

Effect of Thermal History on Rheological Properties of Partially Hydrolyzed Polyacrylamide/Anionic Surfactant SDS Complex Systems

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Abstract: The effects of thermal history on the rheological properties of partially hydrolyzed polyacrylamide/ sodium dodecyl sulfate complex aqueous solutions have been studied using both steady shear and dynamic temperature sweep characterizations. An abnormal rheological behavior was found that dynamic moduli of the aqueous solutions increased, while the viscosity decreased after thermal treatment, which could help to gain insight into the micro-phase evolution of the polymer/surfactant complex aqueous solutions and its dependence on temperature.

Keywords: Partially hydrolyzed polyacrylamide, sodium dodecyl sulfate, supramolecular structure, thermal history, rheological properties

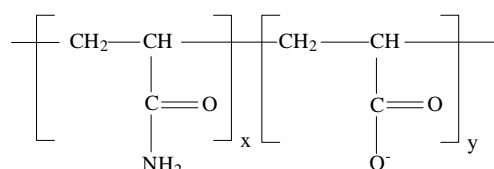
Partially hydrolyzed polyacrylamides (PHPAM) with varied hydrolysis degree are commonly used as thickening agents in industrial processes of food industry, pulp and paper industry, as well as the others. The addition of small quantities of PHPAM can substantially increase the viscosity of their aqueous solutions. Owing to this prominent performance, PHPAM is extensively used in mobility control of fluids in porous media, especially in enhanced oil recovery (EOR). In EOR, surfactants are usually added into the PHPAM aqueous solutions to lower surface or interface tensions. It was found that there existed a complex interaction between PHPAM and the surfactants¹⁻⁴, thus influencing the rheological behavior of the solutions. Much of the previous studies were concentrated on the effects of surfactant type, surfactant concentration and polymer chain structures and concentration, while the effect of thermal history has been scarcely reported. In this work, we selected partially hydrolyzed polyacrylamide/sodium dodecyl sulfate complex aqueous system as a model to study the effects of thermal history on the rheological behaviors.

Experimental

Partially hydrolyzed polyacrylamide (provided by Daqing Petroleum Company) has molecular weight about 2.1×10^7 of 26.4% hydrolysis degree as specified by the supplier. The chemical structure is shown in **Scheme 1**. The sample was ambient dried in vacuum for 1 day *prior* to use. Sodium dodecyl sulfonate ($C_{12}H_{25}SO_4Na$, SDS) was

analytically pure (99%) from Acros. SDS aqueous solutions were prepared by mixing the required amount of SDS in deionized water.

Scheme 1 The chemical structure of PHPAM



$$\text{Hydrolysis degree} = y / (x + y)$$

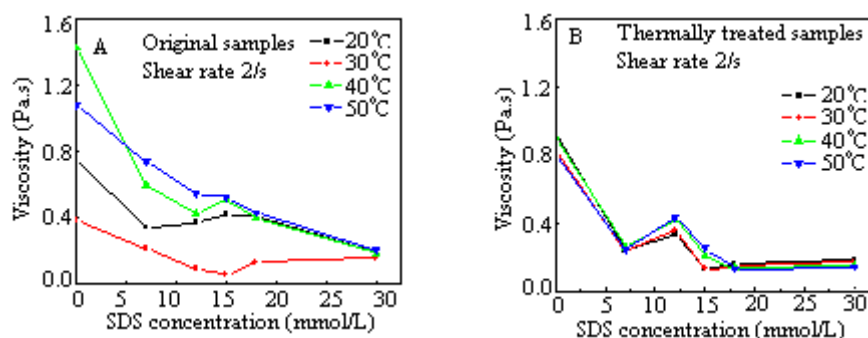
The polymer solutions were prepared by dissolving required amounts of PHPAM in the SDS aqueous solution gradually, and then gently vibrated for 48 h. The polymer concentration was fixed at 2 g/L with varied SDS concentrations. The as-prepared solutions were equilibrated for another 48 h to eliminate air bubbles, thus homogeneous solutions were obtained, and preserved at ambient temperature about 28°C. For thermal treatment, the solutions were heated to and kept at 40°C for 5 h. Afterwards, the solutions were cooled down to ambient temperature and maintained for another 72 h before measurement.

