

Synthesis and Aqueous Solution Properties of Hydrophobically Modified Polyacrylamide

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ABSTRACT: Hydrophobically modified polyacrylamide (HMPAM) is synthesized by a free radical micellar polymerization method with low amounts of anionic long-chain alkyl, sodium 9-(and 10)-acrylamidostearate (NaAAS), which is derived from a renewable resource material, oleic acid. In this progress, the molar ratio of Sodium dodecyl sulfate (SDS) to NaAAS is adjusted, so polymers with different lengths of the hydrophobic blocks (NH = 3 and NH = 6) are obtained. The copolymers are characterized by ¹H NMR, and the polymer weight and polydispersity are determined by gel permeation chromatography. The solution behaviors of the copolymers are studied as functions of concentrations, pH, and added electrolytes by steady-flow and oscillatory experiments. The viscosities of these HMPAMs increase enormously above the critical concentration (*c**). The sample with longer hydrophobic blocks exhibits better thickening effect. The rheological behaviors of aqueous solutions of HMPAMs are also investigated at different pH and brine environments. Low pH or the presence of brine promotes the intramolecular associating of hydrophobes for the both copolymers in semidilute solutions. The introduction of ionizable carboxylic group on the long hydrophobic side chain significantly influences the aggregation behaviors of the copolymers, leading to unique solution behaviors of the poly(AAm/NaAAS) copolymers. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40754.

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INTRODUCTION

Water-soluble polymers exhibiting high viscosities at rather low concentrations of dissolved materials find uses in a wide variety of applications in oil recovery, drilling fluids, coatings, pharmaceuticals, cosmetics, and food.^{1–5} Particularly, water-soluble polymers with hydrophobic substituents have been paid much attention because of the ability to produce highly viscous aqueous solutions above a threshold value of polymer concentration, *C**. The viscosity enhancement of the hydrophobically modified water-soluble polymers (HMWSPs) is much higher than that of the unmodified precursor under the same conditions, which could be attributed to the formation of intermolecular aggregations between hydrophobic parts in aqueous solutions.^{6–11}

Presently, there are substantial synthetic efforts with regard to hydrophobically associating copolymers in which hydrophobic monomers of low levels are incorporated.^{12,13} However, the wide-range use of the hydrophobically associating polymers is usually hindered by their poor solubility; sometimes, even phase separation and precipitation happen because of the interplay between the strong association of the hydrophobic groups and

the high water solubility of the hydrophilic parts of the chains. Therefore, some methods are proposed to synthesize polymers with both the high association property and good water compatibility. One method is that electrolytical comonomers, such as sodium 2-sulfoethyl methacrylate, sodium 3-acrylamido-3-methylbutanoate, and sodium acrylate are introduced to copolymerize the hydrophobic monomers.^{14–19} However, the presence of the electrolytical comonomers may weaken the hydrophobic effect of the polymers. The other method is that ionic monomers with long alkyl chain length are used instead of the hydrophobic monomers to synthesize the HMWSPs.^{20–24} A series of copolymers have been obtained based on this kind of monomers and the fluorescence properties and rheological properties of these polymers were studied. In these systems, the molecular structure of the monomers, such as the length of the alkyl chain, the position of the polymerizable groups at molecular backbones significantly influences the aqueous behaviors of the HMWSPs.^{25–29}

Hydrophobically modified polyacrylamides (HMPAMs) are important types of associating polymers. In our previous work,²² we have got HMPAMs with ionic monomer with long

alkyl chain, sodium 11-acrylamidoundecanoic acid (C11AM), a monomer obtained by the Ritter Reaction from acrylonitrile and sodium 10-undecenoic, and the aqueous solution properties of the HMPAMs were studied. The incorporation of C11AM into the copolymers leads to the enhancement of molecular coil size and high viscosity values of the polymer solutions in semidilute regime. In this paper, a new ionic monomer, with a longer alkyl chain and the polymerizable group in the middle of its molecule backbone, sodium 9-(and 10)-acrylamidostearic acid (NaAAS) was synthesized by Ritter reaction from acrylonitrile and oleic acid. A series of HMPAMs based this monomer were obtained by the micellar copolymerization in the presence of SDS which was used to adjust the length of hydrophobic blocks in copolymer backbone.³⁰ We focus on the rheological properties of these copolymers mainly in semidilute aqueous solutions. The impact of the polymer microstructure on the rheological behavior in water is highlighted, and the impact of small electrolytes and pH on the rheological behavior is also studied.

EXPERIMENTAL

Materials

Oleic acid (UA, Alfa Aesar 99%) and acrylonitrile (Shanghai SSS Reagent Co., Ltd.) were used as received. Acrylamide (Beihua Fine Chemicals Co., Ltd.) was twice recrystallized from acetone and vacuum dried at room temperature. Potassium persulphate (Guaranteed Reagent) was used as initiator without further purification. Sodium dodecyl sulfate (SDS) was twice recrystallized from ethanol. Other reagents were used as received.

