

Study on a Polymer Profile Control Agent with Controllable Swelling Time

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Abstract: The study provided a microsphere profile control agent, which can smoothly go deep into the stratum by using the hydrophobic shell structure as the “protective film”. While the solution time in simulated brine was prolonged, water molecules went deep into the inside of the microsphere particles through the pore structure, and combined with hydrophilic groups. Because of the combination, the microsphere polymer started to swell, and opened the shell into long chain for days, and then at the end, its hydrophilic-hydrophobic block groups were all exposed in the solution, which resulted in self-thickening property. The dissolution time after entering into the stratum, *i.e.* the shell “rupture” time can be controlled by adjusting the carbon chains length of hydrophobic groups in the synthetic process. The agent can not only prolong the depth of plugging and provide a stable plugging rate, but also enlarge the water swept volume after dissolution. This method can stabilize the oil production and control the water cut. The function of delayed thickening ability makes the stratum sealed but kept at a certain permeability.

Keywords: Controllable swelling time, Polymer, Profile control agent, Shell structure, Self-thickening.

1. INTRODUCTION

With acceleration of oilfield exploitation, most oilfields in China and even in the world have entered into the stage of high water-cut, which puts forward new requirements and challenges for how to further improve oil recovery. Now, the profile control in water injection well has become an important technical means of improving oilfield water injection effects and stabilizing well production [1-3]. At present, the research about the existing profile control agent has been increasingly wide, including chromium, zirconium gel system, phenolic resin system, clay/cement dispersion, lime milk, water swelling polymer. Normally, the profile control agent is applicable to low-permeability reservoir, such as silicic acid, aluminum hydroxide gel microspheres, etc. [1-6].

A traditional profile control agent for polymer flooding in oil field was composed of polymer aqueous solution and regulator, *e.g.* β -cyclodextrin, chitosan or heavy alkyl benzene petroleum sulfonate [2, 3]. It can improve the adaptability between polymer molecular aggregates and reservoir heterogeneity by controlling the quantity of hydrophobic groups. The oil recovery efficiency of the synthetic profile control agent system was about 7.0~11.5% [4, 5]. A secondary crosslinking

profile control was composed of partially anionic hydrolyzed polyacrylamide and resorcinol - formaldehyde secondary crosslinking agent.

However, most of the profile control agents started swelling before injected into the reservoir. There were many explanations mentioned in the researches, such as the great initial particle sizes, the short crosslinking time, the quick viscosity increment rate, and the poor mobility, etc. [6-11]. The earlier swelling behavior led the profile control particles to be ruptured by the stratum shear force and sieve tube in the pumping process. Therefore, the traditional profile control agents can only be used in the shallower horizon from the water injection well. The deep profile control technique for high permeability oilfield is still a problem to be further studied.

The profile control polymer designed in this study can control the swelling time by using the hydrophilic-hydrophobic double comb-shaped structure. The profile control agent is supposed to have the ability to go deep into the stratum, as the hydrophilic chains are wrapped by the “protective shell” and isolated with water molecules.

The acrylamide sulfonate, as multifunctional anionic monomer, has good polymerization activity as well as salt-resistant ability [12]. The S-O coordination bond contained in the sulfonic acid group can effectively impede external cations from attacking, consequently

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to improve the temperature resistance and resistance to salinity of the polymer. The hydrophobic group is designed as alkylene oxide with long branched chains. A lot of experiments prove that, if the carbon quantity in the alkyl chain is greater than 6, the required hydrophobic character will be realized. Herein, the hydrophobic group is preferably selected as long chain epoxy, which are supposed to act as a shell to limit the viscosity performance of the polymer. Alkylene oxide belongs to a three-membered ring, because of its high tension and the polar effect of C-O bond, which may be subjected to rupturing and ring opening under acid. The pendant group of long-chain alkane after ring opening serves as the main hydrophobic group.

2. EXPERIMENTAL WORK

2.1. Materials

Acrylamide (AM, industrial grade), 2-acrylamide-2-methylpropanesulfonic acid (AMPS, industrial grade), 1,2-epopentane (C₅H₁₀O), 1,2-octane oxide (C₈H₁₆O), 1,2-epoxydecane (C₁₀H₂₀O), 1,2-epoxydodecane (C₁₂H₂₄O) were obtained from Changjiu Agricultural Chemical Industry co., Ltd (China). Lewis acid, emulsifier agent-Tween 20 and diethanol amine (C₄H₁₁NO₂), ammonium hydroxide (NH₃·H₂O, 25%), n-hexane lipophilic solvent (n-C₆H₁₄, 99.9%), N,N'-diethylethylenediamine (C₁₀H₂₄N₂, DEAEA), n-hexane lipophilic solvent (analytically pure), potassium persulfate (K₂S₂O₈, analytically pure), sodium hydrogen sulfite (NaHSO₃, analytically pure), were purchased from Shanghai McLean biochemical technology co., Ltd (China).

