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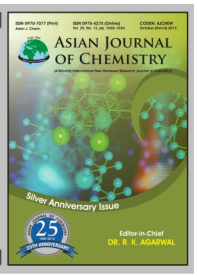

Preparation and Characterization of Poly(aspartic Acid) Derivatives as Biodegradable Water Treatment Agents

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Two poly(aspartic acid) derivatives (PASP-GLU and PASP-SEA-GLU) were prepared from polysuccinimide (PSI), taurine (SEA) and glutamic acid (GLU). The structure of poly(aspartic acid) derivatives were characterized by means of FTIR. The performance of scale inhibition, dispersion and biodegradation were studied. The results showed that PASP-SEA-GLU and PASP-GLU both have better scale inhibition and dispersion performance than PASP and PASP-GLU has better scale inhibition performance; PASP-SEA-GLU has better dispersive performance. PASP-SEA-GLU and PASP-GLU were easily biodegradable. The crystal samples of calcium carbonate were characterized by SEM. The results showed that the crystal form of calcium carbonate was global vaterite after poly(aspartic acid) derivative was added.

Key Words: Ammonolysis, Scale-inhibition, Dispersion, Biodegradation.

INTRODUCTION

It's well known that most water treatment agent are only slightly biodegradable, which might possibly produce significant damage to the environment. Therefore, they should be designed to be completely biodegradable and thus removed from the environment.

Poly(aspartic acid) (PASP) is of potential interest for use as a biodegradable water-soluble poly(carboxylic acid). Recently, we reported that a high molecular weight Poly(succinimide) (PSI) with a linear structure was synthesized by the thermal polycondensation of ASP and then easily hydrolyzed to PASP with a high biodegradability[1,2]. However, the Fe_2O_3-dispersion property, which is one important property for a dispersant or detergent builder, was not enough to use PASP in place of poly(acrylic acid). So it is important to improve its performance of dispersion and scale by research on modified PASP. Poly(succinimide) (PSI) was easily reacted with a primary amine to produce poly(asparatamide) with functional groups in the side-chain[3-8]. For example, Neri *et al.*[9] reported that PSI was prepared by the polycondensation of L-aspartic acid (ASP) in a large amount of orthophosphoric acid and then reacted with ethanolamine to produce poly[(2-hydroxyethyl)-aspartamide] as a plasma expander. Gao *et al.*[10] introduced hydroxyl and sulfonic acid into poly(aspartic acid) molecules.

Thus, PSI that reacted with suitable amounts of taurine (SEA) and glutamic acid (GLU) or only with glutamic acid (GLU) might be converted into an amphiphilic PASP with high Fe_2O_3-dispersion property.

In this paper, functional groups are introduced in the side chain of PASP in order to develop an environmentally friendly and high-efficient water treatment chemical use in industrial circulating cooling water system.

EXPERIMENTAL

L-Aspartic acid (ASP), N,N-dimethylformamide (DMF), taurine (SEA), glutamic acid (GLU), constant temperature magnetic stirrer water bath, type 722 visible spectrophotometer, FEI 3D scanning electron microscopy (SEM), type Nicolet 5700 Fourier infrared spectrometer.

Poly(succinimide) (PSI) was prepared by the thermal polycondensation of ASP in accordance with the description in a previous paper[11].

Preparation of poly(aspartic acid) (PASP): The poly(succinimide) (10.0 g, 103 mmol) was added into the molar ratio of 1.2 times MeOH (14, wt %) , stirring 1 h at 20 ºC. As the solution pH is 7.0, alcohol (AR) was dropwised to solution. Then yellowish-brown solid-state PASP was obtained by filtering. After filtration, the precipitate was washed with ethanol (30 mL × 2) and vacuum dried at 80 ºC.

The average molecular weight of PASP is 1.67×10^4, determined by viscometry in accordance with the description in a previous paper[12].

