

Preparation and Characterization of Polyacrylamide Nanomicrospheres and its Profile Control and Flooding Performance

Chuanjin Yao, Guanglun Lei, Lei Li, Xuemei Gao

Department of Reservoir Engineering, School of Petroleum Engineering, China University of Petroleum (East China), No. 66 Changjiang West Road, Economic and Technological Development Zone, Qingdao 266580, Shandong, China
Correspondence to: C. Yao (E-mail: ycj860714@yahoo.com.cn)

ABSTRACT: In this study, a new profile control and flooding agent “polyacrylamide nanomicrospheres” with particle size of 120–180 nm was prepared by inverse microemulsion polymerization. The viscoelasticity of polyacrylamide nanomicrospheres and the swelling property of polyacrylamide nanomicrospheres in aqueous solution were characterized. Using sand pack models, the profile control and flooding performance of polyacrylamide nanomicrospheres was studied. The results show that the polyacrylamide nanomicrospheres have better elasticity; the polyacrylamide nanomicrospheres have obvious swelling property, which depends on the concentration of NaCl and temperature; the polyacrylamide nanomicrospheres can plug sand pack effectively and have better ability of transporting and plugging in porous media; the polyacrylamide nanomicrospheres prefer to plug high permeability layer selectively so as to increase the swept volume and enhance oil recovery of low permeability layer and low permeability area in high permeability layer; the polyacrylamide nanomicrospheres can enhance oil recovery by 11–14%. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: polyacrylamide nanomicrospheres; viscoelasticity; migration property; plugging property; profile control and flooding; enhanced oil recovery

Received 13 December 2011; accepted 18 March 2012; published online 00 Month 2012

DOI: 10.1002/app.37727

INTRODUCTION

The oil recovery of reservoirs is mainly controlled by the sweep factor and oil displacement efficiency. For the heterogeneous oilfields, the sweep factor of sweep factor of water flooding is an important evaluation parameter. It not only represents the sweep status of water flooding status of water flooding, but also influences the ultimate recoverable reserves and oil recovery.

In recent years, many profile control and flooding agents have been used to control water and enhance oil recovery in high water-cut stage of heterogeneous oilfields. Koch and McLaughlin¹ used inorganic gels to control profile for water injection wells successfully. Chen² researched nonpolymer gels for water control treatment of reservoir treatment of reservoir. However, due to nonorganic gels was not selective on oil, the success rate of construction was low and the selective profile control and flooding technology based on polymer or crosslinked polymer gels got a better development and application. Nanda et al.³ studied the characteristics of polyacrylamine-Cr⁶⁺ gels used for reducing water/oil ratio. Liang et al.⁴ found that gels could reduce water permeability more than oil permeability. Herbas et al.⁵ set up a model to study polymer gels treatment test to

improve the injection profile and the sweep factor in a water injector. Gels for high-temperature water control^{6–8} and *in situ* gels have also been studied in recent years. Cheng et al.⁹ obtained “colloidal dispersion gels” by crosslinking low concentration polymer solution with small amount of chromium acetate or aluminum citrate. Chauveteau et al.^{10–12} invented the microgels for water control. The microgels are colloidal particles of acrylamide-based polymeric gels crosslinked with zirconium whose properties are affected by salinity, pH, shear rate etc. Therefore, their resistance is weak. Particle gels^{13–15} have also been used to improve the water injecting profile, but the particle gel had no define shape.

The relationship between sandstone permeability (k , μm^2), porosity (ϕ , function), and average radius of pore throats (r , μm) can be expressed by the equation¹⁶:

$$r = \sqrt{8k/\phi} \quad (1)$$

For the sandstone formation with permeability of 0.001–10 μm^2 and porosity of 30%, the average radius of pore throats is 0.163–16.3 μm . The result shows that the pore throats of

Table I. A Recipe for Preparing Polyacrylamide Nanomicrospheres

Phase	Material	Mass/g
O	[D] m(Sapn80) : m(Tween60) = 3 : 2 (emulsifier)	9.80
	<i>n</i> -Hexane (dispersion agent)	65.30
W	[AM] Acrylamide (monomer)	3.30
	[MBA] <i>N,N'</i> -methylene bisacrylamide (crosslinking agent)	0.08
	[APS] Ammonium persulfate (initiator)	0.16
	Deionized water	21.35

