

Dispersion Polymerization of Acrylamide with 2-Acrylamido-2-methyl-1-propane Sulfonate in Aqueous Solution

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ABSTRACT: The copolymer of acrylamide (AM) and 2-acrylamido-2-methyl-1-propane sulfonate (AMPS) was synthesized through the free radical dispersion polymerization in an aqueous solution of ammonium sulfate and in the presence of poly(2-acrylamido-2-methyl-1-propane sulfonate) as stabilizer. The average particle size of the copolymer ranged from 1 to 4 μm , and the molecular weight was from 2.0×10^6 to $7.0 \times 10^6 \text{ g mol}^{-1}$. By analyzing apparent viscosity and particle size, the swelling property of the dispersion copolymer was studied. When the dispersion was diluted with salt water in which the ammonium sulfate concentration kept equal with that of the original dispersion, particle size and particle size distribution of the diluted dispersion

changed a little, compared with that of the original dispersion. While diluted with deionized water, particle size and particle size distribution could expand several times. The effects of varying concentrations of the stabilizer, the monomer, the salt and the initiator on particle size, and molecular weight of the copolymer were investigated, respectively. The reaction conditions for preparing stable dispersion were concentrations of 20–28% of the salt, 6–14% of monomers, and 1.8–2.7% of the stabilizer. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2379–2385, 2006

Key words: dispersion; acrylamide; 2-acrylamido-2-methyl-1-propane sulfonate; aqueous solution

INTRODUCTION

The water-soluble polymers and copolymers of acrylamide (AM) had extensive applications in many fields. These polymers were used, for example, as flocculants and biocides in wastewater treatment, the retention aids in papermaking and the polymer floods in the enhanced oil recovery, etc.^{1–4} In these fields, the polyacrylamides with high molecular weight were anticipated for their higher effectiveness and lower price. However, these polymers were nonionic usually. If a polymer had charged groups on its molecular chain, it would be more effective when used as a flocculant or retention aid.

The traditional polyacrylamide in solid form was difficult to dissolve, and its solution was also difficult to handle. The products of the inverse emulsion and the inverse microemulsion overcame the problems above. However, surfactants and other organic solvents used in the course of preparation were harmful to the environment and so the application ranges of these prod-

ucts were restricted.^{5–8} Another method of overcoming the problems of solution application was dispersion polymerization in water or in organic medium.^{9–11}

The dispersion polymerization of hydrophobic polymers in organic media had been studied.^{12–14} However, there were only a few works on the dispersion polymerization of water-soluble polymers in aqueous media. Ray and Mandal^{9,10} had reported the dispersion polymerization of AM in water/*tert*-butyl alcohol media. Ye et al.¹¹ had also synthesized the dispersion polyacrylamide in a similar mixed media mentioned above. Up to now, the dispersion polymerization of AM in water without organic solvents has been investigated only in a few patents. For this system, water was used as the reaction medium, and it presented a number of practical advantages, such as avoiding fire risk, free of toxic and odor effect, etc.

Dispersion polymerization was a unique method due to the inherent simplicity of the single-step process in which particles ranged from 0.1 to 15 μm were formed. Before polymerization, monomer, stabilizer, initiator, salt, and solvent formed an originally homogeneous reaction mixture. Then the initiator decomposed and the free radicals reacted with monomer to form oligomeric radical. At a critical chain length, the oligomer precipitated and adsorbed the stabilizer to form stable particle nuclei. Once particles had been

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formed, they absorbed monomers from the continuous phase and polymerization mainly occurred in the surface of particles. Reaction media was a key factor. Appropriate solvent was insoluble for the formed polymer particles but soluble for the stabilizer and monomers. Salt added in water played a great role in the preparation of dispersion polymer, and it acted as the phase-out reagent by the salting-out effect.¹⁵

