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Hydrophobically associating polyacrylamides and their partially hydrolyzed derivatives prepared by post-modification. 2. Properties of non-hydrolyzed polymers in pure water and brine

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Abstract

Dilute and semi-dilute solution properties of polyacrylamide (PAM) and its hydrophobically modified analogues (HAPAMs) in both pure water and brine were compared by means of viscometry, light scattering and fluorescence spectrometry. In dilute solution, large differences in reduced viscosity and apparent molecular weight $\bar{M}_{\text{wapp}}$ of HAPAMs were found between pure water and 0.1 M NaCl solutions, while no significant differences were observed for PAM. In addition, in pure water, intrinsic viscosity and $\bar{M}_{\text{wapp}}$ of HAPAMs are higher than those of PAM. In semi dilute regime, with increasing salinity, the reduced viscosity of PAM remains almost unchanged, whereas enhanced viscosity was observed for the HAPAM polymers in both monovalent and divalent cation aqueous environment. HAPAM solutions behave as classical shear-thinning fluid in pure water, whereas addition of NaCl induces shear-thickening response for these polymers. The experimental results are interpreted in terms of the hydrophobe distribution and its influence on the formation of intra- and intermolecular associations. The differences between the behaviors described in this paper and those usually obtained with HAPAMs characterized by a blocky hydrophobe distribution are discussed.

Keywords: Hydrophobically modified polyacrylamide; Associating polymers; Solubility

1. Introduction

Water-soluble polymers modified with a few mole percent of hydrophobic moieties have been in the focus of considerable research over the past two decades in both academic and industrial laboratories [1–9]. Of particular interest among such novel hydrosoluble materials is hydrophobically modified associating polyacrylamide (HAPAM) that derives from polyacrylamide by incorporating a relatively small amount (generally less than 2 mol%) of hydrophobic groups onto acrylamide backbone [8–22]. In aqueous environments, the non-polar alkyl groups have a strong tendency to associate together through intra- and intermolecular interactions, because the contact of hydrophobic units and water is unfavorable. At high concentration, intermolecular hydrophobic association is predominant, which yields a transient network structure to offer excellent viscosity building capacity.

It is speculated [23] that upon applied shear stress the HAPAM does not degrade mechanically since the intermolecular non-covalent hydrophobic junctions would dissociate under high shear before any irreversible degradation could occur. When shear is decreased or removed, the hydrophobic bonds could reform and high viscosity could be regained. This property of associating polymers enables to avoid the irreversible chain scission that typically occurs to high molecular weight polyacrylamide (PAM), when subject to high shear stress. Furthermore, when temperature or salinity increases, higher viscosity can be expected because the polarity of the solution is enhanced, which strengthens the hydrophobic interactions. All these unusual properties enable us to consider HAPAM as a new family of promising candidates as thickeners or rheology modifiers in many fields

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particularly in chemically enhanced oil recovery [11,13,19–29].

Practically, most of acrylamide-based polymers used in petroleum exploitation activities are actually partially hydrolyzed to introduce some carboxylic groups into the chain. The presence of these charged units improves water solubility and increase hydrodynamic volume of the chain due to the mutual repulsion of the negative charges [30–32]. The effect of charged groups introduced into the acrylamide backbone of HAPAM remains a matter of debate in literature. To the best of our knowledge, only a few studies so far dealt with HAPAMs containing both hydrophobic and carboxylic groups from hydrolysis process [33–39]. However, almost all these HAPAMs were prepared via micellar copolymerization that leads to blocky distribution of hydrophobes along polymer backbone [10]. For the HAPAMs prepared by an alternative strategy, post-modification, a common method for preparing some other associative polymers, the effect of charges in the main chain is not well documented [18]. Statistical distribution of hydrophobes along the HAPAM main chain can be expected from this method since the reaction media is quite homogeneous in contrast to micro-heterogeneous environment encountered in micellar copolymerization process [18,40,41]. Moreover, the properties of HAPAMs and their hydrolyzed derivatives prepared via post-modification still have to be comprehensively studied due to recent introduction of the method [18,41]. Hence, there is a lack of fundamental understanding on the association behaviors of this HAPAM system.

An attempt to prepare HAPAMs and their hydrolyzed analogues via post-modification and hydrolysis of the amide groups in order to introduce hydrophobic and charged moieties simultaneously has been made in our laboratory. By this method, one can tune the microstructure parameters of the polymer while keeping other variables unchanged. For example, the hydrolyzed samples can inherit the same molecular weight and molecular weight distribution, hydrophobe content and hydrophobe distribution from their non-ionic parent polymer. Thereby, more convincible comparative studies can be preformed. The synthesis and characterization of a series of HAPAMs and their hydrolyzed derivatives [41], as well as some preliminary steady rheological results [42], have been reported previously. In the present paper, we focus on the aqueous solution behavior of non-hydrolyzed associative polymers in pure water and brine, while the properties of hydrolyzed polymers will be discussed in a forthcoming paper of this series. Here we examine the properties of HAPAMs in dilute and semi dilute concentration regimes by combination of viscometry, fluorescence spectrometry and static light scattering measurements. In order to unravel the influence of hydrophobe structure and content on the properties of the HAPAM in solution, we compare our results systematically to those obtained for unmodified parent PAM.

2. Experimental

2.1. Materials

Four polymer samples were used in this work: Polyacrylamide (PAM) and its three hydrophobically modified derivatives H00C8-1.0, H00C12-1.0 and H00C12-0.5. In the nomenclatures corresponding to HAPAMs used in this work, ‘H’ and the following number refers to ‘hydrolysis’ and ‘hydrolysis degree’, ‘C’ and the following number stands for ‘hydrophobe’ and the ‘hydrophobe length’, the last number denotes the content of hydrophobic group. For example, the sample code ‘H00C8-1.0’ means a non-hydrolyzed HAPAM with 1.0 mol% octyl alkyl group. The preparation and structural characterization of all these polymers have been detailed in a previous paper [41], and their physical compositions were reproduced in Table 1.

Pyrene (98%, Aldrich), analytical grade of NaCl (ACROS) and $CaCl_2$ (Aldrich) were used as received. The water used was doubly distilled with an all-glass apparatus.

2.2. Viscometric measurements of dilute solutions

Viscometric properties of dilute polymer solutions were measured by an automatic Ubbelodhe capillary viscometer at 25 ± 0.1 °C. The diameter of the capillary tube is 0.56 mm and an average shear rate in the tube is about 1500 s^{-1}. All the solutions were prepared in the same way as described below for light scattering experiments. The solvents were filtered through 0.1 μm Millipore filters.

2.3. Rheological measurements of semidilute polymer solutions

Concentrated stock polymer solutions were prepared by dissolution of an appropriate amount of polymer powder in distilled water. The powder was pre-hydrated overnight, which was followed by gentle magnetic stirring for more than 2 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 polymer solutions were obtained by diluting the stock solution with distilled water. In the examination of effects of salts, designated amount of NaCl or $CaCl_2$ fine

Table 1
Chemical composition and physical parameters of the polymers [41]

Sample code	Hydrophobe (mol%)	[η] (ml g^{-1}) (in 0.1 M NaCl)	M_w (in formamide)	Note
PAM	0	520	2.0×10^6	Polyacrylamide
H00C8-1.0	1.0	300	1.9×10^6	HAPAM
H00C12-1.0	1.0	–	–	
H00C12-0.5	0.5	–	–	

powders was directly added into the solutions, following by mixing rotationally for 1 day. These solutions were kept standing overnight for equilibrium prior to measurements.

