Study of a Novel Self-Thickening Polymer for Improved Oil Recovery

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ABSTRACT: The utilization of self-thickening polymer (STP) in conformance control was first investigated. Results show that these STP solutions exhibit an increase in viscosity (even like gel) under certain conditions. The optimized application conditions of this novel STP are as follows: mass concentration, 0.25−0.30 wt %; salinity, 4.0−8.0 wt %; and temperature range, 40−70 °C. Environmental scanning images demonstrate that a clear and solid skeleton network structure is formed and the higher the salinity of the brine, the more compact the three-dimensional (3D) network structure. In addition, in-depth flow diversion and water permeability reduction were the main mechanisms of water shut-off treatment for improved oil recovery in oil displacement experiments. Finally, this novel STP with the ability to create a gel-like system is cost-competitive, simpler to apply, and more environmentally friendly than the current polymer−cross-linker system. It provides an alternative candidate for conformance control treatments at injection or production wells.

1. INTRODUCTION

Oil and gas, as efficient sources of energy, play an important role in the world economy.1−3 With the rapid growth of the world economy, the demand for oil and gas is on the rise. Exploration on new reservoirs has become more difficult in recent years, which makes it necessary to improve oil and gas recovery in mature oil fields. Additional oil and gas supplies from stripper wells can be an important contributor to national energy security. Excess water production accompanied by low oil production result in unpro

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0.25−0.30 wt %; salinity, 4.0−8.0 wt %; and temperature range, 40−70 °C. Environmental scanning images demonstrate that a clear and solid skeleton network structure is formed and the higher the salinity of the brine, the more compact the three-dimensional (3D) network structure. In addition, in-depth flow diversion and water permeability reduction were the main mechanisms of water shut-off treatment for improved oil recovery in oil displacement experiments. Finally, this novel STP with the ability to create a gel-like system is cost-competitive, simpler to apply, and more environmentally friendly than the current polymer−cross-linker system. It provides an alternative candidate for conformance control treatments at injection or production wells.

The most common conformance control technology is using bulk gel, which is an in situ multicomponent chemical (polymer with cross-linker). However, it has many disadvantages, such as a lack of gelation time control, uncertainty of gelling due to shear degradation, chromatographic fractionation, or change of gelant compositions, and dilution by formation water.11,12 Therefore, there are other chemicals developed to overcome these disadvantages, including preformed particle gel (PPG),13−16 microgels,17−20 swelling millimeter-sized polymer grains, and swelling submicrometer-sized polymers.21,22 However, they are typically expensive and/or not able to treat the thief zones in relatively lower permeability reservoirs. This novel polymer, synthesized in our research laboratory, is expected to have the desirable physical properties and is suitable for water shut-off treatments at both injection and production wells. The novel chemical is designed to thicken quickly (within hours) to a gel-like condition. Furthermore, this chemical has the unique advantage that it is a single chemical, which means that it is cost-competitive, easier to apply, and more environmentally friendly, to create the target in situ gel with controlled time and extent, compared with conventional bulk gel systems that include multicomponent polymers and cross-linkers.

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This study is dedicated to evaluate the properties of this novel STP for increasing oil recovery and reducing water production, thereby extending the life of mature wells and, at the same time, reducing environmental impact (by decreasing the volumes of produced water). This novel STP can be triggered in water under target salinity. That is, it will be possible to use produced water as makeup water instead of using it as a valuable freshwater resource. The range of thickening times and selective plugging strengths for different reservoir conditions (temperatures, salinities, permeability, etc.) of this novel chemical and its improved oil recovery (IOR) mechanism are investigated in this study. It provides a scientific basis and technical support for the effective deployment of this novel chemical in oil and gas fields.

2. EXPERIMENTAL SECTION

2.1. Chemicals. The STP acquired from ChemEOR, Inc. is terpolymer, which has a structure of hydrophilic molecular main chains with hydrophobic side chains (acrylamide, (2-acrylamido-2-methyl) propylsodium sulfonate, 1-(2-allyoxy)-eightethoxy)-4-decylbenzene). The relative molecular weight of STP is \( \sim 1.09 \times 10^7 \), and its solid content is \( \sim 95 \) wt%. The molecular structure is shown in Figure 1. The STP is a powder, which is not hydrolyzed. The STP was prepared from free radical micellar copolymerization in the presence of sodium dodecyl sulfate (SDS), using acrylamide (AM) as a skeleton, (2-allyoxy)-eightethoxy)-4-decylbenzene as the hydrophobe.

