

Preparation, Swelling Properties, and Displacement Performance of Functional Amphiphilic Microspheres

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ABSTRACT: Because polymers containing benzyl chloromethyl groups are easily modified for functional production, the dispersion polymerization of acrylamide, 4-vinylbenzyl chloride, and *N,N*-methylene bisacrylamide in dimethylformamide initiated with α,α -azobisisobutyronitrile was carried out to produce amphiphilic microspheres containing benzyl chloromethyl groups. The structure of the amphiphilic microspheres was determined by IR and ¹H-NMR spectroscopy. The polymerization conditions, the temperature, amount of crosslinking agent, and initiator included, were optimized. The size distribution of the microspheres after swelling equilibrium ranged from 4 to 62 μm . The swelling behavior of the microspheres was also investigated. The increase in temperature and the decrease in salinity caused a gradual increase in the swelling ratio. The prepared microspheres were transported uniformly in porous media when the permeability was 0.436 μm^2 . The oil displacement experiments indicated that amphiphilic microspheres had the ability to enhance oil recovery under homogeneous and heterogeneous conditions but was more suitable for heterogeneous formation.

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INTRODUCTION

Polyacrylamide and its modification products are among the most common oilfield chemicals for enhanced oil recovery (EOR). With the unceasing deepening of oilfield development, considerable attention has been paid to profile control deeper into the formations with flooding technology based on polymers derived from acrylamide (AM), usually including a linked polymer solution (LPS),^{1,2} colloidal dispersion gel (CDG),^{3–5} performed particle gel (PPG),^{6,7} and microspheres,^{8,9} also known as microgels.^{10,11} LPS and CDG are prepared by a low-concentration polyacrylamide solution with small amounts of a crosslinking agent, such as Al^{3+} ,^{12,13} Cr^{3+} ,¹ Fe^{3+} , and Zr^{4+} .² Because of the low degree of crosslinking, both of these profile control agents are easily affected by the salinity, pH, temperature, and shear rate⁹ and are not applicable for high-temperature and high-salinity reservoirs. The preparation method of PPG is composed of the following steps: gel formation, crushing, granulation, screening, drying, and the production of the products. Benefiting from a high crosslink density and strength, PPGs are suitable for reservoirs with a high salinity, high temperature, strong heteroge-

neity, and macroscopic throats. However, because of the large size, PPGs are easily accumulated at near-wellbore areas in medium–low permeable reservoirs. It is difficult to for it achieve migration in deep formations for PPG.

To solve the aforementioned problem, an elastic microsphere was proposed and has attracted the extensive concern of scholars.^{8,9,14,15} Microspheres move deeply into the oil formation according to the mechanism of plugging–deformation–migration in the porous media of the reservoir.¹⁶ There is some published literature about polyacrylamide microspheres used for EOR. However, the reported research has focused on the matching relationship between the size of microspheres and the permeability of the reservoir or on the control of the particle size or migration characteristics in porous media. Few researchers have investigated the modification and functionalization of microspheres for EOR except one cationic microsphere particle prepared by Li et al.¹¹

The amphiphilic polymer is prepared by the copolymerization of the hydrophobic and hydrophilic monomers. The dual hydrophilic/hydrophobic nature provides the materials with

unique dissolution characteristics and physical properties.¹⁷ As a result, there has been increasing interest in the preparation of amphiphilic microspheres. A particularly interesting amphiphilic microsphere is the copolymer of AM and other hydrophobic monomers. In these hydrophobic monomers, 4-vinylbenzyl chloride (4-VBC) is a functional styrene with a reactive pendent benzyl group susceptible to Lewis-acid-assisted cation formation and nucleophilic substitution. Additionally, the reactive benzyl chloride group is susceptible to Lewis-acid-assisted cation formation and nucleophilic substitution. Also, the group of benzyl chloromethyl can be used as an initiator of surface-initiated atom transfer radical polymerization. A lot of articles about surface-initiated atom transfer radical polymerization have been published in all kinds of academic journals. However, the quantitative separation of the graft polymer on the surface is not an easy task. So it is still a difficulty to accurately characterize the molecular weight and polydispersity of the surface-attached polymer on the surface. As a rough estimate, most researchers have considered that the molecular weight and polydispersity of the surface-attached polymer are nearly equal to those of the free polymer produced in the solution.^{18,19} Only in minor cases can the information of the graft polymer be accurately determined. For example, the treatment of the silica particle with hydrofluoric acid has been used to cleave off a polymer attached to a surface through dissolution of the substrate.²⁰ In addition, quantitative separation of the surface-attached polymer can be achieved if the cleavage reaction is carried out. If the benzyl group is introduced on the surface of microsphere, it becomes possible to dissociate the side chains from the surface of microsphere to determine the molecular weight and molecular weight distribution of side chains because the C—C bond of benzyl groups is easy to break by the oxidation of potassium permanganate.