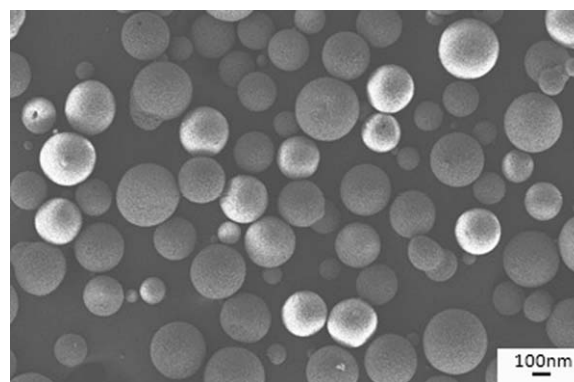
sandstone reservoirs are nanoscale/microscale. Therefore, the size of an ideal profile control and flooding agent should also be nanoscale/microscale. Based on this idea, a new profile control and flooding agent “polyacrylamide nanomicrospheres” was designed.

In this article, the polyacrylamide nanomicrospheres were prepared by inverse microemulsion polymerization. The storage modulus (G') and loss modulus (G'') of the polyacrylamide nanomicrospheres were measured using M5600 HPHT Rheometer. The variation of average particle size was used to characterize the swelling property of polyacrylamide nanomicrospheres in aqueous solution. Using a long sand pack model, the migration and plugging properties of polyacrylamide nanomicrospheres were studied. At last, a series of two-tube heterogeneous sand pack models were used to simulate the heterogeneity of reservoirs, and the profile control and flooding performance of polyacrylamide nanomicrospheres was studied.

EXPERIMENTAL

Materials

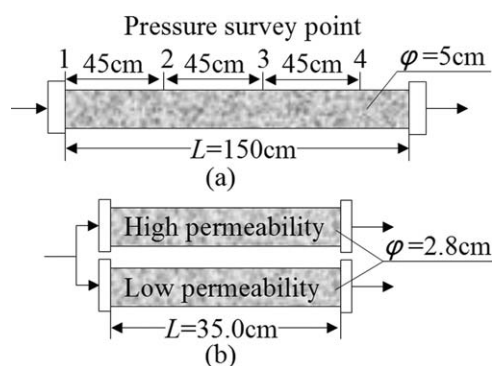
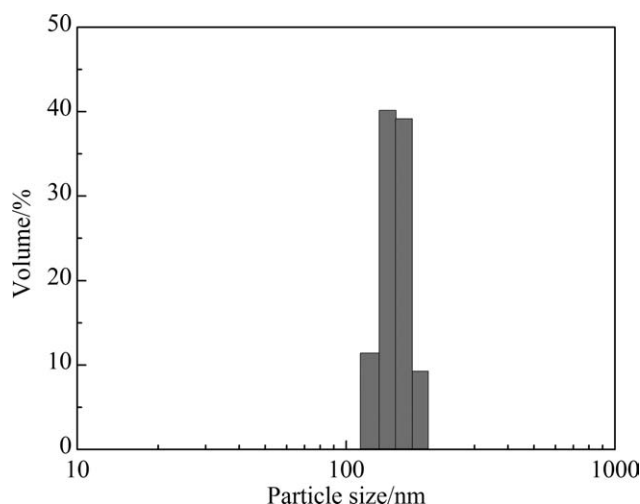
Acrylamide (AM, purity above 98.5%), *n*-Hexane (purity above 99.5%), dispersion stabilizer (D, Span80 and Tween60) and ammonium hydroxide (NH_4OH , purity above 99.5%) were all purchased from Sinopharm Chemical Reagent (China). *N,N'*-methylene bisacrylamide (MBA, purity above 98.0%) was obtained from Shanghai Chemical Reagent Company of Sinopharm (China). Ammonium persulfate (APS, purity above 98.0%) was supplied by Shanghai Aijian Degussa Initiator (China). Sodium

**Figure 2.** SEM micrograph of polyacrylamide nanomicrospheres in aqueous solution.

chloride (NaCl, purity above 99.5%) was obtained from Nanjing Chemical Reagent (China). All reagents were used without any further purification. Deionized water was used for the preparation of all aqueous solutions. The sand of size 10–100 mesh was obtained from Block Gudao in Shengli Oilfield in China. The simulated oil sample with viscosity (μ_o) of 18 mPa s^{-1} and density (ρ_o) of 947.2 kg m^{-3} at 50°C was prepared using degassed crude oil from Block Gudao in Shengli Oilfield in China mixing a certain proportion of kerosene.

