불화계 양친매성 폴리아크릴아마이드의 합성과 용액거동

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Synthesis and Solution Properties of Fluorinated Amphiphilic Polyacrylamide

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Abstract: A series of hydrophobically associating fluorinated amphiphilic polyacrylamide copolymers with remarkably high heat resistance and salt tolerance were synthesized by free radical micellar copolymerization, using acrylamide (AM) and sodium 2-acrylamido-tetradecane sulfonate ($AMC_{14}S$) as amphiphilic monomers, and 2-(perfluorooctyl) ethyl acrylate (PFHEA) as hydrophobic monomer. The structure of the terpolymer was characterized by FTIR, ^1H NMR and ^{19}F NMR. The solution properties of the terpolymers were investigated in details, and the results showed that the terpolymer solution had strong intermolecular hydrophobic association as the concentration exceeded the critical association concentration 1.5 g/L. The terpolymer solution possessed high surface activity, viscoelasticity, excellent heat resistance, salt tolerance and shearing resistance. The viscosity retention rate of copolymer solution was as high as 59.9% under the condition of fresh wastewater, 85 °C and a 60-days aging test.

Keywords: fluorinated amphiphilic polyacrylamide, hydrophobically association, micellar copolymerization, water-soluble polymer, surface tension.

Introduction

The majority of polymers used in enhanced oil recovery process (EOR) are partially hydrolyzed polyacrylamide (HPAM) at present,[1] which is widely applied to increase the viscosity of water phase, to reduce the oil-water mobility ratio, and to improve displacement efficiency.[2] However, HPAM was not suitable for high temperature and salinity reservoir. Li[3] reported that HPAM degraded seriously when the temperature reached up to 75 °C, leading to obvious loss of apparent viscosity. Furthermore, both Molchanov[4] and Panmai[5] had reported that the viscosity of HPAM solution decreased rapidly as the salinity or hardness increased.

Hydrophobically association polyacrylamide (HAPAM)[6-9] and amphiphilic polyacrylamide[10-15] had been developed and applied to various areas with obvious improvement[16] in solu-tion properties including heat resistance, salt tolerance, etc. This achievement encouraged both academic and industrial researchers to synthesize high-performance copolymers with excellent properties for potential applications in field of EOR. Bistline reported the synthesis and characterization of various amphiphilic polymers with different polymerizable surfactants.[17] In comparison to HPAM, amphiphilic polymers not only bear the rheological property of high molecular weight PAM but also have high surface activity.[18,19] For HAPAM, the enhanced hydrophobic association interactions resulted in high viscosity and excellent heat resistance and salt tolerance.[20,21] Hydrophobic monomers with long alkyl chain had been widely used for the preparation of HAPAM, and the solution behavior of the as-prepared HAPAM had been intensively studied.[22,23] However, there were seldom researches focused on fluorinated polyacrylamides. The interaction of hydrophobic associations between fluorocarbon groups is stronger than that of the corresponding hydrocarbon groups of the same carbon chain length because of lower cohesive energy density and sur-

face energy of fluorocarbon groups.[24] Kramer and Steber reported that the hydrophobicity of -CF$_2$- group was equivalent to 1.7 times of that of -CH$_2$- group.[25]

It is generally accepted that the solution of fluorinated water soluble polymers have low surface tension and better hydrophobic associations, which are extremely important for the heat resistance and salt tolerance of flooding polymer. In order to combine the advantages of HAPAM and amphiphilic polyacrylamide, a novel hydrophobically association polyacrylamide with fluorinated unit was developed based on an amphiphilic monomer sodium 2-acrylamido-tetradecane sulfonate (AMC$_{14}$S, as described in the literature).[19] The hydrophobically associating fluorinated amphiphilic polymer was composed of acrylamide (AM), AMC$_{14}$S and 2-(perfluorooctyl) ethyl acrylate (PFHEA), which was synthesized by free radical micellar polymerization. The structure of the terpolymer (abbreviation: PASF) was confirmed by means of FTIR, ^{1}H NMR and ^{19}F NMR. Static laser light scattering (SLS) and dynamic laser light scattering (DLS) were also used to characterize PASF. The experimental results indicated that the performance of polymers solution including surface activity, viscoelasticity, viscosity, salt resistance, temperature resistance, shearing resistance and aging resistance can be remarkably enhanced by introducing fluorinated PFHEA and amphiphilic AMC$_{14}$S into the polymer backbone, which provide the hydrophobically associated fluorinated amphiphilic polyacrylamide with more promising applications in the field of EOR.