In this study, functional amphiphilic microspheres containing benzyl chloromethyl groups were prepared by dispersion polymerization. The structure of the amphiphilic microsphere was analyzed by means of Fourier transform infrared (FTIR) spectroscopy and ¹H-NMR. The effects of the reaction conditions on the properties of the microspheres were investigated. The swelling properties and displacement performance of the amphiphilic microspheres were also studied.

EXPERIMENTAL

Materials

4-VBC from Aldrich Chemical Co. was purified by passage through a column of activated basic alumina to remove the inhibitor, stored over CaH₂, and then vacuum-distilled before use. AM from Sinopharm Chemical Reagent Co. was recrystallized twice from chloroform to remove the stabilizer before use. Dimethylformamide (DMF) from Tianjin Chemical Co. was distilled with the usual techniques. The initiator, α,α -azobisisobutyronitrile (AIBN) from Tianjin Chemical Co., was crystallized from chloroform. Other reagents were analytically pure and were used without further purification. Distilled water was used throughout.

Dispersion Polymerization

The amphiphilic microspheres were synthesized with AM, 4-VBC, and *N,N'*-methylene bisacrylamide (MBA) as crosslink-

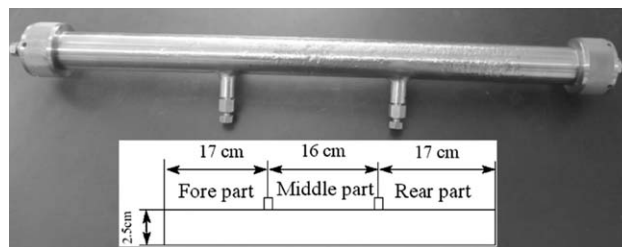


Figure 1. Sandpack with two pressure taps.

ing agents in DMF at different temperatures with a certain amount of AIBN as the initiator. Each reaction was conducted in a 250-mL, three-necked flask equipped with a magnetic stirrer and a nitrogen inlet tube. Then, the products were rinsed by acetone and dried under a primary vacuum at 50°C until a constant weight was attained. The residual monomer content was determined by bromination according to the national standard GB/T 12005.3–1989.

Characterization

¹H-NMR spectra were measured on a Varian Gemini-500 NMR spectrometer with D₂O as the solvent. Chemical shifts were reported in parts per million. A Bruker IFS 66 v/s IR spectrometer was used for FTIR spectroscopy analysis. The parameters we used to obtain the FTIR spectra were as follows: signal-to-noise ratio - 36,000:1, spectral range = 25,000–20 cm⁻¹, and resolution = 0.5 cm⁻¹. The particle size of the amphiphilic microspheres after swelling was measured by a Malvern laser particle size analyzer (MS3000) at 25°C.

Swelling Experiments

The analyses of the equilibrium and dynamic swelling characteristics of all of the amphiphilic microspheres were performed in an excess amount of simulated formation water. A certain quantity of microspheres was put into a small bag made by nickel mesh. Then, the nickel mesh bag with the microspheres was left to swell in buffer solutions under different environments to achieve swelling equilibrium. The swollen microspheres were taken out at regular time intervals, wiped superficially with filter paper, weighed, and placed again in the same immersion bath. The swelling ratio at time *t* (*Q_t*) was calculated by eq. (1):

$$Q_t = \frac{m_t - m_0}{m_0} = \frac{W_t}{m_0} \quad (1)$$

where *m*₀ is the initial weight of the dried microspheres, namely, the weight at *t* = 0, *m_t* is the weight after a time *t*, and *W_t* is the weight of water uptake at a time *t*.

