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Hydrophobically associating polyacrylamides and their partially hydrolyzed derivatives prepared by post-modification.

1. Synthesis and characterization

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Abstract

Hydrophobically associating polyacrylamides (HAPAMs) or hydrophobically associating hydrolyzed polyacrylamides (HHAPAMs) are generally prepared by micellar copolymerization which leads to a blocky distribution of hydrophobes and drifted compositions. In the present study, a series of HAPAMs were prepared by direct N-alkylation of the amide groups of a parent polyacrylamide (PAM) in DMSO with alkyl bromide in the presence of potassium *tert*-butoxide. The derivatives HHAPAMs with various charge densities were obtained by partial hydrolysis of HAPAM precursors with 0.25 M NaOH in a 0.1 M NaCl aqueous solution at 50 °C. Molecular weight determination showed no degradation occurred in both processes. ^{1}H and ^{13}C solution NMR elucidations of hydrophobic group incorporation and degree of hydrolysis showed good agreements with feed ratio. Statistical hydrophobic group distribution along the polymer backbone was expected. For samples with high viscosity and poor solubility, gel HRMAS NMR was successfully employed. The results indicate that post-modification is a more effective way to control the composition of HAPAMs compared against micellar process. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Hydrophobically associating polyacrylamide; Partially hydrolyzed hydrophobically associating polyacrylamide; Post-modification

1. Introduction

Over the past two decades, hydrophobically modified water-soluble polymers (HMWSPs) have attracted increased interest owing to their practical and fundamental importance [1–9]. This system usually consists of a major part of hydrophilic backbone and a small proportion of hydrophobic groups. When dissolved in aqueous solution, the apolar moieties tend to exclude water and are held together, yielding intra or intermolecular association. In the semi-dilute regime, intermolecular aggregates prevail over intramolecular ones and clusters of hydrophobic domains are formed. This leads to a transitional network structure which induces a substantial increase in solution viscosity. It is speculated that these dynamic junctions are disrupted upon high shear stress, but will reform when the force ceases. Such salient macroscopical rheological features, as well as strong viscosifying ability, enable HMWSPs to be attractive to various industrial uses where the control of fluid rheology is required [1–9], for example, coating and paints, cosmetics, drilling fluid, petroleum recovery and foods. In the concentrated domain, viscoelastic physically linked gel can be obtained [10]. This renders possibilities in applying in drug release and control, agricultural agents, adsorbents, or separation processes, where the hydrophobic microdomains serve as reservoirs for an organic solute to be released over long periods or as sinks for organic solutes permeating an aqueous network [11–13]. Recent studies have also proposed applications as matrixes for immobilization of enzymes and drugs [13], or as supporting materials for hydrophobic chromatography [14]. From a fundamental point of view, characterization of polymer composition and hydrophobic aggregates of HMWSPs pose a set of challenges in that most techniques probe structures in a limited dimensional range [6]. Understanding the relationship between the molecular structure and final polymer properties represent another key respect. A typical example is how the architecture parameters such as the molecular weight of the polymer, the nature and level of the hydrophobe, or the relative placement of the non-polar groups along the polymer skeleton influence the final aqueous solution rheological behaviors.

In general, two topologies of HMWSPs can be classified based on the location of hydrophobic groups. One is that of telechelic associative polymers in which the polymer is

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end-capped with hydrophobic groups. Typical examples are hydrophobic ethoxylated urethane (HEUR) [15,16] and hydrophobically modified poly(ethylene oxide) (HMPEO) [17–19]. The other type, called graft or comb-like, in which the hydrophobic units are incorporated as lateral groups. Of particular interest in this class are hydrophobically associating polyacrylamides (HAPAMs), derived from polyacrylamide by introducing a relatively low amount (generally less than 2 mol%) of hydrophobic pendent groups [9]. Much attention has been focused on HAPAMs as they are regarded as promising candidates for chemically enhanced oil recovery (CEOR) [20–23]. It is believed that HAPAMs can overcome the deficiencies of their unmodified analogues, namely, polyacrylamide or partially hydrolyzed polyacrylamide, which are sensitive to mechanical degradation, the presence of electrolytes and high temperature.

As has been shown [20], the aggregation efficiency and thus the subsequent rheological properties of HAPAMs rely strongly on their structural characteristics, notably on the content and the nature of hydrophobes and their distribution along the polymer chain. Other architectural parameters such as molecular weight and the properties of hydrophilic backbone may play important roles as well. Some of these variables, for instance, hydrophobe distributions and molecular weights can be tuned by synthetic processes.

Basically, there are two ways to incorporate hydrophobic moieties on to water-soluble polymer chains [24], i.e. direct copolymerization of hydrophobic and hydrophilic monomers, or post-modification of the parent water-soluble polymer. For HAPAMs, specialized polymerization techniques are always required since acrylamide and hydrophobic comonomers are mutually incompatible. After attempts using heterogeneous [25,26], inverse emulsion [27], microemulsion [28], and precipitation [29,30] copolymerization processes, the final commonly accepted method is micellar free radical copolymerization in which an appropriate surfactant is used to solubilize the hydrophobic comonomer [31,32]. However, the composition of polymer prepared from micellar process always drifts because of the increased reactivity of the hydrophobic monomer when solubilized in micelles [33]. Furthermore, with this copolymerization technique, even under the identical experimental conditions it is very difficult to get samples of PAM and HAPAM with similar molecular weights. This leads to somewhat difficult comparisons of final properties of unmodified and modified polyacrylamide [33]. Additionally, with the micellar method, the micro-heterogeneous process leads to a polymer with blocky distribution of the hydrophobes along the backbone [32]. While by using post-modification of a preformed polymer, a statistical arrangement of hydrophobes can be expected because of the homogeneous reaction medium [34]. Other favorable characteristics due to post-modification process include that one can control over the parameters of interest such as hydrophobic group content or hydrophobe structure while keeping the molecular weight and hydrophobic group distribution constant, and that commercially available polymers can be used as starting material. These advantages have been witnessed in preparing hydrophobically modified hydroxyethyl cellulose (HMHEC) [35], HMPEO [17–19] and hydrophobically modified poly(acrylic acid) [36]. Despite the merits of post-modification against the problems encountered with the micellar process, relatively few studies have been focused on the polymer modification process to prepare HAPAMs. Very recently, Bromberg [37] developed a novel approach by grafting poly(oxyethylene)-*block*-poly(oxypropylene)-*block*-poly(oxyethylene) on to PAM in melts of acrylamide in the presence of benzoyl peroxide to obtain a self-assembling material. Deguchi and Lindman [38] synthesized HAPAM by direct modification of a low molecular weight PAM with alkyl bromide in DMSO. However for higher molecular weight PAM samples, this method was not reported much.

