

A new approach to the synthesis of hydrophobically associating polyacrylamide via the inverse miniemulsion polymerization in the presence of template

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Abstract. Cationic, hydrophobically associating polyacrylamide (PDA) was synthesized via the inverse miniemulsion polymerization in the presence of template. Dimethyloctane(2- acrylamidopropyl)ammoniumbromide (DOAB) was synthesized via quaternization reaction and used as the hydrophobic monomer. Polyacrylic acid (PAA) was used as template for the oppositely charged DOAB. The distribution of DOAB in the inverse miniemulsion and the solution viscosity behaviors of PDA were investigated. The results showed that the complexes of DOAB and PAA were located not only at the interface of the inverse miniemulsion droplets and oil phase but also in the interior of inverse miniemulsion droplets. PDA prepared with template exhibited remarkable enhancement of solution viscosity (thickening ability). And the optimal thickening ability was obtained when the aqueous phase pH was 6.5 and the ratio of DOAB to PAA was 1. The thickening ability of PDA was improved with increasing DOAB content. PDA prepared with template showed stronger association ability than that prepared without template for its longer hydrophobic block structure, which was further supported by the plots of fluorescence spectra.

Keywords: polymer synthesis, molecular engineering, hydrophobically associating, inverse miniemulsion polymerisation, template

1. Introduction

In recent years, water-soluble, hydrophobically associating polymers have attracted considerable interest for their special properties. Among these polymers, hydrophobically associating polyacrylamide (HAPAM) is especially attractive [1–9]. It is well known that there are intramolecular association and intermolecular association in HAPAM aqueous solution due to the presence of hydrophobic groups. When the concentration of HAPAM is above a certain concentration, intermolecular hydrophobic interaction will lead to the formation of dynamic three-dimensional network structure and supramolecular aggregates, which can dramatically enhance the viscosity (thickening ability)

[10, 11]. These polymers have potential applications in many fields including enhanced oil recovery, drilling fluids, coatings, water treatment, etc. [12–18].

Up to now, micellar polymerization has been the most effective method for the synthesis of HAPAM. This method is extremely attractive since it allows the preparation of polymers with hydrophobic microblock structure [19, 20]. As a result, the polymers exhibit higher thickening abilities than those with random distribution structure at the similar molar mass. However, the major disadvantages for this method are obvious: the initial concentration of the reaction mixture is relatively low because of gel effect during the course of poly-

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merization, and the water solubility of the HAPAM is often poor [10, 21, 22], which makes difficult its practical application.

A variety of techniques have been suggested to overcome the problems mentioned above, such as inverse emulsion polymerization and inverse microemulsion polymerization, which can also be used to obtain HAPAM with higher solid content and better water solubility [23–25]. However, these methods require a large amount of surfactant, which restricts their potential applications. And only a small number of literatures on these techniques have been reported recently.

Inverse miniemulsion polymerization is another promising method that can be applied to obtain water-soluble polymer with low surfactant content. In our laboratory, an attempt has been made to prepare HAPAM via inverse miniemulsion polymerization using cationic hydrophobic monomer. In order to obtain HAPAM with higher thickening ability, we introduce template polymerization method [26–28] to the inverse miniemulsion system. In the presence of template, the oppositely charged monomer can form a longer hydrophobic block along the polymer chains. The products will exhibit higher thickening ability.

In this work, we examined the inverse miniemulsion polymerization of acrylamide with the cationic hydrophobic monomer Dimethyloctane(2-acrylamidopropyl)ammoniumbromide (DOAB) in the presence of template polyacrylic acid (PAA). The distribution of DOAB in the inverse miniemulsion and the solution viscosity behaviors of polymers prepared by varying aqueous phase pH, ratio of hydrophobic monomer to template and hydrophobic monomer content were investigated. Effects of polymer concentration and inorganic salt (NaCl) concentration on hydrophobic associating behavior were examined.