Synthesis of Sodium 9-(and 10)-Acrylamidostearic Acid (NaAAS)

A two-necked round-bottomed flask fitted with a dropping funnel and a reflux condenser was charged with oleic acid (14.12 g, 0.05 mol), and acrylonitrile (20 mL, 0.22 mol). The mixture was slowly added to 96% sulphuric acid (13.5 mL, 0.25 mol) and the system was immersed into an ice-water bath, so that the temperature of the reaction was kept below 5°C. After the addition, the reaction was continued for additional 12 h at ambient temperature and then 200 mL water was added. The organic phase of the obtained mixture was extracted by chloroform. The chloroform solution was washed by water several times and dried over anhydrous MgSO₄; then, filtrated and distilled. The structure of AAS was confirmed by ¹H NMR. NaAAS was obtained by neutralization of AAS with equimolar NaOH.

Polymer Synthesis

The polymers were prepared by free-radical micellar copolymerization of acrylamide (AAM), AAS in aqueous SDS solutions. The total monomer concentration was set to 3% through out the experiments while the AAS content in the feed was kept at 0.8 mol %. The concentration of KPS was set to 0.1 wt % with respect to the monomer feed. AM, NaAAS and SDS in the desired ratio, and 150 mL water were added into a 250 mL three-necked round-bottomed flask equipped with a mechanical stirrer, a condenser and a nitrogen inlet. Then the reactor was heated up to 50°C in a water bath with continuous stirring under nitrogen for 30 min. The set amount of KPS was added

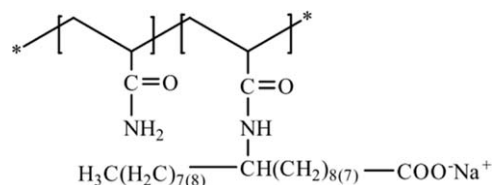


Figure 1. Structural composition of copolymers of acrylamide with sodium 9-(and 10)-acrylamidostearic acid (NaAAS).

with a syringe and the reaction was kept 24 h with nitrogen bubbled at 50°C in this progress.

When the reaction was stopped, gel-like samples were obtained and were precipitated by a large excess of methanol to remove the surfactant, residual initiator, and monomers and then washed by methanol for 1 day at ambient temperature. The polymers recovered by filtration were dried under reduced pressure at ambient temperature for 24 h. Then, the polymers were dissolved in a small amount of water and precipitation, washing, and drying steps were repeated again.

The number of hydrophobic monomers per micelle, N_H , was calculated at the base of the formulation as following:

$$N_H = \frac{[M_H]N_{agg}}{[S] - cmc} \quad (1)$$

where [S] and [M_H] were the molar concentration of the surfactant and the hydrophobic monomer in the feed, respectively, and the aggregation number N_{agg} and cmc for SDS were according to the data reported in the literature ($N_{agg} = 60$ and $cmc = 9.2 \times 10^{-3}$ mol/L at 50°C³⁰). The proportion of hydrophobic monomer in the polymer was set as 0.8 mol % compared with AAM. The polymers coded in this paper take the N_H value (3 and 6) into account. For example, N_3 refers the N_H of the polymer is 3 and N_6 means the N_H of the polymer is 6. The chemical structure of the copolymer is shown in Figure 1.

Molecular Weight Determination

The molecular weights and molecular weight distributions of the polymers were determined with a Gel Permeation Chromatography (GPC) instrument. GPC analysis was performed with a Tosoh HLC-8020 equipped with a Waters 2414 refractive index detector and two Ultrahydrogel (Waters) columns using 0.1 M NaNO₃ aqueous solutions as eluent at a flow rate of 1.0 mL/min. Molecular weights of the copolymers were calibrated with poly(sodium acrylate) standard samples. The elaborate data of the molecular weights were collected in Table I.

¹H NMR Characterization

The product was characterized with ¹H NMR spectroscopy (yield: 87.5%). ¹H NMR (δ : ppm) δ (ppm): 6.1 and 5.6 (—CH=CH₂), 6.4 (—CH=CH₂), 1.27 (—(CH₂)₆₍₅₎—) and (—(CH₂)₆₍₇₎—), 3.98 (—NH—), 0.90 (—CH₃). The content of double bond is about 98%, which was calculated by NMR using the peak areas ratio of the protons of double bond at 6.1–5.6 vs the protons of (—(CH₂)₆₍₅₎—) and (—(CH₂)₆₍₇₎—) at 1.27 and then multiplied by a factor of 6. The NaAAS content was determined by ¹H NMR from the integration of the peaks of the terminal methyl group (≈ 0.8 ppm) of the long alkyl chains and CH group (≈ 2.2 ppm) of the polymer backbone using D₂O as solvent. NMR data

Table I. Reaction Parameters for the Copolymerization of Acrylamide (AM) with Sodium 9-(and 10)-Acrylamidostearic Acid (NaAAS) and Homopolymerization of PAM.