The crude oil from Ansai reservoir, Changqing oilfield (People’s Republic of China), was used for oil displacement experiments. The oil viscosity was 2.2 mPa s at the reservoir temperature of 60 °C measured by a Brookfield DV-II Pro viscometer. The density of the crude oil was 0.777 g/cm³.

2.2. Experimental Methods. 2.2.1. Viscosity. A rheometer (Physica MCR301, Anton Paar Company, Graz, Austria) was used to determine the viscosities of STP solutions at different concentrations, salinities, and temperatures. The measurement was conducted at 7.34 s⁻¹ with CC27 coaxial cylinder test system. 25 Thirty milliliters (30 mL) of each sample solution was transferred to the cylinder, and viscosity data was presented from the mean values of three measurements.

2.2.2. Plugging Capacity. The plugging capacity of STP was investigated by sand-pack coreflooding experiments. The steps are as follows:

- Fill the pack (2.5 cm in diameter and 20 cm in length) with sand and measure the dry weight;
- Saturate the sand pack with brine, and then measure the wet weight and calculate the pore volume (PV);
- Flood the sand pack with brine and measure the stable pressure, then calculate the initial permeability (\( k_1 \));
- Inject 0.3PV STP solutions after brine water flooding;
- Maintain the sand pack at a certain temperature for a certain time; and
- Brine water flooding again and measure the stable pressure, then calculate the permeability (\( k_2 \)) and water shutoff efficiency (\( \eta \)), using the following equation:

\[
\eta (\%) = \frac{k_1 - k_2}{k_1} \times 100
\]

2.2.3. Oil Displacement Efficiency. The IOR experiment was performed in double-layered heterogeneous core with STP. The heterogeneous core size is 30 cm × 4.5 cm × 4.5 cm (length × width × height) as shown in Figure 2; the pore volume of this core is 210 cm³, and the oil saturation is 72%. The high permeability layer is 2.5 μm² and the porosity is 32%, and the low permeability layer is 0.6 μm² and the porosity is 28%. The experimental procedures are as follows:

- Saturate brine water in the double-layered core using a vacuum pump until the bubble production was negligible from the outlet;
- Saturate crude oil in the above core until the water cut produced from the outlet was <1%;
- Brine water flooding until the effluent water cut is >98%;
- Inject 0.3PV STP solution into the cores; and
- Brine water flooding again until the effluent water cut is >98% again.

The pressure data, oil production data, and water production data were all recorded to analyze the recovery ratio and water cut over the injected pore volume.

2.2.4. Environmental Scanning Electron Microscopy. Environmental scanning electron microscopy (ESEM) (Model Quanta 200 FEG, FEI Company, Hillsboro, OR, USA) was employed to observe the microstructure of STP. During the experiment, a drop of STP solution was directly cut over the injected pore volume.

2.2.5. Scanning Electronic Microscopy. To compare the performance of STP before and after injection into the core, a scanning electronic microscopy (SEM) system (Model S-4800, Hitachi, Tokyo, Japan) was used to observe the microstructure of STP in the core. 26 One PV of 0.275 wt% STP solution (made by brine water with a salinity of 8.0 wt%) was injected into an artificial core (25 mm diameter × 80 mm), then the core was placed at a certain temperature for 2 days. The core was quickly transferred to a vacuum cup of liquid nitrogen and frozen at −80 °C for 2 h, sequentially; then, the core was put...
into a lyophilizer for 24 h and the vacuum pressure was 7–8 Pa. After freeze-drying, the core was crushed at 30–40 mm away from the inlet, and then the gel there was investigated with the SEM with an accelerating voltage of 3.0 kV.

3. RESULTS AND DISCUSSIONS

3.1. Optimized Mass Concentration. A series of different mass concentration of STP solutions were made with 6.0 wt % brine water (5.95 wt % NaCl and 0.05 wt % CaCl₂) at room temperature. The Anton Paar Physica MCR301 rheometer then was used to determine the viscosity of the above STP solutions at 40 °C with different aging time. The experimental results were shown in Figure 3.

Figure 3 describes the relationship between viscosity and aging time at different mass concentrations.

Figure 3. Relationship between viscosity and aging time at different mass concentrations.