The limited dissolution ability of HAPAMs will probably impede their popularization in some applications, for instance, in petroleum recovery. It has been reported that weeks are often necessary to dissolve HAPAMs from the dry state [39]. A possible way to overcome this is to introduce charged groups on to the polymer backbone [21]. The presence of charged units can not only impart better hydrosolubility but also elongate the polymer chain to increase its hydrodynamic volume and thus solution viscosity [40]. Nevertheless, incorporation of some charged groups on to HAPAM is not well understood because inadequate results have been discussed. To our knowledge, only a few reports [41–51] so far deal with HAPAMs containing both hydrophobic and carboxylate groups. And again, most of these polymers are prepared via micellar copolymerization of acrylamide, sodium acrylate and a hydrophobic monomer [41–45]. Apparently, these low to moderate charge density polyelectrolytes can offer increased solubilities over non-ionic associative polymers. However, due to electronic interferences between the anion carboxylic groups and the negatively charged micelles during polymerization, much lower levels of hydrophobe incorporation are achieved [42]. And from the micellar process, blocky distribution of hydrophobes and isolated carboxylate placement along polymer chain are anticipated.

In our laboratory, an attempt has been made to prepare higher molecular weight HAPAMs and their partially hydrolyzed derivatives by post-modification. Starting with a PAM, a series of hydrophobic groups with different lengths or different contents were incorporated. Then, these samples were partially hydrolyzed to obtain their derivatives with both hydrophobic groups and charged units. In addition, we have been able to lock more variables, such as molecular weight, hydrophobe content and distribution, so as to directly compare polymers prior and after modification. In the present study, we detail the preparation procedure and structural elucidation of these polymers. Their rheological behaviors in pure water and brines will appear in a following publication [52].

2. Experimental

The general schematic route for the synthesis of the polymers used in this work has been depicted in Fig. 1.

2.1. Materials

Acrylamide (99 + %), potassium persulfate (KPS) (99 + %), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (99%), potassium *tert*-butoxide (95%), dodecyl bromide (97%), octyl bromide (99%), ethyl bromide (99%), anhydrous dimethyl sulfoxide (DMSO) (99.8%) were purchased from Aldrich Chemical Co and used as received. All other reagents and nitrogen gas were obtained from commercial sources. The water was distilled three times with an all-glass apparatus.

2.2. Homopolymerization of acrylamide

Parent polyacrylamide was prepared by a homopolymerization process. The reaction was conducted in a 1 l water-jacketed cylindrical reaction vessel equipped with a motor-drive mechanical stirrer, a thermometer, and a nitrogen inlet and outlet. A given amount (0.25 mol, 17.77 g) of acrylamide was dissolved in 500 ml water followed by 30 min purified nitrogen purge. 2.5 ml of 0.1 mol l^{-1} KPS and TMEDA aqueous solutions were then injected successively. The polymerization was conducted at 30.0 ± 0.1 °C with a thermostatically controlled water circulating bath. After 2 h of stirring under nitrogen atmosphere, the polymerization was terminated by pouring the reaction mixture into seven times excess of methanol with gentle stirring. The precipitated product was filtrated and further dissolved in water and then reprecipitated in methanol. The final product was dried under vacuum at 50 °C for 48 h prior to being stored in a desiccator. Neither methanol nor monomer residing in the polymer was indicated by ^{1}H NMR spectrum (Fig. 2b).

2.3. Hydrophobic modification of polyacrylamide

The incorporation of hydrophobe groups on to the hydrophilic PAM backbone was accomplished by a novel approach proposed by Deguchi and Lindman [38] but with some revision of their work here. A typical procedure for preparing H00C8-1.0 (see Section 2.5.1 later) (Fig. 1) is described as follows: 4.0 g PAM (5.63×10^{-2} mol AM) and 380 ml anhydrous DMSO were introduced into a 1 l, four-necked round flask equipped with a condenser, a nitrogen inlet/outlet, and a mechanical stirrer. When the dissolution of PAM in DMSO was thoroughly complete after 20 h of constant stirring at 80 °C under nitrogen atmosphere, the solution was cooled to room temperature. Then 10 ml of anhydrous DMSO solution containing potassium *tert*-butoxide (0.332 g, 2.81×10^{-3} mol) was added dropwise with active stirring, and the mixture was continuously stirred for 1 h. Afterwards octyl bromide (0.110 g, 0.56×10^{-3} mol) was dissolved in 10 ml DMSO and added dropwise by syringe. The alkylation reaction proceeded at 65 °C with agitation for 24 h. Nitrogen atmosphere was maintained and the reaction mixture remained homogeneous. After terminating the reaction by adding 400 ml of cool water, the final milky reaction mixture was poured into a dialysis cassette with Spectra/Por® cellulose dialysis membrane and dialyzed against continuous tap water for one week, then against distilled water for another week. White solid product was obtained by lyophilizing the dialyzed polymer solution. The same procedure was used for preparing other HAPAMs.

