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Synthesis and properties of hydrophobically modified acrylamide-based polysulfobetaines

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Abstract Acrylamide-based, hydrophobically modified polysulfobetaines containing 3-[*N*-(2-methacroyloylethyl)-*N*,*N*-dimethylammonio]-propane sulfonate (DMAPS) and varying amounts of the hydrophobic monomer stearyl methylacrylate (SMA) were synthesized by micellar copolymerization. The basic physico-chemical properties of the synthesized copolymers were studied by means of surface tension, dynamic laser light scattering, and rheological measurements. All the copolymers showed surface activity when the copolymer concentration was above 0.07 wt%. The dynamic laser light scattering measurement revealed that both zwitterionic and hydrophobic associations were important in copolymer aggregation. The rheological properties of the copolymers in aqueous solution depended on the content of hydrophobic monomer, the copolymer concentration and the addition of salt, which were characteristic of hydrophobically modified polyacrylamide and acrylamide-based polyzwitterions. The critical aggregation concentration of the copolymers was in the range of 0.07–0.1 wt%.

Keywords Water-soluble polymer · Polysulfobetaines · Hydrophobic association

Introduction

In the recent years, an increasing number of studies have focused on the hydrophobic association of water-soluble polymers which contain a relatively small

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number of hydrophobic groups attached along the polymer backbone [1, 2]. The preparation of such materials in a homogeneous solution affords amphiphilic polymers with random distribution of the hydrophobes as isolated units. However, the copolymerization of a water-soluble monomer with a few mole percent of a hydrophobic comonomer in a micellar system [2] results in a statistical distribution of the hydrophobic monomer as small blocks in the hydrophilic polymer chain. The microblocky distribution of the hydrophobes imparts unique rheological and interfacial properties to those associating polymers [3–6]. In aqueous solutions, the hydrophobic groups have a strong tendency to associate through intra- and intermolecular associations to decrease their direct contact with water. In dilute solutions, intramolecular associations are predominant, which lead to coil contraction and viscosity decrease of the solution. At high concentrations (above a certain polymer concentration called critical aggregation concentration CAC), intermolecular associations occur, which lead to an intermolecular physical network structure that causes a viscosity increase [2, 7]. The reversible character of these physical cross-links imparts desirable rheological properties in solution such as shear thinning. The interesting behavior of these associating polymers, such as shear thinning or thixotropy, as a function of shear rate and shear time makes it possible to avoid the irreversible mechanical degradation which occurs for high molecular weight polymers when subjected to high shear stresses [8–11]. The ability to control viscosity at various shear rates render these systems useful in a number of applications including enhanced oil recovery, drilling fluids, coating or cosmetics [2, 7].

In contrast with neutral associating copolymers, hydrophobically associative polyzwitterions (PZs) have unique structures and properties because of the presence of hydrophobic groups and hydrophilic, strongly interacting zwitterionic groups [12–16]. For these polymers, they may be categorized as hydrophobically modified polyampholytes (anionic and cationic charges on separate repeat units) [17, 18] or hydrophobically modified polybetaines (anionic and cationic charges on the same repeat unit) [15, 19–27]. While the electrostatic attractions between the cationic moieties (typically ammonium groups) and the anionic groups (typically sulfonate, carboxylate and phosphonate groups) within a polymer chain leads to coil contraction in water, the interchain electrostatic attractions increase the degree of intermolecular aggregation of the hydrophobic side chains, keeping the hydrodynamic radius large. In presence of added salt (e.g., NaCl), screening of the charges leads to chain expansion and at the same time promotes hydrophobic intermolecular association. Hydrophobically associative PZs may be effective viscosity enhancers in high salinity media, as they combine the properties of hydrophobically modified neutral polymers and PZs [15–17, 28]. The viscosity of hydrophobically modified PZs increases much faster than that for the unmodified polymers because of intermolecular association of hydrophobic parts. This would make them useful in applications where thickeners are required in brine solution, and oil recovery processes. On the basis of the exploitation of these unique properties, practical interest in hydrophobically modified PZs thus stems from their potential use in variety of commercial applications, such as sewage treatment, flocculation, and oil recovery processes.

The synthesis and aqueous solution properties of hydrophobically modified PZs have been studied by several scholars. Liaw et al. [19] studied intramolecular hydrophobic aggregation of amphiphilic polysulfobetaines with various hydrophobic groups in aqueous solution. The reduced viscosity of the copolymers revealed that both zwitterionic and hydrophobic associations were important in polymer aggregation. Umar et al. [24, 29] investigated the effects of zwitterionic charge densities in polymer chains on the viscosity behavior of pH-responsive hydrophobically modified PZs. In one study [24], sulfur dioxide, zwitterionic monomer 3-(*N*,*N*-diallylammonio) propanesulfonate, and a hydrophobic monomer *N*,*N*-diallyl-*N*-octadecylammonium chloride were cycloterpolymerized in dimethyl sulfoxide to afford hydrophobically modified PZs, which were then converted into the corresponding anionic polyelectrolyte by treatment with 1 equiv sodium hydroxide. Subsequent rheological studies revealed that the solution viscosities of the copolymers were highly dependent on the ratio for the zwitterionic and anionic fractions in the polymer chains and on the amount of hydrophobic monomers. The polymer solutions exhibited sharp increase in viscosity with increasing polymer concentrations in salt-free as well as salt-added solutions. Note et al. [27] synthesized a new hydrophobically modified polyampholyte, namely poly-(*N*,*N*-dially-*N*,*N*-dimethyl-ammoniumalt-*N*-octyl-maleamic carboxylate), by alternating free radical copolymerization. The influence of the added polymer on the range of the inverse micellar region (L2 phase) of a SDS-based system was investigated. The polyampholyte proved to be an efficient reducing and stabilizing agent for the formation of gold colloids.

In this article, a micellar synthesis of hydrophobically associating polysulfobetaines composed of acrylamide (AM), 3-[*N*-(2-methacroyloylethyl)-*N*,*N*-dimethylammonio]-propane sulfonate (DMAPS) and stearyl methylacrylate (SMA) is described and their properties in aqueous solution are presented. A combination of static laser light scattering (SLS), ^{1}H-NMR spectroscopy, surface tension, dynamic laser light scattering, and rheological measurements were used to study the solution properties of the synthesized copolymers with various hydrophobe contents. The salt-responsive solution behavior of the synthesized copolymers is interpreted in terms of copolymer composition and microstructure. In our future research, the effects of different surfactants on the properties of these copolymers will be investigated for potential industry applications.

