

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Hydrophobically Associating Polyacrylamides Prepared by Inverse Suspension Polymerization: Synthesis, Characterization and Aqueous Solution Properties

Xiaolan Li<sup>ab</sup>; Xingli Liu<sup>c</sup>; Quansheng Chen<sup>ab</sup>; Yu Wang<sup>ab</sup>; Yujun Feng<sup>a</sup>

<sup>a</sup> Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, Chengdu, P. R. China <sup>b</sup> The Graduate School of the Chinese Academy of Sciences, Beijing, P. R. China <sup>c</sup> College of Chemistry and Environmental Protection Engineering, Southwest University for Nationalities, Chengdu, P. R. China

Online publication date: 12 February 2010

**To cite this Article** Li, Xiaolan , Liu, Xingli , Chen, Quansheng , Wang, Yu and Feng, Yujun(2010) 'Hydrophobically Associating Polyacrylamides Prepared by Inverse Suspension Polymerization: Synthesis, Characterization and Aqueous Solution Properties', *Journal of Macromolecular Science, Part A*, 47: 4, 358 – 367

**To link to this Article:** DOI: 10.1080/10601320903539322

**URL:** <http://dx.doi.org/10.1080/10601320903539322>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

# Hydrophobically Associating Polyacrylamides Prepared by Inverse Suspension Polymerization: Synthesis, Characterization and Aqueous Solution Properties

XIAOLAN LI<sup>1,2</sup>, XINGLI LIU<sup>3</sup>, QUANSHENG CHEN<sup>1,2</sup>, YU WANG<sup>1,2</sup> and YUJUN FENG<sup>1,\*</sup>

<sup>1</sup>Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, No. 9, Section 4, Renmin South Avenue, Chengdu 610041, P. R. China

<sup>2</sup>The Graduate School of the Chinese Academy of Sciences, Yuquan Road, Beijing 100049, P. R. China

<sup>3</sup>College of Chemistry and Environmental Protection Engineering, Southwest University for Nationalities, South Section 4, 1st Circle Road, Chengdu 610041, P. R. China

Received July 2009, Accepted September 2009

Hydrophobically associating polyacrylamides (HAPAMs) were synthesized via inverse suspension polymerization using ammonium persulphate (APS)/tertramethylethylenediamine (TEMED) as the redox initiators, 2-methacryloyloxyethyl n-alkyl dimethyl ammonium bromide (DM-n, n = 8, 12, 16) as the hydrophobic comonomers. The structures of the copolymers were elucidated by FT-IR and ionic chromatographic analysis, respectively. The morphology and particle size of the resultant HAPAMs were characterized by scanning electronic microscope (SEM) and laser particle size analyzer, which revealed that spherical particles were formed and the particle size exhibited Gaussian distribution centered from 25  $\mu\text{m}$  to 162  $\mu\text{m}$ . Furthermore, the solution properties of the copolymers were studied with viscometry and the results showed that HAPAMs synthesized under optimal conditions exhibited an obvious viscosity enhancement in aqueous solution and excellent salt-tolerant capability in brine.

**Keywords:** Inverse suspension polymerization, hydrophobically associating polyacrylamide, polymeric microspheres, hydrophobic interaction, solution properties

## 1 Introduction

Hydrophobically associating water-soluble polymers (HAWSPs) or “associating thickeners” have been the subject of extensive research due to their unique rheological characteristics (1–3). Of particular interest in this class is hydrophobically associating polyacrylamide (HAPAM) that derived by incorporating a relatively small amount of hydrophobic group (generally less than 2 mol%) onto a polyacrylamide backbone (4). The special rheological behavior of HAPAM polymers arises from their ability to produce weak intra- and intermolecular interactions between the hydrophobic groups allocated along the polymer chains. In the dilute concentration regime, intramolecular hydrophobic interactions lead to coil contraction (5); while above critical association concentration (CAC), a transient

network is formed via intermolecular hydrophobic associations, resulting in substantial viscosity enhancement (6), and the associations are reinforced by addition of salt (7). The network structures are disrupted when increasing shear rate and the apparent viscosity of polymer solutions decreases, whereas upon removal of shear, the associations can reform and the viscosities completely recover to their original values (8). Owing to these unique solution properties, HAPAMs possess the potential to be applied in tertiary oil recovery (9–14), flocculation (15,16), coating and paints (17), personal care, etc.

In regard to preparation of HAPAMs, specialized polymerization techniques are always required since AM and hydrophobic comonomers are generally mutually incompatible. Basically, there are two ways to introduce hydrophobic moieties onto PAM chains: direct-copolymerization of the appropriate monomers or chemical modification of a preformed polymer. Over the years, several synthesizing techniques were attempted to prepare HAPAMs, including: micellar copolymerization (4,18,19), aqueous solution polymerization (20), inverse emulsion polymerization (21,22), inverse microemulsion polymerization (23,24) and post-modification (25,26). To date

\*Address correspondence to: Yujun Feng, Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences, No. 9, Section 4, Renmin South Avenue, Chengdu 610041, Sichuan, P. R. China. Tel.: +86 28 8523 6874; Fax: +86 28 8523 6874; E-mail: yjfeng@cioc.ac.cn

however, the most commonly accepted method is micellar copolymerization in which hydrophobic monomer is solubilized within surfactant micelles, while AM is dissolved in the aqueous solution (4). During the polymerization process, when the growing macro-radical head group encounters a monomer swollen micelle, several hydrophobic molecules inside the micelle are added to form a short hydrophobic block and then more hydrophilic molecules in the aqueous phase are added to form a long hydrophilic block. As the polymerization continues, the above processes are repeated again and again. Therefore the final copolymer is characterized by a micro-multiblock structure, compositional inhomogeneity and strong dependence of solution properties on block length (27). In addition, a well-known limitation of micellar polymerization is the relatively low monomer concentration used to prevent a too high viscosity of the reaction mixture, or high monomer concentration with more surfactants resulting in some negative influences, such as low-molecular weight caused by chain transfer effect (28) and side effect on the solution behavior of the resultant polymers due to the residual surfactants (29). Moreover, a large amount of surfactants are consumed in this process, which accretes potential difficulties in the commercial application of the products. Hence, it is still necessary in searching for new routes to prepare HAPAMs.

