Study of P(AM-NVP-DMDA) Hydrophobically Associating Water-Soluble Terpolymer

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ABSTRACT: A new kind of hydrophobically associating water-soluble terpolymer P(AM-NVP-DMDA) was synthesized by free radical terpolymerization. Compared with micellar terpolymerization, this terpolymerization can be conducted in aqueous solution in absence of external surfactant, because the hydrophobic monomer is surface active. Synthesis, structure, and solution properties of P(AM-NVP-DMDA) terpolymer were studied, including its electrolyte effect, rheological behavior, temperature dependence of viscosity, dilute solution property, and the polymer–alkali, polymer–surfactant interaction. The terpolymer shows strong hydrophobic effect, and the terpolymer aqueous brine solution exhibits high viscosity at low polymer concentration. Incorporation of N-vinyl-pyrrolidone into the terpolymer causes an improvement in thermal stability of the terpolymer. The transmission electron photomicrograph analysis of the terpolymer indicates that the presence of the microphase separation of the terpolymer in aqueous solution plays an important role in the viscosification efficiency of the terpolymer. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 211–217, 1999

Key words: hydrophobically associating water-soluble terpolymers; surface-active monomer; aqueous solution terpolymerization; rheological behavior; hydrophobic effect

INTRODUCTION

Hydrophobically associating water-soluble polymers are synthetic water-soluble polymers that incorporate a small amount of hydrophobic groups 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.^{1,2}

Polyacrylamide (PAM) and partially hydrolyzed polyacrylamide (HPAM) are well-known

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water-soluble polymers used for rheology control in enhanced oil recovery (EOR). They rely on a combination of high molecular weight and chain expansion caused by repulsion of ionic groups along the polymer chain to viscosify aqueous fluids. However, when subjected to large elongational or shear stress, or presence of electrolytes, especially divalent cations, they lose significant viscosification efficiency.³ Hydrophobically associating water-soluble polymers exhibit unique rheological behavior and can overcome the deficiencies found in PAM systems. However, the viscosities of hydrophobically associating water-soluble polymers at low polymer concentration are not high enough to be used in oil recovery, which has restricted their uses.^{4,5} In this paper, a lot of work has been done to try to improve the viscosification efficiency of hydrophobically associating watersoluble polymers. A new kind of hydrophobically associating water-soluble polymer was prepared,

Sample	Initiator Conc. (wt %)	Monomer Conc. (wt %)	NVP : DMDA (mol %)	Reaction Temp. (°C)	Reaction Time (h)	Conversion (%)	Apparent Viscosity (mPa s)
APDA-1	0.3	12	30:15	50	10	95.8	2.82
APDA-2	0.3	22	30:15	50	10	96.9	3.32
APDA-3	0.2	22	30:15	50	10	96.7	5.56
APDA-4	0.1	22	30:15	50	10		7.75
							Water
APDA-5	0.1	22	30:15	40	18		insoluble
APDA-6	0.1	22	40:15	30	24	86.3	10.09
APDA-7	0.1	30	50:15	30	24		8.98
							Phase
							separation
							in NaCl
APDA-8	0.08	30	50:15	30	24		solution
APDA-9	0.08	30	50:10	30	24		6.50
APDA-10	0.08	30	45:10	30	24		5.73

Table I Reaction Parameters and Viscosities of APDA Terpolymers

Polymer concentration is 0.2 g/dL.

and viscosification mechanism was probed by studying the relationship between molecular structure and rheological behavior.