Experimental

Materials

Acrylamide (AM, Tianjin Chemical Reagent Co.) was recrystallized twice from acetone and vacuum dried at room temperature. Potassium persulphate (KPS, Beijing Chemical Reagent Co.) was recrystallized twice from deionized water. Sodium dodecyl sulfate (SDS, Shanghai Chemical Reagent Co.), Stearyl methylacrylate (SMA, Zibo Chemical Reagent Co.), 1,3-cyclopropanesultone (CPS, Zibo Chemical Reagent Co.), and *N*,*N*-dimethylaminoethyl methacrylate (DMA, Zibo

Chemical Reagent Co.) were used as received. 3-[*N*-(2-methacroyloylethyl)-*N*,*N*-dimethylammonio]-propane sulfonate (DMAPS) was prepared by the ring opening reaction of CPS with DMA as described previously [30]. DMAPS was obtained in 95% yield. ^{1}H-NMR of DMAPS (400 MHz, D_2O, ppm): δ1.86 (3H, s, $\underline{CH_3}$–C=); δ3.5 (2H, t, –$\underline{CH_2}CH_2CH_2SO_3^-$); δ2.2 (2H, m, –$CH_2\underline{CH_2}CH_2SO_3^-$); δ2.9 (2H, t, –$CH_2CH_2\underline{CH_2}SO_3^-$); δ3.7 (2H, t, O–$\underline{CH_2}CH_2$–); δ4.6 (2H, t, O–$CH_2\underline{CH_2}$–); δ3.14, (6H, s, $\underline{CH_3}N^+\underline{CH_3}$); δ5.67,6.08, (2H, d, d, $\underline{CH_2}$=).

Polymerization

The hydrophobically modified polysulfobetaines were obtained by micellar copolymerization in deionized water following the procedure described by Johnson et al. [15]. A 250 mL, three-neck round-bottomed flask equipped with mechanical stirrer and N_2 inlet/outlet was used for the synthesis. AM was dissolved in 100 mL of water and purged with nitrogen for 30 min at 25 °C. SMA (see Table 1) and SDS were added, stirred and purged with nitrogen for another 30 min. Then the initiator KPS was added. The reaction was allowed to proceed under continuous stirring for 6 h at 50 °C. Briefly, in all cases the initial concentration of total monomer was 1.0 mol.L^{-1}, and the concentrations of DMAPS and SDS were kept constant at 5.0 mol% and 0.1 mol.L^{-1}, respectively. The amount of SMA was 0.3, 0.5, or 1.2 mol%, and the initiator concentration was set to 0.4 mol% relative to monomer feed. For these copolymerization reactions, the copolymer solutions were precipitated twice into an excess of ethanol. The copolymer was recovered after filtration and dried several days under vacuum. Then, the copolymers were re-dissolved in water, purified by dialysis against water using MD55-14 dialysis tubing (molecular weight cutoff = 14000 g.mol^{-1}) for 1 week and freeze dried. As a reference, copolymer lacking DMAPS monomer was synthesized and purified under identical conditions.

Table 1 Characteristics of the samples

Sample	DMAPS[a] (mol%)	SMA[a] (mol%)	Elemental analysis						N_H^c	Conversion (wt%)
			C (wt%)	H (wt%)	N (wt%)	S (wt%)	DMAPS[b] (mol%)	SMA[b] (mol%)		
ADS-1	5	0.3	46.12	6.648	15.48	1.863	5.25	0.25	1.69	93
ADS-2	5	0.5	46.51	6.746	15.45	1.851	5.22	0.42	2.83	90
ADS-3	5	1.2	48.63	6.912	15.43	1.884	5.28	1.12	7.56	89
AS	0	0.5	41.75	7.519	15.58	/	/	0.57	3.85	92

[a] mol% monomer present in the feed ratio

[b] mol% monomer content in the copolymers, measured by elemental analysis

[c] The number of SMA per micelle, calculated according to according to the SMA content determined by elemental analysis

The hydrophobically modified terpolymers were designated as ADS, where A stands for AM, D stands for DMAPS, and S stands for SMA, so that AS is referred to the copolymer composed of AM and SMA.

Characterization

All ^{1}H-NMR experiments were performed on a Bruker AVANCE400 NMR spectrometer. D_2O was used for field-frequency lock, and the observed ^{1}H chemical shifts were reported in parts per million (ppm) relative to an internal standard.

Elemental analyses were performed on an Elementar Vario E1 III analyzer (German).

SLS measurements were performed on a DAWN HELEOS light scattering instrument (Wyatt Technology). The system light source was a linearly polarized gallium arsenide (GaAs) laser (658 nm). The laser is positioned so that the incident beam was vertically polarized. Zimm plots were obtained using Astra software. The copolymers were examined in 0.15 mol.L^{-1} NaCl solution and filtered with a 0.2-μm filter (Millipore). A differential refractive index detector (Optilab-REX) was used to measure the differential refractive indices (dn/dc) of different copolymer solutions at 658 nm and 25 °C.

Surface tension measurements were performed on a Kruss K12 Processor Tensiometer equipped with a Wilhelmy plate at 25 °C.

Dynamic light scattering (DLS) measurements were performed on a multiangle laser photometer equipped with a linearly polarized gallium arsenide (GaAs) laser ($\lambda = 658$ nm; Wyatt Technology Co. DAWN HELEOS), which were conducted at a scattering angle of 99°. In DLS, the Laplace inversion of each precisely measured intensity–intensity–time correlation function $G^{(2)}(t, q)$in the self-beating mode could result in a line width distribution $G(\tau)$ [31, 32]. For a pure diffusive relaxation, $G(\tau)$ can be converted to a translational diffusion coefficient distribution $f(R_h)$ by the Stoke–Einstein equation. In this study, the CONTIN Laplace inversion algorithm in the correlator was used [33]. All the solutions were filtered through Millipore 0.8-μm membranes before the DLS measurements.

Rheological measurements were performed on a HAAKE Rheostress 6000 shear rheometer at 25 °C.

For all measurements, concentrated stock copolymer solutions were prepared by dissolution of an appropriated amount of copolymer powder in deionized water whose electric conductivity was 18.3 MΩ cm or NaCl solutions. The powder was prehydrated overnight; this was followed by gentle magnetic stirring for several days depending on samples and sample concentrations. The solutions were then allowed to stand for some time until any bubbles disappeared. Final desired concentrations of copolymer solutions were obtained by diluting the stock solution with corresponding solvents. Solutions of increasing salt (NaCl) concentration were obtained by addition of concentrated salt solution aliquots to a pure aqueous copolymer stock solution. While adjusting the salt concentration, the copolymer concentration was kept constant by adding an appropriate amount of concentrated copolymer solution. All the solutions were kept standing overnight for equilibrium prior to measurements.