In the present study, an alternative procedure, inverse suspension polymerization, is proposed for the synthesis of HAPAMs. This polymerization procedure is effective in preparing micron-size polymeric microspheres for industrial process (30), and the accumulation of polymerization heat could be avoided because it is easily transmitted throughout the organic phase (31). In addition, the particle size can be easily controlled by regulating the reaction parameters, such as stirring speed, temperature, amount of initiator and dispersant, etc (32). As a result of the above reasons, inverse suspension polymerization has received much attention in fundamental and technological fields in recent years, but it has not been used to prepare HAPAMs to date, although the copolymers obtained by this technique with peculiar spherical structure are worthy of theoretical and applied value. So the primary intention of the present work is synthesizing HAPAMs in the inverse suspension system by the copolymerization of acrylamide with a series of hydrophobic monomers, 2-(methacryloyloxy) ethyl *n*-alkyl dimethyl ammonium bromide (DM-*n*, *n* = 8, 12, 16), which are typical surface-active monomers (surfmers) as their molecules not only have an amphiphilic structure composed of a hydrophobic tail and hydrophilic head group, but contain polymerizable vinyl double bonds (23,24,33). Due to their amphiphilic property which increases the chance of contact between hydrophobic monomers and dispersed AM droplets in organic phase, the incorporated amount of such surfmers is higher than traditional hydrophobic counterparts, and thus imparts the resultant polymer better hydrosolubility and

a strong hydrophobic association effect (34,35). However, these kinds of surfmers so far are mainly utilized to improve emulsion polymerization (36, 37), while other applications, including the preparation of HAPAMs, remain to be developed and studied thoroughly (38). In this work, a series of surfmers with different chain lengths were copolymerized with AM and the properties of the resulting HAPAMs with spherical morphology in term of size and distribution were compared. In addition, the aqueous solution behaviors of the copolymers in pure water and NaCl brine were investigated.

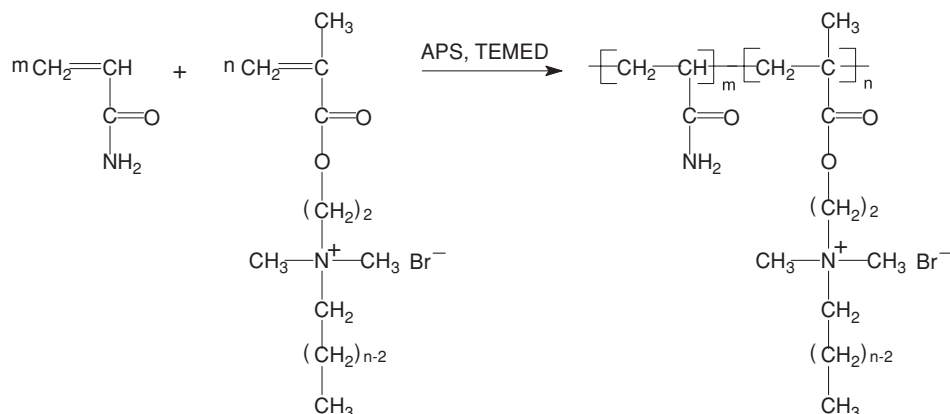
## 2 Experimental

### 2.1 Materials

The surfmers, DM-*n* (*n* = 8, 12, 16), were prepared as described previously (23,24). Acrylamide (AM) was obtained from Changjiu Agri-Scientific Chemicals Co., Ltd. (Nanchang, China) and recrystallized twice with ethanol prior to use. Cyclohexane, ammonium persulfate (APS) (Guanghua Chemical Factory Co., Ltd., China), sorbitan trioleate (Span 85), oleic acid (Sinopharm Chemical Reagent Co., Ltd., China), tetramethylethylenediamine (TEMED) (Shanghai Yuanji Chemical Co., Ltd., China), and other analytical-grade solvents were all used as received without further purification. The water used was triply distilled and N<sub>2</sub> has the purity of 99.999%.

### 2.2 Inverse Suspension Polymerization

HAPAMs were synthesized as described in Scheme 1. The inverse suspension polymerization was carried out in a 500-mL four-necked, round-bottomed flask with mechanical stirrer, nitrogen inlet, reflux condenser and thermometer. About 150 mL of cyclohexane and designed amount of stabilizers (Span 85 and oleic acid) were charged into the flask. After being purged with N<sub>2</sub> for 30 min at 200 rpm to remove the oxygen dissolved, 16.0 g AM, quantitative amount of DM-*n* and the initiator (15 mg) were dissolved in 40 mL and 10 mL distilled water, respectively, and then N<sub>2</sub> was bubbled through the solutions for 15 min. These solutions were introduced into the organic phase successively through a dropping funnel in 30 min, and 20 μL TEMED was then immediately added to the mixture to initiate the polymerization. The reaction was allowed to proceed for 2 h at 60 °C. After polymerization, the microspheres were separated from the oil phase and washed several times with acetone, and left to dry overnight at 45 °C under vacuum. The obtained white powder product was stored in a desiccator for further experiments.



Sch. 1. Synthesis of HAPAMs.  $n = 8, 12, 16$ .

## 2.3 Characterization

### 2.3.1. Infrared Spectroscopy (IR)

The infrared spectra of PAM and HAPAMs were registered in solid state using a KBr pellet method in the transmittance mode. A Nicolet MX-1E FT-IR spectrophotometer (USA) was used to record the spectra within the scanning range of 4000–400  $\text{cm}^{-1}$ .

### 2.3.2. Ion Chromatography (IC)

A designed amount of copolymers was weighed and decomposed by the oxygen flask combustion method using deionized water as the absorbing liquid. Then a trace amount of NaOH and  $\text{H}_2\text{O}_2$  was added to induce the combined bromine ionized completely. An Ion Chromatography (IC) System (ICS-90, Dionex, USA) was utilized to determine the bromine element content in the copolymers, using sodium carbonate aqueous solution as the eluent and dilute sulfuric acid as the regenerates.

### 2.3.3. Gel Permeation Chromatography (GPC)

Weight-average molecular weight ( $M_w$ ) of the copolymers was determined by a gel permeation chromatographic (GPC) system equipped with an OH-pak KB-803 column and a Waters 2410 refractive index detector. The analysis was performed at 20  $^\circ\text{C}$  using 0.1  $\text{mol}\cdot\text{L}^{-1}$   $\text{NaNO}_3$  aqueous solution as the eluent, at a flow rate of 0.8  $\text{mL}\cdot\text{min}^{-1}$ . Poly(ethylene oxide) was used for an initial calibration of the column.

### 2.3.4. Scanning Electron Microscopy (SEM)

The morphology images of the samples were recorded by scanning electron microscopy (SEM), using a model JSM-5900LV (Japan) instrument.

### 2.3.5. Measurement of Particle Size

Particle average diameter and distribution were determined in ethanol using Mastersizer 2000 Laser Particle Size Analyzer (Malvern, UK).

## 2.4 Apparent Viscosity Measurement

Different concentrations of polymer solutions were prepared by dissolution of an appropriate amount of polymer powders in distilled water or NaCl brines, respectively with gentle magnetic stirring. The solutions were then allowed to stand for 1 day until any bubbles present disappeared. Apparent viscosities ( $\eta_{\text{app}}$ ) of polymer solutions were measured at a constant shear rate ( $\dot{\gamma}$ ) of 10  $\text{s}^{-1}$ , using a Brookfield LVDV-III programmable viscometer equipped with SC4-31, SC4-18 and ULA spindles and corresponding adaptors at 25  $^\circ\text{C}$  thermostated with a water circulating bath.

