

Rheological evaluation of synthesized template-hydrophobically modified acrylamide based copolymers in brine

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ABSTRACT: The newly hydrophobically modified associating acrylamide-based copolymers were prepared by the inverse miniemulsion polymerization method in order to investigate the copolymers rheological and associating properties in water and brine solutions. Dimethyldodecane (2-acrylamidopropyl) ammonium bromide (DDPAB) was synthesized and used as a hydrophobic monomer and was later copolymerized with acrylamide in the presence of poly(acrylic acid-co-maleic acid) and various molecular weights of poly(acrylic acid) as templates. The chemical compositions and functional groups of the resulting hydrophobic monomer and copolymers were characterized using the ¹H nuclear magnetic resonance and Fourier transform-infrared spectroscopy. According to the studies on the solutions viscosity behavior, incorporation of small amount of hydrophobic monomer improved the thickening properties due to the intermolecular hydrophobic association. The apparent viscosity of the copolymers with a template was much greater than those prepared without a template. The molecular weight of the template strongly influenced the thickening behaviors of the copolymers. A template copolymer with 1 mol % of a hydrophobic monomer was the one most efficient. The addition of electrolyte saline improved the polarization of the solutions and enhanced the thickening ability. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43588.

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INTRODUCTION

The hydrophobically associating water-soluble polymers containing a few mole percent of hydrophobic comonomers attached directly to the polymer backbone are known as thickeners and rheology-modifiers.^{1–3} These amphipathic copolymers commonly have a structure of hydrophilic molecular groups in the main chains with small parts of hydrophobic groups.^{4,5} Such polymers have been in the center of attention over the past three decades.^{6–9} Among these copolymers, the hydrophobically associating polyacrylamides (HAPAM) are specifically remarkable as they are relatively inexpensive and nontoxic, in addition to providing some unique rheological properties for applications in the enhanced oil recovery.^{10–14} Due to the presence of hydrophobic groups, there are intramolecular and intermolecular associations in the aqueous solution systems.^{15,16} Over a certain polymer concentration, similar to the formation of micelles by a surfactant above its critical micelle concentration, the hydrophobic groups in these polymers coincide and tend to associate in an aqueous solution via the intermolecular hydrophobic interactions. This results in the formation of polymolecular associations, which may dramatically enhance the thickening ability.^{17,18}

Micellar polymerization is the most efficient synthetic method for preparation of HAPAM with multi block structure and

control capability of the blocks' length.¹⁹ The limited initial concentration of the reaction mixture due to the process of gelation during the polymerization is the main difficulty of this method.²⁰ This issue can be resolved with the inverse emulsion polymerization, whereas hydrophobically polyacrylamides should result with more total solid and higher monomer concentrations.^{21–24} The inverse miniemulsion polymerization requires a little amount of surfactant to give more stable and homogeneous latex in comparison with the microemulsion and conventional emulsion polymerization.^{25,26} The microstructure of the polymers in the polymerization can be controlled by means of a proper template.²⁷ In the presence of template, the polymeric chain grows along with the template due to the interactions between the oppositely charged hydrophobic monomer and the template, forming a longer hydrophobic block. In other words, template polymerization tends to produce a multiblocky structure copolymer with stronger association capability. As a result the template copolymer exhibits higher thickening ability than that of the traditional one obtained without a template.^{28,29}

Addition of small amount of electrolyte salt to aqueous solution of hydrophobically modified acrylamide-based copolymers helps to increase the solution polarization, and reinforcing the

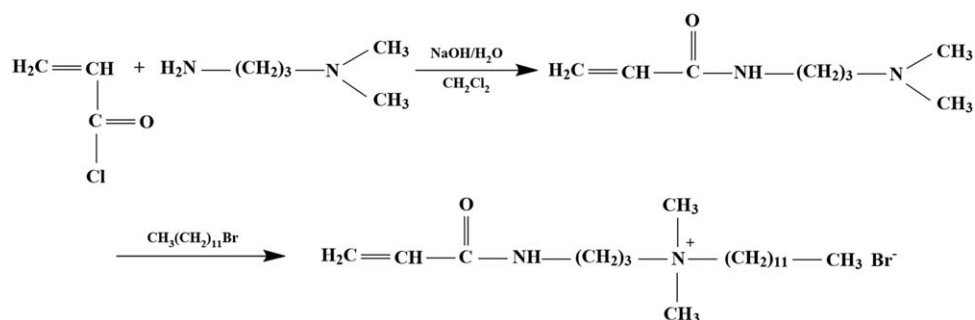


Figure 1. Synthesis route of cationic hydrophobic monomer (DDPAB).

hydrophobic association.^{30,31} As a result of the hydrophobic groups association, the hydrodynamic size of the polymer increases and their aqueous solutions give attractive rheological properties and, simultaneously, further stability in salinity compared with the unmodified one in addition to the viscosity enhancement.^{32,33} Accordingly, these hydrophobically associating copolymers have a great potential to be used as the mobility controller in reservoirs with a high level of brininess and a high concentration of monovalent and divalent ions.^{34–36}