EXPERIMENTAL

Synthesis of Hydrophobic Monomer

To 2-methacryloyloxyethyl-dimethylamine (0.25 mol) was added dropwise an equimolar of 1-bromododecane in 100 mL of acetone. After addition of a small portion of hydroquinone to inhibit any spurious radical polymerization, the reaction mixture was stirred for 48 h at 30°C. The product was crystallized on cooling, collected by filtration, followed by two recrystallizations from acetone. Finally, it was dried under vacuum at room temperature. Analysis calculated for the monomer (abbreviation: DMDA): C, 59.11%; H, 9.85%; N, 3.45%; Br, 19.70%. Found: C, 58.96%; H, 10.92%; N, 3.20%; Br, 20.77%. FITR: -CH₃, -CH₂stretch, 2955–2854 cm⁻¹; --CH₃, --CH₂-bending, 1467 cm⁻¹, 1377 cm⁻¹; C=O stretch, 1724 cm⁻¹; C=C stretch, 1639 cm⁻¹; C-O stretch, 1162 cm^{-1} , 1295 cm^{-1} ; --(CH₂)-bending, 721 cm^{-1} .

Synthesis of AM-NVP-DMDA Terpolymers

The terpolymers of acrylamide (AM), N-vinyl-pyrrolidone (NVP) with DMDA (abbreviation: APDA) were prepared by aqueous solution terpolymerization using ammonium persulphate as the free radical initiator. AM, NVP, and DMDA aqueous solutions were added to the reaction flask and was purged with nitrogen for one-half hour. The solution was heated to temperature, and the initiator was added. The reaction was allowed to proceed for several hours, after which the mixture was cooled and diluted with water. Acetone was then slowly added while stirring to precipitate the terpolymer. The terpolymer was washed with acetone and dried under reduced pressure at 40°C for 5 h. Table I lists the reaction parameters and viscosities of APDA terpolymers.

The solution behavior of APDA-6 terpolymer was carefully studied because of its highest viscosity. A typical Fourier transform infrared spectroscopy (FTIR) spectrum for APDA-6 is as follows: —NH: 3425 cm⁻¹, 3203 cm⁻¹; —CH₃,-CH₂—:, 2955 cm⁻¹, 2854 cm⁻¹, 1371 cm⁻¹, 1460 cm⁻¹; C=O: 1660 cm⁻¹; C=O: 1290 cm⁻¹, 1170 cm⁻¹; —(CH₂)₁₁—: 738 cm⁻¹. Its composition element analysis data are listed in Table II.

Viscometric Analysis

Solution viscosities were measured using the NXE-1 coneplate viscometer and HAAKE RV20

 Table II
 APDA-6 Terpolymer Composition

Monomer	AM	NVP	DMDA
Feed composition (mol %)	45	$\begin{array}{c} 40\\ 23 \end{array}$	15
Polymer composition (mol %)	66		11



Figure 1 Effect of polymer concentration on apparent viscosity of APDA-6 terpolymer.

rotational rheometer. If there is no special statement, the measurement conditions were all as follows: temperature, 25°C; shear rate, 19.2 s⁻¹. The reduced viscosities of the terpolymers were determined as a function of polymer concentration by capillary viscometry at 30°C. Intrinsic viscosities were calculated with Huggins equation and Schulz–Blaschke equation.

TEM Analysis

Electron micrographs were taken with JEOL-100CX transmission analytical electron microscope at 80 kV. The aqueous solution of the terpolymer was applied to the copper grid covered with a collodion film, and the cast film was stained with uranyl acetate solution.

RESULTS AND DISCUSSION

In the terpolymerization described in the experimental section of this paper, the hydrophobic monomer DMDA is surface active and can dissolve in water in the absence of an external surfactant, so AM, NVP, and DMDA monomers were terpolymerized successfully in an aqueous solution. Compared with micellar terpolymerization, in the presence of external surfactant, the aqueous solution terpolymerization process and posttreatment of the product were convenient and easy to conduct. In micellar terpolymerization, incorporation of cosurfactant may dilute the number of hydrophobic groups in each micella; therefore, the blocks of the hydrophobic monomer units in the terpolymer are shortened. The remaining cosurfactant in the terpolymer post-treatment may also effect the solution behavior of the terpolymer.⁶ The hydrophobic monomers used in this study contain hydrophilic ion groups, so the terpolymers remained water soluble when as much as 10-15% mol of DMDA was incorporated into the terpolymer. This is higher than oil-soluble hydrophobic monomers, such as N-alkylacrylamide and acrylic esters, and the terpolymer shows strong hydrophobic association effect.