The rheological measurements of PHPAM/SDS aqueous solutions were conducted on a controlled strain ARES (Advanced Rheology Extension System) rheometer. The concentric cylinder holder with a rotating outer cup of diameter 34 mm and a fixed interior bob of diameter 32 mm was used. Samples were gently loaded into the gap and stayed for 15 min before testing to achieve the temperature equilibrium. The viscosity measurement was conducted in a shear rate range from 0.02 s⁻¹ to 200 s⁻¹, which covered both linear and nonlinear viscoelastic regions. The dynamic temperature ramp tests were conducted within the linear viscoelastic region, *i.e.* at 6.28 rad/s with strain at 20%, and the temperatures were increased from 25°C to 60°C followed by a decrease to 25°C at a rate of 1°C/min.

Results and Discussion

The steady viscosity of the PHPAM/SDS aqueous solutions before and after thermal treatment is depicted in **Figure 1A** and **1B**, respectively.

Figure 1 Viscosity dependence on thermal treatment of PHPAM/SDS aqueous solutions at different temperatures



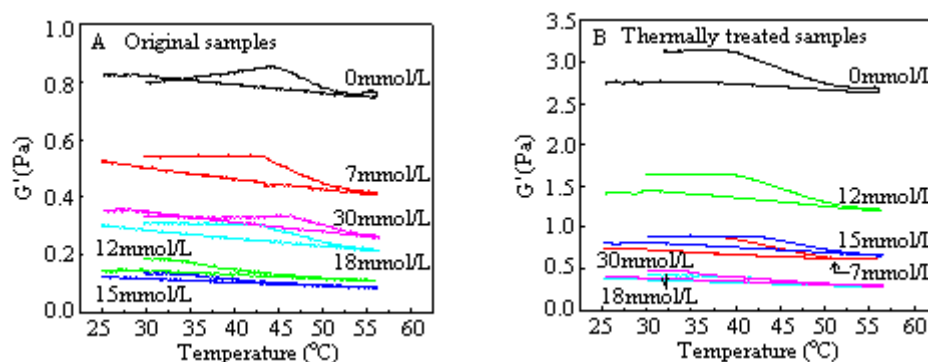
458 Effect of Thermal History on Rheological Properties of Partially Hydrolyzed Polyacrylamide/Anionic Surfactant SDS Complex Systems

Figure 1A shows the steady viscosity of the corresponding solutions before thermal treatment. As SDS concentration increasing, the viscosity first decreases to a minimum, then increases, at last levels off. This trend is remained in the measurement temperature range of 20-50°C. The viscosity measured at 40-50°C is even higher than that at 20°C, and it reaches the lowest value at 30°C. It is difficult to explain this viscosity change with temperature just by hydrogen bond interaction. Thus, PHPAM and SDS should have some complex interaction, which is temperature dependent. The minimum viscosity corresponds to the onset of aggregation between surfactant and polymer, whilst the maximum relates to the saturation of the aggregation. With SDS concentration further increasing to very high value, *i.e.* 30 mmol/L, the viscosity is less affected by temperature. From practical application viewpoint, it is required to retain a high viscosity for the complex solutions containing a designed SDS concentration. From **Figure 1A**, we suggest that SDS concentration should be strictly controlled around the aggregation saturation concentration. In comparison, the viscosity dependence on temperature of the thermally treated solutions is weaker as shown in **Figure 1B**. Viscosity of all the samples is lower than that of their corresponding original ones except that at 30°C. Thus, it is hazardous to preserve the complex solutions at high temperature for long time, which cause severely lost of viscosity. According to our previous results, the ionized polymer entanglement network is weakened *via* electrical shielding owing to the introduction of anionic surfactant SDS *prior* to the formation of aggregation, thus the viscosity decreases significantly. While SDS content increases to a critical value, the “free” surfactant molecules will aggregate into micelles, which cause the weakness of shielding effect until the polymer chains become saturated with surfactant micelles. The micelles also lead to the expansion of polymer hydrodynamic gyration. The weakened shielding effect as well as the expansion of polymer hydrodynamic gyration results in the slower of decreasing trend of viscosity. Then the viscosity increases again mainly due to the expansion of the polymer hydrodynamic gyration caused by the introduction of the micelles. The dependence of viscosity on the temperature is compromised between the shielding effect and the hydrodynamic gyration expansion. At 30°C, the former effect dominates thus the viscosity decreases. While at higher temperature as in the range of 40-50°C, the polymer chains become less hydrophilic, which facilitates the formation of complex micelles to enlarge the hydrodynamic dimension, thus the viscosity increases. During the thermal treatment at high temperature for a long time, the less hydrophilic polymer chains tend to self-aggregate to form a strong network, which is irreversible even the temperature is cooled down to ambient temperature. In this case, the solutions are in quasi-equilibrium state. Besides, the surfactant molecules are easier to form aggregation between the polymer chains of less hydrophilic at high temperature. Therefore, the SDS concentration at viscosity maximum is lower at higher temperatures, which is consistent with the result shown in **Figure 1B**.