Experimental

Materials. Acrylamide (AM, Shandong Polymer Bio-chemicals Co., LTD) was recrystallized twice from acetone and dried at room temperature under vacuum. Potassium persulphate (KPS, Beijing Chemical Reagent Co.), Sodium bisulfite (SBS, Beijing Chemical Reagent Co.), Sodium dodecyl sulfate (SDS, Beijing Chemical Reagent Co.), 2-(Perfluorooctyl) ethyl acrylate (PFHEA, Aldrich Chemical Company). Sodium 2-acrylamido-tetradecane sulfonate (AMC$_{14}$S) was prepared according to a known method with a yield of 95%.[19] ^{1}H NMR of AMC$_{14}$S (400 MHz, D$_2$O, ppm): δ 0.80(3H, -CH$_3$); δ 1.21(20H, -(CH$_2$)$_{10}$-CH$_3$); δ 1.62(2H, -CH$_2$-); δ 3.0(2H, -CH$_2$-SO$_3^-$); δ 4.39(1H, -CH-); δ 5.78(1H, =CH-); δ 6.34(2H, CH$_2$=).

Polymerization. The hydrophobic amphoteric fluorinated polyacrylamide was obtained by micellar copolymerization following the procedure described by Johnson *et al.*.[26] A 250 mL three-necked flask equipped with mechanical stirrer and N$_2$ inlet/outlet was used for the preparation of the copolymers. AM was dissolved in 100 mL of deionized water and purged with nitrogen for 30 min. Sodium dodecyl sulfate (SDS), designated amounts of AMC$_{14}$S and PFHEA (shown in Table 1) were added into three-necked flask, which was then placed in a water bath at 40 °C, while being stirred continuously until a clear homogeneous solution was obtained. Then the initiator KPS and SBS were added. The reaction was allowed to proceed for 12 h at 40 °C under a nitrogen atmosphere. In all cases, the initial concentration of total monomer was 10 wt%, and the concentrations of AMC$_{14}$S and SDS were kept constant at 0.3 mol% and 0.1 mol/L, respectively. The amount of PFHEA was 0.1, 0.2, 0.3, 0.5, or 0.8 mol%, and the amount of initiator was set to 0.1 wt% relative to monomer feed, in which the molar ratio of KPS to SBS was 2. After polymerization, the reaction mixture was diluted with five volumes of distilled water, and two volumes of acetone were then added with stirring to precipitate the polymers. The copolymers were washed with acetone twice and extracted with ethanol using a Soxhlet extractor for two days to remove all traces of water, surfactant, and residual monomers. At last the copolymers were dried under reduced pressure at room temperature for 24 h. For comparison, the AM/AMC$_{14}$S copolymer was also synthesized under identical conditions.

Characterization. ^{1}H NMR and ^{19}F NMR spectra of the polymer samples were performed on a Varian Gemini-500 NMR spectrometer using D$_2$O as the solvent. A Bruker VERTEX 70 infrared spectrometer was used for the Fourier transform infrared (FTIR) spectroscopic analysis.

Elemental analyses were conducted on a Vario MICRO cube Elemental analyzer (German Elementar Co.).

Apparent viscosities were measured using a Brookfield DV-II rotational viscometer. All viscosities were measured at 30 °C in the solution of NaCl 5.0 g/L, and the shear rate was 7.34 s^{-1} unless otherwise stated.

The surface tensions of polymer solutions were measured by DCAT-21 surface tensiometer (Germany Dataphysics Co.) at 25 °C.

Rheological measurements were performed on a HAAKE Rheostress 6000 shearrheometer at 25 °C.

Static laser light scattering measurements (SLS) were performed on a Brookhaven Instruments BI-APD (Brookhaven Instruments Co., USA), using a method of gradually increasing concentration of copolymer. The system light source was a linearly polarized gallium arsenide (GaAs) laser (658 nm) at 25 °C. The copolymer samples were dissolved in de-ionized

water, while being oscillated continuously using the shaking table until a clear solution was obtained, then NaCl crystal was added, and the concentration of NaCl was set to be 0.5 mol/L. The copolymers samples were filtered with a 0.2 μm membrane before test.

Dynamic laser light scattering (DLS) were performed on a Brookhaven Instruments BI-APD (Brookhaven Instruments Co., USA), which were conducted at a scattering angle of 90°. The system light source was a linearly polarized gallium arsenide (GaAs) laser (658 nm) at 25 °C. The intensity-intensity autocorrelation functions were measured by light scattered from copolymer solutions. All the solutions were filtered through a 0.8 μm membrane before the DLS measurement. The hydrodynamic radius (R_h) and distribution of micelles were investigated by the DLS and calculated according to the CONTIN Laplace inversion algorithm.[27]

Results and Discussion

The PASF terpolymer was synthesized by a free radical micellar copolymerization. To evaluate the effects of the terpolymer structure on polymer solution properties, several series of samples with different compositions were prepared by varying the content of PFHEA in the monomer feed (as shown in Table 1). For comparison, the binary copolymer PAS was also synthesized under identical conditions.