Results and discussion

Synthesis and characterization

Hydrophobically modified polysulfobetaines were synthesized by micellar copolymerization using the feed ratios outlined in Table 1 (see Fig. 1). The terpolymers contain sulfobetaine (DMAPS) at 5 mol% incorporation, and the content of the hydrophobic monomer (SMA) was in the range of 0.3–1.2 mol%. Sulfobetaine DMAPS was used as zwitterionic monomer because the persistent charged state of the sulfonate and quaternary ammonium groups allows sulfobetaine-functionalized copolymers to maintain a constant near net-zero charge irrespective of the pH of the medium. To enable comparative studies that distinguish the effects of sulfobetaine comonomer incorporation, control copolymer AS (refer to Table 1 for target compositions) was synthesized. It is known that, the micellar copolymerization should favor the incorporation of the hydrophobic monomer as blocks along the hydrophilic backbone, and the longer the hydrophobic blocks, the greater the thickening efficiency at constant hydrophobe level [34]. The length of the hydrophobic blocks corresponds roughly to the number of hydrophobic monomers contained within a micelle. The key-parameter N_H is calculated from the following relationship:

$$N_H = \left(\left[\mathrm{SMA} \times N_{agg}\right]\right) / \left([\mathrm{SDS}] - \mathrm{cmc}\right)$$

in which N_H is the average number of hydrophobic monomer per micelle, [SMA] is the concentration of SMA (in mol.L^{-1}), N_{agg} is the aggregation number of SDS, and cmc is the critical micelle concentration of SDS. For this system, the N_{agg} of SDS is about 62 and the cmc of SDS is 8.1×10^{-3}mol.L^{-1} [15]. The N_H of SMA monomer of the samples was calculated according to the SMA content determined by elemental analysis and the results were shown in Table 1.

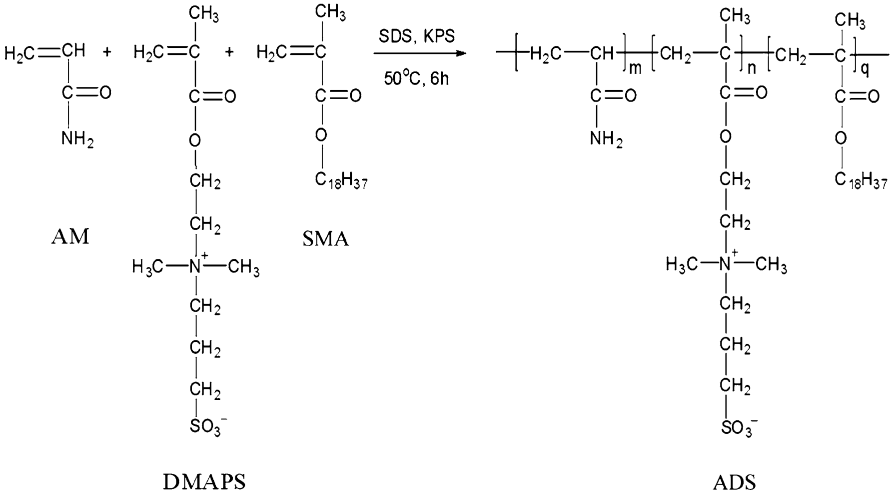


Fig. 1 Synthesis of hydrophobically modified polysulfobetaines

^{1}H-NMR spectrum of ADS sample was shown in Fig. 2. It shows characteristic peaks due to the protons of DMAPS and SMA monomers, indicating the linking of DMAPS and SMA monomers to the polymer backbone. However, it does not give quantitative information on the level of SMA incorporation due to the weak signal strength of the protons of hydrophobic units in the spectrum. The composition of the samples were determined by elemental analysis and shown in Table 1. As evident from Table 1, the hydrophobe incorporations do not match with the feed ratio; the mole percent hydrophobe incorporated in ADS copolymers were always found to be less than the mole percent in the feed.

Static laser light scattering

In SLS measurement, we were able to obtain weight–average mole mass M_{w}, the second-order virial coefficient A_2, and the mean square radius $\langle {r_g}^2 \rangle$ of polymer chains from the angular dependence of the excess absolute scattering intensity, known as the Rayleigh ratio $R(\theta)$, on the basis of

$$\frac{K^*C}{R(\theta)} = \frac{1}{M_{\mathrm{w}}}\left(1 + \frac{1}{3}\left\langle r_g^2 \right\rangle q^2\right) + 2A_2C \tag{1}$$

where $K^* = 4\pi(\mathrm{d}n/\mathrm{d}c)^2\, n_0/(N_A\lambda_0^4)$, and $q = (4\pi n_0/\lambda_0)\sin(\theta/2)$, with n_0, $\mathrm{d}n/\mathrm{d}c$, λ_0, and θ being the solvent refractive index, the specific refractive index increment, the wavelength of the incident light in vacuum and the scattering angle, respectively [35].

The molecular weight determination of the copolymers was performed in 0.15 mol.L^{-1} NaCl aqueous solution. This determination was complicated due to the complex nature of the copolymers. They contain three monomer units along the backbone, one of which is charged, and one is strongly hydrophobic. As a result, we

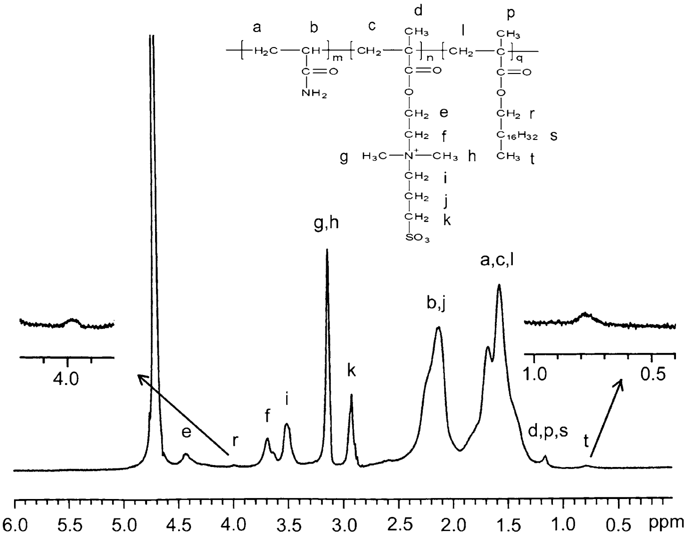


Fig. 2 The ^{1}H NMR spectrum of ADS copolymer

can expect that the light scattering measurements lead to an apparent molecular weight, $M_{\mathrm{w,app}}$, rather than the true average molecular weight, M_{w}. For ADS and AS samples in 0.15 mol.L^{-1} NaCl aqueous solutions, the values of dn/dc are 0.1585 and 0.1620, respectively. Figure 3 shows a typical static Zimm plot of ADS-2 in 0.15 mol.L^{-1} NaCl aqueous solution, where C ranges from 1.83×10^{-5} to 8.82×10^{-5} g.mL^{-1}. Using the projection $\theta = 0$ and $C = 0$, the values of $M_{\mathrm{w,app}}$, $\langle r_g^2 \rangle$, and A_2 calculated on the basis of Eq. 1, which are listed in Table 2. The molecular weights of ADS and AS samples are similar, ranging from 2.379×10^6 to 2.885×10^6 g.mol^{-1}, so a meaningful comparison of their rheological behavior can be made. It is difficult to draw a general trend about the evolution of the second virial coefficient A_2 as a function of the SMA content. However, one can note that A_2 is always negative, indicating that 0.15 mol.L^{-1} NaCl aqueous solution is not a good solvent for both ADS and AS samples. The trend in $\langle r_g^2 \rangle$ was paralleled by $M_{\mathrm{w,app}}$, which could be affected by the content of SMA in ADS samples. Also as expected, one observes that $\langle r_g^2 \rangle$ increases with the increasing the content of SMA, which was caused by the enhancement of the hydrophobic aggregation.