2.2. Preparation of Polymer Profile Control Agent

The preparation of a micro-spherical double comb-shaped block high-molecular polymer profile control agent with controllable dissolution includes following steps.

By molecular fraction, AM, AMPS and hydrophobic associated monomers of epoxy alkanes including: 1,2-epopentane (C₅H₈O), 1,2-octane oxide (C₈H₁₆O), 1,2-epoxydecane (C₁₀H₂₀O), 1,2-epoxy cyclododecane (C₁₂H₂₄O) is prepared at a ratio of 52:15:33 to obtain an aqueous solution with a concentration of 30%. Lewis acid, C₄H₁₁NO₂ and NH₃·H₂O are added to regulate the pH to 7, and the temperature is constant at 5 °C.

High-purity nitrogen of 99.9 % was continuously introduced at a constant 5 °C. After 50min, composite initiator system compositions with a molecular ratio of

each composition of 7:5:1:1 were added in sequence, which comprise Lewis acid, DEAEA, K₂S₂O₈ and NaHSO₃. The inflow of N₂ was maintained during the process, and the addition of composite initiator system compositions was 0.3% of the total amount of monomers, then, seal. The polymer glue was obtained after a 4 h reaction under a sealed condition.

The glue was smashed and aged for 1.5 h at 80 °C, and was subjected to grinding and sieving in 60 °C for 6 h. The preferable number of mesh was 1500. And the prophase sample of profile control agent was obtained.

Taking TQ-5 as an example, the polymerization process was shown as Figure 1.

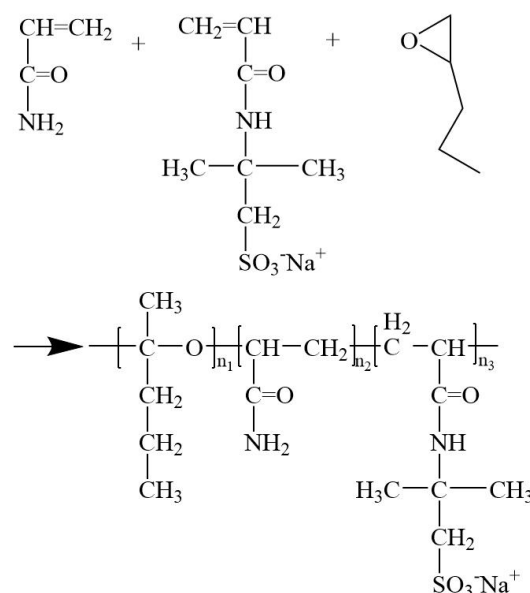


Figure 1: The polymerization process of TQ-5.

The above mentioned fine powdery copolymer was dissolved in n-hexane lipophilic solvent with a concentration of 500 ppm, and is stirred at a bath temperature of 30 °C at a stirring rate of 150 rad/min for 3 h.

The emulsion was preheated to 40 °C, and granulating process was conducted through an aerosol device. Finally, the polymer profile control agent was obtained. According to the carbon number contained in the hydrophobic groups, the samples were named as TQ-5, TQ-8, TQ-10, TQ-12, respectively. The spherification process was shown in Figure 2.

The aerosol device mentioned here was set up in laboratory, which includes: mother liquor tank, spray gun, first sieving tower, second sieving tower, third

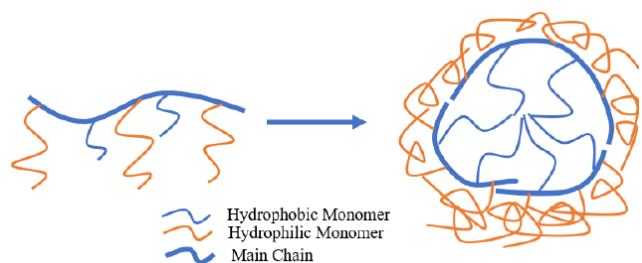


Figure 2: Schematic presentation of micro-spherical profile control agent.

sieving tower, air blower and induced draft fan, see Figure 3.

