

# Synthesis and Aqueous Solution Behavior Of Hydrophobically Modified Polyelectrolytes

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**ABSTRACT:** The hydrophobically modified polyelectrolytes were prepared by a micellar technique from acrylamide, *n*-alkylacrylamides, and a third monomer, sodium acrylate or sodium 2-acrylamide-2-methylpropanesulfonate. Synthesis and solution properties of the terpolymers were studied. In the synthesis process, the type and amount of surfactant and anionic monomers influenced their solution behavior greatly. The terpolymers showed strong synergistic viscosification effects between their ions and hydrophobic groups. Their aqueous brine solutions exhibit high viscosity at low polymer concentration and can maintain the viscosity during aging at a high temperature (80°C). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 3552–3557, 2001

**Key words:** hydrophobic-associating; synthesis; solution properties

## INTRODUCTION

Hydrophobically associating water-soluble polymers are synthetic water-soluble polymers that incorporate a small amount of the hydrophobic group into the polymer molecules. When dissolved in water, the hydrophobic groups aggregate and result in intra- and intermolecular associations. Above a critical concentration ( $C^*$ ), the molecular network formed causes a rapid increase in viscosity. The addition of salt enhances this effect because of the increased polarity of the solvent. These polymers are also insensitive to shear because of their low molecular weight.<sup>1–3</sup>

However, by now, the hydrophobic-associating water-soluble polymers have not been applied widely. Many problems appearing in synthesis and performance limit their uses. For example,

the  $C^*$  is a little high, and their viscosities at low polymer concentration (below  $C^*$ ) are not high enough to be used in oil recovery.<sup>4–7</sup> In this article, a lot of work was done to try to improve the viscosification efficiency. The anionic monomer was incorporated into the polymer and the synergistic viscosification effects between ions and hydrophobic groups was observed.

## EXPERIMENTAL

### Materials and Monomer Synthesis

Analytically pure grade solvents were used without further purification. Acrylamide (AM) was recrystallized twice from  $\text{CHCl}_3$ . Acrylic acid (AA) was purified by recrystallization from deionized water. 2-acrylamide-2-methylpropanesulfonate (AMPS) was obtained from Japan. The alkylacrylamides, including octyl, decyl, and dodecyl ( $N_8$ ,  $N_{10}$ , and  $N_{12}$ ), were synthesized from the reaction of *N*-*n*-alkylamine with acryloyl chloride, with triethylamine as the acid receptor, by using the

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**Table I** Synthesis of AAN<sub>n</sub> Terpolymers

Terpolymer	The Feed Amount of Anionic Monomers (mol %)		The Feed Amount of Hydrophobic Monomers (mol %)		SDS (g)
	AA	AMPS	C <sub>8</sub>	C <sub>10</sub>	
AAN <sub>8</sub> -1	5		0.25		
AAN <sub>8</sub> -2	5		0.50		
AAN <sub>8</sub> -3	5		0.75		
AAN <sub>10</sub> -1	5			0.5	1
AAN <sub>10</sub> -2	15			0.5	1
AAN <sub>10</sub> -3	25			0.5	0.4
AAN <sub>10</sub> -4	25			0.5	0.6
AAN <sub>10</sub> -5	25			0.5	1
AAN <sub>10</sub> -6	25			0.5	2.2
AAN <sub>10</sub> -7	40			0.5	0.4
AAN <sub>10</sub> -8		5		0.5	1
AAN <sub>10</sub> -9		25		0.5	0.4

method described by McCormick et al.<sup>5</sup> The crude product was twice recrystallized from acetone at  $-25^{\circ}\text{C}$ .

Analysis: FTIR (KBr):  $\text{—C—NH}$ ,  $3284\text{ cm}^{-1}$ ,  $1666\text{ cm}^{-1}$ ,  $1540\text{ cm}^{-1}$ ;  $\text{C=C}$ ,  $1627\text{ cm}^{-1}$ ;  $\text{—(CH}_2)_n\text{—}$ ,  $731\text{ cm}^{-1}$ .

### Polymer Synthesis

A micellar polymerization technique was used to prepare polymers using sodium dodecylsulphate (SDS) as the surfactant and ammonium persulphate as the free-radical initiator.<sup>5</sup> The appropriate amount of ionizable monomer (AA or AMPS) was dissolved in deionized water and pH adjusted to 9 with NaOH to form the water-soluble sodium salt (NaA, NaAMPS). AM, SDS surfactant, and the hydrophobic monomer were added, respectively, and stirred under  $\text{N}_2$  until a clear solution was observed. The solution was then heated to  $50^{\circ}\text{C}$ , and the initiator was added. The total monomer concentration was  $0.44\text{M}$ . The polymerization was conducted for 12 h, followed by dilution of the polymer mixtures with water and precipitation into acetone. The polymer was washed with acetone and dried under reduced pressure at  $40^{\circ}\text{C}$  for 5 h.

