# A Novel Thermoviscosifying Water-Soluble Polymer: Synthesis and Aqueous Solution Properties

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**ABSTRACT:** A novel thermoviscosifying water-soluble polymer was synthesized by direct free radical copolymerization of acrylamide with a newly-prepared macromonomer, and its aqueous solution viscosity behavior at different temperatures was preliminarily examined in both pure water and KCl brine in comparison with its homopolyacrylamide counterpart. Thermoviscosifying ability of the copolymer was clearly evidenced in both aqueous media, and the thermoassociative temperature of the copolymer decreased upon increasing KCl content in polymer solution. Under the same conditions, homopolyacrylamide shows only thermothinning behavior and viscosity loss in both pure water and KCl solution. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 116: 3516–3524, 2010

**Key words:** thermoviscosifying polymer; responsive polymer; water-soluble polymer; polyacrylamide; thermoassociation

## INTRODUCTION

Polyacrylamide (PAM), as obtained by free radical homopolymerization of acrylamide, is one of the most widely used and technically important water-soluble polymeric materials.[1] Applications of PAM can be found in various areas, ranging from gel electrophoresis[2] and chromatography column,[3] soil amendment and conditioning,[4,5] coal and mineral processing,[6,7] papermaking,[8] water purification,[9] drag reduction,[10] to oil production processes including oilwell drilling,[11] reservoir stimulation,[12] water shutoff,[13] profile modification,[14] and particularly tertiary oil recovery.[15,16]

When used in petroleum industry, nevertheless, one of the main problems PAM encountered is its poor thermal stability at elevated temperature that is normally found in oil reservoir conditions.[17–21] The amide pendant side in PAM molecule is readily hydrolyzed into carboxylic group in such an extreme environment,[22] and thus efficiency loss is usually witnessed as the resulting hydrolyzed PAM precipitated when contacting $Ca^{2+}$ and $Mg^{2+}$ commonly presented in the oil reservoir brines.[23,24] Given the weeks and often years required in most oil recovery process, Araghi and Doe[24] and Akstinat[25] observed "safe ceiling" temperatures for PAM were only 75 and 80°C, respectively.

Therefore, extensive research efforts from various laboratories have been active in developing improved PAMs by copolymerization of acrylamide with more thermally stable monomers to minimize excessive hydrolysis and thus enhance thermal stability of the products.[26–33] These attempts, to some extent, have gained positive effect in obtaining higher viscosity retention; however, thermal degradation has not been prevented essentially, and there are still some restricts for PAM to be used in hostile oil reservoirs.

An alternative strategy to improve the heat-tolerant performance of water-soluble polymers was the ingenious concept of "thermothickening" or "thermoviscosifying" polymers pioneered by Hourdet and coworkers in early 1990s.[34,35] In these systems, some "blocks" or "grafts" with the character of lower critical solution temperature (LCST) were incorporated onto the hydrosoluble skeleton. The final copolymer is fairly water soluble and behaved as usual macromolecules at room temperature, but the thermosensitive sequences start to self-aggregate into hydrophobic microdomains upon heating to a critical associative temperature ($T_{ass}$), and reversibly switch off hydrophobic interactions when decreasing

temperature to lower than $T_{ass}$. In the semidilute regime, hydrophobic clusters involving LCST grafts covalently linked to different water-soluble backbones should induce above $T_{ass}$ the formation of physical crosslinks between the mainchains, giving rise to a viscosity enhancement macroscopically. Basically, two types of thermosensitive functionalities were introduced onto polymer backbones with grafting technique: one was polyethylene (PEO) or copolymer of PEO and poly(propylene oxide) (PPO) that was grafted via a coupling reaction onto the mainchains of a low-molecular weight hydrosoluble parent polymer, for example, poly(acrylic acid) (PAA),[34,36] PAM,[37] copolymer of AA and 2-acrylamido-2-methyl propanefulfonic acid (AMPS),[38] terpolymer of AM, AMPS, and N-ethyl vinyl acrylamide,[37] even the natural polysaccharide such as carboxymethylcellulose, aliginate, and carboxylated dextran[39]; or copolymerization of acrylamide with PPO-based macromonomers[40,41]; another was N-isopropylacrylamide (NIPAM)-based amino-end functionalized macromonomer,[42] or the oligomer of NIPAM and other comonomers such as AM, AMPS, or butyl methacrylate,[43] which was grafted onto low-molecular-weight PAA backbone through a two-step process. Grafting method used in above functionalizations can control the primary structure of the copolymers and particularly the length and the molecular weight distribution of the backbone, as well as the placement of grafts along the main chain. However, disadvantages of preparation of thermoviscosifying water-soluble polymers with such a "grafting onto" procedure using PEO- and NIPAM-based thermosensitive stickers were also evidenced. First, carboxylic groups was obligatorily necessary in the polymer precursor for most cases[34,37–39,42,44] to couple the reactive amino-end groups; second, the grafting reaction was always conducted at a relative low polymer concentration and with rather low molecular weight parent polymers, for example, the molar mass of PAA was generally less than half million and polymer loading in the reaction system was below 4%[37]; third, the chemicals used in the coupling reaction, such as the thermosensitive monomer NIPAM, the coupling agents dicyclohexylcarbodiimide (DCCI) and N′-(3-dimethylaminopropyl)-N-ethylcarbodiimide hydrochloride (EDC), were fairly expensive; and finally, some specific inorganic salts, mainly $K_2CO_3$, were needed to decrease $T_{ass}$ of PEO-based thermoviscosifying polymers.[34,37–39,44] These limitations may impede large-scale manufacturing of the polymers and acceptance of petroleum engineers who always desire less expensive, high polymer content, and normally high molecular weight acrylamide-based products.

