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Reexamination of Slow Dynamics in Semidilute Solutions: Temperature and Salt Effects on Semidilute Poly(*N*-isopropylacrylamide) Aqueous Solutions

Guangcui Yuan,[†] Xiaohong Wang,[†] Charles C. Han,*[,†] and Chi Wu*[,‡]

Beijing National Laboratory for Molecular Sciences, State Key Laboratory of Polymer Physics & Chemistry, Joint Laboratory of Polymer Science & Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, People's Republic of China, and Department of Chemistry, The Chinese University of Hong Kong, Shatin, N.T., Hong Kong

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ABSTRACT: One fast and one slow relaxation mode were observed in semidilute aqueous solution of poly(*N*-isopropylacrylamide) (PNIPAM) by dynamic light scattering (DLS). The length scale of the slow relaxation was found to be comparable with the observation length (1/*q*) in our DLS measurements. To elucidate its origin, we varied the solution temperature and used different salts to study their effects on such a slow mode because it is known that they can influence the strength of the water−amide hydrogen bonding as well as the icelike structure of liquid water. As the temperature increases, the slow mode was gradually suppressed. Using a strong salting-out salt (Na_2SO_4) and a strong salting-in salt (NaSCN) with the same cation as two model systems, we found that the salting-out salt suppresses the slow dynamics, while the salting-in salt amplifies it. Our results reveal that the slow mode is related to a long-range correlated density or concentration fluctuation, namely, the interaction among the segments in different blobs on chains.

Introduction

For a semidilute solution of linear polymer with a thermodynamically good solvent, the intensity−intensity time correlation function measured by the dynamic light scattering (DLS) is expected to display a single-exponential decay. It is because that under this condition the static and dynamic properties of polymers are determined just by one correlation length of concentration fluctuations (often described as the mesh size), ξ, which is predicted to be molecular weight independent and scaled to the polymer concentration (C) as $\xi \sim C^{0.75}$.[1−3] In additional to this entanglement strand fluctuation mode, it has been found to be generally true that the so-called "slow mode" has also been observed for hydrocarbon polymer in a semidilute solution with Θ-solvent.[4−7] However, various good solvent, semidilute, aqueous systems have also been shown to exhibit a dominant slow mode, such as poly(ethylene oxide)/H_2O,[8,9] poly(vinyl alcohol)/H_2O,[10] and poly(vinylpyrrolidone)/H_2O systems.[11−13] Compared with the chain behaviors in general hydrocarbon systems, the appearance of the slow mode in these aqueous systems seems anomalous and confusing. Sun and King[13] attributed this anomalous behavior to the unique, tetrahedral hydrogen-bonding network of water and showed that denaturing the water through the addition of denaturing agents known to disrupt the water structure could significantly diminish the slow relaxation. Also, the denaturation change through pressure is reversible.

Poly(*N*-isopropylacrylamide) (PNIPAM) is considered as a typical water-soluble polymer which bears both hydrophilic (amide) and hydrophobic (isopropyl) groups, and it has been described as a model system for the cold denaturation of peptides and proteins.[14] The delicate balance between hydration (the formation of hydrogen bonding between polymer and water molecules) and hydrophobic effects is a determining factor in the properties of aqueous PNIPAM solutions.[15] In our previous study, we showed that one fast and one slow relaxation mode were observed in semidilute aqueous solution of PNIPAM by DLS, while there is only one mode in dilute solution.[16] To further elucidate the origin of the slow mode, in this paper, we present experimental investigations of temperature and salt effects on the dynamics of PNIPAM chains in semidilute aqueous solutions, especially on the slow mode, because it is known that both of them can influence the strength of the water−amide hydrogen bonding as well as the icelike structure of liquid water.[17] With respect to the salt effects, a strong salting-out salt (Na_2SO_4) and a strong salting-in salt (NaSCN) with the same cation were chosen as two model systems.