2. Experimental section

2.1. Materials

N,N'-Dimethyl-1,3-propanediamine (98%) and 1-Bromooctane were purchased from Huaian Heyuan Chemical Factory (Huaian, China) and Shanghai Chemical Reagent (Shanghai, China) respectively. Acrylamide (AM), Acryloyl chloride and Sorbitan monooleate (Span80) were obtained from Sinopharm Chemical Reagent Co., Ltd,

(Beijing, China). PAA ($M_n = 1200$ g/mol) and Amphiphilic polymer of poly(oxyethylene-oxypropylene-oxyethylene-oxypropylene)-vinyl diamine (CM38, $M_w = 3800$ g/mol) were supplied by Institute of Chemistry, the Chinese Academy of Sciences, (Beijing, China); 2,2'-azobis[2-(2-imidazolyl)-propane]dihydrochloride (VA-044) was purchased from Fluka (Milwaukee, USA). Deionized water was used throughout the work. All reagents and other solvents were used as received.

2.2. Measurements

FTIR spectrum of the hydrophobic monomer was recorded on a Prestige-21 FTIR spectrophotometer (Shimadzu Corporation, Kyoto, Japan) with KBr pellet in the range of 400–4000 cm^{-1} .

^1H NMR spectrum was measured with a Mercury-plus 400 (Varian Inc., Palo Alto, USA) using Chloroform-D (CDCl_3) as the solvent.

Elemental analysis was carried out using an elemental analyses system, Vario EL III (Elementar Analysensysteme GmbH, Hanau, Germany).

The molar mass of polymer was characterized relatively with intrinsic viscosity, and the intrinsic viscosity of polymer was determined using an Ubbelohde viscometer with 1.0 mol/l NaCl as solvent and the concentrations of the polymer were in the range of 0.02–0.05 g/dl. The measurement process was kept at $30.0 \pm 0.1^\circ\text{C}$. The intrinsic viscosity $[\eta]$ of polymer was obtained with the dilution extrapolation method. The intrinsic viscosity measurement was an approximation method due to the effect of intramolecular hydrophobic interaction on the determination of the viscosity-average molar mass for polymer [29]. The molar mass of polymer was determined by the Mark-Houwink-Sakurada Equation (1):

$$[\eta] = KM_{\eta}^{\alpha} \quad (1)$$

where $K = 4.75 \cdot 10^{-3}$ ml/g and $\alpha = 0.80$.

Droplet size of the inverse miniemulsion was determined at 25°C by a Malvern Zetasizer 3000HS (Malvern Instruments Ltd, Worcestershire, U.K.). Apparent viscosity measurement was conducted by a Brookfield LVDV II+ rotational viscometer (Brookfield Asset Management Inc., Middleboro, USA) with a spindle 1 and a shear rate of 6 rpm at 80°C .

The fluorescence emission spectrum of the probe pyrene was recorded on a HITACHI F-4500 (Hitachi, Ltd., Tokyo, Japan) fluorescence spectrophotometer at 30°C with an excitation wavelength of 335 nm and a slit width of 2.5 nm in a scanning range of 350–450 nm. The ratio of the first band intensity to the third band intensity of pyrene emission, I_1/I_3 , was used as an estimate of micro polarity of pyrene microenvironment. A required volume of stock solution of pyrene in methanol ($1 \cdot 10^{-3}$ mol/l) was pipetted out into a standard flask and a thin film of pyrene was deposited on the side of the flask after the evaporation of solvent by bubbling nitrogen. The concentration of pyrene was maintained at $1 \cdot 10^{-6}$ mol/l in all the solutions and the concentrations of polymers were in the range of 0.1–0.55 g/dl.

All the polymer solutions were prepared by dissolution of the samples in deionized water at room temperature. Afterward, the solution was diluted and polymer aqueous solutions with different concentrations were prepared and kept for 24 h before measurement.

