Colloids and Surfaces A 555 (2018) 621–629

Contents lists available at ScienceDirect

Colloids and Surfaces A

journal homepage: www.elsevier.com/locate/colsurfa

Self-assembly and regulation of hydrophobic associating polyacrylamide with excellent solubility prepared by aqueous two-phase polymerization

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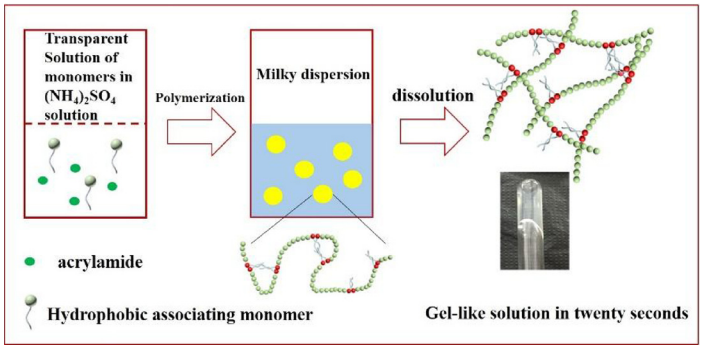
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Hydrophobic associating polymer
Aqueous two-phase polymerization
Solubility
Self-assembly
Viscoelastic regulation

ABSTRACT

The application of hydrophobic associating polyacrylamide (HAPAM) was restricted due to the poor solubility. In order to enhance the solubility of HAPAM and avoid environmental pollution, aqueous two-phase polymerization was used to prepare HAPAM in ammonium sulfate aqueous solution and a milky dispersion was obtained. The HAPAM particles dispersed in the solution spherically and the average particle size was about 7.4 μm. The hydrophobic associating polyacrylamide prepared with aqueous two-phase polymerization exhibited superior solubility and it could dissolve completely in twenty seconds. HAPAM solution could aggregate to network through inter-molecular association, leading significant increase of viscosity. Moreover, the viscosity of HAPAM solution increased with addition of inorganic salt even in nearly-saturated solution, and the viscoelasticity of HAPAM solution also enhanced obviously in the presence of salt, exhibiting excellent salt resistance. Furthermore, anionic surfactant of sodium dodecyl sulfate (SDS) could aggregate with the cationic hydrophobic monomers on the polymer chains via electrostatic attraction to form mixed micelles, which could prompt the polymer from intra-molecular association to inter-molecular association, leading remarkable increase of viscosity and viscoelasticity of the solution. In addition, The HAPAM dispersion doesn't contain any organic solvent and could become solution instantaneously once dilution into water, which provides a green and environmentally friendly strategy for preparation of hydrophobic associating polymers. The HAPAM dispersion was well fit for the hydraulic fracturing in shell gas due to the excellent solubility and environmentally friendly property. These features indicated that HAPAM dispersion would have a great potential application in hydraulic fracturing in shell gas.

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https://doi.org/10.1016/j.colsurfa.2018.07.048
Received 13 May 2018; Received in revised form 26 July 2018; Accepted 28 July 2018
Available online 29 July 2018
0927-7757/

1. Introduction

Hydrophobic associating polymers, with a small amount (generally less than 2 mol %) of hydrophobic monomers onto the polymer backbone [1], has been in the focus of considerable research over the past two decades owing to its excellent rheological characteristics. It was used widely in many fields such as painting, drilling and oil production [2,3].

Up to date, hydrophobic associating polymers were generally prepared with inverse emulsion/microemulsion polymerization [4–7] and micelle polymerization [8–10]. However, the inverse emulsion/microemulsion polymerization needs a large amount of organic solvents and surfactant, causing high cost, potential safety hazard and serious environmental pollution. Micellar copolymerization also needs amount of surfactant and the product needs post treatment to remove the surfactant after the polymerization to obtain purified product. To overcome these disadvantages, water soluble polymerizable surfactant was used as hydrophobic monomer to prepare hydrophobic associating polymer in aqueous solution, which was a kinds of micelles polymerization. Whereas, hydrophobic associating polymers prepared by these methods were difficult to dissolve in aqueous solution owing to the introducing of hydrophobic associating monomers in the polymer, causing wide limitation of application in many fields. There are more hydrophobic monomers in the polymer, the hydrophobic associating polymers were more difficult to dissolve, even leading insoluble when the concentration of hydrophobic monomer exceeded a critical value.