In this work, we developed a method for preparing anionic polyacrylamide dispersion in water media. The anionic dispersion copolymer of AM and 2-acrylamido-2-methyl-1-propane sulfonate (AMPS) was synthesized in aqueous ammonium sulfate media by using 2,2'-azobis(2-amidino-propane) dihydrochloride (V-50) as an initiator and poly(2-acrylamido-2-methyl-1-propane sulfonate) (PAMPS) as a steric stabilizer. Compared with the nonionic stabilizers used in other works,^{9,16,17} the stabilizer used in this work was a polyelectrolyte with sulfonate group. In addition to the steric stabilization, the negative charged end groups in the polymer chains of PAMPS were anticipated to enhance the stabilization of the lattices by electrostatic repulsion. The swelling property of the dispersion copolymer was discussed, and the effects of concentration of the salt, the monomers, the stabilizer, and the initiator on molecular weight and particle size were investigated, respectively. Finally, the optimum conditions for preparing stable dispersion were found out.

EXPERIMENTAL

Materials

Acrylamide (AM) and 2-acrylamido-2-methyl-1-propane sulfonate (AMPS) were industrial materials, used without further purification. Ammonium sulfate (AS) and 2,2'-azobis(2-amidino-propane) dihydrochloride (V-50) were of analytical grade, and used as received. Poly(2-acrylamido-2-methyl-1-propane sulfonate) (PAMPS) was prepared from AMPS in an aqueous solution using V-50 as initiator at 50°C. PAMPS had a molecular weight of $3.0 \times 10^5 - 5.0 \times 10^5 \text{ g mol}^{-1}$. Deionized water was used throughout this work.

Preparation of dispersion polymers

Varying quantities of ingredients containing monomers, AS, PAMPS, and deionized water were added to a 500 mL glass reactor fitted with a stirrer, a reflux condenser, a thermometer and a nitrogen inlet tube. After purging with nitrogen and controlling temperature at 50°C by means of an external heating jacket, the monomers were initiated by drop-feeding V-50 aqueous solution into the reactor uniformly over a period of 1 h. After reacting for 6 h, heating was stopped, and the AM/AMPS dispersion copolymer was obtained. The polymerization was carried out at a constant tempera-

ture of $(50 \pm 2)^\circ\text{C}$, and the stirring speed was fixed at 400 rpm from the beginning to the end.

Characterization of the dispersion copolymer

The apparent viscosity of the aqueous copolymer solution was measured with NDJ-2 rotational viscometer at 25°C in deionized water and in the salt water in which AS concentration kept equal with that of the original dispersion. The intrinsic viscosity $[\eta]$ of the copolymer was determined in 1M NaCl aqueous solution with an Ubbelode capillary viscometer at 30°C. The average molecular weight M_W could be calculated with the Mark-Houwink relationship:

$$M_W = \{10,000 \times [\eta]/3.73\}^{1/0.66}$$

The total monomer conversion could be obtained by determining the residual contents of AM and AMPS with bromating method. About 4.0 g of copolymer dispersion was weighed out in a weighing bottle, and then 100 mL of deionized water was added. After stirring adequately, the sample solution could be obtained. Excessive $\text{KBrO}_3\text{-KBr}$ was added into the sample solution. In the existence of H^+ , KBrO_3 reacted with KBr to produce Br_2 , and then Br_2 could react with residual AM and AMPS in the sample solution for addition reaction. Excessive KI was used to react with the residual Br_2 , and I_2 was formed from the reaction mixture. By titrating I_2 with the standard solution of $\text{Na}_2\text{S}_2\text{O}_3$ and calculating the consumption of $\text{Na}_2\text{S}_2\text{O}_3$, the total residual contents of AM and AMPS could be determined by means of the interrelationships of these ingredients.

The particle size and particle size distribution was determined by a LS230 Sizer of Coulter Company. The samples were usually dispersed by the ultrasonic agitation before measurements. The salt water in which AS concentration was equal with that of the original dispersion was used as circulating water. This ensured that an extended electrical double layer did not artificially increase the size.