## 3 Results and Discussion

### 3.1 Synthesis

Inverse suspension polymerization of acrylamide with DM- $n$  occurs when a concentrated aqueous solution of monomers is dispersed in cyclohexane in which stabilizers are dissolved, since DM- $n$  is water-soluble in spite of the fact that dissolution slows down as the alkyl chain length increases (39). TEMED was used to promote the reaction by accelerating the liberation rate of radicals (40). It is well known that the suspended monomer droplets during inverse suspension polymerization strongly depend on the chemical and physical properties of the dispersing agents or stabilizers blended to achieve an overall HLB of 4–6 (41). In this case, the blend of Span 85 (HLB 1.8, nonionic) and oleic acid (HLB 1.0, anionic) was an optimal stabilizer, owing that DM- $n$  is assumed to possess high HLB due to its hydrophilic property (36). With such a system, a series of HAPAMs were synthesized by inverse suspension polymerization, keeping aqueous phase concentration at 30 wt%, oil phase and water phase volume ratio at 3:1, initiator concentration at 0.1 wt%. The recipe for the series of HAPAM polymers is listed in Table 1.

**Table 1.** Synthesis parameters of inverse suspension polymerization to prepare PAM and HAPAMs ( $C_{\text{aqueous}} = 30 \text{ wt\%}$ ,  $C_{\text{initiator}} = 0.1 \text{ wt\%}$ ,  $V_{\text{organic}}:V_{\text{water}} = 3:1$ ,  $T = 60 \text{ }^\circ\text{C}$ ,  $t = 2 \text{ h}$ )

| Sample        | AM (g) | DM- <i>n</i> |             | Conversion <sup>a</sup> (%) | $M_w^b$ ( $\times 10^{-6}$ ) |
|---------------|--------|--------------|-------------|-----------------------------|------------------------------|
|               |        | <i>n</i>     | Content (g) |                             |                              |
| PAM           | 16     | 0            | 0           | 96.7                        | 6.89                         |
| HAPAM-12-1.0  | 16     | 12           | 0.16        | 92.3                        | 5.89                         |
| HAPAM-12-3.0  | 16     | 12           | 0.64        | 96.7                        | 3.92                         |
| HAPAM-12-5.0  | 16     | 12           | 0.80        | 92.8                        | 3.79                         |
| HAPAM-8-2.25  | 16     | 8            | 0.36        | 55.0                        | 5.66                         |
| HAPAM-12-2.25 | 16     | 12           | 0.36        | 89.2                        | 4.73                         |
| HAPAM-16-2.25 | 16     | 16           | 0.36        | 79.5                        | 2.50                         |

<sup>a</sup>Calculated according to the following equation (22): Conversion (%) = (weight of recovered copolymer/weight of total monomers)  $\times 100\%$   
<sup>b</sup>measured by GPC.

### 3.1.1. Effect of hydrophobe content on $M_w$

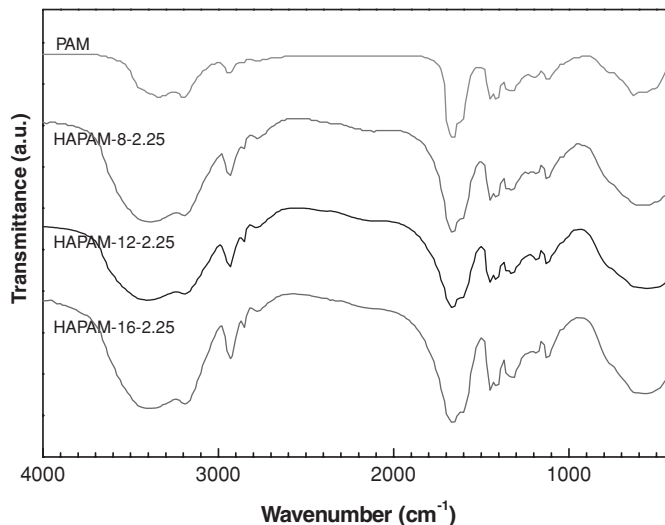
As shown in Table 1,  $M_w$  of the resultant polymers decreases with increasing the content of DM-12 in the feed ratio. For example, when increasing the fraction of DM-12 from 0, 1.0, 2.25, 3.0 to 5.0 percent, the corresponding  $M_w$  decreases from 6.89, 5.89, 4.73, 3.92 to 3.73 million, respectively. Such a reduction in molecular weight can be attributed to the polymerization mechanism. As is well known, inverse suspension polymerization occurs entirely within the aqueous droplets by solution polymerization mechanism (42) and the increase of cationic surfmer-type hydrophobic monomer concentration results in repulsion within a polymer chain which would lead to coil expansion in water (43). Then the amplified interchain steric hindrance inhibits molecular chain bonding and hence, decreases the molecular weight.

### 3.1.2. Effect of hydrophobe length on $M_w$

The same trend for  $M_w$  can be observed as the chain length of hydrophobic group increases. For instance, when keeping the surfmer level at 2.25 wt%, the  $M_w$  decreases from 5.66, 4.73 to 2.50 million as the chain length increases from C8, C12 to C16 (Table 1). After being dispersed in the organic phase, the comonomer with shorter hydrophobic length dissolves in water entirely and was initiated by free radicals, while those with longer hydrophobic length may dissolve out to water-cyclohexane interface because of its hydrophobicity, which decreases the efficiency of chain bonding and results in lower molecular weight.

### 3.1.3. Conversion of comonomers

As listed in Table 1, the conversion of comonomers is pretty high except for HAPAM-8-2.25, in respect that high monomer aggregation of DM-8 in aqueous phase decreased the rate of copolymerization (44), hence induces low conversion in a limited reaction time.



**Fig. 1.** Comparison of FT-IR spectra for PAM and HAPAMs.

## 3.2 Characterization

Elucidation of molecular architecture of HAPAMs by traditional methods such as elemental analysis is difficult owing to the too low percentage of hydrophobic monomer in the polymer, especially for the comonomers consisting of alkyl chains (27). Consequently, the hydrophobe content is assumed to be equal to the initial feed composition in most studies (4,20). This probably induces some overestimation because the composition of HAPAMs prepared by micellar process always drifts. In this work, qualitative and quantitative characterizations of the incorporated hydrophobic groups are confirmed by FT-IR and IC, respectively.

