (10 mL), was added. The polymerization continued for 16 h before it was stopped by precipitating the polymer with acetone. Nitrogen was bubbled through the solution during the polymerization. The polymer was dissolved in 1 M aqueous sodium thiocyanate and precipitated into methanol to get rid of the rest of the oligomer. The unfractionated polymer was redissolved in water, dialyzed against water for several days, and finally freeze-dried. The molecular weight cutoff value of the dialysis tube was about 12 000. By using a high-speed membrane osmometer (Model 502) equipped with a Schleicher and Schuell membrane, the number average molecular weight of PAAA dissolved in 2 M aqueous sodium thiocyanate at 25 °C was determined to be $M_n = 230\,000$. At this condition, it has been argued that the molecular associations are practically eliminated[10,11] and the polymer exists in the form of molecularly dispersed species.

By using the method of cumulants[47] (more details of this procedure are given below), the normalized central moment $\mu_2 \equiv (\gamma - \bar{\gamma})^2/\bar{\gamma}^2$, where $\bar{\gamma}$ is the mean decay rate (see eq 4), can be regarded as a measure[48] of the "degree of polydispersity" providing that the molecular weight distribution is not too broad ($\mu_2 \leq 0.3$). For the present sample of PAAA dissolved in 2 M aqueous sodium thiocyanate solution, the value of $\mu_2 \approx 0.12$ indicates[49] that the polydispersity index M_w/M_n is about 1.5.

At a concentration of 3.6 wt %, this polymer formed a gel in water at 25 °C. This gel point was determined as the temperature where a sample in a test tube showed no flow when turned upside down.

Solution Preparation. All solutions were prepared by weighing and subsequent dilution to the desired concentration. The solutions used for the DLS experiments were filtered in an atmosphere of filtered air through 1 μm glass filters (Gelman Sciences) directly into dust-free NMR tubes of high quality. For the viscosity measurements, the solutions were filtered through 1 μm glass filters (Gelman Sciences) directly into an Ubbelohde viscometer.

Viscometry and Light Scattering. The viscosity measurements were carried out with the aid of an Ubbelohde viscometer. The viscometer was placed into a temperature-controlled water bath at 25.0 ± 0.05 °C. The flow time of the solvent (water) was longer than 300 s.

The beam from an argon ion laser (Spectra Physics Model 2020), operating at the wavelength $\lambda = 488$ nm with vertically polarized light, was focused on the sample cell through a temperature-controlled chamber filled with a refractive index matching silicone oil. All measurements were carried out at 25.0 °C.

The static light scattering experiments were carried out on five different samples of aqueous PAAA at concentrations between 0.03 and 0.46 wt %. Thirteen scattering angles, ranging between 30 and 90°, were used in these experiments, and the total scattered intensity was recorded at each angle. The interval between each angle of measurement was 5°, the duration of each measurement was 10 s, and there were five repetitions at each angle. The intensity was averaged and corrected for by the change in scattering volume as the angle changed by multiplying it with sin θ.

The full homodyne autocorrelation function was collected at several scattering angles, ranging from 25 to 130° with an ALV-5000 multiple tau digital correlator. The correlation functions were recorded in the real time "multiple-τ" mode of the correlator, in which the 256 time channels are logarithmically spaced over an interval ranging from 0.2 μs to almost 1 h.

Analysis of the Intensity Light Scattering Data. The scattered intensity is plotted against the scattering vector q in a double logarithmic plot[30,31,45] (see Figure 9). If the criterion $qL > 1$ is fulfilled, then the plot shows a straight line with a slope yielding the apparent fractal dimension of the scattering object. The results from the dynamic light scattering measurements are also used to confirm that $qL > 1$.