Code	AM (mol %)	[NaAAS] (mol %)	N_H^a	F (mol %) ^b	$10^6 \times M_n^c$	$10^6 \times M_w^c$	M_w/M_n^c	Conv.
N ₃	99.2	0.8	6	0.84	0.29	0.34	1.33	82%
N ₆	99.2	0.8	3	0.83	0.22	0.27	1.33	79%
PAM	100	0	0	0	0.45	0.54	1.17	98%

^aThe number of hydrophobic monomers per micelle.

^bAverage hydrophobes content in the copolymer calculated from ¹H NMR.

^cDetermined by GPC in a 0.1M NaNO₃ solution.

showed that the amount of NaAAS in the copolymer was almost the same as the hydrophobic monomer in the feed.

Rheological Measurements

The polymer solutions for rheological measurements were prepared by the dissolution of polymers in water at room temperature. The polymers were allowed to hydrate and swell for 24 h, and then the solutions were gently stirred magnetically for 1 week. Another 2 or 3 days were needed to remove the air bubbles. All solutions were kept at pH = 7.5 except those prepared for pH responsive experiments.

The viscometry measurements on dilute solutions were performed on a Brookfield DV III⁺ low shear viscometer equipped with different sizes of spindles at temperature of 30°C. Experiments with sufficiently viscous solutions were carried out with a Physica MCR300 controlled stress rheometer equipped with concentric cylinder geometry (CC27 bob radius is 13.33 mm, CC27 cup radius is 14.46 mm, and CC17 bob radius is 8.33 mm). All measurements were implemented with a solvent trap to prevent any evaporation. The temperature was controlled by a TEZ180-C cylinder system (Physica) and was set to 30°C.

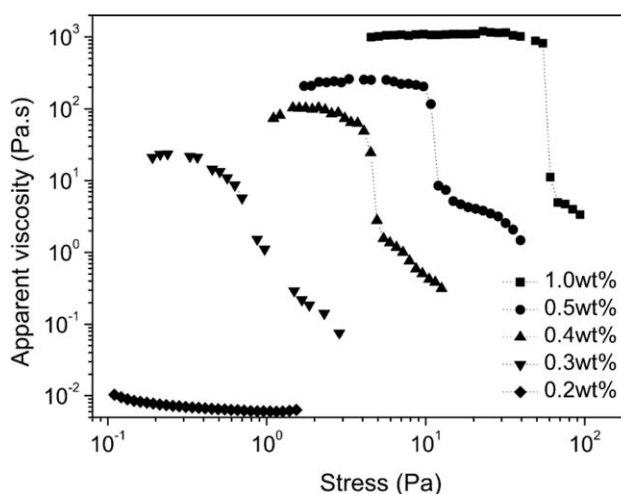
RESULTS AND DISCUSSION

Rheological Behavior in Water

Steady Shear Flow Measurements. The characteristic behavior of associative polymers greatly changes in semidilute regime above the critical concentration (C^*) at which intermolecular associations begin to dominate. Steady shear flow measurements can be used to identify the semidilute regime by observing the steady-state viscosity as a function of the shear stress at different polymer concentrations in aqueous solutions. Figure 2 shows steady-shear viscosities of N₃ copolymers at various concentrations in water as a function of the shear stress. It is apparent that the viscosity increases with an increase of copolymer concentration. Below a polymer concentration of 0.2 wt %, the solution behaves as a Newtonian fluid, which means the associations of copolymer are mainly intramolecular. This is due to the chain contraction resulting from intramolecular associations. However, the flow curves exhibit non-Linear rheology behavior above a concentration of 0.3 wt %. These curves are distinctly separated into two parts, a high viscosity zone at low stress and a low viscosity zone at high stress. Moreover, the discontinuity is observed at intermediary stress. It can be speculated that the copolymer has formed physically cross-linked networks *via* intermolecular associations. The discontinuity observed in the

flow curves at a certain shear stress can be ascribed to the total destruction of the associating network structure. The lifetime of the intermolecular junction can be deduced from the inverse of the shear rate just before the discontinuity.¹⁵ These observations indicate that the gel-like solutions can be easily imposed at high shear stress and can be readily disrupted. In addition, there is a small shear-thickening zone among certain concentration region (0.3 wt %–0.5 wt %) in a narrow concentration range, indicating that there is possibly an increase in the density of the network junctions due to enhanced intermolecular associations.^{15,22}

Figure 3 shows the influence of the polymer microstructure on the rheological properties of the polymers. N₆ and N₃ samples contain the same concentrations of hydrophobic units but they have different microstructures (Table I). For a given concentration, both the viscosity values of the two polymer solutions give values by almost 3 orders of magnitude higher than the viscosity of the unmodified PAM polymer. Furthermore, with a larger incorporated blocks, N₆ sample ($N_H = 6$) exhibits better thickening ability and sustains larger yield stress than the N₃ sample ($N_H = 3$). This result could be ascribed to the intermolecular aggregation which is controlled by adjusting the length of the hydrophobic blocks. The length of hydrophobic blocks influences mainly on the binding energy, which in turn affects the lifetime of hydrophobic associating junctions, consequently the polymer properties are seriously affected.¹⁵

**Figure 2.** Steady shear viscosity of the N₃ samples at various concentrations in water as a function of shear stress in water.