Effect of Polymer Composition

Figure 1 shows the concentration dependence of the solution viscosity for APDA-6 terpolymer in deionized water and in 0.256 mol/L NaCl solution, respectively. In both cases, almost the same solution behavior was observed. As the terpolymer concentration increased, the solution viscosities of the terpolymers obviously increased. A dramatic increase in solution viscosities of APDA terpolymers was observed at about the polymer concentration of 0.35 g/dL, which was attributed to the strong interchain associations. The solution viscosities of APDA-6 terpolymer in 0.256 mol/L NaCl solution was greater than that in deionized water. For example, the apparent viscosity of the terpolymer at concentration of 0.1 g/dL was 6.2 mPa s in NaCl solution, and only 4.5 mPa s in deionized water. The big sidegroup of NVP could disrupt the association of hydrophobically associating water-soluble polymer, and make the C* increase.

Effect of Electrolytes

As shown in Figure 2, With increasing electrolyte concentration, the viscosity of APDA-6 terpoly-



Figure 2 Effect of electrolyte concentration on apparent viscosity of APDA-6 at polymer concentration of 0.2 g/dL.



Figure 3 Effect of temperature on apparent viscosity of APDA-6 at polymer concentration of 0.2 g/dL.

mer initially increased, then decreased followed by an increase. Addition of salt enhanced the intermolecular association attributable to the increased polarity of the solvent.⁵ On the other hand, the hydrophobic monomer units contained ion groups, so addition of salt shielded the intermolecular repulsion and made the polymer molecule contract. These two effects competed with each other.

Temperature Dependence of Viscosity

The effect of temperature on the viscosity is shown in Figure 3. The results are quite dramatic. At first, the solution viscosity slightly decreased, then increased, followed by a decrease. Temperature increase makes the movement of water molecules and hydrophobic groups increase, and the hydration spheres of the hydrophobic groups change a great deal, which is unfavorable for the interchain association of the terpolymers. Hydrophobic hydration is exothermic; whereas, hydrophobe–hydrophobe interaction is endothermic. The viscosity increases observed upon heating are consistent with an entropydriven increase in hydrophobic bonding.^{5,7}

Effect of Shear Rate

Figure 4 shows the apparent viscosity versus shear rate for the APDA-6 terpolymer in 0.25 mol/L NaCl solution at 25°C. The apparent viscosity of the terpolymer decreased with increasing shear rate, and exhibited pseudoplastic behavior. Surprisingly, upon removal of shear, the solution viscosity recovered and was even greater than its original shear value. The very sharp de-



Figure 4 Apparent viscosity versus shear rate of ADA-6 terpolymer at concentration of 0.2 g/dL.

crease in viscosity with shear rate implied that the existence of a network-like loose structure held together by the relatively weak hydrophobic interactions would be disrupted readily upon application of shear. The results indicate that not only do associations recover immediately after removal of shear, but also, the associations are enhanced by the application of shear because of the increasing order of the hydrophobic microdomain.⁵ There exists a dynamic equilibrium between intermolecular association and dissociation. Figure 5 shows the time dependence of viscosity at different shear rate. At low or high shear rate, the solution viscosity increased gradually with increasing shear time.

Effect of Surfactants

The APDA-6 terpolymer contained a large quantity of cationic hydrophobic monomer units, and



Figure 5 Time-dependent apparent viscosity of APDA-6 terpolymer in 0.256 mol/L NaCl solution.