Analysis of the Dynamic Light Scattering Data. After the correlation functions were transformed to $g_1(t,q)$, they were all analyzed by means of the cumulant expansion.[34,49]

$$\ln g_1(t) = -\bar{\gamma}t + \frac{1}{2!}\mu_2(\bar{\gamma}t)^2 - \frac{1}{3!}\mu_3(\bar{\gamma}t)^3 + \ldots \tag{4}$$

The first cumulant $\bar{\gamma}(q)$ equals the initial relaxation rate $\Omega_0(q)$, and $\mu_2 + 1$ yields the polydispersity index M_w/M_n. The other coefficients contain information about higher order moments. However, the full cumulant analysis is not possible if there is more than one relaxation process. In this case, the method can only be applied for the initial part of the correla-

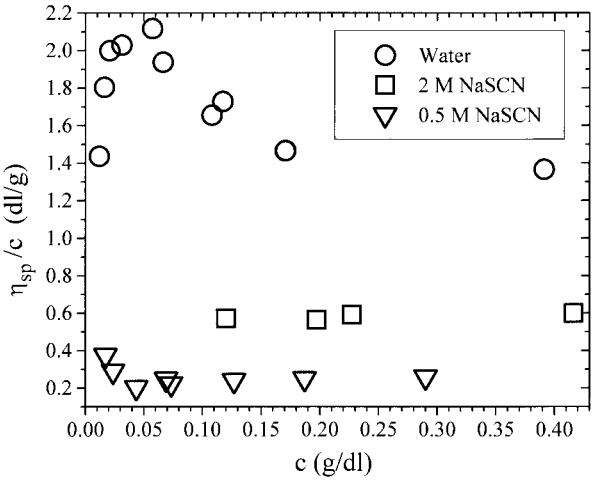

Figure 2. Reduced viscosity of PAAA in water and in aqueous solutions of sodium thiocyanate of different concentration.

tion function, and only the first cumulant contains any physical relevant information. To obtain the coefficients in the cumulant expression, ln $g_1(t)$ was fitted to a polynomial. It proved only possible to use the full cumulant analysis in the analysis of the data from the 2 M aqueous sodium thiocyanate solutions, where only a single, diffusive, relaxation decay was observed. For the other samples, only the initial part of the correlation function was used in the data analysis for the calculation of the first cumulant. In these cases, the order and the time range of the fit depend on the scattering angle. The conditions were selected to keep $\gamma t < 0.5$ and the maximum expansion to the fourth order. The same part of the correlation functions that was used for the cumulant analysis was also fitted to a single stretched exponential[50] for the sake of comparison. The values of the relaxation times of the two methods matched within experimental errors. The q dependence of the initial relaxation rate was determined from a double logarithmic plot. Trials were made to fit the correlation function to both the sum of two stretched exponential functions and the sum of a single and a stretched exponential. These attempts to separate the relaxation processes were unsuccessful. The method of CONTIN was also unsuccessful in the separation of the relaxation modes of the correlation functions.

Results and Discussion

Viscometry. A plot of the reduced viscosity, η_{sp}/c, of PAAA in water and plots in the presence of 0.5 and 2 M aqueous sodium thiocyanate are displayed in Figure 2. For PAAA in water, an anomalous behavior is observed. At low concentrations, the reduced viscosity rises rapidly until a maximum is reached, and after that, the reduced viscosity decreases with increasing concentration. In this context, it should be mentioned that the concentrations were measured in random order, and the reproducibility of the results was checked thoroughly by repeating the measurements at different times with both the same solutions and newly prepared solutions. In all cases, the reproducibility of the viscosity curve with its maximum was good. Therefore, it is unlikely that the observed maximum can be attributed to an artifact. Association of polymer molecules may explain the maximum detected at lower concentrations. The conjecture is that the individual polymer molecules form clusters with an average lifetime longer than the time of the experiment. This results in a rapid increase of the reduced viscosity, because the apparent molecular weight and the hydrodynamic volume of the polymer increase with increasing concentration due to association phenomena. At higher concentrations, the reduced