The polymers (AAN<sub>n</sub>) used in this study are listed in Table I. The composition of the polymers could not be calculated by element analysis because of the small amount of *N-n*-alkylacrylamide incorporated in the copolymer, well below the accurate limit of instrumental detection.

### Solution Studies

Solution viscosities were measured by using the NXE-1 coneplate viscometer and Haake RV20 rotational rheometer. If there is no special statement, the measurement conditions were all as follows: temperature,  $25^{\circ}\text{C}$ ; shear rate,  $19.2\text{ s}^{-1}$ .

## RESULTS AND DISCUSSION

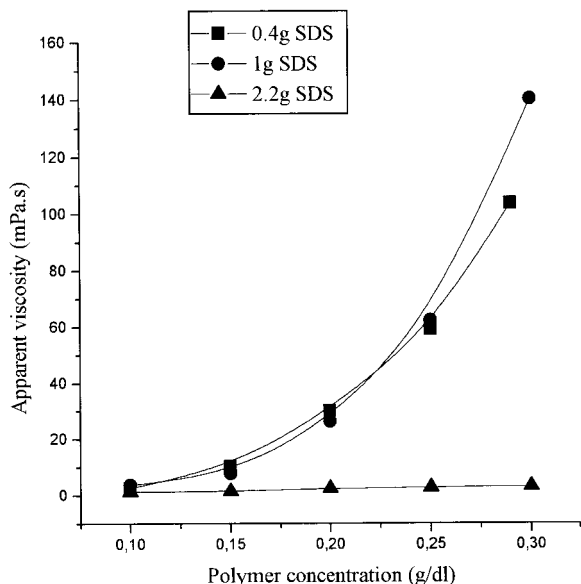
### Synthesis Studies

#### Effect of SDS Amount

The concentration of surfactant used during micellar polymerization can have a significant effect on the resultant hydrophobe-containing polymer, which controls the block length of the hydrophobe groups in the molecule. For the AAN<sub>8</sub> terpolymers containing 0.75 mol % N<sub>8</sub>, the maximum viscosity was achieved at 2 wt % SDS. Increasing the hydrophobe level, 3 wt % SDS was required to achieve maximum viscosity. The low concentrations of surfactant used result in polymers with poor solubility in brine. As shown in Figure 1, it can also be seen that there is an optimum concentration of surfactant at which the maximum solution viscosity is attained.

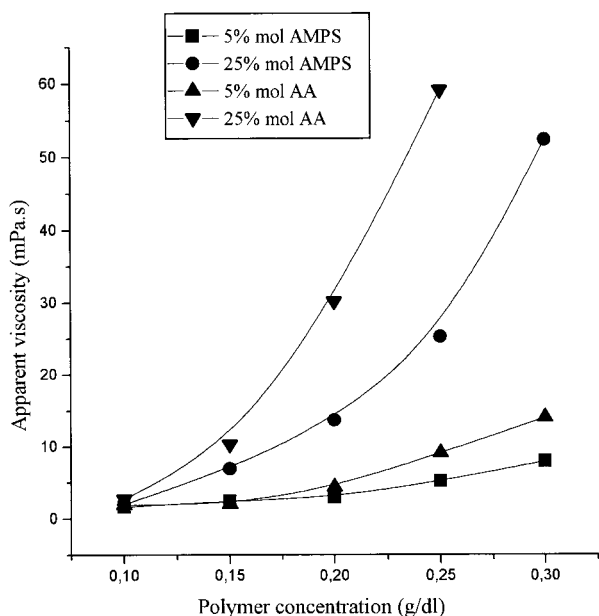
#### Effect of Anionic Monomer Type

As shown in Figure 2, NaA terpolymers have higher viscosities than NaAMPS terpolymers, al-

