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ARTICLE

A Water-Soluble Oil-Displacing Agent with Traced Property for Enhancing Oil Recovery

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A water-soluble fluorescent oil-displacing agent was prepared via copolymerization of acrylamide (AM), acrylic acid (AA) and coumarin derivatives (CO) for the first time. The rigid coumarin unit can be not only used as a fluorescent group for tracer, but also improved the heat-resistant performance of the displacement agent. The copolymer was fully characterized by FTIR, ^{1}H NMR, TG-DSC, UV-Vis and fluorescence measurements. The fluorescence intensity of the polymer exhibited a good linear relationship with its concentration and the linear correlation coefficient reached to 0.9980, which indicated that the copolymer's concentration can be directly determined by measuring the fluorescent intensity. The pH and brine concentration of systems have no significant effect on the fluorescent intensity of the PAAC. It was also found that the viscosity retention rate of PAAC reached up to 42.3% at 100 ^{o}C and PAAC exhibited excellent shear-thickening. Furthermore, up to 13.4% enhanced oil recovery was obtained by 2 g/L PAAC solution according to core flood tests. All results have demonstrated that the tracer copolymer PAAC with fluorescence property exhibits a great potential application for enhancing oil recovery.

1. Introduction

It is well known that polyacrylamides is one of the most widely used polymers in enhancing oil recovery (EOR).[1] Unfortunately, the thermal degradation and hydrolysis of polyacrylamides would occur under high temperature and high salinity, which resulting in the decrease of polymer concentration and further reduction of the oil recovery. [2-7] Until now, there is no effective method to check the polymer concentration at service time. Usually, extra tracers such as radioactive tracers, isotope tracers and fluorescence chemicals are often introduced into polymer solution to monitor the concentration in oil reservoir. However, these additional tracers have many drawbacks such as complicated operation, high cost and adverse effect on polymer solutions.[8] In this context, water-soluble fluorescent polymers are considered as ideal flooding agents because of the additional tracing ability based on the displacement of reservoir oil. Although we have elucidated the preparation and evaluation of many kinds of oil-displacing agent,[9-10] the application of water-soluble fluorescent polymers in EOR has not been reported so far except widely application in water treatment.[11-13] One of the key issue in this area is the selection of the fluorescent group. It should not only play an important role in the tracing process, but also not affect the oil displacement application in oil reservoir.

With this thought in mind, herein we designed a water-soluble fluorescent polymer that prepared as a combination of flooding agent and tracer by introducing a polymerizable rigid fluorescent coumarin monomer in polyacrylamide chains. Coumarin derivatives have been widely studied in brighteners, fluorescent indicator, and fluorescent dyes due to their strong fluorescent intensity and stability.[14-16] As expected, the rigid coumarin unit can be not only used as a fluorescent group for tracer, but also improved the heat-resistant performance of the fluorescent polymer.[17-20] Moreover, the concentration of water-soluble fluorescent tracer polymer can be measured online and controlled at real-time way to improve efficiency and management in the flooding process.

The fluorescent polymer (denoted as PAAC) was prepared by copolymerization of the coumarin derivative ally-7-hydroxyl-4-methyl coumarin (CO) (fluorescent monomer) with acrylamide (AM) and acrylic acid (AA). The effect of temperature, monomer ratio, pH and initiator concentration on the copolymerization was studied in detail. The fluorescent intensity of different concentration of copolymer was determined by fluorescence analysis. And the effect of pH and brine solution on fluorescent intensity of the polymer was also investigated. Furthermore, the shear-thickening and thermal stability of PAAC were investigated by rheological measurement.

2. Experimental

2.1. Materials.

Acrylamide (AM), acrylic acid (AA), sodium hydroxide (NaOH), sodium sulfite (NaHSO$_3$), ammonium persulfate ((NH$_4$)$_2$S$_2$O$_8$), poly(oxyethylene octylphenol ether) (OP-10), partially hydrolyzed polyacrylamide (HPAM), sodium chloride (NaCl), magnesium chloride (MgCl$_2$) and calcium chloride (CaCl$_2$) are all analytical reagent and used directly without further purification. Ally-7-hydroxyl-4-methyl coumarin (CO) were prepared based on the reported method.[21]

