

## Synthesis and Aqueous Solution Properties of Novel Thermosensitive Polyacrylamide Derivatives

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**ABSTRACT:** A series of novel thermosensitive polymers were synthesized with acrylamide and thermosensitive macromonomers by radical polymerization in water solution. The structures of the copolymers were characterized by  $^1\text{H-NMR}$ . The effects of the polymer concentration, NaCl concentration, shear rate, and chemical structure on the thermothickening behavior of the polymer solution were investigated by advanced rheometry. The luminous transmittance of the solution with various polymer concentrations was tested by visible spectrometry. The results show that the thermothickening behavior was due to the phase separation of the polymer solution or intramolecular repulsions between the hydrophobic side chains and hydrophilic backbone at high temperatures. Finally, the thermothickening properties of the novel copolymer were studied under conditions simulating an underground oil reservoir. This novel copolymer is expected to be used as an oil-displacing agent to enhance oil recovery in the future. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 766–775, 2013

**KEYWORDS:** functionalization of polymers; properties and characterization; structure–property relations

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### INTRODUCTION

Acrylamide-based water-soluble polymers have been used as oil-displacing agents for tertiary oil recovery because of their excellent dissolvability and thickening properties. Polyacrylamide (PAM) can enhance the apparent viscosity of its aqueous solution to increase the sweep area and enhance oil recovery.<sup>1</sup> On the other hand, polymer oil-displacing agents have mostly been used at high temperatures, even higher than 80°C, so it is very important for applications to keep the polymer aqueous solution at a high apparent viscosity. However, the viscosity of polymers is one of the most important factors in polymer flooding and may decrease sharply at high temperatures.<sup>2</sup> As a result, the applications of acrylamide-based polymers in oil fields are limited to a great extent.

In recent years, water-soluble thermosensitive polymers have been widely used in many fields, including biomedical materials, temperature-triggered emulsions, and intelligent hydrogels.<sup>3–6</sup> The concept of thermothickening polymers was put forward by Hourdet et al.<sup>7</sup> An aqueous solution of a thermosensitive polymer usually contains special side chains that possess a lower critical solution temperature (LCST). Above the LCST, self-assembly behavior occurs among the polymer molecules in aqueous solution, and thermoinduced micelles or physical networks are formed.<sup>8–12</sup> As a response to this self-assembly

behavior, the apparent viscosity of the polymer solution rises dramatically;<sup>13–15</sup> even an obvious solution–gel transformation appears.<sup>16–19</sup> Accorded to the research of Hourdet and co-workers,<sup>7,10</sup> intermolecular thermoassociative behavior or sol–gel transformation occurs only for semidilute solutions in which there are polymer concentrations higher than the overlap concentration of the chains. In dilute solution, however, intramolecular thermoassociative behavior is induced by heating, and the solution viscosity decreases above LCST. Between dilute and semidilute solution domains, the solution viscosity could remain constant with heating because of the intermolecular associations that start to occur.<sup>20</sup> In addition to the polymer concentration, the thermothickening performance is influenced by the salt concentration of the solution, the chemical structure of the side chains, the surfactant, and the shear rate.<sup>21–24</sup>

A water-soluble polymer can be endowed with thermosensitive abilities by block copolymerization,<sup>25</sup> graft copolymerization,<sup>26</sup> and the grafting of LCST side chains on the water-soluble backbone.<sup>27</sup> Mostly, water-soluble thermosensitive polymers contain *N*-isopropylacrylamide (NIPAM), poly(ethylene oxide) (PEO), or poly(propylene oxide) (PPO) because of their remarkable temperature-response properties.<sup>28</sup> The LCST of poly(*N*-isopropylacrylamide) (PNIPAM) is around 32°C, close to body temperature, so polymers containing PNIPAM are of great interest

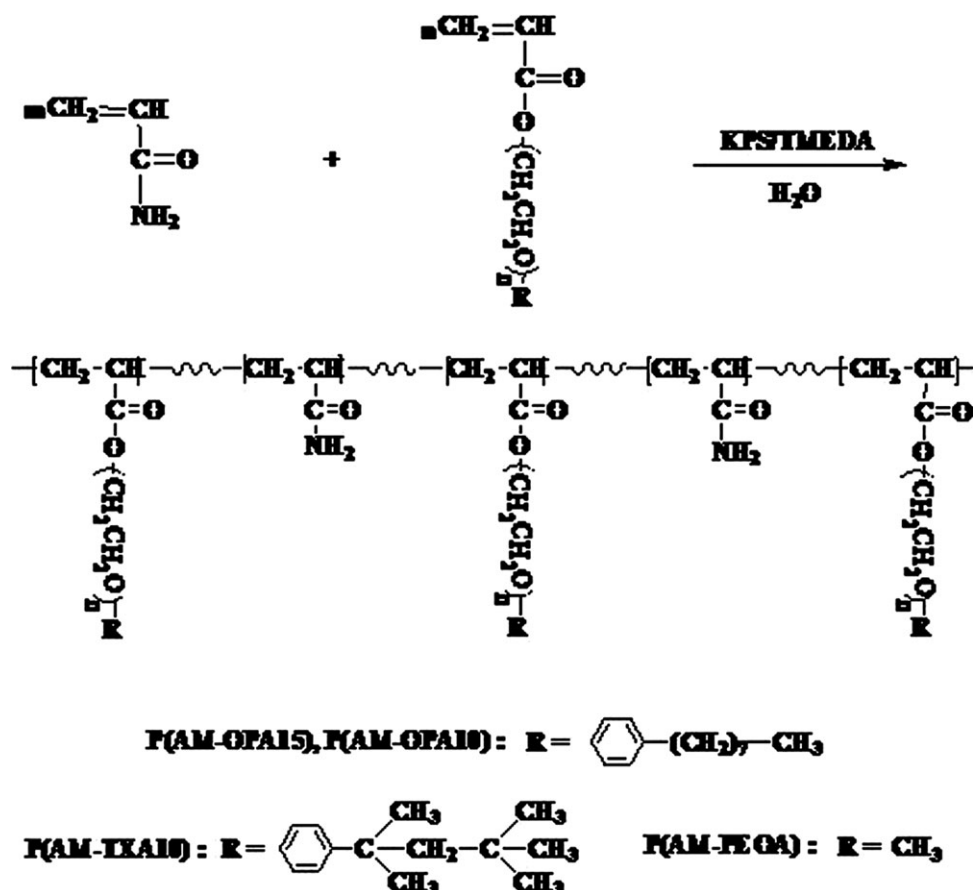


Figure 1. Chemical structures of P(AM-OPA15) ( $n = 15$ ), P(AM-OPA10) ( $n = 10$ ), P(AM-TXA10) ( $n = 10$ ), and P(AM-PEOA) ( $n = 22$ ).