Characterization of PASF Terpolymer. FTIR spectrum of the copolymer was shown in Figure 1. The peak at 3344 cm^{-1} is assigned to the N-H stretching vibration. The peak at 3196 cm^{-1} is attributed to characteristic absorption of -NH$_2$, and the peak at 1451 cm^{-1} is C-N and N-H in-plane bending vibration. The peak at 1663 cm^{-1} is characteristic of C=O
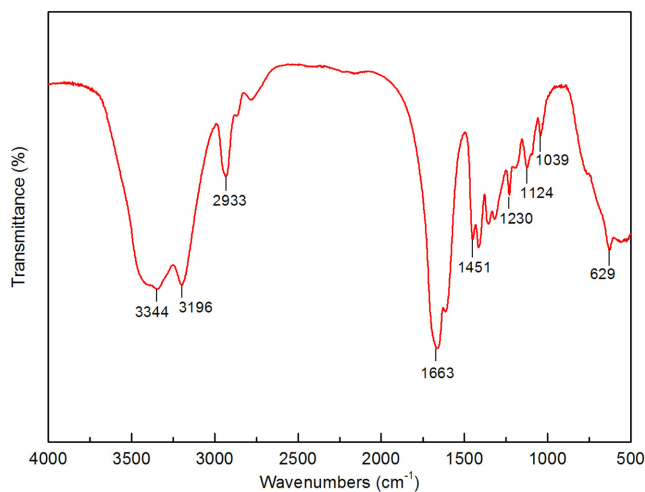

Figure 1. FTIR spectrum of the PASF-4 copolymer.

stretching from the amide group. The peak at 1039 cm^{-1} and 1230 cm^{-1} is attributed to symmetric and asymmetric vibration absorption of -SO$_3^-$, respectively, indicating the presence of AMC$_{14}$S in the copolymer. The peak at 629 cm^{-1} is ascribed to the stretching vibration absorption of -C-S. The peak at 1124 cm^{-1} is due to -C-F stretching vibration, suggesting the incorporation of PFHEA in the polymer backbone.

To get further information concerning the chemical structure and composition, ^{1}H NMR and ^{19}F NMR spectra of the copolymer were further measured, as shown in Figure 2 and Figure 3, respectively. It can be obviously seen that there were characteristic signals of each monomer, demonstrating the existence of PFHEA and amphiphilic AMC$_{14}$S units in the resulted copolymer. According to the analysis of FTIR, ^{1}H NMR and ^{19}F NMR spectra, it could be inferred that the as-prepared polymer product was a terpolymer consisted of three kinds of monomer AM, AMC$_{14}$S and PFHEA.

Table 1. Elemental Analysis Results of the Samples

Sample	AMC$_{14}$S (mol%)	PFHEA (mol%)	Elemental analysis						Conversion (wt%)
			C (wt%)	H (wt%)	N (wt%)	S (wt%)	AMC$_{14}$S (mol%)	PFHEA (mol%)	
PAS	0.3	0	50.82	7.08	19.50	0.13	0.29	/	93.2
PASF-1	0.3	0.1	50.72	7.05	19.41	0.12	0.27	0.09	93.1
PASF-2	0.3	0.2	50.62	7.02	19.33	0.12	0.27	0.16	92.5
PASF-3	0.3	0.3	50.53	6.99	19.24	0.11	0.26	0.25	91.8
PASF-4	0.3	0.5	50.29	6.93	19.02	0.10	0.24	0.46	90.6
PASF-5	0.3	0.8	49.99	6.85	18.72	0.10	0.24	0.74	89.2