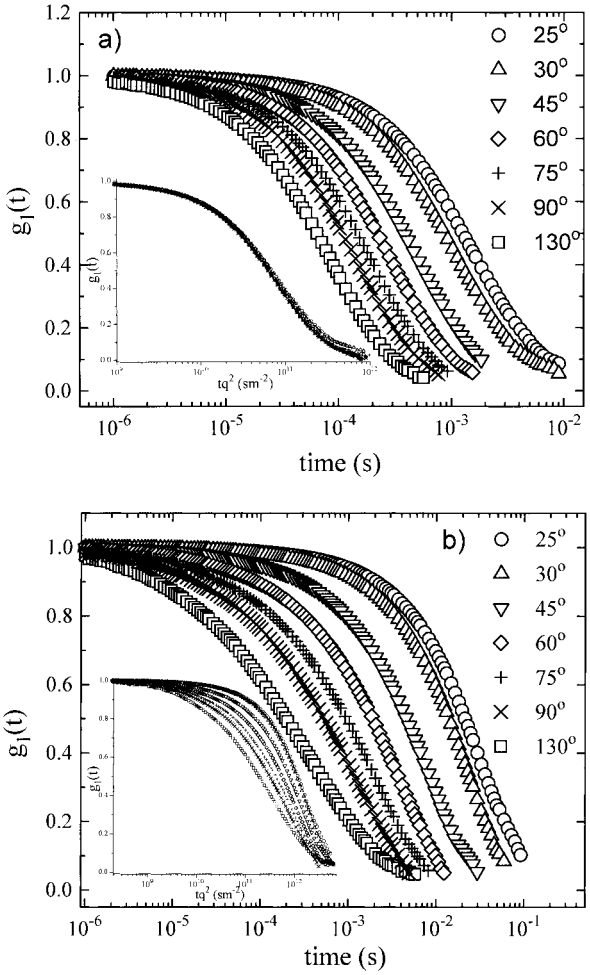

Figure 3. Semilogarithmic plot of the autocorrelation function for 0.46 wt % solutions of PAAA in 2 M aqueous sodium thiocyanate (a) and in pure water (b) at the scattering angles indicated. The inset plots show the same correlation functions versus q^2t.

viscosity drops. This indicates that the specific viscosity η_{sp} increases slower than the concentration. This behavior is only possible if the polymer molecules add to existing aggregates without increasing the hydrodynamic volume of the aggregates. This suggests that clusters grow more dense as the concentration of the polymer is increased. This type of phenomenon has been discussed by Watterson and Elias[51] for associating systems. According to these authors, the viscosity curves ($\eta_{sp}/c = f(c)$) may be concave or convex to the c-axis, may show extrema, or may even be approximately linear, depending on the type of association encountered (closed or open), on the thermodynamics and on the aggregation number.

In Figure 2, it can be seen that the reduced viscosity drops dramatically when thiocyanate is added to the PAAA-water solution. This reagent disrupts the intermolecular associations, so that the clusters break up and the viscosity falls off. This type of reduction of the viscosity has also been observed[52] for a system of a hydrophobically associating fluorocarbon polymer when the solvent is changed from water to a mixture of water−dimethyl formamide (DMF). It was argued that the addition of DMF to water dissociates the polymer aggregates.

Larger values of the reduced viscosity are found when the concentration of the denaturant sodium thiocyanate

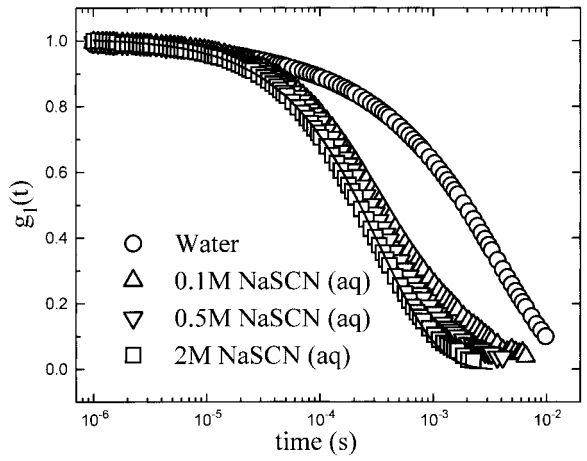

Figure 4. Semilogarithmic plot of the field autocorrelation function for a 0.46 wt % solution of PAAA in water and in aqueous sodium thiocyanate solutions. The solid curve has been fitted to the data from the 2 M sodium thiocyanate solution with the aid of $g_1(t) \sim \exp[-(t/\tau)^{\beta}]$, with $\beta = 0.8$.