for use in biomedical applications.<sup>29,30</sup> For acrylamide-based, water-soluble polymers used as oil-displacing agents, a high molecular weight is required, usually up to  $1.0 \times 10^6$  to  $1.0 \times 10^7$ , to reduce the dosage of PAM. So graft copolymerizing is most suitable for producing thermosensitive PAMs applied in field of tertiary oil recovery. Gouveia et al.<sup>26</sup> synthesized modified PAMs (PAM-PPGMA [poly(propylene glycol) monomethacrylate] copolymers) by aqueous micellar copolymerization using PPO monomethacrylate as the LCST monomer. From 25 to 50°C, the solution of PAM-PPGMA copolymers exhibited a thermothickening behavior. Because of this thermothickening effect, thermosensitive polymers are expected to improve the thickening ability of acrylamide-based, water-soluble polymers used as oil-displacing agents at high temperatures.

In this investigation, novel thermosensitive PAMs were synthesized by graft copolymerization, and the thermothickening behaviors of the copolymer solutions were studied. Thermosensitive PAM derivatives were developed to obtain a novel oil-displacing agent to be applied in tertiary oil recovery. Macromonomers containing PEO were synthesized by esterification. The chemical structures of the macromonomers are shown in Figure 1. Except for methoxypolyethylene glycol acrylate, those macromonomers were unsaturated amphiphilic functional molecules that could enhance the emulsification ability of aqueous solutions.<sup>31</sup> In water, these amphiphilic functional monomers can organize into micelles without the addition of surfactants.<sup>32</sup>

So a micellar copolymerization was adopted to obtain thermosensitive PAMs by the copolymerization of acrylamide and self-made macromonomers. As a result, the effects of the polymer concentration, salt concentration, and chemical structure of the side chains and the chemical structure of the water-soluble backbone on the rheological behavior were investigated. Finally, a novel acrylamide-based polymer exhibiting an obvious thermothickening ability for use as an oil-displacing agent was prepared via optimization of the chemical structure of the side chains.

## EXPERIMENTAL

### Materials

Acrylamide, tetramethylethylenediamine (TMEDA), potassium peroxydisulfate (KPS), and acetone were analytically pure. The macromonomers (OPA-15, OPA-10, TXA-10, and PEOA) were synthesized in our laboratory (Figure 1).<sup>33</sup> TMEDA and KPS were dissolved in deionized water at a concentration of 2 mg/mL.

### Synthesis of the PAM Derivatives

In these polymerization reactions, a redox system was used as the initiating system, in which TMEDA was used as a reductant and KPS was used as an oxidant. Acrylamide (0.3465 mol) and the macromonomers (0.0052 mol) were added to deionized water (75 mL) with mechanical stirring. TMEDA solution (5 mL) was measured accurately and added to the flask. After absolutely dissolution of the acrylamide and macromonomers in deionized water,  $\text{N}_2$  was introduced for at least 30 min to

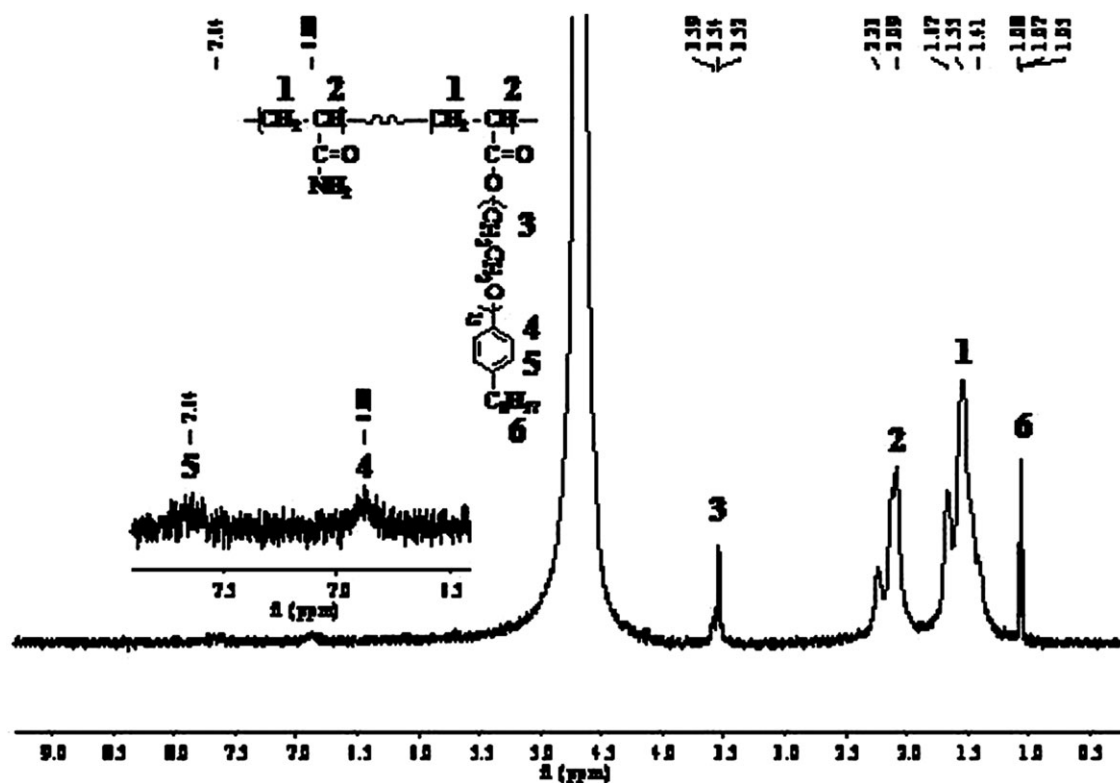


Figure 2.  $^1\text{H-NMR}$  spectrum of P(AM-OPA15).

purge the aqueous solution. Then, KPS solution (10 mL) was added drop by drop at  $50 \pm 1^\circ\text{C}$  from a drop funnel. After 2 h, the product was precipitated in acetone three times to remove residual monomer and dried at  $70^\circ\text{C}$ . For four derivatives [poly[acrylamide-poly(ethylenemethoxyglycol acrylicester)] [P(AM-PEOA)], poly[acrylamide-poly(oxylethyleneoctylphenol ether acrylicester)-10] [P(AM-OPA10)], poly[acrylamide-poly(oxylethyleneoctylphenol ether acrylicester)-15] [P(AM-OPA15)], and P(AM-TXA10)], the intrinsic viscosities were 2108.15, 2373.42, 2301.55, and 2350.62 mL/g, respectively; this indicated that the molecular weight of each derivative was very high and exceeded 10 million. The chemical structures of the four derivatives are shown in Figure 1.