The amphiphilic fluorinated terpolymers were designated as PASF, where A stands for AM, S stands for AMC$_{14}$S, and F stands for PFHEA, so that PAS is referred to the copolymer composed of AM and AMC$_{14}$S. Conversion=(Total mass of copolymer after extraction and drying)×100%/ (Total mass of all monomers).
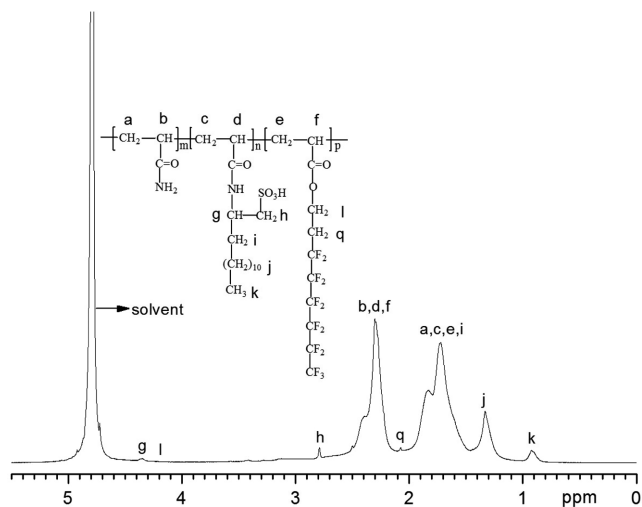
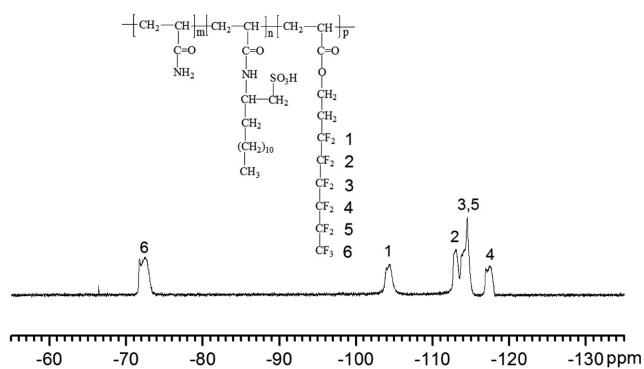**Figure 2.** ^{1}H NMR spectrum of the PASF-4 copolymer.

Figure 3. ^{19}F NMR spectrum of the PASF-4 copolymer.

Static Laser Light Scattering Measurements. Static laser light scattering measurements were performed to characterize the molecular weight of PASF copolymers. As shown in Table 2, the weight average molecular weight (M_w) and mean square radius (R_g) of PASF samples increased with increasing PFHEA contents. As the amount of PFHEA varied from 0.1 to 0.5 mol%, the M_w of PFHEA increased from 6.08×10^6 to 6.77×10^6 g/mol, and R_g increased from 128.5 to 159.7 nm correspondingly. Because of the incorporation of fluorinated hydrophobic monomer into the polymer backbone, M_w and R_g of PFHEA were a little smaller than that of PAS. The second-order virial coefficient (A_2) indicated that NaCl aqueous solution was a good solvent for both PASF and PAS samples. For PASF-5, even higher fluorinated content in the copolymer would result in strong intramolecular associations, leading to poor solubility in salt water.

Dynamic Laser Light Scattering Measurements. The

Table 2. Static Laser Light Scattering Data for the Copolymer Samples

Sample	M_w (10^6 g/mol)	R_g (nm)	A_2 (10^4 mol·mL/g^2)
PASF-1	6.08±0.35	128.5±9.5	2.25±0.82
PASF-2	6.35±0.27	139.4±8.3	2.05±1.24
PASF-3	6.62±0.39	151.2±10.2	1.97±0.58
PASF-4	6.77±0.23	159.7±9.8	1.52±1.49
PASF-5	-	-	-
PAS	7.01±0.28	185.2±6.5	2.53±0.72

aggregation behavior of the copolymer samples with different compositions in the diluted solutions was investigated by dynamic laser light scattering measurement (DLS). Figure 4 showed the influence of copolymer concentration on the hydrodynamic radius (R_h) of the copolymers in 0.5 mol/L NaCl solutions at 25 °C. As shown in Figure 4, at a lower copolymer concentration, the R_h values of the PASF samples decreased gradually with increasing copolymer concentration and reached a minimum at approximately 0.03-0.08 mg/mL. At higher polymer concentration, the R_h values increased steadily as the copolymer concentration increased. In comparison, the R_h values of the PAS sample only changed slightly within the concentration range studied. It could also be found that the R_h values of the PASF samples decreased with increasing content of fluorinated segment at lower copolymer concentration. On the contrary, an opposite trend was observed at higher copolymer concentration. The decrease of R_h values with increasing content of PFHEA indicated that intramolecular hydrophobic association was predominant at lower
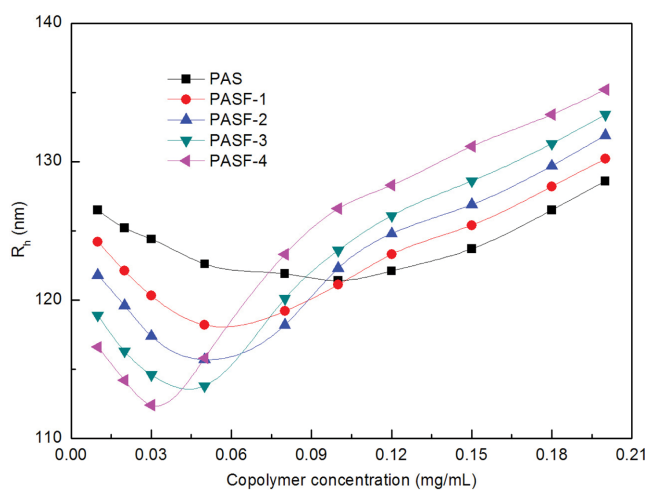