With the increase of aging time, the viscosity first increases quickly and then reaches a plateau. When the mass concentration of the STP solution is <0.20 wt %, almost no thickening phenomenon happened; however, when it reaches 0.25 wt %, the thickening phenomenon occurred, and the viscosity can be stabilized at a relatively high value. With the increase of mass concentration, the thickening effect is more obvious and the viscosity is higher. The thickening process of the STP solution is very much like gel, which could hang on a glass rod. This means that there is no risk of chromatographic separation of components and poor in situ gelation. In addition, this avoids the use of any objectionable cross-linkers, such as those based on chromium. However, when the mass concentration of STP solution is over 0.50 wt %, the viscosity can exceed 10 000 mPa s. The viscosity changes rapidly with aging time; the viscosity can reach up to 2000 mPa s in 1 or 2 days, and the initial viscosity of the STP solution could reach up to 200 mPa s, so it is difficult for this system to inject into the reservoir easily, but it is suitable for conformance control in ultrahigh-permeability reservoirs. In summary, the optimized mass concentration of STP solutions ranges from 0.25 wt % to 0.30 wt %.

This phenomenon is due to the presence of hydrophobic groups in the molecule. At low mass concentration, the association action is weak. The random coils are formed mainly by intramolecular association, as shown in Figure 4. In addition, the coils are separated from each other, as shown in Figure 5a, so the viscosity of the system is low. As the mass concentration increases, more random coils are formed by the increase in intramolecular association, and they get closer to each other and come into contact with each other, so the viscosity increases. There is a corresponding mass concentration, which is called the “critical contact concentration”, as shown in Figure 5b. When the mass concentration of the STP solution continues to increase, the association action comes mainly in the form of intermolecular association, as shown in Figure 4. This results in penetration and overlap of random coils, thus forming a new molecular structure, which exhibits a significant increase in viscosity, as shown in Figure 5c.

3.2. Reasonable Salinity Range. Series of 0.275 wt % STP solutions were prepared with different brines at room temperature. The Anton Paar Physica MCR301 rheometer was used to measure the viscosity of the above STP solutions at 60 °C through different aging time. The experimental results are shown in Figure 6.

Figure 6 shows that the viscosity increases gently at low salinity, up to 200 mPa s. This indicates the occurrence of weak associating action. With increases in brine salinity, viscosity increases constantly, exceeding 2000 mPa s. This is an indication of strong associating action. The higher the salinity of the brine, the higher the viscosity. Similar results are received from the ESEM images shown in Figure 7. A three-dimensional (3D) network structure was formed due to association action triggered by salinity. The network structure is a uniformly porous-like network structure composed by chain bunches, net pores, and nodes. The size of the net pores ranges from several micrometers to tens of micrometers. With the increase of brine salinity, the size of the net pores becomes smaller, and the quantity of the net pores increases significantly per unit volume. The chain bunches around the net pores reveals the continuous skeleton network through the nodes to ultimately form the 3D network structure. The higher the brine salinity, the stronger the association action. Thus, the network structure becomes...
more compact, which has great water holding ability, because of the numerous small net pores. It can be attributed to the clusters of the water-filled porous-like network structure.29−31 This structure can result in lower shrinkage and increase the stability of this system. When this structure is formed in the formation, the 3D network bridges across the pore throats and restricts the flow of water in the high-permeability layer, which has an effect on conformance control and promotes the applicability of STP systems in oilfields.

In the meantime, as the number of aging days increases, the viscosity first increases sharply, then reaches the highest value, remains almost constant, and then no longer decreases. It is also found that the time to reach the maximum viscosity shortens with the salinity increment of the makeup brine. However, when the brine salinity is ≥8.0 wt %, because of the high salinity and STP structure, the cohesive force and intramolecular force of STP strengthens; therefore, it is hard for STP to stretch and dissolve in the brine water with salinity over 8.0 wt %. Therefore, the reasonable salinity range of the makeup water is 4.0−8.0 wt %.

Figure 5. Relationship between the polymer structure and polymer concentration.

Figure 6. Relationship between viscosity and aging time at different brine salinities: sample 1#, 1.95 wt % NaCl + 0.05 wt % CaCl₂; sample 2#, 3.95 wt % NaCl + 0.05 wt % CaCl₂; sample 3#, 5.95 wt % NaCl + 0.05 wt % CaCl₂; and sample 4#, 7.95 wt % NaCl + 0.05 wt % CaCl₂.

Figure 7. Environmental scanning electron microscopy (ESEM) images of STP prepared with brine water.
The reason for this phenomenon is a co-effect of association action and repulsion of electric charges. When the salinity is very low, the repulsion between electric charge is dominant, and association action is relatively weak, so the viscosity is low. When the salinity increases and surpasses the critical association salinity, the association effect is dominant, and the viscosity increases significantly. At the initial stage of the high-salinity range, the repulsion between electric charges are still effective, and the probability of intramolecular association is smaller than that of intermolecular association, which results in the dramatic increase of viscosity. However, when the salinity continues to increase, the repulsion of electric charge barely exists. The probability of intramolecular association is larger than that of intermolecular association, so the viscosity decreases in this situation.