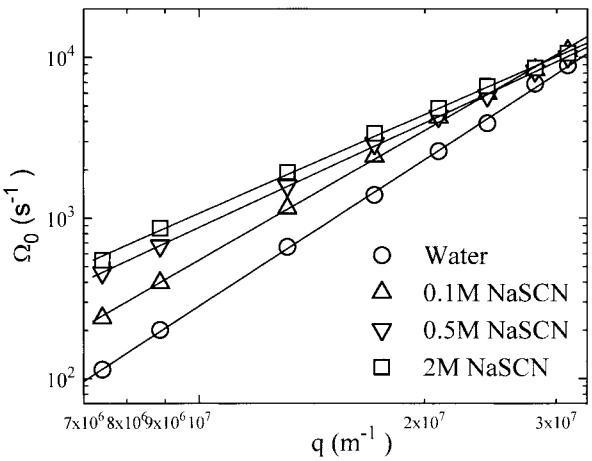

Figure 5. Logarithmic plot of the initial relaxation rate versus the scattering vector in solutions of PAAA in water and in aqueous sodium thiocyanate solutions.

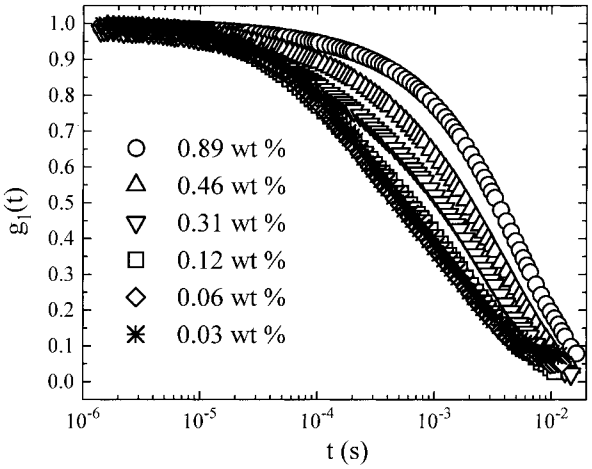

Figure 6. Semilogarithmic plot of the autocorrelation function at different polymer concentrations in water.

is increased from 0.5 to 2 M. If the polymer becomes partially hydrolyzed in the presence of salt, the reverse behavior is expected,[13] since the viscosity of polyelectrolytes decreases with increasing concentration of salt. The results for the present system suggest that the excluded volume effect becomes more dominant as the concentration of sodium thiocyanate is increased. One may say that 2 M sodium thiocyanate is a better solvent (stronger excluded volume effect) than 0.5 M sodium thiocyanate. This result is consistent[13] with similar measurements performed on aqueous poly (acrylamide).

Dynamic Light Scattering. The angular dependence of the correlation function in a 0.46 wt % solution of PAAA in 2 M sodium thiocyanate is displayed in Figure 3a. The inset plot shows the same correlation functions, but they are scaled with q^2. This plot reveals that the relaxation mode is practically diffusive (q^2 dependent). The translational diffusion of individual polymer molecules is observed. The data are easily analyzed by the method of cumulants. From this analysis, both the polydispersity index $M_w/M_n \approx 1.5$ and the mutual diffusion coefficient $D_z = 1.0 \times 10^{-11}$ m^2/s are determined. The latter quantity is calculated from the initial decay through the following relation $\Omega_0(q) = D_z q^2$. Using the Stokes−Einstein relation ($D = k_b T/R_h 6\pi\eta_0$), the value of $R_h = 2.2 \times 10^{-8}$ m was obtained for the apparent hydrodynamic radius.

The angular dependence of the correlation function of a 0.46 wt % solution of PAAA in water is shown in Figure 3b. The inset plot, where the correlation functions are scaled with q^2, reveals that the relaxation modes exhibit much stronger q dependence than that of a diffusive process. The profile of the correlation function changes as the scattering angle is changed. This type of behavior is not observed for PAAA in the presence of 2 M sodium thiocyanate. This is an indication of the presence of two or more relaxation processes, which exhibit a different q dependence. It can be mentioned that if the correlation functions in Figure 3b are scaled with q^3 instead of q^2 (see the inset plot), the correlation functions do not condense because the profile of the curves changes with scattering angle.