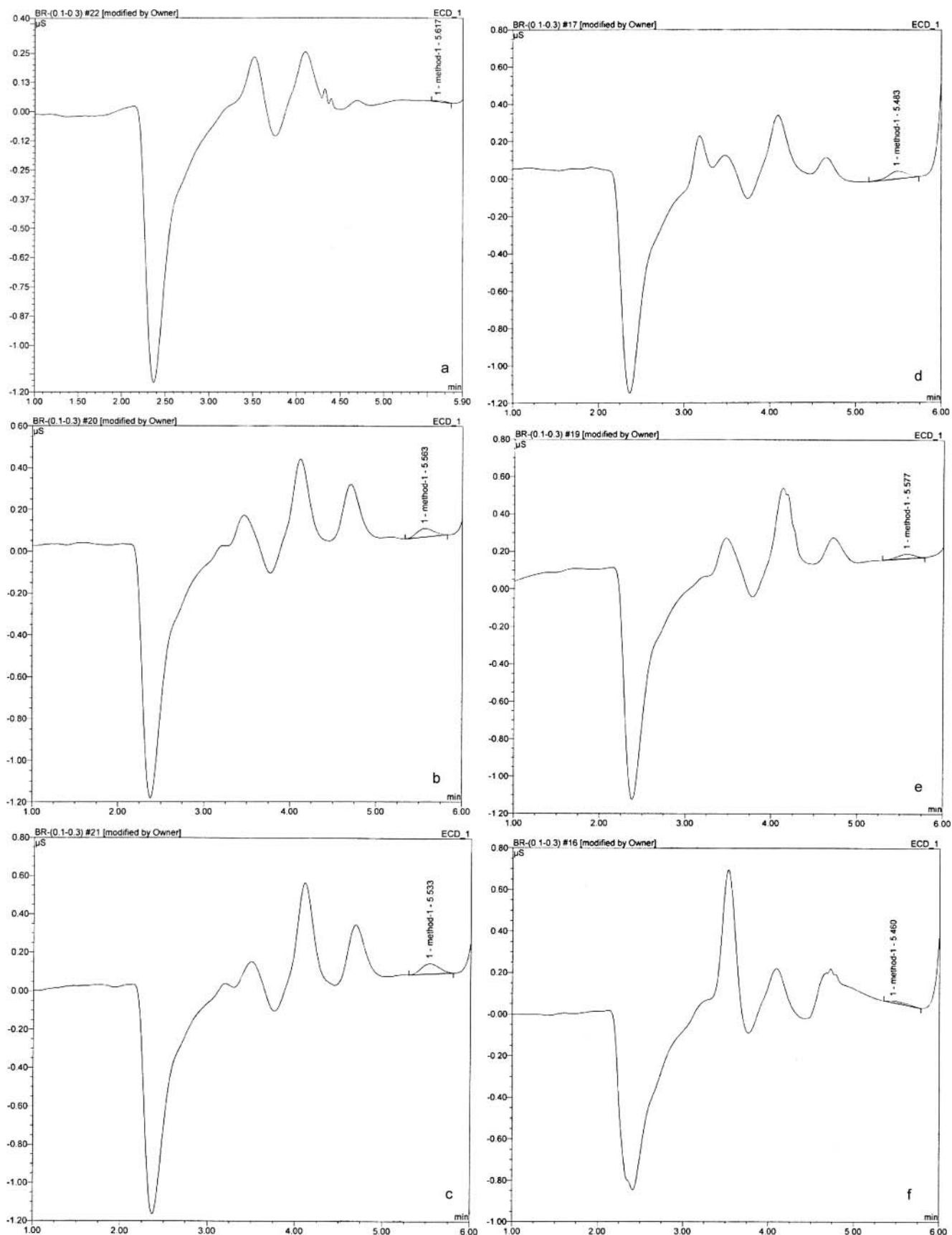
### 3.2.1. FT-IR analysis

Figure 1 presents the FT-IR spectra of PAM and HAPAMs with different hydrophobe length. The spectra of all the polymers show strong stretching vibration peaks at 3358  $\text{cm}^{-1}$  and 1663  $\text{cm}^{-1}$  for the amino group and carbonyl group of amides, respectively. Furthermore, no vibration peaks of C=C were observed. Compared with that of PAM, there is a strong C-H stretch in 2926  $\text{cm}^{-1}$  and 2847  $\text{cm}^{-1}$  in the spectra of HAPAMs, indicating the existence of alkyl group of DM-*n*. So, successful copolymerization between hydrophobic monomers and AM is obtained.

### 3.2.2. IC analysis

As shown in Figure 2,  $\text{Br}^-$  is detected by IC at a retention time range of 5.5-5.7 min and its concentration in polymer solution is obtained by the integration of the peak area. The content of incorporated hydrophobic monomer,  $C_h$ , is equal to the content of  $\text{Br}^-$  in polymer, calculated by the following equation:

$$C_h = \frac{C_{\text{Br}^-}/80 \times M}{C_p - C_{\text{Br}^-}/80 \times M} \times 100\% \quad (1)$$



**Fig. 2.** IC spectra of HAPAMs: (a) HAPAM-12-1.0,  $C_{\text{Br}} = 0.178$  mg/L; (b) HAPAM-12-3.0,  $C_{\text{Br}} = 0.399$  mg/L; (c) HAPAM-12-5.0,  $C_{\text{Br}} = 0.479$  mg/L; (d) HAPAM-8-2.25,  $C_{\text{Br}} = 0.415$  mg/L; (e) HAPAM-12-2.25,  $C_{\text{Br}} = 0.294$  mg/L; (f) HAPAM-16-2.25,  $C_{\text{Br}} = 0.220$  mg/L.

**Table 2.** Quantitative characterization of incorporated hydrophobic comonomer of HAPAMs by IC

| Sample        | n  | DM-n (wt%) |               |
|---------------|----|------------|---------------|
|               |    | Feed ratio | Final content |
| HAPAM-12-1.0  | 12 | 1.0        | 0.75          |
| HAPAM-12-3.0  | 12 | 3.0        | 1.71          |
| HAPAM-12-5.0  | 12 | 5.0        | 2.06          |
| HAPAM-8-2.25  | 8  | 2.25       | 1.52          |
| HAPAM-12-2.25 | 12 | 2.25       | 1.26          |
| HAPAM-16-2.25 | 16 | 2.25       | 1.08          |

where  $C_p$  and  $C_{Br}$  (mg/L) are the concentration of polymer and the detected concentration of  $Br^-$  in solution, respectively, and  $M$  and  $80$  are the molar mass of the comonomer DM-n and bromide, g/mol.

It appears that the amount of hydrophobe in the copolymer is lower than that in feed (Table 2). Furthermore, the difference between feed ratio and final composition becomes larger with increasing the feeding amount of DM-12 and increasing the hydrophobe length at 2.25 wt%.