Experimental Section

The details of sample preparation and laser light scattering spectrometer have been described before.[16] A PNIPAM sample with $M_n = 1.99 \times 10^5$ g mol^{-1} and $M_w/M_n = 1.1$, measured by gel permeation chromatography (Waters) at 20 °C with tetrahydrofuran as eluant, was used in the present study. Na_2SO_4 and NaSCN of analytical chemical reagents grade were used after recrystallization. In DLS, the baseline-normalized intensity−intensity time correlation function $g^{(2)}(t,q)$ in the self-beating mode was measured, where t is the decay time and q is the scattering vector ($q = (4\pi n/\lambda_0)\sin(\theta/2)$). $g^{(2)}(t,q)$ can be related to the normalized first-order electric field time correlation function $|g^{(1)}(t,q)|$ via the Siegert relation as[18]

$$g^{(2)}(t,q) = \beta|g^{(1)}(t,q)|^2 \qquad (1)$$

where $0 < \beta < 1$ is a constant related to the coherence of the detection optics. For broadly distributed relaxation spectrum, $|g^{(1)}(t,q)|$ is related to a characteristic relaxation time distribution $G(\tau)$ as

$$|g^{(1)}(t,q)| = \int_0^\infty G(\tau)e^{-t/\tau}\,d\tau \qquad (2)$$

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* To whom correspondence should be addressed: Ph +86 010 82618089; Fax +86 010 62521519; e-mail c.c.han@iccas.ac.cn; chiwu@cuhk.edu.hk.

[†] The Institute of Chemistry, CAS.

[‡] The Chinese University of Hong Kong.

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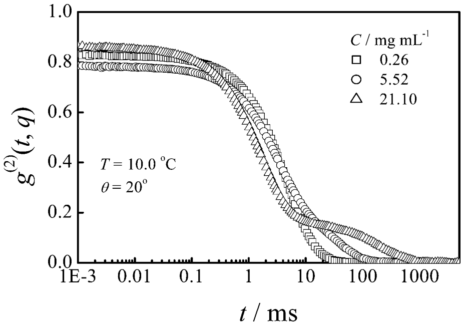

Figure 1. Concentration dependence of intensity−intensity time correlation function $g^{(2)}(t,q)$ of PNIPAM/H_2O in both dilute and semidilute regimes. The overlapping concentration estimated from $3M_w/(4\pi N_A R_g^3) < C^* < M_w/(N_A(\sqrt{2}\ R_g)^3)$ is in the range 1.9−2.8 mg mL^{-1}, where N_A is the Avogadro constant and R_g is the average radius of gyration.

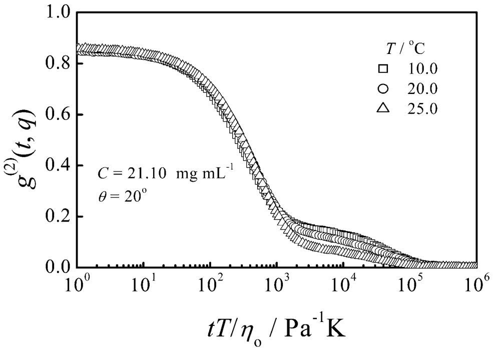

Figure 2. Temperature dependence of intensity−intensity time correlation function $g^{(2)}(t,q)$ of PNIPAM/H_2O in a semidilute solution. The decay time (t) on the x-axis is shifted by (T/η_0) to correct the temperature (T) and the solvent viscosity (η_0), so that the relaxation time at different temperatures can be directly compared.