Figure 4. Effect of copolymer concentration on the average hydrodynamic radius in 0.5 mol/L NaCl solution at 25 °C.
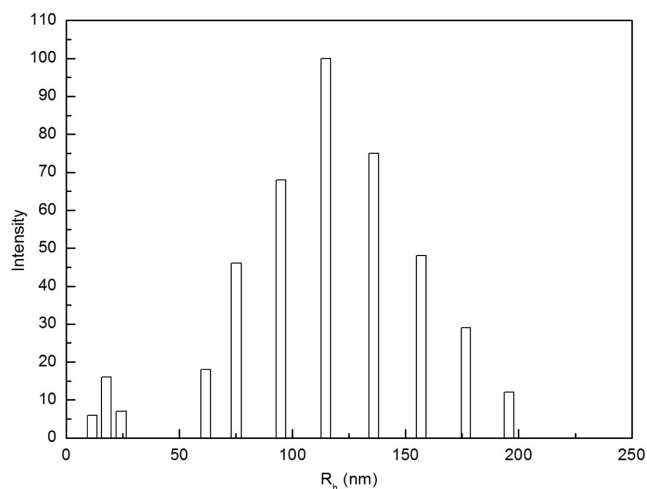
Figure 5. Hydrodynamic radius distribution of PASF-4 sample (0.08 mg/mL) in 0.5 mol/L NaCl solution at 25 °C.

Figure 6. Effect of copolymer concentration on the surface tension of PASF aqueous solution.

copolymer concentration, which resulted in the contraction of polymer chains. While the increase of R_h values at higher concentration could be attributed to the aggregation of copolymer chains due to intermolecular hydrophobic association. The DLS results showed that fluorinated segment may largely promote the hydrophobic association and exhibit excellent increasing viscosity at high copolymer concentration.

The hydrodynamic radius distribution of PASF-4 sample in 0.5 mol/L NaCl solution was further studied by DLS. The result was shown in Figure 5. In the solution of a 0.08 mg/mL copolymer concentration, a bimodal distribution was observed. The first peak with low R_h values was attributed to individual copolymer chains, and the second peak with high R_h values represented polymeric aggregates of intermolecular associations. The average R_h value was about 124 nm.

As shown in Figure 4 and Figure 5, DLS data indicated that hydrophobic associations may occur both intramolecularly and the intermolecularly. At low copolymer concentration, the intramolecular hydrophobic association interactions induced collapse of the polymeric chains and caused decrease of R_h values. While in the case of a higher copolymer concentration, the intermolecular hydrophobic association interactions played a dominant position and resulted in the formation of the polymeric chains aggregation. As the copolymer concentration increased, the number and volume of the aggregations increased, leading to higher R_h values.

Effect of Copolymer Concentration on the Surface Tension. In order to prove that the surface tension can be decreased by the adding of PFHEA monomer, the verification of the surface tension has become the key point. Figure 6
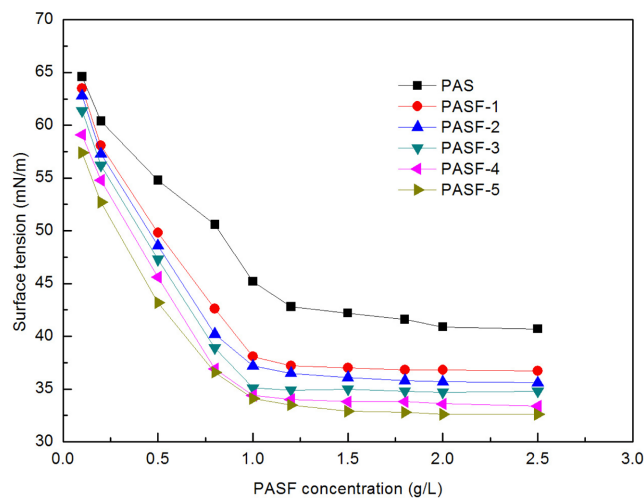
showed the relationship between surface tension and concentration of PASF and PAS samples at 25 °C. With the increased copolymer concentration, the surface tension of the aqueous solutions dropped drastically, and then the surface tension became invariable in the increasing of concentration of copolymer. But the surface tensions of PASF samples were lower than that of PAS sample. PASF samples had high surface activity due to their strong hydrophobic fluorinated modification. The -CF₃ group in the PFHEA monomer provided the copolymer with extremely low surface energy. When the concentration was increased, the ordered distribution of fluorinated groups on the air/water interface and the aggregates like micellar originated from self-association of the side fluorinated groups, caused surface tension to decrease quickly.