Consequently, in recent years, there has been a significant progressive interest about the synthesis and investigation of the solution properties of acrylamide-based copolymers. Many research studies have also been carried out on the mechanism and the microstructure of these template copolymers. A template copolymer of N-isopropylacrylamide and a cationic monomer, N,N-(dimethylaminopropyl)methacrylamide, was prepared using polyacrylate chains as a preliminary template with the purpose of studying the mechanism of the polymerization process and investigating the influence of the template on the polymer microstructure. The molar mass of the template copolymer was found much higher than a similar one prepared without the template.³⁷ Liu's research group has studied the microstructure of acrylamide/methylacrylic acid copolymers in the presence of poly(allylammonium chloride) in aqueous solution by high resolution nuclear magnetic resonance. The results of one-dimensional (1D) and two-dimensional (2D) nuclear magnetic resonance (NMR) studies demonstrate that the microstructure of the template copolymer in aqueous solution depends on the pH solution.³⁸ Acrylamide and 2-methacryloyloxyethyl-trimethylammonium chloride (DMC) was synthesized with polysodium acrylate (PAAS) as a template by Wu *et al.* The results indicated that the block length of the hydrophobic monomer was significantly increased due to the presence of template.³⁹ Zhang *et al.* studied the template's impact on the reaction kinetic of the copolymerization of acrylic acid and acrylamide using polyallylammonium chloride as a template.^{40–42} The copolymers of acrylamide and 4-(*ω*-propenoxyethoxy) benzoic acid were investigated in the presence of poly(allylammonium chloride) as a template in an aqueous medium by viscometry. These template copolymers exhibited remarkable thickening properties due to the effective hydrophobic association.⁴³ The rheological properties of the product of template polymerization of polyacrylamide in aqueous solutions were also investigated by Zhang *et al.*⁴⁴ Gong *et al.* found stronger association ability for copolymers prepared with template for its

longer hydrophobic block structure which was confirmed by the fluorescence spectra.²⁶

In this work, we have synthesized a cationic hydrophobic comonomer; have prepared the hydrophobically associating copolymers, and have investigated the rheological properties of the template copolymers, to study the impact of copolymer's microstructure on its rheology in water and brine solutions. First, a novel cationic hydrophobic monomer, namely, dimethyl dodecyl-(2-acrylamidopropyl) ammonium bromide was synthesized via the quaternization reaction. Then, the hydrophobically modified associating water-soluble multiblock copolymers of acrylamide with the synthesized hydrophobic comonomer, were prepared using an inverse miniemulsion polymerization technique in the presence of poly(acrylic acid) and poly(acrylic acid-*co*-maleic acid) as templates. The infrared spectroscopy (IR) and ¹H NMR were conducted to characterize the association structures of monomer and copolymers. The solution viscosity behaviors of copolymers have been investigated with respect to the molar percentage of hydrophobic monomer and the templates with various molecular weights. The influence of NaCl and CaCl₂ on the rheological properties of the template copolymers is also discussed.

EXPERIMENTAL

Materials

The hydrophobically modified copolymers and hydrophobic monomer, dimethyldodecane (2-acrylamidopropyl) ammonium bromide (DDPAB) were synthesized in our laboratory according to the methods described in the literatures.^{4,26} Acrylamide (AM) with purity higher than 99% was purchased from Merck. Sorbitan monooleate (Span 80) (Merck), poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol) (Pluronic 31R1) ($M_n \sim 3300$ g/mol) (Aldrich), and kerosene (Fluka) were used as surfactant, stabilizer, and continuous phase respectively. The initiator for the synthesis of copolymers was 2,2'-azobis[2-(2-imidazolin-2-yl)-propane] dihydrochloride (AIPC), supplied from Energy Chemical company. Poly(acrylic acid) (PAA) with molecular weights of 1800 and 5000 g/mol and poly(acrylic acid-*co*-maleic acid) [poly(AA-*co*-MA)] with molecular weight of 3000 g/mol were obtained from Aldrich and used as templates. All reagents were used as received without any further purification. The brine used in this work was prepared with the inorganic salts, NaCl and CaCl₂. Deionized water was used throughout the experiment.

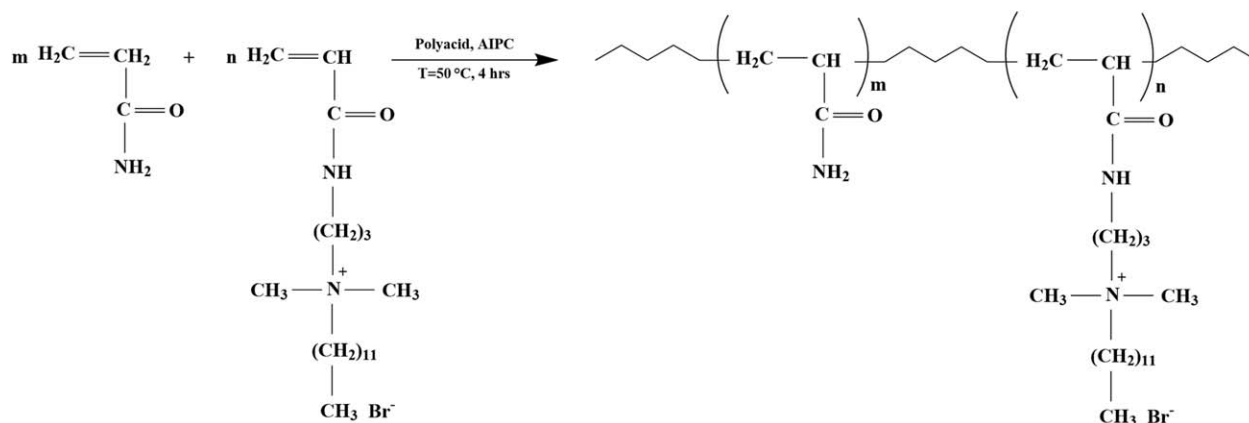


Figure 2. Synthesis route of hydrophobically associating template copolymer (AM/DDPAB).