#### Structural Characterization of the PAM Derivatives

The PAM derivatives were purified by a solvent extraction method to thoroughly remove small molecular compounds. The polymers were pulverized, put in a Soxhlet extractor (Shanghai, China), mixed with acetone as a solvent, and then heated at  $70^\circ\text{C}$  in a reflux condenser for about 48 h. Then, the derivatives were characterized by  $^1\text{H-NMR}$  spectroscopy (Shanghai, China) with a Bruker AV 600-MHz spectrometer with  $\text{D}_2\text{O}$  as the solvent.

#### Viscosity Measurement

The PAM derivatives were dissolved in an aqueous solution at a certain concentration with or without the addition of NaCl. The polymer solutions were heated at  $50^\circ\text{C}$  with continual stirring for 2 h to accelerate polymer dissolution. The aqueous solution properties were tested with an AR2000ex advanced rheometer

(TA Instruments, Ltd.) equipped with a parallel plate (diameter = 60 mm, gap = 1 mm). The shear rate was  $0.01 \text{ s}^{-1}$ , and scanning was performed at  $2^\circ\text{C}/\text{min}$  for viscosity measurement.

#### Luminous Transmittance of the Polymer Solution

The luminous transmittance of the polymer solution was tested by a visible spectrometer (Brookhaven BI-200SM Laser Light Scattering Spectrometer, Brookhaven, Mississippi), and the wavelength adopted in these tests was 500 nm. Before testing, the polymer solution was laid in a constant-temperature equipment for at least 10 min to stabilize the temperature of the solution. The mass concentration of NaCl was 15%.

## RESULTS AND DISCUSSION

#### Synthesis and Structural Analysis of the PAM Derivatives

In this study, four macromonomers containing different PEO and hydrophobic groups were designed and synthesized (Figure 1). PEOA possessed the longest PEO chain but no hydrophobic groups in its chemical structure. The length of the PEO chain of poly(oxylethyleneoctylphenol ether acrylicester)-15 (OPA15) was longer than that of poly(oxylethyleneoctylphenol ether acrylicester)-10 (OPA10), and the hydrophobic groups of OPA15 were the same as those of OPA10. The chemical structure of poly(oxylethylenetert-octylphenol ether acrylicester)-10 (TXA10) was a little different than that of OPA10. The hydrophobic group of OPA10 was *n*-octyl phenol, whereas the hydrophobic group of TXA10 was *tert*-octyl phenol. The  $^1\text{H-NMR}$  spectra and structural analysis of the macromonomers are shown in Figures 2–5. The methylene protons of the backbones

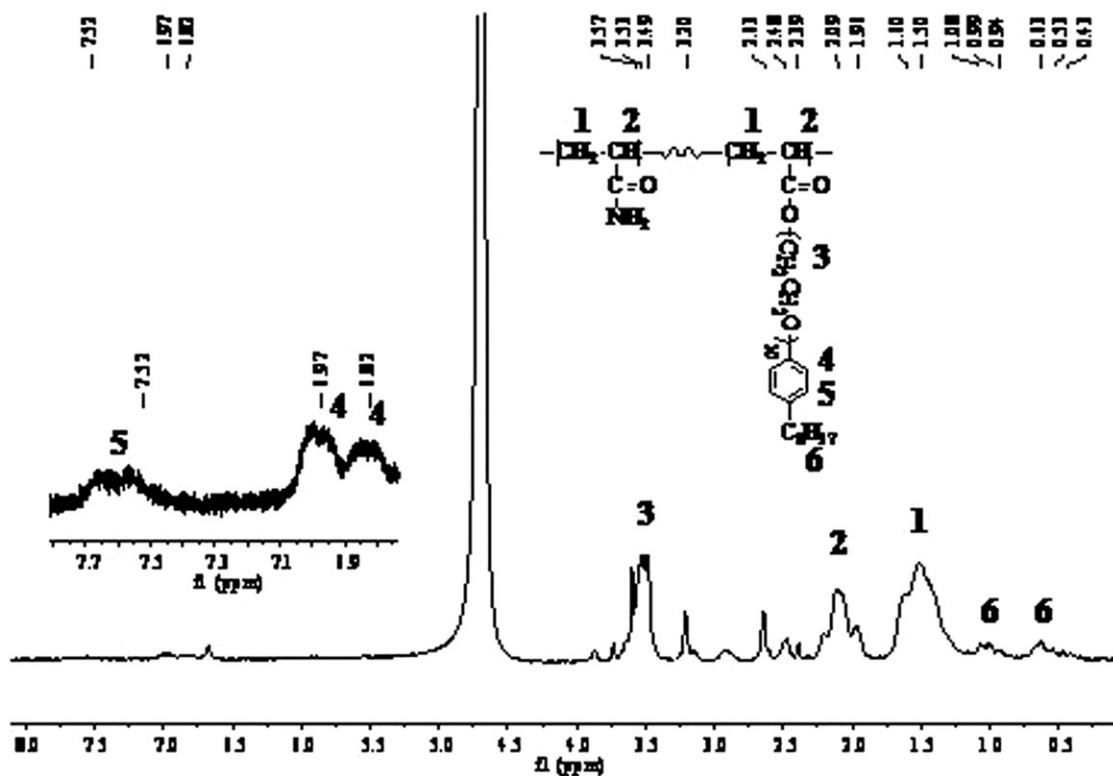


Figure 3. <sup>1</sup>H-NMR spectrum of P(AM-OPA10).