Preparation of Polyacrylamide Nanomicrospheres

The polyacrylamide nanomicrospheres were prepared through inverse microemulsion polymerization.^{17,18} The polymerization was carried out in a 250 mL three-neck flask. The flask was equipped with mechanical stirrer, reflux condenser, dropping funnels, and constant temperature water bath. A typical recipe for the inverse microemulsion polymerization is presented in Table I. First, 65.30 g of *n*-Hexane (dispersion agent) and 9.80 g of emulsifier [m (Sapn80) : m (Tween60) = 3 : 2] were introduced into the three-neck flask. The flask was then placed in the water bath at the constant temperature of 33°C with a stirring rate of 360 rpm. After complete dissolution of the

**Figure 1.** Basic parameter of (a) long sand pack model and (b) heterogeneous sand pack model.**Figure 3.** Particle size distribution of polyacrylamide nanomicrospheres.

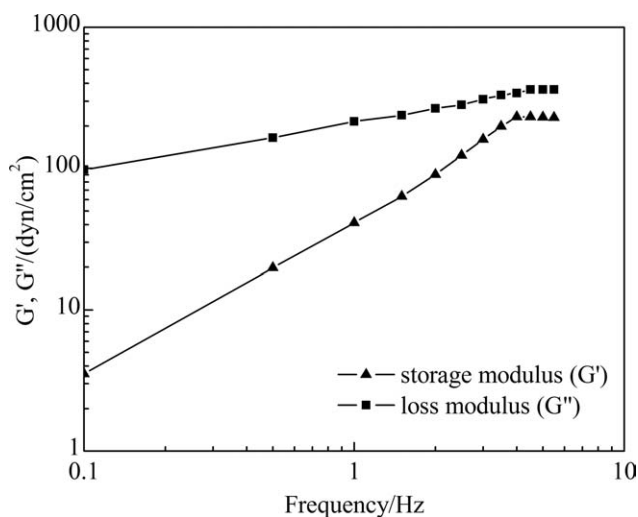


Figure 4. Storage modulus (G') and loss modulus (G'') of polyacrylamide nanomicrospheres (without solvent) versus frequency at 50°C.

emulsifier in *n*-Hexane, the aqueous solution of AM, MBA, and APS (3.30 g of AM, 0.08 g of MBA, and 0.16 g of APS were dissolved in 21.35 g deionized water) in the dropping funnel was dripped into the reactor with an appropriate dripping rate (1–2 drops per second). Simultaneously, the mixture in the flask was stirred with a stirring rate of 360 rpm. When the water phase was suspended in the oil phase completely to form W/O microemulsion, the temperature was increased to 75°C to initiate the polymerization of monomers. NH₄OH (20 wt %) was added to adjust the pH to about 7.0. Then the temperature was kept at 75°C for 60 min. Finally, the mixture in the flask was cooled and filtered. Thus, polyacrylamide nanomicrospheres were obtained.

Characterizations

EVO 18 scanning electron microscopy (Carl Zeiss, Germany) was used to analyze the physical structure of the polyacrylamide

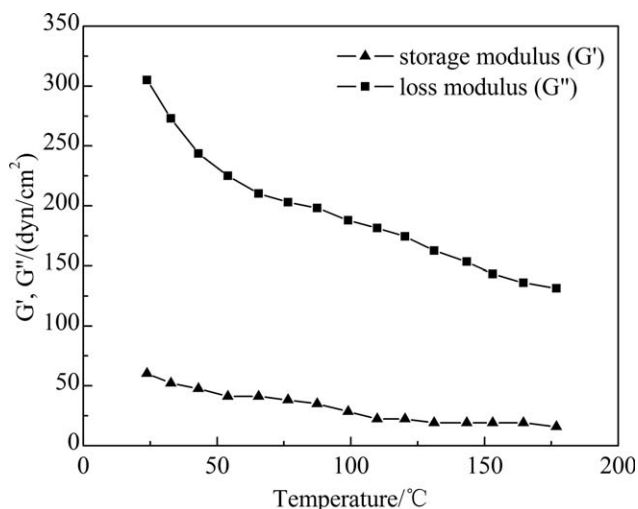


Figure 5. Storage modulus (G') and loss modulus (G'') of polyacrylamide nanomicrospheres (without solvent) versus temperature at 1 Hz.