2.2. Synthesis of PAAC.

A certain amount of AM, CO and OP-10 were dissolved with appropriate distilled water in the

three-necked flask. 1 mol/L NaOH was used to adjust pH of AA solution to indicated conditions and then the AA solution was added into the reaction flask. The mixture was stirred in N_2 atmosphere for half an hour. The reactant solution was heated in water bath at constant temperature, then NaHSO$_3$-(NH$_4$)$_2$S$_2$O$_8$ with molar ratio of 1/1 was added in. The reaction was allowed to occur at indicated times. The final solution was clear and highly viscous. The mixture was isolated by precipitation with ethanol and dried *in vacuum* at 40 °C for 2 days to give the corresponding PAAC (Figure 1a). The effect of mass ratio of AM to AA, CO concentration, pH, initiator concentration, temperature and reaction time on copolymeration of copolymer is investigated. The results are shown in Fig S1. It was found that the best results could be obtained by the ratios of AM to AA was 8:2, CO 0.2 wt% , initiator was 1 wt%, pH was 7, temperature was 50 °C and reaction time was 10 h corresponding apparent viscosity up to 294.5 mPa·s. When the concentration of CO was over 0.02, the water solubility of copolymer was poor due to the hydrophobicity of CO.

2.3. Instrumentation. The structure of copolymers was characterized by FTIR spectroscopy. FTIR spectra of the samples were measured with KBr pellets in a NICOLET-560 FTIR spectrophotometer. ^{1}H NMR spectra of the samples were measured by a Bruker AV III-400 NMR spectrometer (Bruker, Switzerland) in D$_2$O. The UV-Vis spectrum was recorded on a UV-240 spectrophotometer. The photoluminescence property was studied for the copolymers solution using VARIAN-Cary Eclipse Fluorescence spectrophotometer. The apparent viscosity of polymer solutions was measured by a Brookfield DV-III + Pro viscometer (Brookfield, USA) at room temperature. The effect of share rate and temperature on apparent viscosity was measured by RheoStress6000 rheometer. Thermogravimetry and differential scanning calorimetry (TG-DSC) of the polymer were equipped with a STA449 F3 synchronous thermal analyser (Netzsch, Germany) from 40 to 700 °C at a heating rate of 10 °C/min under air atmosphere.

3. Results and discussion

3.1. Characterizations of copolymer PAAC. The structure of the PAAC was confirmed by FTIR spectroscopy (Figure 1b). The characteristic absorptions of –C=O stretching vibrations (1676.80 cm^{-1}) and the characteristic absorption of N–H (sharp peak at 3424 and 3188 cm^{-1}) in the spectrum of PAAC were obvious presented. The characteristic peaks related to –COO$^-$ group are observed at 1558 and 1407 cm^{-1}. The absorption bands at 2938 and 2781 cm^{-1} are due to the stretching vibration of C–H group, and the absorption band 1455 cm^{-1} assigns to the bending vibration of C–H group in polymer chains. And the absorption band at 1118 cm^{-1} assigns to C–O stretching vibrations of CO monomer. The ^{1}H NMR spectrum of PAAC (Figure 1c) displayed the chemical peaks from 7.69 to 6.86 ppm were assigned to the protons of the coumarin ring, and the distinct peak at 2.48 ppm was due to the protons of –CH$_3$ linked in CO. The peak at 1.53 ppm assigned to the protons of aliphatic –CH$_2$– of polymeric chain, and the protons of the aliphatic –CH– of polymeric chain appeared around 2.13 ppm. As expected, the FTIR and ^{1}H NMR spectra confirmed the presence of repeated units in the PAAC.

   As shown in Figure 1d, TG-DSC curves were also explored to compare the thermal degradation of the copolymers PAAC and HPAM. For PAAC, the first weight loss of 10.45% from 40 to 218 °C was due to the loss of the moisture. The second process occurs from 218 to 372 with a mass loss of 29.11%

which was due to the decomposition in the side chain of polymer. The third step took place beyond 372 °C with the mass loss of 38.96 % caused by the breakage of the C-C skeleton. For HPAM, the first stage takes place in the range of 40-215 °C with a loss of 16.26%. The second one occurs in 215-384 °C with a mass loss of 23.14 wt%, which could be ascribed to the amide groups and the
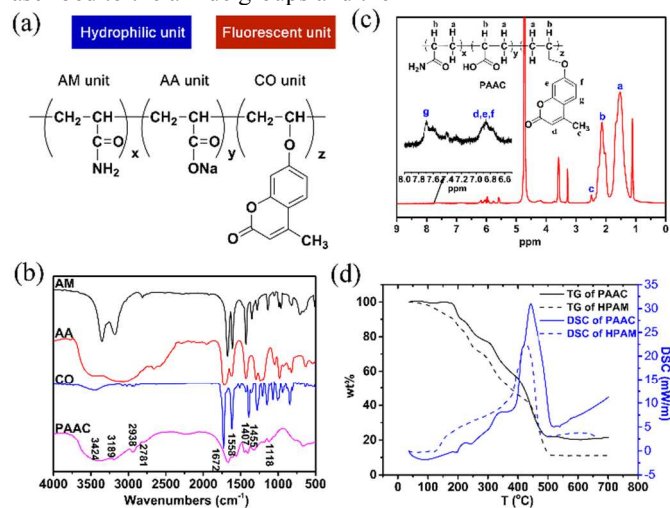