Displacement Tests

The displacement tests were conducted with sandpack models 50 cm in length and 2.5 cm in diameter with two pressure taps (Figure 1). Sand of 250–300 mesh was wet-packed in the sandpack. The synthetic brine (total dissolved solids = 20,000 mg/L) was first injected into the sandpack at a constant rate of 1 mL/min by a constant flow pump until the pressure reached a stable value. After that, a certain amount of microsphere solution (2500 mg/L) was injected at the same flow rate. Subsequently, the brine was injected into the sandpack again. Throughout the entire process, the pressures were monitored to evaluate the

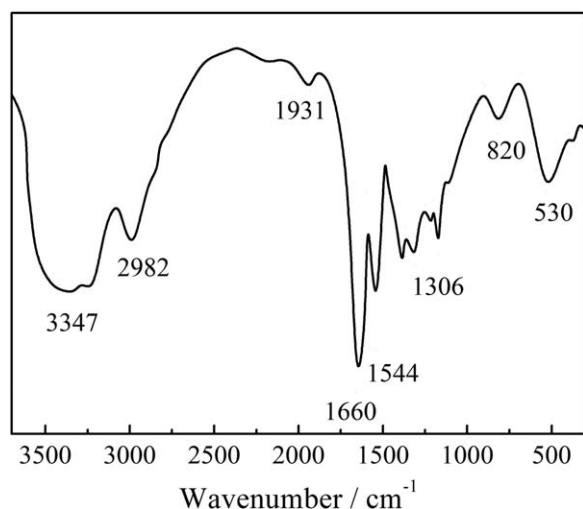


Figure 2. FTIR spectrum of the AM/4-VBC copolymer microspheres.

injection and migration performance of the microspheres in the porous medium.

The laboratory oil displacement experiment was carried out as follows. The wet-packed sandpack was flooded with the oil sample until the water production ceased. Thereafter, brine flooding continued until the water cut was greater than 98%. After that, a 0.3 pore volume (PV) of the microsphere solution slug was injected (2500 mg/L); this was followed by water flooding until the water cut of the efflux reached 98% again.

RESULTS AND DISCUSSIONS

Characterization of the Amphiphilic Microspheres

The IR spectrum of the microsphere is reported in Figure 2. The broad band observed around 3347 cm^{-1} was the characteristic peak of the —NH_2 stretching from the amide group. The peak at 1660 cm^{-1} was characteristic of C=O stretching from the amide group. The peak observed at 2982 cm^{-1} was assignable to the C—H stretching from the phenyl group, and the peak at 1544 cm^{-1} was due to the benzene skeleton vibrations. The peak

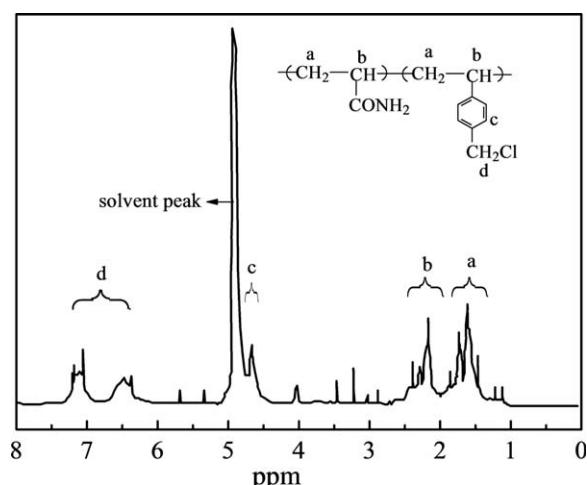


Figure 3. Expansion of the 500-MHz $^1\text{H-NMR}$ spectra of the AM/4-VBC copolymer microspheres with D_2O as the solvent.