Preparation of taurine (SEA) and glutamic acid (GLU) modified poly(aspartic acid) (Fig. 1): A typical procedure for the preparation of the taurine and glutamic modified poly(aspartic acid) is as follows: The taurine (7.5 g, 60 mmol) and glutamic acid (5.88 g, 40 mmol) was added into the molar ratio of 1.2 times (25, wt %) in MeOH separately. To a solution of poly(succinimide) (10 g, 103 mmol) in water (30 mL) was added 2-aminoethane sulfonate and sodium glutamate drops. After stirring 22 h at 20 ºC, the reaction mixture was poured into ethanol (500 mL). After filtration, the precipitate was washed with ethanol (30 mL × 2) and vacuum dried at 80 ºC. Dilute sulphuric acid was added into the remaining reaction mixture to separate out the taurine (isoelectric point was 5) and glutamic acid(isoelectric point was 3.22). The grafting ratio of taurine and glutamic acid were 54.2 and 39.8 %.

Preparation of glutamic acid (GLU) modified poly(aspartic acid): The glutamic acid(14.7 g, 100 mmol) was added into the molar ratio of 1.2 times (25, wt-%) MeOH. The solution of poly(succinimide) (10 g, 103 mmol) in water (30 mL) was added sodium glutamate drops. After stirring 25 h at 25 ºC, alcohol (AR) was added drop wise to solution. Then yellowish-brown solid-state PASP-GLU was obtained by filtering. After filtration, the precipitate was washed with ethanol (30 mL × 2) and vacuum dried at 80 ºC for 5 h. To the remaining reaction mixture was added dilute sulphuric acid to separate out glutamic acid (isoelectric point was 3.22). The grafting ratio of glutamic acid was 36.8 %.

Scale inhibition ability of modified poly(aspartic acid): The scale inhibition ability was evaluated by static anti-scaling method. The feed solution was prepared by dissolving in distilled water appropriate amounts of $CaCl_2$ (4 mmol L^{-1}) and $NaHCO_3$ (8 mmol L^{-1}). Added 500 feed water and a certain concentration of scale inhibitor to Erlenmeyer flask (500) to boil for 10 h at 80 ºC. A blank test was made with no scale inhibitor. An aliquot of the supernatant liquid was withdrawn for analysis to determine the concentration of soluble calcium ions using a standard solution of EDTA titration. The efficiency of scale inhibition was calculated based on the concentration of calcium ions remaining in the supernatant liquid from the flask containing no inhibitor and the flask containing a known amount of the inhibitor, respectively. The efficiency of scale inhibition was calculated as follows:

$$\text{Efficiency of scale inhibition} = \frac{C_M - C_1}{C_0 - C_1} \times 100$$

where C_M is the concentration of soluble calcium ion, mg/L; C_1 is the concentration of soluble calcium ion in blank solution, mg/L; C_0 is the concentration of soluble calcium ion in feed solution, 400 mg/L.

Dispersion capacity of modified poly(aspartic acid): The dispersion capacity was evaluated by ferric(III) oxide powder[13]. The sample, (75 mg) $CaCl_2$, (250 mg) $Na_2B_2O_7$, (35 mg) $FeSO_4 \cdot 7H_2O$ and H_2O (500 mL) was added into flask (500 mL) boiled for 5 h at 50 ºC in the constant temperature water bath. An aliquot of the supernatant liquid was withdrawn for analysis to measure transmittance at 420 nm. The smaller the light transmittance, the better is the dispersion.

Biodegradability of modified poly(aspartic acid): The biodegradability of modified poly (aspartic acid) was estimated using shaking-bottle incubating test in accordance with the description in a previous paper[13].