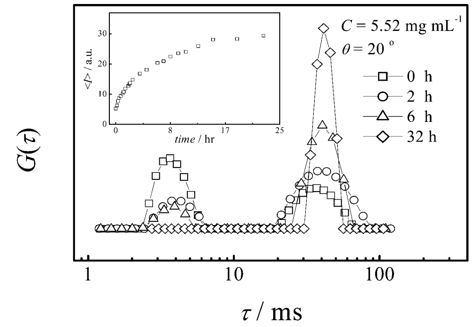

Figure 3. Time dependence of characteristic relaxation time distribution function $G(\tau)$ of a semidilute aqueous of PNIPAM after its temperature was jumped from 29.0 to 30.0 °C. The inset shows the time dependence of averaged intensity of scattering light under the same condition. Note that here $C/C^* \approx 2$ and the extent of overlapping between polymer chains is rather limited.

$G(\tau)$ can be calculated from the Laplace inversion of the measured $g^{(2)}(t,q)$ on the basis of eqs 1 and 2. In this study, the CONTIN program supplied with the correlator was used.[18]

Results and Discussion

Figure 1 shows the typical intensity−intensity time correlation function of PNIPAM aqueous solutions in both dilute and semidilute regimes. In dilute solution, only one relaxation mode is observed, which is related to the mutual diffusion of fully dispersed polymer chains. As the polymer concentration increases, one additional slow mode appears in the semidilute regime. Previous studies showed that the characteristic relaxation rate (Γ_f) of the fast mode is proportional to q^2, indicating that it is diffusive, while the characteristic relaxation rate of the slow mode (Γ_s) is scaled to q as $\Gamma_s \sim q^{\alpha_s}$ with $2 < \alpha_s < 3$, indicating that the slow relaxation involves a length scale which is comparable with the observation length ($1/q$) used in our DLS measurements.[16] The slow mode becomes more and more dominant, and its characteristic relaxation time shifts toward the slow direction with an increasing concentration.

In this system, besides water as a special solvent that can form some clustering structures via intermolecular hydrogen bonding,[17] PNIPAM itself can form intra- and interchain hydrogen bonding as well as form hydrogen bonding with water molecules. As expected, PNIPAM chains or segments interact directly or indirectly with each other in semidilute solutions. Güven and Eltan[19] have illustrated such interaction in their viscometric study of association behavior of poly(vinylpyrrolidone) in water. Therefore, it is possible that such a long-range segment−segment interaction might not be completely “screened” out by overlapping, especially when the extent of chain overlapping is not too high in semidilute solutions.

It has been well documented that temperature can significantly alternate the solubility of nonionic polymers in water. For PNIPAM, it has a lower critical solution temperature (LCST) around 32 °C in water. Figure 2 shows the temperature dependence of the intensity−intensity time correlation function obtained from a semidilute solution of PNIPAM in water at temperature lower than its LCST. The slow mode becomes more evident in amplitude and shifts toward a longer relaxation time as the solution temperature decreases. Note that water is a better solvent for PNIPAM at lower temperature. Therefore, the slow mode cannot be related to chain aggregations or the formation of some real chain clusters. Since the chains have a more swollen conformation at a lower temperature, they are more overlapped with each other, so the slow mode should be related to the chain entanglement. Presumably, as we suggested before, it is due to some long-range correlated density or concentration fluctuations. In the classical semidilute solution theory, the motions of segments between different blobs are screened and therefore not correlated. Such an assumption may be broken down when there is some interaction (hydrogen bonding in water) or strong interaction between chains in poor solvents.

Figure 3 shows the characteristic relaxation time distribution at different times for a semidilute aqueous solution of PNIPAM after its temperature was jumped from 29.0 to 30.0 °C. The solution was kept at 29.0 °C for 48 h to reach its corresponding equilibrium state before temperature jump. The reason for choosing 30.0 °C instead of a higher temperature is that we had to construct a balance between the phase transition temperature and the observation of phase separation by DLS. Namely, at 30.0 °C, the solution remains clear within 3 days. At the temperatures higher than 30.0 °C (e.g., 31.0 °C), the solution becomes cloudy within a few minutes. The inset in Figure 3 shows the time dependence of the time averaged intensity of scattering light ($\langle I \rangle$) after the solution temperature reaches 30.0 °C. It is clear that $\langle I \rangle$ increases with time due to the phase separation; i.e., the chains start to aggregate. In Figure 3, the intensity contribution of the slow mode (i.e., the peak area) increases with time. Finally, the fast mode disappears or becomes not measurable. As discussed before, the fast mode is related to the cooperative diffusion of segments inside each “blob”. The chain collapse at 30.0 °C suppresses such a motion. On the other hand, the chain shrinkage also reduces the interchain entanglement and destroys the transient network. It has been found that the chain aggregation and contraction in a poor solvent could lead to the formation of mesoglobules made of a limited number of chains.[20] As more and more polymer