- The mother liquor tank is connected with a first sieving tower, and a spray gun is provided between the mother liquor tank and the first sieving tower.
- The first sieving tower, second sieving tower and third sieving tower are sequentially connected.
- The blower and the first sieving tower are connected.
- The induced draft fan and the third sieving tower are connected.

- The head of spray gun is preferably provided at the inner upper of the first sieving tower.
- The evaporation capacity is selected according to the demand of bottom porosity to select different spray guns. Therefore, the number of the spray gun could be chosen as one, three, four, six or eight.

2.3. Experimental Procedure

In the present work, all the presented data have been characterized and evaluated in the laboratory with standard equipment. The experimental procedures have been demonstrated as followed.

The simulated brine mentioned in the present work contained a total mineralization of 1.28×10^5 mg/L and a combined concentration of Ca^{2+} and Mg^{2+} of 425 mg/L.

The particle size was measured by Beckman Laser diffraction analyzer LS 13320 XR. The prepared micro-spherical polymer mentioned in the study was added to prepare a polymer brine solution with a concentration of 1000 mg/L.

All the apparent viscosity tests were measured on a RPV-1(2)-RA fully automatic molecular weight measuring instrument. The apparent viscosity of TQ

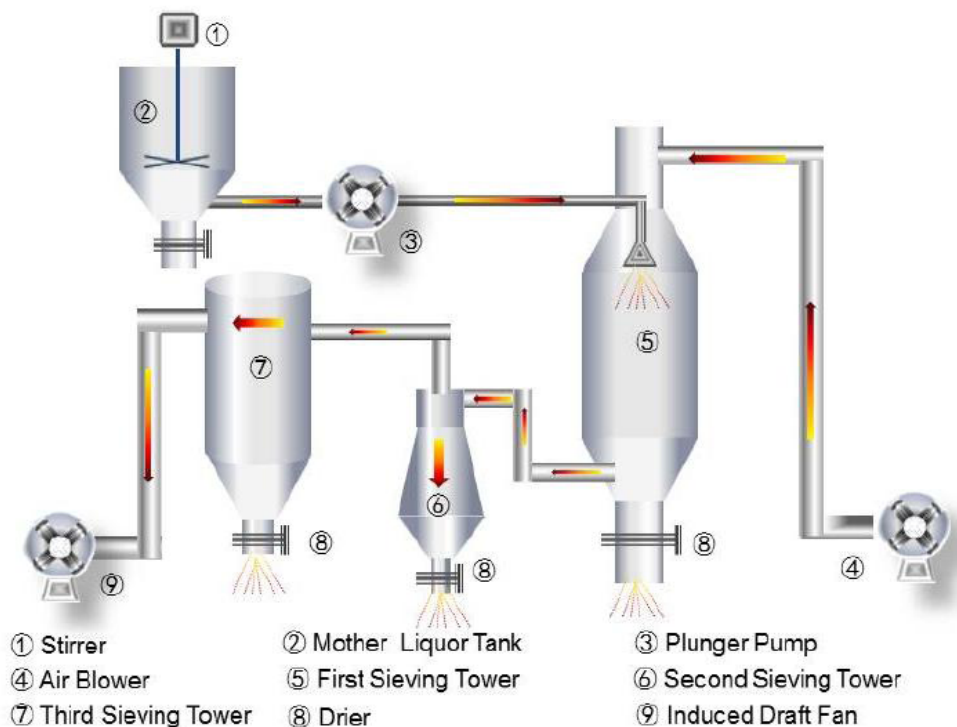


Figure 3: Model of aerosol device.

series was measured under the condition of 85 °C, 7.34 s⁻¹ and a concentration of 1500 mg/L.

The anti-aging stability of micro-spherical polymer flooding agents was tested as the following process. The polymer microspheres samples were fully dissolved by simulating underwater, and then diluted to 1500 ppm, recording the initial viscosity of the samples at 85 °C, with a shearing rate at 7.34 s⁻¹. Aging the above solutions with the treatment temperature of 85 °C and an inspection cycle of 90 days.

The TQ-10 sample was selected for simulated core plugging experiment. The operating equipment was shown in Figure 4. The experimental process was shown as follows.

(a) Core sampling: the length of sampling from a block in Kazakhstan oilfield was 25 cm and its diameter was 3.5 cm.

(b) Kazakhstan high-mineralization simulation water: total mineralization was 1.28×10⁵ mg/L, and total concentration of Ca²⁺ and Mg²⁺ was 4.25×10² mg/L.

(c) Determination of water phase permeability before blocking: the core was evacuated and injected by Kazakhstan high mineralization brine. Then, the core was flushed by water flooding with 1000 mL/min

flow, after saturation. The water phase permeability of the core was measured and recorded as K₀.