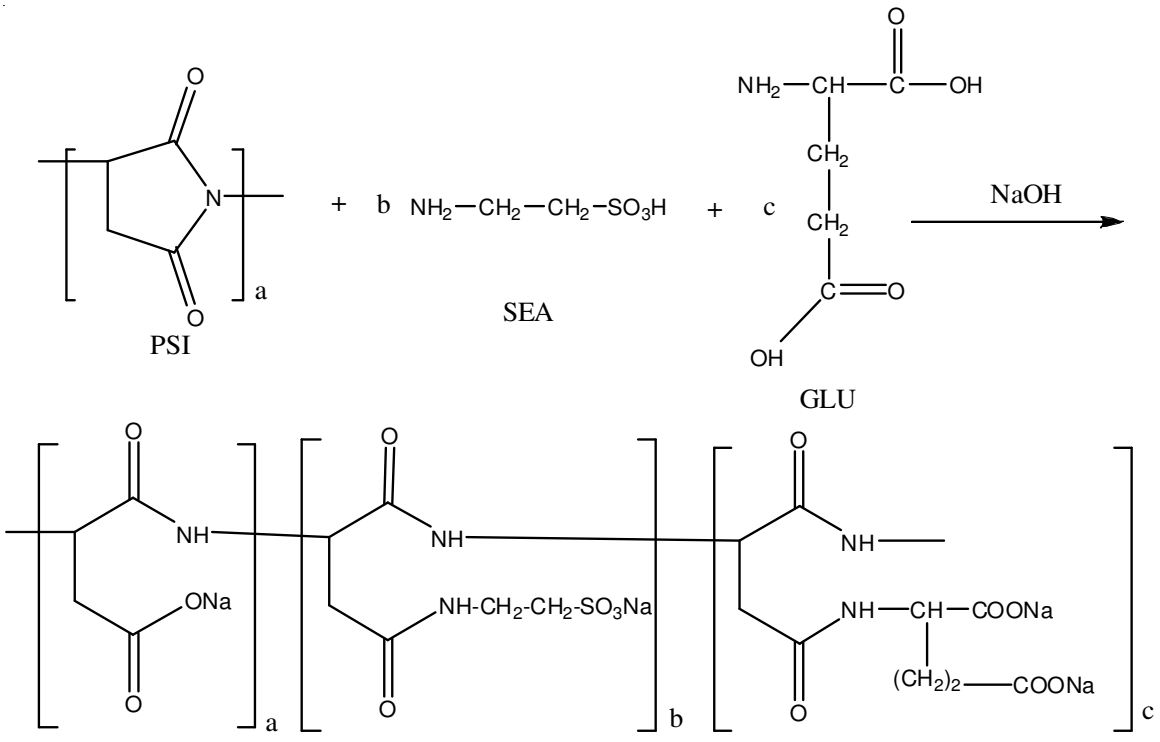


Fig. 1. Chemical structure of PASP-SEA-GLU

RESULTS AND DISCUSSION

The reaction of poly(succinimide) (PSI) with taurine and glutamic acid were carried out for the purpose of introducing factional groups into PSI. Fig. 2 shows IR spectrum of PASP and PASP-SEA-GLU. Comparing the IR spectrum of PASP with that of PASP-SEA-GLU, it is observed in the IR spectrum of PASP-SEA-GLU, 1045 cm^{-1} the characteristic absorption peak of $-SO_3Na$ prove that PSI has reacted with taurine; in the IR spectrum of PASP-SEA-GLU 1130cm^{-1} characteristic absorption peak of C-N bond much stronger and displacement than the PASP shows that C-N bond in the PASP-SEA-GLU is a lot more than PASP. In the IR spectrum of PASP-SEA-GLU 1656 cm^{-1} the C=O absorption peak compare with PASP happened displacement. The IR spectrum of PASP-SEA-GLU 3402 cm^{-1} shows the N-H characteristic absorption peaks in the amide much stronger and displacement than the PASP. As a result of the work mentioned above, PSI reacted with SEA and GLU generated PASP-SEA-GLU.

