The Degradation of P(AM-AMPS) Microspheres Synthesized by Emulsion Polymerization

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Abstract. Anionic polyacrylamide microspheres P (AM-AMPS) were synthesized by emulsion polymerization with 2-acrylamide-2methylpropanesulfonic acid (AMPS) and acrylamide (AM). The degradation experiments were designed at 80 °C. The degradation products of this microspheres were analyzed by scanning electron microscopy, thermogravimetric analysis, infrared spectrum, dynamic light scattering, pH and viscosity measurement. The results showed that, in the first four hours, radical oxidative degradation rapidly broke the main polymer chain of microspheres and decreased the solution viscosity sharply, while the hydrolysis reaction relatively moved slowly and pH kept steady around 2.75. Four hours later, the radical oxidative degradation approached to termination and the hydrolysis reaction of amide began to raise pH by self-acceleration of amide group in acidic condition. The out-layer polymer branch of microspheres degraded in 4 hours and then the inner main chain began to break, resulting in the following faster size decrease.

Keywords: polyacrylamide, microspheres, degradation, hydrolysis.

1. Introduction
Microspheres can be used for profile control and sewage treatment in oil field. [1] The water produced by Daqing oilfield, China, contains polyacrylamide and other organic high-molecular substances which are viscous and difficult to degrade. It is also difficult to meet the water quality requirements of reinjection. By studying gel breaking and degradation behavior of cationic polyacrylamide acid thickener P(DMC-AM) in higher temperature acid, Chen [2] indicated P(DMC-AM) is mainly characterized by broken chain of the main chain, accompanied by break of ester bond and amide bond. Zhang[3] revealed the degradation behavior of zwitterionic acid thickener CXS in high temperature acid and indicated CXS is mainly characterized by broken chain of the main chain, accompanied by break of ester bond and amide bond. DB[4] studied the hydrolysis of polyacrylamide (PAM) in an alkaline-surfactant-polymer flooding under alkaline conditions. By studying the radical oxidative degradation of polyacrylamide used in EOR, DB [5] indicated that the acrylic backbone was cleaved by free radical mechanism, resulting in a decrease in molecular weight and a corresponding decrease in viscosity. However, the degradation of polyacrylamide microspheres have seldom been studied. In this paper, anionic polyacrylamide microspheres were prepared by emulsion polymerization. The high temperature degradation experiments were designed and the degradation of microspheres was analyzed.
2. Experimental Section

2.1. Experimental Materials
2-Acrylamido-2-methylpropane sulfonic acid (AMPS), white oil, acrylamide (AM), sodium hydrogen sulfite, ethanol and cyclohexane are all analytical grade. Tween 60 and Span 80 are both chemically pure. The above chemicals are all produced by Shanghai Sinopharm Chemical Reagent Co., Ltd. Made with deionized water.

2.2. Experimental methods

2.2.1 Polymerization method and degradation. A certain proportion of Span80, Tween 60, white oil was added into a three-necked flask equipped with a thermometer, a stirrer and a nitrogen protection device. This mixture was uniformly stirred by an electric mixer, and then 10% aqueous solution of AMPS monomer was added to initiate polymerization. The reaction was carried out at 30 °C for 1 hour and finally obtain microsphere emulsion of 10% P (AM-AMPS). The microsphere emulsion was washed several times with absolute ethanol, and then dried in a vacuum oven at 60 °C for 5 hours to constant weight to obtain microsphere particles. The 0.5% P (AM-AMPS) solution was prepared and degraded in a blast oven at the constant temperature of 80 °C for 1 h, 2 h, 4 h, 1 d, 5 d, 10 d.

2.2.2 SEM morphological characterization. A trace amount of 10% P(AM-AMPS) microspheres were dispersed in an appropriate amount of cyclohexane and ultrasonically dispersed to obtain a uniform microsphere cyclohexane dispersion. Germany Zeiss Supra 55 SEM were used to examine the microsphere morphology.

2.2.3 Infrared spectroscopy characterization. The infrared spectroscopy of the microsphere samples before and after degradation was tested on Germany Bruker Equinox 55 Fourier infrared spectrometer.

2.2.4 pH analysis. The degradation rate and degree of 0.3% P (AM-AMPS) polymer and 0.5% P (AM-AMPS) microsphere solution were measured by lightning magnetic PHS-3c pH meter, using Shanghai Leici Company equipment.

2.2.5 Viscosity measurement. The viscosity of 0.5% P (AM-AMPS) microsphere solution was measured at the constant temperature of 25 °C by American Brookfield LVDV3T rotational viscometer.

2.2.6 Particle size characterization. The particle size of 0.5% P(AM-AMPS) was measured by a dynamic light scattering, using British Malvern Instrument Co., Ltd. equipment.