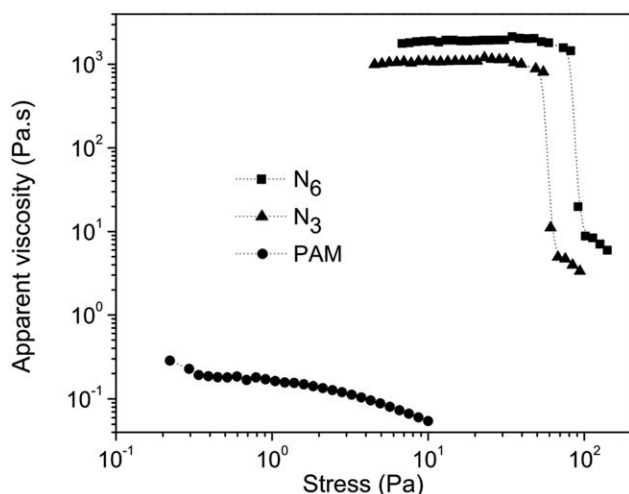


Figure 3. Apparent viscosity as a function of shear stress for copolymers (N_6 and N_3 sample, 1.0 wt %) and for the homopolymer (PAM, 1.0 wt %)

The dependences of the zero-viscosity on polymer concentrations in pure water for homopolyacrylamide and the two copolymers containing different lengths of hydrophobic blocks are plotted in Figure 4. The viscosity increases with increasing polymer concentration for all the polymers, while the transition between dilute and semidilute regime is more significantly for HMPAMs. The abruptly rising of viscosity, nearly 2 orders for copolymer samples, indicates the transition from intramolecular association to intermolecular association. The intramolecular interactions of the associative polymer tend to shrink its hydrodynamic volume in the dilute regime. While above the critical concentration (C^*) a temporary interconnected network of clusters forms by a percolation progress.²² These thermodynamic properties mainly result from the hydrophobic associated interactions drove by entropy. From Figure 4, it can be seen that the C^* of the N_3 sample is 0.25 wt %, and the C^* of the N_6 sample decreased to 0.1 wt %. The different critical concentrations (C^*) of N_3 and N_6 are due to the different intramolecular interac-

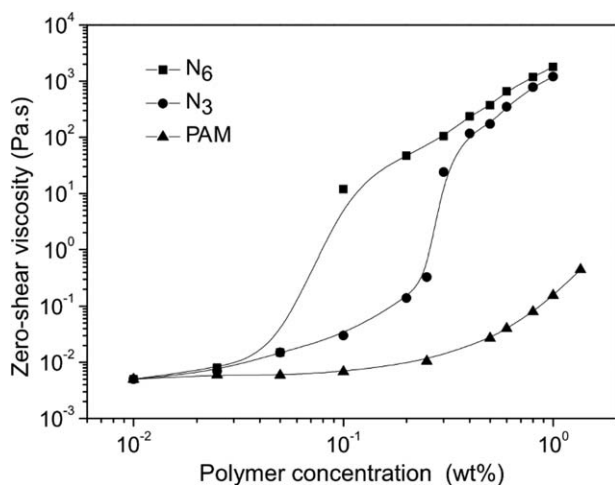


Figure 4. Effect of the concentration on zero-shear viscosity of samples for copolymer (N_6 and N_3 sample) and for the homopolymer (PAM) in water.

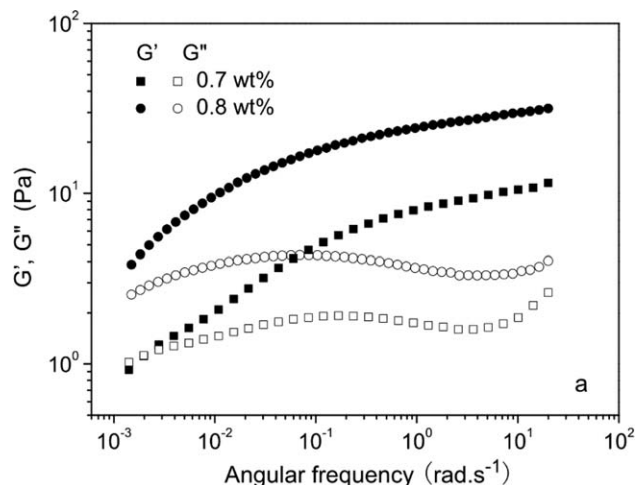


Figure 5. G' and G'' as functions of the frequency for the N_3 sample at concentration of 0.7 wt % and 0.8 wt % in water.

tions for the two samples with different lengths of hydrophobic blocks.