Attempts have been made in our laboratory to overcome the above deficiencies, and presented in this work are the preliminary results of synthesis and thermothickening behaviors of a novel thermoviscosifying water-soluble polymer prepared via direct free radial copolymerization of AM and a newly-prepared thermoresponsive macromonomer.

## EXPERIMENTAL

### Materials

Acrylamide (AM, 99.5%, Changjiu Agri-Scientific, Nanchang, China), N-(1, 1-dimethyl-3-oxobutyl)-acrylamide (diacetone acrylamide, DAAM, >98%, Liangxi Fine Chemicals, Wuxi, China), 2-amino ethanethiol hydrochloride (AET · HCl, 98%, Aldrich), acryloyl chloride (>98%, Shanghai Shunqiang Biology, China) were used as received. N,N′-dimethylformamide (DMF), potassium persulfate (KPS), and other solvents were all analytical grade and obtained from Shanghai Chemical Reagent, China. The water used was doubly distilled with an all-glass apparatus, and $N_2$ has the purity of 99.999%.
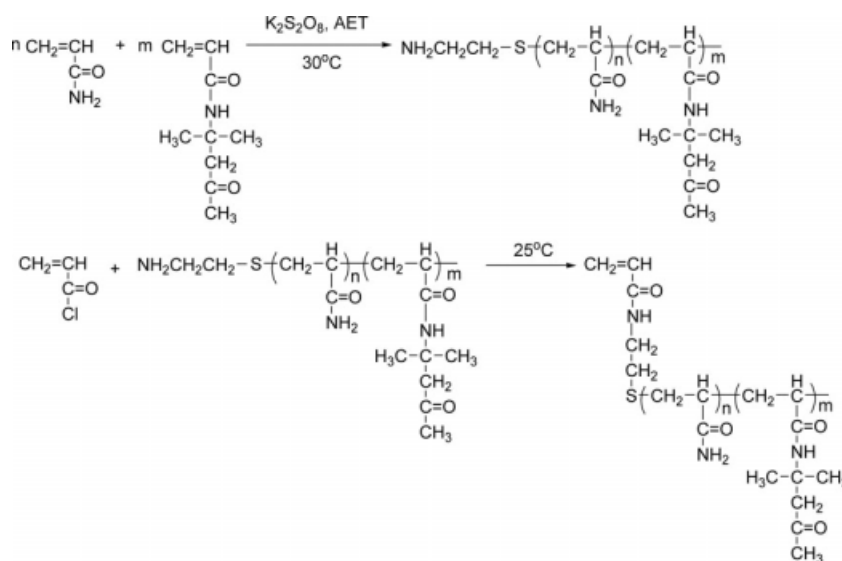
### Synthesis of macromonomer

The novel AM-based macromonomer (MPAD) was prepared through a two-step reaction (Scheme 1) following the NIPAM-telomerization protocol proposed by Chen and Hoffman,[45] but revised in this work. AM (25.56 g, 0.36 mol) and DAAM (74.36 g, 0.44 mol) were firstly copolymerized in water (230 mL) at 30°C under $N_2$ atmosphere for 8 h using KPS (0.80 g, 2.97 mmol) as initiator, and AET · HCl (1.09 g, 9.62 mmol) as chain transfer agent (CTA). The intermediate with a terminal amino group, P(AM-co-DAAM)-NH₂, was obtained by precipitating the reaction solution in acetone, followed by repeated precipitation in acetone and freeze-drying, and 80.25 g of P(AM-co-DAAM)-NH₂ was finally obtained with a yield of 80.31%.

