A novel polymer of $\text{Al}_2(\text{SO}_4)_3$ -poly(acrylamide-co-2-acrylamido-2-methyl-1-propanesulfonate) ionic hybrid prepared by dispersion polymerization

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Abstract. A novel polymer $\text{Al}_2(\text{SO}_4)_3$ -poly(acrylamide-co-2-acrylamido-2-methyl-1-propanesulfonate) ($\text{Al}_2(\text{SO}_4)_3$ -P(AM/AMPS)) had been synthesized by dispersion polymerization in an aqueous solution of ammonium sulfate and aluminum sulfate, using poly(2-acrylamido-2-methyl-1-propanesulfonate) P(AMPS) as stabilizer, acrylamide (AM) and 2-acrylamido-2-methyl-1-propanesulfonate (AMPS) as monomers, poly(2-acrylamido-2-methyl-1-propanesulfonate) (PAMPS) as stabilizer and [2-(2-imidazdino-2-yl)propane]dihydrochloride (VA-044) as initiator. The average particle size of polymer dispersion ranged from 0.2 to 0.3 μm , the molecular weight was from $4.3 \cdot 10^6$ to $5.7 \cdot 10^6 \text{ g} \cdot \text{mol}^{-1}$. The polymer was characterized by infrared (IR) spectroscopy, thermogravimetry (TGA) and transmission electron microscopy (TEM). The swelling property of the dispersion polymer was studied by particle size distribution. When the polymer dispersion was diluted with deionized water, particle sizes decreased several times. When the polymer dispersion was diluted with salt water, the particle size increased with increasing concentration of salt. The effects of $\text{Al}_2(\text{SO}_4)_3$ and stabilizer on the particle size and the relative molecular weight of the polymer were investigated, respectively. The optimum conditions for the stable $\text{Al}_2(\text{SO}_4)_3$ -P(AM/AMPS) dispersion were that the concentration of $\text{Al}_2(\text{SO}_4)_3$ was 1.12 wt%, the concentration of PAMPS stabilizer was 3 wt% and the concentration of initiator was $0.2 \text{ mol} \cdot \text{l}^{-1}$ and the monomers concentration was 14 wt%.

Keywords: smart polymers, dispersion polymerization, polyacrylamide, organic-inorganic hybrids, aluminum sulfate

1. Introduction

As attractive materials, organic-inorganic hybrids that could have high performance or high function due to synergism of two components have been widely used, such as photochromic films, optical functionalities, flocculants and process aids for low-grade oil sand ore [1–4]. Several methods have been used to prepare organic-inorganic hybrids such as sol-gel reaction [5, 6], intercalation polymerization [7, 8], melt-processing [9, 10], and *in situ* polymerization [11, 12].

The first condition for preparation of organic-inorganic hybrids with enhanced performance is to guarantee uniform distribution of inorganic parti-

cles within the polymer matrix. Dispersion polymerization has been considered as a promising and preponderant approach in preparing nearly monodisperse polymer particles in a single step [13]. In dispersion polymerization, the organic polymer can be uniformly dispersed in the form of particles whose size ranged from 0.1–15 μm , which can ensure the inorganic particles uniformly dispersed as much as possible in the system.

To our knowledge, little research has been reported on inorganic/polyacrylamide hybrids. Feng *et al.* [1] prepared photochromic nanocomposite thin films by entrapping polyoxometalate in a polyacrylamide matrix via the ultrasound technique. Mat-

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suura *et al.* [2] had synthesized polysilane-acrylamide block copolymers by photopolymerization of acrylamide monomers. Yang *et al.* [3] had synthesized $\text{Al}(\text{OH})_3$ -polyacrylamide using a redox initiation in aqueous medium. However, there existed little works about the hybrid $\text{Al}_2(\text{SO}_4)_3$ -poly(acrylamide-co-2-acrylamido-2-methyl-1-propanesulfonate) ($\text{Al}_2(\text{SO}_4)_3$ -poly(AM/AMPS)) by dispersion polymerization in aqueous medium. In this work, a novel dispersion polymer $\text{Al}_2(\text{SO}_4)_3$ -poly(AM/AMPS) ionic hybrid was synthesized by using 2,2'-azobis(2-(2-imidazolin-2-yl) propane) dihydrochloride (VA-044) as an initiator and poly(2-acrylamido-2-methyl-1-propanesulfonate) (PAMPS) as the stabilizer through dispersion polymerization and ionic bond between $\text{Al}_2(\text{SO}_4)_3$ and poly(AM/AMPS) was characterized by thermogravimetric analysis and IR spectroscopy. Compared with the nonionic stabilizer used in other works, the negative charged end groups in the polymer chains of PAMPS were anticipated to enhance the stability of the lattices by electrostatic repulsion as well as to interact with $\text{Al}_2(\text{SO}_4)_3$ with positive charge. The effects of concentration of $\text{Al}_2(\text{SO}_4)_3$, the stabilizer and initiator on molecular weight, particle size distribution and the overall conversion of the monomers were investigated, and the swelling property of the dispersion polymer was discussed. The difference between P(AM/AMPS) and $\text{Al}_2(\text{SO}_4)_3$ -poly(AM/AMPS) was discussed in terms of the stabilizer concentration and particle size distribution.