Polymerization Procedures

Synthesis of Cationic Hydrophobic Monomer. DDPAB with the following structure as shown in Figure 1 was synthesized via the two-step reaction.^{4,26}

An indicated amounts of dichloromethane with *N,N'*-dimethyl 1,3 propanediamine and sodium hydroxide were added into a stainless steel Buchi reactor and were simultaneously mixed and purged with nitrogen for 15 minutes. When the bath temperature dropped below 10 °C, dichloromethane with acryloyl chloride were slowly added from a funnel while the temperature was kept below 10 °C. Finally, after titration, the reaction proceeded at the room temperature for 5 h. The organic phase was then separated, washed twice with saturated sodium carbonate aqueous solution, and then the aqueous phase was extracted with dichloromethane after adding excessive sodium chloride. The organic phase was dried for 4 h with anhydrous magnesium sulphate. The solvents were removed by a rotary evaporator and a liquid product with a yellowish color was obtained. Finally, the product was purified by the vacuum distillation in the presence of a small amount of copper as inhibitor. Some colorless oil was collected from the reaction vessel at 140–150 °C under a vacuum of 0.5 mmHg. *N*-[3-(Dimethylamino)-propyl]acrylamide was then treated with dodecyl bromide, degassed with gentle bubbling of N₂ for about 10 minutes in a 100 mL round flask and then the reaction proceeded at room temperature for

about 48 h. Afterward, the excess dodecyl bromide was decanted and then the transparent gel precipitated and converted into a white solid by acetone. Additional purification of the product was performed by the mixture solvent of acetone and ether for several times. The solvents were removed by a rotary evaporator, and then the raw product was dried into a constant weight in a vacuum oven at room temperature for about 48 h. As a result, a white powder of DDPAB was obtained (m. pt. ~122–128 °C).

Synthesis of Template Hydrophobically Modified Copolymers. Template copolymers of AM/DDPAB were prepared using inverse miniemulsion polymerization in the presence of PAA and poly(AA-*co*-MA) as templates, according to the literatures.²⁶ Figure 2 illustrates the synthetic route of the hydrophobically modified copolymers.

The aqueous phase was prepared according to a certain mass ratio of the template, aqueous solution of two monomers (DDPAB and AM), and the initiator AIPC. The solution was then adjusted to a neutral pH with sodium hydroxide solution (0.5M). The aqueous phase was mixed with oil phase prepared by predissolving surfactant Span 80 and stabilizer Pluronic 31R1 in kerosene. The mixture was pre-emulsified by magnetic stirring and then homogenized by ultrasonication in an ice water bath to prevent polymerization. The synthesis was carried out in a 600 mL stainless steel Buchi reactor equipped with a

Table I. Abbreviations and Correlative Data of the Synthesized Polymers Used in this Study

Sample	Template	DDPAB/AM (mol %)	$M_w \times 10^{-6}$
^a PAM	-	-	3.4
^b CHPA	-	0.5	3.1
^c TCHPA-24	PAA 1800	0.5	3.3
TCHPA-21	PAA 1800	1	3.1
TCHPA-27	Poly(AA- <i>co</i> -MA)	1	3.2
TCHPA-20	PAA 1800	3	2.5
TCHPA-25	PAA 5000	0.5	3.5

^a Polyacrylamide.

^b Cationic hydrophobically polyacrylamide.

^c Template cationic hydrophobically polyacrylamide.

Table II. Characteristic Data for Preparation of Template Hydrophobically Copolymer (TCHPA-24)

Sample	AM (g)	DDPAB (g)	Template (g)	H ₂ O (mL)	Kerosene (g)	Span 80 (g)	Pluronic 31R1	AIPC (g)	RT (h)
TCHPA-24	10	0.29	1.27	20	70	3	0.3	0.012	4

mechanical stirrer, an attachment for bubbling N₂, reflux condenser, and a heating system. The polymerization reaction proceeded at 50 °C for 4 h. Next, the resulting polymer was precipitated by slowly pouring the solution into the constantly stirred mixture of ethanol and acetone, and washed with ethanol and acetone separately three times. After filtration, the crude product was dried into a vacuum oven at room temperature for 24 h and then a fine powder of polymer was obtained. The abbreviations and correlative data of the polymer and copolymer samples prepared are summarized in Table I.

The characteristic data for some template hydrophobic copolymer (TCHPA-24), as a representative, is presented in Table II.

For all the samples, the molar ratio of hydrophobic monomer to template was considered unity, and the molar ratio of hydrophobic monomer to AM was given in Table I. The specific value of acrylamide, the hydrophobic monomer, and template for the other samples may be calculated accordingly.

Characteristic Analysis

¹H NMR and FT-IR. The structure of hydrophobic monomer and AM/DDPAB copolymers was detected using the ¹H NMR and FT-IR spectroscopy. The ¹H NMR experiments were measured using Chloroform-D (CDCl₃) and water-D (D₂O) as solvents, simultaneously. The FT-IR spectra were recorded on a Bruker FT-IR spectrophotometer with KBr pellet in solid state with the purified polymer samples in the range of 500–4000 cm⁻¹.

Intrinsic Viscosity and Molecular Weight Determination. The intrinsic viscosity [η] of the polymer's aqueous solution was characterized using an automatic capillary viscometer (Ubbelohde), Lauda Model PV15 at 30 °C with 1M NaCl solution as a solvent. The concentrations of the polymer were in the range of 0.05–0.2 g/dL. The viscosity of each solution was automatically measured three times by the same viscometer. The intrinsic viscosity was determined by extrapolating the reduced viscosity to zero concentration according to the Flory–Huggins eq. (1). The reduced viscosity is a linear function of polymer concentration as follows:

$$\frac{\eta - \eta_0}{\eta_0 C} = [\eta] + k'[\eta]^2 C \quad (1)$$

The polymer's molecular weight was determined relative to the intrinsic viscosity using the Mark–Houwink–Sakurada eq. (2) where $K = 4.75 \times 10^{-3}$ mL/g and $\alpha = 0.8$.²⁶ Whereas, the weight and viscosity average molecular masses, M_w and M_v , are considered equal in dilute solutions, M_w were calculated from the same formula.⁴⁵

$$[\eta] = k[M_w]^\alpha \quad (2)$$

Viscosity Measurement. The rheological measurements were carried out on a rotational rheometer (MCR 500). The solution

viscosity of the copolymers was investigated at different polymer concentrations, shear rate, and salinity. All the samples were separately prepared by dissolving an appropriate amount of the polymers into pure water or saline at room temperature. The mixtures were stirred for 2 h and then the polymer solutions were left for complete dissolution for 24 h before measurements. All the solutions appeared to be transparent and homogeneous.