The purified P(AM-co-DAAM)-NH₂ (25.00 g) was then dissolved in DMF (100 mL), and the solution was purged with $N_2$ and cooled down to 5°C. Acryloyl chloride (5 mL, 0.055 mol) dissolved in DMF (10 mL) was added dropwise in the above solution over a duration of 40 min under continuous stirring. When finishing the addition of acryloyl chloride, the reaction was proceeded at 25°C under $N_2$ atmosphere for 12 h, and the reactant was poured into a large excess of acetone to get raw product. Afterward, 18.35 g purified macomonomer MPAD was obtained by repeated precipitation in acetone and freeze-drying.

### Preparation of polymers

The copolymer was prepared by direct free radical copolymerization of AM and macromonomer MPAD

**Scheme 1** Synthesis route of macromonomer MPAD.

in water (Scheme 2): MPAD (3.00 g) and AM (7.00 g) were dissolved in 90 mL water and the pH was adjusted at 7–8 using NaOH followed by 30 min of $N_2$ purge. A total of 0.5 mL of 1% (w/v) KPS aqueous solutions was then injected. The polymerization was proceeded at 50°C with a thermostatically controlled water circulating bath under $N_2$ atmosphere for 10 h. The resulting product was obtained by dropwise addition into fivefold excess of acetone and repeatedly washed with acetone, following with freeze-drying, and 8.15 g of the final product was obtained. For comparison, homopolyacrylamide, PAM, was prepared under the identical conditions.

### Structural characterization

#### Elemental analysis

The elemental analysis of macromonomer MPAD and copolymer was performed using a Carlo Erba 1160 elemental analyzer (Italy), and the final composition of copolymer could be calculated from

$$\frac{56.8\%w_1 + \dfrac{3 \times 12.01}{71.08}w_2}{w_1 + w_2} \times 100\% = 47.2\% \quad (1)$$

$$\frac{9.7\%w_1 + \dfrac{14.01}{71.08}w_2}{w_1 + w_2} \times 100\% = 16.1\% \quad (2)$$

where $w_1$, $w_2$ were the mass content of macromonomer units and AM in the copolymer, and 12.01, 14.01, 71.08 referred to the atomic weight of C, N and molecular weight of AM, respectively.

#### IR spectroscopy

IR spectrum of intermediate P(AM-co-DAAM)-NH$_2$ was registered with a Nicolet MX-1E FTIR (USA) spectrophotometer in the scanning range of 4000–400 cm$^{-1}$ using a KBr pellet method.
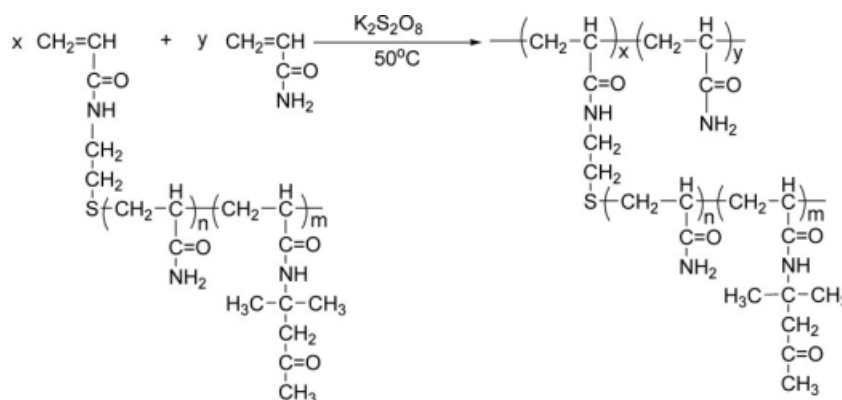


**Scheme 2** Copolymerization of AM and macromonomer.

## Nuclear magnetic resonance

^{1}H-NMR spectra of both intermediate P(AM-co-DAAM)-NH$_2$ and copolymer were recorded on a 300 MHz Bruker spectrometer in DMSO-d$_6$ and D$_2$O, respectively. ^{1}H-NMR spectrum of macromonomer MPAD was recorded on a 600 MHz Bruker spectrometer in D$_2$O.

## GPC measurement

Number- and weight-average molar mass of the macromonomer MPAD were determined by 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°C using 0.1 mol L$^{-1}$ NaNO$_3$ aqueous solution as the eluent, at a flow rate of 0.8 mL min$^{-1}$. Poly(ethylene oxide) (PEO) was used for an initial calibration of the column.

## Determination of intrinsic viscosity

Intrinsic viscosity, [η], of both copolymer and homopolymer, was determined by an Ubbelhode capillary glass viscometer with capillary inner diameter 0.56 mm at 25°C ± 0.2°C using five-spot method. Initial stock polymer solutions were prepared by dissolving appropriate amount of polymers in 0.1 mol L$^{-1}$ NaCl aqueous solution with gentle magnetic agitation.