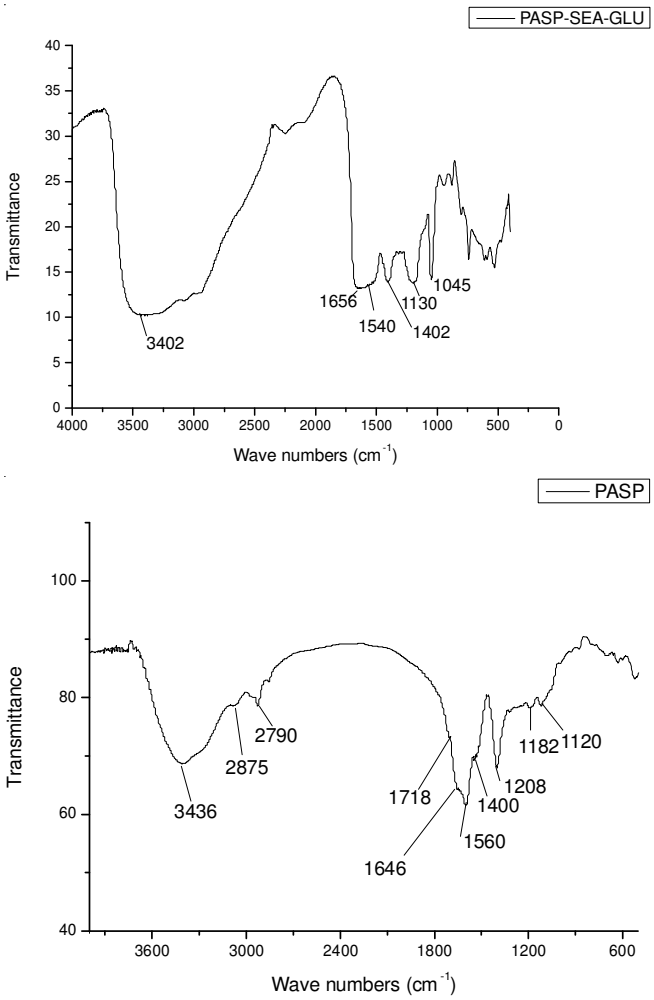


Fig. 2. IR spectrum of PASP-SEA-GLU and PASP

Comparing the IR spectrum of PASP-GLU with that of PASP, it is observed in the IR spectrum of PASP-GLU 1139 cm^{-1} the characteristic absorption of C-N much stronger and displacement than the PASP show C-N bond in the PASP-GLU is more than PASP. In the IR spectrum of PASP-GLU 1540 cm^{-1} the characteristic absorption peak of -COONa has a strong displacement than PASP. In the IR spectrum of PASP-GLU 1660 cm^{-1} the C=O absorption peak in amide compare with PASP happened displacement. In the IR spectrum of PASP-GLU, 1716 cm^{-1} the C=O characteristic absorption peaks in the carboxyl much stronger and displacement than the PASP show C=O in the PASP-GLU is more than PASP. In the IR spectrum of PASP-GLU peaks at 2960 and 2870 cm^{-1} the saturated hydrocarbons characteristic absorption peak displacement about 100 cm^{-1} than PASP. In the IR spectrum of PASP-GLU, 3392 cm^{-1} the N-H characteristic absorption peaks in the amide compare with PASP happened displacement. As a result of the work mentioned above, PSI reacted with GLU generated PASP-GLU.

The results of scale inhibition and Fe_2O_3-dispersion property are listed in Tables 1-3.

TABLE-1
SCALE INHIBITION AND Fe_2O_3-DISPERING PROPERTY OF PASP

Dosage (mg/L)	Scale-inhibition rate (%)	Fe_2O_3-Dispersion property (transmittance, %)
2	83.64	94.6
4	83.64	90.1
6	85.10	87.9
8	86.00	80.2
10	83.64	78.9
12	86.20	77.5

TABLE-2
SCALE INHIBITION AND Fe_2O_3-DISPERING PROPERTY OF PASP-SEA-GLU

Dosage (mg/L)	Scale-inhibition rate (%)	Fe_2O_3-Dispersion property (transmittance, %)
2	70.99	78.8
4	74.28	70.3
6	76.21	60.3
8	79.22	58.0
10	85.13	61.2
12	86.61	63.5

TABLE-3
SCALE INHIBITION AND Fe_2O_3-DISPERING PROPERTY OF PASP-GLU

Dosage (mg/L)	Scale-inhibition rate (%)	Fe_2O_3-Dispersion property (transmittance, %)
2	63.25	87.6
4	80.34	75.4
6	86.32	68.2
8	93.17	64.1
10	80.16	66.5
12	79.00	74.0

Tables 1-3 showed that the scale inhibition property is in the order PASP-GLU > PASP-SEA-GLU > PASP and the Fe_2O_3-dispersion property is PASP-SEA-GLU > PASP-GLU > PASP. It is evident that PASP-SEA-GLU and PASP-GLU both have better scale inhibition and Fe_2O_3-dispersion property than PASP. The results also indicated that in the sample that sulfonic acid and carboxylic acid common grafted onto the side chain of poly(succinimide) has a good Fe_2O_3-dispersion property but scale inhibition property isn't as good as the introduction of carboxylic acid sample. This can prove that sulfonic acid contribution larger to improve dispersion property