2.4. Hydrolysis of HAPAM and PAM

Hydrolyzed derivatives of HAPAMs were prepared in a similar fashion to hydrolyzed PAM reported previously [53]. HAPAMs were firstly dissolved into a 0.1 M NaCl aqueous solution in a well-stirred double-jacket conical flask and polymer concentration was kept at 0.1 M. Then, solid NaOH was added with its concentration 0.25 M in the solution. The reaction time lasted for 15, 75 and 240 min at 50 °C corresponding to the hydrolysis degree 10, 25 and 40 mol% as reported by Truong et al. [53]. The final mixtures were precipitated in excess of ethanol and washed several times by acetone and then dried under the same conditions mentioned earlier. For comparison, partially hydrolyzed polyacrylamides (HPAMs) with different charge densities were prepared under identical experimental condition.

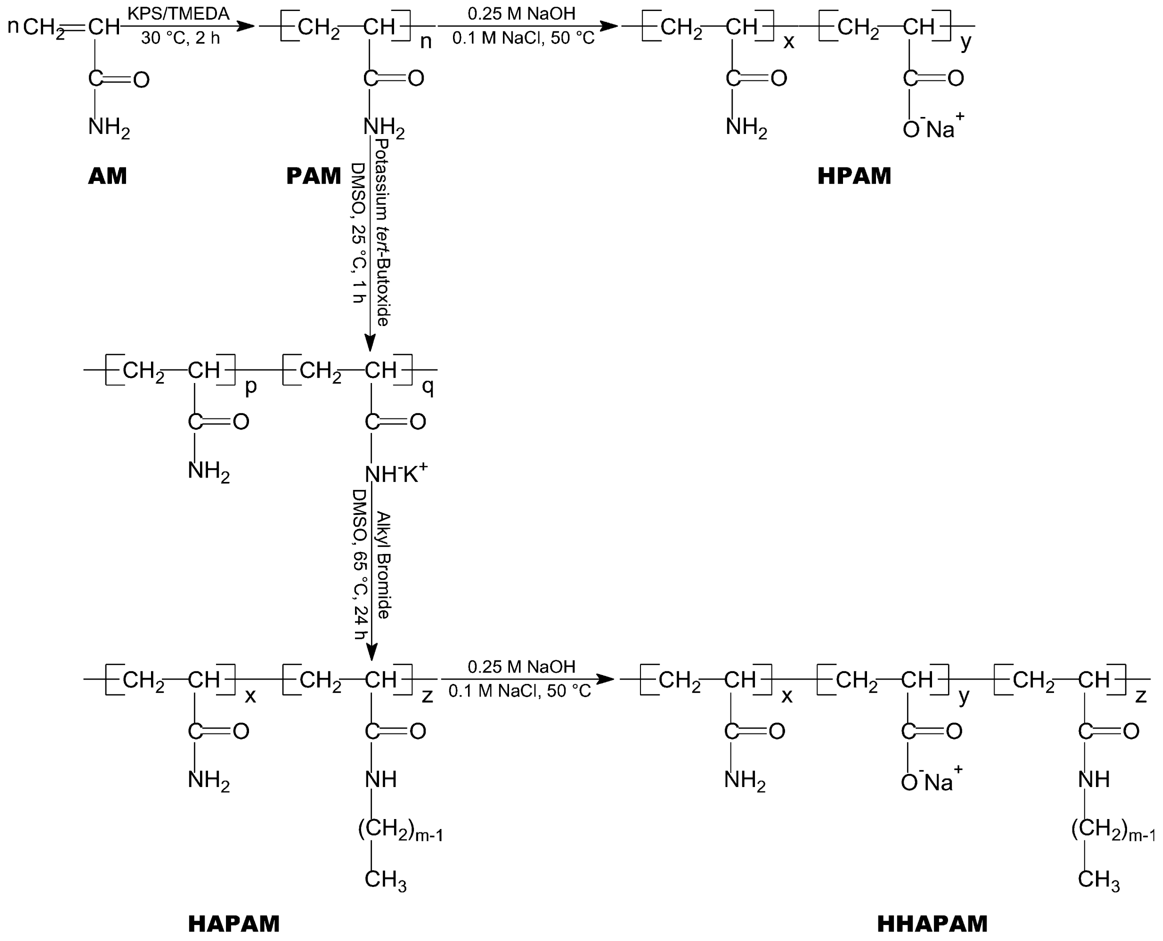
2.5. Composition characterization

2.5.1. Nomenclature

As listed in Fig. 1, the sample codes refer to the hydrolysis degree, hydrophobe length and content of polymers. For example, in the sample code for ‘H25C8-1.0’, ‘H’ stands for hydrolysis, the number ‘25’ followed means the hydrolysis degree, mol%; ‘C’ stands for hydrophobic group, ‘8’ means hydrophobic length, and the final number ‘1.0’ indicates the hydrophobe content, mol%.