2.3. Synthesis of cationic hydrophobic monomer DOAB

2.3.1. Synthesis of

N,N'-dimethylpropylacrylamide

N,N'-dimethylpropylacrylamide was synthesized according to the literature [22]. Dichloromethane solution (20 ml) with predissolved N,N'-dimethyl-1,3-propanediamine (4.17 g, 0.04 mol) and sodium hydroxide solution (7 ml, 6 mol/l) were added to a round bottom flask, cooled by ice-water bath and purged with nitrogen for 30 min at the same time. Then dichloromethane solution (20 ml) with predissolved acryloyl chloride (3.71 g, 0.041 mol) was titrated slowly. The temperature was kept below 5°C. After titration, the system was kept still for 5 h at the room temperature. Then the organic phase was washed twice with saturated sodium carbonate aqueous solution and aqueous phase was extracted with dichloromethane after adding excessive sodium chloride. The organic phase and the extract liquid of dichloromethane were dried for 24 h with magnesium sulfate, solvents were removed by vacuum distillation, and liquid product was obtained (yield 74%).

2.3.2. Synthesis of DOAB

DOAB was prepared via quaternization reaction [22, 30] of N,N'-dimethylpropylacrylamide and 1-Bromooctane according to the following method: In a round-bottom flask with a magnetic bar, acetone (60 ml) with predissolved N,N'-dimethylpropylacrylamide (4.5 g, 0.029 mol) and 1-Bromooctane (6.4 g, 0.033 mol) was added under the purge of nitrogen. The reaction proceeded at 55°C for 24 h before being quenched. The initial product was precipitated and purified by the mixture solvent of absolute ether and acetone. Solvents were removed by vacuum distillation and the crude product was dried to a constant weight in a vacuum oven at room temperature, then power DOAB was obtained (yield 81%). FTIR (KBr, cm^{-1}): $\nu = 3434$ (N–H stretching), 3041 (C=CH stretching), 1670 (C=O stretching), 1626 (C=C stretching), 1410 (C–N stretching), 726 ($(\text{CH}_2)_n$, $n \gg 2$, rocking). ^1H NMR (CDCl_3 , ppm): $\delta\text{H} = 8.3$ (1H, s), 6.5 (1H, s), 6.3 (1H, m), 5.6 (1H, s), 3.9 (2H, d), 3.5 (2H, s), 3.3 (2H, s), 3.2 (6H, s), 2.1 (2H, s), 1.8 (2H, s), 1.3 (10H, m), 0.9 (3H, s). Elemental analysis: Calculated for $\text{C}_{16}\text{H}_{33}\text{N}_2\text{O}$ (269.45 g/mol): 71.32 (C%), 12.34 (H%), 10.40 (N%). Found: 71.30 (C%), 12.76 (H%), 10.32 (N%).

2.4. Synthesis of cationic hydrophobically associating polyacrylamide (PDA)

PDA was synthesized as described below. Aqueous phase consisting of a certain amount of template PAA, monomers DOAB, AM solution (15 g, 50 g/dl), initiator VA-044 (6 mg) was prepared and adjusted to pH 6.5 with sodium hydroxide solution (Unless otherwise defined, pH used herein was about 6.5). Then aqueous phase was mixed with oil phase prepared by predissolving surfactant Span80 (1.5 g) and stabilizer CM38 (0.15 g) in kerosene (35 g). The mixture was pre-emulsified by magnetic stirring and purged with nitrogen for 1 h. Then the mixture was homogenized by ultrasonication for 180 s with a Branson sonifier W450 Digital (Branson Ultrasonics Corporation, Danbury, USA) at 70% amplitude in an ice-water bath to prevent polymerization. The inverse miniemulsion thus prepared was subsequently transferred into a round bottom flask, and purged with nitrogen for 15 min. Then the reaction proceeded at 50°C for 4 h. The

Table 1. Correlative data of the polymers prepared via inverse miniemulsion polymerization

Sample	DOAB [mol%] ^a	DOAB/PAA [mol/mol]	M _n ·10 ⁻⁶ [g/mol]
PAM	–	–	5.06
PDA-1	0.5	–	5.13
PDA-2	0.1	1.0	4.93
PDA-3	0.3	1.0	4.75
PDA-4	0.5	1.0	4.38
PDA-5	0.5	0.5	4.11
PDA-6	0.5	2.0	4.67

^aThe molar ratio of DOAB to AM

initial product was dropped into the mixture solvent of ethanol and acetone and then washed with absolute ethanol for three times. After filtration, the rude product was dried to a constant weight in a vacuum oven at room temperature, and then power polymer was obtained. The correlative data about the polymer samples were presented in Table 1.