Viscoelastic Behaviors. Dynamic rheology measurements, which were performed within the linear viscoelastic regime, were used to obtain the information of polymeric networks under small oscillatory deformations in the semidilute solutions. The frequency (ω) dependences of G' and G'' measured at a shear stress of 1 Pa with respect to N_3 samples of different concentrations are shown in the Figure 5. For the N_3 sample in the moderate concentrations, the crossover frequency (ω_R), at which $G' = G''$, presents in very low frequency regime. The increase of polymer concentrations enhances both modulus values and ω_R shifts lower. When the concentration reaches up to 0.8 wt %, the behavior in the terminal zone could not be observed because of the experimental setup limitations, indicating that the solution behaves like a highly elastic gel. Moreover, at the same concentration, the moduli of N_6 are higher than those of N_3 sample, and the relaxation spectra of the N_6 polymer doesn't show a terminal zone with a crossover frequency in

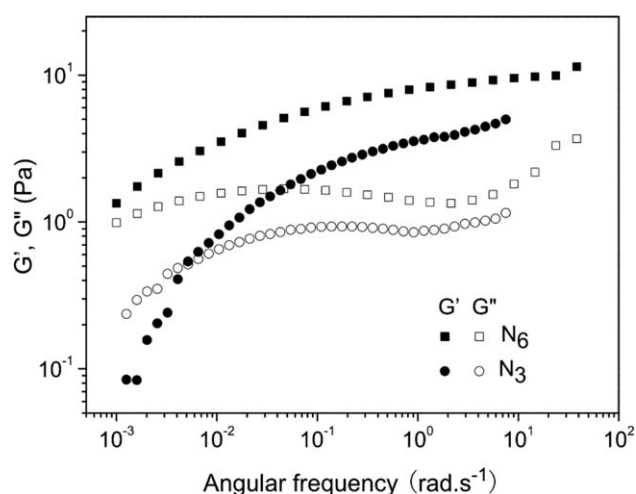


Figure 6. G' and G'' as functions of the frequency for the N_3 and N_6 samples at concentration of 0.5 wt % in water.

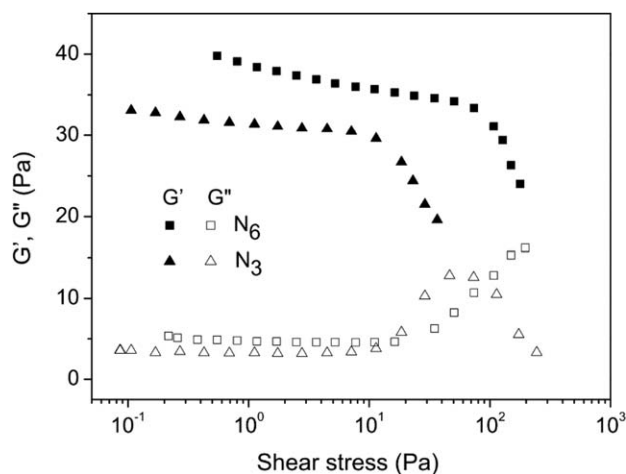


Figure 7. Stress amplitude sweep results of 1.0 wt % solutions of N_6 and N_3 samples at constant angular frequency of 10 rad/s.

the experimentally accessible range, in contrast to the behavior of the N_3 sample (Figure 6). This is because that the sample with longer hydrophobic blocks is a more powerful thickening agent. The viscoelastic properties are strongly influenced by physical cross-link due to hydrophobic association.

The elastic and viscous components of dynamic shear modulus, G' and G'' for unshared state of the two copolymers are plotted against strain in Figure 7 at constant angular frequency of 10 rad / s. For the two copolymers, the storage modulus decreases dramatically with the increasing of the stress in a critical value. According to a simple theory for transient networks or reversible physical bonds in which the network can break and recombine, it can be inferred that G' reflects the number density of mechanically active junctions while G'' reflects the effect volume occupied by the mechanically active polymer network. Thus, the discontinuity of both G' and G'' at high stress, a phenomenon has been reported by other authors, is due to the absolutely destruction of the network junctions at first and then total rupturing of the network.^{20,25}

Association strength that is the relative strength of network junctions of the polymers can be compared by the critical stress from Figure 7. The network structure of N_3 sample is severely ruptured at much lower stress compared with that for N_6 sample, indicating that the strength of its hydrophobic associations is weaker than that of N_6 sample. The fact that the increase in G'' for N_6 sample is larger compared with N_3 sample indicates that the N_6 sample needs more time to relax to the equilibrium state than the N_3 sample, also proving that the strength of hydrophobic associations and the binding strength of hydrophobe in a junction increase with the length of hydrophobic blocks.

