

# Investigation on preparation of poly (AM/SSS/AMPS) microspheres by dispersion polymerization system

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**Abstract.** The present work had the purpose of developing a class of terpolymer plugging microspheres for petroleum engineering. The terpolymer microspheres were prepared by dispersion copolymerization of acrylamide (AM), sodium 4-styrenesulfonate (SSS) and 2-acrylamido-2-methyl propane sulfonic acid (AMPS), using ethanol/deionized water as dispersion medium, polyvinyl pyrrolidone (PVP) as dispersant, N,N-methylenebisacrylamide (MBA) as crosslinking agent and potassium persulfate (KPS) as initiator. The influences of dispersion medium volume ratio, concentration of dispersant, pH value and stirring speed on the stability of dispersion system were investigated. The results showed that the stable dispersion system was obtained when ethanol-water ratio was 50:50 (v: v), the dispersant content was 15 wt. % (total mass of monomers), pH value was 7 and stirring speed was 200 r/min, which was suitable for ternary dispersion polymerization. FTIR spectrum and SEM images indicated the structure and surface morphology of microspheres.

## 1. Introduction

Up to now some of the water based drilling muds used natural polymers or modified natural polymers as plugging agent, like xanthan gum [1], guar gum [2], tamarind gum [3,4], polyanionic cellulose (PAC) [5] or sodium carboxymethyl cellulose (NaCMC) [6,7]. However, this class of products is not very stable at salty and high temperature conditions. Therefore, it is important to develop new additives for water based muds (WBM) that would turn working fluids applicable throughout the whole drilling proceed. Polyacrylamide based microspheres have been widely used in the depth profile of oilfield in recent years [8, 9]. Because of their good elasticity, they can present elastic deformation under certain pressure and migrate through deep pore throat, arousing the wide attention of drilling engineering, especially for plugging micron scale cracks in fractured reservoir. Besides, these water-soluble polymers can control fluid loss and improve inhibition without large changes in fluid rheology. Compared with natural polymers, polyacrylamide based microspheres which are copolymerized with SSS and AMPS can also exhibit better thermal stability and salt tolerance due to the  $\text{SO}_3^-$ .

There are many methods for synthesizing polyacrylamide based microsphere such as inverse-phase suspension polymerization [10], inverse-phase emulsion polymerization [11], inverse-phase microemulsion polymerization [12] and dispersion polymerization [13]. Among these methods,



dispersion polymerization shows lower apparent viscosity, faster dissolution speed, lower vaporization heat of medium and simpler production process [14], which makes it have broad application prospects in the process of oilfield development.

In this paper, we have prepared poly (AM/SSS/AMPS) microspheres by dispersion polymerization. The present research is to investigate the influence of dispersing medium, dispersant dosage, pH value and stirring rate on the molecular weight, gel strength and conversion rate of the microsphere plugging agent. The obtained system presented good stability and some available conclusions are put forward as below.

## 2. Experimental sections

### 2.1. Raw materials

Acrylamide (AM, 98 %, CP), sodium 4-styrenesulfonate (SSS, 98 % CP) and 2-acrylamido-2- methyl propane sulfonic acid (AMPS, 98 %, CP) were purchased from Beijing Bei Hua Fine Chemical Co., Ltd.. Absolute ethanol (99.5 %), potassium persulfate (KPS, 98 %, CP) and polyvinyl pyrrolidone (PVP, 98 %, CP) were provided by Tianjing Guangfu Fine Chemical Research Institute, China. N, N-Methylene-bis-acrylamide (MBA, 99 %, AR) were provided by Aladdin Industrial Corporation, China. Deionized water was used for all experiments.

### 2.2. Synthesis of poly (AM/SSS/AMPS) microspheres

Firstly, the AM, SSS, AMPS monomers (20 wt.% of total system) and MBA (0.25 wt.% of monomers) soluted with deionized water (50 mL) were taken into a 100 mL beaker, using NaHCO<sub>3</sub> solution to adjust pH value. Secondly, desired amount of PVP was added into ethanol solution (50 mL) in a 250 mL three-necked flask equipped with a condenser. Then, the monomer solution was added slowly to the 250 mL three-neck flask with continuously stirred for 30 min at 50 °C. Finally, the KPS initiator was taken into the mixture with stirring. The reaction was carried out in nitrogen gas and maintained at 70 °C for 8 h. The sample was filtered and rinsed with ethanol for several times, and dried in vacuum at 80 °C for 24 h. The product was ground and sieved in the screen of 200 mesh.

