Research Article

Synthesis and Evaluation of a Water-Soluble Hyperbranched Polymer as Enhanced Oil Recovery Chemical

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A novel hyperbranched polymer was synthesized using acrylamide (AM), acrylic acid (AA), *N*-vinyl-2-pyrrolidone (NVP), and dendrite functional monomer as raw materials by redox initiation system in an aqueous medium. The hyperbranched polymer was characterized by infrared (IR) spectroscopy, ¹H NMR spectroscopy, ¹³C NMR spectroscopy, elemental analysis, and scanning electron microscope (SEM). The viscosity retention rate of the hyperbranched polymer was 22.89% higher than that of the AM/AA copolymer (HPAM) at 95°C, and the viscosity retention rate was 8.17%, 12.49%, and 13.68% higher than that of HPAM in 18000 mg/L NaCl, 1800 mg/L CaCl₂, and 1800 mg/L MgCl₂·6H₂O brine, respectively. The hyperbranched polymer exhibited higher apparent viscosity (25.2 mPa·s versus 8.1 mPa·s) under 500 s⁻¹ shear rate at 80°C. Furthermore, the enhanced oil recovery (EOR) of 1500 mg/L hyperbranched polymer solutions was up to 23.51% by the core flooding test at 80°C.

1. Introduction

Polymer flooding plays an important role in enhanced oil recovery (EOR) [1–7]. However, the most widely used water-soluble polymers, polyacrylamide and partially hydrolyzed polyacrylamide, are not suitable for high temperature, high salinity, and high flow rate injection owing to hydrolysis, decomposition, degradation, shear damage, and so forth [1, 6, 8–11]. With the growing demand for petroleum resources, the water-soluble polymer, which displays perfect temperature-resistance, salt-resistance, and shear-resistance in harsh conditions, is a challenge to the oil field chemists [12].

In recent decades, many studies demonstrated that acrylamide (AM) copolymerized with an applicable functional monomer, such as *N,N*-dimethylacrylamide, methacrylamide, *N*-vinyl-2-pyrrolidone (NVP), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), sodium allylsulfonate, acrylic acid (AA), and ethylenesulfonic acid, could obtain more satisfying polymer possessing better temperature-resistance and salt-resistance for EOR [12–17]. What is more, dendrite polymers, star polymers, and hyperbranched polymers, which may exhibit excellent

shear-resistance performance due to their special network structure, have been reported widely in many other applied fields [18–25]. This special network structure may reduce the effect of shear on polymer molecular chain, which may recover to a certain extent after being cut and eventually obtaining higher viscosity retention rate.

Keeping in mind all the above points, herein, a novel hyperbranched polymer was synthesized by free radical polymerization based on AM, AA, NVP, and dendrite functional monomer aiming to obtain satisfying temperature-resistance, salt-resistance, and shear-resistance.

2. Experimental

2.1. Chemicals and Reagents. Ethylenediamine (EDA, AR), methyl acrylate (AR), methanol (AR), ethanol (AR), *N,N*-dimethylformamide (DMF, AR), maleic anhydride (AR), acrylic acid (AR), acrylamide (AR), *N*-vinyl-2-pyrrolidone (NVP, AR), sodium hydroxide (AR), sodium hydrogen sulfite (NaHSO₃, AR), ammonium persulfate ((NH₄)₂S₂O₈, AR), sodium chloride (NaCl, AR), calcium

SCHEME 1: The synthesis route of the hyperbranched polymer.

chloride anhydrous (CaCl_2 , AR), magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, AR), potassium chloride (KCl, AR), sodium sulfate (Na_2SO_4 , AR), and sodium bicarbonate (NaHCO_3 , AR) were purchased from Chengdu Kelong Chemical Reagent Factory (Sichuan, China). All chemicals and reagents were used as received without any further purification.