Surface tension measurements

Figure 4 showed the relationship between surface tension and concentration of ADS and AS samples at 25 °C. All samples were surface-active above a threshold concentration (above 0.07 wt%). Differences among the surface activity of the various samples were minimal. The surface tensions of the aqueous solutions of ADS samples were higher than that of AS sample, indicating that the incorporation of the zwitterionic group into the copolymer decreased the surface activity of the corresponding hydrophobically modified copolymers. Among the ADS samples, ADS-3 was the most effective in reducing the surface tension of the water. The surface tension tended to decrease with increasing copolymer concentration, without reaching a plateau value, which may be taken as an indication that the aggregates of the ADS samples formed in water are polydisperse and that aggregation and adsorption at the air–water interface take place simultaneous [36]. For solutions of

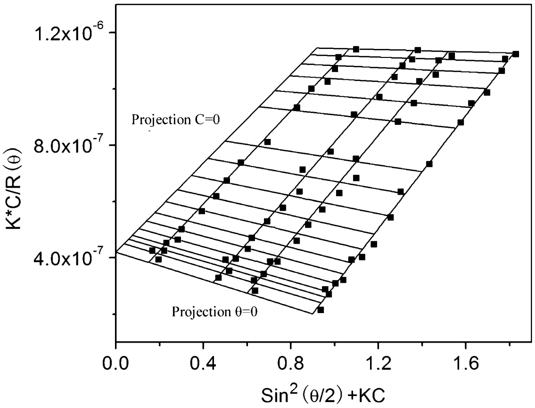


Fig. 3 Typical Zimm plot for the copolymer ADS-1 in 0.15 mol.L^{-1} NaCl aqueous solution

Table 2 Static laser light scattering data for the samples

Sample	$M^{a}_{w,app}$ (10^{-6} g.mol^{-1})	$\langle r_g^2 \rangle$ (nm)	A_2 (10^4 mol mL.g^{-2})
ADS-1	2.379 ± 0.164	91.6 ± 9.2	−9.783 ± 1.396
ADS-2	2.819 ± 0.208	93.4 ± 6.9	−3.588 ± 0.177
ADS-3	2.875 ± 0.241	113.9 ± 9.4	−9.898 ± 1.324
AS	2.885 ± 0.234	158.4 ± 11.3	−2.288 ± 0.535

[a] Apparent molecular weight measured by light scattering

ADS and AS samples, the concentration corresponding to the onset of decrease in surface tension corresponds closely to the onset of association concentration determined by rheological measurements.

Dynamic laser light scattering

The aggregation behavior of ADS samples of different compositions in the dilute regime was studied by dynamic laser light scattering (DLS) measurement. Figure 5 shows the copolymer concentration dependence of average R_h of four different copolymer samples in aqueous solution. It is seen that the R_h of ADS samples decreases rapidly when the copolymer concentration is below 0.08 mg.mL^{-1}, and then keeps almost constant when the copolymer concentration is above 0.08 mg.mL^{-1}; while the R_h of AS sample decreases initially with increasing copolymer concentration up to 0.06 mg.mL^{-1}, and then increase monotonically with further increasing copolymer concentration. The R_h values of ADS samples are smaller than that of AS sample in the concentration range studied. These phenomena can be explained by considering the hydrophobic interactions of copolymer hydrophobic moieties and the electrostatic interactions between the opposite charges of the sulfobetaine units. On one hand, hydrophobic interactions of copolymer hydrophobic moieties are mainly intramolecular hydrophobic association at low

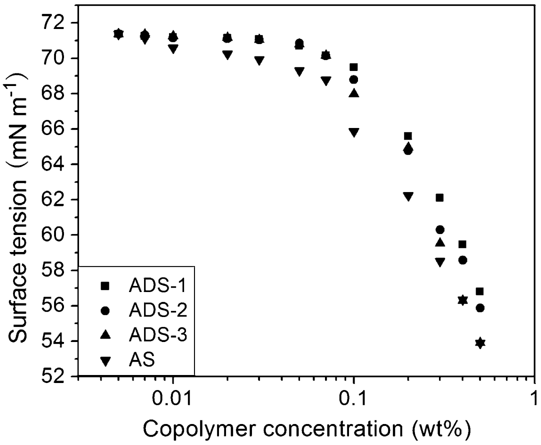


Fig. 4 Changes in the surface tension of copolymer solutions as a function of copolymer concentration at 25 °C

concentrations, which lead to coil contraction and the decrease of the R_h. While at high concentrations, intermolecular hydrophobic association occurs, which lead to the increase of the R_h. On the other hand, while the electrostatic attractions between the cationic moieties (typically ammonium groups) and the anionic groups (typically sulfonate groups) within a polymer chain leads to intramolecular association, causing the shrinkage of the copolymer chain and increasing the degree of intramolecular aggregation of the hydrophobic side chains, leading to the decrease of the R_h, the interchain electrostatic attractions increase the degree of intermolecular aggregation of the hydrophobic side chains, keeping the hydrodynamic radius large. Our experiment results show that the intramolecular association is dominative when the copolymer concentration is low (below 0.06 mg.mL^{-1}), leading to the chain shrinkage and the decrease of the R_h of all the copolymer samples. When the copolymer concentration is above 0.06 mg.mL^{-1}, the increase of the R_h of AS sample is due to the intermolecular hydrophobic associations of the long-chain hydrophobe with 18 carbon segments [37]. While for ADS samples, the intrachain electrostatic attractions between the opposite charges of sulfobetaine units are dominative and suppress the intermolecular hydrophobic associations of the long C_{18} hydrophobe, which lead to little change of the R_h with increasing the copolymer concentration. Also, Fig. 5 reveals that the intramolecular hydrophobic association is directly related to the N_H value, i.e., the hydrophobic block length of the copolymers. At the same copolymer concentration, the larger the N_H value is, the smaller the average R_h is. This is because that the intramolecular hydrophobic association dominates due to the intrachain electrostatic attractions between the opposite charges of sulfobetaine units, which is enhanced by increasing the length of the hydrophobic block length [38].