3. Results and discussion

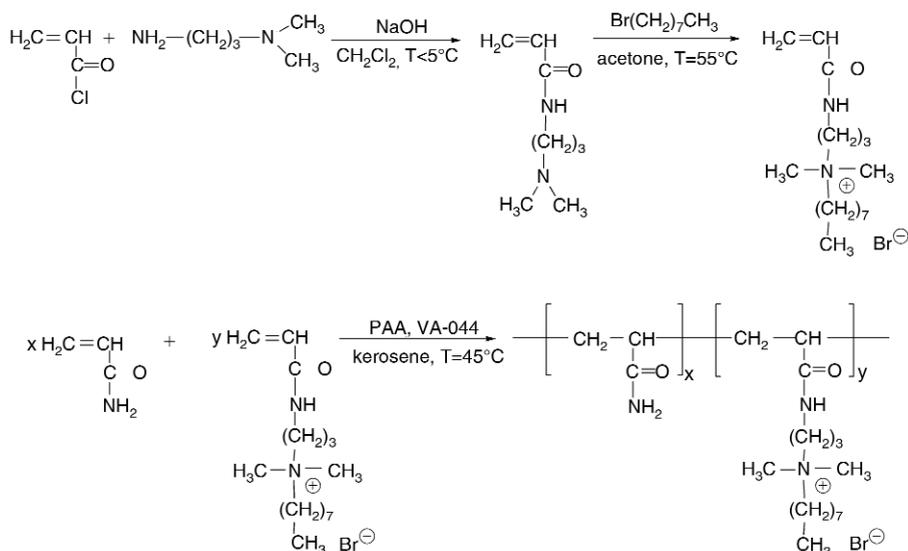
3.1. Molecular design for PDA

The synthetic route for PDA is shown in Figure 1. We firstly synthesized cationic monomer DOAB. PDA with hydrophobic block was then obtained by the inverse miniemulsion polymerization with PAA as template.

In the inverse miniemulsion system with template PAA, cationic hydrophobic monomer DOAB was soluble in aqueous phase, namely the inverse miniemulsion droplets. DOAB strongly interacted with template PAA due to electrostatic interaction

and formed a tight complex. This complex could be completely dissolved in aqueous solution, even when pH varied from 5 to 8. It could be assumed that the polymerization of DOAB adsorbed on template followed a zip mechanism rather than a pick-up mechanism for the strong ionic interaction. Under the same conditions, the neutral monomer AM had no interaction with PAA. When DOAB adsorbed on template PAA was initiated by a growing macroradical headgroup in the aqueous phase, polymerization would proceed along the PAA chain to form a hydrophobic block and then initiated AM in the aqueous phase to form a hydrophilic block. These steps were repeated many times, so the structure of the product was multiblock [31]. The length and density of the hydrophobic block in the HAPAM chain depended on the pH of the aqueous phase and the ratio of hydrophobic monomer to template. Under proper conditions, products with high hydrophobically associating ability could be obtained through the template process. The polymerization process was illustrated in Figure 2.

Unfortunately, it was impossible to separate PDA from template PAA completely [32], and the exact sequence distribution of hydrophobic groups along the polymer chain could not be detected by ¹H NMR and FTIR since the length of the hydrophobic blocks was too large [23] and the amount of hydrophobic groups was too small [31]. So we compared the PAA-PDA complexes obtained by inverse miniemulsion polymerization with the complexes obtained by mixing of equimolar solutions of the two polymers at the following experi-

**Figure 1.** Synthetic route for PDA

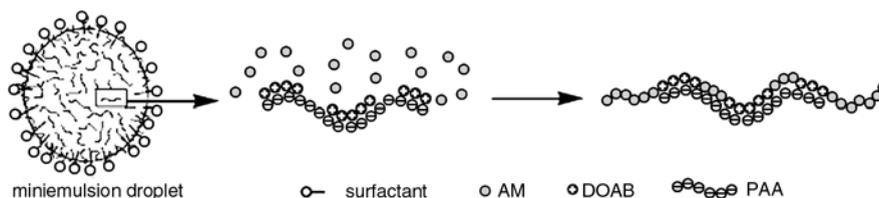


Figure 2. Representation of inverse miniemulsion polymerization in the presence of template

ments and studied the sequence distribution indirectly by the hydrophobic associating behavior of the polymers.