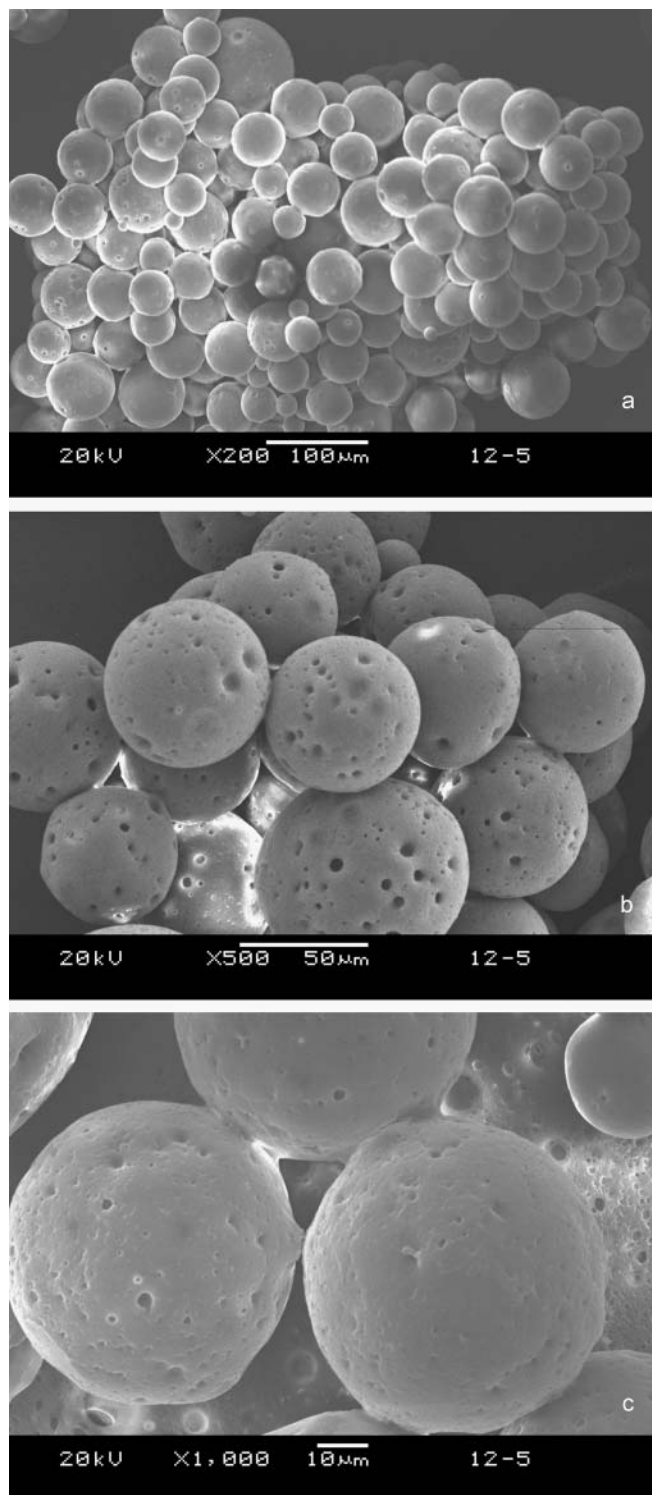
### 3.3 Morphology

Exhibited in Figure 3 are SEM images of HAPAM-12-5.0 with different magnifications, showing the typical morphology of HAPAMs prepared by inverse suspension polymerization. The SEM image of Figure 3(a) indicates that spherical particles were readily formed from this polymerization procedure. It can be seen from Figure 3(b) and Figure 3(c) that the surface of the microspheres is smooth with microspores on it, which is consistent with the morphology of non-associative polymeric microspheres prepared in previous work using the same technique (45,46). In addition, it is expected that the porous surface structure may be convenient for the penetration of water molecules into the network, thus accelerating the dissolution rate of the polymers (47).

### 3.4 Particle Size and Distribution

#### 3.4.1. Effect of hydrophobe content on particle size and distribution

Table 3 and Figure 4(a) present the particle diameter and uniformity of PAM and HAPAM microspheres. It is obvious that the distribution of the particle size exhibits Gaussian distribution. The particle size decreases slightly from  $162 \mu\text{m}$  to  $149 \mu\text{m}$  and the uniformity index increases from 0.32 to 0.42 with increasing DM-12 content. The difference in the particle size is resulted from the shift in polymerization domain from inverse-suspension to inverse-emulsion (48,49). As the content of surfmer increases, a transition accompanied by a change in the locus of nucleation from the monomer droplets to micelles process



**Fig. 3.** SEM images of HAPAM-12-5: (a)  $\times 200$ ; (b)  $\times 500$ ; (c)  $\times 1000$ .

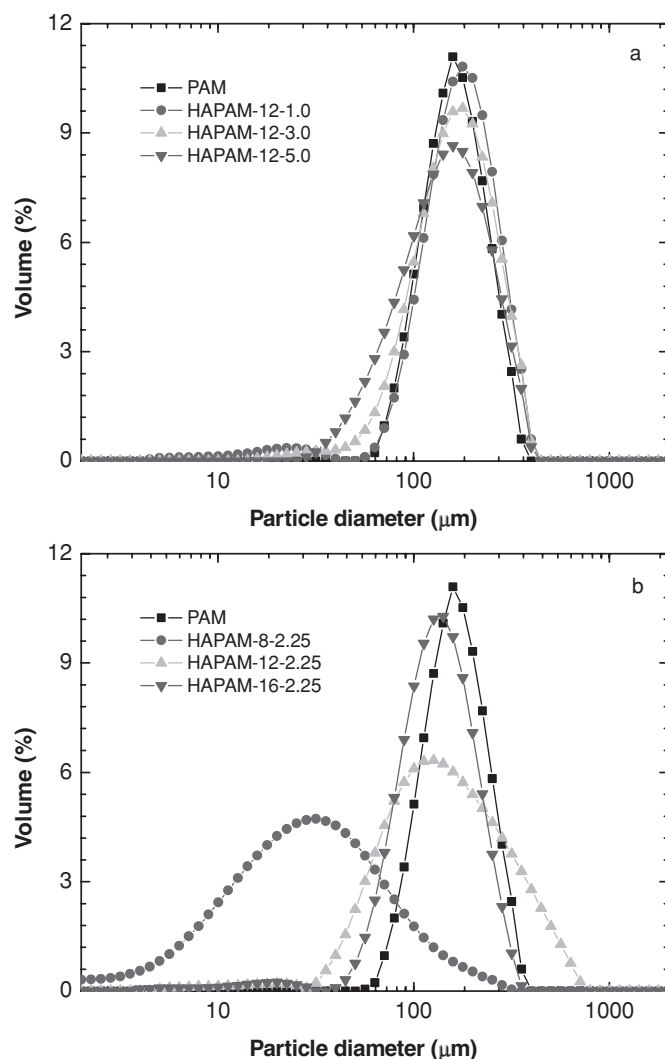
occurs with a corresponding decrease in particle size (50). Additionally, the discrepancy between two different nucleation mechanism leads to the particles more and more inhomogeneous.