RESULTS AND DISCUSSIONS

Effect of the salt concentration

In the article, the effects of AS concentration on molecular weight and particles size of the dispersion copolymer were studied in the range of 20–30%, while the monomers, the stabilizer, and the initiator concentration were kept constant at 14%, 1.8%, and $1.0 \times 10^{-4} \text{ mol L}^{-1}$, respectively. As shown in Table I, the increasing dosage of AS did not seem to have strong effects on molecular weight and monomers conversion. Contrary to this, the particle sizes yet took on the decreasing tendency at the same condition.

TABLE I
Effect of Salt Concentration on Dispersion Copolymers

| AS (% w/v) | M_w (10^6 g mol ⁻¹) | Conversion (%) | PD (μ m) |
|------------|--------------------------------------|----------------|---------------|
| 18 | coagulated | | |
| 20 | 6.73 | 93.3 | 4.6 (1.0–7.6) |
| 22 | 6.89 | 93.9 | 4.2 (1.0–6.5) |
| 25 | 6.93 | 93.1 | 3.0 (1.2–5.8) |
| 28 | 6.83 | 92.8 | 3.1 (1.1–6.0) |
| 36 | coagulated | | |

PD, average of particle diameter (range of particle diameter). Polymerization conditions: AM/AMPS (mol ratio), 80/20; total monomer, 14%; PAMPS, 1.8%; V-50, 1.0×10^{-4} mol L⁻¹.

According to the Electrical Double Layer Thesis of Colloids, AS was added into the reaction system as an electrolyte, and it would reduce the thickness of diffusion electrical double layer of the copolymer molecules. As a result, the ζ -potential of molecules decreased, and the electrostatic repulsion between molecules was weakened. So molecules tended to aggregate into the colloid particles that possessed a higher electrostatic stability in the water medium, and actually the dispersion copolymer was about to form. What discussed above was just about why AS was used in this reaction system. When the AS concentration was below 20%, we could not get a stable dispersion but a high yield of coagulum. Because of the insufficient salt-out effect, the behavior of weakening the electrostatic repulsion between particles was not efficient enough, and copolymer particles would not precipitate but dissolve in water, thus resulted in the generation of a homogeneous gel. Song et al.¹⁸ argued when AS concentration was lower, the extent of ionization would be higher, and the stabilization of stabilizer would be diminished. Meanwhile, the precipitation of stable nuclei would be deterred to some extent until the polymer chain length was large enough. After that, the formed particles might coalesce at a rapid rate. When the concentration of AS increased, the precipitation of polymer would occur when the polymer chains were shorter and so smaller colloid particles were obtained. Gradually, the stable dispersion could be produced successfully. However, the AS concentration could not be too high, and the anticipated dispersion could not be obtained on that condition. When AS concentration was above 30%, excessive salting-out effect would neutralize the electrostatic repulsion between particles. At this time, the electrostatic attraction became the main force between particles, which resulted in the coagulation of particles, and a high yield of the coagulum was obtained in the form of agglomerated lumps separated from the medium.

In the system, the varying concentration of AS could affect the polymerization, especially the activeness of the initiator V-50. As the initiator decomposed, free rad-

icals were produced, and they reacted with monomers to form oligomeric radicals. When the concentration of AS was higher, stronger electrostatic effect might make the radicals difficult to move. So the probability of collision between radicals and monomers was reduced. That is, it required more reaction time to a similar degree, compared with that of lower salt concentration. Under that condition, properly increasing initiator concentration was necessary to make reaction time reasonable.

Effect of the monomer concentration

The effects of the monomer concentration on molecular weight, monomer conversion, and particle size of the dispersion copolymer were shown in Table II. It was seen that molecular weight, monomer conversion and particle size all increased with the increase of the monomer concentration. This was the expected trend reported in some literatures.^{19–22} When the monomer concentration was higher than 16%, the dispersion was so unstable that coagulation occurred. As increasing the monomer concentration, the salt-out effect and the stabilization of AS would be weakened, the instability of copolymer particles in the medium increased, and dispersion coagulated gradually.