## Apparent viscosity measurement

Concentrated stock polymer solutions were prepared by dissolution of an appropriate amount of polymer powders in distilled water with gentle magnetic stirring. The solutions were then allowed to stand for some time until any bubbles disappeared. Final desired concentrations of polymer solutions were obtained by diluting the stock solution with distilled water. In the examination of effects of salts, designated amount of KCl fine powders was directly added into the solutions, following by mixing rotationally for 1 day. These solutions were kept standing overnight for equilibrium before measurements. Apparent viscosity (η$_{app}$) of polymer solutions was measured at a constant shear rate ($\dot{\gamma}$) of 10 s$^{-1}$ in the temperature range of 20–80°C with a Brookfield LVDV-III programmable viscometer equipped with SC4-31 spindle and corresponding adaptor. Temperature was regulated with a thermal stable water circulating bath and detected instantaneously using a temperature probe connected between adaptor and viscometer.

## RESULTS AND DISCUSSION

### Synthesis and characterization

Macromonomer

As illustrated in Scheme 1, amido-end functional intermediate was obtained by copolymerization of AM and DAAM in aqueous medium, and the terminal amino group was then substituted by acryloyl chloride to get the final macromonomer MPAD. The key points to obtain the thermoresponsive macromonomer MPAD were the concentration of DAAM in the feed ratio must be carefully controlled within an appropriate range so as to avoid crosslinking during telomerization, and the utility of AET · HCl as an efficient CTA to get both defined functionality and desired molecular weight.[42,44]

Both FTIR and ^{1}H-NMR spectra were used to elucidate the molecular structure of the amido-end functional intermediate P(AM-co-DAAM)-NH$_2$. As its IR spectrum shown in Figure 1, the peak at 1662.4 cm$^{-1}$ was the characteristic absorption bands of carbonylamide in AM and DAAM units, and the band at 1705.8 cm$^{-1}$ was due to the stretching vibration of C=O from ketone in DAAM. It could be seen that two bands located at around 3366.2 and 3415.4 cm$^{-1}$ were attributed to the stretching of N—H; whereas a strong signal at 1542.8 cm$^{-1}$ was resulted from the bending vibration N—H. No more existence of C=C band in the telomer could be verified by the absence of the stretching vibration of =C—H at 3100 cm$^{-1}$ and the absorption bands at 1800 cm$^{-1}$. All these characteristics affirmed the successful copolymerization AM and DAAM.

^{1}H-NMR spectrum of the macromonomer intermediate P(AM-co-DAAM)-NH$_2$ in DMSO-d$_6$ was reproduced in Figure 2 where all the peaks could be assigned to the hydrogen atoms of the repeating unit: protons in the methylene units (—CH$_2$—) along the backbone and in the gemini methyl groups



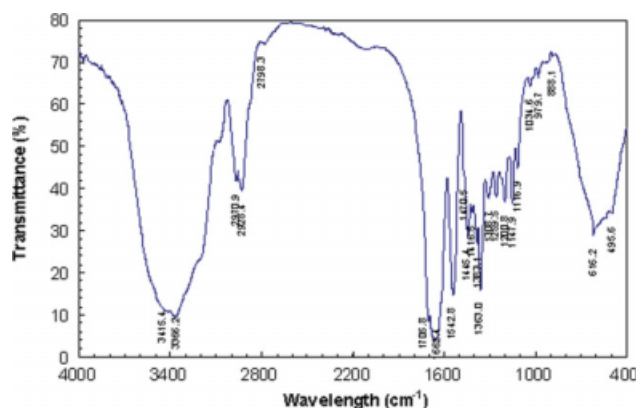**Figure 1** FIIR spectrum of intermediate P(AM-co-DAAM)-NH$_2$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
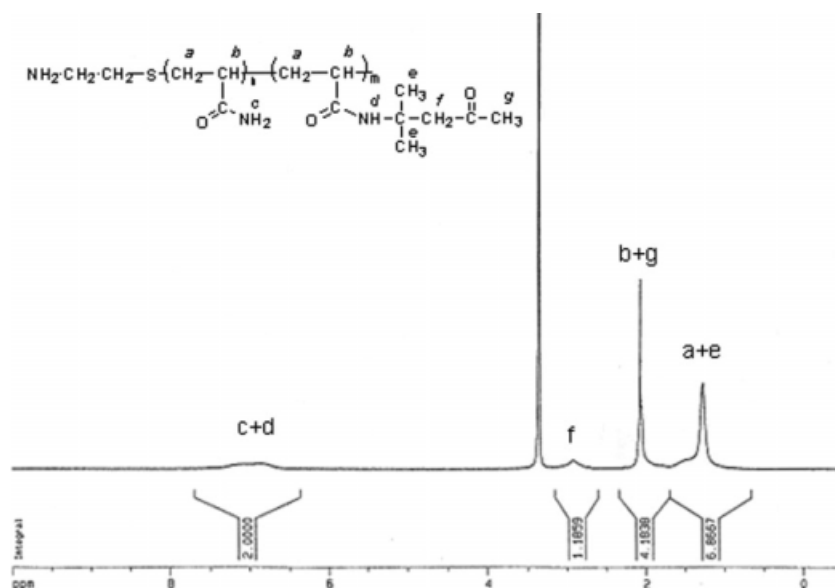
**Figure 2** $^1$H-NMR spectrum of intermediate P(AM-*co*-DAAM)-NH$_2$.