RESULTS AND DISCUSSION

Characterization

The cationic, hydrophobically associating polyacrylamides were synthesized in the presence of PAA and poly(AA-co-MA) as templates via the inverse miniemulsion polymerization. DDPAB was synthesized via the quaternization reaction and used as a hydrophobic monomer. The ¹H NMR and FT-IR were used to characterize the structures of the hydrophobic monomer and copolymers. Figure 3(a,b) represent the ¹H NMR spectrum of hydrophobic monomer and copolymer (TCHPA-24) in CDCl₃ and D₂O, respectively. All the resonances of protons were determined on the related spectrum of the monomer and copolymer.

As is seen in the Figure 3(a), the chemical shift value at 0.8253 is assigned to the proton CH₃ (proton k). The characteristic peak at 1.2091 is due to the proton (CH₂)_n marked as j. The protons—CH₂ (i, f, g, and e) in the chain are appeared at 1.6783, 2.1219, 3.3791, and 3.7181. The proton CH₃—N—CH₃ (h) is seen at 3.2366. The proton —NH (d) is at 8.3264. The 5.5707, 6.2510, and 6.4555 protons (a, b, and c) belong to =C—H. The result of ¹H NMR showed that the hydrophobic monomer was synthesized. The ¹H NMR of the template copolymer (TCHPA-24) was shown in Figure 3(b). As is obvious, the characteristic peaks observed at 0.7337 is related to CH₃ (proton k) and the proton (CH₂)_n (j) is appeared at 1.1328. The protons =C—H are shifted to 1.5236 and 1.6160 (protons a, a), and 2.0790 and 2.2097 (protons c, c) due to the reduction of carbon–carbon double bonds. The chemical shift values at 7.6123 and 7.8120 are due to the protons NH₂ and NH (protons d' and d), respectively. Therefore, the obtained ¹H NMR spectra confirmed the template cationic hydrophobically associating acrylamide based copolymers' structure.

The FT-IR spectra of monomers (AM and DDPAB), copolymer (TCHPA-24), and all three together were shown in Figure 4(a–c), respectively. The characteristic FT-IR adsorption peaks of hydrophobic monomer (DDPAB) are as follows: —NH stretch (3424.68 cm⁻¹), =C—H stretch (2924.20 cm⁻¹), —C—H stretch (2853.51 cm⁻¹), C=O stretch (1640.14 cm⁻¹), C=C (1561.34 cm⁻¹), C—N (1385.31 cm⁻¹), (CH₂)_n n > 2 (720.91 cm⁻¹), and C—Br (641.31 cm⁻¹). The functional groups observed in AM spectra are: —NH₂ stretch (3353.33 cm⁻¹), =C—H stretch (2812.71 cm⁻¹), —C—H stretch (2734.71 cm⁻¹),