In recent decades, aqueous two-phase polymerization has received great attention as an environmentally friendly approach for the preparation of polyacrylamide [11–16]. Generally, two kinds of solvents, ammonium sulfate aqueous solution and polyethylene glycol solution, were used in aqueous two-phase polymerization. Polyethylene glycol solution was limited due to high cost. Ammonium sulfate aqueous solution was widely used as solvent owing to the low cost and low pollution. The aqueous dispersions in ammonium sulfate aqueous solution didn't contain any organic solvent [17–19]. Aqueous two-phase polymerization avoided the environmental pollution in inverse suspension polymerization and inverse emulsion/microemulsion polymerization, and also overcame the poor solubility of hydrophobic associating polymer powder [17]. Due to the superior performances, aqueous two-phase polymerization was underwent a rapid development in recent years and it was widely used in many fields, such as food processing [20–23], material preparation [24–28], control release [29–32], oil production [33] and other fields [34,35]. As far as our information goes, however, there exists few works about the dispersion of hydrophobic associating polyacrylamide in aqueous ammonium sulfate solution.

In this work, hydrophobic associating polyacrylamide (HAPAM) with excellent solubility was prepared via aqueous two-phase polymerization. The dispersion was characterized by inverted fluorescence microscope without eyepiece and the average particle size was measured with laser particle size analyzer. The critical association concentration was firstly determined and the solubility was also investigate. Furthermore, the effect of salt, shear rate and surfactant on the viscosity of HAPAM were discussed, respectively. Moreover, the viscoelasticity and temperature resistance properties of HAPAM were also studied. The results indicated that HAPAM prepared by aqueous two-phase polymerization exhibited superior properties on aspect of viscosity, temperature resistance, shear resistance and solubility.

2. Experiment section

2.1. Materials

N, N-dimethyl-allyl-hexadecyl ammonium chloride (CD_{16}) was prepared in the lab. Acrylamide (AM), 2,2′-Azobis(2-methylpropionamide)dihydrochloride(V-50), Ammonium sulfate ($(NH_4)_2SO_4$), Sodium chloride(NaCl), Calcium chloride($CaCl_2$), Magnesium chloride ($MgCl_2$), Methacryloxyethyltrimethyl ammonium chloride(DMC), Sodium dodecyl sulfate(SDS) and ethanol were analytical grade purchased from Kelong Chemical Reagent Factory (Chengdu, China) without further purification.

2.2. Preparation of the HAPAM dispersion

The stabilizer (PDMC) was firstly prepared with DMC and the detail was described in supporting information. Then the $(NH_4)_2SO_4$, AM, stabilizer and deionized water were added into a 250 ml round-bottomed three-neck flask and the mass concentration of the $(NH_4)_2SO_4$, AM and PDMC was 25%, 15% and 3%, respectively. Then the solution was injected with nitrogen for 1 h to remove oxygen in the solution. Afterwards, the hydrophobic monomer (CD_{16}) was added into the solution with the molar concentration of 0.75% relative to AM. Subsequently, initiator (V-50) was also added into the solution with the concentration of 0.05% relative to the monomer mass. The flask was sealed with rubber plug and the polymerization proceeded with stirring at 45 °C. After one hour, the prepared polymer gradually separated from the solution and the transparent solution change to a milky dispersion. The dispersion of hydrophobic associate polymer was obtained after 24 h. Finally, a part of the dispersion (20 mL) was taken out and washed with ethanol/deionized water (1:1) to remove ammonium sulfate and residual monomers, and then the polymer was dried in vacuumoven for 48 h (Scheme 1).

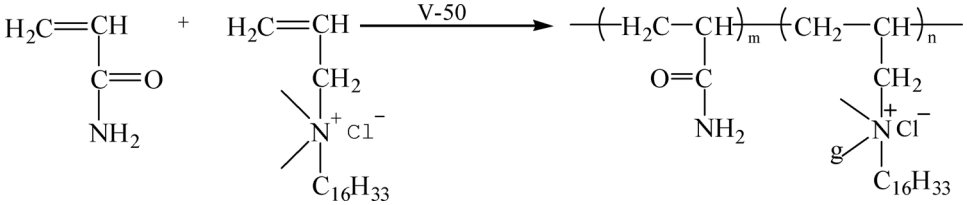
2.3. Characterization and measurements

The morphology of the aqueous dispersion was characterized with inverted fluorescence microscope without eyepiece. The distribution of the particle size of dispersion was measured by Melvin laser particle size analyzer with the medium of $(NH_4)_2SO_4$ solution at the same concentration of the dispersion at 25 °C. Infrared spectroscopy analysis and ^{1}H-NMR spectra were carried out to confirm the chemical structures of the polymer. The aggregation of HAPAM solution was characterized with scanning electron microscope (SEM). The size of aggregation of HAPAM was measured using dynamic light scattering (DLS). Viscoelasticity, viscosity and shear resistance of the polymer solution were measured with HAAKE RS600 rational rheometer.

3. Results and discussion

3.1. Characterization of the dispersion

The mechanism of the aqueous two-phase polymerization was similar with the conventional dispersion polymerization (Scheme 2). The only difference was the solvent used in the reaction. In the conventional



Scheme 1. the reaction scheme of HAPAM preparation.