connected to the quaternary atoms (—(CH$_3$)$_2$C—) were evidenced by the peak at 1.39 ppm, and the protons in methine (—C$\boldsymbol{H}$—) of the backbone and terminal methyl groups (—CH$_3$) of the DAAM unit could be found at 2.08 ppm. The wide peak at 6.86–6.88 ppm was resulted from the protons in the amido groups in AM and DAAM units (—N$\boldsymbol{H}_2$, —N$\boldsymbol{H}$) respectively, and the small peak at 2.88 ppm could be attributed to the protons in the methylene group between carbonyl group and quaternary carbon atom (—C$\boldsymbol{H}_2$CO—). This $^1$H-NMR result further confirmed the copolymerization of AM and DAAM.

The molecular structure of the final macromonomer MPAD was also characterized by $^1$H-NMR in D$_2$O. As exhibited in Figure 3, the peak at 2.99 ppm could be attributed to the protons in the methylene (—C$\boldsymbol{H}_2$—) between the quaternary carbon atom and carbonyl group, and the high peak at 2.09 ppm is the combination of the protons in the terminal methyl (—C$\boldsymbol{H}_3$) and methine (—C$\boldsymbol{H}$—) groups along the backbone. The wide peak centered at 1.45 ppm was the combination of the gemini methyl groups in DAAM unit and the methylene groups (—C$\boldsymbol{H}_2$) in the copolymer mainchain. Significantly, the peaks detected at 5.8–6.5 ppm by local magnification were the characteristic double carbon bond of the end-capped acrylamido-terminal, indicating that a polymerizable end group was successfully introduced into the amido-end functional intermediate P(AM-*co*-DAAM)-NH$_2$.

The number- and weight-averaged molar masses of the macromonomer MPAD were determined by GPC to be 5657 and 8274 g mol$^{-1}$, respectively, and its polydispersity index (PDI) was 1.46.

**Polymers**

The thermoviscosifying water-soluble copolymer, P(AM-*co*-MPAD), was synthesized by the copolymerization of macromonomer MPAD and AM. Like in the preparation of the macromonomer, the concentration of MPAD must be carefully controlled to an appropriate level so that the copolymer solution exhibited only microphase separation other than macro-phase separation upon heating, and preliminary experiments indicated that the copolymerization was very sensitive to the polymerization conditions, since crosslinking occurred at low conversions giving rise to highly swollen gels. Chain transfer to DAAM unit of macromonomer MPAD was considered to be the most important factor for gel formations, and therefore, a number of experiments were run preliminarily to optimize the recipe.

The molecular structure of the obtained copolymer was elucidated by $^1$H-NMR spectroscopy. As shown in Figure 4, the NMR signals together with their allocation were attributed to different protons, particularly the characteristic peaks at 3.08 ppm (—C$\boldsymbol{H}_2$CO—), 2.14 ppm (—COC$\boldsymbol{H}_3$, —C$\boldsymbol{H}$CO—) and 1.36 ppm (—C$\boldsymbol{H}_2$, —C$\boldsymbol{H}_3$).

However, it was difficult to quantitatively determine the final compositions of macromonomer and copolymer because of the complex molecular structures and the ambigious integrals in the $^1$H-NMR spectra, and elemental analysis was, therefore, used to help accurate determination of monomer contents in the copolymer.