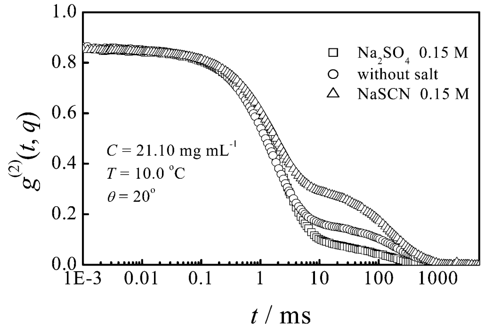

Figure 4. Salt effect on intensity−intensity time correlation function $g^{(2)}(t,q)$ of PNIPAM/H_2O in a semidilute solution.

chains are pulled away from the entangled transient network, more and more mesoglobules (real clusters) are formed. Note that here the slow mode at the later stage represents large aggregates of the chains, i.e., real cluster. This process is reversible.

To further our study of the interaction between chains and the effect of chain conformation, we added different salts into the PNIPAM aqueous solution. The effects of salts on the PNIPAM chain conformation and its LCST have been investigated in depth by many experimental techniques and found to be consistent with the Hofmeister series,[21−23] which originally categorized simple inorganic salts in regard to their relative ability to precipitate proteins from aqueous solution. Anions have a more pronounced effect on such a behavior than cations. The effect of Hofmeister anions on the PNIPAM solvation can be explained by different interactions of anions with the chain and its hydration water molecules; namely, the salting-out effect (the decrease of the LCST) is induced by weakening the hydrogen bonding between water molecules and the amide group via polarization and by increasing the surface tension of the cavity surrounding the chain backbone and the isopropyl side group. On the other hand, the salting-in effect (the increase of the LCST) is induced by strengthening the hydrogen bonding when anions bind directly to the amide group.[23] SO_4^{2-} is a strong salting-out ion, which has a high surface charge density and forms a complex of tightly bound water molecules, which is considered as a solvent worse than pure water. Contrary to this, SCN^- is a strong salting-in ion, and its complex with water is a better solvent for PNIPAM.[24] Figure 4 shows the intensity−intensity time correlation function of semidilute solutions with an identical polymer concentration, but with and without different salts (Na_2SO_4 and NaSCN) at 10.0 °C, which is well below the LCST. The addition of SCN^- anions increases the relative amplitude of the slow mode, but the addition of SO_4^{2-} anions has an opposite effect on the slow mode. This is expected because SCN^- anions increase the solubility of PNIPAM in water and contribute to the extension of chains, which has a similar effect as the decreases of the solution temperature. All of our results consistently showed that the better the solubility of PNIPAM in water, the more pronounced the slow mode.

Conclusion

The slow relaxation mode was observed by DLS in semidilute polymer solutions when the solvent is not thermodynamically good or there exists some interaction stronger than the van der Waals interaction, such as the hydrogen bonding. In the present study, by changing the solution temperature or adding different salts, we have demonstrated that the slow relaxation mode in semidilute aqueous solutions of PNIPAM below the LCST is not related to a possible chain aggregation or formation of real clusters, but to a long-range interaction between the segments in different blobs on chains. Hence, it might be due to the hydrogen bonding. It seems that more extension of the chains or more overlapping of the chains will lead to a more pronounced slow mode.

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