In Figure 4, the autocorrelation functions of PAAA in water and with different amounts of sodium thiocyanate are depicted. A comparison of the correlation functions clearly shows that the decay is shifted toward shorter times as the level of sodium thiocyanate addition is increased. For these concentrations of sodium thiocyanate, the decay of the correlation function can be described by a single stretched exponential of the form $g_1(t) \sim \exp[-(t/\tau)^{\beta}]$, with $\beta = 0.8$ in the presence of 2 M sodium thiocyanate (see Figure 4). This deviation from a single exponential can directly be attributed to the intrinsic molecular weight distribution of the polymer fraction. These findings suggest that the slow relaxation mode gradually disappears when sodium thiocyanate is added. The conjecture is that the clusters formed in the intermolecular association process of PAAA in water give rise to the slow relaxation mode. In the presence of sodium thiocyanate, the clusters are progressively disrupted as the concentration of the denaturant increases.

Figure 5 shows a log−log plot of the initial relaxation rate Ω_0 as a function of the scattering vector. For PAAA in water, Ω_0 exhibits a q^3 dependence at all the considered concentrations. This observation suggests that relaxation[36] of internal motions in the Zimm limit is probed. The hydrodynamic interactions between monomers remain dominant, and the condition $qL > 1$ is fulfilled. To satisfy this criterion, R_h must be larger than 1.3×10^{-7} m, which is more than six times the value of the hydrodynamic radius found for a single polymer molecule in 2 M aqueous sodium thiocyanate.

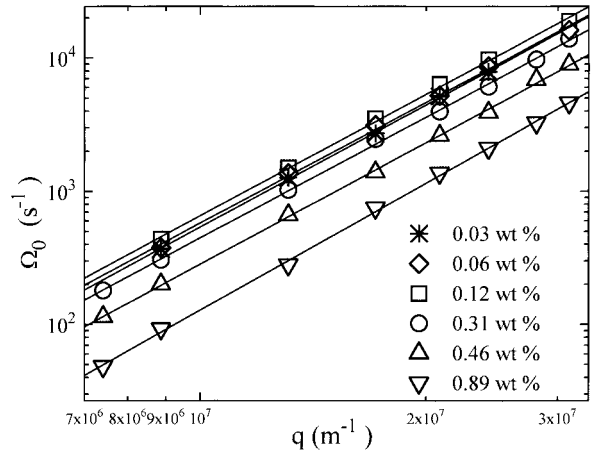

Figure 7. Logarithmic plot of the initial relaxation rate versus the scattering vector for PAAA in water at the concentrations indicated.

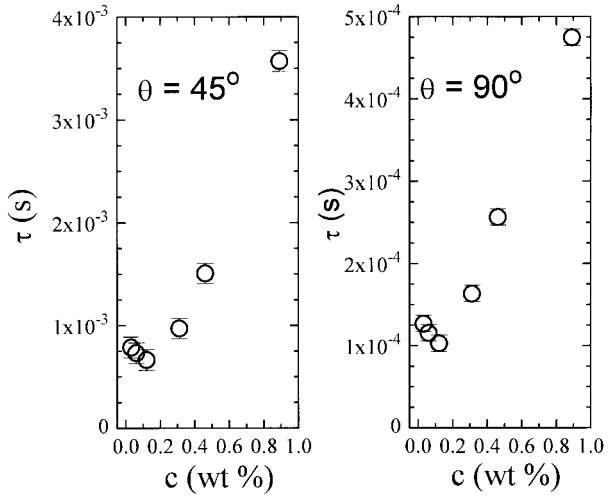

Figure 8. The initial relaxation time $\tau = \Omega^{-1}$ plotted against concentration for solutions of PAAA in water.