2.2. Synthesis of Dendrite Functional Monomer. Synthesis of 0.5 generation dendritic macromolecule ($\text{DM}_{0.5}$): 113.5 g methyl acrylate was added into a three-necked flask with methanol as solvent, and then 9.0 g ethylenediamine was dripped into the stirred solution in the three-necked flask. The reaction time was 24 h at 25°C . After reaction, the product was purified by vacuum distillation and silica gel column. Then the $\text{DM}_{0.5}$ was obtained [18, 20].

Synthesis of 1.0 generation dendritic macromolecule ($\text{DM}_{1.0}$): 40.0 g ethylenediamine was added into a three-necked flask with methanol as solvent, then 20.2 g $\text{DM}_{0.5}$ was dripped into the stirred solution in the three-necked flask.

The reaction time was 48 h at 25°C , and the product was the $\text{DM}_{1.0}$, which was purified by vacuum distillation and silica gel column [18, 20].

Modification of $\text{DM}_{1.0}$: 4.4 g maleic anhydride was added into a round-bottom flask with N,N-dimethylformamide as solvent, and 8.0 g $\text{DM}_{1.0}$ was dripped into the round-bottom flask. The reaction time was 8 h at 70°C , and the dendrite functional monomer was obtained by vacuum filtration.

2.3. Synthesis of Hyperbranched Polymer and HPAM. Firstly, 7.00 g AM, 2.95 g AA, 0.01 g dendrite functional monomer, 0.04 g NVP, and 1.65 g sodium hydroxide were added into a 100 mL three-necked flask with 38.35 mL distilled water as solvent. Secondly, 0.04 g $\text{NaHSO}_3 \cdot (\text{NH}_4)_2\text{S}_2\text{O}_8$ initiator (mol ratio = 1:1) was taken along with distilled water in the three-necked flask. And then, the copolymerization was carried out for 4 h at 50°C under nitrogen atmosphere. Finally, the hyperbranched polymer was obtained by ethanol washing, drying, and pulverizing. The synthesis route of the hyperbranched polymer is shown in Scheme 1.

TABLE 1: TDS and chemical composition of the brine.

Composition	NaCl	KCl	CaCl ₂	MgCl ₂ ·6H ₂ O	Na ₂ SO ₄	NaHCO ₃	TDS
Content (g/L)	8.007	0.155	0.762	2.183	0.138	0.516	10.599

The AM/AA copolymer (HPAM) was synthesized using 7.00 g AM and 2.95 g AA as raw materials through the same synthesis method.

2.4. Characterization. Infrared (IR) spectra of the dendrite functional monomer and hyperbranched polymer were measured with KBr pellets using Perkin Elmer RX-1 spectrophotometer (Beijing Rayleigh Analytical Instrument, China). ¹H NMR spectroscopy and ¹³C NMR spectroscopy of the dendrite functional monomer, hyperbranched polymer, and HPAM were recorded on Bruker AC-E 200 spectrometer (Bruker BioSpin, Switzerland) at 400 MHz with D₂O as solvent. The elemental analysis of the hyperbranched polymer and HPAM was carried out through Vario EL III elemental analyzer (Wuxi Chuangxiang Analytical Instrument, China). The microstructures of the hyperbranched polymer and HPAM were observed via Quanta 450 scanning electron microscope (SEM, FEI Company, USA).

2.5. Weight-Average Molecular Weight. The weight-average molecular weight (M_w) of the hyperbranched polymer and HPAM was determined by a BI-200SM wide angle dynamic/static laser light scattering apparatus at 25°C. The laser wavelength was 532 nm. The M_w of the hyperbranched polymer and HPAM can be obtained by the following equation [26, 27]:

$$\frac{KC}{R_{90}(q)} \cong \frac{1}{M_w} \left(1 + \frac{1}{3} \langle R_g \rangle^2 q^2 \right), \quad (1)$$

where C is the concentration of polymer solution, g/mL; K is a constant; $\langle R_g \rangle$ is the average radius of gyration, nm; $R_{90}(q)$ is the Rayleigh ratio; and $q = (4\pi n/\lambda_o) \sin(\theta/2)$ with n , λ_o , and θ being the solvent refractive index, the wavelength of laser in vacuo, and the scattering angle, respectively.