2.5.2. NMR elucidations

Hydrophobe incorporation and hydrolysis degrees were determined by both ^{1}H and ^{13}C NMR spectroscopy in D_2O. All spectra were recorded on a Bruker AVANCE 400 MHz spectrometer. ^{1}H spectra were obtained at 400 MHz while ^{13}C at 100 MHz. For the polymers with higher viscosities and poor solubilities, gel HRMAS (high resolution magnetic angle spinning) technique was used. Bubbles inside gels removed by centrifugation at



Designation

AM acrylamide

PAM polyacrylamide

HPAM partially hydrolyzed polyacrylamide

y=10 mol%, HPAM10

y=25 mol%, HPAM25

y=40 mol%, HPAM40

HAPAM hydrophobically associating polyacrylamide

m=8, z=1.0 mol%, H00C8-1.0

m=12, z=1.0 mol%, H00C12-1.0

m=12, z=0.5 mol%, H00C12-0.5

HHAPAM partially hydrolyzed hydrophobically associating polyacrylamide

m=8, z=1.0 mol%, y=10 mol%, H10C8-1.0

m=8, z=1.0 mol%, y=25 mol%, H25C8-1.0

m=8, z=1.0 mol%, y=40 mol%, H40C8-1.0

m=12, z=1.0 mol%, y=25 mol%, H25C12-1.0

m=12, z=0.5 mol%, y=25 mol%, H25C12-0.5

Fig. 1. Schematic route to prepare HMPAMs, HPAMs and HHAPAMs.

20000 rpm for about 10 min prior to characterization. All spectra were recorded at 27 °C. Chemical shifts are reported as ppm downfield from 4,4-dimethyl 4-silapentane sodium sulfonate (DSS).

2.5.3. Viscometry

An automatic Ubbelohde capillary viscometer (Fica) was employed to measure the intrinsic viscosity of parent PAM and the hydrophobically modified polymer, H00C8-1.0.

Measurements were performed at 25 ± 0.1 °C. The capillary diameter was 0.56 mm. All the solutions prepared in the same way as described below for light scattering experiment. The solvents are filtrated through 0.1 μm Millipore filters.

2.5.4. Static light scattering

Carefully prepared stock polymer solutions (6×10^{-3}g ml^{-1}) were ultracentrifuged at 20000 rpm for 9 h in a SIGMA 3K30 centrifugator at 15 °C. All solvents were filtrated 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 was varied between 30 and 150°.

3. Results and discussion

3.1. Hydrophobic modification of PAM

The synthesis of HAPAM in DMSO was firstly used by Deguchi and Lindman [38], and derived from a method developed by Jannasch and Wesslén [54] to alkylate the copolymer of styrene and acrylamide in 2-ethoxyethyl ether. In spite of the poor solvent quality of DMSO for PAM at room temperature, it was confirmed [38] that PAM could be easily dissolved into DMSO at 80 °C with vigorous stirring over a long period. Our work also verified this result. But it seems that the solubility of PAM in DMSO relies mainly on molecular weight and concentration of PAM used. In their work, Deguchi and Lindman [38] found complete dissolution in DMSO for a PAM with M_W 4.8×10^5 g mol^{-1} after 1 day agitation at 80 °C. Under identical conditions in this work, for the higher molecular weight PAM ($M_W = 2.25 \times 10^6$ g mol^{-1}) prepared in this work, even after 2 days of vigorous stirring, we just observed swelled gel rather than homogeneous solution. But when decreased its concentration to 1 wt%, a homogeneous solution can be obtained after only 20 h of stirring at 80 °C.

It is reported that only one of the two hydrogens in the primary groups of PAM is active [54]. In presence of *tert*-butoxide anions, the amide groups were attacked and partially ionized (Fig. 1). This could be verified by increased viscosity after adding potassium *tert*-butoxide into the dissolved PAM solution, because the ionized amide groups along the polymer chain repulse each other. The ionized amide groups are strongly basic and nucleophilic, and part of these ionizing amide groups can be utilized as sites for nucleophilic substitution reactions with alkyl bromide to give N-alkylated PAM. The bromide anion, which can be regarded as good leaving group in SN2 reactions, does not take part in any side reactions [54]. Remaining anions subsequently revert to amide groups when in contact with water.