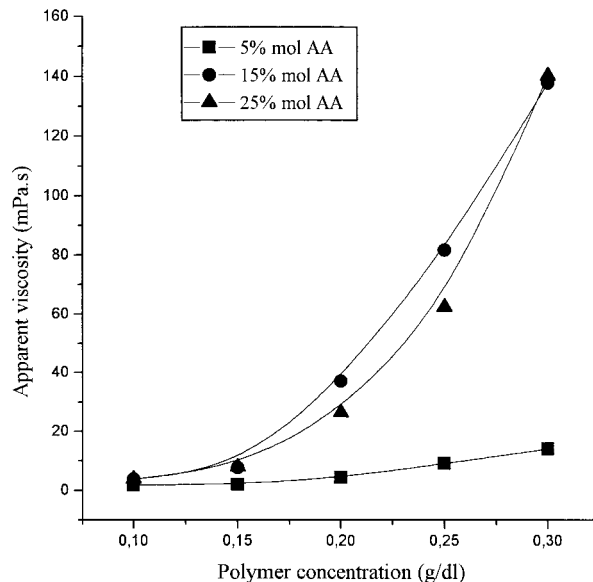


**Figure 1** The effect of SDS content on the apparent viscosity of AAN<sub>10</sub> polymers solution.

though NaAMPS terpolymers are less shielded by counterions. The distance of the ionic group from the backbone may influence hydrophobic association. The NaAMPS monomer allows charged groups to extend out farther from the polymer backbone, apparently preventing associations among hydrophobic groups, whereas the NaA



**Figure 2** The effect of anionic monomer on the apparent viscosity of AAN<sub>10</sub> polymer solution.

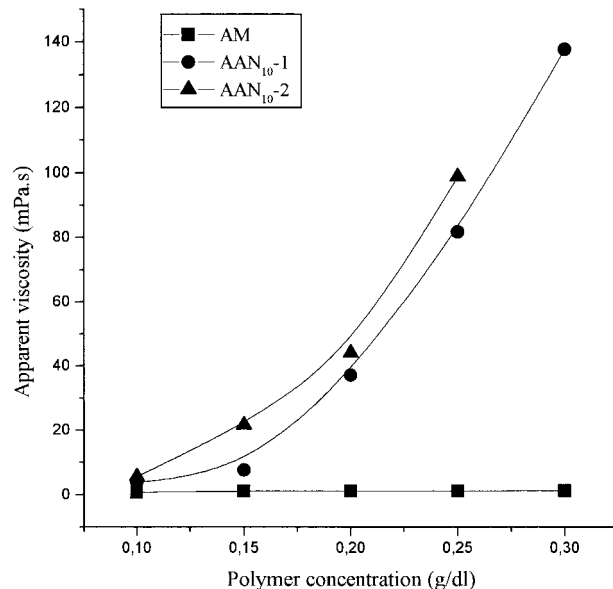


**Figure 3** The effect of AA amount on the apparent viscosity of AAN<sub>10</sub> polymer solution.

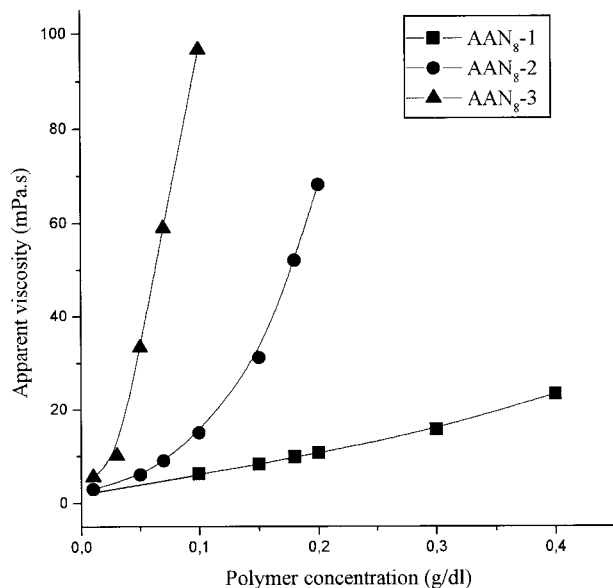
monomer, with charges much closer to the backbone, has less disruption of the hydrophobic effect.

**Effect of AA Amount**

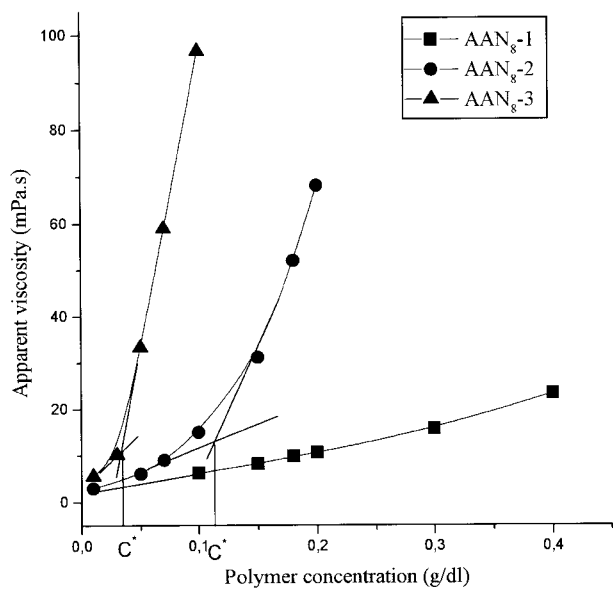
As shown in Figure 3, 15 mol % NaA terpolymer (AAN10-2) has higher viscosity than other terpolymers. The incorporation of ion groups into