Listed in Table I were the elemental analysis results of C and N contents in the macromonomer
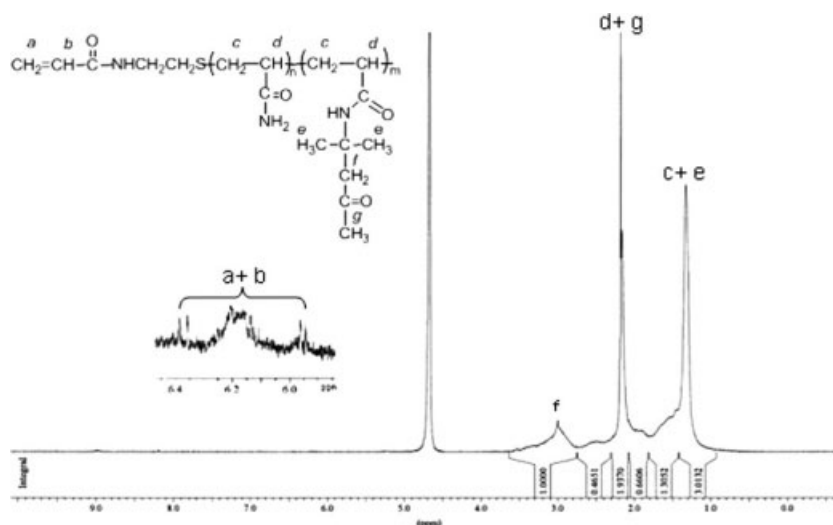
**Figure 3** ¹H-NMR spectrum of macromonomer MPAD.

and final copolymer. Based on these results, one could get the mass percentages of AM and MPAD in both feed ratio and final composition from eqs. (1) and (2). As given in Table II. The macromonomer unit content in the copolymer was 19.9%, lower than 30.0% (see the Experimental section) in the feed recipe. This was in agreement with the copolymerization results of AM and NIPAM-based macromonomer reported by Hourdet and coworkers.[46] In addition, the intrinsic viscosity of P(AM-co-MPAD) was also lower than that of PAM prepared under identical synthetic conditions. These results implied that incorporation of macromonomer decreased molecular weight of the copolymer and a significant drift occurred in reaction, which mainly due to the large difference of reactivity between AM and mac-

romonomer, like the NIPAM-based macomonomer and AM reported by Petit et al.[44]

### Effect of temperature on polymers in pure water

Exhibited in Figure 5 are the viscosity behaviors of P(AM-co-MPAD) and PAM in pure water upon heating for polymer concentrations ($C_p$) between 0.25% and 1.00% (w/w, the same below). As shown in Figure 5a, P(AM-co-MPAD) solutions have a clear thermoviscosifying property and such a behavior strongly depends on the copolymer concentrations: at $C_p = 0.25\%$, $\eta_{app}$ remains nearly unchanged when temperature changes from 20 to 80°C; however, the thermoviscosifying behavior appears clearly when at high polymer concentrations, and $T_{ass}$ decreased
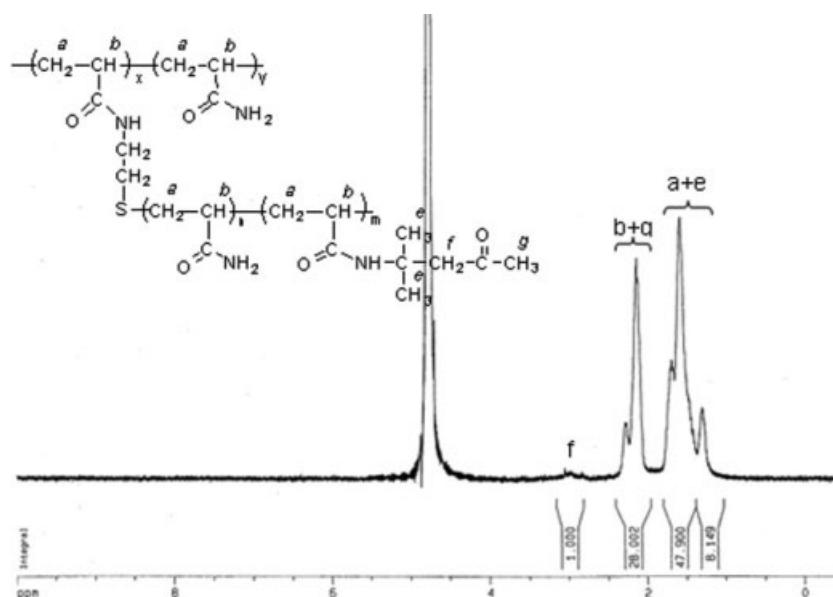