Effect of the stabilizer concentration

In the system, a water-soluble homopolymer PAMPS was used as a steric stabilizer. Table III showed the effect of PAMPS concentration on the dispersion copolymers. When PAMPS content was less than 1.2%, stable copolymer particles were few, and an agglomerating system was obtained. The result might be caused by the insufficient adsorption on the polymerized phase. As the content of the stabilizer increased to a certain value, more stable copolymer particles were produced. When the stabilizer concentration was larger than 3.0%, the stability of the dispersion became very poor, and some coagulated lumps separated from the medium. Cho et al.²³ argued that the extra stabilizer

TABLE II
Effect of Monomer Concentration on Dispersion Copolymers

| Monomer (% w/v) | M_w (10^6 g mol ⁻¹) | Conversion (%) | PD (μ m) |
|-----------------|--------------------------------------|----------------|---------------|
| 6 | 4.84 | 89.0 | 2.4 (1.0–4.9) |
| 8 | 5.33 | 90.3 | 2.7 (1.0–4.8) |
| 10 | 5.68 | 91.7 | 2.9 (1.0–5.3) |
| 12 | 6.17 | 93.2 | 2.9 (1.2–5.6) |
| 14 | 6.93 | 93.1 | 3.0 (1.2–5.8) |
| 16 | coagulated | | |
| 18 | coagulated | | |

PD, average of particle diameter (range of particle diameter). Polymerization conditions: AM/AMPS (mol ratio), 80/20; PAMPS, 1.8%; AS, 25%; V-50, 1.0×10^{-4} mol L⁻¹.

TABLE III
Effect of Stabilizer Concentration
on Dispersion Copolymers

| PAMPS (% w/v) | M_w (10^6 g mol $^{-1}$) | Conversion (%) | PD (μ m) |
|------------------|-----------------------------------|-------------------|------------------|
| 0.60 | coagulated | | |
| 0.96 | coagulated | | |
| 1.2 | coagulated | | |
| 1.8 | 6.93 | 93.1 | 3.0 (1.2–5.8) |
| 2.1 | 6.01 | 90.8 | 2.8 (1.1–5.4) |
| 2.4 | 5.80 | 89.4 | 2.5 (1.3–5.5) |
| 2.7 | 5.63 | 92.7 | 2.4 (1.2–5.1) |
| 3.0 | coagulated | | |
| 3.6 | coagulated | | |

PD, average of particle diameter (range of particle diameter). Polymerization conditions: AM/AMPS (mol ratio), 80/20; total monomer, 14%; AS, 25%; V-50, 1.0×10^{-4} mol L $^{-1}$.

molecules presented links between copolymer particles, which resulted in larger particles and ultimately caused flocculation. As shown in Table III, when the concentration of PAMPS was below 1.2% or above 3.0%, the copolymer dispersion would coagulate. The suitable PAMPS concentration was from 1.8 to 2.7%.

The molecular weight of copolymers decreased with the increase of PAMPS concentration when stable dispersion copolymers were obtained. The result was just contrary to some authors' works. Ye et al. reported that molecular weight had the opposite tendency with the varying stabilizer concentration. He explained that it was the result of gel effect.¹¹ In Ye et al.'s opinion, as the polymerization took place to a considerable degree, the particle phase captured oligomeric radical from the continuous phase, and the molecular weight of copolymer would increase rapidly. With a higher concentration of stabilizer, particle size became smaller at the beginning of polymerization, and the rate of solid-phase polymerization became faster as a result of faster access of monomer. It might lead to solid-phase polymerization of high molecular weight because of the restricted radical termination in the gel particles. In this work, however, it did not seem that the gel effect was so significant. An important distinction was the use of *tert*-butanol (*t*-BA), which was not used in this work. The copolymer and the oligomeric radical of AM and AMPS are soluble in water, but they are insoluble in *t*-BA; therefore, they tend to move to aqueous phase or water-soluble particle phase while they repulse *t*-BA.

Just corresponding to this article, the molecular weight decreased as described in some other authors' articles.²⁴ Cho et al.²³ found that the molecular weight of polymers obtained by dispersion polymerization was lower than that obtained by either solution polymerization or precipitation polymerization, and molecular weight decreased with the increase of stabilizer concentration. Moreover, one noticeable difference between the three systems was the use of stabilizer, which was

only used in dispersion polymerization. Therefore, one possible explanation was that PAMPS, used as stabilizer in this work, could act as a chain-transfer agent, which led to the lower molecular weight with the increasing concentration of the stabilizer.