**Figure 4** The effect of polymer concentration on the apparent viscosity of polymer solution (1.5% NaCl).



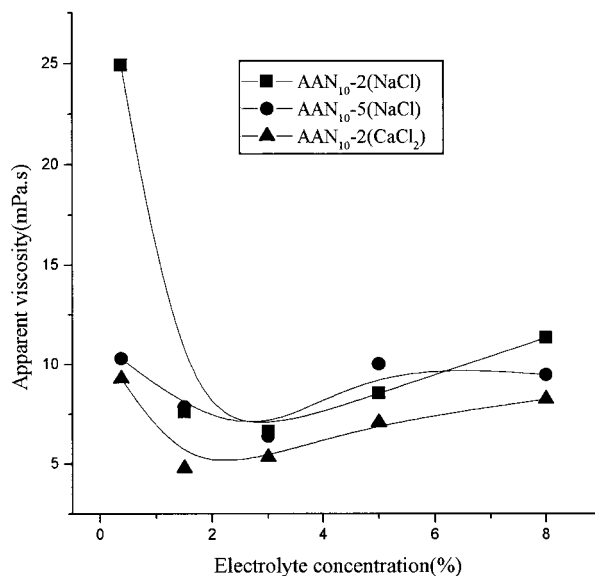
(a)



(b)

**Figure 5** The effect of polymer concentration on the apparent viscosity of polymer solution (aqueous solution).

polymer chains may enhance the solubility of terpolymers, and the electrostatic repulsion of the ionic groups results in chain expansion, which may favor the intermolecular associations of hydrophobic groups. This is called synergistic effects. However, too many ionic groups along the polymer chain may be susceptible to the small electrolytes and disrupt hydrophobic associations.



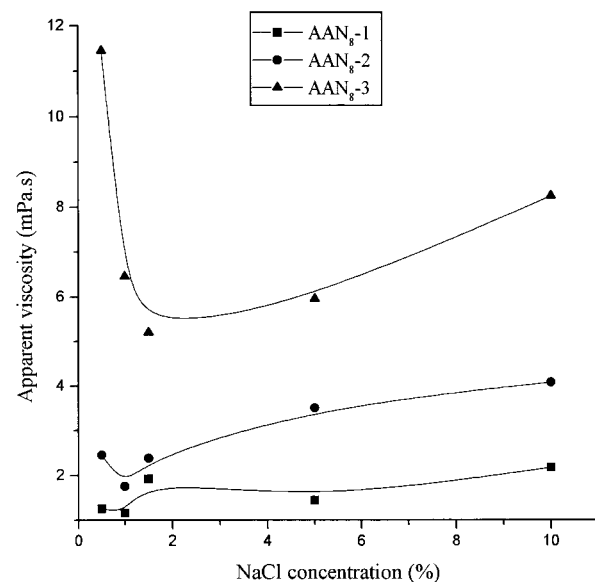
**Figure 6** The effect of electrolytes on the apparent viscosity of polymer solution (polymer concentration: 0.1 g/dl).

Therefore, it is important to determine the suitable AA amount.

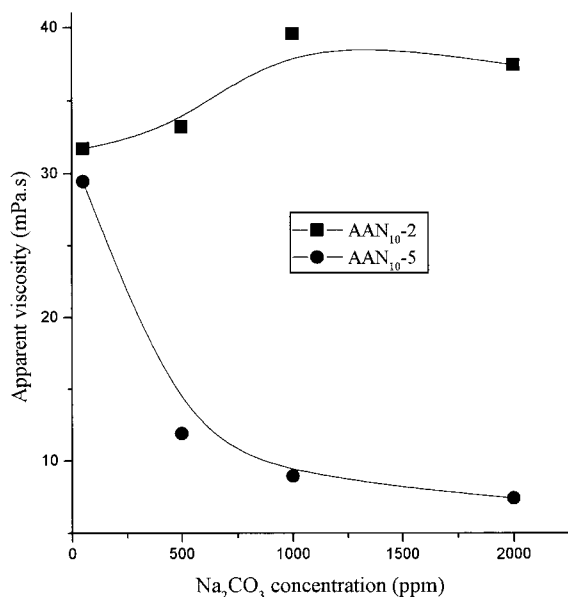
**Solution Behavior**

*Effect of Polymer Concentration*

Figure 4 and 5 show the concentration dependence of the solution viscosity for AM, AAN<sub>8</sub>, and



**Figure 7** The effect of NaCl concentration on the apparent viscosity of AAN<sub>8</sub> terpolymers (polymer concentration: 0.1 g/dl).