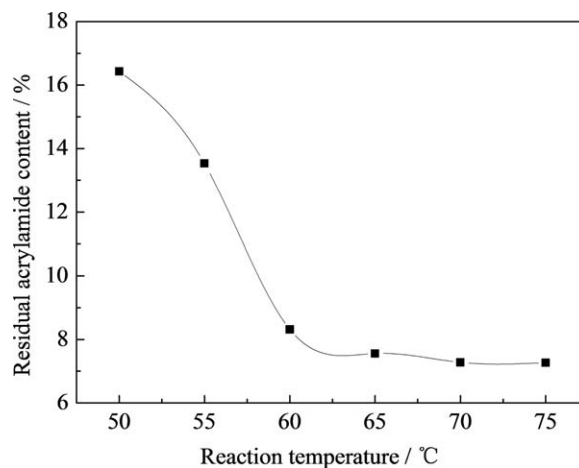


Figure 4. Influence of the reaction temperature on the residual monomer amount.

at 820 cm^{-1} was due to the out-of-plane bending vibrations of C—H from the *p*-substituent benzene. The FTIR spectrum showed that AM and 4-VBC were copolymerized to form the microspheres. In addition, the complete $^1\text{H-NMR}$ spectrum (Figure 3) assignment was straightforward: methylene protons H [Figure 3(a)] at 1.1–1.9 ppm, methane proton H [Figure 3(b)] at 2.0–2.5 ppm, chloromethyl protons H at 4.7 ppm, and phenyl protons H [Figure 3(c)] at 6.4–7.3 ppm. The peak at 4.9 ppm belonged to deuterium from the D_2O solvent. According to the analysis of the FTIR and $^1\text{H-NMR}$ spectra, the prepared product was indicated to be a microsphere copolymer of 4-VBC and AM.

Preparation of the Microspheres

The influence of the concentration of the AIBN initiator on the conversion rate at 60°C was studied. When the AIBN concentration was lower than 0.2% (weight percentage of the total monomer), the reaction rate was low, and the conversion rate was no more than 80% in 10 h. However, if the AIBN concentration exceeded 0.7%, the reaction rate was very high, and the gel block began to appear at the bottom of the flask. So, the amount of initiator fell somewhere between 0.2 and 0.7%. In addition, the influence of the temperature on the residual monomer content in 12 h is shown in Figure 4. With increasing temperature, there was a reducing trend of the residual AM content. However, when the reaction temperature rose above 60°C , the decrease of the residual monomer was not obvious. In this study, the conversion rate was up to 92.0% when the reaction temperature was controlled to between 65 and 75°C in 12 h. Additionally, the influence of the dosage of the MBA crosslinking agent on the size of the microspheres was studied, as shown in Figure 5. The size of the microspheres after swelling equilibrium increased at first, then decreased to flatten with increasing amount of crosslinking agent. When the concentration of MBA was low, the degree of crosslinking was too low to form granular material. The size of the particle measured was small or not accurate. As the concentration of crosslinking agent increased, there was an optimal degree of crosslinking around 1.0%. When the concentration of MBA was higher than this value, the crosslinking degree of the microsphere was too high; this led to a decrease in the median diameter of the microspheres.

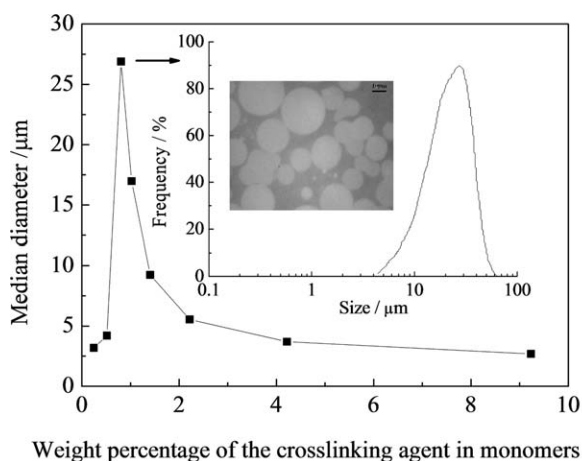


Figure 5. Relationship of the amount of the crosslinking agent to the microsphere size. (The scale bar is 10 μm .)

The morphology photo of the microspheres in pure water and the size distribution curve of the swollen microspheres are also shown in Figure 5. Most of the microsphere particles were closely spherical and could be highly dispersed in pure water. The size distribution of particles after swelling equilibrium ranged from 4 to 62 μm . The sample in subsequent experiments was prepared under the following conditions: the initiator concentration was 0.5%, the reaction temperature and time were 70°C and 12 h, and the concentration of crosslinking agent was 1.0%.