Effect of the initiator concentration

The V-50 concentration was changed between 1×10^{-4} and 4.5×10^{-4} mol L $^{-1}$. Table IV showed that the molecular weight decreased with the increase of initiator concentration. This was an expected line.^{18,25} Odian²⁶ argued that the kinetic chain length of a radical chain polymerization was determined as the average number of monomer molecules consumed per each radical, which initiated a polymer chain. It was proportional to the radical concentration. So the increase of V-50 concentration resulted in a lower polymer molecular weight.

It also could be seen that particle size increased with the increase of the initiator concentration. This was an expected behavior, yet the mechanism of initiation was still debatable. Ye et al.¹¹ argued that a higher initiator concentration would lead to grafts of shorter oligomer chain length that had greater solubility in the reaction medium. The adsorption of the grafted stabilizer on the particles would therefore be retarded, thus larger sized particles were formed. On the other hand, Song and coworkers^{23,27,28} believed that higher initiator concentration led to a greater rate of generation of unstable oligomeric radicals. As the generation rate of the oligomeric radicals was much faster than the adsorption rate of the stabilizer, the oligomers would tend to aggregate and form the larger particle nuclei of various sizes, before enough stabilizers were adsorbed to make them stable. When the two views were compared, our work was more consent to that of Song et al.

Apparent viscosities of the diluted copolymer dispersion

An apparent viscosity test was made to study the swelling property of the diluted dispersion of the AM/

TABLE IV
Effect of Initiator Concentration
on Dispersion Copolymers

| V-50 (mol L $^{-1}$) | M_w (10^6 g mol $^{-1}$) | Conversion (%) | PD (μ m) |
|--------------------------|-----------------------------------|-------------------|------------------|
| 1.0 | 6.93 | 93.1 | 3.0 (1.2–5.8) |
| 2.0 | 6.37 | 93.5 | 3.1 (1.3–5.9) |
| 3.0 | 5.84 | 94.6 | 3.4 (1.0–6.1) |
| 4.0 | 5.14 | 95.7 | 3.6 (1.1–6.1) |
| 4.5 | 4.07 | 95.9 | 3.9 (1.0–6.0) |

PD, average of particle diameter (range of particle diameter). Polymerization conditions: AM/AMPS (mol ratio), 80/20; total monomer, 14%; AS, 25%; PAMPS, 1.8%.

TABLE V
The Apparent Viscosities of the AM/AMPS Copolymer Aqueous Solutions Diluted with the Deionized Water

| Concentration (%) | 6 rpm (mPa s) | 12 rpm (mPa s) | 30 rpm (mPa s) | 60 rpm (mPa s) |
|-------------------|---------------|----------------|----------------|----------------|
| 12 | 4,400 | 2,750 | 1,800 | 990 |
| 10 | / | / | / | / |
| 8 | / | / | / | / |
| 6 | / | / | / | / |
| 4 | 30,000 | 20,250 | 12,900 | 9,350 |
| 2 | 3,900 | 2,950 | 1,920 | 1,360 |
| 1 | 850 | 725 | 535 | 387.5 |
| 0.5 | 140 | 127.5 | 109 | 92.5 |

"/": beyond the max. measuring range of the NDJ-2 rotational viscometer.

AMPS copolymer in deionized water and in the salt water in which the AS concentration kept equal with that of the original dispersion, as shown in Tables V and VI.

From Table VI, it could be found that the apparent viscosities of solutions diluted with the salt water were all less than that of the original dispersion (12% concentration), and they reduced gradually with the decreasing diluted concentration. However, when diluted with deionized water, the tendency shown in Table V was more different from what we just discussed above. At several special consistencies (10, 8, 6, 4%), the apparent viscosities were all larger than that of the original dispersion. Especially at 10, 8, and 6%, the viscosities were so large that they exceeded the range of the viscometer and could not be determined. When Table V was compared with Table VI, it could also be seen that the apparent viscosity of the former was much larger than that of the latter at a specific rotational speed.