(d) Simulation of core displacement test Under the constant temperature of 85 °C, inject a certain block dewatered oil of the Kazakhstan oilfield, and the core was saturated, with water flooding to residual oil state for 24 h.

(e) Inject 2PV TQ-10, and keep it under the constant temperature of 85 °C for 200 h. The measured water phase permeability after plugging was measured and recorded as K₁.

3. RESULTS AND DISCUSSION

3.1. Granularity Test

As shown in Table 1, the average size of initial polymer profile control agents was controlled within about 1~3 μm through the aerosol technique. The result indicates that the sphere particles might enter into the inner stratum easily and successfully owing to the micro particle size.

Table 1: Initial Particle Size of TQ Series

No.	TQ-5	TQ-8	TQ-10	TQ-12
Particle Size/μm	0.33	0.97	1.26	2.82

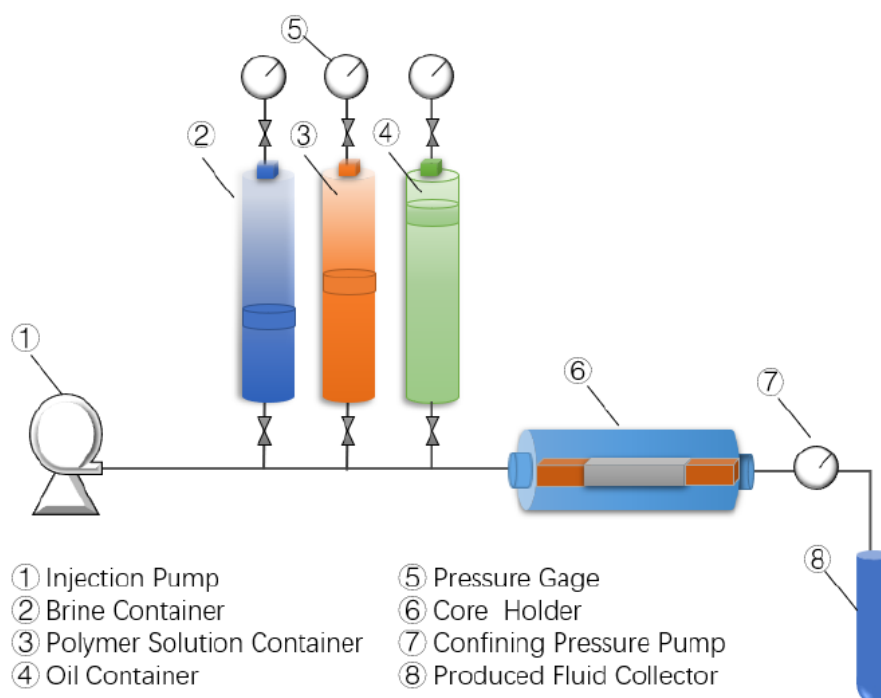


Figure 4: Model of core plugging Equipment.

3.2. Viscosity Increasing Rate Test

As shown in Figure 5, the viscosity increasing rate of the TQ series was measured. Under the temperature of 85 °C, for polymer saline solution, their initial apparent viscosity was negligible. According to continuous testing, the apparent viscosity gradually elevated and remained at a fixed range stably. It indicates that the external layer of the polymer agent is wrapped by long-chain hydrophobic alkyl as “protective film”, so that the sphere can smoothly go deep into the stratum without viscoelastic resistance. With the extension of time, water molecules get through micro-spherical polymer wrapped by the hydrophobic group combines with the center of the inner hydrophilic group, resulting in the micro-spherical material gradually dissolving, eventually all opening and forming a stretch of hydrophilic-hydrophobic groups of the block copolymer. The longest delay thickening time can be extended to 96 hours. The hydrophilic groups are completely exposed in the brine, while hydrophobic groups start to aggregate because of hydrophobic association effect. High-molecular chains are made to associate with each other, in order to form dynamic physical cross-linked network, which greatly increases the hydrodynamic volume and the solution viscosity. The result indicates that the viscosity of the polymer not only could enter into deeper formation, but also exert a stable viscosity enhancement ability.