Swelling Behavior

The swelling behavior of the microspheres depended on the nature of the microspheres and the environmental conditions, including the salt concentration and the temperature. The swelling ratios as a function of time for the microspheres in solutions with different salinities are shown in Figure 6. As shown in this figure, there was a decreased swelling ratio with increasing water salinity. The lower the NaCl concentration was, the faster the swelling rate and the shorter the time needed for reaching swelling equilibrium were. This was expected because the effect of

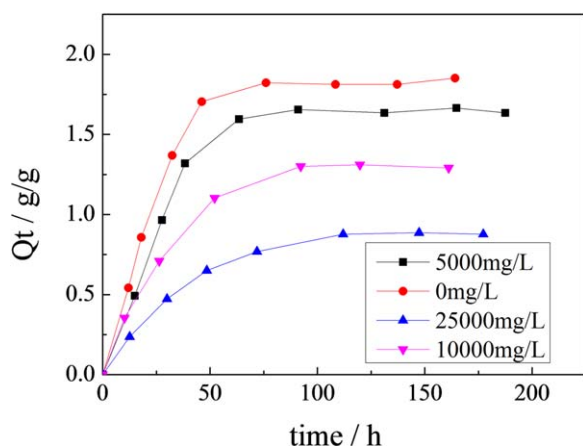


Figure 6. Swelling ratios of the microspheres in different water salinities (25°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

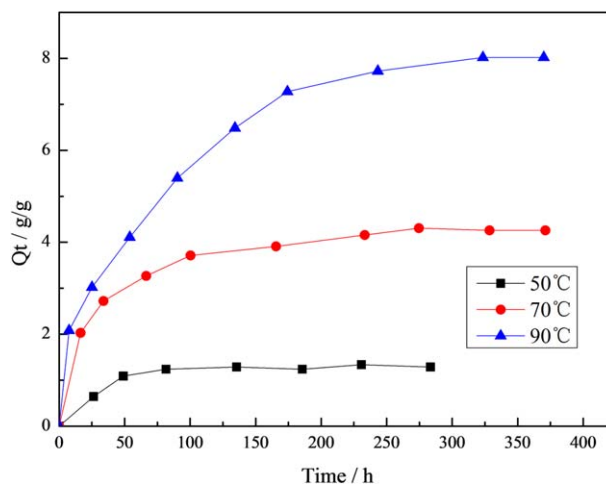


Figure 7. Swelling ratios of the microspheres at different temperatures in 25,000 mg/L brine. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

compressing the thicknesses of the electric double layer and hydration layer of the ionic groups in the microspheres was caused by the electrolytes; this reduced the repulsion and caused macromolecular chain contraction with smaller hydrodynamic volumes and resulted in a decrease in the swelling ratio.

The swelling ratios gradually increased with increasing temperature, as shown in Figure 7. Although the hydrogen bonding force between the water and the polymeric chain in the microspheres decreased with increasing temperature, the entropy of the water and macromolecular chain increased with increasing temperature, and the dispersion force of the water molecules was smaller than the attraction force of the water and macromolecular chain. As a result, the free water moved from the surrounding into the microspheres.

Displacement Performance

The flow of the microsphere system in porous media was of considerable practical importance in applications such as tertiary oil recovery.

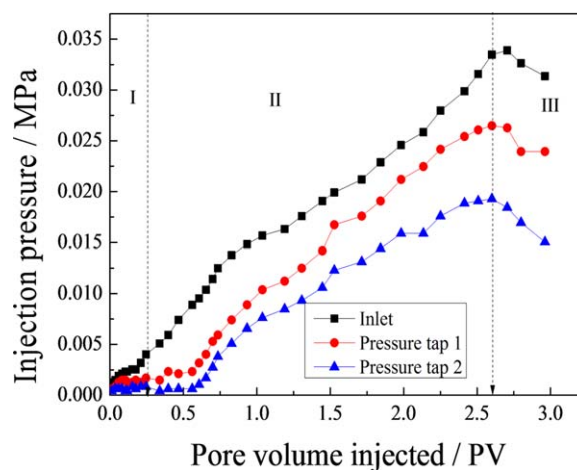


Figure 8. Variation of the injection pressures during the injection of the 2500 mg/L microsphere solution. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Summary of the Microsphere Flooding and Polymer Flooding Tests in the Sandpack Model (2500 mg/L)