3.2. Distribution of DOAB in the inverse miniemulsion

The distribution of DOAB in the inverse miniemulsion can be reflected by the variation of inverse miniemulsion droplet size. Figure 3 shows the droplet sizes of the inverse miniemulsions prepared with (DOAB/PAA ratio was 1) and without template PAA. It can be noted that the initial droplet size of the inverse miniemulsion prepared without template decreased with the increase of DOAB content. And in the presence of template, the initial droplet size decreased firstly and then kept nearly constant. These results indicated that DOAB was located at the interface of the inverse miniemulsion droplet and oil phase for its surface activity, while the complexes of DOAB and PAA were located not only at the droplets interface but also in the interior of inverse miniemulsion droplet. Indeed, if the complexes were located at the interface, the interfacial tension and therefore the droplets size would be modified [23].

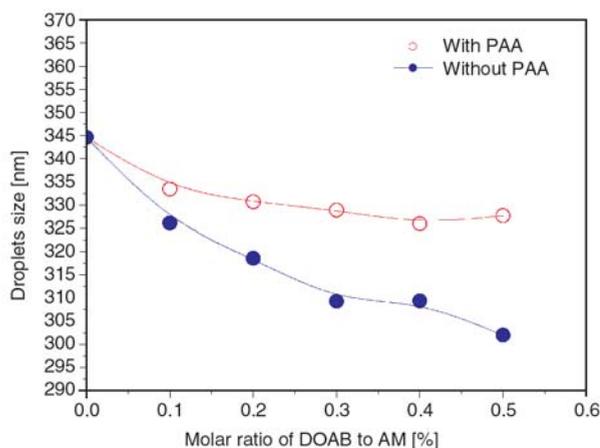


Figure 3. Effect of PAA on the droplets size of the inverse miniemulsion

3.3. Influencing factors of the inverse miniemulsion polymerization in the presence of template

3.3.1. Aqueous phase pH

Figure 4 shows the effect of aqueous phase pH on the molar mass and apparent viscosity of PDA solution (0.5 g/dl). The content of DOAB was 0.5 mol% (relative to AM) and the DOAB/PAA ratio was 1. The molar mass and apparent viscosity of PDA solution firstly increased and then decreased with increasing aqueous phase pH. The largest molar mass was obtained at pH 7.0, but the optimal thickening ability was obtained at pH 6.5. At the same hydrophobic group content, PDA prepared at pH 6.5 must have a longer hydrophobic block structure than that of prepared at pH 7.0. In the inverse miniemulsion system, aqueous phase pH determined the ionization degrees of DOAB and PAA, which significantly influenced their interaction. Under strong acid or strong basic conditions, the interaction between DOAB and PAA was weakened due to the fact that one of their ionization degrees was decreased. This led to a decreasing quantity of DOAB preadsorbed on PAA and the number of hydrophobic groups randomly distributed in the PDA chain increased, and therefore the thickening ability of PDA decreased.