### 3.3. Reasonable Temperature Range

A series of 0.275 wt% STP solutions were prepared with 8.0 wt% brine water at room temperature. The Anton Paar Physica MCR301 rheometer then was used to measure the viscosity of the above STP solutions at different temperatures through different aging times. The experimental results are shown in Figure 8.

![Figure 8](image)

**Figure 8.** Relationship between the viscosity and aging time at different temperatures.

Figure 8 shows that the viscosity increases at 40−70 °C and reaches 2000 mPa s; when temperature is over 70 °C, the viscosity begins to decline, to a small extent. When the temperature is 90 °C, the viscosity decreases dramatically. The reason for these phenomena is that, in the range of 40−70 °C, with the increase of temperature, the interaction between molecules is endothermic, the process is entropy-driven, and the association action increases as the temperature increases. With the increase in the thermal motion of ionic groups and the weaker interaction between anionic and cationic groups, the molecule chains stretch, which favors increasing viscosity. However, when the temperature continues to increase, the thermal motion of hydrophobic groups in the molecule also increases, which weakens the hydrophobic association; meanwhile, the thermal motion also changes the structure and state of water molecules around hydrophobic groups, the molecule chains shrink, and the viscosity decreases. When the temperature is 90 °C, the association among molecules is very weak, and the association structure is destroyed, which leads to no thickening effect.

### 3.4. Reasonable Permeability Range

A series of 0.275 wt% STP solutions were composed of 8.0 wt% brine water at room temperature. Different permeability sand-pack cores were used to evaluate the plugging ability of STP as a conformance control agent. The experimental results are shown in Table 1.

<table>
<thead>
<tr>
<th>Core No.</th>
<th>Porosity (%)</th>
<th>Core Permeability (D)</th>
<th>Water Shutoff Efficiency, η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>37.4</td>
<td>0.50</td>
<td>0.0135</td>
</tr>
<tr>
<td>2</td>
<td>36.9</td>
<td>1.13</td>
<td>0.0655</td>
</tr>
<tr>
<td>3</td>
<td>36.4</td>
<td>2.1</td>
<td>0.200</td>
</tr>
<tr>
<td>4</td>
<td>35.9</td>
<td>4.0</td>
<td>0.740</td>
</tr>
<tr>
<td>5</td>
<td>34.0</td>
<td>5.3</td>
<td>1.350</td>
</tr>
</tbody>
</table>

Table 1 describes the relationship between the water shutoff efficiency and the permeability of the sand-pack cores. As the permeability increases, the pore size of the core becomes larger, which leads to weaker plugging ability. Especially when the permeability is over 4 D, the water shutoff efficiency is below 80%. Therefore, this system is more suitable for conformance control in the reservoir, with a permeability of <4 D, which can effectively lower the formation heterogeneity and improve sweep efficiency. The microstructure of the gel-like state of STP in porous media is demonstrated from the SEM results in Figure 9. Comparing with the results using distilled water as makeup water, a clear and solid skeleton network structure of STP that appeared in porous media was formed. The skeleton structure is thicker and more solid in pores and throats than that in distilled water; some branched chains among this structure can be tightly locked together to form a compact and continuous network. Thus, the gel-like state of STP is triggered to form in core, and the thick and solid network restricts the water flow by bridging across the pores and throats. When the following water contact with STP system, the gel-like network inflates and strengthens water flow resistance to reduce the water permeability in the formation. Therefore, the STP system can block the high-permeability layer in the formation. However, with the increasing of formation permeability, the pores and throats in the formation become larger, the skeleton network structure becomes slimmer and softer than that in the small pores and throats. Although the skeleton network is not too compact and the bridging becomes more difficult in the large pores and throats, the water flow resistance is increased and the water permeability is reduced in the formation. So the water shutoff efficiency decreases as the permeability increases.

### 3.5. Coreflooding Experiment

The oil displacement experiment was conducted via a coreflooding equipment, and the diagram of oil displacement experiment is shown in Figure 10. Rubber sleeve liners are present in the core holder. The heterogeneous core was inserted into the rubber sleeve and placed in the core holder. A seal test was carried out by injecting water in the annulus of the core holder with the maintained overburden pressure at 2−3 MPa from the top valve of the core holder. The oil displacement result is shown in Figure 11.