2. Experimentals

2.1. Materials

Acrylamide (AM) and 2-acrylamido-2-methyl-1-propane sulfonate (AMPS) were industrial materials purchased from Dia-Nitrix Co. Ltd. (Japan) and Zhenxing Fine Chemicals Inc. Henan (China), respectively. Aluminium sulfate ($\text{Al}_2(\text{SO}_4)_3$) and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) were analytical grade. Deionized water was used throughout the experiments. 2,2'-azobis(2-(2-imidazolin-2-yl) propane) dihydrochloride (VA-044, A. R. Grade) was purchased from WAKO Pure Chemical Industries Ltd. (Japan). Poly(2-acrylamido-2-methyl-1-propanesulfonate) (PAMPS) was prepared from AMPS in an aqueous solution using VA-044 as initiator at 40°C under nitrogen atmosphere for

4–5 h. The molecular weight of PAMPS was $3.0 \cdot 10^5$ – $7.0 \cdot 10^5$ g·mol⁻¹. In this work we used PAMPS whose molecular weight was around $3.5 \cdot 10^5$ g·mol⁻¹.

2.2. Preparation of polymer dispersion

Varying quantities of the ingredients containing monomers, aluminium sulfate, ammonium sulfate, PAMPS and deionized water were added to a 250 ml four-neck flask fitted with a stirrer, a reflux condenser, a thermometer and a nitrogen inlet tube. After purging with nitrogen for 30 min and controlling the temperature at 60°C by means of an external heating jacket, the monomers were initiated by drop-feeding VA-044 aqueous solution into the reactor evenly over a period of 1 h. After reacting 6 h, heating stopped and the $\text{Al}_2(\text{SO}_4)_3$ -P(AM/AMPS) hybrids were obtained. The stirring speed was fixed at 120 rpm in all experiments.

2.3. Characterization of dispersion copolymer

$\text{Al}_2(\text{SO}_4)_3$ -P(AM/AMPS) dispersion was dissolved in water. Then, the polymer was washed with acetone. These operations were repeated several times to remove the inorganic salts, unreacted monomers and PAMPS. Then the copolymer precipitated was dried to a constant weight at 50°C under vacuum. The dried sample was used to determine the intrinsic viscosity $[\eta]$ of the copolymer was determined in a 1 mol/l NaCl aqueous solution with an Ubbelohde capillary viscometer at 30°C. The concentration used for the measurement of viscosity was 0.0005–0.001 g/ml. The viscosity-average molecular weight M_v could be calculated with the Mark-Houwink relationship (Equation (1)):

$$M_v = \left(1000 \cdot \frac{[\eta]}{3.73} \right)^{1/0.66} \quad (1)$$

The method to determine PAMPS molecular weight was the same as in the case of $\text{Al}_2(\text{SO}_4)_3$ -P(AM/AMPS).

Particle size and particle size distribution were measured with Coulter LS230 particle size analyzer. The samples were usually dispersed by ultrasonic agitation before measurements.

FT-IR spectra were recorded on a spectrophotometer (AVATAR 360, Nicolet, USA) using KBr pellets. The thermal degradation test was conducted on

TGA (TG209, NETZSCH, Germany) at a heating rate of 10°C/min under static N₂ atmosphere. Weigh 5 mg Al₂(SO₄)₃ and 5 mg P(AM/AMPS) and then mix them together. All samples (10.0 mg) used had been dried in vacuum at 110–120°C for 8 h. The change in weight differential difference with temperature was recorded. The particle morphology of Al₂(SO₄)₃-P(AM/AMPS) and P(AM/AMPS) were measured by TEM (JEM-1200EX, JEOL, Japan).