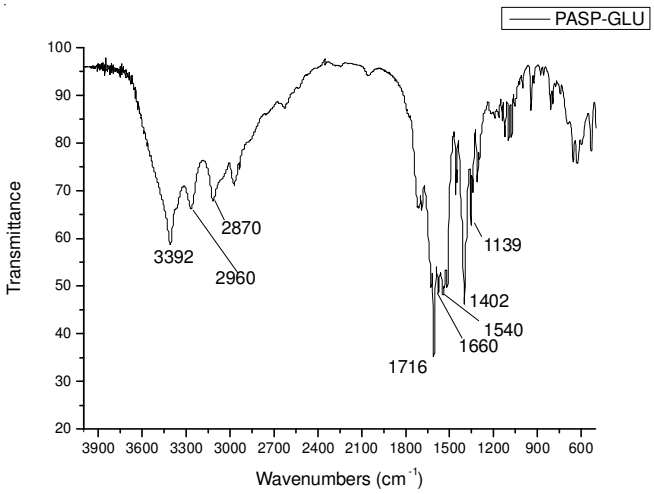
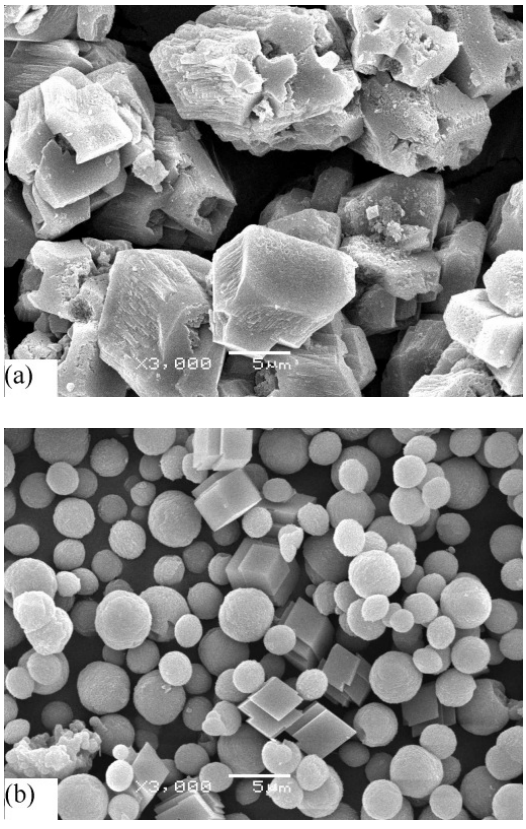


Fig. 3. IR spectrum of PASP-GLU

but reduce the scale inhibition performance. Carboxylic acid contribution larger to improve scale inhibition property but common dispersion property.

Fig. 4 shows the SEM micrographs of $CaCO_3$ formed in the solution after boiling 10 h at 80 ºC. As can be seen from the graph, in the absence of inhibitor, $CaCO_3$ exhibits rhombohedron shape and particle size is very large, loose edge has defect. This is ascribed to the fact that an uneven distribution of ion in the solution with no inhibitor, large piece of precipitation appears. When adding PASP scale inhibitor, $CaCO_3$ exhibits regular rhombohedron and spherical shape, particle size becomes small. When adding PASP-SEA-GLU scale inhibitor, $CaCO_3$ exhibits smaller fragment. When adding PASP-GLU scale inhibitor, $CaCO_3$ exhibits spherical shape and fragment.