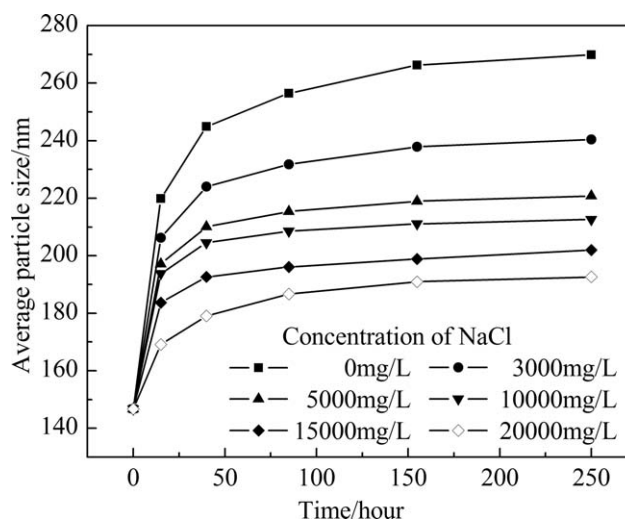


Figure 6. Variation of average particle size of polyacrylamide nanomicrospheres in aqueous solution versus time at different salinity (50°C).

nanomicrospheres. The particle size of the polyacrylamide nanomicrospheres was measured by Rise-2008 laser particle size analyzer (Jinan Runzhi Science and Technology Corporation, China) at 25°C. M5600 HPHT rheometer (Grace) was used to measure the storage modulus (G') and loss modulus (G'') of the polyacrylamide nanomicrospheres (without solvent) versus temperature and frequency. The variation of particle size was measured to characterize the swelling property of polyacrylamide nanomicrospheres in aqueous solution. Long sand pack model with four survey points was used to characterize the migration and plugging properties of polyacrylamide nanomicrospheres in porous media. Using a series of two-tube heterogeneous sand pack models, the profile control, and flooding performance of polyacrylamide nanomicrospheres in heterogeneous reservoirs.

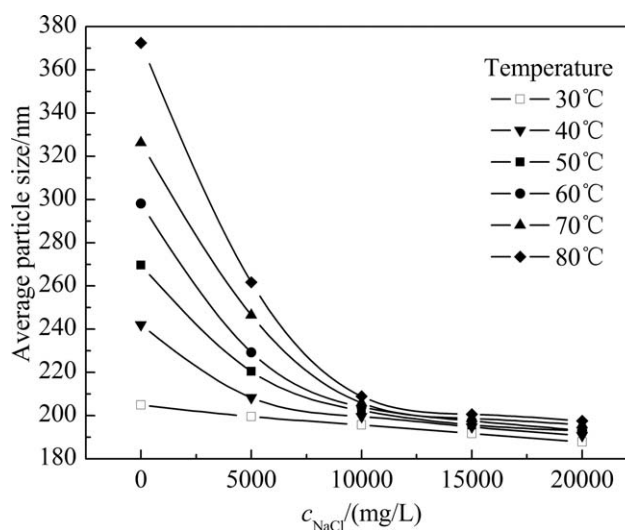


Figure 7. Variation of average particle size of polyacrylamide nanomicrospheres in aqueous solution versus salinity at different temperature (250 h).

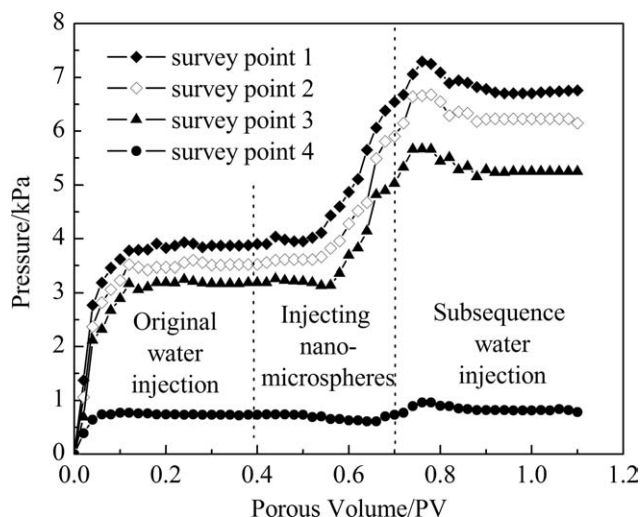


Figure 8. Variation of pressure at each survey point during polyacrylamide nanomicrospheres moving in long sand pack model at 30°C.