**Figure 4** ¹H-NMR spectrum of copolymer P(AM-co-MPAD).

**TABLE I**
**Analysis Results of C and N Contents in Macromonomer and Final Copolymer**

|  | Elemental analysis results (wt %) | |
| --- | --- | --- |
| Element | Macromonomer | Copolymer |
| C | 56.8 | 47.2 |
| N | 9.7 | 16.1 |

when increasing polymer concentration. For example, the $T_{ass}$ is shifted from 55 to 35°C when increasing $C_p$ from 0.50 to 1.00%. The thermoviscosifying behavior of P(AM-co-MPAD) solutions can be related to the thermoassociative interaction of macromonomer unit induced by an LCST type phase separation taking place at a local scale.[34,35,39] Nevertheless, the viscosity of PAM solution decreases with increasing temperature [Fig. 5(b)], with a general trend following Arrhenius' law.[47]

### Effect of temperature on polymers in 2% KCl solution

Figure 6 shows the variation of $\eta_{app}$ with temperature for different concentrations of P(AM-co-MPAD) and PAM in 2% KCl brine. When comparing temperature effect on the copolymer in pure water [Fig. 5(a)] and that in 2% KCl solution [Fig. 6(a)], one can easily find: (1) at $C_p = 0.25\%$, the addition of KCl almost does not influence the viscosity behavior of the copolymer between 20 and 80°C; (2) at higher concentrations ($C_p > 0.25\%$), the addition of KCl decreases $T_{ass}$, for example, $T_{ass}$ in pure water is 55°C at $C_p = 0.50\%$ while lowered to 30°C in 2% KCl solution; (3) the magnitude of the thermothickening effect was largely enhanced, for example, at $C_p = 1.00\%$, $\eta_{app}$ is 489.1 mPa s in pure water, but exceeds the measurement limit (1020 mPa s) of the LVDV-III Brookfield viscometer when in 2% KCl solution. Nevertheless, for other thermothickening copolymers[39,44,48] at similar conditions, neither was the viscosifying magnitude found nor was the viscosity increased at high temperature in the presence of added salt.

The comparison between Figures 5b and 6b illustrates the influence of the 2% KCl on the viscosity

**TABLE II**
**Physical Parameters of PAM and Copolymer P(AM-co-MPAD)**

| | Feed ratio (wt %) | | Final composition (wt %) | | |
| --- | --- | --- | --- | --- | --- |
| Polymer | AM | MPAD | AM | MPAD | $[\eta]$ (mL g$^{-1}$) |
| PAM | 100 | 0 | 100 | 0 | 672 |
| Copolymer | 70.0 | 30.0 | 80.1 | 19.9 | 445 |

behavior of PAM solutions upon heating. For instance, when at $C_p = 0.50\%$ and 50°C, the viscosity of PAM solution is 28.6 mPa s in puer water, and only 14.3 mPa s in 2% KCl solution. This viscosity loss of PAM solutions is due to the contraction of the polymer coils caused by the screening effect of KCl.[49]

### Effects of temperature and salt on apparent viscosity of polymer solutions

The viscosity-temperature curves for P(AM-co-MPAD) and PAM at $C_p = 0.5\%$ with different KCl contents are given in Figure 7. As KCl concentration goes from 0 to 5%, the $T_{ass}$ of the copolymer decreases from 40°C down to a value lower than 20°C. At the same time, the magnitude of the viscosifying effect is enhanced with increasing KCl concentration. For instance, at 40°C, the viscosity of P(AM-co-MPAD) solutions is enhanced from 9.2 to 118.3 mPa s when increasing KCl level from 1 to 5%. Nevertheless, when KCl concentration is above 1%,
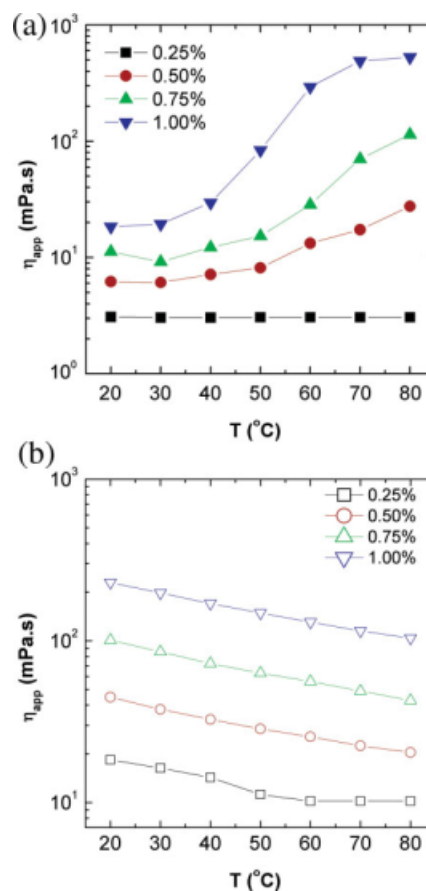


**Figure 5** Apparent viscosity plotted as a function of temperature for P(AM-co-MPAD) (a) and PAM (b) in pure water at different polymer concentrations ($\dot{\gamma} = 10$ s$^{-1}$) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the viscosifying effect seems to be unaffected by KCl concentration when temperature is higher than 60°C.