The steady shear rheological properties of polymer semidilute solutions were measured using a low-shear Contraves LS30 viscometer (Couette type) equipped with the bob-cup system T1–T1 (inner radius = 5.5 mm, height = 20.0 mm and outer radius = 6.0 mm). This apparatus works with controlled shear rate ranging from 0.017 to 128.5 s^{-1}. For high concentration and high viscosity polymer solutions, controlled-rate mode of an Bohlin CVOR150 rheometer with a cone-plate geometry (radius = 40.0 mm, angle = 0.096 rad, gap = 0.150 mm) was used. All these measurements were performed at 25 ± 0.1 °C. The systems were allowed to reach steady state at each shear rate prior to registering the measured values.

2.4. Static light scattering

Carefully prepared stock polymer solutions were ultracentrifugated at 20,000 rpm for 9 h in a SIGMA 3K30 centrifuge at 15 °C. All solvents were filtered through 0.1 μm Millipore filters. Static light scattering experiments were performed with a spectrogoniometer (SEMATech) equipped with an argon laser source operating at $\lambda =$ 514.5 nm. The scattering angle θ was varied between 30 and 150°.

2.5. Fluorescence spectrometry

Steady fluorescence spectra were recorded on an LS50B luminescence spectrometer (Perkin–Elmer). A series of solutions were prepared by dissolution of dry polymer sample in pyrene-saturated distilled water. All measurements were performed at room temperature. Emission spectra were obtained with an excitation wavelength 335 nm and a slit width of 2 nm. The ratio I_1/I_3 of the intensities of the first and the third vibronic peaks for the emission spectrum provides an estimate of relative hydrophobicity of the local environment.

3. Results

3.1. Solubility of associative polymers in water

Solubility is the primary consideration for the applications of water-soluble polymers due to the fact that most of their utilizations arise from aqueous based systems. For example, in oil recovery process, solubility of polymer in water is one of the most important and critical requirements [32]. The relative poor solubility of HAPAM polymers may be one of the most important impedances for petroleum engineers to accept this type of materials.

However, there is no generally-accepted quantitative method to determine the solubility of water-soluble polymers in aqueous media. Some researchers proposed spectrometric [43–45] and conductometric [46] techniques, but the former method is limited to much diluted solutions and the latter one is influenced by many factors such as particle size, stirring speed, temperature, and ionic group content. Here we just give a semi-quantitative description of the hydrosolubility of the series of polymers by visual observation.

In general, the solubility of an associative polymer is governed mainly by its architecture and chemical composition. The polymerization degree and the hydrophobe distribution of all polymers used in this work are identical [41], so we will only examine the effects of hydrophobe length and content, as well as the influence of added salt on polymer solubility.

At polymer concentration 0.50 wt% and at agitation speed of 300 rpm, 5 and 24 h were required for dissolution of non-ionic associative polymers H00C12-0.5 and H00C12-1.0. McCormick and co-workers [47] reported that HAPAM polymers containing more than 0.50 mol% hydrophobes, prepared by micellar copolymerization, are insoluble. This clearly indicates that hydrophobe content and distribution play important roles in the solubility of associative polymers.

For polymers with different hydrophobe length but identical chemical structure, the solubility is different. For example, associative polyacrylamide with hydrophobe contents of 0.50 or 0.75 mol% is only soluble for less than 12 carbons in the aliphatic group [48]. We observed similar phenomena for our polymers: At 0.50 wt% polymer concentration, it took 8 and 24 h of continuous magnetic stirring at 300 rpm for dissolving H00C8-1.0 and H00C12-1.0, respectively. Peiffer [38] examined the solubility characteristics of a series of hydrophobic comonomers with surfactant nature. With increasing the hydrophobe chain length, the monomers were less water-soluble as anticipated from increased hydrophobic character and apparent inability to form micellar-type aggregates. This behavior is also manifested when these monomers were incorporated into a polymer. Compared with C12, the C8 hydrophobe modified polyacrylamide H00C8-1.0 has much better solubility. Therefore, in the following experiments, we will mainly focus on H00C8-1.0.

Other external factors influencing water solubility of associative polymers include the nature of solvent and preparation process of the solution. We tried to dissolve H00C12-1.0 samples directly in 0.5 M NaCl aqueous solution at polymer concentration 0.15 wt%, but finally only swelled particles suspending in the solution were observed even if one-week vigorous agitation has been applied. Other researchers also found that the associative polymers are very slow to dissolve from dry state into an aqueous solution in the presence of small molecular weight electrolytes [48]. Therefore, in this work, we directly added salt powder into the well-dissolved pure water polymer solutions in order to obtain the salted aqueous solutions.

Remarkably, when we stirred the polymer/water mixture immediately after putting the polymer powder into water, it was more difficult to dissolve the polymer and many bubbles can be observed in a turbid solution. One can assume that under the agitation, unhydrated parts of the polymer powders were wrapped into the hydrated layer. The solvent molecules penetrate slowly into the unhydrated part because of the high viscosity. But if we let the mixture stand for one night prior to agitating, the final solutions were more homogeneous and did not contain bubbles.

3.2. Rheological properties in aqueous solution

Viscometric properties of polymer solutions were used extensively to gain insight into the structure and conformation of polymers in solution. The dependence of zero-shear apparent viscosity, η_0, on polymer concentration for PAM and its hydrophobically modified analogues HAPAMs in pure water are presented in Fig. 1(a).

These curves exhibit the following distinctive features: (i) η_0 for all the polymers increases with increasing polymer concentration; (ii) the transition between dilute and semi dilute regime (concentration range, where a viscosity sharply increases) is shifted towards smaller concentrations when the length of hydrophobe increases at constant molar fraction of hydrophobic groups in the chain and (iii) viscosity increases with increasing molar fraction of hydrophobes or the hydrophobe length in both dilute and semi-dilute regimes.

The plots of reduced viscosity, η_{red}, versus polymer concentration provide more representative information about the chain conformation. Fig. 1(b) clearly indicates that, in pure water, η_{red} of modified polymers is much higher than that of PAM in the whole range of concentration. Remarkably the enhancement of viscosity of HAPAMs with respect to that of parent PAM occurs in the dilute regime. This finding confronts earlier observations that η_{red} of HAPAM is lower than that of the parent PAM [49–52]. As one can see from Fig. 1(b) the crossover concentration between dilute and semi dilute regimes varies roughly as $1/[\eta]$, where $[\eta]$ is the intrinsic viscosity (i.e. extrapolated to zero concentration reduced viscosity).

Hence, the rheological behaviour of HAPAMs studied in present work is markedly different from that studied so far, at least in pure water. In Fig. 1(b), no 'polyelectrolyte effect' is found for both PAM and HAPAMs, indicating that no charged groups were introduced in the PAM chain during the chemical modifications. The peculiar behavior of our polymers in water can be attributed to the distribution of the hydrophobes which differs from that usually obtained by micellar polymerization: it is well-known that the hydrophobes place as random 'micro-block' in HAPAMs prepared from micellar process [10], while disperse statistically along the backbone of associative polymers from the post-modification [40].