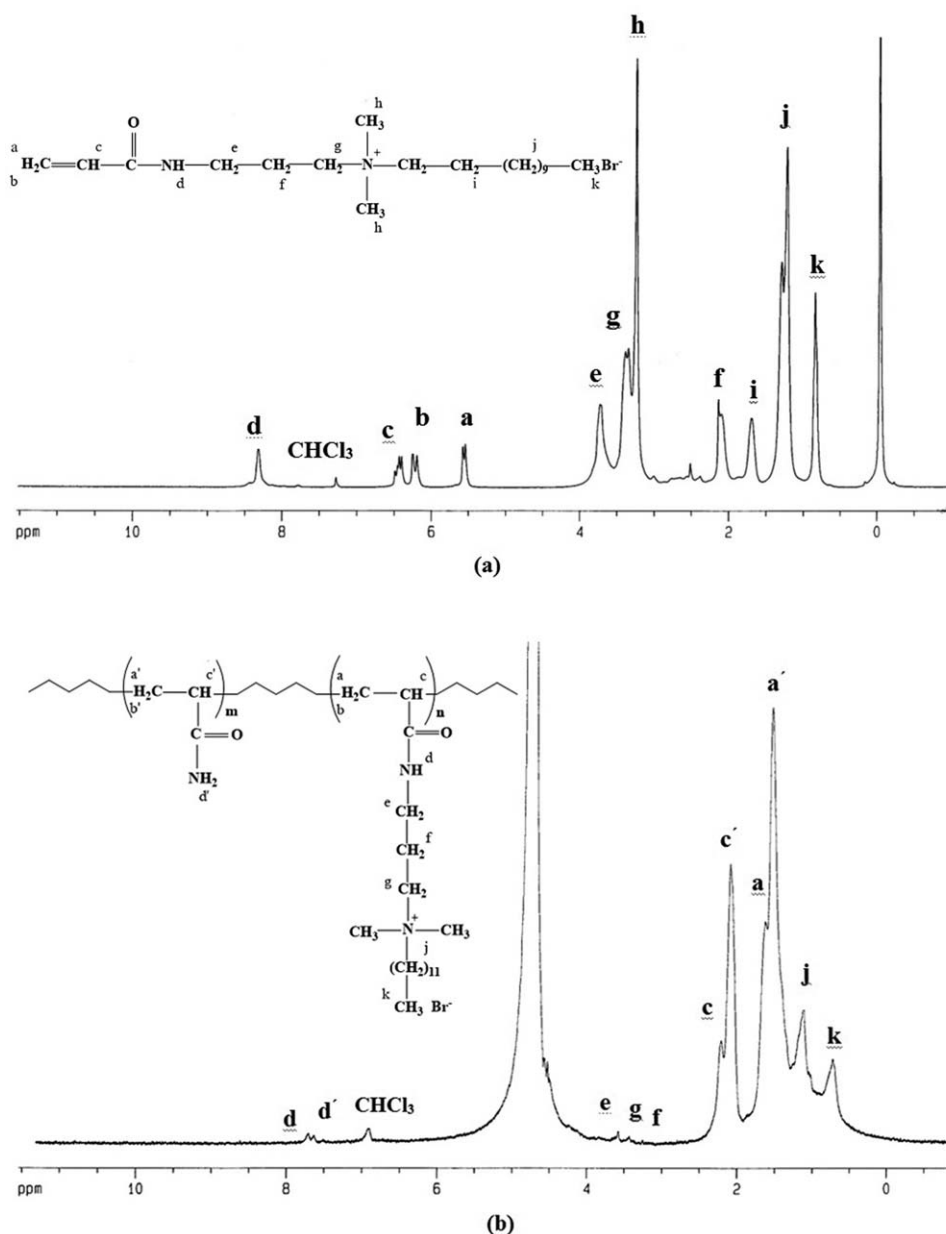


Figure 3. ^1H NMR of (a) hydrophobic cationic monomer (DDPAB); (b) template cationic hydrophobically copolymer (TCHPA-24).

$\text{C}=\text{O}$ stretch (1672.92 cm^{-1}), and $\text{C}=\text{C}$ (1612.65 cm^{-1}). The major functional groups identified on TCHPA-24 are confirmed by the strong absorptions at 3354.34 and 1662.68 cm^{-1} ; these are attributed to the stretching vibration of $\text{N}-\text{H}$ and $\text{C}=\text{O}$ bonds, respectively, in the $-\text{CONH}_2$ group. The peak at 1452.18 cm^{-1} is due to the stretching vibrations of $\text{C}-\text{N}$ and that at 2855.86 cm^{-1} is assigned to the stretching vibrations of $\text{C}-\text{H}$ bond. $\text{C}-\text{Br}$ exhibited adsorption at 634.95 cm^{-1} . All these bands confirm that those monomers have been properly introduced into the polymer chain and the hydrophobically modified cationic polymers were successfully synthesized.

It is worth to mention that as PAA is a polyelectrolyte, in water solution, the majority of the side chains of this polyacide would lose protons and acquire negative charges. Therefore, PAA is

converted during the reaction, and should not exist anymore or, more likely; only a small trace of PAA may be present, not observable by the NMR or FT-IR. PAA generates negative charges in water solution and interacts strongly with the cationic hydrophobic monomer (DDPAB). It acts the same as a coupling agent, steers the reaction and helps to have a longer hydrophobic block structure along the polymer chain resulting in an increase in the viscosity.

Rheological Behaviors

Viscosity of Different Polymers. Figure 5 compares the apparent viscosities of polyacrylamide (PAM), hydrophobically polyacrylamide (CHPA), and template hydrophobically polyacrylamide (TCHPA-24) in different concentrations. As shown, the apparent viscosities for the copolymers prepared with a

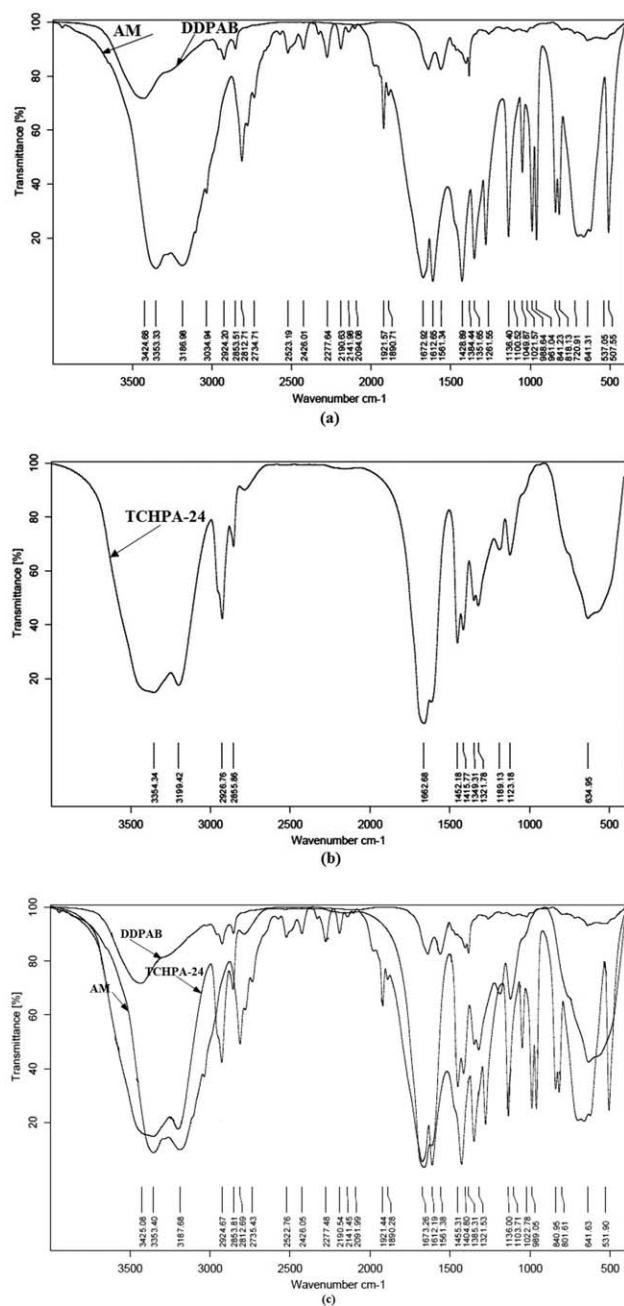


Figure 4. FT-IR spectra of (a) DDPAB and AM monomers; (b) hydrophobically associating template copolymer (TCHPA-24); (c) DDPAB/AM/TCHPA-24.

template are much higher than those prepared without a template, and much higher than polyacrylamide. In the presence of PAA, the block length of DDPAB was significantly increased in the copolymer due to the electrostatic interaction between the DDPAB and PAA, making it easier to form an intermolecular association at the concentration above the critical point.²⁶ As a result the polymer would have a greater thickening ability.