The long sand pack model and two-tube heterogeneous sand pack models were all packed with sand from Block Gudao in Shengli Oilfield, China. Figure 1 shows the basic parameters of long sand pack model and two-tube heterogeneous sand pack model.

RESULTS AND DISCUSSION

Physical Property and Structure

The polyacrylamide nanomicrospheres are milk-white. The effective content is 95–98%. The density is about 1.0 g cm⁻³. The viscosity of polyacrylamide nanomicrospheres solution is <1.5 mPa s⁻¹ and the pH value is 6.0–8.0. Figure 2 is SEM micrograph of the polyacrylamide nanomicrospheres in aqueous solution. Figure 2 shows that the polyacrylamide nanomicrospheres are spherical particles. The particle size distribution of the polyacrylamide nanomicrospheres is shown in Figure 3. It can be seen that the particle size of the polyacrylamide nanomicrospheres is 120–180 nm, and the average value is 146.7 nm.

Viscoelasticity of Polyacrylamide Nanomicrospheres

The storage modulus (G') and loss modulus (G'') of the polyacrylamide nanomicrospheres (without solvent) versus frequency and temperature are given in Figures 4 and 5. It can be seen that the storage modulus and loss modulus of polyacrylamide nanomicrospheres increase with the increase of frequency and decrease with the increase of temperature. When the frequency is 1 Hz and the temperature is 25°C, the storage modulus (G') is 59.25 dyn cm⁻² and the loss modulus (G'') is 300.71 dyn cm⁻². The storage modulus (G') and loss modulus (G'') are still large even at a high temperature. At 175°C and 1 Hz, the storage modulus (G') is 132.07 dyn cm⁻² and the loss modulus (G'') is 16.46 dyn cm⁻². The results indicate that the polyacrylamide nanomicrospheres have better viscoelasticity and can be used in the high-temperature reservoir. Because of the elasticity, the polyacrylamide nanomicrospheres can easily transport into the deep area of oil formation, resist water to change the flow direction, and increase the sweep efficiency of oil reservoirs.

Swelling Property of Polyacrylamide Nanomicrospheres in Aqueous Solution

The polyacrylamide nanomicrospheres can swell through absorbing water. The original average particle size of polyacrylamide nanomicrospheres is 146.7 nm. The variation of the average particle size of polyacrylamide nanomicrospheres in aqueous solution is given in Figures 6 and 7. Figure 6 shows that the average particle size increases with the increase of time and obtains the maximum value when the time is about 250 h. Figure 7 shows that the average particle size increases with the increase of temperature. Figures 6 and 7 also show that the average particle size decreases with the increase of concentration of NaCl. When the concentration of NaCl is >10,000 mg L⁻¹, the variation of average particle size is not obvious. In fact, polyacrylamide nanomicrospheres are crosslinked particles with three-dimensional network structure and many free hydrophilic groups (—CONH₂) inside. Polar water molecules can combine with these groups easily, and cause nanomicrospheres to swell.

Table II. Enhanced Oil Recovery of Polyacrylamide Nanomicrospheres in Heterogeneous Sand Pack Model

Model No.	Concentration of nanomicrospheres (wt %)	Sand pack type	k (μm^2)	Recovery of water flooding (%)		Recovery of nanomicrospheres (%)		EOR (%)	
				Single	Total	Single	Total	Single	Total
1	1000	High permeability tube	1.81	48.86	40.80	54.90	52.08	6.04	11.28
		Low permeability tube	0.73	32.73		46.35		13.62	
2	1500	High permeability tube	1.75	45.83	37.97	52.60	50.32	6.77	12.35
		Low permeability tube	0.68	30.11		45.97		15.86	
3	2000	High permeability tube	1.92	51.92	40.62	57.24	54.18	5.32	13.56
		Low permeability tube	0.71	29.31		45.52		16.21	
4	2500	High permeability tube	1.68	49.56	39.05	55.68	52.85	6.12	13.80
		Low permeability tube	0.66	28.53		44.88		16.35	
5	3000	High permeability tube	1.72	50.23	40.09	55.41	53.95	5.18	13.86
		Low permeability tube	0.75	30.15		46.18		16.03	