It is worth noting the importance of the purification

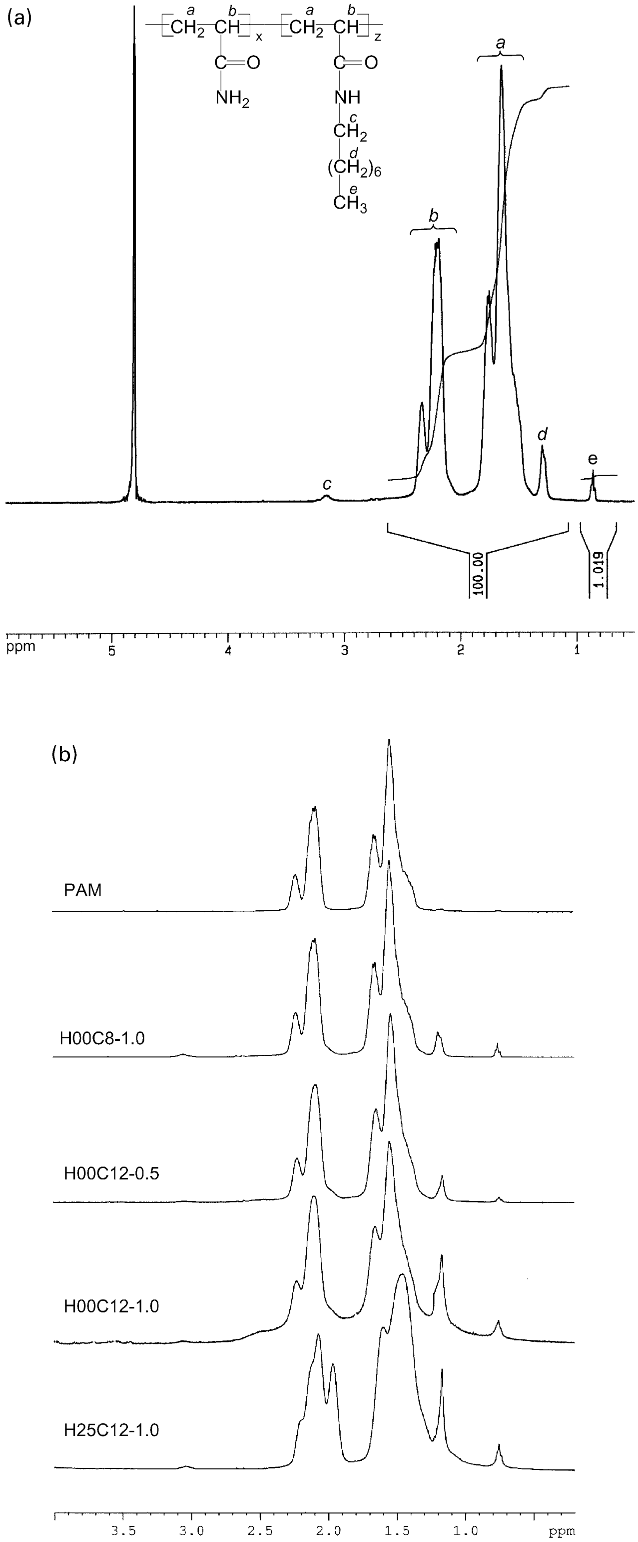


Fig. 2. ^{1}H NMR characterization of PAM, HAPAMs and HHAPAM: (a) H00C8-1.0; (b) comparisons for PAM, HMPAMs and HHMPAM (H25C12-1.0 characterized by gel HRMAS NMR).

methods used. When the coupling reaction was terminated by introducing equal amount of cool distilled water, the final solution immediately became a milky mixture. And this mixture could not be precipitated in solvents used for precipitating PAM, such as methanol, ethanol or acetone or mixture of them because of the low concentration, high viscosity of HAPAM and micellization. Even with a dialysis bag against distilled water (changed every 2 or 3 h), it was very difficult to remove all the reaction residues. After 20 days of dialysis, some milky residues suspending on the top of dialysis bag column can still be observed. For this reason, we employed a two-compartment dialysis cassette which was divided into two equal cabins, one for polymer solution and the other for water. One piece of dialysis membrane (M_W cut-off 12000–14000) was inserted into the joint of the two parts. Gentle continuous magnetic agitation was applied in the compartment of polymer solution mixture during dialysis and the water in the other compartment was continuously renewed. This method allowed us to efficiently remove the low molecular weight molecules, such as the unreacted 1-bromoalkanes, potassium *tert*-butoxide and DMSO. Two weeks later, as shown by ^{1}H NMR spectra of Fig. 2(a) and (b), no unreacted chemicals resided in the final polymers.

3.2. Characterization

3.2.1. Hydrophobe content

Elucidation of molecular architecture of HAPAMs by traditional methods such as elemental analysis is difficult due to the too low percentage of hydrophobic monomer in the polymer. Consequently in most studies the hydrophobe content is assumed to be equal to the initial feed composition [32]. This probably leads to some error because the composition of HAPAMs prepared from the micellar process always drifts. Incorporation of a hydrophobic comonomer containing a chromophore such as phenyl or other aromatic groups allows detection by ultraviolet spectroscopy accurately [32].

In this work, we confirmed that it is possible to detect the content of non-chromophore hydrophobe as low as 0.5 mol% with careful ^{1}H NMR characterization. ^{1}H NMR spectra of the polymers prepared in this work are reproduced in Fig. 2(a) and (b). Compared with the unmodified PAM, the spectrum of HAPAM shows three additional peaks due to the hydrophobe protons. As shown in Fig. 2(a) corresponding to H00C8-1.0, protons in the methylene connected to acrylamido group ($-NH-CH_2-$) were evidenced by the weak peak at 3.2 ppm. The protons in other methylenes ($-(CH_2)_n-$) in alkyl side chains can be found at 1.3 ppm and the end methyl ($-CH_3$) at 0.9 ppm. The peak of terminal methyl groups of the hydrophobe is sufficiently separated to yield the hydrophobe content from their area ratio (Fig. 2(a) and (b)). So, for example, the hydrophobe content in H00C8-1.0 can be calculated by using Eqs. (1) and (2).

$$S_e/(S_a + S_b + S_d) = 3z/(3x + 15z) \tag{1}$$

$$x + z = 100 \tag{2}$$

as indicated in Fig. 2(a), where S_e, S_d, are the integrating areas of protons in $-CH_3$ and $-(CH_2)_n-$ of alkyl side chain, S_a and S_b are integrating areas of protons in polymer backbone. x and z stand for acrylamide and hydrophobe contents respectively, in mol%. The hydrophobe content for all other HAPAMs was calculated in the same manner and the results were given in Table 1. In the unhydrolyzed samples H00C8-1.0, H00C12-1.0 and H00C12-0.5, z was found to be 1.0, 1.0 and 0.5 mol%, respectively, which corresponds exactly to the feed compositions, meaning that the chemical modification is a quantitative reaction. Further, the absence of the triplet at 3.6 ppm (α-methylene protons of an alkyl bromide) indicates that the product is free of the unreacted alkyl bromide. Wang et al. [36] reported for a hydrophobically