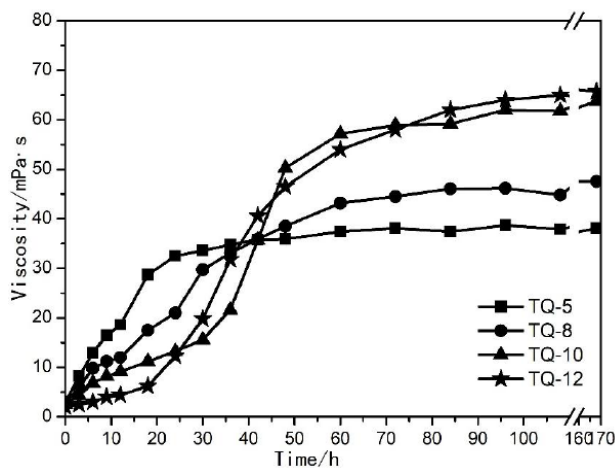


Figure 5: Viscosity Rate of TQ series.

In addition, it is noteworthy that the dissolution rate of the micro-spherical polymer profile control agent is inversely correlated with the length of the hydrophobic chain. As shown in Figure 5, the dissolution rate is summarized as follows: TQ-5 > TQ-8 > TQ-10 ≈ TQ-12, which indicating the shorter the hydrophobic group

chain, the faster the dissolution rate. It is speculated that, at the same proportion, the increase of hydrophobic chain length causes the outer shell structure to be more closely wrapped outside the hydrophilic core, hindering the hydration process of microspheres, which manifests as a slower viscosity increase rate. Once the carbon content of the hydrophobic chain exceeds 10, the rate of delayed thickening does not change anymore. It can be speculated from the hydrated layer shell density of TQ-10 and TQ-12 is close to saturation as the carbon content more than 10 when the size of the hydrophilic long chain kernel is approximately the same. It is indicated that hydrophobic agent with 1,2-epoxydecane (C₁₀H₂₀O) performances the ultimate delayed thickening rate under this ratio.

Furthermore, under the premise of the same block proportion, the longer the carbon chain of the hydrophobic group is, the higher its viscosity retention rate acts, shown in Figure 5. It is indicated that the polymer structure with longer C-C chain has the stronger association ability and stability. It is supposed to be two reasons: the larger volume branched groups could inhibit the main chain from curling. On the other hand, longer carbon chains could provide more carbon sites to help increase the probability of intermolecular association. The scheme is displayed in Figure 6.

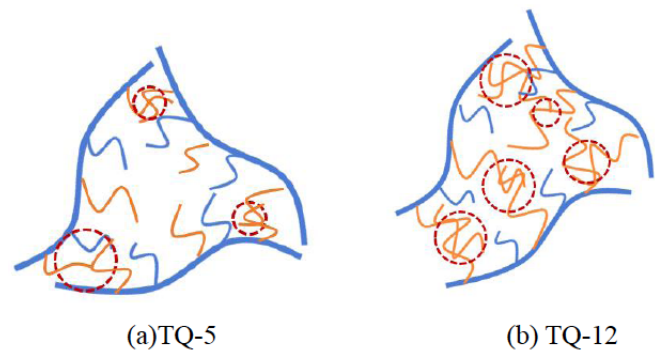


Figure 6: Schematic presentation of the association state of TQ series with different hydrophobic chain length.

3.3. Anti-aging Capability

The aging stability results are as shown in Table 2. After 90 days of processing, all the viscosity retention rates of TQ series can maintain at 90%~96% around, which displays the excellent anti-aging capability at 85 °C.

3.4. Simulation of Core Displacement Test

The measured water phase permeability of core K₀ was 1.96×10² mD. With the comparison of water phase

permeability after plugging was 5.3 mD. The plugging rate was 97.3 % by using Kazakhstan high mineralization brine for continuous displacement. It is indicated that the TQ-10 sample has high efficient plugging ability.

Table 2: Viscosity Retention after Aging Treatment

No.	Viscosity Retention (%)
TQ-5	92.8
TQ-8	94.2
TQ-10	95.8
TQ-12	94.1

CONCLUSIONS

The study mainly aims at water blocking profile control and polymer flooding techniques for oil reservoir, as well as provides a new type of deformation material with controllable swelling time. In order to form a micron-scale “controllable dissolved distortion sphere”, the profile control agent is designed as a hydrophilic-hydrophobic block spherical polymer, which can plug channels, meanwhile keep them at a certain permeability. Additionally, the agent could accomplish an excellent blocking effect at 85 °C under a high salinity condition, and the viscosity retention rate after 90 days is as high as 92~96%. According to the core oil displacement test, the plugging rate of TQ-10 can maintain as high as 98%, which provides the possibility for deep profile control with a required retarding thickening time. Therefore, the polymer profile control agent can effectively achieve both the abilities of oil production stabilization and the water cut control.

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