However, inorganic ions can compress the hydration layer and reduce the hydration degree. Thus, the particle size is smaller when the concentration of NaCl is higher. The particle size of polyacrylamide nanomicrospheres varies with the concentration of NaCl. High temperature will lead to the polymer network outward expansion, and the water absorption will increase too. The result shows that polyacrylamide nanomicrospheres have better swelling property. This property can increase their plugging capacity in deep formation of reservoirs.

Migration and Plugging Properties in Long Sand Pack Model

In this study, the permeability of the long sand pack model was $1.71 \mu\text{m}^2$. First, the brine water with salinity of 2000 mg L^{-1} was injected for 0.4 PV. Then, the polyacrylamide nanomicrospheres solution (1000 ppm) was injected for 0.3 PV. At last, only brine water was injected for 0.4 PV. Meanwhile, the pressure at each survey point was measured by pressure sensor (Qingdao Keeasy Biotech, China), respectively. The injection rate was 1 mL min^{-1} and the experimental temperature was 30°C .

The variation of pressure at each survey point is shown in Figure 8. It can be seen that during the injection of polyacrylamide nanomicrospheres solution, the pressure at survey point 1 increases first, then the pressure at survey point 2–4 increases in turn. The pressure does not increase until the moving front of polyacrylamide nanomicrospheres reaches. This result shows that the polyacrylamide nanomicrospheres can transport into the deep area of sand pack gradually. In the process of subsequent water injection, the pressure at each survey point increases further. This is caused by the swelling property of polyacrylamide nanomicrospheres in the sand pack. At the end of subsequent water injection, the injecting pressure (survey point 1) keeps about 7.0 kPa, and the resistant factor is three times more than that of the original water injection. Besides, the pressure near the exit end (survey point 4) is still lower than 0.8 kPa. This result shows that the polyacrylamide nanomicrospheres in the deep area of sand pack can be retained in the sand pack and plug the sand pack effectively. These results indicate that the polyacrylamide nanomicrospheres have better migration and plugging properties in porous media.

Profile Control and Flooding Performance in Heterogeneous Sand Pack Model

In this study, the polyacrylamide nanomicrospheres was hydrated in NaCl solution of $10,000 \text{ mg L}^{-1}$ for 10 days at 80°C . First, the brine water with salinity of 3000 mg L^{-1} was injected in sand pack model until the water-cut of output was 98%. Then, the polyacrylamide nanomicrospheres solution was injected for 0.5 PV. At last, only brine water with salinity of 3000 mg L^{-1} was injected until the water-cut of output was 98%. Meanwhile, the output volume of oil and water was measured by measuring cylinder, respectively. The injection rate was 1 mL min^{-1} and the experimental temperature was 30°C .

The parameter of the five heterogeneous sand pack model and the experimental results are given in Table II. Table II shows that the oil recovery of water flooding is 38–41%. After the pro-

file control and flooding of polyacrylamide nanomicrospheres, the oil recovery is up to 50–54%. The enhanced oil recovery (EOR) of polyacrylamide nanomicrospheres is 11–14%. Increasing the concentration of polyacrylamide nanomicrospheres solution can enhance oil recovery further. However, when the concentration of polyacrylamide nanomicrospheres is more than 2500 mg L^{-1} , the enhanced oil recovery becomes very small. Comparing the oil recovery of the high permeability tube with the low permeability tube in each model, it can be seen that the oil recovery mainly comes from the low permeability tube. This result indicates that the polyacrylamide nanomicrospheres prefer to plug high permeability layer selectively to improve the swept volume of low permeability layer. Besides, the polyacrylamide nanomicrospheres can also improve the sweep condition and flooding effect of low permeability area in high permeability layer.