2.6. Temperature-Resistance and Salt-Resistance. Hyperbranched polymer and HPAM solutions (5000 mg/L) were prepared with distilled water. The apparent viscosity of these polymers solutions was tested using Brookfield DV-III viscometer at different temperatures. The salt-resistance performance was studied by increasing salt (NaCl, CaCl₂, or MgCl₂·6H₂O) concentration, and then the apparent viscosity of these polymers solutions was measured via Brookfield DV-III viscometer at 20°C.

2.7. Shear-Resistance. Shear-resistance of the hyperbranched polymer and HPAM solutions (5000 mg/L) was measured using HAAKE RS 6000 rotational rheometer (Thermo Fisher Scientific, Germany) at 80°C [12, 15–17]. The samples were prepared with distilled water.

2.8. Core Flooding Experiments. Two Berea sandstone cores were used to study the EOR ability of these copolymer solutions (1500 mg/L) prepared with brine. Total dissolved solids (TDS) and chemical composition of the brine are listed in Table 1. The core was placed into Hassler core holder with 1.0 MPa backpressure and 3.0 MPa confining pressure. It was saturated with the brine, and then it was saturated with crude oil (62.2 mPa·s at 80°C) at different injection rate (0.1–0.2 mL/min) until irreducible water saturation (S_{wi}) was established. After 96 h of aging, the brine was injected at 0.2 mL/min to displace the crude oil until water cut reached 95%, and then the polymer solution was injected at 0.2 mL/min to obtain water cut 95% once more. The EOR of polymer solutions is calculated with the following equation:

$$EOR = E - E_w, \quad (2)$$

where EOR is enhanced oil recovery of polymer solution, %; E is the oil recovery of water flooding and polymer flooding process, %; E_w is the oil recovery of water flooding process, %.

All core flooding experiments were conducted at 80°C. The maximum work pressure of the ISCO pump is 50 MPa, and its maximum and minimum displacement rates are 50.000 and 0.001 mL/min, respectively. The pressure drop was recorded by a pressure sensor with a precision of ± 0.0001 MPa. And flow chart of the core flooding tests is shown in Figure 1.

3. Results and Discussion

3.1. IR Spectra Analysis. The structures of the dendrite functional monomer and hyperbranched polymer were confirmed by IR spectra as illustrated in Figure 2. The dendrite functional monomer, which was prepared using EDA, methyl acrylate, and maleic anhydride, was confirmed by strong absorptions at 3383.78 cm⁻¹ (–NH stretching vibration), 2949.63 cm⁻¹ (–CH₂ stretching vibration), 1646.91 cm⁻¹ (C=O stretching vibration and carbon double-bond stretching vibration), and 1554.98 cm⁻¹ (C–N stretching vibration and –NH bending vibration) in the IR spectroscopy of the dendrite functional monomer. Pure NVP exhibited a very strong absorption at 1703.01 cm⁻¹, which reflected the carbonyl stretching; at 1629.32 cm⁻¹, which was a carbon double-bond stretching vibration; and at 1445.11 cm⁻¹, which was the characteristic absorption peak of NVP. The characteristic absorptions of the dendrite functional monomer and NVP were clearly presented, and the carbon double-bond was not detected in the IR spectroscopy of the hyperbranched polymer. As expected, the IR spectra demonstrated that the hyperbranched polymer was successfully synthesized.

FIGURE 1: Flow chart of the core flooding tests.

FIGURE 2: IR spectra of the dendrite functional monomer, NVP, and hyperbranched polymer.