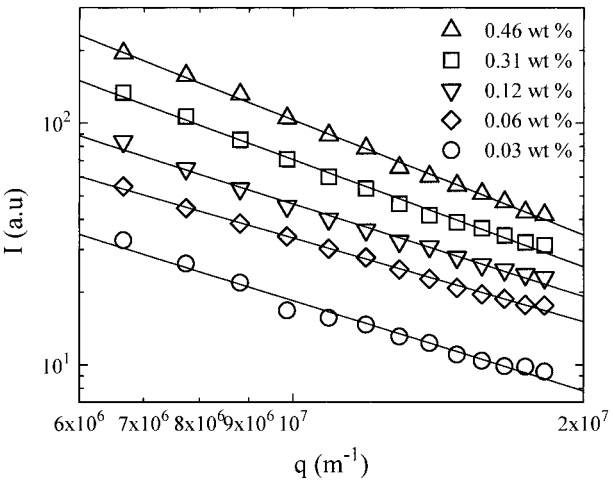

Figure 9. Logarithmic plot of the scattered intensity versus the scattering vector for PAAA in water at the concentrations indicated.

In addition to relaxation of the internal motions, it is believed that a diffusive relaxation mode is hidden in the correlation functions for the PAAA-water systems. This relaxation mode represents the translational diffusion of the polymer clusters. Unsuccessful attempts have been made to separate the different relaxation processes.

A close inspection of Figure 4 reveals that the decay of the correlation function for PAAA in the presence of 0.1 and 0.5 M sodium thiocyanate contains a small contribution of a long-time tail. This tail is most pronounced for PAAA at the lowest denaturant concentration (0.1 M) but is virtually absent for PAAA in the 2 M sodium thiocyanate solution. This result may indicate the presence of a limited aggregation process at low concentrations of sodium thiocyanate. This hypothesis of limited cluster formation in solutions of low sodium thiocyanate content is consistent with the observation of excess scattering from the static light scattering measurements at low angles for these solutions. Our surmise is that the clusters are small and that the interaction between the polymer molecules is weak.

This picture of the association process seems to be supported by the results in Figure 5, where the initial relaxation rate Ω_0 is plotted against the scattering vector in a log−log plot. The q dependence of Ω_0 for solutions of PAAA changes from q^2 in 2 M sodium thiocyanate to q^3 for PAAA in water. Again, this behavior is an indication of the presence of large clusters for the PAAA-water system, and dispersed polymer molecules for the PAAA−2 M sodium thiocyanate system. The presence of aggregates may explain why Ω_0 shows a q dependence that lies between q^2 and q^3 for the solutions with small amounts of sodium thiocyanate. It seems that the limited cluster formation in these solutions is responsible for the observed crossover effect. The radius of the scattering object is about the size of the scattering volume, $qL \approx 1$. The observed initial decay is composed of a mixture[53] of translational diffusion and internal modes.

The effect of changing the concentration of PAAA in water on the correlation function is depicted in Figure 6. The autocorrelation functions of six different polymer concentrations, ranging from 0.03 to 0.89 wt %, are shown. Evidently the relaxation is slowed down and the slow relaxation mode becomes more pronounced as the concentration of the polymer increases. This type of slowing down has been observed previously, e.g., when the concentration of an associating polymer increase, or when the gel point[54−56] of a system is approached. The q dependence of the initial relaxation rate of all these correlation functions is displayed in Figure 7. The general feature is that Ω_0 scales with q^3 for all the considered concentrations. The initial relaxation rate is dependent on the concentration.

The concentration dependence of the initial relaxation time, $\tau = \Omega^{-1}$ for PAAA in water at two different scattering angles is shown in Figure 8. Within experimental errors, the relaxation time is independent of concentration in the low concentration range, but at c > 0.12 wt %, the relaxation time becomes markedly slower as the concentration of polymer increases. From DLS experiments performed on high molecular weight polystyrenes, a concentration dependence of the initial relaxation time has been reported.[57] Below a certain concentration, the initial relaxation rate was found to be constant. Above that point, a gradually slower relaxation time was observed with increasing polymer concentration. The crossover concentration was located at about half the overlap concentration.