As seen from Figure 7(b), one can find that at lower salinity (<2%)' the viscosity of PAM solution decreases with increasing KCl concentration; but at higher salinity, see, above 2%, the viscosity increases with increasing KCl concentration, which is in line with the results reported by Shanks et al.,[50] and can be attributed to the competition of salting-out effect of nonpolar section and salting-in effect of amide groups in the PAM molecule.

## CONCLUSIONS

In this work, a novel thermoviscosifying copolymer was synthesized by free radical copolymerization of AM and a newly-prepared acrylamide-based temperature-sensitive macromonomer. A comparative study shows that the resulting copolymer exhibits obvious thermoviscosifying behavior in both pure
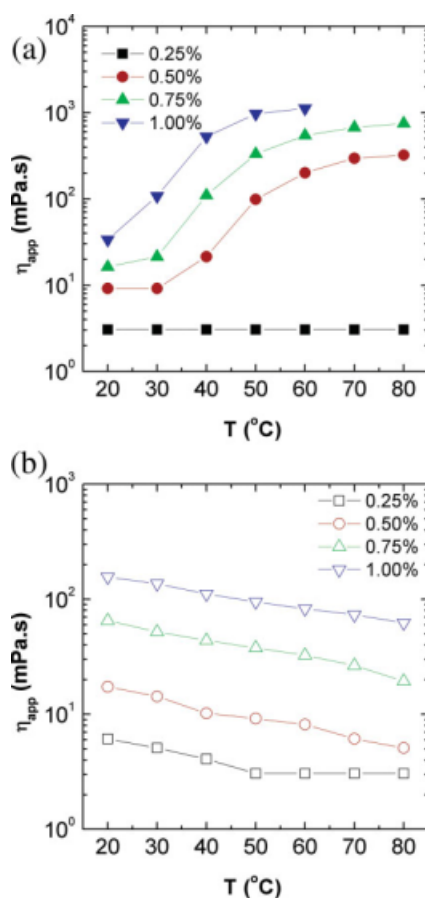


**Figure 6** Apparent viscosity plotted as a function of temperature for P(AM-co-MPAD) (a) and PAM (b) in 2% KCl solution at different polymer concentrations ($\dot\gamma = 10 \text{ s}^{-1}$) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
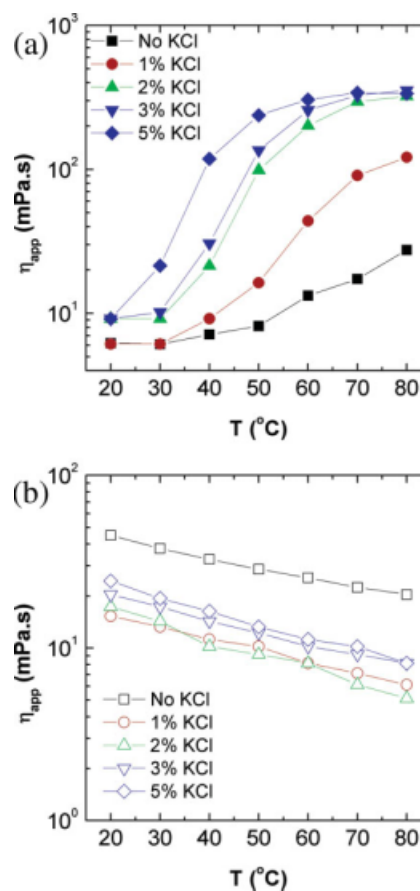


**Figure 7** Apparent viscosity plotted as a function of temperature for P(AM-co-MPAD) (a) and PAM (b) in different KCl solutions ($C_p = 0.5\%$, $\dot\gamma = 10 \text{ s}^{-1}$) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

water and KCl brine, whereas homopolyacrylamide shows only monotonous thermothinning property at identical conditions. Moreover, the thermoassocitive temperature of copolymer can be tuned by changing salinity of the polymer solution. These peculiar thermoviscosifying properties enable this type of acrylamide-based copolymers to find potential applications in severe conditions such as in high-tmperture and high-salinity oil reservoirs.

In respect to the preparation of the copolymer, nevertheless, the feed ratio and polymerization parameters should be well controlled so as to avoid crosslinking because of the chain transfer character of the macromonomer to copolymer, and composition drift was evidenced during the polymerization owing to the reactivity difference of AM and macromonomer.

Preparations of macromonomers with different LCST and thus copolymers themselves with different thermoassociative temperatures are undergoing in our laboratory.

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