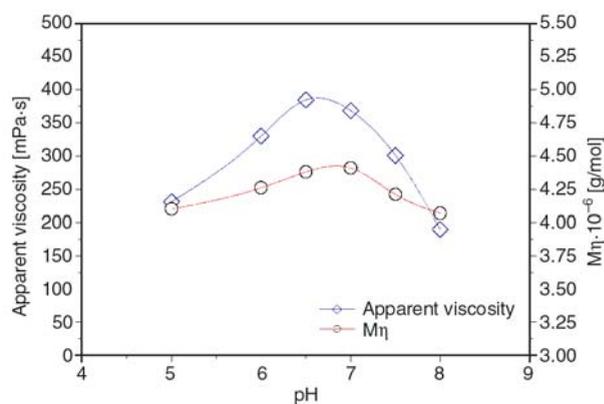


Figure 4. Effect of aqueous phase pH on the molar mass and apparent viscosity of PDA solution

3.3.2. Ratio of hydrophobic monomer to template

Figure 5 shows the effect of the molar ratio of DOAB to PAA on PDA solution viscosity as a function of polymer concentration. When the molar ratio of DOAB to PAA was equal to 1, the thickening ability was the best. In this case, most DOAB molecules were preadsorbed on PAA chains. When the ratio was higher than 1, part of DOAB molecules were dissolved in the aqueous phase for the absence of template, which led to a decrease of the number of hydrophobic blocks along the macromolecular chains and the thickening ability. When the ratio was lower than 1, most DOAB molecules were preadsorbed on the PAA chains, but the length and density of the hydrophobic blocks decreased, so the thickening ability decreased. It was apparent that the viscosities enhanced sharply when PDA solution concentrations attained approximately 0.30 g/dl. This suggested that 0.30 g/dl (or a value around 0.30 g/dl) was a critical concentration for the three polymers, at which intramolecular association transformed into intermolecular association, i.e., the critical association concentration (C^*). When the polymer concentrations increased further, intermolecular association was strengthened because of the shortening of the distance between macromolecules, and the viscosity enhanced rapidly.

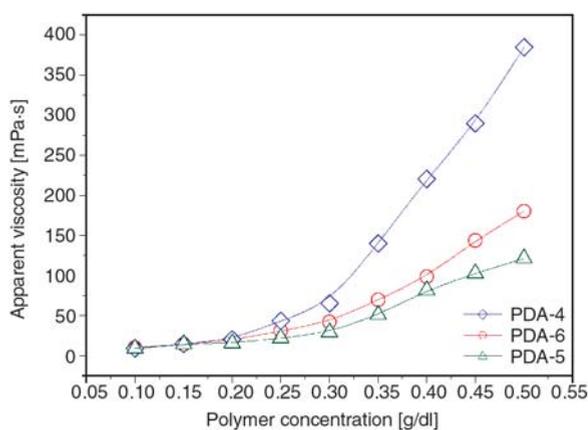


Figure 5. Effect of DOAB to PAA ratio on the apparent viscosity of PDA solution

3.3.3. Hydrophobic monomer content

Figure 6 shows the effect of hydrophobic monomer content on the viscosity of PDA solution. It was found that the apparent viscosity increased and the C^* decreased with the increase of hydrophobic

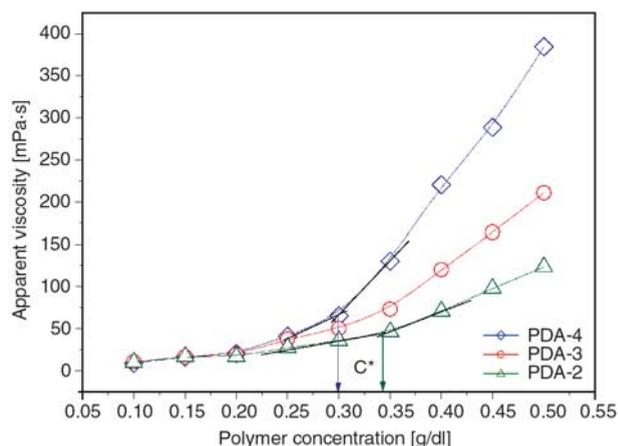


Figure 6. Effect of hydrophobic monomer content on the apparent viscosity of PDA solution

monomer content. The C^* were about 0.30 and 0.34 g/dl for PDA-4 and PDA-2 respectively. The solution viscosity of PDA prepared with higher content of DOAB increased rapidly at the concentration above C^* . This could be explained by the higher hydrophobic block density along the PDA chain, which led to a larger quantity and probability of hydrophobic groups that participated in association.