Figure 6 Apparent viscosity versus CTAB concentration of APDA-6 terpolymer in aqueous solution at concentration of 0.2 g/dL.

phase separation appeared when adding the anionic surfactant (SDS), which may be the result of the coulombic attraction of the positive and negative charges. The effects of cationic (CTAB) and nonionic (OP) surfactants on the viscosity of the terpolymer solution were studied (Figs. 6 and 7). In the range of both surfactant concentrations investigated, there were a sharp initial decrease of solution viscosity followed by an increase, and then a decrease again. The association of surfactant with the hydrophobic groups of the terpolymer competed with intermolecular polymer-polymer association. The hydrophobic association was disrupted when adding surfactant. With increasing surfactant concentration, the surfactant micelle formed and may crosslink the hydrophobic groups effectively, which caused the viscosity to increase; however, too many surfactant micella at high surfactant concentration may not combine



Figure 7 Apparent viscosity versus OP concentration of APDA-6 terpolymer in aqueous solution at concentration of 0.2 g/dL.



Figure 8 Effect of alkalinity on apparent viscosity of APDA-6 terpolymer in aqueous solution.

hydrophobic groups effectively, and may disrupt the interchain association of hydrophobic groups.^{8,9}

Effect of Alkali

As the literature reports addition of alkali would make the viscosity of partially hydrolyzed HPAM decrease greatly. For APDA-6 terpolymer, as shown in Figure 8, the solution viscosity obviously increased with increasing alkali (NaHCO₃).

Thermal Stability of Terpolymer Solution

Figure 9 shows the aging effect of APDA-6 terpolymer in 0.256 mol/L NaCl solution at 50°C (saturation oxygen). During the first 7 days, the solution viscosity decreased slowly, and changed slightly afterward. The viscosity of APDA-6 terpolymer was 4.82 mPa s after 56 days' aging, and the original value was 7.1 mPa s before aging.



Figure 9 Aging effect of APDA-6 terpolymer in 0.256 mol/L NaCl solution.



Figure 10 Reduced viscosity versus concentration of APDA-6 in its aqueous solution.

Dilute Solution Property

Figure 10 shows the plots of the reduced viscosity of APDA-6 terpolymer as a function of terpolymer concentration in deionized water. With increasing polymer concentration, the reduced viscosity decreased and showed a behavior typical of ionized polyelectrolytes. In addition to salt, the solution behavior was the same as the nonionic polymer, and the reduced viscosity can be described with the Huggins equation. Table III lists the intrinsic viscosities $[\eta]$ and Huggins parameters K_H of the APDA-6 terpolymer in 0.256 mol/L NaCl solution. The $[\eta]$ of the terpolymer is very low, because of the shielding of the ionic repulsion and the strong intramolecular association of the hydrophobic groups, which make the molecular chain contract. The high values of $K_{\rm H}$ and β reflect the strong tendency for the macromolecules to form intermolecular association.^{5,7}

TEM Analysis of the Terpolymer

Figure 11 compares electron micrographs of APDA-6 terpolymer in deionized water and in

Table III Intrinsic Viscosity and Huggins Parameters of APDA-6 Terpolymer in 0.256 mol/ L NaCl Solution

Sample	[η] (dL/g)	K _H 2.0 1.48	
APDA-6ª APDA-6 ^b	$\begin{array}{c} 1.35\\ 1.37\end{array}$		

^a Calculated by Huggins equation: $\eta_{SP}/C = [\eta] + K_H [\eta]^2C$. ^b Calculated by Schulz–Blaschke equation: $\eta_{SP}/C = [\eta] + K_H [\eta] \eta_{SP}$.



in deionized water



in NaCl solution

Figure 11 Transmission electron photomicrographs of APDA-6.

0.256 mol/L NaCl solution. The cast films of the terpolymer were stained with uranyl acetate, and the unstained white portions were hydrophobic microdomains. In both cases, microphase structures are clearly observed. The microdomains were small in deionized water and large in salt solution. The hydrophobic groups tended to aggregate and associate with one another so as to attain the smallest surface area exposed to the aqueous phase and to release the structured water around them.¹⁰ In salt solution, the polarity of the solution increased, and the hydrophobic association appeared strong. The presence of the microphase separation of the terpolymer in aqueous solution make the terpolymer exhibit high viscosification efficiency and excellent salt tolerance.

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