3. Results and Discussion

3.1. SEM analysis

![Figure 1. 10% P (AM-AMPS) microsphere scanning electron micrograph](image)

Figure 1. 10% P (AM-AMPS) microsphere scanning electron micrograph
Figure 1 is a SEM photograph of 10% P (AM-AMPS). As shown, the synthesized microspheres are spherical. The 10% P(AM-AMPS) microspheres have a particle size of 70 nm. The average particle size of 10% M (AM-AMPS) was 124.93 nm as measured by laser particle sizer. SEM and optical dynamic scattering experiments show that the synthesized microspheres are uniformly distributed and the particle size is moderate.

3.2. Infrared analysis

The infrared spectrums before and after degradation of P(AM-AMPS) are shown in Figure 2. According to Figure 2, 3323 cm\(^{-1}\) and 3192 cm\(^{-1}\) are characteristic absorption peak of primary amide in amido group. The strong absorption peak at 1656 cm\(^{-1}\) is stretching vibration absorption peak of carbonyl group in the amide group. The absorption peaks of 2960 cm\(^{-1}\), 2923 cm\(^{-1}\) and 2854 cm\(^{-1}\) are the asymmetry and symmetric stretching vibration absorption peaks of saturated-CH\(_3\) and -CH\(_2\). The absorption peaks caused by methylene scribble bending vibration is at 1420 cm\(^{-1}\). The absorption peak at 1450 m\(^{-1}\) is C-N stretching vibration absorption peak. 1182 cm\(^{-1}\), 1038 cm\(^{-1}\), and 620 cm\(^{-1}\) are the symmetric and asymmetric stretching vibration absorption peaks of -SO\(_3^\text{2-}\). [6]

Compared these two spectrum, the C=O absorption peak in the amide group at 1656 cm\(^{-1}\) was weakened, indicating that the C=O bond was degraded. The C-N absorption peak at 1450 m\(^{-1}\) was weakened, indicating that the C-N bond at the amide group and the ester group were degraded. At 2960 cm\(^{-1}\), 2923 cm\(^{-1}\), 2854 cm\(^{-1}\) and 1420 cm\(^{-1}\), the absorption peaks of -CH\(_3\) and -CH\(_2\) were weakened, indicating that the main chain or the branch was broken. The -SO\(_3^\text{-}\)-absorption peak at 1182 cm\(^{-1}\), 1038 cm\(^{-1}\), and 620 cm\(^{-1}\) was weakened, indicating that the branches with the -SO\(_3^\text{-}\) bond were broken.

3.3. pH analysis

The pH curves of the polymer and microspheres are shown in Figure 3. According to infrared spectrum analysis, the amide group and ester group in the polymer chain both degraded. The ester bond of sulfonate group is hydrolyzed to form carboxyl group (-COOH) and sulfonate, and amide group (-CONH\(_2\)) is hydrolyzed to form carboxyl group (-COOH) and NH\(_3\). Due to the steric hindrance of the tert-butyl group on the AMPS structure, it has high hydrolysis resistance [7]. The hydrolysis reaction was slower and the pH increased slowly before 4h.
Figure 3. P(AM-AMPS) microspheres and polymer solution degrading pH changes

The hydrolysis process under acidic conditions exhibits self-acceleration \[^{[8]}\], because carboxyl group produced by hydrolysis accelerates hydrolysis of amido group. Accordingly, pH rose faster after 4h. This phenomenon is different from the linear polyacrylamide, where the -OH catalyzed hydrolysis of the amide group (-CONH\(_2\)) under neutral and weakly basic conditions. Due to electrostatic repulsion, the amide group and the ester group are hydrolyzed to -COO- which hinders -OH catalysis of adjacent amide groups and ester groups. \[^{[9]}\] Thus, the polymer pH rises slower.

3.4. Viscosity analysis

Figure 4. Viscosity change of 0.5% P (AM-AMPS) microsphere solution

The viscosity of P(AM-AMPS) solution versus degradation time at 25 °C is shown in Figure 4. As shown in Figure 4, the viscosity of P(AM-AMPS) solution decreased to 32.45% compared to its initial viscosity after the first 2 hours. This rapid decrease can be ascribed to the residue initiator in the polymerization, which may initiate radical oxidative reaction to form a small molecular polymer segment. \[^{[10-11]}\] Combined with the infrared spectrum analysis, the microsphere main chain or branch chain is broken. The free radical-induced oxidation reaction is very fast and the viscosity drops rapidly in the first 2 h.

After 2 h, the rate of oxidative chain scission reaction slowed down close to termination and then its viscosity decreased very slowly. This slowing down attributed to the increasing hydrolysis degree of this microspheres, shown in Figure 5. Due to the hydrolysis of carboxylic acid groups in the polymer...
chain, the charge density increased and microsphere swelled by the repulsion among polymer chain and the osmotic pressure. This swelling relieve the decreasing trend of viscosity. One day later, its viscosity decreased to several cent poises.