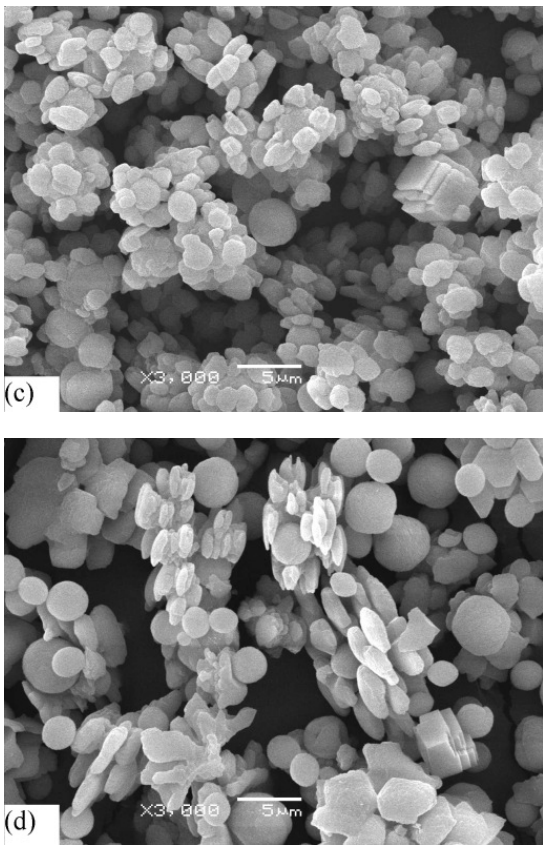


Fig. 4. SEM micrographs of $CaCO_3$ formed in the solution after boiling 10 h at 80 ºC (a) in the absence of inhibitor, (b) in the presence of 10 mg/L PASP, (c) in the presence of 10 mg/L PASP-SEA-GLU, (d) in the presence of 10 mg/L PASP-GLU

$CaCO_3$ scale formation is a heterogeneous crystallization nucleation process on the solid-liquid interface. During $CaCO_3$ crystal growth the inhibitor molecules or ions containing sulfonic acid or carboxylic acid groups (PASP, PASP-SEA-GLU and PASP-GLU) can adsorb onto the active growth sites of the crystal surface to disturb the regular outgrowth of $CaCO_3$ crystal. Accordingly the lattice distortion occurs in the presence of the inhibitors the crystal morphology and structure are changed[14]. In addition, the tiny particles adsorbed inhibitor crystals can form the electric double layer changing the charge state of the particle surface; in static state, the particles are mutually exclusive to avoid particle collisions deposits so can particles disperse in the water. Electronegativity of sulfonic acid group is larger than the carboxylic acid group, so dispersion better.

The results of biodegradability are listed in Tables 4 and 5.

TABLE-4
BIODEGRADABILITY OF PASP-SEA-GLU

Time (day)	ρCOD_{Mn} (PASP-SEA-GLU, mg/L)	ρCOD_{Mn} (blank, mg/L)	Biodegradability (removed ρCOD_{Mn},%)
0	18.24	16.71	0
4	19.158	18.24	40.0
8	20.29	19.45	45.0
12	28.089	27.35	48.4
16	25.075	24.31	50.0
20	19.40	18.69	53.8
28	18.88	18.24	58.0

TABLE-5
BIODEGRADABILITY OF PASP-GLU

Time (day)	ρCOD_{Mn} (PASP-SEA-GLU, mg/L)	ρCOD_{Mn} (blank, mg/L)	Biodegradability (removed ρCOD_{Mn},%)
0	18.24	16.71	0
4	18.995	18.24	50.0
8	20.03	19.45	62.0
12	27.748	27.35	74.0
16	24.647	24.31	78.0
20	18.96	18.69	82.1
28	18.47	18.24	85.0

The biodegradability of modified poly (aspartic acid) was evaluated by the removed COD value. The 8 day values for the PASP-SEA-GLU and PASP-GLU were 45 % (> 30 %) and 62 % (> 30 %). The results indicated that both PASP-SEA-GLU and PASP-GLU are easily biodegradable.

Conclusion

The modified poly (aspartic acid) PASP-SEA-GLU and PASP-GLU were obtained by ammonolysis of polysuccinimide. PASP-SEA-GLU and PASP-GLU had good scale inhibitor and Fe_2O_3-dispering property than PASP. The scale inhibiton property of PASP-GLU was better than PASP-SEA-GLU. The Fe_2O_3-dispering property of PASP-SEA-GLU was better than PASP-GLU. PASP-SEA-GLU and PASP-GLU were easily biodegradable. These results suggested that PASP-SEA-GLU and PASP-GLU had the possibility of being used as biodegradable water treatment agents.

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