Fig. 2 compares the variation of zero-shear reduced viscosity, η_{red}, as a function of polymer concentration for PAM and H00C8-1.0 in pure water and 0.1 M NaCl.

In the presence of 0.1 M NaCl, as expected, η_{red} of PAM remains unchanged. However, the η_{red} of H00C8-1.0 decreases upon addition of salt by almost one order of magnitude in the diluted regime compared to that in pure water and becomes smaller than that of PAM. Hence, in the presence of salt, the 'classical' behavior of HAPAMs in dilute regime (observed earlier both in pure water and in the presence of salt and attributed to intra-molecular association) is recovered. This result implies that for the polymers studied here the chain collapses due to intra-molecular hydrophobic association only when the strength of hydrophobic interactions is reinforced by the 'salting out' effect. In the semi-dilute region, i.e. above a given concentration close to $1/[\eta]$, the η_{red} of HC00C8-1.0 increases strongly in the presence of salt and becomes much higher than that of PAM and even superior to that in pure water. This is usually observed and normally attributed to the enhancement of intermolecular hydrophobic associations.

It is generally assumed that the effect of salts on the hydrophobic interactions depends only on the ionic strength but is independent of the nature of the ionic species. The effects of NaCl and $CaCl_2$ on η_{red} for H00C8-1.0 and PAM in semi-dilute region are shown in Fig. 3. As anticipated, upon increasing salt content, η_{red} of PAM does not vary while that of H00C8-1.0 increases continuously. An increase in viscosity upon addition of $CaCl_2$ seems to be higher than that of NaCl for the same molar concentration. However, if the ionic strength is considered, both curves become superimposed, which confirms that the hydrophobic interactions depend on the ionic strength but are independent of the charge of ions.

Fig. 4 gives the shear rate dependence of the apparent viscosity, η_{app}, of semi-dilute solution ($C_p = 0.50$ wt%) for both PAM and H00C8-1.0 in pure water and in 0.1 M NaCl. In both solutions, PAM behaves nearly as a Newtonian fluid; namely, the apparent viscosity does not change upon increasing shear rate. On the contrary, solutions of H00C8-1.0 in pure water behave as a pseudo-plastic fluid: Upon increasing shear rate, the apparent viscosity experiences a Newtonian plateau and then a shear-thinning region. This behavior is different from that of the polymers prepared by micellar copolymerization, which exhibit a shear thickening behavior in pure water at high polymer concentrations [37,43,52]. This finding implies that distribution of hydrophobes along the skeleton strongly affects not only the reduced viscosity but also the shear rate response of aqueous solutions of associative polymers. In our particular case, when hydrophobes are isolated and do not form sequences, an increase in the shear rate does not provoke the chain expansion responsible for the shear thickening behavior in pure water.

However, upon addition of salt, the rheological behavior of associative polymer solutions studied here changed

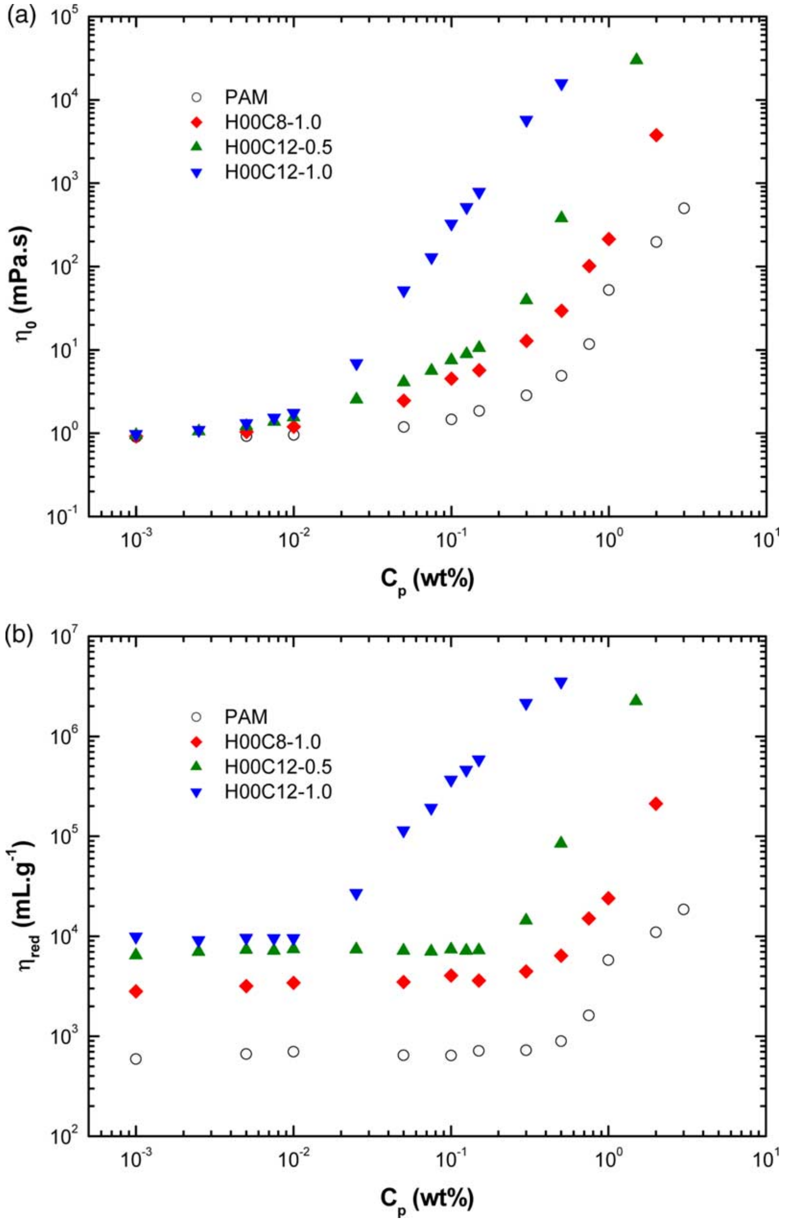

Fig. 1. (a) Zero-shear reduced viscosity plotted as a function of polymer concentration for PAM and its hydrophobically modified derivatives in pure water ($T=25$ °C). (b) Reduced viscosity of PAM and its hydrophobically modified derivatives in pure water ($T=25$ °C).

dramatically. As shown in Fig. 4, in the presence of 0.1 M NaCl, the curve of apparent viscosity versus shear rate for the H00C8-1.0 solution exhibit three regions: First, a Newtonian plateau, then a shear-thickening region, where apparent viscosity goes up to a maximum point, and finally, a shear thinning regime. This phenomenon was repeatedly observed in our experiments and was preliminary reported in Ref. [42]. In addition, this unique rheological response is more pronounced in semi-dilute solutions of partially hydrolyzed associative polyacrylamides, which will be discussed in detail in the next publication.

To summarize these rheological observations, HAPAM polymers prepared by post-modification differ significantly from the HAPAM generally investigated in pure water but the usual behaviors are observed upon addition of salts. One has to understand why these polymers which chemically differ from the other ones only by the statistical distribution of the hydrophobes exhibit peculiar behaviors in pure water.