Effect of Template Molecular Weight. Figure 6 shows the effect of the molecular weight of templates on the viscosity. Comparing viscosity thickening capacities for different templates, it was

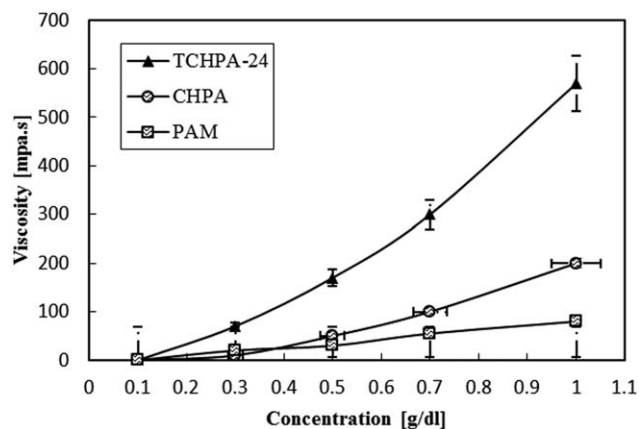


Figure 5. Comparison of PAM, CHPA, and TCHPA-24 viscosities in different concentrations.

found that viscosity increases when the molecular weight of templates increases. The length of large blocks in a chain depends on the molecular weight of the template in polymerization⁴³; a longer hydrophobic block structure has a stronger hydrophobic association ability. When the template's molecular weight increases, so does the solution viscosity. This is an indication that the average size of the hydrophobic blocks is more effective than their block number. The viscosity variations of the poly(AA-co-MA) template with a molecular weight of 3000 and the PAA with a molecular weight of 5000 g/mol are almost alike. It can be related to the stronger electrostatic interaction between poly(AA-co-MA) and DDPAB due to losing more protons and acquiring further negative charges, forming a tighter complex and longer hydrophobic block structure.

Effect of Hydrophobic Content. Figure 7 indicates the influence of hydrophobic monomer content on the viscosity of copolymer solutions. A template copolymer with 1 mol % of a hydrophobic monomer has been the most efficient copolymer. With the increase in the molar percent of the hydrophobic monomer from 0.5 to 1 mol %, the viscosity increased from 330 to 780 (mPa.s) and then decreased to 570 (mPa.s) at 3 mol %. Increasing the hydrophobic monomer from 0.5 to 1 mol % increased the density of the hydrophobic block during the

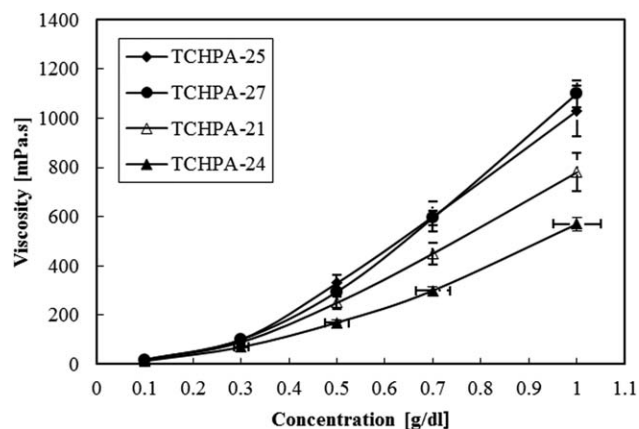


Figure 6. Effect of templates' molecular weight on the viscosity of template hydrophobically copolymers in different concentrations.

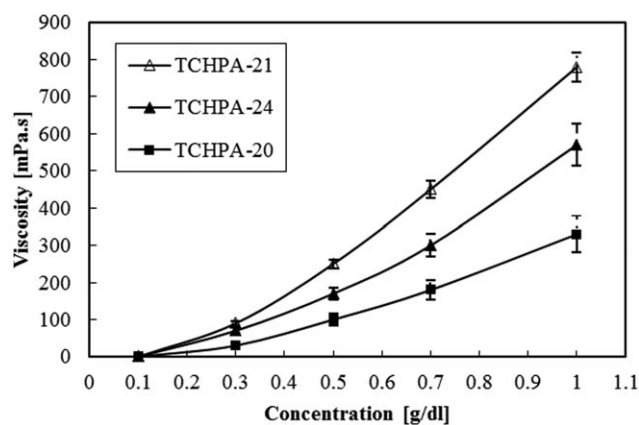


Figure 7. Effect of hydrophobic monomer (DDPAB) content on the viscosity of template hydrophobically copolymers in different concentrations.

copolymerization, leading to a larger quantity and probability of hydrophobic groups participating in the association. A reduction in viscosity observed for 3 mol % hydrophobic monomer may be related to the more amount of template in the copolymer composition. Since the molar ratio of the hydrophobic monomer to the template was constant; the amount of template increased in copolymers with increasing the hydrophobic monomer content. It then acted as a chain-transfer agent, which decreased the molar mass and viscosity, subsequently. In addition, the literature shows that the viscosity of the copolymer solution after template separation is slightly higher than that of the one with template.²⁶ This indicates that an increase in the viscosity with copolymer concentration is mainly due to the hydrophobic interaction between the hydrophobic monomer units.