**Table 3.** Particle size and uniformity of HAPAMs microspheres

| Sample        | <i>n</i> | <i>d</i> (0.5) ( $\mu\text{m}$ ) | uniformity |
|---------------|----------|----------------------------------|------------|
| PAM           | 0        | 161.375                          | 0.32       |
| HAPAM-12-1.0  | 12       | 162.457                          | 0.34       |
| HAPAM-12-3.0  | 12       | 153.320                          | 0.38       |
| HAPAM-12-5.0  | 12       | 149.043                          | 0.42       |
| HAPAM-8-2.25  | 8        | 25.110                           | 0.98       |
| HAPAM-12-2.25 | 12       | 121.316                          | 0.87       |
| HAPAM-16-2.25 | 16       | 139.040                          | 0.36       |

### 3.4.2. Effect of hydrophobe length on particle size and distribution

The Gaussian distribution is also observed from Fig. 4(b), with a curve centered from 25  $\mu\text{m}$  to 139  $\mu\text{m}$ , smaller than that of PAM particles. Table 3 shows that the particle size increases significantly, but the uniformity index



**Fig. 4.** Particle size distribution of polymers with (a) different hydrophobe content and (b) different hydrophobe length.

decreases, with increasing alkyl chain length. Owing to its amphiphilicity, the incorporated surfmer increases interface between monomer droplets and dispersed phase, thus larger numbers of particles with smaller diameter than PAM are achieved (37). As mentioned above, the surfmer with shorter hydrophobe length tends to nucleate in a micelle locus owing to its higher HLB, whereas the surfmer with longer hydrophobe length tends to nucleate in monomer droplets due to its lower HLB. As a result, larger particles are obtained using hydrophobic monomer with longer alkyl chain length. As to the better uniformity with increasing hydrophobe length, it is due to the fact that one nucleation process plays a dominant during the polymerization.

## 3.5 Aqueous Solution Properties

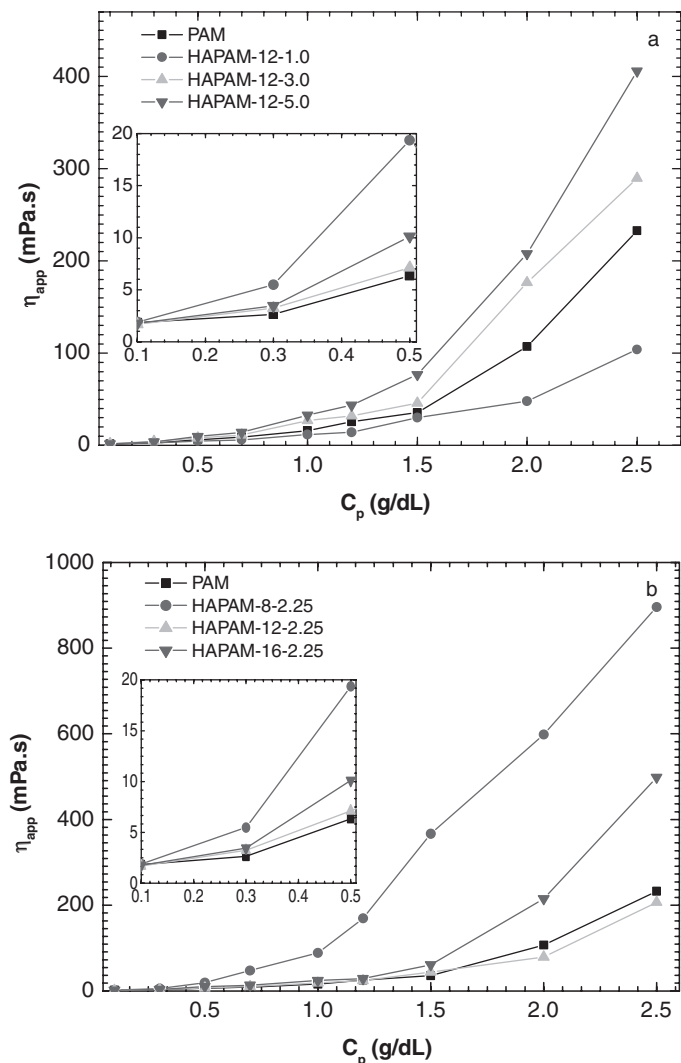
### 3.5.1. Effect of hydrophobe content and length on apparent viscosity

Figures 5(a) and (b) present the concentration dependence of the aqueous solution viscosity for HAPAMs with different hydrophobe content and hydrophobe length in deionized water. PAM is used for comparison and the inset presents the variation in the lower concentration range. The following distinctive features can be found from both figures: (i) the apparent viscosity of all polymer solutions increases with increasing polymer concentration; (ii) viscosity increases with increasing incorporated hydrophobe amount; (iii) a dramatic increase in solution viscosity of HAPAMs occurs, when hydrophobe length or hydrophobe content is fixed, at about the concentration of 0.3 g/dL, which is assumed as the CAC.

It must be pointed out that the thickening capability of HAPAMs is relevant to many factors, such as effectively incorporated hydrophobe and molecular weight, which may have discrepancy with that as expected owing to the difference in reactivity of hydrophobic comonomers under the same conditions. For instance, the thickening efficiency of HAPAM-12-1.0 and HAPAM-12-2.25 is weaker than that of PAM accidentally. It is probably due to their lower molecular weight, which leads to fewer physical entanglements of molecular chains, and this effect is greater than the intermolecular association with lower incorporated hydrophobe content. In addition, when the feed ratio of hydrophobic monomer remains constant, the viscosity does not increase with increasing hydrophobe length as expected. The unexpected excellent solution property of HAPAM-8-2.25 may result from its higher molecular weight and well incorporated hydrophobe amount than the others.

Additionally, the viscosity of HAPAMs aqueous solutions, except for HAPAM-12-1.0 and HAPAM-12-2.25, is higher than that of PAM in both dilute and semi-dilute regions. This unusual phenomena disagrees with the behavior of HAPAMs prepared with AM and other hydrophobic