3.2. ^1H NMR and ^{13}C NMR Analyses. The ^1H NMR spectrum and ^{13}C NMR spectrum of the dendrite functional monomer are shown in Figures 3(a) and 3(b), respectively. In Figure 3(a), the chemical shift value at 2.44 ppm is assigned to the $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{NH}-$ protons. The chemical shift value at 2.60 ppm is due to the $-\text{CH}_2-\text{N}(\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-)_2$ protons. The $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{NH}-$ protons appear at 2.79 ppm. The chemical shift value at 3.04 ppm is assigned to the $-\text{NH}-\text{CH}_2-\text{CH}_2-$ protons. The $-\text{NH}-\text{CH}_2-\text{CH}_2-$ protons appear at 3.42 ppm. The chemical shift value at 5.95 ppm is due to the $-\text{C}(\text{O})-\text{CH}=\text{CH}-\text{C}(\text{O})-$ protons. In Figure 3(b), the chemical shift value at 171.11 ppm is due to C_6 . The chemical shift value at 164.96 ppm belongs to C_5 . The chemical shift value at 134.49 ppm is due to C_4 . The characteristic peak at 48.88 ppm belongs to C_3 . The characteristic peak at 36.90 ppm is due to C_2 . The chemical shift value at 31.01 ppm is assigned to C_1 . The results of ^1H NMR spectrum and ^{13}C NMR spectrum showed that the dendrite functional monomer was synthesized.

The ^1H NMR spectrum and ^{13}C NMR spectrum of the hyperbranched polymer are shown in Figures 4(a) and 4(b), respectively. In Figure 4(a), the chemical shift value at 3.23 ppm is due to the $-\text{NH}-\text{CH}_2-\text{CH}_2-$ protons and

the $-\text{C}(\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ protons. The chemical shift value at 2.65 ppm is assigned to the $-\text{CH}_2-\text{N}(\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-)_2$ protons. The $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{NH}-$ protons and the $-\text{CH}(\text{C}(\text{O})-)-\text{CH}(\text{C}(\text{O})-)-$ protons appear at 2.49 ppm. The chemical shift value at 2.16 ppm is assigned to the $-\text{C}(\text{O})-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ protons, the $-\text{CH}_2-\text{CH}_2-\text{C}(\text{O})-\text{NH}-$ protons, and the $-\text{CH}_2-$ protons which are obtained from the carbon double-bonds of AM, AA, and NVP. The $-\text{CH}-$ protons, which are free radical polymerization products of the carbon double-bonds of AM, AA, and NVP, appear at 1.54 ppm. In Figure 4(b), the chemical shift value at 182.96 ppm belongs to C_8 . The chemical shift value at 179.79 ppm is due to C_7 . The chemical shift value at 178.63 ppm is assigned to C_6 . The chemical shift value at 44.80 ppm is due to C_5 . The characteristic peak at 42.30 ppm belongs to C_4 . The characteristic peak from 35.11 to 36.95 ppm is due to C_3 . The chemical shift value at 31.80 ppm is assigned to C_2 . And the characteristic peak of C_1 is observed at 17.62 ppm. ^1H NMR spectrum and ^{13}C NMR spectrum indicated that the hyperbranched polymer was successfully synthesized.

The ^1H NMR spectrum and ^{13}C NMR spectrum of HPAM are shown in Figures 5(a) and 5(b), respectively. In Figure 5(a), the chemical shift value at 2.12 ppm is assigned to the $-\text{CH}-\text{CH}_2-$ protons. The characteristic peak of the $-\text{CH}-\text{CH}_2-$ protons appears at 1.55 ppm. In Figure 5(b), the chemical shift value at 183.12 ppm belongs to C_4 . The chemical shift value at 179.58 ppm is due to C_3 . The characteristic peak at 41.95 ppm belongs to C_2 . The chemical shift value at 34.99 ppm is assigned to C_1 .