**Figure 8** The effect of alkali concentration on the apparent viscosity of the polymer solution (polymer concentration: 0.1 g/dl).

AAN<sub>10</sub> terpolymers. A dramatic increase in solution viscosity was observed at about 0.15 g dl<sup>-1</sup> for AAN<sub>10</sub> AAN<sub>8</sub>-2, and AAN<sub>8</sub>-3 terpolymers. The critical association concentration (*C*<sup>\*</sup>) of polyacrylamide and the AAN<sub>8</sub>-1 (0.25 mol % N<sub>8</sub>) could not be clearly observed in the concentration range investigated. As shown in Figure 5, the concentration dependence of the viscosity became greater as the N<sub>8</sub> content in the copolymer increased. The solution viscosity of AAN<sub>10</sub>-4 terpolymer at concentration of 0.15 g dl<sup>-1</sup> and shear rate of 9.6 s<sup>-1</sup> can reach 21.6 mPa s.

#### Effect of Additives on the Viscosity

##### NaCl and CaCl<sub>2</sub>

As shown in Figures 6 and 7, a minimum solution viscosity of the terpolymers appeared with increasing NaCl concentration in the range of 0–10%. Addition of salt shielded the intermolecular repulsion of the ion groups and made the

**Table III** The Relationship of Solution Viscosity and Heating Time of AAN<sub>10</sub> Copolymer Under 80°C

Copolymer Viscosity (mPa s)	Heating Time (Days)					
	0	10	40	42	80	115
AAN <sub>8</sub> -3	18.1	6.2	8.9		7.9	7.3
AAN <sub>10</sub> -4	3.8	5.7		5.6		

*Note.* The polymer concentration of AAN<sub>8</sub>-3 is 0.15 g/dl; the polymer concentration of AAN<sub>10</sub>-4 is 0.1 g/dl.

polymer molecule contract, resulting in the decrease of the solution viscosity. However, with an increase of salt concentration, the shielding effect tends to reach equilibration, and the intermolecular association of the hydrophobic groups increased, which caused the increase of the solution viscosity.<sup>4,5</sup> A similar effect was observed for CaCl<sub>2</sub> with concentration in the range of 0–8%.

##### Na<sub>2</sub>CO<sub>3</sub>

The alkali–polymer complex is often used in enhanced oil recovery. As shown in Figure 8 for AAN<sub>10</sub>-5 terpolymer, the solution viscosity decreased with increasing Na<sub>2</sub>CO<sub>3</sub> concentration, whereas for AAN<sub>10</sub>-2 terpolymer, addition of Na<sub>2</sub>CO<sub>3</sub> yielded little change in the solution viscosity, which may be due to the smaller content of ion groups in the AAN<sub>10</sub>-2 terpolymer.

##### Surfactant

The effect of anionic surfactant SDS on the solution viscosity of AAN<sub>10</sub>-2 terpolymer was investigated (Table II). Its solution viscosity increased remarkably upon addition of SDS. Further addition of SDS made the solution viscosity decrease. The association of surfactant with the hydrophobic groups of the terpolymer competed with intermolecular polymer–polymer association. With increasing surfactant concentration, the surfactant micelle formed and effectively crosslinked the hy-

**Table II** The Effect of SDS Concentration on the Apparent Viscosity of the Polymer Solution

SDS concentration (ppm)	0	50	100	200	300	400
AAN <sub>10</sub> -2 viscosity (mPa s)	7.60	32.23	47.74	31.60	17.09	2.38

*Note.* The polymer concentration is 0.1 g/dl.

drophobic groups, which caused the viscosity to increase; but too many surfactant micelles at high surfactant concentration may not combine hydrophobic groups effectively and disrupted the inter-chain association of hydrophobic groups.<sup>8</sup>

#### ***Thermal Stability of Terpolymers Solution***

Table III shows the aging effect of the terpolymers in 0.256M NaCl solution at 80°C. For AAN<sub>8</sub>-3 terpolymer, the solution viscosity decreased remarkably during the first 10 days and changed slightly afterward. For AAN<sub>10</sub>-4 terpolymer, the solution viscosity remains almost stable during the testing time (42 days).

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