Figure 6 shows the copolymer concentration dependence of R_h for four different copolymer samples in 0.05 mol.L^{-1} NaCl solutions. As shown in Fig. 6, at low polymer concentration, the R_h values of all the samples decrease slightly with the increase of polymer concentration. Whereas, at higher copolymer concentration (above 0.08 mg.mL^{-1}), the R_h values of all the samples increase sharply as copolymer concentration increases. The decrease of R_h is attributed to the shrinkage

Fig. 5 Variation of the average hydrodynamic radius with copolymer concentration in deionized water at 25 °C

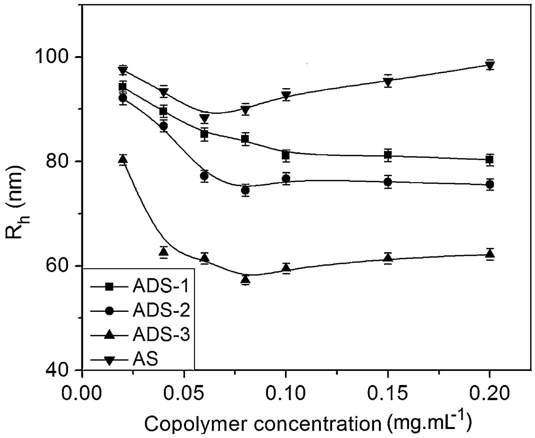
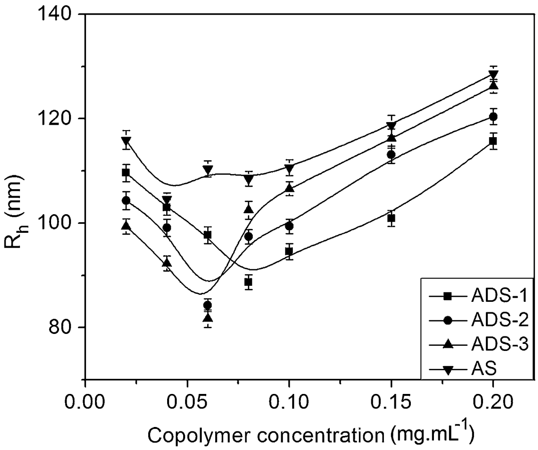


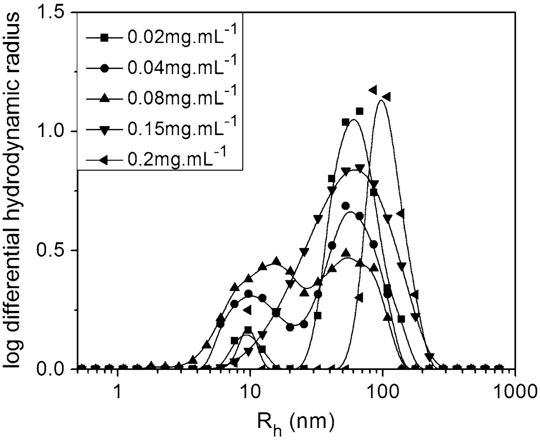
Fig. 6 Variation of the average hydrodynamic radius with copolymer concentration in 0.05 mol.L^{-1} NaCl solution at 25 °C



of copolymer chains due to intramolecular association. R_h increases sharply at high copolymer concentration, revealing the intermolecular association is dominant with the increase of copolymer concentration.

The distribution of the hydrodynamic radius of ADS-1 in 0.05 mol.L^{-1} NaCl solution obtained by DLS is shown in Fig. 7. A bimodal distribution of the average R_h is observed when the copolymer concentration is 0.02 mg mL^{-1}. The peak with lower R_h could represent individual copolymer chains, whereas that with a higher R_h value could be attributed to their interchain aggregates [37]. It can be seen that when the copolymer concentration increases from 0.02 to 0.08 mg.mL^{-1}, the individual chain peaks shift to lower R_h and their scattering intensity increases, indicating the enhancement of the intramolecular associations. When the copolymer concentration is above 0.08 mg.mL^{-1}, the aggregation peak shift toward the higher R_h direction, and the scattering intensity of interchain aggregates increases with further increase of the copolymer concentration, reflecting the enhancement of interchain aggregates.

Fig. 7 The hydrodynamic radius distribution of ADS-1 in 0.05 mol.L^{-1} NaCl solution at different copolymer concentration



From Figs. 6 and 7, we know that the aggregation between copolymer chains could be dominated by either the intrachain or the interchain aggregation. The hydrophobic and electrostatic interactions can induce both the intrachain and the interchain associations [19, 39, 40]. At low copolymer concentration, the mutual dipolar–dipolar intrachain interactions between the positive and negative charges cause bending of the polymeric main chains and promote the intramolecular hydrophobic association, leading to the decrease of the average R_h. While in the case of a high copolymer concentration, the intermolecular electrostatic and hydrophobic interactions become dominant and apparent. The intermolecular interactions result in the intermolecular aggregation of the copolymer chains. With the increase of the copolymer concentration, these aggregations further collide with each other or with individual copolymer chain, leading to even larger aggregations.

The effects of added sodium chloride on the average hydrodynamic radius of all the copolymer samples are shown in Fig. 8. The R_h of all the copolymer samples increases as a consequence of increased intermolecular association with the increase of the concentration of NaCl, which correlates well with the known effects of NaCl on the hydrophobic and zwitterionic associations [37, 41, 42]. Further more, the R_h of ADS samples is larger than that of AS sample in the NaCl concentration range, and increases with the increase of the N_H value of ADS samples. These results indicate that the incorporation of the zwitterionic groups promotes hydrophobic intermolecular association in the presence of added salt, and the hydrophobic intermolecular association is enhanced by increasing the length of the hydrophobic block length [43].

Rheological measurements

The rheological behavior of ADS samples of different compositions in the moderately semi-dilute were evaluated at 25 °C. Figure 9a, b, and c displayed the variation of viscosity with concentration of ADS-1, ADS-2, and ADS-3, respectively, in deionized water at various shear rates. As evident from Fig. 9a, the critical

Fig. 8 Variation of the average hydrodynamic radius with salt concentration at 25 °C ($C_{copolymer} = 0.2$ mg.mL^{-1})