Because of the serious heterogeneity of this core, the injected STP solution almost all entered the high-permeability layer. Therefore, the higher water production, along with the high-permeability layer, was plugged to remedy the reservoir.
heterogeneity; then, the water cut decreased significantly and the reservoir pressure increased sharply. Water flood was diverted into the low-permeability layer to displace the remaining oil; thus, the ultimate oil recovery was much higher than that of the first water flooding.

From Figure 11, we can see that the recovery rate of water flooding is $\sim 36\%$ while final recovery rate is $\sim 60\%$. The enhancement in the oil recovery rate is $\sim 24\%$. Because of its good integrality, which is similar to weak gel after 2 days of gelation, the ability of STP to control high-permeability layer is better than that of conventional polymer. The STP can lead the subsequent water flooding into the low-permeability layer and increase the final oil recovery. That is caused by its physical properties. This novel STP can be triggered in certain brines and becomes a gel-like system with viscoelastic properties, and realizes moveable in-depth conformance control and better oil displacement process. Figure 12 shows the diagram of the moveable in-depth conformance control and oil displacement process of gel-like STP in the sandstone reservoir.

In mature water flooding oilfield, the injection water prefers to flow through the high-permeability layer or large pores and throats. Thus, potentially, a large amount of oil remains in the middle-to-low-permeability layer or small pores and throats. The STP solutions can be easily injected into the high-permeability layer or large pores and throats, then become gel-like systems after being triggered in brine, which can temporarily shut off water in the high-permeability layer or large pores and throats near wellbore (even where the pressure gradient is very high) and divert the water flow and displace the remaining oil to the middle- and low-permeability layer or small pores and throats. When the pressure gradient is high enough, the polymer will deform and transport in the porous media of the high-permeability layer or large pores and throats, and quickly recover to its original shape. Finally, the polymer could move into the deep area of oil formation and effectively plugs the high-permeability layer or large pores and throats there, because of the relatively low pressure gradient. Thus, the water

Figure 9. SEM images of STP makeup by (a) brine and (b) distilled water.

Figure 10. Diagram of oil displacement experiment.
flow is diverted again and again, and the oil that remains in the deep area of oil formation is displaced.

4. CONCLUSIONS

In this work, a new concept in conformance control is proposed. The unique features of a novel STP (increase in viscosity, and even to a gel state in some cases), which are due to strong association action, were comprehensively investigated in both bottle test and core flooding experiments. The main new understandings are as follows:

① When the mass concentration of STP solution is <0.20 wt %, almost no thickening phenomenon happens. However, thickening phenomenon occurs when the mass concentration reaches up to 0.25 wt %, and the viscosity can be stabilized at a relatively high value. With the increase in mass concentration, the thickening effect is more obvious and the viscosity is higher. Taking the injectivity into account, the optimized mass concentration of STP solutions ranges from 0.25 wt % to 0.30 wt %.

② As the brine salinity increases, the viscosity obviously increases: the higher the salinity of the makeup brine, the higher the viscosity. A three-dimensional (3D) network structure investigated with environmental scanning electron microscopy (ESEM) was formed because of association action triggered by salinity. The higher the salinity of the makeup brine, the stronger the association action. Thus, the network structure becomes more compact at high salinity, which has great water-holding ability, because of the numerous small net pores. Considering the solubility, the reasonable salinity range of the makeup brine is 4.0–8.0 wt %.

③ The viscosity of the system increases at 40–70 °C and reaches values up to 2000 mPa s; when the temperature is >70 °C, the viscosity begins to decline, to a small extent. When the temperature is 90 °C, the system viscosity decreases dramatically. This is determined by both the association action and the thermal motion of the ionic groups.

④ The results of the plugging experiments show that, as the permeability increases, the pore size of core becomes larger, which leads to the weaker plugging ability. Therefore, this system is more suitable for conformance control in the reservoir with the permeability being <4 D, which can effectively improve the formation heterogeneity and improve the sweep efficiency. SEM images also illustrated the microstructure of gel-like state of STP in porous media. The thick and solid network bridge across the pores and throats leads to restriction of water flow.

⑤ The oil displacement experiments demonstrate that, after STP treatment, the higher-level channels of water production, along with the high-permeability layer, were plugged to remedy the reservoir heterogeneity, then the water cut was significantly decreased, and the following water was diverted into the low-permeability layer to produce the remaining oil. In-depth flow diversion and water permeability reduction were the main mechanisms of the gel-like system formed by STP in water shut-off treatment for improved oil recovery from oil displacement experiments.

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Notes
The authors declare no competing financial interest.

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