Research Article

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Investigation on the effect of active-polymers with different functional groups for EOR

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Abstract: Active-polymer attracted increasing interest as an enhancing oil recovery technology in oilfield development owing to the characteristics of polymer and surfactant. Different types of active functional groups, which grafted on the polymer branched chain, have different effects on the oil displacement performance of the active-polymers. In this article, the determination of molecular size and viscosity of active-polymers were characterized by Scatterer and Rheometer to detect the expanded swept volume ability. And the Leica microscope was used to evaluate the emulsifying property of the active-polymers, which confirmed the oil sweep efficiency. Results show that the Type I active-polymer have a greater molecular size and stronger viscosity, which is a profile control system for expanding the swept volume. The emulsification performance of Type III active-polymer is more stable, which is suitable for improving the oil cleaning efficiency. The results obtained in this paper reveal the application prospect of the active-polymer to enhance oil recovery in the development of oilfields.

Keywords: active-polymer; viscosity; emulsification property; molecular size; EOR

1 Introduction

Active polymers as a new type of chemical oil displacement agent have the advantages of both surfactant and polymer,

which can increase the viscosity to expand the sweep efficiency and reduce the interfacial tension between oil and water to improve the oil washing efficiency (1-4). Because of the increase of the viscosity of the driving fluid, the water-oil fluidity ratio and local pressure gradient can be improved to expand the sweep volume. What is more, active polymer can change the wettability of porous which is helpful to improve oil recovery. The emulsification of active polymer can also reduce the flow resistance of crude oil (4,5). In conclusion, different types of active polymers can enhance oil recovery in different ways.

In recent years, the evaluation methods of active polymer flooding include core experiment and field data (6-9). In these results of core displacement experiments, the recovery rate of Henan Oilfield is expected to reach about 16%. The recovery rate of oil can reach 18.8% and the water cut of production well can drop up to 60% in Daqing oilfield. Therefore, active polymer flooding has been proved to be a potential oil recovery technology. However, the mechanism of producing oil by active polymers with different functional groups is not clear, which greatly restricts the application of active polymers in exchange for more oil production.

In this article, Scatterer and Rheometer were used to measure molecular size and viscosity of active polymers named Type I and Type III active polymer, respectively. The experiment of molecular size and viscosity established that the ability of enlarging flooding swept volume. The Leica microscope was used to evaluate emulsifying ability of oil displacement efficiency.

2 Materials and methods

2.1 Materials

The active-polymers which respectively named Type I and Type III were purchased from Haibo Company (Shanghai, China). The active ingredient was up to 90% and the molecular weight was 1200×10^4 . The oil with a viscosity of 9.8 mPa·s at 45°C, composed of

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dehydration crude of oil Daqing oilfield and kerosene oil. Experimental water is taken from the Daqing oilfield and the ion composition in water is shown in Table 1.

2.2 Preparation of the active polymer solution

The polymer powder and salt water required for the preparation of the 5000 mg/L solution were respectively determined by the precise balance. The polymer was dissolved in sewage stirred in 400 rpm for 3 h. Moreover, the polymer solution with a concentration of 5000 mg/L is diluted to 1500 mg/L stirred in 400 rpm for 1 h as the target solution for the experiments.

2.3 Molecular structure detection of the active polymer

The Fourier transform infrared spectroscopy (FTIR) spectra of the active polymers were observed by a 1615 FTIR spectrometer (Perkin Elmer, Waltham, MA, USA). The instrument measures the optical components in the range of 15000-350 cm^{-1} without manual insertion and replacement. Firstly, the air conditioner is turned on before the sample is tested, so that the room temperature can be maintained at about 24°C and the appropriate humidity is maintained. Then the polymer dry powder and potassium bromide were separately ground to pulverization, and then these two kinds of powder were pressed into tablets, finally the tablets were placed in the infrared spectrometer to detect the molecular structure.

2.4 Molecular size detection of the active polymer solution

The BI-200SM type wide-angle static and dynamic light scattering instrument was used for the determination of polymer molecular size (D_h), the equipment for the experiment was measured by Brookhaven Instruments Company, USA. The working power of the argon ion laser

is 200 mW, the scattering angle is 90° and the wavelength is 532.0 nm. The polymer solution was cleaned with ultrasonic for 5 min after removing dust with a 0.85 μm diameter microporous membrane. The test vessel was placed in a scattering pool for testing at a constant temperature. The laser wavelength was 532.0 nm and the dynamic light scattering angle was 90°.