The total monomer conversion could be obtained by determining residual contents of AM and AMPS with bromating method [14].

3. Results and discussion

3.1. Effect of Al₂(SO₄)₃ concentrations

Effect of Al₂(SO₄)₃ concentration on the relative molecular weight, particles size and conversion of monomers were shown in Table 1. As shown in Table 1, with increasing concentration of Al₂(SO₄)₃, molecular weight increased, but the particle size and the particle size distribution decreased. When Al₂(SO₄)₃ concentration was between 0 and 1.86 wt%, stable dispersion could be obtained. Al₂(SO₄)₃ and (NH₄)₂SO₄ can form a complex salt called AlNH₄(SO₄)₂·12H₂O whose solubility in water is much lower than any of them. So, in our

experiments, the concentration of Al₂(SO₄)₃ in aqueous (NH₄)₂SO₄ solution is less than 1.86% to avoid precipitation. But the reaction temperature between Al₂(SO₄)₃ and (NH₄)₂SO₄ was 100°C, in our experiment the temperature was around 60°C. So there was little AlNH₄(SO₄)₂ in the system. Compared with Al₂(SO₄)₃ concentration, the AlNH₄(SO₄)₂ could be ignored. According to Electric Double Layer Theory, the thickness of diffusion electrical double layer reduced with adding Al³⁺ into the reaction system. As a result, the molecular chain of polymer crimples seriously, at the same time, and the number of mature particles does not change [15], so the particle sizes decreased. Moreover, Al₂(SO₄)₃ also has the precipitation effect. The precipitation effect became stronger with increasing Al₂(SO₄)₃ concentration, so the particles size decreased with Al₂(SO₄)₃.

3.2. Effect of stabilizer concentrations

A series of experiments were carried out to examine the effect of stabilizer concentrations on the hybrid. As shown in Table 2, when PAMPS content was less than 1.5%, it could not provide enough electrostatic repulsion and steric stabilization and an agglomerating system was obtained. With increasing PAMPS, the relative molecular weight

Table 1. Effect of salt concentration on the properties of dispersion polymers

Al ₂ (SO ₄) ₃ [wt%]	M _w [10 ⁶ g·mol ⁻¹]	Conversion [%]	P.D. [μm]	Notes
0.00	4.33	93.3	0.30(0.10–0.7)	
0.37	4.42	93.5	0.27(0.07–0.7)	
0.75	4.57	93.2	0.25(0.07–0.6)	
1.12	4.76	93.4	0.23(0.07–0.8)	
1.49	5.12	93.2	0.21(0.07–0.6)	
1.86	5.22	92.1	0.20(0.07–0.7)	
1.93	–	–	–	precipitated

Polymerization conditions: AM/AMPS (mole ratio), 5/1; total monomer 14%; PAMPS 1.8%; VA-044 0.01 wt%; (NH₄)₂SO₄ 25%. P.D., average of particle diameter (range of particle diameter).

Table 2. Effect of stabilizer concentrations on dispersion polymer

PAMPS [wt%]	M _w [10 ⁶ g·mol ⁻¹]	Conversion [%]	P.D. [μm]
1.5	coagulated	–	–
2.0	4.12	89.1	0.27(0.07–0.7)
3.0	4.76	93.6	0.26(0.07–0.7)
4.0	4.36	92.3	0.24(0.07–0.6)
5.0	4.62	90.3	0.23(0.07–0.6)
6.0	4.83	89.4	0.22(0.07–0.6)
8.0	5.74	88.4	0.20(0.07–0.6)

Polymerization conditions: AM/AMPS (mol ratios) 5/1; total monomer, 14%; (NH₄)₂SO₄ 25%; Al₂(SO₄)₃ 1.12%; and VA-044, 0.01 wt%

had a slowly increasing tendency, but the particle sizes decreased.