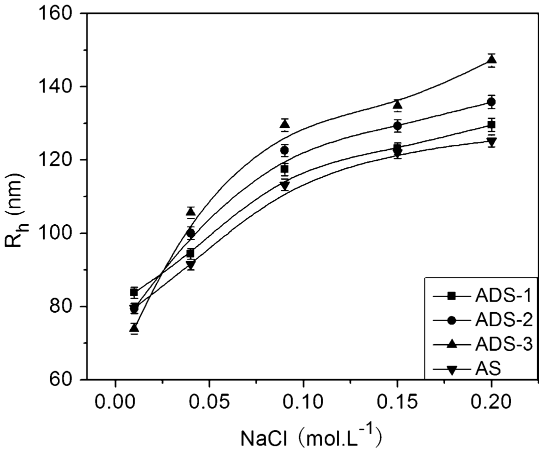
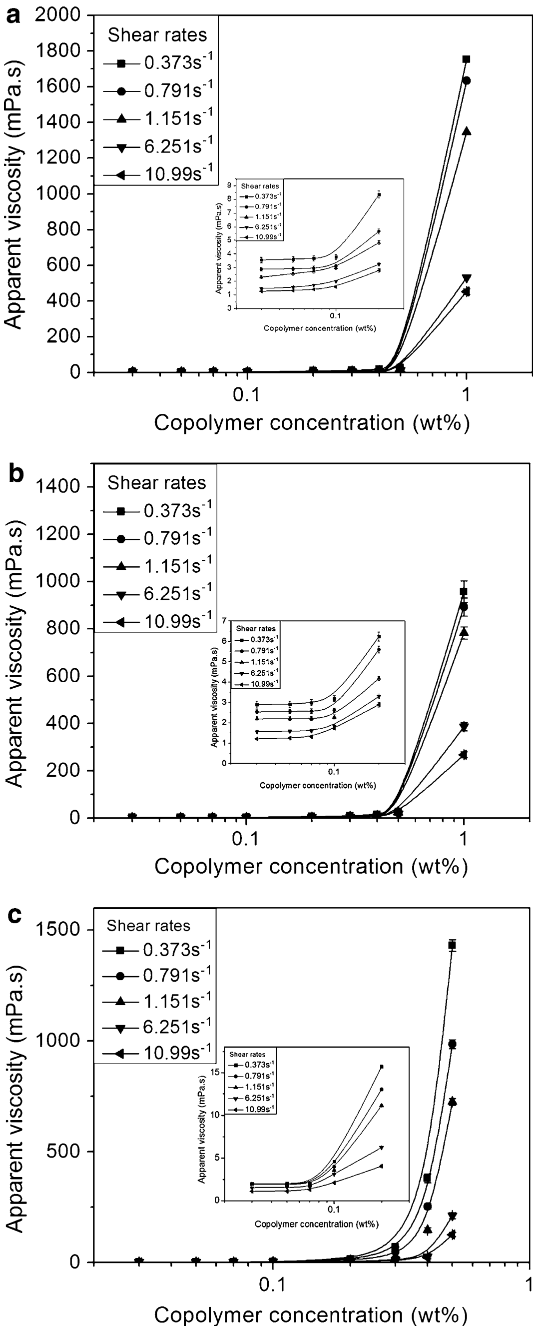


Fig. 9 Variation of viscosity with copolymer concentration at various shear rates in deionized water at 25 °C (*inset* showing the variation in the lower concentration range): **a** ADS-1, **b** ADS-2, **c** ADS-3



association concentration (CAC) was found to be around a copolymer concentration of 0.1 wt%; when the copolymer concentration changed from 0.1 to 0.2 wt%, the viscosity increased by a factor of 2.21 at the shear rate of 0.373 s^{-1}. It is more pronounced for the association behavior of the copolymers in the lower shear rate range as expected since higher shear rates lead to disruption of hydrophobic associations. Similar observations have been frequently observed for hydrophobically modified associative polymers [44, 45]. When the copolymer concentration passes CAC, intermolecular associations occur, which lead to an intermolecular physical network structure that contributes significantly to the thickening. The CAC for ADS-2 was also found to be around a copolymer concentration of 0.1 wt% (Fig. 9b). The viscosity increased by a factor of 1.97 at a shear rate of 0.373 s^{-1} by changing the copolymer concentration from 0.1 to 0.2 wt%, which was a little smaller than that of ADS-1, and may be attributed to the gradual switchover from a mainly intra- to intermolecular associations [46]. For ADS-3, a relatively low CAC value of around 0.07 wt% was found (Fig. 9c), due to the increase of the hydrophobic block size [47].

Figure 10 displayed the variation of viscosity with concentration of ADS and AS samples in deionized water at the shear rate of 10.99 s^{-1} at 25 °C. A meaningful comparison may be made between ADS and AS samples because they did not present significant differences in molar mass among them. For ADS samples, when the copolymer concentration was blow 0.1 wt%, the viscosity was low (about 1.3 mPa.s) and did not change with increasing the copolymer concentration. Furthermore, the viscosity decreased with increasing N_H values of ADS samples, i.e., ADS-3 solution was less viscous than the other two ADS samples. However, when the copolymer concentration was above 0.1 wt%, a dramatic increase in solution viscosities of ADS samples was observed which was contributed to the strong interchain associations. As the N_H values of ADS samples increased, the solution viscosities obviously increased, and the concentration dependence of the viscosity became greater. These phenomena might be explained by considering intra- and intermolecular associations induced by the hydrophobic interactions. Hydrophobic moieties in hydrophobically modified polymers leaded to intramolecular associations, resulting in the coil contraction and viscosity decreases in dilute solutions. On the other hand, at high-enough concentrations (above CAC), intermolecular associations occurred, which led to an intermolecular physical network structure that caused a viscosity increase. Our experimental results indicated that intramolecular associations were dominant when the copolymer concentration was below CAC, and the increase of hydrophobe content caused the increase of intramolecular associations which led to the viscosity decreases, in agreement with the results of McCormick et al. [48]. When the copolymer concentration was above CAC, the hydrophobic interactions were mainly of intermolecular associations which resulted in viscosity increase, and the viscosity increase became more pronounced with increasing the N_H values of ADS samples. Furthermore, it can also be seen from Fig. 6 that for ADS-2 and AS, which had similar molecular weight and N_H values, the viscosity of ADS-2 was lower than that of AS when the copolymer concentration was below CAC. However, when the copolymer concentration was above CAC, the viscosity of ADS-2 was higher than that of AS sample. This provided evidence that the incorporation of zwitterionic monomer was beneficial to the promotion of intramolecular associations in dilute solutions and intermolecular associations at high concentrations, due to the strong

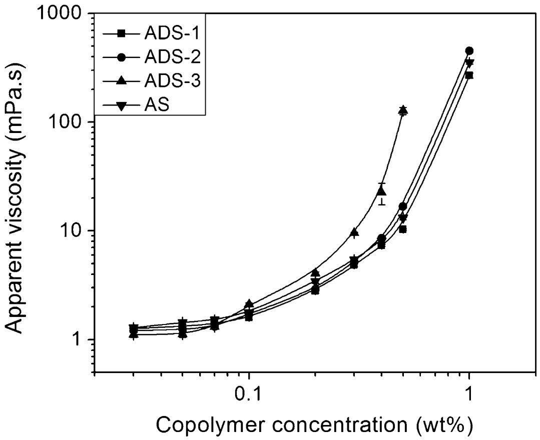
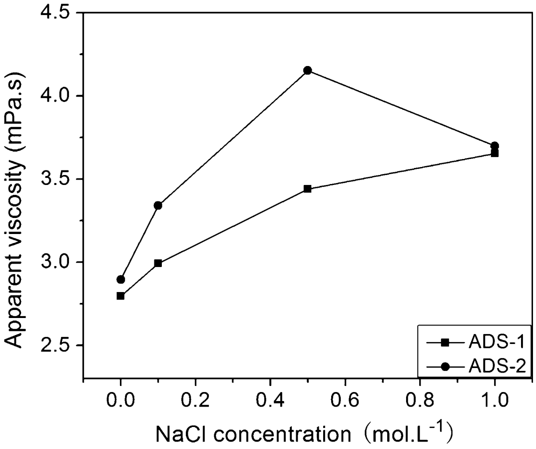


Fig. 10 Variation of viscosity with copolymer concentration at the shear rate of 10.99 s^{-1} in deionized water at 25 °C

dipolar interactions between the opposite charges of sulfobetaine units, which is in agreement with the results of DLS measurements.