Figure 1. (a) Structure representation of PAAC; (b) FTIR spectrum of PAAC; (c) ^{1}H NMR spectrum of PAAC; (d) Thermal gravimetric curves comparison of HPAM and PAAC.

decompositions of amide groups. The last stage occurs beyond 384 °C with the mass loss of 37.26 wt% which could be attributed to the carbonization. A strong exothermic peak occurring at 442.7 °C was observed in the DSC curve of PAAC, while occurring at 419.8 °C in DSC curve of HPAM, which indicated that the decomposition temperature of the PAAC polymer skeleton increased due to the introduction of rigid CO monomer. The TG-DSC results showed that PAAC had an ideal thermal stability.

3.2. Spectra study of PAAC. The UV-Vis and fluorescence experiments were performed to better understand the optical character of PAAC. Figure 2a displayed the UV spectrum of PAAC (600 mg/L) dissolved in deionized water. The characteristic absorption peak at 322 nm is attributed to the coumarin group in PAAC. This also indicates that CO was incorporated into the polymer chains. The excitation and emission spectra of PAAC were shown in Figure S2, it can be found that the excitation and emission wavelengths of polymer are 322 nm and 383 nm, respectively. And the excitation and emission spectra demonstrated a good mirror-image relationship indicating that the molecules change little when transiting from the ground state to the excited state, and had the same interval of vibration level. Most importantly, the fluorescent intensity should be presented good proportional to the concentration of PAAC and good reproducibility during the practical quantitative analysis process. The fluorescent intensity of PAAC was increased stepwise by varying the polymer concentration from 40 to 1000 mg/L (Figure 2b). It was also found that the fluorescent intensity and the concentration of the polymer exhibited a good linear relationship, which is y = 10.6010 +1.00796 x with a linear correlation coefficient up to 0.9980. Therefore, the fluorescent intensity can be used as quantitative analysis of polymer concentration which indicating that measuring the fluorescent intensity of the copolymer can determine the concentration of the polymer directly.

Generally, at high salinity, especially high metal ion content of the reservoir, have dramatically effect on the fluorescent intensity of some fluorescent material. In this section, the effect of NaCl, $MgCl_2$ and $CaCl_2$ concentration on the fluorescent intensity of copolymer was studied. The concentration of copolymer is 600 mg/L. As shown in Figure 2c, with the increase in metal ion concentration from 0 to 12000 mg/L, the fluorescence intensity of PAAC remained steady. The result revealed that despite the increase of NaCl, $MgCl_2$ and $CaCl_2$ concentration, the fluorescent intensity of the copolymer almost kept the original value, indicating that the fluorescence intensity of the PAAC was relatively stable at high salinity. Figure 2d demonstrated the fluorescent intensity of the copolymer with different pH values at the concentration of 600 mg/L. It was found that when the pH values was in the range of 2 and 6, the fluorescent intensity of the polymer was relatively stable, and when the pH value at the range of 7 to 8, the fluorescent intensity increased slowly and reached the maximums at pH value of 7. Further increasing the pH value to 11, the fluorescent intensity finally decreased. However, the fluorescent intensity of PAAC changed less than 9% within the entire pH range and displayed lower value under acidic condition, which probably because the oxygen of the ketone and ether of the monomer CO with lone electron pair was readily affected by acidic environment.
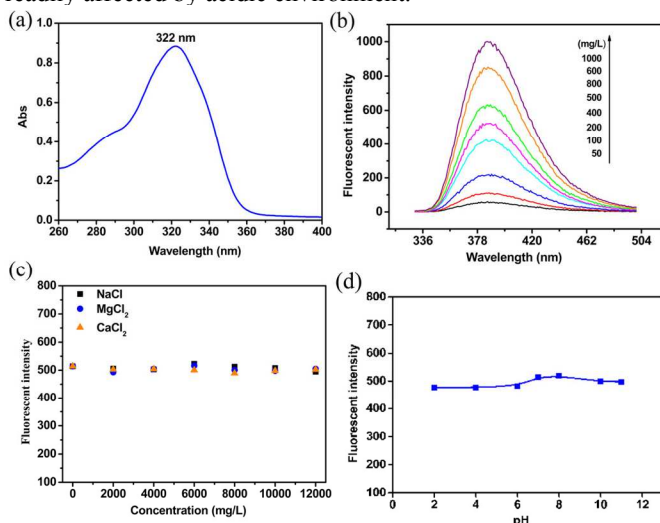