### 2.3. Characterizations

Fourier transform infrared spectroscopy (FTIR) spectrum of sample was obtained at wave numbers ranging from 4,000 to 400 cm<sup>-1</sup> using a FTS-3000 spectrophotometer (American Digilab). Monomer conversion was measured by gravimetry method as formula (1). Viscosity was performed on a rheometer (HAAKE RheoStress600, Germany). All rheological measurements were performed at a temperature of 25 °C by using a Z41 cylinder-to-cylinder sensor in steady shear mode and were conducted with shear rate of 1000 s<sup>-1</sup>. Molecular weight of the sample was calculated by the empirical formula (2) through limiting viscosity measured by Ubbelohde viscometer. Scanning electron microscope (SU8010, HITACHI, Japan) was used to study the surface morphology of samples at an operating voltage of 5 KV.

$$P_y = (W_1/W_2) \times 100 \% \quad (1)$$

Where  $P_y$  is the synthetic yield,  $W_1$  is the weight of the dry samples (g), and  $W_2$  is the initial weight of the monomers (g).

$$[\eta] = 3.73 \times 10^{-4} M^{0.6} \quad (2)$$

Where  $\eta$  is the limiting viscosity,  $M$  is the molecular weight.

### 3. Results and Discussion

#### 3.1. FTIR analysis

FTIR spectrum of (AM-SSS-AMPS) terpolymer particles was shown in Fig. 1

In Fig. 1 for (AM-SSS-AMPS) terpolymer, transmittance bands at 2,925 represented C-H stretching, and a strong band at 3431  $\text{cm}^{-1}$  corresponded to N-H in AM. 1,662  $\text{cm}^{-1}$  represented C=O.

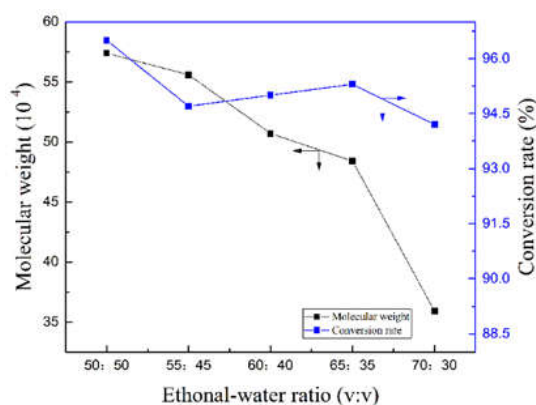


Fig. 1 FTIR spectrum

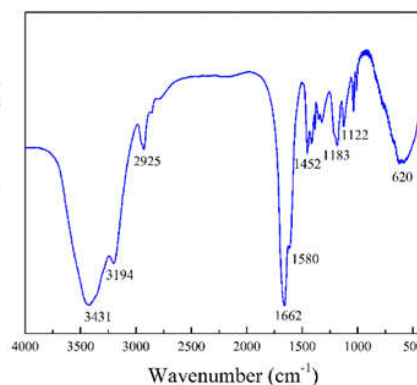


Fig. 2 Influence of ethanol-water ratio

Stretching vibration and antisymmetric stretching. Transmittance bands at 1452  $\text{cm}^{-1}$  represented the C-N stretching of AM and AMPS. 1,183  $\text{cm}^{-1}$  and 1,122  $\text{cm}^{-1}$  absorption peaks corresponded to the  $-\text{SO}_3$  antisymmetric stretching and stretching vibration of SSS. The peak of 620  $\text{cm}^{-1}$  may represent  $-\text{CH}_2$  rocking vibration. These showed that the AM, SSS and AMPS were synthesized successfully.

#### 3.2. Influence of ethanol-water ratio on the conversion rate and molecular weight

Through the previous experiments, it was found that ethanol-water mixed solvent can meet the requirements of AM dispersion polymerization, and aiming at the requirements of the ternary monomer dispersion system, ethanol-water solvent was still optimum. But when the ethanol volume percentage of the mixed solvent was more than 70%, the stability of the dispersion emulsion was poor and would appear layered phenomenon after a certain period. This was because ethanol presents poor solubility for PVP, and the more ethanol existed in the medium, the stronger PVP molecule chains contracted, which produced less stable effect of PVP on the whole system. When ethanol volume percentage of the dispersion medium was less than 50%, the product was easy to form gel-formation. This was because water was a good solvent for monomers, the more water existed in the medium, the more overlapping area of monomers molecular chains in solution, increasing the chance of cross-linking molecular chain by touching each other. Such situation can lead to form gel in dispersion emulsion. Thus, the ethanol volume percentage in the dispersed system should be controlled between 50% - 70%, the product can form a stable and milk-white emulsion.