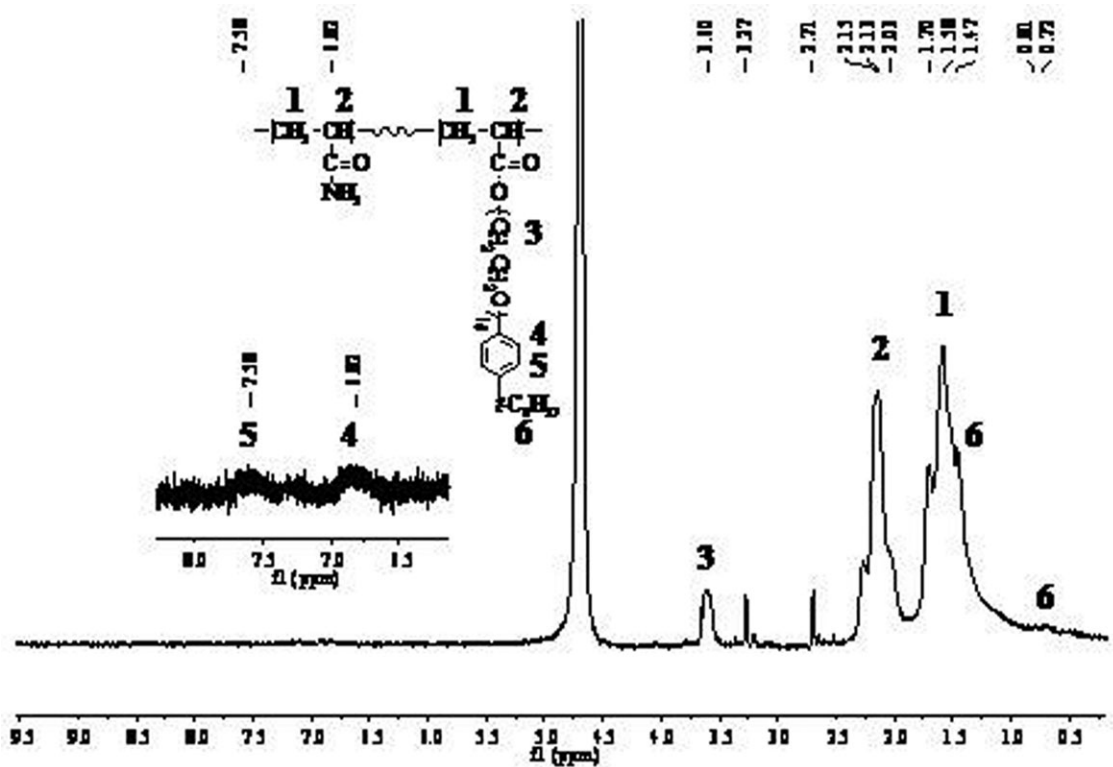


Figure 4. <sup>1</sup>H-NMR spectrum of P(AM-TXA10).

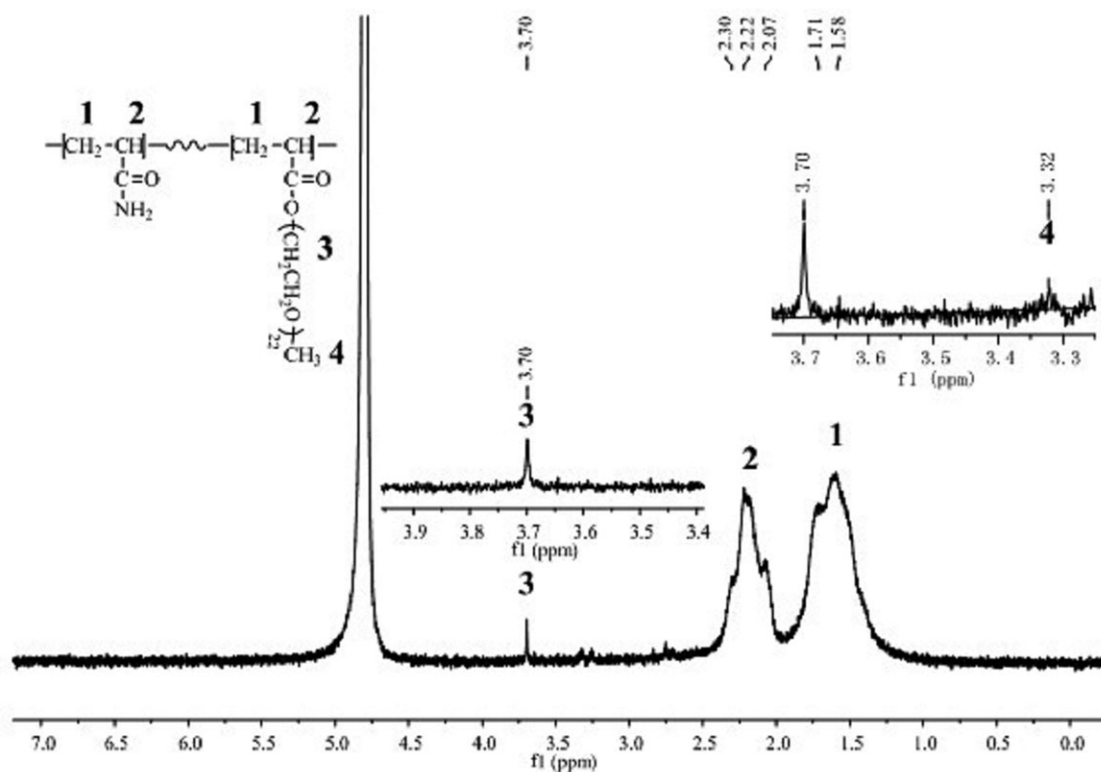


Figure 5.  $^1\text{H}$ -NMR spectrum of P(AM-PEOA).

could be distinguished at 1.25–1.75 ppm, whereas the methyldyne protons of the backbones appeared at 1.75–2.25 ppm. The protons belonging to PEO appeared around 3.60 ppm, whereas the phenyl protons of P(AM-OPA15), P(AM-OPA10), and P(AM-TXA10) appeared around 6.80 and 7.60 ppm (as shown on the enlarged spectra). Those peaks appearing at 0.25–1.25 ppm were ascribed to protons of alkyl groups on the side chains.