Figure 2. (a) UV-Vis spectrum of PAAC; (b) Fluorescent spectra of PAAC solution at various concentration; (c) The effect of brine on fluorescent intensity of PAAC; (d) The effect of pH on fluorescent intensity of PAAC.

3.3. Effect of temperature and shear rate on viscosity of PAAC.

The apparent viscosities versus temperature for 2 g/L PAAC solution at the shear rate 7.34 s^{-1} (Figure 3a). It can be found that the apparent viscosity decreased when the temperature increased from 20 to 120 ^oC due to the coiling of polymer chain at the increased temperature. The viscosity retention rate could reach up to 42.3% when the temperature as high as 100 ^oC. Further to increasing the temperature, a sharply decline in apparent viscosity occurred. The result revealed that the copolymer PAAC in the temperature range of 30-100 ^oC exhibited a better temperature stability than HPAM due to the relatively larger hydrodynamic volume of PAAC incorporated with rigid structure.

It can be observed from Figure 3b that the 2 g/L PAAC solution exhibited non-Newton behaviors. The viscosity of polymer solution decreases with the increasing of shear rate,

and keep balanced viscosity when shear rate remained a value for 4 minutes. First from 7.34 to 170 s^{-1}, then from 510 s^{-1} to 7.34 s^{-1}. It can be observed that the viscosity of PAAC almost recovered the original value exhibiting moderate shear resilience varied with shear rate. The rigid structure of unit in PAAC polymer chains enhance the strength of chain entanglement which possessed better shear resistance in comparison of HPAM.
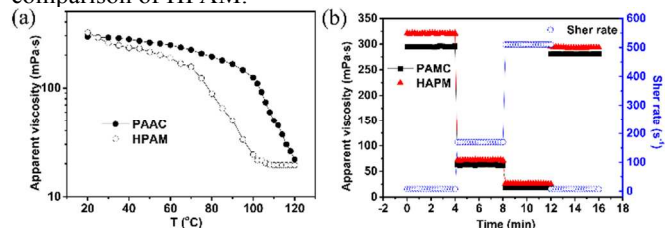

Figure 3. (a) Effect of temperature on apparent viscosities of PAAC solution; (b) Effect of shear rate on apparent viscosity of copolymer solution;

3.4. Viscoelasticity and salt resistance.

We further aimed at exploration of the viscoelasticity behaviors of the polymers PAAC and HPAM. It could be found that viscous modulus (G″) and elastic modulus (G′) of PAAC are both higher than that of HPAM, and that G′ of two polymers surpassed its G″ at higher frequency, which indicated that the elastic modulus of polymer solution played a crucial role than viscous modulus (Figure 4a). The result displayed that the viscoelasticity of two polymers solutions was governed by chain entanglement.
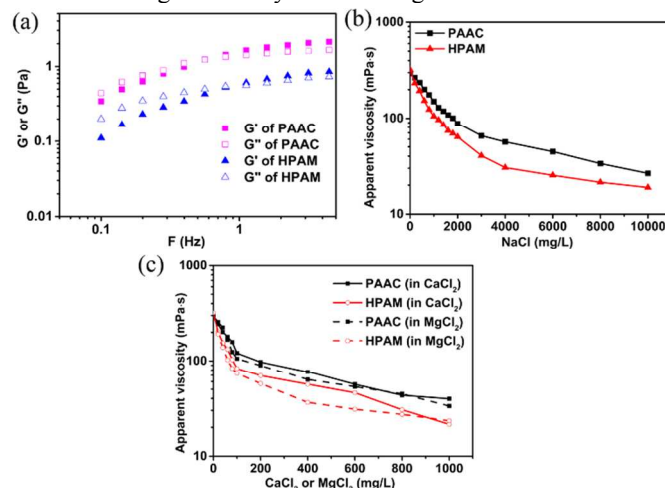