Additionally, the surface tension of PASF aqueous solution decreased as the hydrophobe content of PFHEA increased. PASF-5 was the most effective in reducing the surface tension of the water solution. When copolymer concentration reached to 1.0 g/L, surface activity of copolymer solution decreased to 32 mN/m. This contributed to more fluorinated groups in the polymer chains, resulted ordered arrangement on the air/water interface.

Dynamic Rheological Property of Copolymer Solution. The viscoelasticity of copolymer solution can be characterized using storage modulus (G') and loss modulus (G''). G' represents elasticity and G'' represents viscosity of copolymer solution. When the fluid flowed through porous media, the driving force of fluids coming from the elasticity of copolymer solution, could change part residual oil to movable oil, and thus improve oil displacement efficiency.[28] As shown in Figure
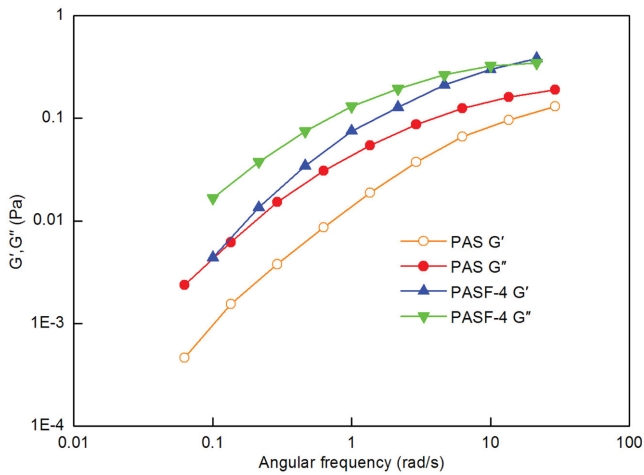
Figure 7. Dynamic rheological property of copolymer solution (copolymer concentration 2.0 g/L, NaCl concentration 5.0 g/L).

Figure 8. Effect of copolymer concentration on the apparent viscosity of PASF aqueous solution.

7, G' and G'' increased with the increasing angular frequency, but the increment rate of G' was bigger than that of G'', and then a cross-over appeared. At low range of angular frequency, G' was lower than G''. The result indicated that the copolymer solution was dominated by viscosity, contrarily, that was elasticity. Meanwhile, the lower cross-over value indicated that the copolymer solution had good viscoelasticity.[29] By contrast, the elasticity and viscosity of PASF-4 sample was better than that of PAS, because the incorporation of fluorinated groups into the copolymer chains largely strengthened interaction of hydrophobic association, which was benefit for improving viscoelasticity.

Effect of Polymer Concentration on the Viscosities. Relationships between apparent viscosity and copolymer concentration in water solution are depicted in Figure 8. The curves showed that the viscosities increased sharply as the polymer concentration was higher than around 1.5 g/L, which was the critical association concentration ($[C^*]$) for copolymers. When the concentration was above $[C^*]$, three-dimensional network structures with large hydrodynamic volumes were formed due to strong intermolecular hydrophobic associations, which contributed significantly to the higher viscosity. The more the content of fluorinated segment in the copolymer, the higher the viscosities of solutions could be observed, which resulted in the increment of the hydrodynamic radius (R_h). This result was consistent with that of DLS. However, the solution viscosity of PASF-5 was much lower because of strong intramolecular association caused by higher fluorinated contents in the copolymer. By contrast, the solution viscosity of PAS prepared under the identical condition was obviously
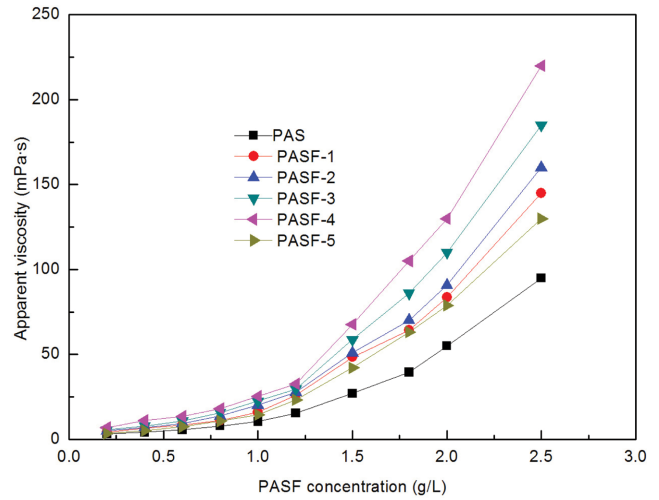
lower than that of terpolymers, and these results indicated that fluorinated amphiphilic polyacrylamide had significant capacities of hydrophobic association and increasing viscosity.