Effect of Polymer Concentration. Figure 8 depicts the viscosity of all synthesized samples as a function of concentration in aqueous solutions. It is clear that the viscosities of hydrophobically modified associating copolymers have been enhanced sharply with rising concentration as reached approximately to 0.3 g/dL called the critical concentration. However, the viscosity variations of polyacrylamide were happened gently without any transition. This high thickening behavior of the associating copolymers is resulted due to the transformation of intramolecular association into intermolecular association at a certain range. With further increasing of polymer concentration, the intermolecular association is strengthened due to the shortening of the macromolecules distance. It caused the formation of some supermolecular aggregates which can greatly enhance the viscosity. These results are the same as what are frequently reported for hydrophobically modified associative polyacrylamides.^{46–50} Comparing the thickening property, the highest viscosity enhancement was found for the copolymers synthesized in the presence of template. Among the template copolymers, TCHPA-27 with 1 mol % hydrophobic monomer prepared with poly(AA-co-MA) as a template demonstrated the maximum apparent viscosity that was almost similar to that of TCHPA-25 in terms of thickening ability. Having more amounts of hydrophobic monomer with higher molecular weight of the template assign to a longer hydrophobic block structure and

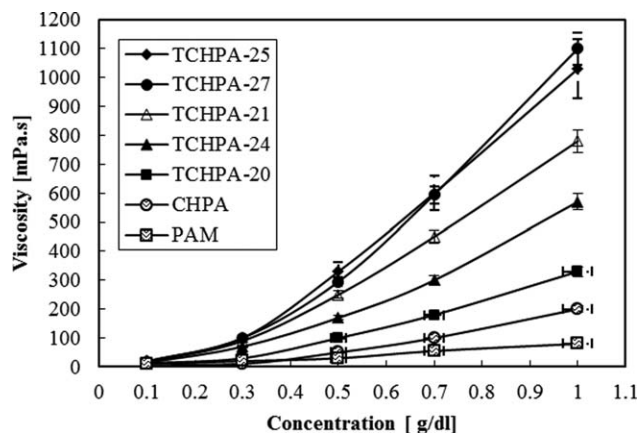


Figure 8. Viscosity of polymers as a function of concentration in aqueous solutions.

stronger association ability causing the further aggregate volume, and finally increasing the apparent viscosity. In contrast, TCHPA-20 with 3 mol % hydrophobic monomer showed reduction in viscosity and molar mass because of the chain-transfer phenomenon that decreases the hydrophobic block density and chain length, thus reducing the viscosity.

Effect of Brine Concentration. Since, adding salt ions have a considerable effect on the rheology of associated copolymers, Figures 9 and 10 illustrate the effect of different concentrations of inorganic ions (Na^+ , Ca^{2+}) on the shear viscosity of the TCHPA-24 copolymer. The viscosities of the copolymer were measured in 0.05, 0.5, 1, 2, 3, and 4M NaCl aqueous solutions. The concentrations of CaCl_2 solutions were 0.01, 0.05, 0.1, and 0.2M. All the samples were prepared at a concentration of 0.7 g/dL.

The effect of sodium salt (NaCl) concentration on the viscosity of TCHPA-24 solution is shown in Figure 9. Adding salt has an electric-shielding effect on the electrostatic resistance of the polymer ions, causing the polymer chains to coil up.^{5,51} This decreases the viscosity of the polymer solution while increasing the salt concentration. For our synthesized hydrophobically

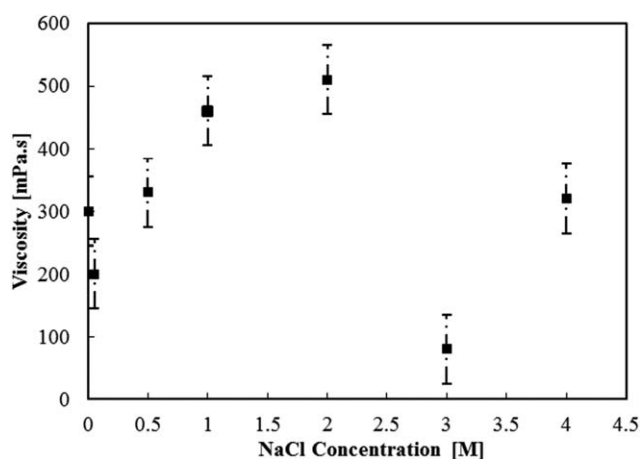


Figure 9. Effect of NaCl concentration on the solution viscosity of TCHPA-24.

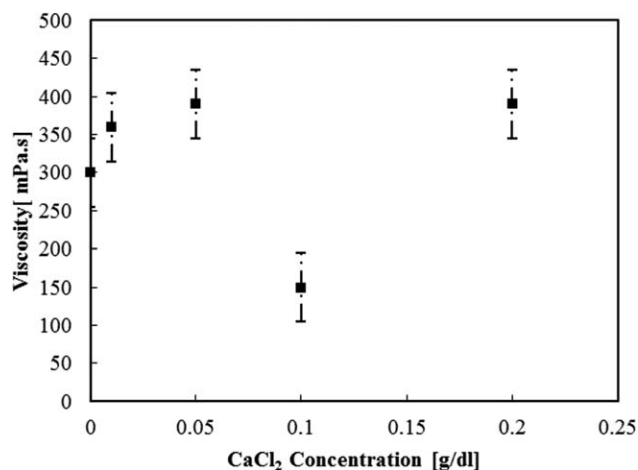


Figure 10. Effect of CaCl_2 concentration on the solution viscosity of TCHPA-24.