One can also note that the molar mass of PDA prepared with template decreased with increasing hydrophobic monomer content (Table 1). This could be mainly attributed to the presence of PAA, which was known to act as a chain-transfer agent. This assumption was supported by the comparison with PDA-1. The fact of PDA with lower molar mass and higher thickening ability due to the template effect was described in the next section.

3.4. Apparent viscosity of different polymer solutions

The relationships between apparent viscosity and polymer concentration for different polymers can be seen in Figure 7. A strong template effect was evidenced by the different trends of the curves. The solution viscosity of PDA prepared with template showed a significant dependence of the viscosity on concentration. The viscosity of PDA-4 solution was higher than that of PDA-1 solution at the concentration above C^* (0.30 g/dl), opposite trend was shown at the concentration below C^* . This result indicated that PDA prepared with template exhibited a longer hydrophobic block characteristic,

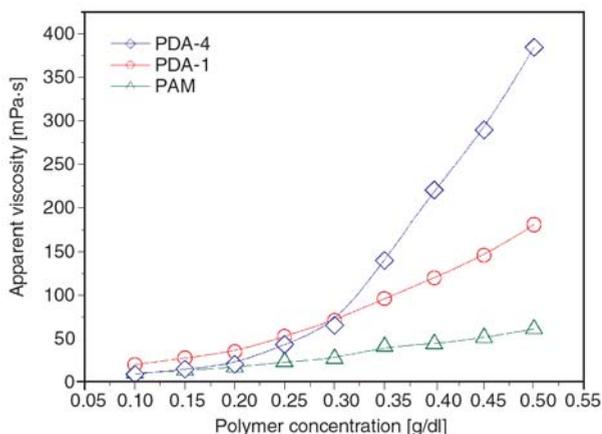


Figure 7. Relationships between apparent viscosity and polymer concentration for different polymers

which made it more easily to form intermolecular association at the concentration above C^* and intramolecular association at the concentration below C^* [8, 33, 34].

It was interesting to note that the viscosity of PDA was higher than that of PAM without hydrophobically modified at the concentration below C^* . The unusual phenomenon disagreed with the behavior generally described for HAPAM. Viscosity of HAPAM was often found to be either equal to or lower than that of PAM [16] at the concentration below C^* due to the formation of intramolecular hydrophobic association. The explanation of this discrepancy could be related to the presence of template PAA. In the polymer solution, PAA was absorbed on the hydrophobic chain of PDA through electrostatic interaction and formed the PAA-PDA complexes, which enhanced the viscosity of the polymer solution.

The apparent viscosity reflects the hydrophobic association ability from a macroscopic property, whereas the fluorescence probe experiments can investigate their hydrophobic association ability from the molecular level. It is known that the value of I_1/I_3 is extremely sensitive to the polarity of the probe microenvironment. The weaker the polarity of the microenvironment around the pyrene molecule, the lower the value of I_1/I_3 .

Figure 8 shows the value of I_1/I_3 as a function of polymer concentration in aqueous solution. For PAM, the value of I_1/I_3 had no remarkable changes in whole concentration region, but for PDA, the value of I_1/I_3 decreased with increasing polymer concentration. Especially in the range of higher concentrations, the I_1/I_3 value of PDA was much