3.3. Static light scattering

Static light scattering (SLS) measurements with the standard Zimm analysis can provide information about such properties as molecular weight ($\overline{M_w}$), radius of gyration (R_g) and the second virial coefficient (A_2) for polymers in the diluted regime. The basic relation for static light scattering is

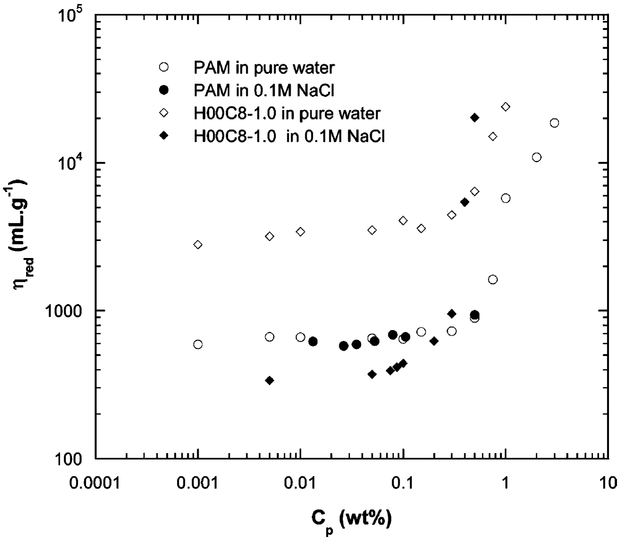

Fig. 2. Comparison of the reduced viscosity-polymer concentration relationship for hydrophobically modified and unmodified polyacrylamides in pure water and 0.1 M NaCl ($T=25$ °C).

$$\frac{KC}{\Delta I}=\frac{1}{\overline{M_w}}\left(1+\frac{q^2R_g^2}{3}\right)+2A_2C \tag{1}$$

where $K\left(=4\pi n_0^2(\mathrm{d}n/\mathrm{d}C)^2/N_A\lambda_0^4\right)$ is an optical constant with N_A, n_0 and λ_0 being Avogadro number, the solvent refractive index, and the wavelength of the light in a vacuum, respectively. C is the polymer concentration, g mL^{-1} and ΔI is intensity difference between polymer solution and solvent. A_2 refer to the second virial coefficients. The scattering vector is defined as $q=4\pi n\,\sin(\theta/2)/\lambda$.

Light scattering characterization of PAM of high molecular weight in water has been often considered to be difficult, due to its tendency to form aggregates. On the other hand, due to the high polarity of the amide groups, few solvents are able to well disperse PAM. Formamide was found to be a good solvent for PAM and the same values of molecular weight in formamide and water were obtained, if special care was taken for the preparation of the aqueous solutions [53]. Obviously, characterization of HAPAM by static light scattering really represents a challenge for the normal solvents used for water-soluble polymers since hydrophobic groups induce aggregation, which often leads to more or less erroneous results [10, 41]. A unambiguous molecular weight determination requires to search appropriate solvent(s) in which HAPAM is molecularly dispersed, i.e. where no aggregates exist [10]. Formamide was found again to be such a candidate [52] and continuously employed in Candau's group [43,54,55]. Blagodatskikh et al. [56] claimed recently that aqueous $NaNO_3$-acetonitrile mixed solvent can weaken or disrupt the association in HAPAM dilute solutions and some results from both static light scattering and gel permeation chromatograph are comparable. Static light scattering results obtained from different solvents for both PAM and H00C8-1.0 in this work are compared and summarized in Table 2.

Static light scattering results for both PAM and H00C8-1.0 in formamide have been reported in a previous paper [41]. Similar $\overline{M_w}$ were found for both polymers in such a solvent, where no association was expected for HAPAM polymers [52]. This can be verified by the regular diagram [41] of H00C8-1.0, where the Zimm plot (not shown here) does not exhibit any anomaly, and by the fact that, as claimed by Biggs et al. [52], the values of index increment, dn/dc, of a series of HAPAMs with different hydrophobic contents in formamide were close to that of pure PAM. Similar values of $\overline{M_w}$ for both modified and unmodified polyacrylamides also indicate that no degradation occurred

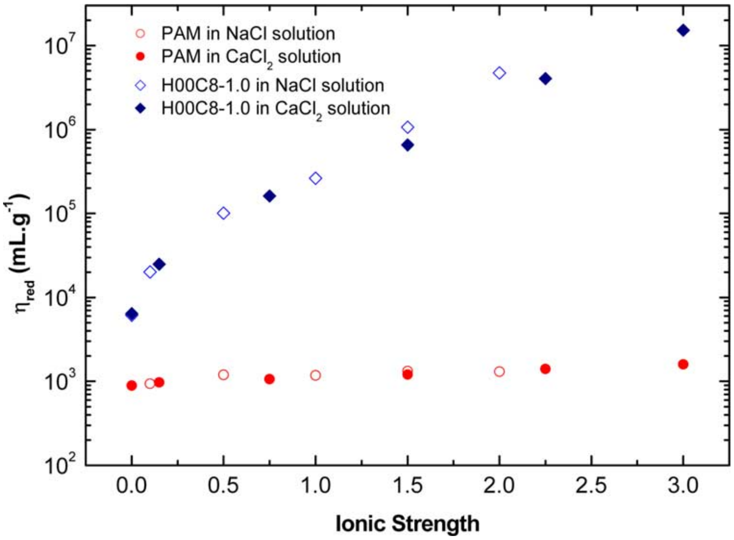

Fig. 3. Effect of mono- and divalent inorganic salts on reduced viscosity of hydrophobically modified and unmodified polyacrylamides ($C_p=0.50$ wt%, $T=25$ °C).

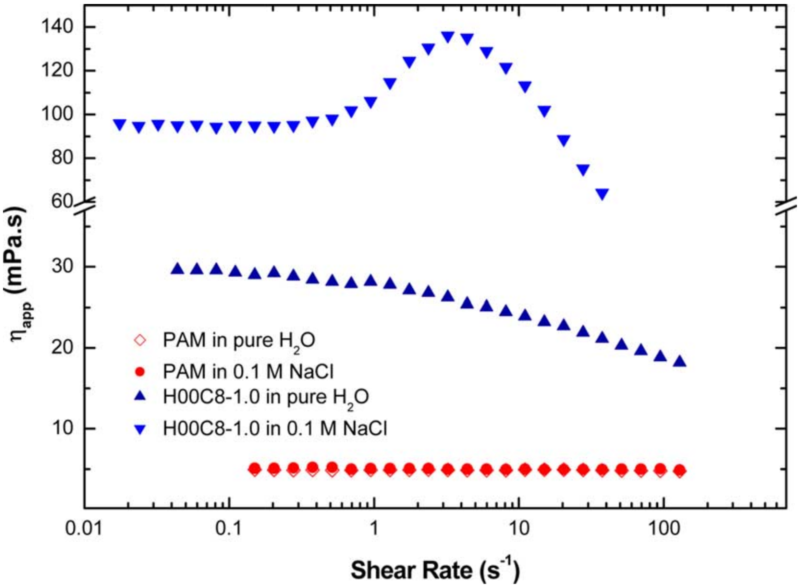

Fig. 4. Comparison of rheological behaviors of hydrophobically modified and unmodified polyacrylamides in pure water and 0.1 M NaCl ($C_p = 0.50$ wt%, $T = 25$ °C).

in the process of preparation for H00C8-1.0 from PAM, in other words, the HAPAM analogues inherited the same molecular weight from their parent polyacrylamide.