The effect of thermal history on storage modulus (G') is shown in **Figure 2**. Loss modulus G'' (not shown here) has the same tendency as that of G' . From **Figure 2**, the information about structural change with temperature could also be provided. For the original samples as shown in **Figure 2A**, modulus G' decreases with SDS concentration until obtaining a minimum at 15 mmol/L then increases again. At 15 mmol/L SDS concentration, the storage modulus *vs* temperature hysteresis is the smallest, meaning that the sample is lest elastic. In the temperature range of 40-50°C, G' greatly decreases with temperature. While in the high to low temperature ramp procedure, G' gradually increases with temperature decreasing without an abrupt change, which means the transformation is irreversible, or at least incompletely reversible. Surprisingly, as shown in **Figure 2B**, values of G' of the thermally treated samples are larger than those of original samples, indicating a great increase in elastic response after thermal treatment.

This is another verification of supramolecular structure formed during thermal treatment rather than polymer chains scission. There exists a minimum and a maximum storage modulus at 18 mmol/L and 12 mmol/L SDS concentration respectively, which is similar to that as shown in **Figure 1B**. The storage modulus hysteresis of the thermally treated samples is larger than that of the original ones, meaning the existence of static structure after thermal treatment. Moreover, the storage modulus measured from high to low temperature scanning was higher than the corresponding value measured from low to high temperature scanning test. This is consistent with the conjecture of irreversible self-aggregation among the polymer chains at high temperature. It is reasonable that the cohesive entanglement among the polymer chains is facilitated at high temperature for long time.

Figure 2 Storage modulus G' as a function of temperature



In conclusion, the rheological behaviors of PHPAM/SDS complex aqueous solutions are significantly influenced by thermal history. Steady viscosity decreased after the solutions were thermally treated, while storage and loss moduli increased. This was closely related with the self-aggregation of the polymer chains as well as the change of interaction between the surfactant molecules and polymer with temperature. This experimental finding may help to understand the interaction of surfactant between polymer chains, and the conformation of the polymer chains in aqueous solutions at high temperature. It can also contribute to design flooding fluids in enhanced oil recovery.

Acknowledgments

This work was supported by 973 Project "Fundamental Study on Enhanced Oil Recovery" (G1999022500).

References

1. L. Wang, C. Tiu, T. J. Liu, *Colloid. Polym. Sci.*, **1996**, 274, 138.
2. J. Y. Zhang, X. P. Wang, H. Y. Liu, *et al.*, *Colloid. Surf. A*, **1998**, 132, 9.
3. K. Y. Mya, A. M. Jamieson, A. Sirivat, *Polymer*, **1999**, 40, 5741.
4. H. Z. Yuan, S. Zhao, J. Y. Yu, *et al.*, *Colloid. Polym. Sci.*, **1999**, 277, 1026.

Received 17 August, 2001