#### Effect of the Polymer Concentration on the apparent viscosity

Figure 6 shows the apparent viscosity of P(AM-OPA15) as a function of the mass percentage of polymer at different temperatures in a 15% NaCl aqueous solution. The apparent viscosity of the aqueous solution increased with increasing polymer concentration. Above a polymer concentration of 1.0%, the apparent viscosity increased dramatically due to the microscopic phase-separation behavior of P(AM-OPA15) in aqueous

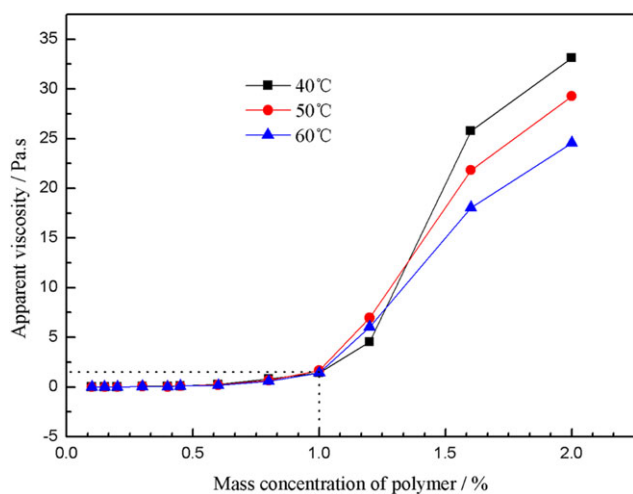


Figure 6. Apparent viscosity of P(AM-OPA15) as a function of the mass percentage of the polymer at different temperatures in a 15% NaCl aqueous solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

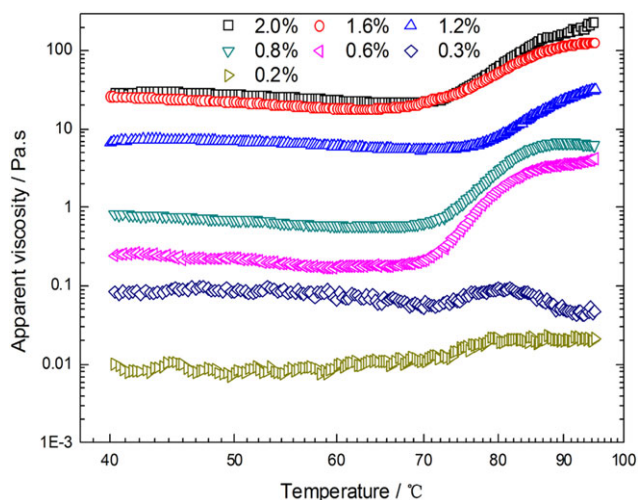
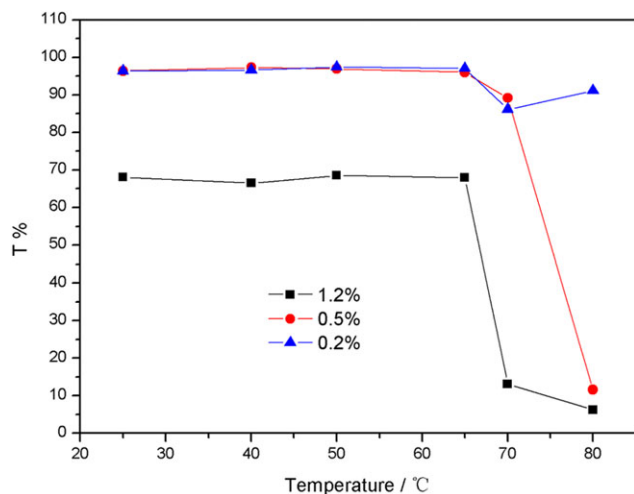


Figure 7. Apparent viscosity as a function of the temperature with different concentrations in a 15% NaCl aqueous solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** Luminous transmittance of the solution as a function of the temperature with different polymer concentrations in a 15% NaCl aqueous solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

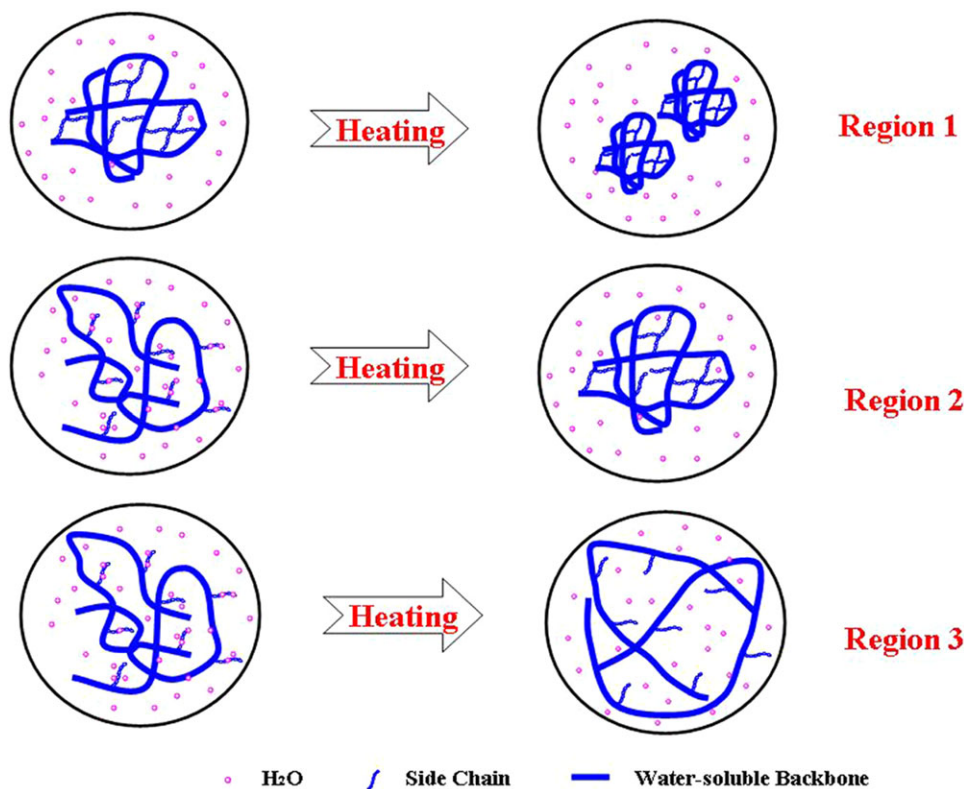
solution at 40, 50, and 60°C. As a result, a polymer concentration of 1.0% was set as the critical phase-separation concentration.