Zimm plots for PAM and H00C8-1.0 in pure water are compared in Fig. 5. The Zimm plot of PAM (Fig. 5(a)) is acceptable though it is not as good as those in 0.1 M NaCl and in formamide [41] (not shown here) because the points are slightly scattered due to incomplete removal of dust. The fact that $A_2 > 0$ (Table 2) is indicative of a good solvent quality. The values of $\overline{M_w}$ and R_g found for PAM in pure water are in excellent agreement with those determined in formamide. However, the Zimm plot corresponding to H00C8-1.0 in pure water (Fig. 5(b)) is rather different from that of PAM: The curves $KC/\Delta I = f(C)$ for the different angles are no more parallel and those for different concentration exhibit some curvature at high angle range, indicating the existence of aggregation in the solution.

As shown in Table 2, $\overline{M_w}$ and R_g of PAM determined in 0.1 M NaCl are identical with those found in formamide and pure water. When adding salt, good Zimm plot is also obtained for H00C8-1.0 [41]. However, the values of $\overline{M_w}$ for H00C8-1.0 in 0.1 M NaCl are higher than those of PAM in 0.1 M NaCl and that of H00C8-1.0 in formamide, whereas the value of R_g is smaller than that of PAM in 0.1 M NaCl and that of H00C8-1.0 in formamide.

The extrapolation of $KC/\Delta I$ to $q = 0$ in Eq. (1) provides variations of the $\overline{M_{w,app}}$ parameter, the so-called apparent weight-average molecular weight [57] against concentration:

$$\left(\frac{KC}{\Delta I}\right)_{\theta=0} = \frac{1}{\overline{M_{w,app}}} = \frac{1}{\overline{M_w}} + 2A_2C \qquad (2)$$

Fig. 6 shows the evolution of $\overline{M_{w,app}}$ with polymer concentration in pure water for both PAM and H00C8-1.0. In pure water, $\overline{M_{w,app}}$ of PAM increases slightly with dilution of the polymer solution which reflects a positive second virial coefficient, while $\overline{M_{w,app}}$ of H00C8-1.0 increases very sharply under the identical experimental conditions. As the $\overline{M_w}$ values of H00C8-1.0 and PAM are exactly the same when measured in formamide, results obtained with the H00C8-1.0 in pure water clearly indicate formation of large aggregates, even in the very diluted regime considered in light scattering measurements. In the presence of NaCl, this aggregation phenomenon is less pronounced since the $\overline{M_w}$ value of H00C8-1.0 is not so different from that of PAM; remarkably a lower value of radius of gyration is observed which indicates a collapse of the chains.

By taking into account the experimental points in the lower range of scattering angle, one could find that for

Table 2
Static light scattering results of PAM and H00C8-1.0 in different solvents

Sample	In pure H_2O			In 0.1 M NaCl			In formamide		
	$\overline{M_w}$ (10^6 g mol^{-1})	R_g (nm)	A_2 (cm^3 mol g^{-2})	$\overline{M_w}$ (10^6 g mol^{-1})	R_g (nm)	A_2 (cm^3 mol g^{-2})	$\overline{M_w}$ (10^6 g mol^{-1})	R_g (nm)	A_2 (cm^3 mol g^{-2})
PAM	2.0	95	0.00044	2.2	95	0.00051	2.0	96	0.00063
H00C8-1.0	–	–	–	3.1	85	0.00013	1.9	100	0.0009

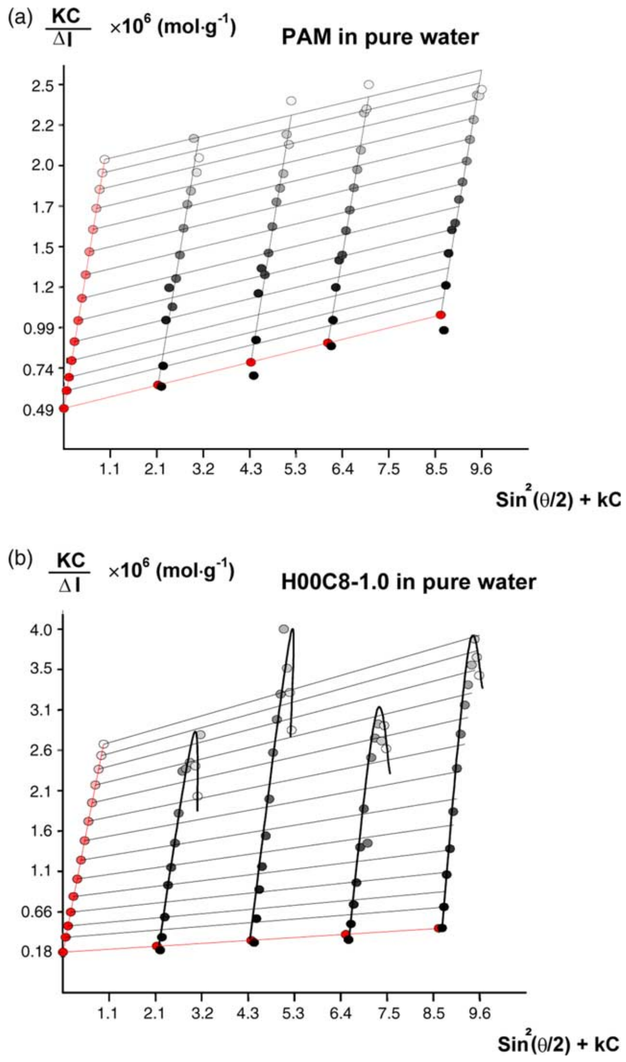

Fig. 5. Zimm-plots of hydrophobically modified and unmodified polyacrylamides in formamide ($T=25$ °C): (a) PAM; (b) H00C8-1.0.

H00C8-1.0 in pure water: $\overline{M_w} \geq 6\times 10^6$ g mol^{-1} and $R_g \geq 200$ nm.

3.4. Fluorescence spectrometry

Fig. 7 presents the ratios of fluorescence intensities of the first and the third emission peaks (I_1/I_3) for PAM, H00C8-1.0 and H00C12-1.0 as a function of polymer concentration, in pure water. I_1/I_3 of PAM in the concentration range remains unchanged and is close to the characteristic value two for pyrene in pure water [56], which means that pyrene is not influenced by the presence of amide functions in aqueous solution. On the contrary, when polymer concentration increases, the ratio I_1/I_3 for H00C8-1.0 and H00C12-1.0 decreases from about 1.9 down to 1.2 which is indicative of pyrene solubilized in hydrophobic aggregates in aqueous solutions of different associative polymers [58–60]. Values of I_1/I_3 of H00C8-1.0 and H00C12-1.0 lower than those of PAM suggest that hydrophobic nano-domains (able to solubilize pyrene) can form even at very low concentrations. This effect is of marginal importance for H00C8-1.0 but is more significant for H00C12-1.0. From Fig. 7, one can also find that in the whole concentration range the ratio I_1/I_3 for H00C12-1.0 is lower than that for H00C8-1.0, and the decrease in the I_1/I_3 curve for H00C12-1.0 appears at smaller polymer concentration (about 0.025 wt%) than in that of H00C8-1.0 (about 0.05 wt%). These findings are in agreement with the fact that hydrophobic side groups in H00C12-1.0 is longer than those in H00C8-1.0, thus stronger tendency for both intra- and intermolecular hydrophobic associations is expected in the former case than in the latter.