2.5 Viscosity characterization of active polymer solution

The viscosity of active polymer solution was measured by type RS150 rheometer(HAAKE, Berlin, Germany). The temperature range of the instrument is 0-500°C. The polymer solution was added to the cone plate system when the water temperature was constant at 45°C and the data of viscosity was automatically controlled by a computer.

2.6 Emulsifying performance of active polymer solution

The active-polymer solutions and the crude oil were mixed in four proportions according to 4:1, 3:1, 2:1, 1:1 respectively, and the mixture will form an emulsion at a stirring speed of 2000 r/min. The change of precipitation ratio and emulsion type with time were measured by Leica microscope which was produced by Karl Zeiss Company of Germany at the experimental temperature of 45°C.

2.7 Enhanced oil recovery

The porous media with a diameter of 2.5 cm, a length of 10cm were used to determine the profile control capacity and enhanced oil recovery of active polymers. The permeability of cores were measured by water, the cores with permeability of $1500 \times 10^{-3} \mu\text{m}^2$ and $500 \times 10^{-3} \mu\text{m}^2$ were selected as the research object. The core was soaked in benzene for 24 h to extract the oil in porous media, then extracted by ethanol until there is no oil in the solution, and then placed in a 120°C incubator until the weight remains constant.

The experimental equipment mainly includes the displacement pump, the pressure collection system, the

Table 1: Ions in brine.

Electrolyte	Total	CO_3^{2-}	HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	$\text{Na}^+ + \text{K}^+$	PH
Concentration (mg/L)	4697.6	75.0	2135.7	895.4	96.1	16.1	4.9	1474.5	8

Figure 1: Diagram of oil displacement experiment.

core holder, the middle container. The oil displacement system is produced by Hai'an Petroleum Equipment Company, China. The equipment is temperature resistant to 100°C and pressure is 30 MPa. The used in the oil displacement experiments include homogeneous models and heterogeneous models. The heterogeneous model consists of two cores with different permeability, the shunt rate and recovery ratio is calculated to reflect the swept volume of the active-polymers. The homogeneous model can reflect the displacement efficiency of active-polymers with the same viscosity. All equipment remained in the constant temperature of 45°C. The experimental apparatus are shown in Figure 1.

3 Results

3.1 Molecular structure of the active polymer

The FTIR spectra are based on the principle of atomic vibration in molecules to analyze functional groups in organic matter. By grafting different types of functional groups to the polymer branching, the active-polymer can be subjected to different properties, such as reduced interfacial tension and emulsification. The results of is illustrated in Figure 2.

The characteristic absorption peaks of olefinic double bonds appeared at 963.76 and 858 cm^{-1} , which

proves that Type I active-polymer is obtained by polymerization and the double bond were remained in the polymerization process. The Type III active-polymer also has the molecular structure of polymer that the characteristic absorption peaks of olefin double bonds appeared at 967.40 and 849.16 cm^{-1} . The characteristic peaks of sulfonates presented at 1238.96 and 1027.25 cm^{-1} , which is attributed to the hydrophilic groups in Type I active-polymer. The characteristic absorption peaks of methyl groups appear in 3000-2800 cm^{-1} , which indicates that there are lipophilic groups in the molecular structure of active-polymers. Hydrophilic and lipophilic groups proved the existence of the active groups in the molecular structure of the active-polymers. Therefore, the Type I active-polymer have both the molecular structure of surfactant and polymer, and this conclusion is also applicable to Type III active-polymer.

Although the functional groups of these two types of active-polymers are essentially the same, but their characteristic absorption peak position and the peak area are slightly different. The weak characteristic absorption near the peak of 725 cm^{-1} proves that there are more than 7 methylene carbon numbers representing the hydrophobic group, while the Type III active-polymer is no such characteristic absorption. The difference of molecular structure proves the location and number of functional groups, molecular weight of these two products are not all the same.

(a) Type I active-polymer

(b) Type III active-polymer

Figure 2: Infrared spectrogram of active-polymers.

3.2 Molecular size of the active polymers

The molecular clusters of the active-polymers with a concentration of 1500 mg/L were analyzed by light scattering instrument. The solution should be diluted to a concentration of 100 mg/L for convenience of molecular size. The distribution of D_h are shown in Figure 3.