Effect of Temperature on the Viscosities. The apparent viscosity of flooding polymer at different temperature, especially at high temperature was a significant factor for the application in the field of EOR. The relationship between temperature and apparent viscosity of copolymer aqueous solutions are shown in Figure 9, as the temperature increased from 25 to 85 ℃. As the temperature increased, the apparent viscosity of copolymers solution increased gradually. After reaching a maximum at approximately 35-50 ℃, the viscosity decreased with the temperature further increasing. The interaction of hydrophobic association played an important role in the whole temperature range. Because hydrophobic association was an endothermic process accompanied by an entropy increase,[30] the hydrophobic association of inter-macromolecule chains led to increase viscosity as the temperature became higher. However, with the temperature continuous to increase the fast movement of macromolecule chains and water molecules weakened the interaction of hydrophobic association and undermined the "iceberg structure" around the hydrophobe segments which finally led to a decrease of the copolymer solution viscosity.[31]

As shown in Figure 9, the transition temperature of PAS corresponding to the maximum of apparent viscosity was only about 35 ℃. The transition temperature of PASF-4 sample reached up to 50 ℃ due to the incorporated of the hydrophobic fluorinated monomers. Furthermore, the transition temperature
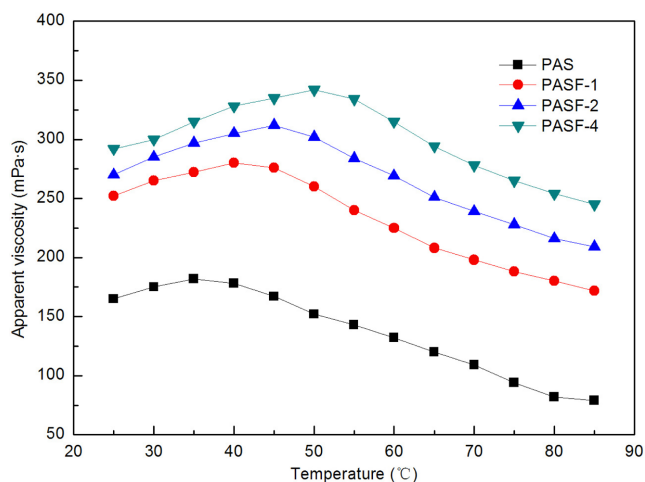
Figure 9. Effect of temperature on the apparent viscosity of PASF aqueous solution (copolymer concentration 3.0 g/L).

of PASF-1- PASF-3 was 40, 45 and 50 °C, respectively, in accordance with the increasing content of hydrophobic PFHEA. The temperature dependence of viscosity for PASF indicated that the fluorinate modification could significantly improve the temperature resistance performance of flooding polymer.

Effect of Salinity on the Viscosities. The effect of NaCl concentration on the apparent viscosity of the copolymer solutions had been investigated, and the results were summarized in Figure 10. As shown in Figure 10, the apparent viscosities of copolymer solution increased firstly and then decreased after reaching the peak as NaCl concentration increased gradually. This is probably due to the solvent's polarity change as
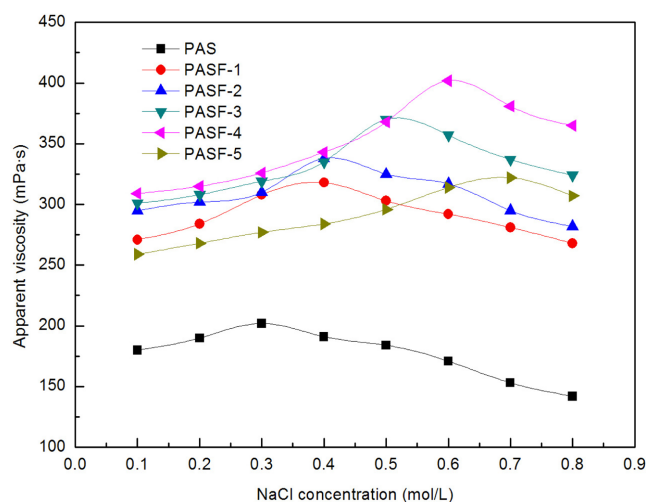
a consequence of the addition of NaCl, which weakened the electrostatic attraction between charges in the polymer chains. Relatively high NaCl concentration led to an extension of the polymer chain and reinforced intermolecular hydrophobic associations and dimensional network, as a result the copolymers showed excellent salt thickening property. However, with further increase of NaCl concentration, the hydrophobic microstructures become contraction, and then the polymer chains associate to form larger aggregates, resulted in the subsequently phase separation and the apparent viscosity loss.

Additionally, as shown in Figure 10, in comparison to the bipolymer PAS, it can be clearly seen that the salt tolerance capacity of PASF is much better than that of PAS. Meanwhile, with increasing fluorinated content, the salt concentrations corresponding to maximum values of the apparent viscosity increased accordingly, indicating the enhancement of intermolecular associations due to increasing content of hydrophobic PFHEA.