Figure 7 shows the apparent viscosity as a function of the temperature with different concentrations in a 15% NaCl aqueous solution. For most of the PAM solution, the apparent viscosity

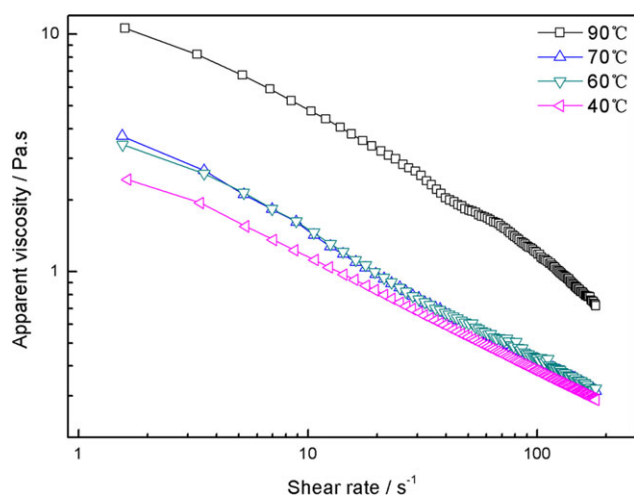
decreased with increasing temperature because of the shrinking of the macromolecules upon heating.<sup>34,35</sup> However, the aqueous solutions of P(AM-OPA15) exhibited thermothickening characteristics (Figure 7) because of the PEO existing in the side chains. OPA15 is known to undergo a phase-separation under heating because of the dehydration process of PEO. For P(AM-OPA15), the hydrogen bonds between water and ether oxygen were disrupted by heating, and the water molecules left the hydration shell around the PEO to move freely. At the same time, the side chains of P(AM-OPA15) were made hydrophobic at high temperatures to induce phase-separation behavior or intramolecular repulsion between the hydrophobic side chains and hydrophilic backbone. For concentrated polymer solutions (0.6, 0.8, 1.2, 1.6, and 2.0%), the apparent viscosity increased dramatically above 70°C because phase-separation behavior appeared at high temperatures. However, the apparent viscosity of the dilute solutions (0.2 and 0.3%) increased gently above 70°C because of the microscopic phase-separation behavior that started to occur.

#### Effect of the Polymer Concentration on the Phase-Separation Behavior

The luminous transmittance as a function of the temperature in the 15% NaCl aqueous solution is shown in Figure 8. The luminous transmittance of the polymer solution decreased when the phase-separation behavior appeared in the solution. For the 0.5% polymer solution, the luminous transmittance of the aqueous solution decreased quickly above a certain temperature. The

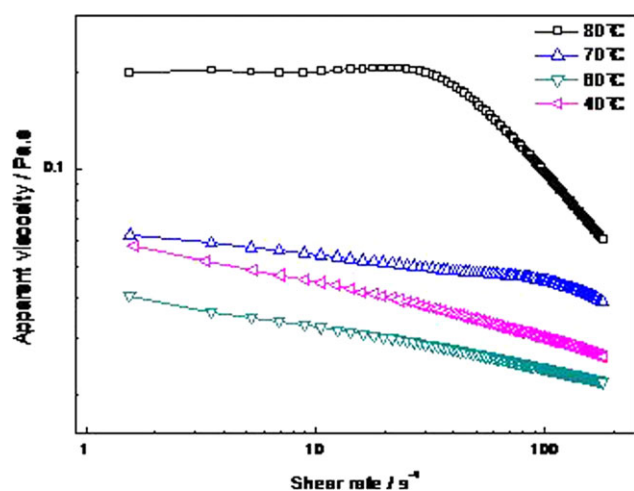


**Figure 9.** Microstructure of P(AM-OPA15) in a 15% NaCl aqueous solution. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

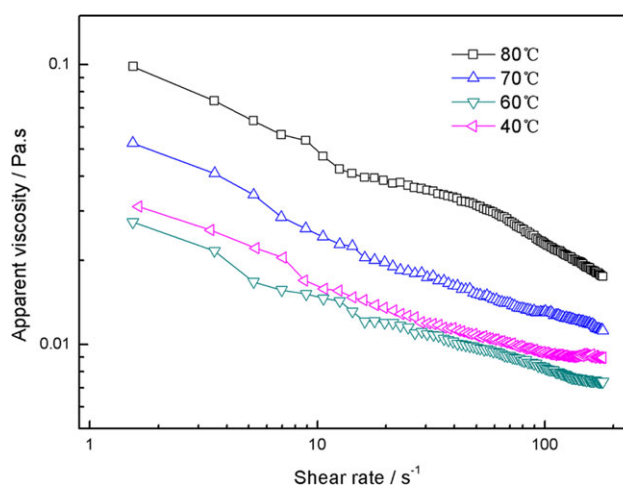


**Figure 10.** Apparent viscosity of the 1.2% polymer solution as a function of the shear rate at different temperatures with 15% NaCl. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

temperature was the LCST of P(AM–OPA15), and the LCST was around 70°C. The hydrogen bonds were disrupted by heating, and the solubility of P(AM–OPA15) was poorer above the LCST and induced phase-separation behavior. At 70°C, the luminous transmittance of the 1.2% polymer solution was much lower than those of the 0.5 and 0.2% solutions because of the existing phase-separation behavior. However, at the same temperature, the luminous transmittance of the 0.5 and 0.2% solutions remained very high; this only decrease a little compared to that below 65°C because microscopic phase separation occurred. So, this suggested that the 1.2% polymer solution had a lower temperature than the 0.5 and 0.2% solutions, in which phase separation occurred. Furthermore, the phase separation was enhanced by heating because of the poor solubility of P(AM–OPA15), and the luminous transmittance decreased rapidly. On



**Figure 11.** Apparent viscosity of the 0.5% polymer solution as a function of the shear rate at different temperatures with 15% NaCl. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 12.** Apparent viscosity of the 0.2% polymer solution as a function of the shear rate at different temperatures with 15% NaCl. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the other hand, phase-separation behavior appeared neither above LCST nor below LCST for the 0.2% polymer solution, so the luminous transmittance of the aqueous solution remained constant with heating.

According to the polymer concentration, the polymer solutions could be divided into three concentration regions (Figure 9): regions 1, 2, and 3. In region 1 (the polymer concentration was above the critical phase-separation concentration), phase-separation behavior appeared below LCST and was enhanced by heating, so the apparent viscosity increased dramatically above LCST. In region 2 (0.5, 0.6, and 0.8% polymer solutions), phase-separation behavior appeared, and the apparent viscosity increased rapidly above LCST. In region 3 (0.2 and 0.3% polymer solutions), the hydrogen bonds were broken by heating, and PEO was changed into hydrophobic chains. The thermodynamic repulsion between the hydrophobic side chains and the hydrophilic backbone made the macromolecules have large hydrodynamic volumes at high temperatures. As a result, the apparent viscosity of the polymer solution was enhanced at high temperatures.