As shown in Figure 3, the comparison of D_h distribution of Type I active-polymer is larger than the value of Type III active-polymer with the same concentration. The wider distribution of D_h indicates that Type I active-polymer is more suitable for complex heterogeneous reservoirs with complex pore structures.

The polymer molecules with large particle size flow into large pore in formation for increasing the flow resistance, small molecule polymer can have the opportunity to enter the small channel, thus expanding the swept volume of heterogeneous reservoir.

3.3 Viscosity of the active polymers

We compared the viscosity of two types of active-polymers with the concentration of 1500 mg/L, which were shown in Figure 4. In the case of active-polymer declines rapidly with the increase of shear rate.

Figure 3: D_h distribution of active-polymers.

Figure 4: Curve of viscosity change with shear rate.

As shown in Figure 4, the solution viscosity of Type I active-polymer is higher than the value of Type III active-polymer at the same shear rate, which indicates that viscosity shear stability of Type I active-polymer is better than the Type III active-polymer. A large number of molecular chains and functional groups of active-polymer in the solution can be combined to form a multi-layered network structure under the force of the Van der Waals. The cross-linked network structure increases the viscosity of the active-polymer solution. There are more molecular groups in the Type I active-polymer, so that the network structure is more compact and the viscosity of the solution is bigger.

3.4 Emulsifying performance of the active polymers

In this section, the stability of emulsions which formed by active-polymer and crude oil are determined by microscope. The experimental principle is through the

difference between the transmission of crude oil and water to determine the type of emulsion medium phase. The inner phase of the O/W emulsion is oil, whereas the inner phase of the W/O emulsion is water. The results were illustrated in Table 2. According to Table 2, both the Type I and Type III active-polymers are all oil in water emulsions under four different oil-water ratios, which is conducive to improving oil displacement efficiency.

The water separation of emulsions (Figure 5) with different oil-water ratios is determined periodically in a 45°C incubator to evaluate the stability of emulsion, which were illustrated in Figure 6. As can be seen from the Figure 6, the separation degree of water increases gradually with the increase of the static time, which is due to the role of repulsion between molecules to break the oil-water interface membrane. With the increase of water/oil ratio, the separation degree of water gradually increases. This is because the proportion of the active-polymer in the emulsion is larger, the interface membrane is more unbalanced, the interfacial membrane is more

Table 2: Dentification result of emulsion type.

Active-polymer	Concentration (mg/L)	Catalyst oil ratio	Type
Type I	1500	4:1	O/W
		3:1	O/W
		2:1	O/W
		1:1	O/W
Type III	1500	4:1	O/W
		3:1	O/W
		2:1	O/W
		1:1	O/W

Figure 5: Microscopic imaging of emulsion between active polymer and oil.

Figure 6: Curve of water separation proportion change with time.

Table 3: Oil recovery of homogeneous core.

Active-polymer	Permeability ($\times 10^{-3} \mu\text{m}^2$)	Concentration (mg/L)	Viscosity (mPa·s)	Water flooding recovery (%)	Polymer flooding recovery (%)
HPAM	1535	1900	84.8	48.5	12.2
Type I	1512	835	84.8	48.9	15.2
Type III	1532	1500	84.8	48.3	18.4

Table 4: Oil recovery of heterogeneous cores.

Active-polymer	Concentration (mg/L)	Injection volume (PV)	Core	Permeability ($\times 10^{-3} \mu\text{m}^2$)	Water flooding recovery (%)	Polymer flooding recovery (%)
Type I	1500 mg/L	0.7	1	1503	50.5	14.6
			2	498	39.9	16.8
			Total/		46.2	15.8
Type III	1500 mg/L	0.7	3	1495	51	12.1
			4	512	40.5	14.1
			Total/		45.8	12.8

likely to break and cause oil and water separation. Compared with these two kinds of active-polymer emulsion with the same concentration, the emulsion stability of the Type III active-polymer and crude oil is stronger.

3.5 Profile control ability and enhanced oil recovery

In this section, the oil washing efficiency of two kinds of active polymers with the same viscosity was studied in homogeneous cores with the same permeability. Comparison of oil recovery between active polymers

and polyacrylamide (HPAM) with the same viscosity, the experimental results are listed in Table 3. The same polymer solution viscosity eliminates the effect of the flow ratio on the recovery ratio, so that the difference in oil recovery in Table 4 is mainly due to the discrimination in the emulsifying properties of the two types of active-polymers. The results show that the oil recovery of the Type III active-polymer solution with the same viscosity is better, which is mainly attributed to the formation of emulsion in the oil displacement process is more stable and remaining oil is more likely to be carried out of the formation. Therefore, the Type III active-polymer is more suitable for improving the oil displacement efficiency in homogeneous reservoir.