3.3. Elemental Analysis of the Hyperbranched Polymer and HPAM. The elemental analysis of the hyperbranched polymer and HPAM was carried out by Vario EL III elemental analyzer. The content of different elements can be calculated by detecting the gases, which are the decomposition products of these copolymers at high temperature. Theoretical values of the hyperbranched polymer are 50.49% (C%), 6.53% (H%), 30.12% (O%), and 12.86% (N%); found values of the hyperbranched polymer are 45.46% (C%), 6.12% (H%), 26.73% (O%), and 11.36% (N%). Theoretical values of HPAM are 50.50% (C%), 6.60% (H%), 29.03% (O%), and 13.87% (N%); found values of HPAM

FIGURE 3: (a) ^1H NMR spectrum of the dendrite functional monomer in D_2O ; (b) ^{13}C NMR spectrum of the dendrite functional monomer in D_2O .

are 45.91% (C%), 6.04% (H%), 26.19% (O%), and 12.03% (N%).

3.4. Microscopic Structure Analysis by SEM. The microscopic structures of the HPAM and hyperbranched polymer solutions (2000 mg/L) prepared with distilled water were observed through SEM at room temperature. Among these

images, Figures 6(a)–6(c) are HPAM solutions at different scan sizes ($20\ \mu\text{m}$, 5000x; $10\ \mu\text{m}$, 10000x; $5\ \mu\text{m}$, 20000x, resp.). Similarly, the images of hyperbranched polymer solutions are shown in Figure 6(d) ($20\ \mu\text{m}$, 5000x), Figure 6(e) ($10\ \mu\text{m}$, 10000x), and Figure 6(f) ($5\ \mu\text{m}$, 20000x). As shown in Figure 6, it could be obviously observed that there were space net structures in the images of the hyperbranched polymer

FIGURE 4: (a) ^1H NMR spectrum of the hyperbranched polymer in D_2O ; (b) ^{13}C NMR spectrum of the hyperbranched polymer in D_2O .

solutions. Moreover, it could be found that the microscopic reticular structures of the hyperbranched polymer solutions were much more compact than those of HPAM solutions in the same scan size. The much denser networks of the hyperbranched polymer solutions may help to reduce the effect of shear on the hyperbranched polymer molecular chain and

improve the viscosity retention rate of the hyperbranched polymer at high shear rate.

3.5. Weight-Average Molecular Weight. 2 mg/L copolymer solution was prepared using distilled water and filtered by a $0.5\ \mu\text{m}$ Millipore Millex-LCR filter. As shown in Figure 7,

FIGURE 5: (a) ^1H NMR spectrum of HPAM in D_2O ; (b) ^{13}C NMR spectrum of HPAM in D_2O .

FIGURE 6: SEM images of HPAM and hyperbranched polymer: (a) HPAM solution at 20 μm , 5000x; (b) HPAM solution at 10 μm , 10000x; (c) HPAM solution at 5 μm , 20000x; (d) hyperbranched polymer solution at 20 μm , 5000x; (e) hyperbranched polymer solution at 10 μm , 10000x; (f) hyperbranched polymer solution at 5 μm , 20000x.

TABLE 2: The parameters of cores and the results of core flooding tests.

Polymer	Cores	Length (cm)	Diameter (cm)	Porosity (%)	Permeability (mD)	S_{wi} (%)	E (%)	E_w (%)	EOR (%)
HPAM	1#	8.95	3.79	23.75	985.28	20.42	47.63	30.97	16.67
Hyperbranched polymer	2#	8.87	3.78	23.69	980.15	20.16	54.33	30.82	23.51

FIGURE 7: $KC/R_v(q)$ versus q^2 for the hyperbranched polymer and HPAM.

the weight-average molecular weight of the hyperbranched polymer and HPAM was 5.72 and 5.64×10^6 g/mol, respectively. The hyperbranched polymer has higher weight-average molecular weight than HPAM due to its hyperbranched structure.