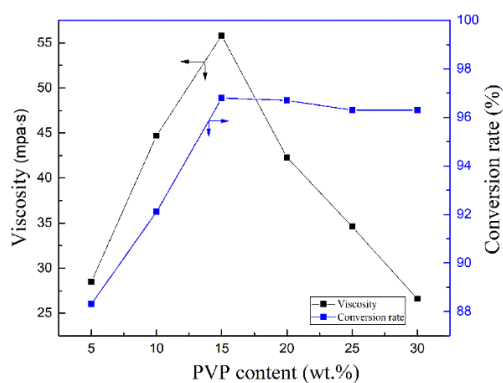
Ternary copolymerization was carried out by adjusting ethanol-water mixed ratio (v:v) as 50:50, 55:45, 60:40, 65:35 and 70:30, respectively. The obtained products presented uniform white latex and Fig. 2 showed the conversion rate and molecular weight. It can be seen from the Fig. 2, with the increase of ethanol in the mixed solvent, the molecular weight of products in the whole system was on the decline and monomer conversion rate changed not obviously. This was mainly because with the increase of ethanol-water ratio, rate of dispersion polymerization decreased, leading to the increase of particle diameter. In order to get the balance of molecular weight and conversion rate, ethanol-water ratio should keep at 50:50 (v:v).

### 3.3. Influence of PVP content on the conversion rate and viscosity

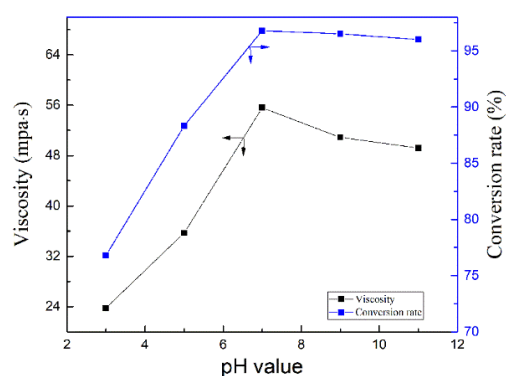
The effect of PVP content on conversion rate and gel strength of terpolymer microspheres was shown in Fig. 3. According to Fig. 3, with the increase of the dosage of PVP, the conversion rate of terpolymer microspheres gradually increased, and apparent viscosity increased to a maximum and then decreased. That was because, when PVP content was more than 15%, particle size of terpolymer microspheres further reduced, which increased the contact area between the particles and enhanced mutual acting force, leading to hindering the diffusion of monomer to the solid phase. Therefore, PVP content should be controlled appropriately about 15 wt. %.

### 3.4. Influence of pH value on the conversion rate

It was found from Fig. 4 that it was hard to form stable dispersion liquid under low pH value which also impacted the speed of droplet nucleation significantly during the dispersion process. Thus, the dispersion emulsion easily stratified. At first, the stability of the dispersion liquid increased with the increase of pH value and the dispersion liquid formed at the pH value of 6-7 can kept stable for a long time. When  $\text{pH} > 8$ , the system stability did not change obviously with the increase of pH value and the conversion rate changed slightly. It can be seen that the high pH value impacted little on the stability of dispersion system. However, with the increased of alkaline value in reaction system, the poor soluble gel produced more during the polymerization process. So, the pH value of water was useful to control the stability of dispersion and its value could be determined between 7 and 8.



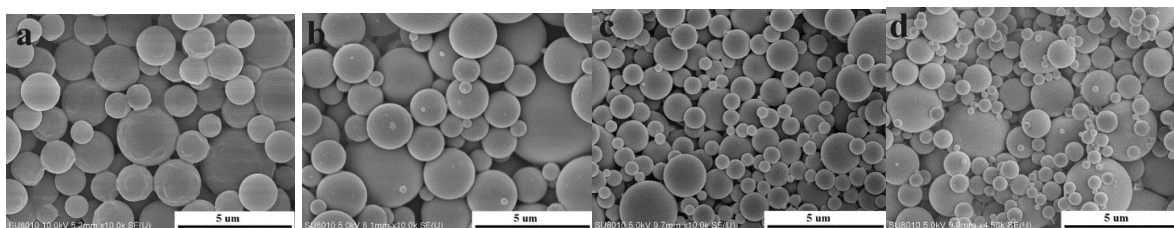
**Fig. 3** Influence of different PVP loading