As we discussed above, AS acted as phase-out reagent by the salting-out effect in the system. When diluted with the salt water, the concentration of AS changed few, and salting-out effect was equal with that diluted before. So the dispersion was still stable, and its apparent viscosity changed few. While diluted with deionized water, AS concentration decreased. Because of the insufficient AS concentration, the salting-out effect was weakened. The stability of the colloid particles was destroyed and so the particles were dissolved in water. Therefore, the molecular chains of the particles expanded, and hydrodynamic volumes enlarged, which resulted in the viscosity of the diluted dispersion becoming larger.

Particle size of the copolymer dispersion

As shown in Figure 1, the average particle size of the original dispersion (12% consistency) ranged from 1.1 to 3.8 μm , and that of the dispersion diluted with the salt water was also in the range of 1.0–4.0 μm . That is, when diluted with the salt water, both particle size and

particle size distribution of the dispersion kept consistent essentially. On the other hand, when diluted with deionized water, the average particle size ranged from 1.1 to 20.0 μm , which changed more compared with those of the original dispersion and the dispersion diluted with the salt water. Particularly, the particle size became large, and particle size distribution was broader than that diluted before.

Just corresponding to what we discussed above, AS was a key factor in the system. When diluted with the salt water, the salting-out effect changed a little. So the dispersion were stable, the colloid particles also kept their electrostatic stability in the water medium, and particle sizes and particle size distributions kept consistent essentially. While diluted with deionized water, AS concentration decreased. Because of the insufficient salt concentration, the behavior of weakening to the electrostatic repulsion between particles was not efficient enough, the molecular chain expanded, and the particle size became larger.

CONCLUSIONS

The copolymer of AM and AMPS was synthesized through free radical dispersion polymerization in an aqueous solution of AS and in the presence of PAMPS as stabilizer.

The concentrations for obtaining stable dispersion copolymer of AM/AMPS were as follows: for AS, it ranged from 20 to 30%, and the monomers were in the range of 6–16%, while the suitable PAMPS concentration ranged from 1.8 to 2.7%. The optimum concentrations for AS, the total monomers and PAMPS were 25, 8–14, and 1.8%, respectively. The average particle size of the aqueous dispersion obtained was between 1 and 4 μm , and the molecular weight was from 2.0×10^6 to $7.0 \times 10^6 \text{ g mol}^{-1}$.

When diluted with the salt water in which the AS concentration kept equal with that of the original dispersion, the particle size was in the range of 1.0–4.0 μm . Compared with the range of 1.1–3.8 μm of the original dispersion, it changed a little. The apparent viscosities of diluted dispersions were all less than that of the orig-

TABLE VI
The Apparent Viscosities of the AM/AMPS Copolymer Aqueous Solutions Diluted with the Salt Water

| Concentration (%) | 6 rpm (mPa · s) | 12 rpm (mPa · s) | 30 rpm (mPa · s) | 60 rpm (mPa · s) |
|-------------------|-----------------|------------------|------------------|------------------|
| 12 | 4400 | 2750 | 1800 | 990 |
| 10 | 2530 | 1637.5 | 970 | 710 |
| 8 | 750 | 512.5 | 326 | 237.5 |
| 6 | 225 | 175 | 106 | 80 |
| 4 | 70 | 60 | 55 | 51 |
| 2 | 30 | 22.5 | 18.4 | 16.4 |
| 1 | 20 | 15 | 10.4 | 9.8 |
| 0.5 | 10 | 7.5 | 6.8 | 6.0 |