Table 1. Variation of the Fractal Dimension with Polymer Concentration

concentration (wt %)	0.03	0.06	0.12	0.31	0.46
d_m	1.2	1.2	1.3	1.5	1.6
d_f	1.5	1.5	1.6	1.9	2.0

Static Light Scattering. The total scattered intensity for five aqueous solutions of PAAA is plotted versus q in a log−log plot in Figure 9. The q dependence of the scattered intensity can be well described by a power law. The criterion qL > 1 is fulfilled and the measured fractal dimension d_m may be found from the slope of the lines, $I(q) \propto q^{-d_m}$. The numerical values are collected in Table 1. At the highest concentration, $d_m = 1.6$. This value is predicted for a dilute solution of polydisperse clusters if $d_m = d_f(3 - \tau)$ (see eq 3) and $\tau = 2.2$ (percolation theory). In this case, the fractal dimension of a single swollen cluster is $d_f = 2.0$. This is the value of the fractal dimension[30] of swollen percolation clusters below the gelation threshold. The fractal dimensions at the other concentrations are calculated in the same manner and the results are shown in Table 1.

Since the mass inside the radius of a cluster is dependent upon the fractal dimension through the following relation: $M \propto R^{d_f}$, the fractal dimension is a measure of the compactness of a cluster. As the fractal dimension increases, the object will become more compact. As can be seen from Table 1, the fractal dimension increases with increasing concentration, indicating that the clusters assume a more dense structure. This finding is consistent with the behavior observed for the reduced viscosity in Figure 2. The scattered intensity does not follow a power law in q for the polymer solutions containing sodium thiocyanate. In this case, the criterion qL > 1 is not fulfilled over an extended q range.

Summary and Conclusions

In this study, viscometry as well as static and dynamic light scattering measurements have been carried out on solutions of poly (*N*-acetamido acrylamide) in water and in the presence of various amounts of sodium thiocyanate.

From the viscosity results, there is a strong indication of aggregation of PAAA in water at low polymer concentrations and contraction of the clusters at higher concentrations. Addition of sodium thiocyanate breaks up the clusters.

The results from static light scattering on PAAA-water solutions also indicate the presence of large clusters. The scattered intensity exhibits a power law in q. A progressively stronger q dependence of the intensity is observed with increasing polymer concentration, indicating that the fractal dimension of the clusters increases, i.e., the clusters become more compact. This concentration-induced contraction of the clusters is consistent with the viscosity results.

The DLS experiments show that the decay of the correlation function is shifted toward shorter times when sodium thiocyanate is added to a solution of PAAA in water. When the amount of denaturant is increased, the decay is shifted even further toward shorter times. A long-time tail behavior of the correlation function can be traced in the PAAA solutions containing low concentrations of sodium thiocyanate. This may be a sign of an incipient cluster formation process. At these conditions, the initial relaxation rate shows a stronger q dependence than that of a diffusive process. However, the data from the viscosity measurements gave no indication of aggregation at low levels of denaturant addition. It is possible that the shear forces operating in the Ubbelohde viscometer are strong enough to disrupt these weak clusters. When the amount of denaturant is increased to 2 M, the long-time tail of the correlation function disappears completely and the initial relaxation rate shows a q^2 dependence; i.e., the relaxation mode is diffusive.

The results from the DLS experiments in water clearly indicate the presence of large clusters. The initial decay rate exhibits a q^3 dependence. This relaxation mode is caused by internal motions, where the hydrodynamic interactions are dominating. To fulfill the criterion qL > 1, the value of R_h of a cluster must be at least 6 times larger than that of a single polymer coil. If $d_f = 1.5$, which is the value of the fractal dimension at the lowest concentration of polymer in water (0.03 wt %), then the mass of a cluster (calculated from eq 1) must increase more than 14 times to give rise to an increase of the radius of the cluster of 6 times.

The polymer PAAA is a hydrophilic associating polymer. The presence of clusters is observed in water, even at very low polymer concentrations. As the concentration increases, the number of clusters increases and they shrink. In this type of system, we expect that the attractive forces between the individual polymer molecules give rise to enhanced molecular association. These forces are most likely due to hydrogen bonding between the amide groups on the polymer backbone. This surmise is supported by the fact that these bonds are disrupted in the presence of sodium thiocyanate, which is a hydrogen-bond-breaking agent.

References and Notes

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