Table 3 lists the values of I_1/I_3 in semi-dilute solution ($C_p=0.50$ wt%) of H00C8-1.0 in various brine. One can find that addition of 0.1 M NaCl induces a decrease of I_1/I_3, but further decrease is not evident upon increasing salinity. However, the result is in agreement with the fact that salt is considered to have enhancing effect on hydrophobic interactions and association.

4. Discussion

In general, macroscopic aqueous solution properties of polymers are strongly determined by the conformations of polymer chains. The observed macroscopic behaviors, such as solubility and rheological response, are affected by macromolecular architecture, external conditions (e.g. salinity), as well as polymer-solvent interactions. As we anticipate below, all these factors affect the balance between intra- and intermolecular association.

4.1. Solubility of polymer in pure water and brine

Pure polyacrylamide has relatively simple chemical structure which carries a strong hydrophilic amide group (–CONH$_2$). These amide groups are easily hydrated because the hydrogen bonds can be formed between the hydrogens in amide groups and the oxygen in water molecules, and the dipole interactions can be generated by the amide groups [61]. However, when hydrophobes are introduced into PAM backbone, the apolar alkyl groups tends to avoid contacts with water molecules and induce ordering of water molecules around themselves, such as a cage like or clathrate structure or 'icebergs' [62,63]. This is why the dissolution time of HAPAMs, such as H00C8-1.0 and H00C12-1.0, is much longer than that of polyacrylamide.

Although positive values of A_2 (Table 2) indicate good solvent conditions for both PAM and H00C8-1.0 in 0.1 M NaCl, the addition of salt such as NaCl enhances the polarity of the medium, which promotes hydrophobic association and thus slows down the dissolution. For associative polymer with longer hydrophobe length, such as H00C12-1.0, this effect becomes even stronger: It is insoluble in

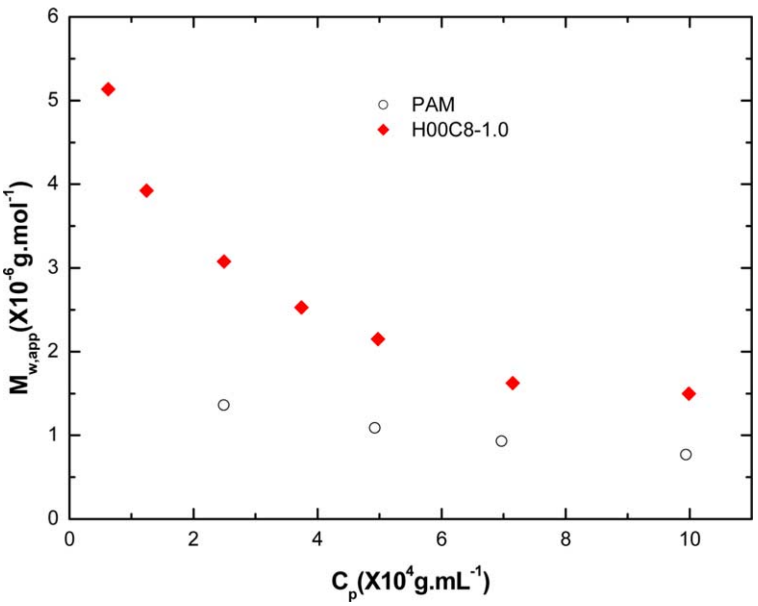

Fig. 6. Apparent molecular weight of hydrophobically modified and unmodified polyacrylamides varies with polymer concentration in pure water ($T = 25$ °C).

0.5 M NaCl even at such a low polymer concentration as 0.15 wt%.

We found that the HAPAM polymers can be well dissolved in formamide. This is in good agreement with a recent report of Xue et al. [64] who found that HAPAM polymers can be dissolved in formamide whatever the hydrophobe content or hydrophobe block length.

It should be borne in mind that the optical observation is a very rough method of determination of the solubility characteristics for the series of polymers, and it is uneasy to obtain a solubility phase diagram like that of hydrophobically modified poly(ethyl oxide) [65] because of the strong hydrophilic feature of amide groups.

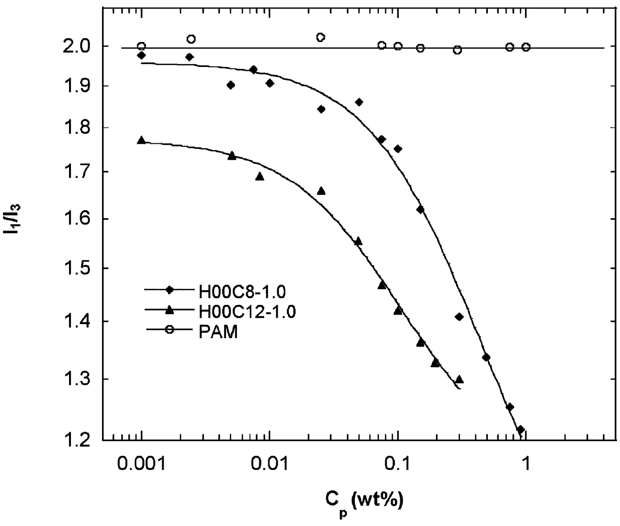

Fig. 7. I_1/I_3 varies with polymer concentration for PAM and H00C8-1.0 in pure water.

4.2. Dilute solution properties

One of the most interesting findings of this work is the fact that in dilute solution, the presence of hydrophobes in the PAM chain strongly enhances the viscosity of the dilute polymer solution in pure water while earlier studies indicated on the contrary a decrease in viscosity in comparison to that of parent PAM. Remarkably, such a decrease in viscosity is observed for our HAPAM polymers in the presence of salts.

As stated in introduction, two modes of hydrophobically-drive aggregation, i.e. the intra- and the intermolecular aggregation have to be considered in order to explain the rheological behaviors of the associative polymers. A decrease in viscosity of the HAPAM solution in dilute regime with respect to that of the parent polymer is unambiguously attributed to a partial chain collapse due to intramolecular association. However, few works analyzed whether the measured viscosity corresponds to isolated collapsed chains or to aggregates of collapsed chains. In order to make an unambiguous conclusion, additional measurements of molecular weight or hydrodynamic radius by static or dynamic light scattering are necessary. When the reduced viscosity of the solutions of associative polymers much higher than that of the parent polymer solutions is observed, this indicates either expansion of individual chains or aggregation of several chains. The first alternative is not reasonable when hydrophobic groups are present along the chain. Light scattering measurements of HPAM in pure water have clearly demonstrated the existence of aggregates: The apparent molecular weight of H00C8-1.0 is approximately three times higher that that of PAM with a much higher radius of gyration. On the basis of this observation, we can assume that: (i) In pure water,

Table 3
Effect of NaCl content on I_1/I_3 for H00C8-1.0 ($C_p = 0.50$ wt%)

Sample	I_1/I_3 in different solvents					
	Pure H_2O	0.1 M NaCl	0.5 M NaCl	1.0 M NaCl	1.5 M NaCl	2.0 M NaCl
PAM	1.93	–	–	–	–	–
H00C8-1.0	1.34	1.26	1.21	1.25	1.22	1.24

the statistical distribution of hydrophobes does not lead to intra-molecular association and (ii) there is formation of loose intermolecular aggregates by weak intermolecular association.