Condition	Displacing fluid	Permeability (μm^2)	Permeability ratio	Recovery of water flooding (%)	Final oil recovery (%)	Tertiary recovery (%)
Homogeneous	Microsphere system	0.403	—	46.3	61.5	15.2
		0.595	—	47.9	62.3	14.4
		0.791	—	49.3	65.7	16.4
	SL3230	0.414	—	46.9	61.1	14.2
	DH102	0.802	—	50.1	65.0	14.9
Heterogeneous	Microsphere system	0.812/0.413	1.97	41.2	61.5	20.3
		1.324/0.396	3.34	37.9	56.4	18.5
		0.804/0.386	2.08	40.5	56.1	15.6

The flow experiment was designed to measure the transport property of the microspheres in porous media. We performed the flow test at 3000 mg/L, but the experiment failed because of serious blockage. So, the flow experiment was carried out at a concentration of 2500 mg/L because if the microspheres could transport successfully in porosity medium at 2500 mg/L, it could also transport at concentrations below this limit. Figure 8 shows the variation of the injection pressures along the sandpack with the injection volume. In stage II, with increasing PV injected, the pressure of each measurement point increased gradually. This showed that the microspheres prepared could transport uniformly in porous media without partial blocking when the permeability was $0.436 \mu\text{m}^2$. When the pressure no longer rose, the dynamic retention reached equilibrium, but the balance was difficult to achieve. In our experiment, the injection pressure still increased continuously; even the PV of the injected microsphere flooding reached 20.

The ability to enhance the oil recovery of the microspheres at 80°C was also investigated in this study. The oil sample used in this study was dehydrated oil (asphaltenes = 7.8%, resins = 33.9%, oily constituents = 58.3%) from Shengli Oilfield, and its viscosity was 56 mPa s at 80°C . A series of oil-displacement experiments were carried out at 80°C with homogeneous and heterogeneous sandpack models ($\Phi = 2.5 \times 20 \text{ cm}^2$). It was necessary to state that the heterogeneous sandpack model was simulated by two parallel sandpacks ($\Phi 2.5 \times 20 \text{ cm}$) with different permeabilities. This model can amount to the kind of formation with an aquifuge between the two permeability zones. The tertiary recovery of microsphere flooding and the final oil recovery of each flood test are shown in Table I. Under our laboratory conditions, the ability to enhance the oil recovery (18.5–20.3%) of the microsphere under heterogeneous conditions (permeability ratio = 1.97–3.34) was higher than that (15.2–14.6%) under homogeneous conditions (permeability range = $0.4\text{--}0.8 \mu\text{m}^2$). In similar conditions, the experiments of polymer flooding were carried out for comparison with microsphere flooding. Two polymer samples were used in this study: ultra-high-molecular-weight polyacrylamide (SL3230) and hydrophobically associating polyacrylamide (DH102). The intrinsic viscosities of SL3230 and DH102 were 2317 and 1355 mL/g, respectively. From the data in Table I, the tertiary recovery of the microsphere system was

observed to be slightly better than that of polymer flooding under homogeneous conditions. However, under heterogeneous conditions, the tertiary recovery of the microsphere system (20.3%) was far greater than that of polymer flooding (12.6%) within a suitable range of permeability ratios (1.97–2.08). The results indicate that the microsphere synthesized enhanced the oil recovery and would be more suitable for heterogeneous formation. Research into the modification and properties based on this amphiphilic microsphere is scheduled for the future.

CONCLUSIONS

Functional amphiphilic microspheres containing benzyl chloromethyl groups were prepared by the suspension polymerization of AM, 4-VBC, and *N,N*-methylene bisacrylamide (MBA) in DMF with AIBN as an initiator. The structure of the amphiphilic microspheres were determined by means of FTIR spectroscopy and $^1\text{H-NMR}$. The amount of initiator should have been somewhere between 0.2 and 0.7%. The reaction temperature should have been controlled at between 65 and 75°C in 12 h. There was an optimal degree of crosslinking when the amount of crosslinking agent was 1.0%. The size distribution of microspheres after swelling equilibrium ranged from 4 to $62 \mu\text{m}$. The swelling ratio decreased with increasing water salinity. The swelling ratios gradually increased with increasing temperature. The displacement tests showed that the prepared microspheres transported uniformly in porous media without partial blocking when the permeability was $0.436 \mu\text{m}^2$ and would be more suitable for heterogeneous formation in EOR.

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