Table 1
Chemical parameters of PAM, HPAM, HAPAM and HHAPAM

Sample code	Composition				Yield (%)
	Feed ratio (mol%)		Final product (mol%)		
	Hydrophobe	COO^-	Hydrophobe	COO^-	
PAM	0	0	0	0	92.1
HPAM10	0	10	0	10.6	–
HPAM25	0	25	0	30.2	–
HPAM40	0	40	0	45.3	–
H00C12-1.0	1.0	0	1.0	0	–
H00C12-0.5	0.5	0	0.5	0	93.4
H00C8-1.0	1.0	0	1.0	0	96.2
H25C12-1.0	1.0	25	1.0	30.1	–
H25C12-0.5	1.0	25	0.5	28.1	–
H10C8-1.0	1.0	10	1.0	12.0	–
H25C8-1.0	1.0	25	1.0	29.2	–
H40C8-1.0	1.0	40	1.0	40.1	–

modified poly(acrylic acid) a 100% modification was attained. Lindman group [38] obtained similar results in preparing HAPAM by post-modification. These reports, together with our results in this work, show that it is more efficient to control the graft ratio by using a post-modification process, in other words, the composition does not drift as the reaction media is homogeneous.

For comparison, the incorporation of hydrophobes in H25C12-1.0 was also determined, as shown in Fig. 2(b) and Table 1, which was well consistent with its precursor H00C12-1.0. This means that the hydrolysis procedure does not cut the hydrophobic side groups.

3.2.2. Hydrolysis degree

Potentiometric titration is a classical way to determine charge content in partially hydrolyzed polyacrylamides [53]. However, for the partially hydrolyzed HAPAMs used in this work, we found very limited solubilities when they are in the acid form after exchange with cationic resin. Another effective approach to determine hydrolysis degree of HPAM is ^{13}C NMR [53] and its validity has been confirmed previously in good agreement with elemental analysis results [55]. Nevertheless, characterization of hydrolyzed HAPAMs by solution ^{13}C NMR represents a challenge even though this technique has been successfully employed in elucidation of composition of HPAMs [53,55]. In general, solution ^{13}C NMR necessitates concentrations of 5–20 wt% in D_2O to obtain good quality spectra. For high molecular weight ($>10^6$ g mol^{-1}) HAPAMs and their hydrolyzed derivatives, preparation of homogeneous solutions at such high concentrations requires a considerable amount of time and the resulting high viscosity induces a broadening of the NMR peaks. Though ultrasonic treatment was suggested for acrylamide-based high molecular weight polymers to prompt rapid dissolution and to decrease the solution viscosity to manageable levels [56], it may degrade the hydrophobic side chains in the case of HMWSPs. To overcome this problem, Gelman et al. [57] have shown methanol can suppress hydrophobic aggregation in aqueous solutions of HMCMC. Magny et al. [34] followed this method to characterize hydrophobically modified poly(acrylic acid), but they found the viscosity still remains high and phase separation may occur. Finally they successfully determined the microstructure by using a mixture of D_2O/CD_3OD. Deguchi and Linman [38] reported the ^{13}C NMR characterization of HAPAMs by dissolving them into DMSO-d_6 at 50 °C. We tried to use these two methods to characterize our polymers but consequently we found that poor solubility and resolution remained [58], due probably to the high molecular weight of our samples.

Finally, we used two different methods to solve these problems: (i) the polymer concentration was decreased and the scanning time was increased to yield a proper signal-to-noise ratio (approximately, three days of accumulation to get the ^{13}C results for sample H40C8-1.0 at 2 wt% in D_2O). We obtained a satisfactory spectrum as shown in Fig. 3(a); (ii) ^{13}C gel HRMAS NMR technique was used for some samples, such as H25C8-1.0 and H25C12-1.0. This method allows an increase of the solid content of polymer samples in D_2O as high as 50 wt% to obtain a better resolution. Hydrolysis degree was determined for all hydrolyzed samples by calculating the ratios of the integrated areas of the peaks at 181 and 184 ppm which correspond to the carbons in carbonyl groups in acrylamide and acrylate units, respectively. This agrees very well with the ratio of areas of carbons in the methyne groups in acrylamide and acrylate unites (b_1