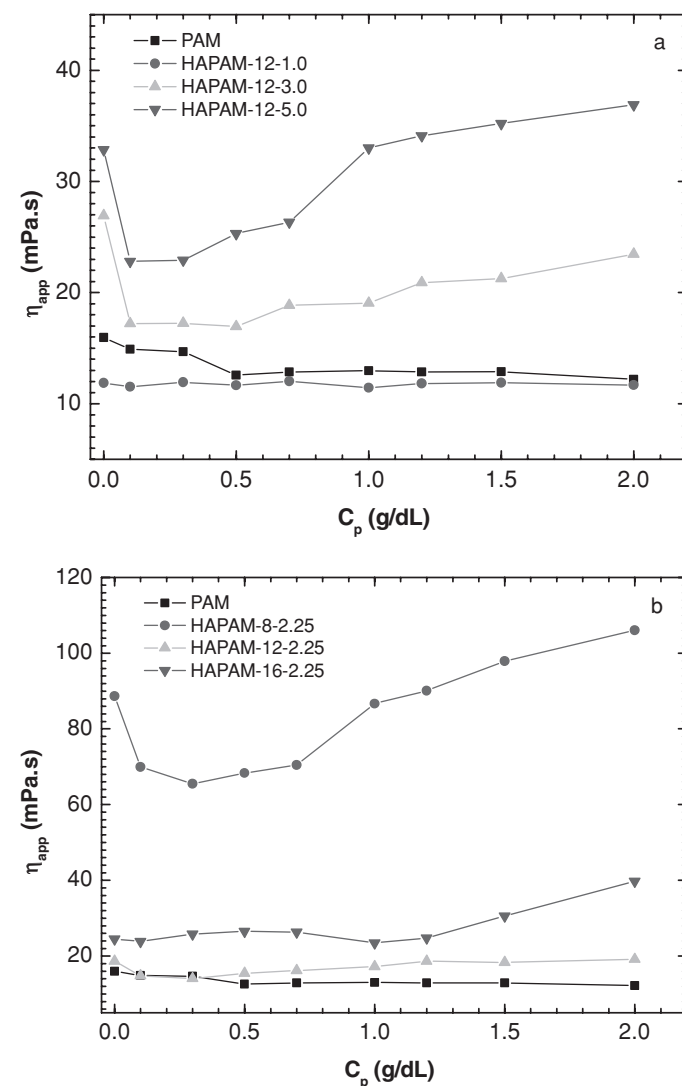
**Fig. 5.** Effect of polymer concentrations with (a) different hydrophobe content and (b) different hydrophobe length on apparent viscosity in pure water ( $T = 25\text{ }^{\circ}\text{C}$ ,  $\dot{\gamma} = 10\text{ s}^{-1}$ ).

monomers. Viscosity of dilute solution of HAPAMs is often found to be lower than that of PAM because of intramolecular association (51). As the copolymer concentration increases, hydrophobic intermolecular associations become predominant, giving rise to a network structure of polymer chains by approaching each other, leading to higher solution viscosity than that of PAM (52). The explanation of this discrepancy could be related to the structure of DM- $n$  possessing an ionizable group. Owing to the polyelectrolyte nature of the copolymers, relatively higher apparent viscosity is observed at low polymer concentration due to the coulombic repulsions between the cationically charged comonomers. Another important factor is the way the hydrophobe distributes along the backbone of HAPAMs. As discussed above, inverse suspension polymerization occurs entirely within the aqueous droplets where chain propagation occurs. Hence, the incorporated alkyl chain of such

type of HAPAMs may distribute along the skeleton randomly like that prepared by solution polymerization. It is difficult to associate intramolecularly for this kind of polymers in dilute solution. As a result, the aqueous viscosity is higher than that of PAM.

### 3.5.2. Effect of hydrophobe content and length on salt tolerance

The influence of NaCl on solution viscosity of HAPAMs is presented in Figure 6. It can be observed: (i) upon addition of NaCl, the viscosity decreases firstly, and then increases at higher salt concentrations; (ii) the capability of salt tolerance increases with increasing hydrophobe content; (iii) viscosity of polymers in NaCl brine varies positively with the molecular weight and effectively incorporated a hydrophobe amount at different hydrophobe length.



**Fig. 6.** Effect of NaCl concentration on apparent viscosity of polymers with (a) different hydrophobe content and (b) hydrophobe length at concentration of  $1.0\text{ g/dL}$  ( $T = 25\text{ }^{\circ}\text{C}$ ,  $\dot{\gamma} = 10\text{ s}^{-1}$ ).

It is notable that HAPAMs exhibit excellent salt-resistance capability than PAM because of the incorporation of hydrophobic monomer except for HAPAM-12-1.0 and HAPAM-12-2.25, the solution viscosity of which is almost invariant with salinity owing to the above mentioned reasons. This result can be explained by the following reasons: intramolecular hydrophobic associations are enhanced at low NaCl concentration due to electrostatic screening of the small charged groups, leading to a marked reduction of hydrodynamic volume, thus decreasing the solution viscosity. However, with the increase of NaCl concentration, the solution polarity induced by electrolyte increases, resulting in reinforced intermolecular associations of the hydrophobic groups, thus higher apparent viscosity is obtained macroscopically.

#### 4 Conclusions

A series of HAPAMs with different hydrophobe content and length were synthesized by inverse suspension polymerization for the first time, using surfmers (DM-n) as the hydrophobic moieties, keeping the aqueous phase concentration at 30 wt%, oil phase and water phase volume ratio at 3:1, initiator concentration at 0.1 wt%. The molecular weight of the resultant polymers decreases with increasing hydrophobe content and/or length.

IC analysis revealed that the final amount of hydrophobe in the copolymers was lower than that in feed. The discrepancy between feed ratio and final composition becomes larger with increasing feeding amount at invariable hydrophobe length or increasing hydrophobe length at a constant amount. SEM and particle size analysis show that HAPAMs prepared by this technique possess spherical structure and the distribution of particles exhibit Gaussian distribution with a curve centered from 25  $\mu\text{m}$  to 162  $\mu\text{m}$ .

The thickening performance in pure water and salt-resistance capability in brine of HAPAMs increase with increasing incorporated hydrophobe amount, while it varies positively with the molecular weight of copolymers and the effectively incorporated hydrophobe amount at different hydrophobe length.

HAPAMs synthesized under optimal conditions, like HAPAM-8-2.25, exhibits an obvious viscosity enhancement in aqueous and excellent salt-resistance capability in brine, which implies that copolymers prepared by this method may have potential applications in oil field exploitations, including drilling, polymer flooding and profile modification.

#### Acknowledgements

The authors gratefully acknowledge the financial supports from the application-oriented fundamental research

program of Sichuan Provincial Bureau of Science and Technology (2008JY0002), opening fund from State Key Laboratory of Oil/Gas Reservoir Geology and Exploitation Engineering (PLN0605), as well as the key project in natural sciences (09NZD002) of Southwest University for Nationalities.