associating template copolymer, the viscosity of copolymers first decreased when NaCl was added and then increased when the sodium concentration increased up to 2M. Adding sodium salt improves the polarization of the solution, making it easier for the nonpolar hydrophobic groups to come in contact. It enhances the intermolecular association effect of the hydrophobic group and the solution viscosity.^{52,53} Increasing viscosity by salt is attributed to the strength of hydrophobic association. After increasing the salt to 3M, the viscosity was decreased sharply. With increasing the monovalent ion to 4M, an increment in the viscosity was observed once again although it was less than the viscosity of the solution with 2M NaCl concentration. A possible explanation for these cases is that the additional ionic charges act as electrostatic shields, destroying the template copolymer complexes making the copolymer chains stick to one another and shrink. This phenomenon reduced the size of the macromolecular chain and decreased the solution viscosity that was more obvious at the concentration of 3M saline.^{54,55}

Figure 10 shows the variation in viscosity for TCHPA-24 with different concentrations of CaCl_2 solutions. The viscosity was increased in 0.05M of Ca^{2+} and then decreased when the divalent ion reached 0.1M. In the case of 0.2M concentration, the viscosity was similar to that of 0.05M. A strong interaction between the polyelectrolyte solution and divalent ions causes a weaker repulsion between the molecules and a smaller hydrophobic association that results in a decrease of hydrodynamic radius and viscosity.⁴⁴ This suggests that the viscosity of the copolymer solution in the CaCl_2 brine is lower than the viscosity in the NaCl brine because of the lower degree of association.

As compared the viscosities of the TCHPA-24 in pure water and brine solutions, it was observed that the viscosities of the copolymer in saline enhanced dramatically with increasing the salt concentration. This observation demonstrated that the polarity of the hydrophobic microdomains in the brine solutions of copolymer is much stronger than the polarity in pure water. Increasing the aqueous solution polarization by adding the electrolyte molecule can promote the hydrophobic association, and increase the solution viscosity; however, this effect is limited.

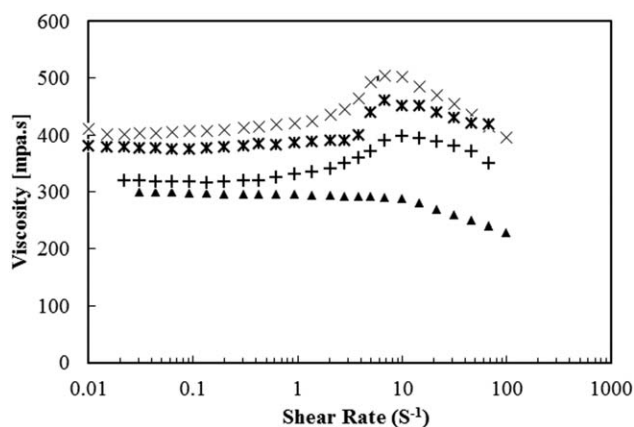


Figure 11. Comparison of TCHPA-24 solution viscosities in monovalent ion (x), divalent ion (+), mixture of both ions (x), and pure water (▲).

Effect of Shear Rate. Figure 11 compares the apparent viscosity of TCHPA-24 in the mixture of both monovalent and divalent ions solution with 2M Na^+ and 0.2M Ca^{2+} as a function of shear rate. The viscosity of copolymer in the mixed ions is between the viscosities of copolymer in the separate ion solutions but is closer to the Na^+ saline. This indicates that the electrostatic shield effect of the monovalent, as an opposite ion for the repulsion between anions, is stronger than the divalent ion. Hence, the viscosity in the NaCl brine is much higher than that in the CaCl_2 brine. This results have been reported in some other research as well.^{30,44}

In pure water, the polymer solution shows classical behavior including, Newtonian plateau at low shear rates, and the typical behavior of pseudo-plastic fluid that viscosity is decreased with increasing the shear rates to 10 s^{-1} .³⁶ In brine solutions the flow curve of copolymer was changed due to the hydrophobic association. It exhibits three regions including a Newtonian plateau at low shear rate where the viscosity is constant, shear thickening region where the viscosity rises with shear rate to a maximum point, and finally a shear thinning regime that viscosity decreases with increasing the shear rate. This particular behavior is due to the balance shifting of intra- and intermolecular hydrophobic associations with shear stress.^{6,35} The shear thickening behavior can be explained by stretching the polymer chains at high shear rate that can enhance the intermolecular association, and increase the viscosity.³⁵ However, this expansion can only occur in the limited shear rates and the shear thinning phenomenon would happen upon increasing the shear rate.

CONCLUSIONS

The hydrophobically modified associating copolymers of acrylamide and DDPAB were synthesized through inverse miniemulsion polymerization in the presence of PAA and poly(AA-co-MA) as templates. DDPAB was prepared via a two-step reaction and used as a hydrophobic monomer. The structures of hydrophobic monomer and copolymers were justified by the ¹H NMR and FT-IR. The properties of copolymers were investigated under different conditions in order to study the relation between the copolymers structure and their solution viscosity

behavior. Association of hydrophobic groups in aqueous solutions, due to the intermolecular hydrophobic interaction and formation of polymolecular network structure, results in improving the viscosity. The copolymers were prepared with a template demonstrated remarkable thickening ability. In the presence of a template a longer hydrophobic blocks appears causing stronger association ability and viscosity. The rheological studies indicated the viscosity of copolymers effectively depends on the hydrophobic content, template type, molecular weight, polymer concentration, and salinity. The apparent viscosity of solution was increased sharply when the concentration is above a critical value, indicating an excellent thickening ability of the copolymers.

Addition of saline prominently improved the viscosity due to inducing more hydrophobic association, and coil expansion formed by the electrostatic repulsions. Therefore, the copolymers exhibited excellent salt-resistance. NaCl was figured out to be more efficient than CaCl₂ in viscosity enhancement. The hydrophobically associating template polyacrylamide solutions exhibited shear thickening behavior at intermediate shear rate in brine solutions.

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