**Fig. 4** Influence of different pH value

### 3.5. SEM Characterization

SEM images and surface behavior of poly (AM/SSS/AMPS) terpolymer were shown in Fig. 5. Fig. 5(a) - (d) showed SEM images of poly (AM/SSS/AMPS) microspheres with different stirring from 100 r/min to 400 r/min under overview. It was seen that dispersity and exterior morphology of the microsphere under 200 r/min were the best. In Fig. 5(a), it was evidently seen that the copolymer particles were of spherical shape with sticky surface due to monomer or oligomer residues and unsatisfied nucleation. In Fig. 5(d), at 400 r/min, the microsphere collisions were very serious among particles and surface smoothness was seriously affected due to the adhesion of small particles. Such surface roughness of these polymer microspheres can be eliminated by adjusting the stirring speed. Consequently, the microspheres with satisfactory surface behaviors were prepared when the stirring speed was 200 r/min.



**Fig. 5** SEM images of poly (AM/SSS/AMPS) microspheres under different stirring speed (a) 100 r/min, (b) 200 r/min (c) 300 r/min and (d) 400 r/min

#### 4. Conclusion

Poly (AM/SSS/AMPS) microspheres were successfully synthesized by dispersion polymerization. The optimized system was obtained when ethanol-water ratio was 50:50 (v:v), the dispersant content was 15 wt.% (total mass of monomers), pH value was 7, stirring speed was 200 r/min. The spherical surface and dispersity of the terpolymer microspheres was well tuned by adjusting the stirring speed. These spherical terpolymer microspheres can be the candidate materials for plugging formation microchannels or cracks.

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#### References

- [1] F.G. Ochoa, V.E. Santos, J.A. Casas, E. Gómez, Xanthan gum: production, recovery, and properties, *Biotechnol. Adv.* 18 (2000) 549-579.
- [2] R.M. Pérez, S.Siquier, N.Ramírez, A.J. Müller, A.E. Sáez, Non-Newtonian annular vertical flow of sand suspensions in aqueous solutions of guar gum, *J. Petrol. Sci. Eng.* 44 (2004) 317-331.
- [3] V. Mahto, V.P. Sharma, Rheological study of a water based oil well drilling fluid, *J. Petrol. Sci. Eng.* 45 (2004) 123-128.
- [4] S. Parija, M. Misra, A.K. Mohanty, Studies of natural gum adhesives extracts: an overview, *J. Macromol. Sci. Polym. Rev.* 41 (2001) 175-197.
- [5] R. Caenn, G.V. Chillingar, Drilling fluids: state of the art, *J. Petrol. Sci. Eng.* 14 (1996) 221-230.
- [6] M. Dolz, J. Jiménez, M.J. Hernández, J. Delegido, A. Casanovas, Flow and thixotropy of non-contaminating oil drilling fluids formulated with bentonite and sodium carboxymethyl cellulose, *J. Petrol. Sci. Eng.* 57 (2007) 294-302.
- [7] M.V. Kok, G. Iscan, Effect of carboxy methyl cellulose and determination of pore throat criteria for water-based drilling fluids. *Energ. Source. Part A: Recovery Utilization Environ. Eff.* 31 (2009) 396-405.
- [8] J.Q. Ji, C.L. Zeng, Y. C. Ke, Y. Pei. Preparation of poly (acrylamide-co-acrylic acid)/silica nanocomposite microspheres and their performance as a plugging material for deep profile control, *J. Appl. Polym. Sci.* 134 (2017) 45502.
- [9] M.Q. Lin, G.Q. Zhang, Z. Hua, Q. Zhao, F.F. Sun, *Colloids Surf. A Physicochem. Eng. Asp.* 477 (2015) 49.
- [10] J.Q. Ji, Y.C. Ke, Y. Pei, G.L. Zhang, Effects of highly exfoliated montmorillonite layers on the properties of clay reinforced terpolymer nanocomposite plugging microspheres, *J. Appl. Polym. Sci.* 134 (2017) 44894.
- [11] H. Kawaguchi. Functional polymer microspheres. *Prog. Polym. Sci.* 25 (2000) 1173-1175.
- [12] I. Kaneda, A. Sogabe, H. Nakajima. Water-swellaable polyelectrolyte microgels polymerized in

an in-verse microemulsion using a nonionic surfactant. J. Colloid. Interf. Sci, 275 (2004) 450-451.

[13] S. Cuha, B. Ray, B.M. Mandal, Polym. Sci. Part A: Polym Chem. 39 (2001) 3434-3442.

[14] M. Sairam, V.R. Babu, B.V.K. Naidu, T.M. Aminabhavi, Encapsulation efficiency and controlled release characteristics of crosslinked polyacrylamide particles. Int. J. Pharmaceut, 320 (2006) 131-136.