Figure 7: Relationship between shunt rate and pore volume.

However, all reservoirs are heterogeneous, which is the main reason for the formation of remaining oil. In this paper, the recovery and split flow rate of high and low permeability cores are tested respectively to determine the expansion recovery of active polymer to heterogeneous model volume, the results are presented as Table 4 and Figure 7. According to Figure 7, the shunt rate of high permeability reservoir decreases rapidly during the process of active polymer flooding, while the result of low permeability reservoir is just the opposite. The shunt rate of low permeability layer is increased greatly of the Type I active-polymer flooding, which indicates a better profile control ability. As can be seen in Table 4, the water flooding recovery increases with the increase of core permeability and the remaining oil is mainly concentrated in the low permeability layer. Active polymers can greatly improve the residual oil recovery of the heterogeneous core, especially the crude oil in the low permeability layer. Compared with the oil recovery of two kinds of active-polymers, the Type I have a higher production rate of oil in low permeability.

Considering the recovery and shunt rate, it can be seen that the Type I active-polymer has a great effect on enhancing oil recovery, which is mainly due to the larger size and wider distribution of the Type I active-polymer molecular size. The polymer molecules first enter the high permeability layer to increase the permeation resistance so that the subsequently injected polymer molecules begin to flow to the low permeability layer. Because all reservoirs are heterogeneous, improving the viscosity of displacement phase and profile control is the primary problem of oilfield development.

On this basis, improving the oil washing ability of the displacement agent can further improve the oil recovery.

4 Conclusions

In this paper, two active polymers with different functional groups have been studied to improve oil recovery. The wider distribution of D_h indicates that Type I active-polymers are more suitable for complex heterogeneous reservoirs with complex pore structures. The emulsion stability of the Type III active-polymer and crude oil is stronger, which is suitable for the water absorption profile of heterogeneous reservoirs. In the development of heterogeneous reservoirs, the oil recovery is increased by 15.8%, which is 3% higher than the value of Type III active-polymer.

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References

1. Pi Y.F., Gong Y., Liu Y.J., A Study on Oil Displacement Effect of Polymer Surfactant Flooding and the Change of Seepage Field after Polymer Flooding. *Int. J. Simul.*, 2016, 17, 12.1-12.6.
2. Zhang J.H., Wang Y., Chen X. L., Qu Z.W., Qin D.K., The Effect of Following Water after Polymer Flooding on the Displacement Efficiency with Alternately Injecting Slug of Gel and Polymer/ Surfactant. *Adv. Mat. Res.*, 2013, 737, 1290-1293.

3. Sun L.Y., Shi H.D., Yang H., Zhang J.C., Evaluation of Potential of Remaining Oil after Polymer Flooding. *Adv. Mat. Res.*, 2013, 737, 1189-1195.
4. Zhang W., Zhai B., Song K.P., Wang M., Research on Injection Capacity of Polymer Flooding in Sublayers in Daqing Oilfield. *Adv. Petrol. Explor. Dev.*, 2015, 10, 27-32.
5. Stuart M.A.C., Scheutjens J.M.H.M., Fleer G.J., Polydispersity effects and the interpretation of polymer adsorption isotherms. *J. Polym. Sci. A2*, 1980, 18, 559-573.
6. Chen T., Wan W., Modified Polymer Gels for Creating a Horizontal Barrier to Block Off Water Coning. *The Petroleum Society*, 1996, 14, 1-5.
7. Giordano R.M., Slattery J.C., Effect of interfacial viscosities upon displacement in capillaries with special application to tertiary oil recovery. *Aiche J.*, 1983, 29, 483-492.
8. Guo Y., Lv B., Wang J., Analysis of Chuanxiong Rhizoma and its active components by Fourier transform infrared spectroscopy combined with two-dimensional correlation infrared spectroscopy. *Spectrochim. Acta A*, 2016, 153, 550-559.
9. Qu L., Chen J.B., Zhou Q., Zhang G.J., Sun S.Q., Guo Y.Z., Identification of authentic and adulterated *Aquilariae Lignum Resinatum* by Fourier transform infrared (FT-IR) spectroscopy and two-dimensional correlation analysis. *J. Mol. Struct.*, 2016, 1124, 216-220.