Effect of Shear Rate on the Viscosities. The variation of apparent viscosity as a function of shear rate for PASF-4 and PAS solutions are shown in Figure 11. With the increase of shear rate, the apparent viscosity of the two copolymer solutions both decreased sharply, which was due to the disruption of the weak and reversible intermolecular physical network structure. On the other hand, the recovery of intermolecular association was a time-dependent process and finally the apparent viscosity tended to be constant because of the balance between intermolecular association and disassociation, which exhibited pseudo-plastic behavior. In contradistinction to PAS,
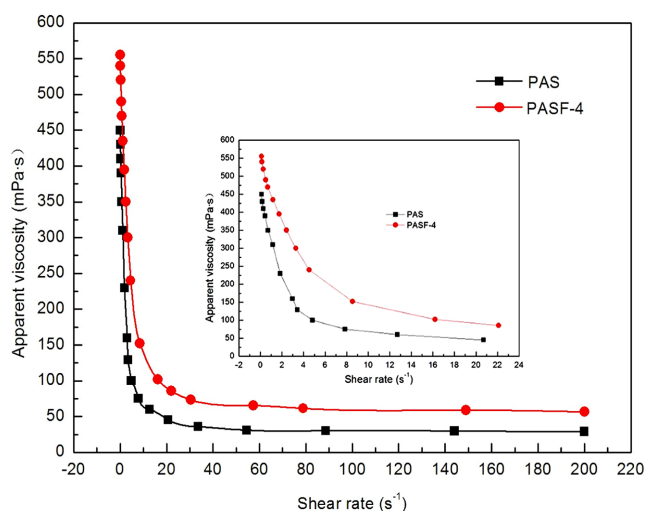

Figure 10. Effect of NaCl concentration on the apparent viscosity of PASF solution (copolymer concentration 3.0 g/L).

Figure 11. Effect of shear rate on the apparent viscosity of PASF solution (copolymer concentration 3.0 g/L).

Table 3. Aging Property of Copolymer (mPa·s)

Sample	Aging time (d)						
	0	1	7	15	30	45	60
PASF-4	118.2	105.4	99.8	85.5	78.4	73.8	70.8
PAS	57.4	49.5	43.1	34.0	30.6	27.5	24.8

the apparent viscosity of PASF-4 was higher at any shear rate, and decrease amplitude was smaller. That is to say, terpolymers exhibited better shearing resistance.

Effect of Aging on the Solution Viscosity. In order to optimize injection allocation technology and improve injection efficiency, flooding polymer solution was prepared by dissolving the polymer in reservoirs fresh wastewater. The wastewater contains plenty of H_2S and Fe^{2+}, which consequently results in degradation of polymer in solution. Meanwhile, the residence time of flooding polymer in reservoir was quite long. For adapting the above oil field condition, the aging property of copolymer solution should be necessarily studied with the reservoirs fresh wastewater. PASF-4 and PAS samples with a concentration of 2.0 g/L were used to investigate the influence of aging on the solution viscosity. The relationship between apparent viscosities and the aging time is shown in Table 3. After aging for 60 days at 85 °C, the viscosity retention ratio of PASF-4 solution was 59.9%, which was higher than that of PAS (43.2%). This result indicated that PASF exhibited excellent anti-aging performance because of the incorporation of PFHEA into the copolymer chains. The PFHEA moieties had lower cohesive energy density, which might be beneficial to intermolecular amphiphobic interaction and mitigate polymer chain breaking.

Conclusions

In conclusion, The hydrophobically associating fluorinated amphiphilic polyacrylamide (PASF) with obvious improvement in both the heat resistance and salt tolerance were synthesized by free radical micellar copolymerization technique in aqueous solution. The amount of PFHEA remarkably affected the apparent viscosity of PASF solutions because of strong intermolecular hydrophobic associations, and the apparent viscosity increased dramatically as the concentration of the copolymer was above the critical associating concentration (approximate 1.5 g/L) in aqueous solution. Additional, the terpolymer solution possessed high surface activity, viscoelasticity. Results from temperature and salinity measurement

indicated that the incorporation of fluorinated groups into the copolymer could improve heat resistance and salt tolerance of flooding polymer. At the same time a gradually increase in the apparent viscosity accompanied an increase in a low temperature range or in the mass fraction of NaCl. The results of shear rate measurement indicated that the PASF copolymer has excellent pseudo-plastic and anti-shearing behavior. Moreover, the PASF copolymer showed good anti-aging property in fresh wastewater solutions at 85 °C, the viscosity retention rate of copolymer solution was as high as 59.9%.

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