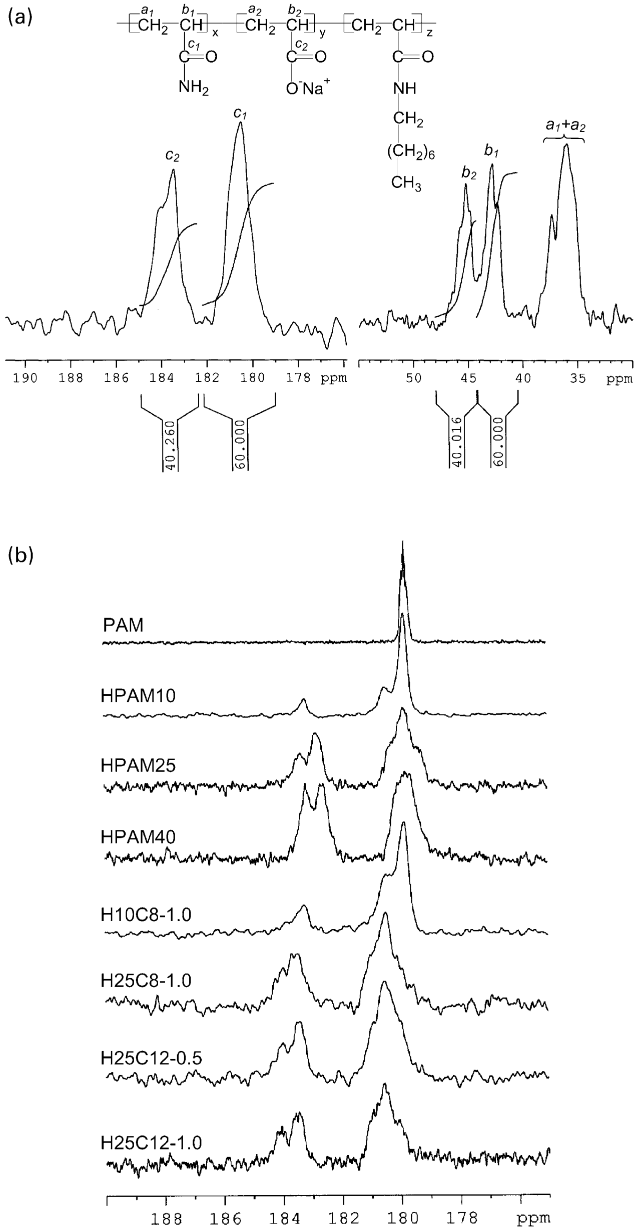


Fig. 3. ^{13}C NMR characterization of PAM, HAPAM and their hydrolyzed derivatives: (a) H40C8-1.0; (b) comparisons for PAM, HPAMs, HAPAMs and HHAPAMs (H25C8-1.0 and H25C12-1.0 characterized by gel HRMAS NMR).

Table 2
Molecular weight of modified and unmodified polyacrylamide in various solvents

Sample	In pure water (d*n*/d*c* = 0.165)[68]		In 0.1 M NaCl (d*n*/d*c* = 0.164)[68]		In formamide (d*n*/d*c* = 0.095)[68]	
	M_W	$[\eta]$ (ml g^{-1})	M_W	$[\eta]$ (ml g^{-1})	M_W	$[\eta]$ (ml g^{-1})
PAM	1.99×10^6	522	2.25×10^6	520	2.01×10^6	–
H00C8-1.0	–	–	3.05×10^6	300	1.93×10^6	–

and b_2 in Fig. 3a). The carbons in the carbonyl group of hydrophobic unit could not be identified because of the too low content of hydrophobic units. All the results are listed in Table 1.

3.2.3. Monomer distribution

Statistical hydrophobic sequences in hydrophobically modified poly(acrylic acid) has been confirmed by ^{13}C NMR [34]. Based on this result, Deguchi et al. [38] deduced similar hydrophobic placement existed in HAPAMs prepared in DMSO in the presence of potassium *tert*-butoxide. This seems reasonable because we observed a homogenous solution throughout the reactions. However, we insist that a direct evidence is necessary because hydrophobe arrangement along HAPAM chain prepared by this route depends not only on coupling reactions of alkyl bromide and ionized amide groups, but also on the ionization process of amide groups (see Fig. 1). In other words, both the arrangement of ionized amide groups and the attacking manner of alkyl bromide to these ionized groups influence the final hydrophobic group distribution. Unfortunately, the classical kinetic and NMR methods seem ineffective in these two processes to detect the incorporation of alkyl groups because of too low hydrophobic content. For this reason, the preparation of a series model HAPAMs with much lower molecular weight and shorter hydrophobic group length but much higher hydrophobic content is undergoing in this laboratory. These polymers are prepared under identical conditions as described earlier, and the final products will be specially used for elucidation of hydrophobic group distribution along polymer backbone.

As for placement of acrylates in the hydrolyzed derivatives, it is well known [53] that alkaline hydrolysis of amide group in PAM is an auto-retarded reaction which leads to a monomer distribution where the carboxylate groups are isolated along the chain. This has been confirmed by ^{13}C NMR.

3.2.4. Molecular weight

To verify that no degradation occurred in both hydrophobic modification and hydrolysis processes, it is necessary to confirm no changes in the degree of polymerization of PAM, HAPAM and HHAPAM. If their molecular weight can be determined precisely under identical conditions, this problem can be solved because their degrees of polymerization can be computed from their molecular weight providing the known hydrophobic content and hydrolysis degree. However, as reviewed by Candau et al. [32], little information is provided on the molecular weight determination in most papers reported so far because of the intermolecular association effect. For hydrophobically modified polyelectrolytes like HHAPAMs, this is more important since there are two opposing effects existed simultaneously: hydrophobic aggregation and Colombic repulsion. In the diluted regime, the first interaction leads to intramolecular association which decreases the polymer hydrodynamic volume while the latter force expands polymer coils and thus the hydrodynamic volume. Adding salt can screen out the polyelectrolyte effect [46,59], though, the hydrophobic intramolecular association will be enhanced at the same time. Some authors reported static light scattering measurements by disrupting intermolecular hydrophobic association with additives, such as methanol [60], or surfactants [61,62]. While these results, to some degree, can be used for relative comparison, some researchers [63] recently found in other associative polymer systems that both organic solvents and co-solvents do not remove all hydrophobic associations, and addition of surfactant will alter the polymer structure. Alternatively, Biggs et al. [64] claimed that formamide can satisfy the requirements of determination of molecular weight of HAPAMs in that values of index increment, d*n*/d*c*, of a series of HAPAMs with different hydrophobic contents in formamide were equal to that of pure polyacrylamide. We followed this idea to compare the results of PAM and H00C8-1.0. It seems that it is difficult to disrupt hydrophobic aggregates for the molecular weight of H00C8-1.0 is slightly lower than that of pure PAM (Table 2) and the dusts are very difficult to remove completely for the points in Zimm plot of H00C8-1.0 (Fig. 4b) are more scattered than those of PAM (not shown here). In 0.1 M NaCl, we obtained very beautiful Zimm plots for both H00C8-1.0 (Fig. 4a) and PAM (not shown here). But the measured molecular weight of H00C8-1.0 is much higher than that of PAM as shown in Table 2. This is due to the addition of NaCl induces hydrophobic aggregates. In pure water, it is very difficult to remove all the dusts in the solution of H00C8-1.0, even by centrifuge at 20,000 rpm for 9 h.