Figure 11 showed the viscosity of 0.2 wt% solutions of ADS-1 (a) and ADS-2 (b) samples at various NaCl concentrations at 10.99 s^{-1} shear rate. For ADS-1, the viscosity values increased with the increase in salt concentration. On one hand, the addition of NaCl increased the solution ionic strength, weakened the electrostatic attraction between the charges in the polymer chains, and broke up intramolecular zwitterionic associations, leading to an extension of the polymer chain, and as a result the viscosity was expected to increase with increasing concentration of the added NaCl. On the other hand, the presence of NaCl made the aqueous system more hostile to the hydrophobes thus forces them to associate inter- or intramolecularly. In the case of ADS-1, the increase in viscosity values with increasing concentration of NaCl implied the greater significance of the intermolecular hydrophobic associations in an environment increasingly hostile to the hydrophobes than the intramolecular hydrophobic associations. A contrasting salt effect was observed in the case of the sample ADS-2. In contrast to ADS-1, the viscosity values thus increased considerably for the sample ADS-2 by changing the solvent from salt-free water to 0.5 mol.L^{-1} NaCl. While the viscosity value decreased in 1.0 mol.L^{-1} NaCl in compare to the viscosity in 0.5 mol.L^{-1} NaCl, it still remained higher than that in salt-free water; exactly the same result of adding more NaCl to a polyampholytic copolymer solution has been discovered by other workers [24]. In the presence of added salt (NaCl), the increase in viscosity correlated well with the known effects of NaCl on the association of hydrophobic modified polybetaines [15]. At the highest NaCl concentration (1.0 mol.L^{-1}), the decrease in viscosity may be attributed to the salt-out effect of NaCl: the solubility of the hydrophobic parts of the molecule decreased, the polymer chains were unable to manifest effective intermolecular associations and the viscosity decreased. The polymer containing more hydrophobes even tended to precipitate in salt solutions, such as ADS-3, which gave cloudy solution in 0.1 mol.L^{-1} NaCl as result of the salt-out effect. Further more, the viscosity values of ADS-2 sample are larger than

Fig. 11 Variation of viscosity of ADS-1 (**a**) and ADS-2 (**b**) copolymers ($C_{\text{copolymer}} = 0.2$ wt%) with NaCl concentration at the shear rate of 10.99 s^{-1} at 25 °C



that of ADS-1 sample in the studied NaCl concentration, indicating the enhancement of intermolecular associations due to the increment of hydrophobe content of the samples.

Conclusions

A series of novel hydrophobically modified polysulfobetain terpolymers were synthesized by micellar copolymerization along with corresponding control copolymer. The basic physico-chemical properties such as surface tension, aggregation, and rheological properties were studied as a function of copolymer concentration and NaCl concentration. Results from surface tension measurement indicated that all samples were surface-active above a threshold concentration of 0.07 wt%, and the surface tension became lower with increasing N_H values of the samples. The results of DLS measurement indicated that the incorporated zwitterionic groups would promote intramolecular hydrophobic associations in deionized water, and promote intermolecular hydrophobic associations in saline solution, which provide intra-/intermolecular associations due to the electrostatic interactions between the opposite charges of the zwitterionic groups. The rheological behavior of the samples was very dependent on the chemical composition of the monomer feed. With increasing N_H values, the critical aggregate concentration CAC decreased from 0.1 to 0.07 wt%. When the copolymer concentration was low (below 0.1 wt%), both the increment of N_H values and the incorporation of DMAPS monomer led to the decrease of viscosity, due to the promotion of intramolecular associations in dilute solutions. When the copolymer concentration was high (above 0.1 wt%), both the increment of N_H values and the incorporation of DMAPS monomer led to the increase of viscosity, indicating the enhancement of intermolecular associations at high concentrations. When NaCl concentration increased, the viscosity of the samples with low N_H values (ADS-1) increased, while the viscosity of the samples with high N_H values firstly increased and then decreased, indicating that the structure had important role on the rheological properties of these copolymers.

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References

1. Glass JE (1989) Polymers in aqueous media: performance through association. Advances in Chemistry Series. American Chemical Society, Washington, DC, pp 223
2. Candau F, Selb J (1999) Hydrophobically-modified polyacrylamides prepared by micellar polymerization. Elsevier, Amsterdam, pp 149–172 (and references cited therein)
3. Yahaya GO, Ahdab AA, Ali SA, Abu-Sharkh BF, Hamad EZ (2001) Solution behavior of hydrophobically associating water-soluble block copolymers of acrylamide and N-benzylacrylamide. Polymer 42:3363–3372
4. Shaikh S, Ali SA, Hamad EZ, Abu-Sharkh BF (1999) Synthesis and solution properties of poly (acrylamide-styrene) block copolymers with high hydrophobic content. Polym Eng Sci 39:1962–1968
5. Biggs S, Hill A, Selb J, Candau F (1992) Copolymerization of acrylamide and a hdydrophobic monomer in an aqueous micellar medium: effect of the surfactant on the copolymer microstructure. J Phys Chem 96:1505–1511
6. Dowling KC, Thomas JK (1990) A novel micellar synthesis and photophysical characterization of water-soluble acrylamide-styrene block copolymers. Macromolecules 23:1059–1064
7. Volpert E, Selb J, Candau F (1996) Influence of the hydrophobe structure on composition, microstructure, and rheology in associating polyacrylamides prepared by micellar copolymerization. Macromolecules 29:1452–1463
8. Winnik MA, Yekta A (1997) Associative polymers in aqueous solution. Curr Opin Colloid Interface Sci 2:424–436
9. Glass JE (2000) Associative polymers in aqueous media. American Chemical Society, Washington, DC
10. Hester RD, Squire DR (1997) Rheology of waterborne coatings. J Coat Technol 69:109–114
11. Taylor KC, Nasr-El-Din HA (1998) Water-soluble hydrophobically associating polymers for improved oil recovery: a literature review. J Pet Sci Technol 19:265–280
12. Kudaibergenov SE (2002) Polyampholytes: synthesis, characterization, and application. Kluwer/Plenum, New York, p 220
13. Wang C, Tam KC, Jenkins RD (2002) Dissolution behavior of HASE polymers in the presence of salt: potentiometric titration, isothermal titration calorimetry, and light scattering studies. J Phys Chem B 106:1195–1204
14. Dobrynin AV, Colby RH, Rubinstein M (2004) Polyampholytes. J Polym Sci B 42:3513–3538
15. Johnson KM, Fevola MJ, McCormick CL (2004) Hydrophobically modified acrylamide-based polybetaines. I. Synthesis, characterization, and stimuli-responsive solution behavior. J Appl Polym Sci 92:647–657
16. Johnson KM, Fevola MJ, Lochhead RY, McCormick CL (2004) Hydrophobically modified acrylamide-based polybetaines. II. Interaction with surfactants in aqueous solution. J Appl Polym Sci 92:658–671
17. Kujawa P, Rosiak JM, Selb J, Candau F (2001) Micellar synthesis and properties of hydrophobically associating polyampholytes. Macromol Chem Phys 202:1384–1397
18. Kudaibergenov SE, Didukh AG, Ibraeva ZE, Bimendina LA, Rullens F, Devillers M, Laschewsky A (2005) A regular, hydrophobically modified polyampholyte as novel pour point depressant. J Appl Polym Sci 98:2101–2108
19. Liaw DJ, Huang CC, Sang HC, Kang ET (1999) Intramolecular hydrophobic aggregation of amphiphilic polysulfobetaine with various hydrophobic groups in aqueous solution. Langmuir 15:5204–5211