#### Effect of the Shear Rate on the Apparent Viscosity

The shear-thinning properties of a polymer solution are more visible when a microscopic phase-separation behavior appears because phase separation is weakened by shearing. Figures 10–12 show the apparent viscosities of the 1.2, 0.5, and 0.2% polymer solutions as a function of the shear rate at different temperatures. In region 1, the microscopic phase-separation behavior existed at 40, 60, 70, and 80°C. By contrast, no microscopic phase-separation behavior appeared at any temperature in region 3. As a result, the apparent viscosity of the polymer solution decreased with increasing shear rate, and the downward tendency of each curve was similar in regions 1 and 3. In region 2, however, the apparent viscosity of the aqueous solution declined rapidly when the shear rate exceeded 30 s<sup>-1</sup> at 80°C. Nevertheless, the curves below LCST decreased gently because there was no phase-separation behavior at lower temperatures.

**Table I.** Values of  $K$  and  $n$  at Different Temperatures

	Region 1				Region 2				Region 3			
	80°C	70°C	60°C	40°C	80°C	70°	60°	40°C	80°	70°C	60°C	40°C
$K$	20.01	4.89	4.59	3.39	1.68	0.07	0.04	0.07	0.11	0.06	0.03	0.03
$N$	0.47	0.47	0.49	0.49	0.38	0.90	0.87	0.83	0.66	0.67	0.72	0.72

For a non-Newtonian fluid, the viscosity curve could be fitted by a power-law equation to obtain the viscous coefficient ( $K$ ; Pa s) and rheological index ( $n$ ). For shear-thinning polymers, the value of  $n$  represents the non-Newtonian property of fluid and is always less than 1:

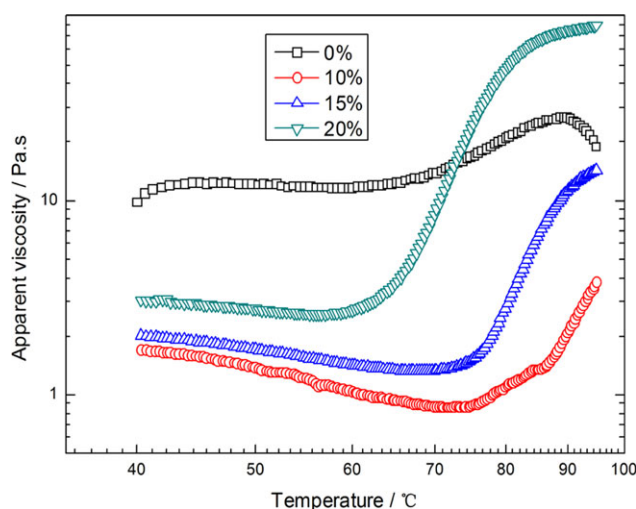
$$\eta = K\dot{\gamma}^{n-1} \quad (1)$$

where  $\eta$  is the apparent viscosity (Pa s) and  $\dot{\gamma}$  is the shear rate ( $s^{-1}$ ).

Table I shows the values of  $K$  and  $n$  at different temperatures. The differences of  $n$  in region 1 or 3 were very small, but the values of  $n$  in region 1 were lower than that in region 3 because of the existence of phase-separation behaviors in region 1. For  $n$  of a non-Newtonian fluid, the lower the  $n$  is, the higher the sensitivity to shearing will be. In region 2,  $n$  at 80°C was obviously lower than that at 70, 60, and 40°C. The microscopic phase-separation behavior was caused by heating in region 2, and the phase separation was weakened under the effect of high shearing. As a result, the apparent viscosity of the polymer solution was more sensitive to shearing than that at lower temperature, and  $n$  was lower than that at high temperature.

#### Effect of NaCl on the apparent viscosity

The apparent viscosity of the 1.0% polymer solution as a function of the temperature at different concentrations of NaCl is shown in Figure 13. Compared to the polymer solution without

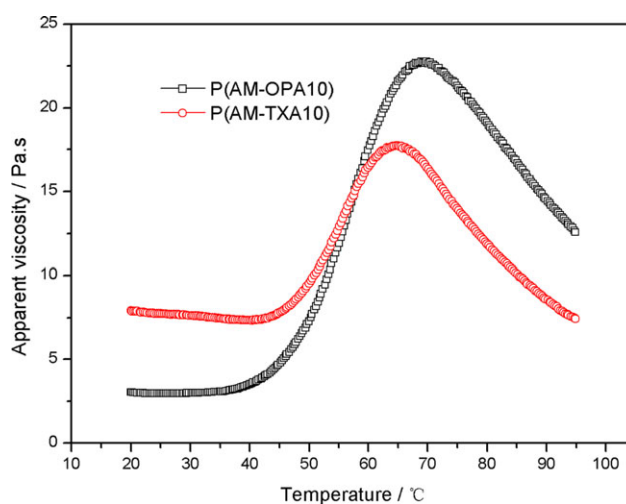


**Figure 13.** Apparent viscosity of the 1.0% polymer solution as a function of the temperature at different concentrations of NaCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

salt, the apparent viscosity showed a sharp decline when NaCl was added to the aqueous solution. The reason was that some amido groups hydrolyzed into carboxylic acids in the procedure of synthesis and dissolution, and the apparent viscosity was decreased by the polyelectrolyte effect in brine. On the other hand, the viscosity increased with increasing NaCl, and the thermothickening properties were enhanced by the addition of NaCl. The viscosity of the aqueous solution with 15% NaCl increased dramatically above 75°C, but that of the aqueous solution with 20% NaCl increased above 65°C. The polarity of the aqueous solution was reinforced by NaCl, and the strength of hydrogen bonds between water and ether oxygen weakened at the same time. Consequently, the hydrogen bonds were easily broken by heating, and phase separation formed in a hurry at lower temperatures.

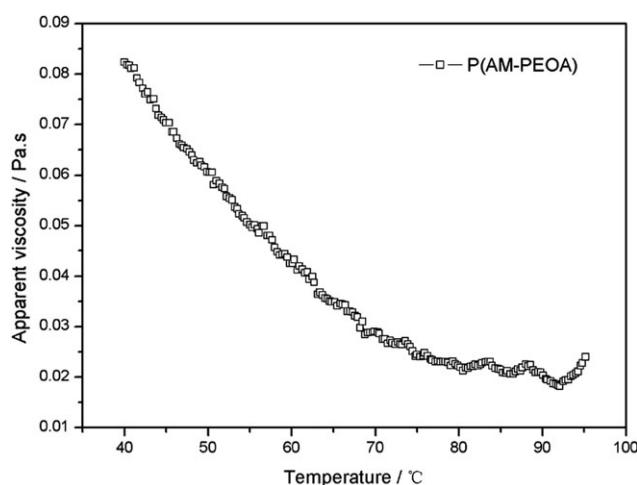
#### Effect of the Chemical Structure on the Apparent Viscosity

Figure 14 shows the apparent viscosities of the 1.0% P(AM-OPA10) and P(AM-TXA10) solutions as a function of temperature with 15% NaCl, and that of 1.0% P(AM-PEOA) as a function of the temperature with 15% NaCl is shown in Figure 15. Compared to the thermothickening properties of the P(AM-OPA15) solution, the apparent viscosities of P(AM-OPA10) and P(AM-TXA10) increased dramatically when the temperature was above 45°C. The turning point of P(AM-OPA15) was 75°C under the same conditions (Figure 13), and phase separation appeared at lower temperatures in the P(AM-OPA10) and P(AM-TXA10) solutions than in the P(AM-OPA10) solution.