3.6. Temperature-Resistance. The apparent viscosity versus temperature curves of the hyperbranched polymer and HPAM solutions is shown in Figure 8. Compared with HPAM, the hyperbranched polymer displayed better temperature-resistance (apparent viscosity: 558.6 mPa·s versus 260.3 mPa·s and viscosity retention rate: 45.01% versus 22.12%) at 95°C. This phenomenon may be explained by the inelasticity structure of pyrrole ring which can improve the thermal stability of the hyperbranched polymer.

3.7. Salt-Resistance. The influences of salt (NaCl, CaCl_2 , or $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) on apparent viscosity of the HPAM and hyperbranched polymer solutions were carried out at 20°C. As shown in Figures 9(a)–9(c), with the increase of salt concentration (NaCl, CaCl_2 , or $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), the apparent viscosity of HPAM solutions decreased rapidly, and then it is kept at a low value. Similarly, the measure of the hyperbranched polymer solutions displayed similar phenomena. However, compared with HPAM solution, the hyperbranched polymer solutions displayed better antisalt due to higher apparent viscosity under the same conditions. These results

FIGURE 8: Apparent viscosity versus temperature for HPAM and hyperbranched polymer solutions (5000 mg/L).

reveal that the hyperbranched polymer can withstand higher salt concentration than HPAM. This characteristic may be well explained by the special network structure which can enhance the interaction between the hyperbranched polymer chains, and crimping degree of the polymeric chains will be smaller than HPAM at the same salt concentration. Thus the hyperbranched polymer exhibits higher apparent viscosity and retention rates.

3.8. Shear-Resistance. Shear-resistance of the polymer solutions was conducted on HAAKE RS 6000 rotational rheometer at 80°C by changing the shear rate from 170 s^{-1} to 500 s^{-1} and from 500 s^{-1} to 170 s^{-1} around. As shown in Figure 10, the viscosity retention rate of the HPAM and the hyperbranched polymer was 61.95% and 91.64%, respectively, when one cycle was completed. The phenomena may support the microscopic reticular structures of the hyperbranched polymer which can reduce the effect of shear on the hyperbranched polymer molecular chain during shear process and restore the structures of the hyperbranched polymer after being sheared.

3.9. Enhanced Oil Recovery. As shown in Table 2, the EOR of the hyperbranched polymer solutions and HPAM solutions was 23.51%, and 16.67%, respectively. This phenomenon may support higher viscosity retention rate of the hyperbranched polymer contributes to expand injection water sweeping volume and enhance oil recovery. As shown in Figure 11,

FIGURE 9: Salt-resistance ((a) NaCl, (b) CaCl₂, and (c) MgCl₂·6H₂O) of HPAM and hyperbranched polymer solutions (5000 mg/L) at 20°C.

FIGURE 10: Shear-resistance of HPAM (a) and hyperbranched polymer (b) at 80°C (5000 mg/L).

FIGURE 11: EOR results of the HPAM and hyperbranched polymer solutions at 80°C.

compared with HPAM, the hyperbranched polymer revealed stronger ability of establishing flow resistance and reducing water cut in polymer flooding. This phenomenon may support the sweep efficiency which is obviously improved by the hyperbranched polymer due to its excellent temperature-resistance, salt-resistance, and shear-resistance.

4. Conclusions

A novel hyperbranched polymer possessing microscopic reticular structure was successfully synthesized using AM, AA, NVP, and dendrite functional monomer as raw materials under mild conditions. Compared with HPAM, the hyperbranched polymer exhibits obvious advantages in temperature-resistance, salt-resistance, and shear-resistance due to the introduction of pyrrole ring which can reduce the influence of high temperature on the polymer molecular chain and the introduction of the reticular structures which can be favorable to decrease the crimping degree of polymeric chains under high shear rate and high salinity. Thus, the EOR capability of the hyperbranched polymer is improved remarkably even in a harsh condition.

Conflict of Interests

The authors declare no possible conflict of interests.

Acknowledgments

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