Compared with the system without adding $\text{Al}_2(\text{SO}_4)_3$ in the syntheses media, obviously different results were found. We have reported [14] that when PAMPS concentration was below 1.2 or above 3.0%, the copolymer dispersion would coagulate. Suitable PAMPS concentration was from 1.8 to 2.7%. In this system, even if PAMPS concentration was up to 8%, the system was still stable. It could be attributed to $\text{Al}_2(\text{SO}_4)_3$ colloid with positive charge interacting with the with negatively charged stabilizer filling. There was an obvious tendency that the particle sizes decreased and the molecular weight increased as the stabilizer concentration increased. It was different from the results of Cho *et al.* [15] and Chen *et al.* [16] but in correspondence with the results of dispersion polymerization Ray and Mandal's [17, 18] reported in the literature. The particle size decreased with increasing stabilizer concentration. The increasing of molecular weight was the contribution of the solid phase polymerization increase associated with the gel effect. As for a given quantity of polymer smaller particles present greater surface area, so the particle phase captures oligomeric radical from the continuous will increase, and the molecular weight of the polymer would increase. Furthermore, PAMPS used as stabilizer was incorporated in the final dispersion copolymer and may influence the final molecular weight. The influence maybe very small because the molecular weight of the PAMPS was too low compared with the dispersion copolymer.

As shown in Table 2, the overall conversions decreased with PAMPS concentration increasing. Since with increasing PAMPS, the viscosity of the continuous phase increased correspondingly, which prevented monomer radicals freely transferred between nature particles and continuous phase. So, the overall conversion was reduced.

3.3. Effect of initiator concentrations

Experimental sets in Table 3 showed the effects of initiator concentration from 1.0 to 4.5 $\text{mol}\cdot\text{l}^{-1}$, whereas the monomer, stabilizer, $(\text{NH}_4)_2\text{SO}_4$, and $\text{Al}_2(\text{SO}_4)_3$ concentrations were fixed at 14, 3, 25, and 1.12%, respectively. As shown in Table 3, the relative molecular weight decreased with increasing VA-044. While the rate of polymerization increases with increase of initiator concentration, the average numbers of monomer molecules consumed per each radical become smaller, resulting in the lower molecular weight [19].

It also could be seen that particle size increased with increasing the initiator concentration which was commonly observed in dispersion polymerization. The most commonly offered explanation was that a higher initiator concentration would lead to a greater rate of generation of unstable oligoradicals or dead polymer molecules. These primary particles are not stabilized enough by the stabilizers, resulting in a greater rate of coagulation, yielding larger size particles [14].

3.4. Particle size of dispersion polymers

As shown in Figure 1, the average particle size of the original dispersion ranged from 0.03 to 0.8 μm , while those diluted with different salt water and deionized water were in the range of 0.01–0.1, 1.3–2.7 and 0.007–0.05 μm , respectively. The results were contrary to some works reported. We have reported that when diluted with deionized water the particle size became large [15]. It was explained that the insufficient salt concentration weakening the electrostatic repulsion between particles led to expanded molecular chains, and the particle size became larger.

Chen *et al.* [16] said that oligomeric radicals and monomers could enter the particles through solvent channel. It also could be understood as the inorganic salt could enter the particles. Through

Table 3. Effect of initiator concentrations on dispersion polymer

VA-044 [$10^{-4} \text{ mol}\cdot\text{l}^{-1}$]	M_w [$10^6 \text{ g}\cdot\text{mol}^{-1}$]	Conversion [%]	P.D. [μm]
1.0	4.76	93.6	0.26(0.07–0.7)
2.0	4.59	94.2	0.27(0.07–0.7)
3.0	4.44	94.9	0.29(0.1–0.8)
4.0	4.21	95.3	0.31(0.1–0.9)
4.5	4.05	95.7	0.35(0.1–0.9)

Polymerization conditions: AM/AMPS (mol ratios) 5/1; total monomer, 14%; $(\text{NH}_4)_2\text{SO}_4$ 25%; $\text{Al}_2(\text{SO}_4)_3$ 1.12%, PAMPS 1.8%

Figure 1. Particle size distribution of different solutions: (a) solution diluted with deionized water, (b) solution diluted with 15% $(\text{NH}_4)_2\text{SO}_4$ solution, (c) solution diluted with original solution, and (d) solution diluted with 30% $(\text{NH}_4)_2\text{SO}_4$ solution

Brownian diffusion the concentration of inorganic salt inside the particles and outside the particles must be consistent. When diluted with the lower concentration of salt water, the inorganic salt could diffuse from the particle to the continuous phase, so the particle size decreased. Similarly, when diluted with high concentration of salt water, the inorganic salt diffused from continuous phase to the particles, so the particle size increased.

3.5. Characteristics of $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$

Figure 2 represented the FT-IR spectra of $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$ and P(AM/AMPS) , respectively. Curves ‘b’ displayed almost the same characteristic bands as curves ‘a’ except for the

Figure 2. IR spectra of $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$ and P(AM/AMPS)

nuances of 940 and 713 cm^{-1} . $\text{Al}_2(\text{SO}_4)_3$ has absorbance at 940 and 713 cm^{-1} , assigned to $\nu_{\text{Al-SO}_3}$ and $\nu_{\text{Al-O}}$, respectively. It indicated that the sample was an organic-inorganic hybrid of $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$.