Some researchers estimated the molecular weight of HAPAMs from intrinsic viscosity measurements in pure water by using the relationship established for the unmodified PAM [65–67]. However, as the single polymer coil of HAPAM is more compact than that of unmodified PAM due to hydrophobic intramolecular interactions, the viscosity-averaged molecular weight values are underestimated.

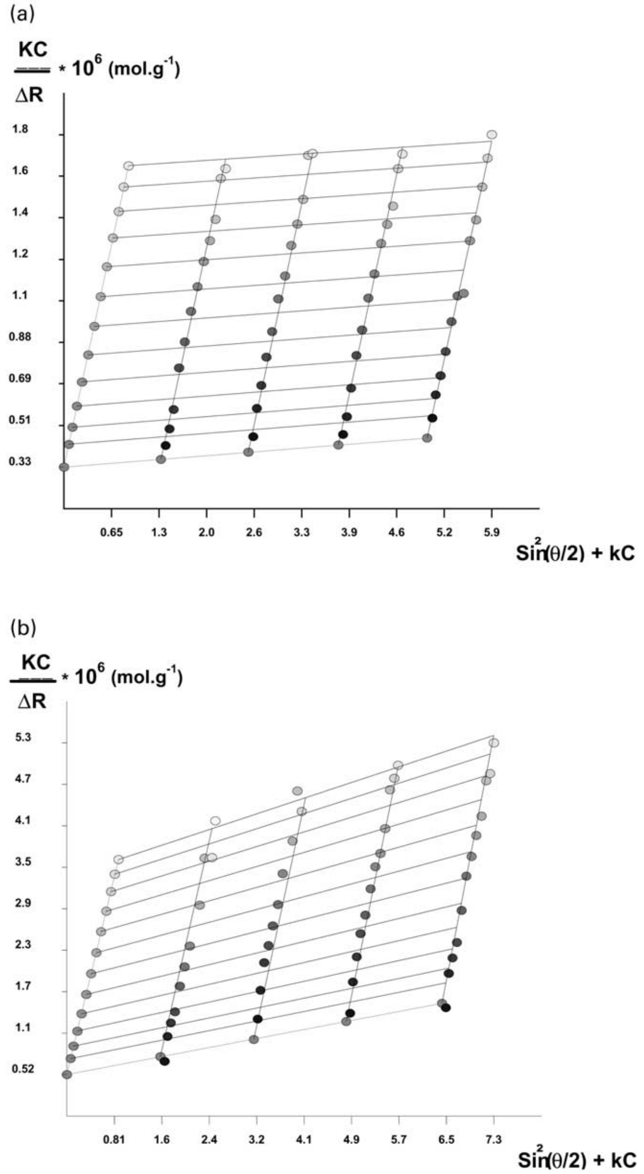


Fig. 4. Zimm plot for H00C8-1.0 in different solvents: (a) in 0.1 M NaCl; (b) in formamide.

This becomes very obvious when measuring the intrinsic viscosity in brine, for example, as shown Table 2, in 0.1 M NaCl aqueous solution, the intrinsic viscosity of H00C8-1.0 is nearly two times lower than that of pure PAM. If we use the classical intrinsic viscosity-molecular weight relationship $[\eta] = 9.33 \times 10^{-3} M^{0.75}$ [68] to calculate the molecular weights of PAM and H00C8-1.0, we will found, the calculated molecular weight of PAM (2.13×10^{6}) agrees very well with that of measured by static light scattering (2.25×10^{6}). On the other hand, even in very dilute solution, hydrophobic aggregates still remain, which result in much larger intrinsic viscosity of HAPAM than that of unmodified PAM [52].

For HHAPAMs, molecular weight determination by both static light scattering and viscometry are more difficult because it is not well known that the parameters k and α in Mark–Houwink equation or the refractive index increment dn/dc for hydrolyzed polyacrylamide exhibit strong dependence on hydrolysis degrees [69,70]. The literature data for HPAMs are usually only suitable for a certain hydrolysis degree rather. For our series of hydrophobically modified polyelectrolytes, the comparison of their molecular weights appears difficult because there are no k and α values available for their Mark–Houwink relationship. For these reasons, we used an indirect method to verify that no degradations occurred during the processes of hydrobical modification and hydrolysis. During the preparation of H00C12-1.0, after adding the potassium *tert*-butoxide into PAM–DMSO mixture but before the coupling reaction, 50 ml of reaction mixture was extracted and dialyzed against distilled water and then freeze-dried. The intrinsic viscosity of this product determined in 0.1 M NaCl at 25 °C is 507 ml g^{-1} which is comparable to that (520 ml g^{-1}) of the parent PAM if we consider experimental error. This shows that there is no degradation occurring in the hydrophobic modification process. This confirmation agrees with the result reported by Deguchi et al. [38] who verified no degradation by dissolving low molecular weight PAM in DMSO at the identical experimental conditions for hydrophobic modification. Muller et al. [71] confirmed by light scattering that no degradation occurred during hydrolysis of PAM at 63 °C. Based on this conclusion, there should be no degradation of our polymers hydrolyzed under milder conditions (50 °C).

4. Conclusions

In this work, a series of hydrophobically modified polyacrylamides and their hydrolyzed derivatives have been prepared via polymer post-modification or/and post-hydrolysis. Molecular weight determination shows that no degradation occurred during these reactions, and ^{1}H and ^{13}C NMR elucidation of polymer microstructures displayed a good agreement with feed ratio. This means, compared with micellar copolymerization, post-modification process is a more effective route to control the amount of grafted groups.

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