The first assumption can be supported by the following simple arguments based on the model of intramolecular associations proposed in Ref. [66]. The formation of intramolecular aggregate via association of hydrophobic sequences into hydrophobic domains is favored by the gain in the free energy due to reduced contacts of hydrophobes with water replaced by hydrophobic environment. At the same time it is penalized by conformation entropy losses and additional crowding of spacers forming loops.

Let $[H]$ be the fraction of hydrophobic units in the chain. Each hydrophobic unit comprises a pendant aliphatic chain of n carbons. The hydrophobes are grouped into sequences each comprising p hydrophobes (Fig. 8). Then the average number of hydrophilic monomers in the main chain segment separating neighboring hydrophobic sequences is $p/[H]$.

The gain in the free energy due to transfer of group of p hydrophobes from water into a hydrophobic domain is $\sim\gamma(pn)^{2/3}$. Here the exponent 2/3 reflects the fact that hydrophobic domains are collapsed (water content inside the domains is negligible) and γ is the surface tension at the interface between collapsed hydrophobic domain and water. The latter is an increasing function of temperature and of the ionic strength in the solution, because both are increasing polarity of water and thus increasing the strength of hydrophobic attraction.

The conformational entropy and the steric repulsion penalty for association of a group of hydrophobes into a hydrophobic domain is $\sim kTN_{\mathrm{agg}}^{1/2}\ln(p/[H])$. Then the intramolecular aggregates are formed if $kT\ln(p/[H]) \leq \gamma(pn)^{2/3}$. At a given number p of hydrophobes in a sequence, the latter condition implies that the fraction of hydrophobic units in the chain should exceed the characteristic value $[H]_{\mathrm{min}} \sim p\exp[-\gamma(pn)^{2/3}/kT]$. Hence, when $p>1$ the value of $[H]_{\mathrm{min}}$ is a decreasing function of p, i.e. grouping of hydrophobic monomers in sequences at constant $[H]$ promotes intramolecular association.

These arguments imply that the probability of intramolecular association decreases when p decreases and provide an explanation why no signatures of intramolecular association have been observed in dilute salt-free aqueous solution with our polymers in which $p=1$.

However, addition of salt leads to an increase in the strength of hydrophobic attraction and, consequently, to an increase of the surface tension γ. As a result, the minimal fraction of hydrophobes necessary to be included in the chain in order to make for intramolecular association thermodynamically favorable also decreases. Hence, for a given chemical composition (fraction of hydrophobes), addition of salt may trigger intramolecular aggregation even if this aggregation does not occur in the salt-free solution. This type of salt-induced intramolecular aggregation, manifested in significant drop in reduced viscosity with respect to that of the parent PAM, occurs apparently for HAPAM with statistical distribution of hydrophobes studied here.

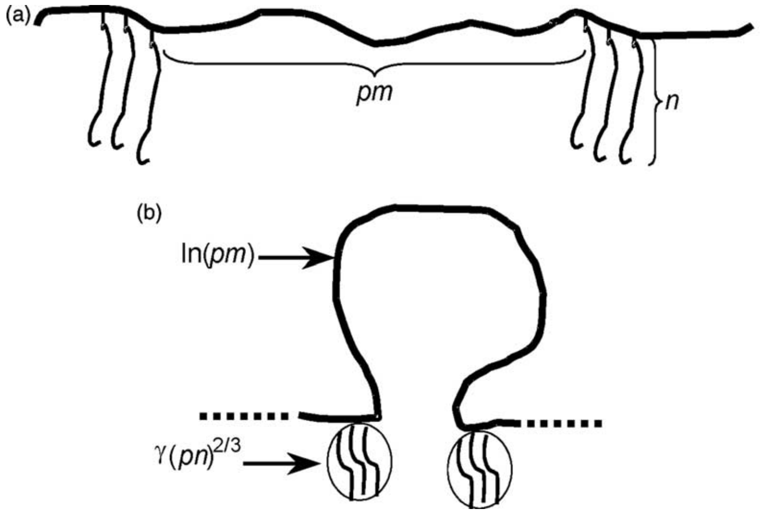

Fig. 8. Model of intramolecular association in associative polymers, $m=1/[H]$.

We should remark that due to random distribution of hydrophobes along the chain we can not exclude formation of small intramolecular aggregates within 'more hydrophobic' segments of the chain, where fraction of hydrophobic monomers may exceed significantly the average value. However, this effect is weak and does not lead to detectable (in viscosity) collapse of chain.

On the other hand, due to the presence of small number of statistically appearing segments with enhanced hydrophobicity within individual chains, the possibility to form loose intermolecular aggregates in dilute solution (below the overlap concentration of individual chains) arises.

This behavior is similar to that of hydrophobically one- or two-end modified (telechelic) poly(ethylene oxide) based polymers (PEOAP) which start to micellize at CAC which is much lower than C^*, depending on their composition (respective length of PEO and aliphatic end groups). In the latter case, each polymer chain possesses one or two hydrophobic groups and micellization occurs highly cooperatively, i.e. with well-defined CAC and large aggregation numbers in micelles with a hydrophobic core and star-like or flower-like shape of the corona [67]. Due to random positioning of sequences with enhanced (but still relatively weak) hydrophobicity along the statistically modified HAPAM chains (and between the chains), the intermolecular association in dilute solution of HAPAM occurs less cooperatively, i.e. there is no indication of CAC in our case.

Moreover, the fluorescence study indicates no presence of strongly hydrophobic domains in dilute solution in pure water (no noticeable decrease in the I_1/I_3 ratio), in contrast to what is observed in salty solution. This observation indicates that intramolecular association in dilute solution occurs via formation of a small number of relatively loose hydrophobic clusters.

It is a difficult experimental task to find average aggregation number in our case. In this work, with our samples H00C8-1.0, light scattering measurements give an average number of chains per aggregate of approximately 3, but if one takes into account the reduced viscosity of samples H00C12-05 and H00C12-1.0, the aggregates are probably much larger. This is consistent with the higher hydrophobicity of aliphatic chain with 12 carbons. However, complementary experiments should be made in order to check the effect of the method of preparation of the solutions and a new theoretical approach should be developed to understand the intermolecular association mechanism in the dilute regime of the associative polymers.

Remarkably, it has been observed that as soon as salt favors intramolecular association (manifested a decrease in intrinsic viscosity), the intermolecular association is suppressed (kinetically hindered) since the apparent molecular weight found from SLS measurements in the salt-added solution is the same as in formamide or for the parent sample. This suggests that practically all the hydrophobes are involved in intramolecular association.