#### References

- Glass, J.E., Ed. *Polymers in Aqueous Media: Performance through Association*. Advances in Chemistry, Series 223, American Chemical Society: Washington, DC, 1989.
- Glass, J.E., Ed. *Associative Polymers in Aqueous Media*. ACS Symposium, Series 765, American Chemical Society: Washington, DC, 2000.
- Gouveia, L.M., Grassl, B. and Müller, A.J. (2009) *J. Colloid Interface Sci.*, 333(1), 152–163
- Candau, F. and Selb, J. (1999) *Adv. Colloid Interface Sci.*, 79(2–3), 149–172.
- Ma, J., Liang, B., Cui, P., Dai, H. and Huang, R. (2003) *Polymer*, 44(4), 1281–1286.
- Grassl, B., Billon, L., Borisov, O. and Francois, J. (2006) *Polym. Int.*, 55(10), 1169–1176.
- Gao, B., Jiang, L. and Kong, D. (2007) *Colloid Polym. Sci.*, 285(8), 839–846.
- Yahaya, G.O., Ahdab, A.A., Ali, S.A., Abu-Sharkh, B.F. and Hamad, E.Z. (2001) *Polymer*, 42(8), 3363–3372.
- Chagas, B.S., Machado, D.L.P., Haag, R.B., de Souza, C.R. and Lucas, E.F. (2004) *J. Appl. Polym. Sci.*, 91(6), 3686–3692.
- Maia, A.M.S., Borsali, R. and Balaban, R.C. (2009) *Mater. Sci. Eng. C-Biomimetic Supramol. Syst.*, 29(2), 505–509.
- Zhong, C., Luo, P., Ye, Z. and Chen, H. (2009) *Polym. Bull.*, 62(1), 79–89.
- Feng, Y., Luo, P., Luo, C. and Yan, Q. (2002) *Polym. Int.*, 51(10), 931–938.
- Lu, H., Feng, Y. and Huang, Z. (2008) *J. Appl. Polym. Sci.*, 110(3), 1837–1843.
- Taylor, K.C. and Nasr-El-Din, H.A. (1998) *J. Petro. Sci. Eng.*, 19(3), 265–280.
- Dragon, S., Maftuleac, A., Dranca, I., Ghimici, L. and Lupascu, T. (2002) *J. Appl. Polym. Sci.*, 84(4), 871–876.
- Ren, H., Li, Y., Zhang, S., Wang, J. and Luan, Z. (2008) *Colloid Surf. A-Physicochem. Eng. Asp.*, 317(1–3), 388–393.
- Lesota, S., Lewandowski, E.W. and Schaller, E.J. (1989) *J. Coat. Technol.*, 61(7), 135–138.
- Lara-Ceniceros, A.C., Rivera-Vallejo, C. and Jimenez-Regalado, E.J. (2007) *Polym. Bull.*, 59(4), 499–508.
- Gao, B., Guo, H., Wang, J. and Zhang, Y. (2008) *Macromolecules*, 41(8), 2890–2897.
- Lee, K.E., Poh, B.T., Morad, N. and Teng, T.T. (2009) *J. Macromol. Sci. Part A-Pure Appl. Chem.*, 46(3), 240–249.
- Pabon, M., Corpart, J.M., Selb, J. and Candau, F. (2004) *J. Appl. Polym. Sci.*, 91(2), 916–924.
- Shang, H., Liu, J., Zheng, Y. and Wang, L. (2009) *J. Appl. Polym. Sci.*, 111(3), 1594–1599.
- Lu, H. and Feng, Y. (2008) *J. Macromol. Sci. Part A-Pure Appl. Chem.*, 45(5), 372–380.
- Lu, H. and Feng, Y. (2007) *E-Polymers*, no.099, 1–13.
- Feng, Y., Billon, L., Grassl, B., Khoukh, A. and Francois, J. (2002) *Polymer*, 43, 2055–2064.
- Feng, Y., Grassl, B., Billon, L., Khoukh, A. and François, J. (2002). *Polym. Int.*, 51(10), 939–947.
- Volpert, E., Selb, J. and Candau, F. (1996) *Macromolecules*, 29(5), 1452–1463.

28. Zhang, Y.X., Fang, Q., Fu, Y.Q., Da, A.H., Zhang, Y.B., Wu, C. and Hogen-Esch, T.E. (2000) *Polym. Int.*, 49(7), 763–774.
29. Zhu, Z., Ouyang, J., Paillet, S., Desbrieres, J. and Grassl, B. (2007) *Eur. Polym. J.*, 43(3), 824–834.
30. Huang, Z., Lu, H. and Zhang, T. (2007) *E-Polymers*, no.153, 1–12.
31. Dimonie, M.V., Boghina, C.M., Marinescu, N.N., Marinescu, M.M., Cincu, C.I. and Oprescu, C.G. (1982) *Eur. Polym. J.*, 18(7), 639–645.
32. Bajpai, S.K., Bajpai, M. and Sharma, L. (2007) *Des. Monomers Polym.*, 10(2), 181–192.
33. Summers, M. and Eastoe, J. (2003) *Adv. Colloid Interface Sci.*, 100, 137–152.
34. Ye, L., Luo, K. and Huang, R. (2000) *Eur. Polym. J.*, 36(8), 1711–1715.
35. Schulz, D.N., Kaladas, J.J., Maurer, J.J., Bock, J., Pace, S.J. and Schulz, W.W. (1987) *Polymer*, 28(12), 2110–2115.
36. Jin, L, Q. Liu, Z., Xu, Q. and Li, Y. (2006) *J. Appl. Polym. Sci.*, 99(3), 1111–1116.
37. Cao, N., Wang, X., Song, L. and Zhang, Z. (2007) *J. Polym. Sci. Pol. Chem.*, 45(24), 5800–5810.
38. Gao, B., Jiang, L. and Liu, K. (2007) *Eur. Polym. J.*, 43(10), 4530–4540.
39. Nagai, K. and Ohishi, Y. (1987) *J. Polym. Sci. Pol. Chem.*, 25(1), 1–14.
40. Kiatkamjornwong, S., Siwarungson, N. and Nganbunsri, A. (1999) *J. Appl. Polym. Sci.*, 73(11), 2273–2291.
41. Kiatkamjornwong, S. and Phunchareon, P. (1999) *J. Appl. Polym. Sci.*, 72(10), 1349–1366.
42. Dowding, P.J., Vincent, B. and Williams, E. (2000) *J. Colloid Interface Sci.*, 221(2), 268–272.
43. Ren, H., Chen, W., Zheng, Y. and Luan, Z. (2007) *React. Funct. Polym.*, 67(7), 601–608.
44. Nagai, K., Ohishi, Y., Inaba, H. and Kudo, S. (1985) *J. Polym. Sci. Pol. Chem.*, 23(4): 1221–1230.
45. Lu, S., Cheng, G. and Pang, X. (2006) *J. Appl. Polym. Sci.*, 100(1), 684–694.
46. Pang, X., Cheng, G., Li, R., Lu, S. and Zhang, Y. (2005) *Anal. Chim. Acta*, 550(1–2), 13–17.
47. Li, P., Zhang, J. and Wang, A. (2007) *Macromol. Mater. Eng.*, 292(8), 962–969.
48. Benda, D., Snuparek, J. and Cermak, V. (1997) *J. Dispersion Sci. Technol.*, 18(2), 115–121.
49. Capek, I., Fialova, L. and Berek, D. (2008) *Des. Monomers Polym.*, 11(2), 123–137.
50. Hunkeler, D., Candau, F., Pichot, C., Hemielec, A.E., Xie, T.Y., Barton, J., Vaskova, V., Guillot, J., Dimonie, M.V. and Reichert, K.H. (1994) *Adv. Polym. Sci.*, 112, 115–133.
51. Hill, A., Candau, F. and Selb, J. (1993) *Macromolecules*, 26(17), 4521–4532.
52. Feng, Y., Billon, L., Grassl, B., Bastiat, G., Borisov, O. and Francois, J. (2005) *Polymer*, 46(22), 9283–9295.