CONCLUSIONS

A new profile control and flooding agent “polyacrylamide nanomicrospheres” with particle size of 120–180 nm, effective content of 95–98%, and density of 1.0 g cm^{-3} is prepared by inverse microemulsion polymerization. The polyacrylamide nanomicrospheres have better viscoelasticity even at 175°C and can be used in the high-temperature reservoir. The polyacrylamide nanomicrospheres have obvious swelling property. How large they can expand depends on the concentration of NaCl and temperature. The polyacrylamide nanomicrospheres have better migration and plugging properties in porous media. The polyacrylamide nanomicrospheres prefers to plug high permeability layer selectively and improve the sweep condition and flooding effect of low permeability layer and low permeability area in high permeability layer. The polyacrylamide nanomicrospheres can enhance oil recovery by 11–14%. The results are very useful for the application of polyacrylamide nanomicrospheres in the profile control and flooding of heterogeneous reservoirs.

ACKNOWLEDGMENTS

The research was supported by “the Fundamental Research Funds for the Central Universities” (No. 11CX06025A) and Graduate Innovation Fund Supported Project of China University of Petroleum (East China) (No. CXZD11-04).

REFERENCES

1. Koch, R. R.; McLaughlin, H.C. Paper No. SPE 2847, SPE Practical Aspects of Improved Recovery Techniques Symposium, Fort Worth, Texas, USA, March 8–9, 1970.
2. Chen, K. S. Paper No. SPE 17674, Offshore South East Asia Show, Singapore, February 2–5, 1988.
3. Nanda, S. K.; Kumar, R.; Sindhvani, K.L.; Goyal, K.L. Paper No. SPE 16253, SPE International Symposium on Oilfield Chemistry, San Antonio, Texas, USA, February 4–6, 1987.
4. Liang, J.; Sun, H.; Seright, R. S. Paper No. SPE 24195, SPE/DOE Enhanced Oil Recovery Symposium, Tulsa, Oklahoma, USA, April 22–24, 1992.

5. Herbas, J.; Moreno, R.; Amaury, M. T.; Romero, M. F.; Coombe, D. Paper No. SPE 92025, SPE International Petroleum Conference in Mexico, Puebla Pue., Mexico, November 7–9, **2004**.
6. Peng, B.; Li, M. Y.; Ji, S. L.; Wu, Z. L. *Chem. Eng.* **1998**, *45*, 171.
7. Li, M. Y.; Wu, Z. L. *Chem. Oilfield* **2000**, *33*, 343.
8. Wang, D. M.; Seright, R. S.; Shao, Z. B., Wang, J. M. *SPEE* **2008**, *11*, 1117.
9. Chang, H. L.; Sui, X. G.; Xiao, L.; Guo, Z. D.; Yao, Y. M.; Xiao, Y. G.; Chen, G.; Song, K. P.; James, C. M. *SPEE* **2004**, *49*, 664.
10. Chauveteau, G.; Omari, A.; Tabary, R.; Renard, M.; Veerapen, J.; Rose, J. Paper No. SPE 64988, SPE International Symposium on Oilfield Chemistry, Houston, Texas, USA, February 13–16, **2001**.
11. Chauveteau, G.; Tabary, R.; Bon, C.; Renard, M.; Feng, Y. J.; Omari, A. Paper No. SPE 82228, SPE European Formation Damage Conference, Hague, Netherlands, May 13–14, **2003**.
12. Chauveteau, G.; Tabary, R.; Blin, N.; Renard, M.; Rousseau, D.; Faber, R. Paper No. SPE 89390, SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA, April 17–21, **2004**.
13. Bai, B. J.; Huang, F. S.; Liu, Y. Z.; Seright, R. S.; Wang, Y. F. Paper No. SPE 113997, SPE/DOE Symposium on Improved Oil Recovery, Tulsa, Oklahoma, USA, April 20–23, **2008**.
14. Dalrymple, D.; Eoff, L.; Vasquez, J.; Eijden, J.V. Paper No. SPE 114886, SPE Russian Oil and Gas Technical Conference and Exhibition, Moscow, Russia, October 28–30, **2008**.
15. Wu, Y. S.; Bai, B. J. Paper No. SPE 115678, SPE Annual Technical Conference and Exhibition, Denver, Colorado, USA, September 21–24, **2008**.
16. Chen, J. J.; Yang, J.; Tian, L. *Adv. Earth Sci.* **2007**, *22*, 997.
17. Zhao H. Z.; Wu, Z. L.; Zheng, X. Y. *Fine Chem.* **2005**, *22*, 62.
18. Cao, T. Y.; Dai, B.; Dai, J. Y. *Polym. Bull.* **1995**, *8*, 174.