A weak gel may have macroscopic properties of fluids (the flow) and rheological properties of gels (the elastic modulus is much greater than the viscous modulus). The mechanical spectra of weak gels are slightly different from those of conventional gels in two respects: the modules are a little frequency dependent, and the magnitude of G' is often 10 times less than that of G'' .^{27,28} Both the N_3 and N_6 samples show the characteristic of

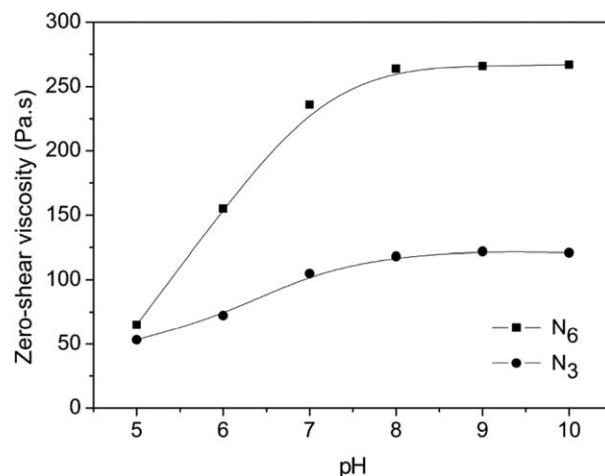


Figure 8. Zero-shear viscosity of N_6 and N_3 samples at different pH at concentration of 0.5 wt %.

physical cross-linked weak gels at a concentration of 1 wt %. To our knowledge, whether the physical cross-linked weak gels for the HMPAMs solutions form or not is determined by several factors about polymer structures. First of all, the polymer chains must be solubilized to some extent in the solvent in respect that the concentration of side chains in solution is the all-important driving force to form intermolecular associations. This requirement poses difficulties for HMPAMs based on AM and alkylacrylamide due to the differences in polarity of the backbones and side chains. Although the polymers with long side chains have a higher driving force for aggregation due to their poor compatibility to water, however, macroscopic phase separation may be observed due to their relatively insolubility in solution when the polymer itself is only marginally soluble. A high level of charge on the polymer backbone will help to overcome this handicap by enlarging its radius gyration in solutions, however, the backbone charge will also resistant to intermolecular hydrophobic aggregation due to electrostatic repulsion, giving rise to a very complex relation between gel properties and various aspects of polymer architecture.¹¹ In this system, a long surfmer was incorporated into PAM macromolecular backbone and the weak gels could be conveniently obtained by control copolymer concentrations and the length of hydrophobic blocks.

The Effect of pH on Rheological Behavior

The presence of carboxylic acid group on the copolymers allows controlling the solution behavior by adjusting pH. To investigate the effect of pH on solution viscosity for poly (AM/NaAAS), the zero-shear viscosities of the N_6 and N_3 samples at a concentration of 0.5 wt % were examined in buffer solution (Figure 8). The zero-shear viscosities of the both polymers increase with increasing pH and then nearly keep constant at high pH values. For the N_3 sample, a slighter increase in viscosities is observed compared with the N_6 sample. At a pH value of 4, both the samples precipitate from aqueous solution, because the phase separation happens. Between higher pH values of 5 and 7, the zero-shear viscosities are small which indicated that the copolymer chains adopt a collapsed conformation and intramolecular associations come into being. Hydrophobic

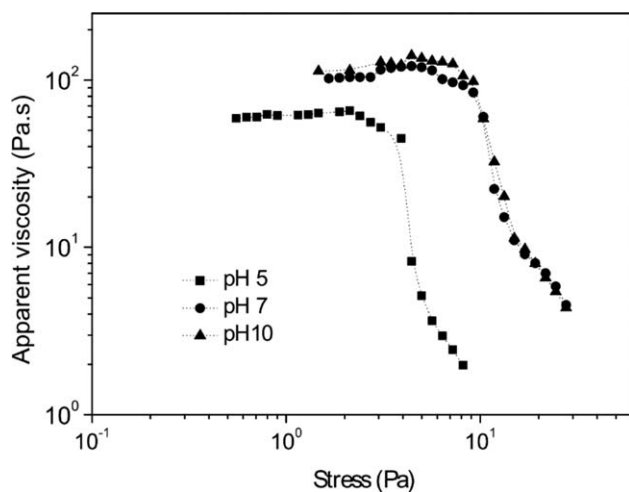


Figure 9. Apparent viscosity as functions of shear stress for the N_3 sample with different pH at concentration of 0.5 wt %.

effects due to uncharged hydrocarbon portions of the ionic and intramolecular hydrogen bonding association between the protonated pendent acid groups account for this behavior. With increasing pH values, the protonated pendent acid groups became ionized, the compact conformations of the polymer chains expand to open conformations, and the intramolecular hydrophobic associations change into the intermolecular associations, thus the zero-shear viscosities of the both samples come to a plateau value.

The influence of the pH on the stability of the physical networks of the N_3 sample was investigated by steady-shear measurements and plotted in Figure 9. The frangible network structures for N_3 samples at low pH also indicate the existence of intramolecular associations when the backbones of the copolymer are taken as a compact conformation.