4.3. Crossover between dilute and semi dilute regimes

The strong increase of viscosity of aqueous solutions of HAPAM above a given concentration threshold is exploited in a variety of practical applications and is of great interest for the application in enhanced oil recovery. It is then important to understand the association mechanisms at the molecular level to be able to control these industrial processes. However, there are controversies in literature concerning interpretation of the experimental results on viscosity of semi-dilute HAPAMs solutions.

As shown in Fig. 1(a) and (b), a significant deviation from slow variation of viscosity at small concentration is observed for the various HPAM in pure water at concentrations C_η roughly equal to $1/[\eta]$ which is much lower than the critical overlap concentration C^*_{PAM} of the parent polymer. Using the empirical law $[\eta]=9.33\times10^{-3}\,\overline{M}_{\mathrm{w}}^{0.75}$, one can calculate for our parent PAM the intrinsic viscosity $[\eta]$ and $C^*=2\times10^{-3}\mathrm{g\ mL^{-1}}$ or 0.2 wt%, which is well consistent with the measured viscosity curve of this polymer. However, for H00C12-1.0, H00C12-0.5 and H00C8-1.0 polymers, the concentration C_η at which viscosity starts to increase sharply can be determined as 0.01, 0.05 and 0.07 wt%, respectively. This result is consistent with the high value of intrinsic viscosity measured in pure water for these polymers. The onset of the increase in viscosity occurs when loose aggregates already present in solution at lower concentration start to overlap. At larger concentration the number of the hydrophobic domains (per unit volume) increases, resulting in an increase of viscosity, as demonstrated by Shaskhina et al. [22].

Regalado et al. [68] have compared various HAPAM samples prepared by micellar polymerization (i.e. with blocky distribution of hydrophobes) by varying molecular weight as well as the molar fraction of hydrophobes $[H]$ and the number of hydrophobes per block p. A sharp transition between the dilute regime and the semi-dilute unentangled regime for a value of concentration C_η which depends on molecular weight of PAM but is independent of p and $[H]$ has been observed. However, the conformation of these polymers in the dilute regime is strongly affected by intramolecular association resulting in a decrease in reduced viscosity, which should lead to an increase of C_η.

It is again interesting to note that the crossover behavior of our polymers differs in pure water from that of the blocky associative polymers, but becomes similar in the presence of salt.

Finally, we can suggest that the formation of intermolecular associations upon an increase in concentration in dilute regime may be a quite general feature. Even when the dilute regime is dominated by intramolecular association, the expected increase of C_η is compensated by the aggregation phenomenon which tends to decrease C_η. Then the observations of Regalado et al. [68] may be fortuitous and be the result of such compensation.

4.4. Semidilute regime

In the semidilute solutions of linear homopolymers, one can distinguish between the region $C^* < C < C_e$, where C_e represents the characteristic concentration at which polymer chains start to entangle, and the region for $C > C_e$, where the viscosity follows the power law $\eta \propto C^4$. In the latter (entangled) regime, the viscoelasticity of the solutions is described by a reptation model.

For HAPAM characterized by a blocky distribution of hydrophobes, Regalado et al. [68] have reported these two distinctive regimes. Their findings indicate that in the concentration range $C^* < C < C_e$, the rate of an increase of viscosity as a function of C depends on the values of p and $[H]$. For large values of p and $[H]$, the slope of $\log \eta$ versus $\log C$ is higher than that observed in the same regime for parent PAM and can even exceed 4. At higher concentrations, the viscosity is always much larger than that of PAM solutions of the same concentration and follows a universal power law as a function of concentration with the exponent 4 which represents the characteristics of the entangled regime of linear polymers.

The behavior of our polymers in pure water above C_η is similar to that described by Regalado et al. [68] for the lowest value of p ($p = 2$): A slow variation of viscosity in the intermediate regime $C^* < C < C_e$ and an exponent which tends to 4 for $C > C_e$ is observed. We have to stress once again that polymers prepared by post-modification behave in the presence of salts similar to HAPAM with blocky distribution of hydrophobes in pure water. This observation again illustrates the enhancing effect of salt on the hydrophobic interactions.

As follows from the survey of results of different experimental studies on rheological behavior of associative grafted copolymers, there is no complete understanding of their viscoelastic behavior of the aqueous solutions up to now. The reason of this lack of a comprehensive picture may be due to numerous factors, which influence viscosity. There is no quantitative explanation of the fast increase of viscosity in the region $C^* < C < C_e$, which is observed for the high values of p (blocky distribution). This behavior is reminiscent to that described for telechelic polymers. In these cases, at the concentration when the ‘flower-like’ micelles start to overlap, viscosity jumps by several orders of magnitude in a very narrow range of concentration. This jump is attributed to the formation of intermolecular bridges [69]. Semenov et al. [69] have predicted an increase of viscosity by the factor of $\exp(B)$, B being the energy of disengagement of one hydrophobe extremity from a micelle. In the case of grafted polymers with high values of p, the fast increase of viscosity should be also attributed to formation of intermolecular associations and the energy of disengagement may strongly vary with the parameter p, the number of hydrophobes in a block.

In the entangled regime, Regalado et al. [68] propose to apply the model of reversible network developed by Leibler et al. [70]. However, this approach strictly applies to binary physical crosslinks while fluorescence experiments show that the hydrophobic domains in associative grafted polymers have aggregation number as high as 80.

Finally, one must point out that it is difficult to perform accurate viscosity measurements in the semidilute regime with such polymers. The reproducibility of the measurements, the shift of viscosity with time and the method of preparation of the solution should always be emphasized in all the experimental reports.

4.5. Salt-induced shear thickening effect

Unique rheological behaviors of HAPAM polymers in brine have been discussed in detail in our preliminary studies [42], that is, shear-thickening behavior is evidenced upon addition of salt. These phenomena can be interpreted by a combination of balance of shifting from intra- to intermolecular associations and the participation of free hydrophobes into aggregative clusters under shear.

5. Conclusions

The aqueous solution properties of non-hydrolyzed PAM and its hydrophobically modified associating analogues prepared by post-modification were investigated by viscometry, rheometry, static light scattering and fluorescence spectrometry in absence and in presence of salt and compared to those of HAPAMs prepared by micellar copolymerization. In dilute region, the reduced viscosity of HAPAM polymer in pure water is higher than that of PAM, which indicates formation of loose intermolecular aggregates. Presence of such aggregates is also confirmed by light scattering.

The observed behavior differs from that described in literature for HAPAMs prepared by micellar polymerization and can be explained by specific feature of the molecular architecture of the HAPAMs prepared by post-modifications (single hydrophobs instead of hydrophobic sequences along the chain), that prevents intra-molecular aggregation in the dilute solution.

The addition of salt significantly decreases reduced viscosity and radius of gyration of HAPAM polymer measured by light scattering. In the semidilute domain, dramatic increase in viscosity for HAPAM polymers upon increasing salinity, and unique shear-thickening behaviors are evidenced when introducing salt into HAPAM polymer aqueous solutions. At low shear rate, the viscosity is high compared with PAM as a result of hydrophobic association in aggregates. When shear rate increases, viscosity drops due to disconnection of the chain entanglement.

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