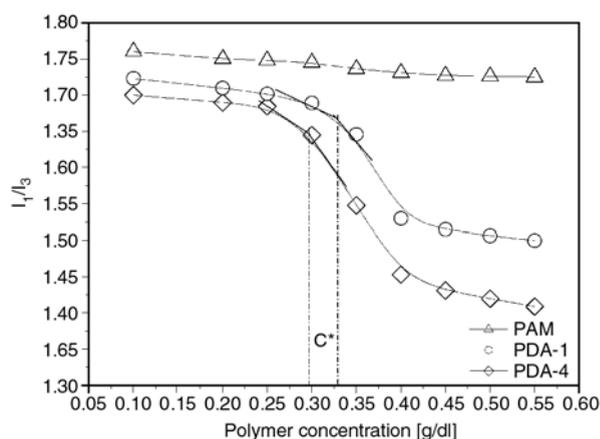


Figure 8. Variation of the I_1/I_3 value with polymer concentration

lower than that of PAM. This indicated that the hydrophobic microdomains have formed in polymer solution due to the intramolecular associating at lower concentrations and intermolecular associating at higher concentrations. It could be found that the I_1/I_3 values of PDA-4 and PDA-1 decreased abruptly at a concentration of about 0.30 and 0.33 g/dl (C^*) respectively. At the same concentration, the I_1/I_3 value of PDA-4 was lower than that of PDA-1, especially at the concentration above C^* . This difference should be attributed to the different microstructures of polymers. As mentioned above, polymer with longer hydrophobic block structure had stronger hydrophobic association ability. Therefore the polarity of the hydrophobic microdomains for PDA-4 was weaker, resulting in the lower value of I_1/I_3 .

3.5. Effect of inorganic salt concentration on apparent viscosity of polymers solution

Figure 9 shows the effect of inorganic salt (NaCl) concentration on the apparent viscosity of polymer solution (0.5 g/dl). It was found that NaCl has a significant effect on the values of apparent viscosity. The expected viscosity decrease was observed for PAM solution, which generally attributed to the thinning of hydration film around the macromolecular chain and the size shrinkage of the macromolecular by the increasing polarity of solvent. At the concentration above 1.0 g/l, the viscosity of PAM solution became insensitive to the increasing NaCl concentration due to the slightly change of the shrunken macromolecular chain size.

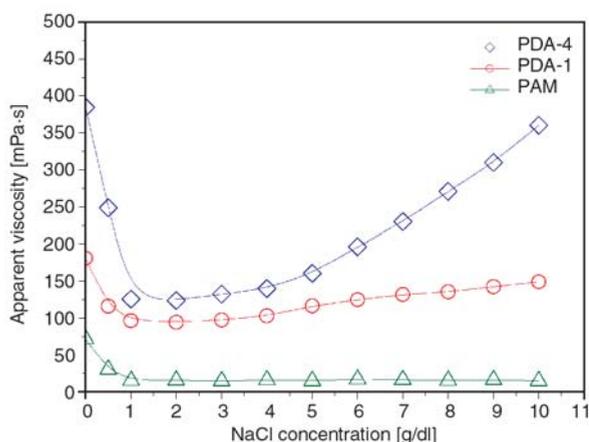


Figure 9. Effect of salt concentration on the apparent viscosity of polymer solution

As far as PDA was concerned, the viscosity decreased sharply with the addition of NaCl. It was believed that the added ionic charges acted as electrostatic shields had destroyed the PAA-PDA complexes, leading to a reduction in the macromolecular chain size and the decrease of solution viscosity, which was accelerated by the thinning of hydration film. With the increase of NaCl concentration, the viscosity of PDA solution increased. The addition of salt increased the polarity of solvent, which made the nopolar hydrophobic groups more easily to contract, resulting in the enhancement of intermolecular association and the solution viscosity. PDA prepared with template had a more significant salt thickening effect for its longer hydrophobic block structure.

4. Conclusions

A new approach was carried out to synthesize HAPAM via inverse miniemulsion polymerization in the presence of template. DOAB was synthesized via quaternization reaction and used as the hydrophobic monomer. PAA was used as template for the oppositely charged DOAB. In the inverse miniemulsion system, DOAB strongly interacted with template PAA and formed tight complexes. The complexes were located not only at the interface of the inverse miniemulsion droplets and oil phase but also in the interior of inverse miniemulsion droplets. The results from viscosimetry indicated that PDA prepared with template exhibited remarkable thickening ability in aqueous solution and aqueous salt solution. The thickening ability strongly depended on the chain structure, which

was dominated by aqueous phase pH, ratio of hydrophobic monomer to template and hydrophobic monomer content. Furthermore, fluorescence spectra of pyrene probe revealed that PDA prepared with template showed stronger association ability for its longer hydrophobic block structure.

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