Figure 4. (a) Viscous modulus (G″) and elastic modulus (G′) as a function of frequency for polymers; Effect of (b) NaCl; (c) $CaCl_2$ and $MgCl_2$ concentration on apparent viscosities of copolymers

Figure 4b-4c displayed the effect of NaCl, $CaCl_2$ and $MgCl_2$ concentration on solution viscosity of the PAAC and HPAM. The concentration of copolymers is 2 g/L. With the increasing of all brine concentration, the solution viscosity of copolymer decreases sharply, and further increases brine concentration, the solution viscosity decreases slowly and no precipitation and phase separation behavior is observed. Generally, the thickening capability of copolymer in mainly lies in hydrodynamic chain entanglement and electrostatic repulsion. The presence of electrostatic charges in solution results in a reduction in electrostatic eventually leading to the decrease of the viscosity. The larger side chain and larger hydraulics volume of PAAC make them stretch polymer chain more stable in the presence of monovalent and even divalent ions compared

with HPAM. This is suggesting that PAAC have excellent compatible to slat.

3.5. Core flood tests. To further shed light on the flooding property of the fluorescent polymer, simulation experiment was performed to measure the oil displacement efficiency. A schematic diagram of the experimental set up for the study of the oil recovery by the injection of the polymer solution was shown in Figure 5a. The core assembly was a stainless steel cylinder of length 50 cm and an internal diameter 2.5 cm packed with sand. The differential pressure between the inlet and the outlet during the recovery was monitored. After the packed dry core apparatus was assembled, the sand pack was saturated with distilled water. The permeability of sand pack is about 1550 mD. The core was then flooded with oil to a connate water saturation. An initial water flood was conducted until no additional oil was produced by the continuous water injection. Then it was flooded with the 0.2 PV polymer solution to recover increasing residual oil. It can be seen that about 10.8% enhanced oil recovery has been obtained by injecting 2 g/L HPAM solution after the breakthrough of the water flood at 60 °C (Figure 5b). Higher enhance oil recovery of 13.4% afforded by using 2 g/L PAAC solution. The results suggested that PAAC was an excellent candidate for potential application in enhanced oil recovery compared with HPAM due to the introduction of the monomer CO to improving the rigid of polymer chains. The PAAC solution which exhibits higher viscosity than HPAM can improve the mobility ratio of oil and displacing fluid which enhance oil recovery ultimately under the salinity and temperature conditions. And according to Figure 5c, the concentration of fluorescent polymer could be determined by fluorescent intensity at service time.
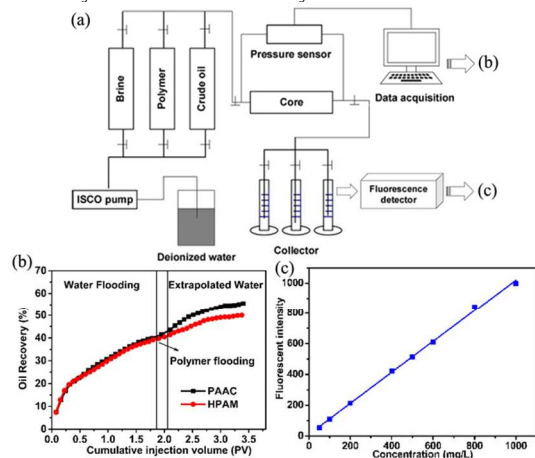

Figure 5. (a) A schematic diagram of the experimental set up; (b) Results of core flood tests at 60 °C; (c) The relationship of fluorescent intensity and the concentration of PAAC.

Conclusions

A water-soluble fluorescent copolymer PAAC was synthesized with AM, AA and CO by free radical polymerization process. The copolymer was fully characterized by FTIR, ^{1}H NMR, TG-DSC, UV-Vis and fluorescence measurements. The fluorescent intensity of PAAC displays a good linear relationship with its concentration, which suggesting the concentration of PAAC can be obtained by measuring the fluorescent intensity of copolymer. The pH and brine concentration of systems had no significant effect on the fluorescent intensity of the PAAC. The displacement agent also exhibited shear thinning and reversible shear thickening behavior, superior thermal stability, and salt-tolerance. Moreover, EOR results showed that 13.4% enhanced oil recovery rate can be obtained by PAAC. These results suggested that the fluorescent copolymer PAAC can be not only used as a tracer detecting the polymer concentration in EOR, but also used as excellent candidate for potential application in enhanced oil recovery.

Notes and references

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