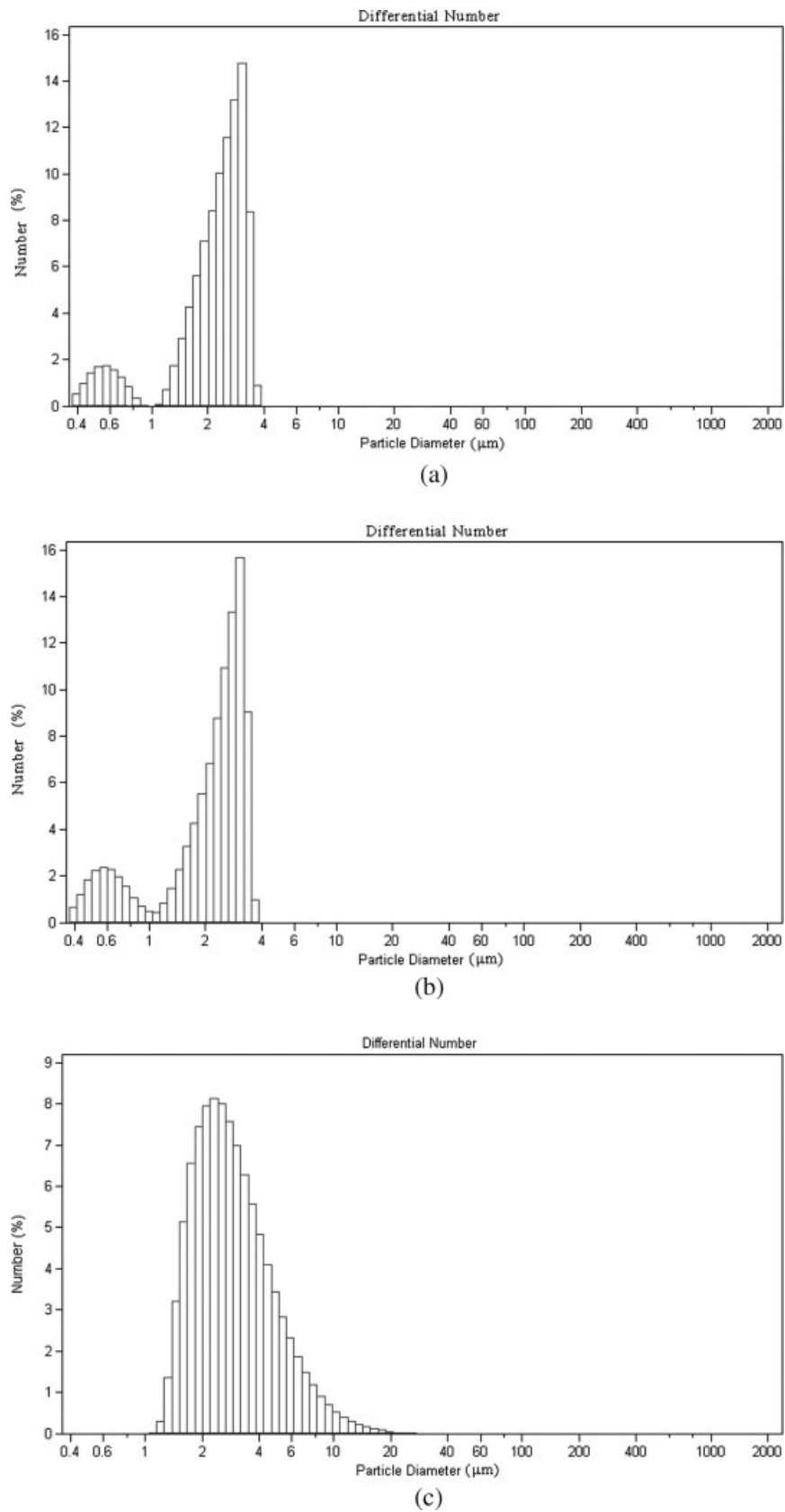


Figure 1 Particle size distribution of different solutions (a) original solution, (b) solution diluted with salt water, and (c) solution diluted with deionized water.

inal dispersion, and they reduced gradually with the decreasing concentration of diluted solution. While diluted with deionized water, the particle size ranged between 1.1 and 20 μm , which was several times broader than that of the original dispersion. Meanwhile, their apparent viscosities were all much larger than that of the original dispersion.

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