The Effect of Brine on Rheological Behavior

Shear-flow experiments allow one to localize the semidilute regime as illustrated in Figure 10(a), which gives the variation of the steady-state viscosity as a function of shear rate for a HMPAM at different concentrations in 0.1 M NaCl solution. In

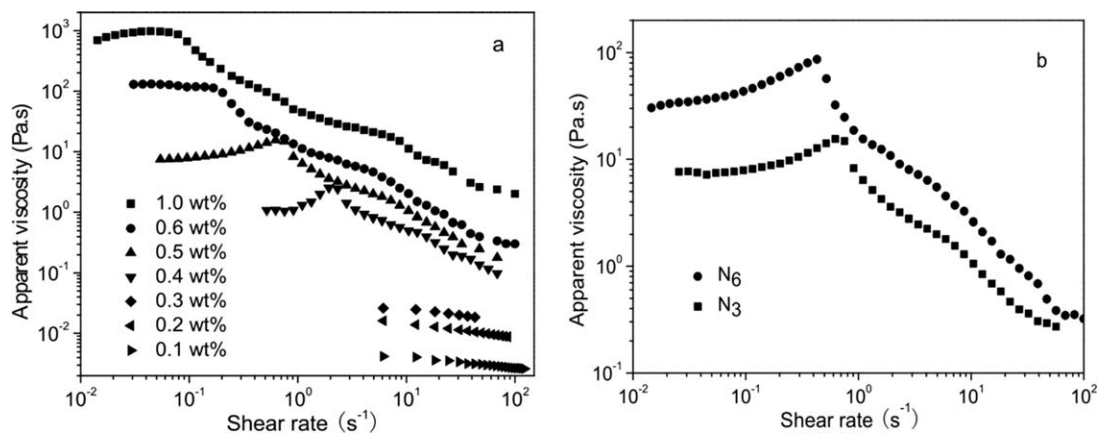


Figure 10. (a) Steady-shear viscosity versus shear rate for N_3 sample at various concentrations in 0.1 M NaCl (b) Steady-shear viscosity versus shear rate for N_3 sample and N_6 samples at concentrations of 0.5 wt % in 0.1 M NaCl.

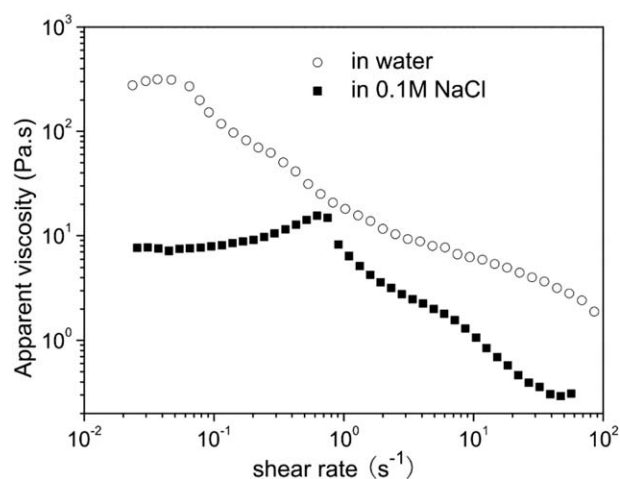


Figure 11. Flow curves for the N_3 sample of different structure at concentration of 0.5 wt % in water and in 0.1 M NaCl solutions.

the dilute regime ($C < 0.3$ wt %), the system is Newtonian, meaning there is no obvious variation of viscosity with shear rate. Slightly above this crossover concentration, one can observe a shear-thinning behavior, as in the previously reported studies,^{11–13} following a weak shear-thickening effect. Moreover, the crossover shear rate, where the viscosity departs from the limiting plateau value, is a decreasing function of the concentration. The N_6 sample exhibits the similar shear behavior as the N_3 sample and the crossover shear rate of the former is much smaller than that of the latter [Figure 10(b)].

At 0.5 wt % concentrations of the N_3 sample from Figure 11, large low-shear viscosities and a highly shear-thinning behavior are observed at lower shear rates in water, a characteristic typical of associative thickeners with a hydrophobe comb-type structure attached along the main backbone.^{25,31,32} To compare the rheology behaviors of the sample in pure water and in brine solutions, steady-shear viscosity versus shear rate for N_3 sample at the same concentrations in brine is also shown in Figure 11. The sample shows a lower viscosity in brine solution and the shear rate curve exhibits higher crossover shear rate than that in water. An explanation of the shear behavior of the system in semidilute regime involves the change between the relative