3.5. Particle size analysis

![Figure 5. P(AM-AMPS) particle size change chart](image)

Figure 5. P(AM-AMPS) particle size change chart

The particle size evolution with degradation time of P (AM-AMPS) is shown in Figure 5. The particle size of P(AM-AMPS) microsphere solution showed a decreasing trend with the change of degradation time. In the first four hours, the initial particle diameter was 774 nm, and the degradation particle size after 4 hours was reduced to about 650 nm. The solution viscosity decreased by far faster than the shrink of effective volume of microspheres. This behavior can be attribute to the morphology change of microspheres. The crosslinking density of polymer microspheres is decreasing from inner to outer layer, (Fig.6a) and there are random polymer branches protruding into solvent when they are swollen in the water (Fig.6b). This protruding branches are apt to be anionic polymer chain due to their hydrophilic character. In this four hours, the radical oxidation reaction occurred not only in the inner but also the outer layer. Thus the protruding branches were decomposed and diminished particle size, shown in Fig.6c. Simultaneously, the electric viscous effect and inter-tangling effect reduced, which aggravated the viscosity decrease. After four hours, the microspheres began to break into pieces and showed a sharp decrease in particle size, shown in Fig.6d.

![Figure 6. microsphere degradation process](image)

Figure 6. microsphere degradation process (a. Initial shape of microspheres b. Microspheres swelling morphology c. Microspheres degradation d. Branching after microspheres degradation)
4. Conclusion
A uniform P(AM-AMPS) microspheres with particle size about 70nm were synthesized by emulsion polymerization. The degradation mechanisms of these microspheres are shown as follows:
Radical oxidative degradation went fast at first four hours and accordingly decreased the solution viscosity rapidly. After four hours, the hydrolysis reaction began to increase pH of solutions.
According to the particle size analysis by DLS, the out-layer polymer branch of microspheres degraded at first 4 hours and then the inner main chain appeared to be broken, resulting in the following faster size decrease.

Acknowledgments
This work was financially supported by National Natural Science Foundation of China. The development of the new low-damage fracturing fluid gelled with associating nano-microspheres (51504215).

References
[1] W Lin, Y.H Chen., M. Cao. Performance evaluation and application of deep profile control agent YG polymer microspheres, J. Oilfield Chemistry.28(2011)327-330.
[2] K. Chen, Y.S. Zhang, J.Y.He. Effect of ionicity on gel breaking and acid degradation of acrylamide (AM) and methacryloylxyethyl trimethyl ammonium chloride (DMC) copolymers, J.Oilfield Chemistry .34 (2017) 234-240.
[3] Y.S. Zhang, X.Lin, K.Chen. Synthesis and Acid Degradation of Zwitterionic Acid Thickener, J.Oilfield Chemistry.33(2016) 210-214.
[4] DB Levitt, GA Pope. Chemical Degradation of Polyacrylamide Polymers Under Alkaline Conditions, J Spe Reservoir Evaluation & Engineering.14 (2016) :281-286.
[5] DB Levitt, WS Slaughter, GA Pope. The Effect of Redox Potential and Metal Solubility on Oxidative Polymer Degradation, J.pe Reservoir Evaluation & Engineering.14 (2011) :287-298.
[6] Z.S. Yu, Y.M.Xia. Analysis of the Content of Acrylamide Copolymers by Infrared Spectroscopy, J.Fine Petrochemicals .29(2012): 79-82.
[7] H. Kheradmand, J.Francois ,V.Plazanet. Hydrolysis of polyacrylamide and acrylic acid-acrylamide copolymers at neutral pH and high temperature, J.Polymer.29(1988):860-870.
[8] W.L. Kang, Y.Lu, Z.Li. Study on Micro-rheological Properties of Partially Hydrolyzed Polyacrylamide, J.Oil and gas chemical industry.44(2015), 75-78.
[9] L.Y. Zhu, Z.Y. Chang, M.Z.Li, E.J.Wang. Oxidative degradation of partially hydrolyzed polyacrylamide in aqueous solution, J. Effect of temperature. Polymer Materials Science and Engineering.01(2000): 113-116.
[10] M.T. Bao, Q.G. Chen, N.Wang, S.X. Guo, X.M.Li. Study on degradation mechanism of polyacrylamide (Hpam) in oilfield wastewater, J.Polymer Bulletin.02(2008): 1-9.
[11] L.Y. Zhu, C. Ma, M.Li. High temperature hydrolysis of water-soluble AM /AA /AMPS copolymers, J.Applied Chemistry.17 (2000): 117-120.