**Figure 14.** Apparent viscosity of the 1.0% P(AM-OPA10) and P(AM-TXA10) solutions as a function of the temperature with 15% NaCl. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

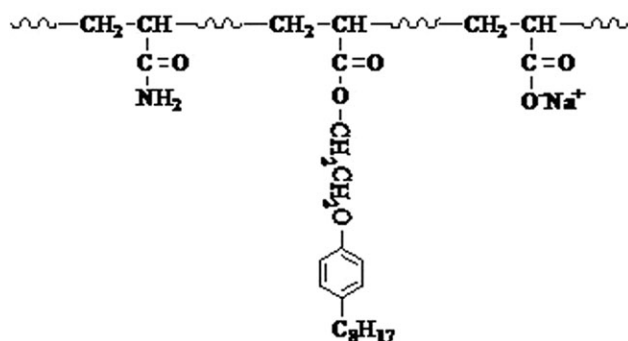




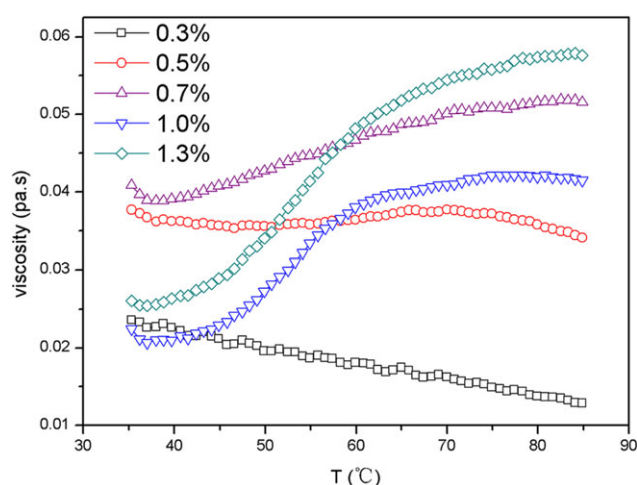
**Figure 15.** Apparent viscosity of the 1.0% P(AM-PEOA) solution as a function of the temperature with 15% NaCl.

On the other hand, the P(AM-PEOA) solution did not exhibit thermothickening behavior in the range from 40 to 90 °C. The length of the PEO chain in P(AM-OPA10) was equal to that in P(AM-TXA10), but the length was shorter than that of P(AM-OPA15). The hydrophilicity of the side chains in P(AM-OPA10) and P(AM-TXA10) was poorer than that in P(AM-OPA15), so phase-separation behavior was caused at lower temperatures in the P(AM-OPA10) and P(AM-TXA10) solutions. On the contrary, the length of the PEO chain in P(AM-PEOA) was the longest among these copolymers. Moreover, there was neither octyl nor phenyl groups on the side chains of P(AM-PEOA). As a result, the amount of hydrogen bonding between water and ether oxygen was the greatest, and the side chains on P(AM-PEOA) were the most hydrophilic among the copolymers. In the range from 40 to 90 °C, P(AM-PEOA) was too hydrophilic to form phase separation.

In conclusion, shortening the length of PEO on the side chain enhanced the thermosensitivity of the copolymer. A novel thermosensitive macromonomer, OPA7, was designed and synthesized in our laboratory. Then, thermosensitive copolymers based on OPA7 were obtained, and a partially hydrolyzed structure was introduced into the copolymer by a posthydrolysis process to improve the solubility of the bipolymer. This copolymer, named P(AM-AA-OPA7), exhibited thermosensitive properties



**Figure 16.** Chemical structure of P(AM-AA-OPA7).



**Figure 17.** Apparent viscosity of the 1.0% polymer solution as a function of the temperature ( $T$ ) with different OPA7 contents (salinity = 32,868 mg/L). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

in simulated reservoir conditions. The chemical structure of P(AM-AA-OPA7) is shown in Figure 16, and the apparent viscosity of the 1.0% P(AM-AA-OPA7) solution (salinity = 32,868 mg/L) as a function of the temperature is shown in Figure 17, in which all of the hydrolysis was 16%. The aqueous solution was prepared by simulation of the conditions of an underground oil reservoir in which large numbers of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were included ( $[\text{NaCl}] = 29,678.3$  mg/L,  $[\text{MgCl}_2 \cdot 6\text{H}_2\text{O}] = 1467.1$  mg/L,  $[\text{CaCl}_2] = 1934.6$  mg/L). The apparent viscosity of the P(AM-AA-OPA7) solution remained constant with heating when the content of OPA7 was 0.7 mol % because of intramolecular repulsion between the hydrophobic side chains and hydrophilic backbone at high temperature. An obvious thermothickening phenomenon appeared when the content of OPA7 was above 0.7 mol % because phase-separation behavior appeared above 60 °C in the aqueous solution. We concluded that a 0.7% content of OPA7 was the best concentration for this series of polymers. We expect this to be used as a novel oil-displacing agent to enhance oil recovery in the future.

## CONCLUSIONS

A series of thermosensitive polymers were prepared by the copolymerization of acrylamide with macromonomers in aqueous solution. The chemical structures of those thermosensitive polymers were characterized by  $^1\text{H-NMR}$ . For P(AM-OPA15), the LCST was around 70 °C in saline solution. In semidilute solution, phase-separation behavior was induced or enhanced by the heating of the solution above LCST; this dramatically increased the apparent viscosity of the polymer solution. In dilute solution, however, the hydrodynamic volume of P(AM-OPA15) was enhanced by intramolecular repulsion between the hydrophobic side chain and the hydrophilic backbone above LCST. As a result, the polymer solution retained a high apparent viscosity at high-temperatures. The thermosensitive properties were enhanced by the addition of NaCl; this shortened the length of PEO on the side chain to a certain extent. Finally, the

thermothickening properties of the novel copolymer were studied under conditions of simulating an underground oil reservoir.

#### ACKNOWLEDGMENTS

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