20. Miyazawa K, Winnik FM (2002) Synthesis of phosphorylcholine-based hydrophobically modified polybetaines. Macromolecules 35:2440–2444
21. Miyazawa K, Winnik FM (2002) Solution properties of phosphorylcholine-based hydrophobically modified polybetaines in water and mixed solvents. Macromolecules 35:9536–9544
22. Didukh AG, Koizhaiganova RB, Bimendina LA, Kudaibergenov SE (2004) Synthesis and characterization of novel hydrophobically modified polybetaines as pour point depressants. J Appl Polym Sci 92:1042–1048
23. Konno T, Watanabe J, Ishihara K (2004) Conjugation of enzymes on polymer nanoparticles covered with phosphorylcholine groups. Biomacromolecules 5:342–347
24. Umar Y, Abu-Sharkh BF, Asrof Ali S (2005) The effects of charge densities on the associative properties of a pH-responsive hydrophobically modified sulfobetaine/sulfur dioxide terpolymer. Polymer 46:10709–10717
25. Colak S, Tew GN (2008) Synthesis and solution properties of norbornene based polybetaines. Macromolecules 41:8436–8440
26. Yu X, Wang Q, Yang JC, Buch I, Tsai CJ, Ma B, Cheng SZD, Nussinov R, Zheng J (2009) Mutational analysis and allosteric effects in the HIV-1 capsid protein carboxyl-terminal dimerization domain. Biomacromolecules 10:390–399
27. Note C, Koetz J, Wattebled L, Laschewsky A (2007) Effect of a new hydrophobically modified polyampholyte on the formation of inverse microemulsions and the preparation of gold nanoparticles. J Colloid Interface Sci 308:162–169
28. Kujawa P, Rosiak JM, Selb J, Candau F (2000) Synthesis and properties of hydrophobically modified polyampholytes. Mol Cryst Liq Cryst Sci Technol A 35:401–407
29. Umar Y, Abu-Sharkh BF, Ali SA (2005) The effects of zwitterionic and anionic charge densities in polymer chains on the viscosity behavior of a pH-responsive hydrophobically modified ionic polymer. J Appl Polym Sci 98:1404–1411
30. Liaw DJ, Lee WF, Whung YC, Lin MC (1987) Aqueous solution properties of poly [3-dimethyl (methacryloyloxyethyl) ammonium propane sulfonate]. J Appl Polym Sci 34:999–1011
31. Chu B (1974) Laser light scattering. Academic Press, New York
32. Berne BJ, Pecora R (1976) Dynamic light scattering. Wiley, New York
33. Provencher SW (1976) A Fourier method for the analysis of exponential decay curves. Biophys J 16:27–41
34. Regalado EJ, Selb J, Candau F (1999) Viscoelastic behavior of semidilute solutions of multisticker polymer chains. Macromolecules 32:8580–8588
35. Zimm BH (1948) The scattering of light and the radial distribution function of high polymer solutions. J Chem Phys 16:1093–1099
36. Maltesh C, Xu Q, Somasundaran P, Benton WJ, Hung N (1992) Aggregation behavior of and surface tension reduction by comblike amphiphilic polymers. Langmuir 8:1511–1513
37. Mozumder MS, Alnaizy RS, Umar Y, Ali SA, Abu-Sharkh BF (2005) Influence of hydrophobe content and salt concentration on dilute solution behaviour of hydrophobically modified ionic polymers from diallylammonium salts/sulfur dioxide cyclocopolymerization: light scattering and fluorescence spectroscopy. Eur Polym J 41:2224–2231
38. Volpert E, Selb J, Candau F (1998) Associating behaviour of polyacrylamides hydrophobically modified with dihexylacrylamide. Polymer 39:1025–1033
39. Schulz DN, Peiffer DG, Agarwal PK, Larabee J, Kaladas JJ, Soni L, Handwerker B, Garner RT (1986) Phase behaviour and solution properties of sulphobetaine polymers. Polymer 27:1734–1742
40. Liaw DJ, Huang CC (1997) Dilute solution properties of poly (3-dimethyl acryloyloxyethyl ammonium propiolactone). Polymer 38:6355–6362
41. McCormick CL, Salazar LC (1992) Water soluble copolymers. 46: hydrophilic sulphobetaine copolymers of acrylamide and 3-(2-acrylamido-2-methylpropanedimethyl-ammonio)-1-propanesulphonate. Polymer 33:4617–4624
42. Kathmann EE, White LA, McCormick CL (1997) Water soluble polymers: 69. pH and electrolyte responsive copolymers of acrylamide and the zwitterionic monomer 4-(2-acrylamido-2-methylpropyldimethyl-ammonio) butanoate: synthesis and solution behaviour. Polymer 38:871–878
43. Gao B, Jiang L, Liu K (2007) Microstructure and association property of hydrophobically modified polyacrylamide of a new family. Eur Polym J 43:4530–4540
44. Kopperud HM, Hansen FK, Nystrm B (1998) Effect of surfactant and temperature on the rheological properties of aqueous solutions of unmodified and hydrophobically modified polyacrylamide. Macromol Chem Phys 199:2385–2394

45. Gouveia LM, Paillet S, Khoukh A, Grassl B, Müller AJ (2008) The effect of the ionic strength on the rheological behavior of hydrophobically modified polyacrylamide aqueous solutions mixed with sodium dodecyl sulfate (SDS) or cetyltrimethylammonium p-toluenesulfonate (CTAT). Colloids Surf A 322:211–218
46. Ali SA, Umar Y, Al-Muallem HA, Abu-Sharkh BF (2008) Synthesis and viscosity of hydrophobically modified polymers containing dendritic segments. J Appl Polym Sci 109:1781–1792
47. Molyneux P (1983) Water-soluble synthetic polymers: properties and behavior. CRC Press, Boca Raton
48. Chang Y, McCormick CL (1994) Water-soluble copolymers: 57. Amphiphilic cyclocopolymers of diallylalkoxybenzyl-methylammonium chloride and diallyl-dimethyammonium chloride. Polymer 35:3503–3512