Figure 3 showed the TGA curves of $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$, $\text{Al}_2(\text{SO}_4)_3\text{/P(AM/AMPS)}$ mixture and P(AM/AMPS) . As shown in Figure 3, $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$ hybrid had two peaks of pyrolysis rate (T_p) at 280 and 739°C, respectively, while $\text{Al}_2(\text{SO}_4)_3\text{/P(AM/AMPS)}$ mixture and the pure P(AM/AMPS) had peaks at 269, 654.5 and 225, 598.1°C, respectively. Activation energies (E_a) of these samples could be evaluated from TGA data according to Flynn and Wall method [20]. The results of T_p and E_a are shown in Table 4. Accord-

Figure 3. Different TGA curves of $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$, $\text{Al}_2(\text{SO}_4)_3\text{/P(AM/AMPS)}$ mixture and P(AM/AMPS)

Table 4. T_p and E_a of $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$, $\text{Al}_2(\text{SO}_4)_3/\text{P(AM/AMPS)}$ mixture, and P(AM/AMPS)

Samples	T_p [°C]		E_a [KJ/mol]	
	First stage	Second stage	First stage	Second stage
$\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$	280	739.5	176.1	292.3
$\text{Al}_2(\text{SO}_4)_3/\text{P(AM/AMPS)}$	269	654.5	152.2	273.9
P(AM/AMPS)	225	598.1	141.8	246.3

ing to the results from Yang and coworkers [3, 21], high T_p and large E_a of the $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$ were also attributed to the ionic bond formed between $\text{Al}_2(\text{SO}_4)_3$ and P(AM/AMPS) chains.

When researching the interaction between colloidal particles and polyelectrolyte with opposite charge, Hou *et al.* [22] found that the presence of these colloidal particles increased the degree of ionization of the polyelectrolyte. According to this, heat resistance of the $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$ and FTIR spectra indicated that the negative end group of P(AM/AMPS) chain could form an ionic bond with $\text{Al}_2(\text{SO}_4)_3$ with positive charge.

Figure 4 showed the TEM micrograph of $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$ and P(AM/AMPS) . Compared with Figure 4a and 4b significant differences were shown. Figure 4a had a bright rim structure around the surface of the particles but Figure 4b did not have such structure. The very different between the two samples was that one with $\text{Al}_2(\text{SO}_4)_3$ in it, the other was not. So, we indicate that the $\text{Al}_2(\text{SO}_4)_3$ particles were present outside of the particles.

4. Conclusions

The main conclusions from this work are as follows:

- (1) $\text{Al}_2(\text{SO}_4)_3\text{-poly(AM/AMPS)}$ ionic hybrid was synthesized by dispersion polymerization in an aqueous solution of $\text{Al}_2(\text{SO}_4)_3$ and $(\text{NH}_4)_2\text{SO}_4$ in the presence of PAMPS as stabilizer. Ionic bonds between $\text{Al}_2(\text{SO}_4)_3$ and poly(AM/AMPS) chains in $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$ are displayed.
- (2) The optimum conditions for obtaining stable dispersion polymer of $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$ were as follows: the concentration of $\text{Al}_2(\text{SO}_4)_3$ was 1.12%, the concentration of the PAMPS stabilizer was 3%, and the concentration of initiator was $0.2\text{ mol}\cdot\text{l}^{-1}$, respectively. With increasing the concentration of $\text{Al}_2(\text{SO}_4)_3$, the molecular weight increased but the particle sizes decreased, respectively. With increasing the concentration of the stabilizer, the particle sizes decreased and the molecular weight increased.
- (3) The swelling property of the dispersion polymer was studied by particle size distribution.

Figure 4. TEM micrograph of $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$ and P(AM/AMPS) : (a) $\text{Al}_2(\text{SO}_4)_3\text{-P(AM/AMPS)}$ content $\text{Al}_2(\text{SO}_4)_3$ 1.12 wt%; (b) P(AM/AMPS)

When diluted with different concentrations of $(\text{NH}_4)_2\text{SO}_4$ solutions the particle size increased with the $(\text{NH}_4)_2\text{SO}_4$ concentration increased, and when diluted with deionized water the particle size minimized.

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