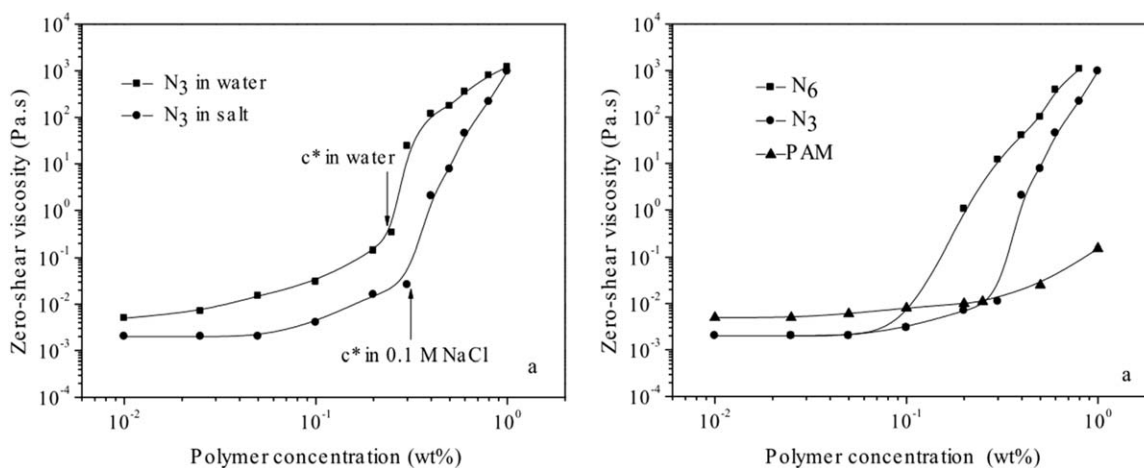


Figure 12. (a) Zero-shear viscosity vs. polymer concentration for N₃ samples in water and 0.1M NaCl solutions and (b) comparisons of zero-shear viscosity of N₃, N₆ and PAM samples in 0.1M NaCl solutions.

amount of intra- and inter-molecular associations with shear. By the addition of brine, a part of transition from inter- to intra-polymer associations happens. Therefore, one can observe a longer shear thickening zone in brine solutions.

A comparison of the variations of the viscosity versus the polymer concentration for N₆ and N₃ sample in water and in 0.1M NaCl solution is shown in Figure 12(a). It is apparent that the addition of NaCl causes a substantial decrease of the zero-shear viscosity, and the critical concentration where onset of the hydrophobically driven association shifts to a higher region. Rheological studies indicate that a partly transition from inter- to intra-polymer associations happens. In the presence of electrolyte, the solubility of polymers is reduced, that is so-called salting out effect, which is generally attributed to the enhanced intramolecular hydrophobic associated interactions. On the other hand, because of a little amount of hydrophobic electrolyte in polymer backbone, the addition of salt leads to shielding of the ionic charges and screening of the electrostatic repulsions, that is so-called shielding effect or screening effect, which also facilitates the formation of the intramolecular associations at the expense of intermolecular junctions. Thus, below the critical entanglement concentration, the presence of salt influences the dynamics of the polymers, resulting in significant reductions of the zero-shear viscosity and rheology behaviors. It is found these behaviors happen even in the dilute region, lead to the lower viscosity of the copolymer than that of PAM [Figure 12(b)], and the viscosities of the two samples are much higher than that of PAM in NaCl semidilute solutions. It is also noted that these behaviors tend to disappear above the critical entanglement concentration, above which the chains would be interpenetrated.

CONCLUSIONS

Hydrophobically modified polyacrylamide copolymers based on an anionic surfimer NaAAS and AM were prepared. The two samples investigated were set with the same molecular composition but with different hydrophobic blocks lengths. The molecular composition of the copolymers was indicated by ¹H NMR

and the molecular weight of the polymers were in a comparable regime based on gel permeation chromatography.

Rheology measurements were used to study the association behaviors of the copolymers in aqueous solutions. Above critical concentration of the two copolymers, pronounced shear viscosity enhancement was observed. The order of magnitude increased in viscosity of the copolymers was attributed to intermolecular associations leading to the formation of transient network. N₆ sample exhibited better thickening ability and sustains larger yield stress than the N₃ sample. Furthermore, the critical concentrations of the copolymers at which the viscosity enhanced shifted to low concentrations with the increase of the length of hydrophobic blocks. The N₆ samples showed as a physical cross-linked gel in semidilute solutions but the N₃ samples exhibited soft gel behaviors by adjusting the polymer concentrations in viscoelastic measurements. Moreover, the associated polymer displayed a terminal viscoelastic behavior as the networks of the gels were completely disrupted by higher applied stress.

The gel behaviors of the two samples could be adjusted by pH of the solutions. At acid pH, the viscosity was lower and the weak gels were brittle for the presence of hydrogen bond between the amide groups and prorogated acrylamidostearic acid caused intra-polymer associations. As NaCl was added into solutions of NaAAS copolymers, the viscosity value decreased and the critical concentrations shifted to higher value for both of the copolymers. Both of the salting out effect and screening effect promoted the transformation of the copolymers from intermolecular associations to intramolecular associations at semidilute solutions. Nevertheless, the viscosity of the two samples was much higher than that of PAM in NaCl semidilute solutions.

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