RESEARCH NOTES

Microwave-assisted Synthesis of Modified Polyaspartic Acid in Solvent[*]

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Abstract   Polyaspartic acid (PASP) is suitable for the inhibition of scale deposition from water. To enhance its inhibition efficiency, PASP was modified by reacting aspartic acid (Asp) with glutamic acid (Glu) to provide Asp-Glu copolymer under microwave irradiation. The influence of reaction parameters on conversion, molecular weight and inhibition of $CaCO_3$ precipitation was investigated Infra-red. (IR), ^1H nuclear magnetic resonance (^1H NMR) and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectroscopies were used to characterize the copolymer. The results show that copolymerization of aspartic acid and glutamic acid is catalyzed by a small amount of phosphorous acid (H_3PO_4) in solvent, the product conversion is 98.05% under the following conditions: the molar ratio of glutamic acid to reactant [Glu/(Asp+Glu)] is 0.3 and that of catalyst (Cat) to reactant [Cat/(Glu+Asp)] is 0.05 (0.65ml H_3PO_4), the volume of solvent dimethylformamide is 16ml, the microwave power used is 720W and the reaction for 3 min. The weight average molecular weight of copolymer synthesized under these conditions is 2709 and the inhibition rate for $CaCO_3$ is 97.75%.

Keywords   microwave irradiation, aspartic acid, glutamic acid, copolymer, conversion ratio, scale inhibition

1 INTRODUCTION

Polyaspartic acid (PASP) is a representative product in new-era of green chemistry. PASP can be produced from base hydrolysis of polysuccinimide that aspartic acid (Asp) is thermally polymerized to. Its biodegradability makes it particularly valuable from the point of view of environmental acceptability and waste disposal[1]. PASP is used widely as mineral scale [such as $CaSO_4$, $BaSO_4$[2] $CaCO_3$ and $Ca_3(PO_4)_2$[3]] inhibitor in water treatment applications[4] and as dispersing agents in detergents, paints and papermaking processes. Some studies indicate that as a scale inhibitor, the scale inhibiting capability of PASP is poorer than that of phosphorus-containing inhibitor[5,6], which is especially obvious in application of inhibitors to the oilfield produced water. In order to improve scale-inhibiting capability of PASP and widen its application, studies on modified PASP have been carried out in some countries.

Methods are known for the modification of PASP. As a scale mineral inhibitor, modified PASP are mainly prepared by the copolymerization of aspartic acid with a selected polyfunctional monomer. The catalytic copolymerization of aspartic acid with tartaric acid, adipic acid[7,8], citric acid, succinic acid[9] or 1,2,3,4-butanetetra-carboxylic acid [10] produces succinimide copolymer in the presence of various catalysts and organic solvent. Modified PASP is then obtained from base hydrolysis of succinimide copolymer. The chosen monomers have the same polyfunctional group- carboxyl, and there are two or more carboxyl groups in each monomer unit. Functional group carboxyl (COOH) on the unit of PASP and modified PASP is thought to be primarily responsible for inhibition of mineral scale precipitation. However, the scale-inhibiting capability of the copolymers reported in the literature compared with PASP is not greatly enhanced. These methods rely mainly on an inefficient process of heat transfer during copolymerization, namely the traditional method of heating the reactants. Another disadvantage of these methods is the large amount of catalyst and/or dehydrating agent required for copolymerization.

There is an ongoing need, therefore, for an acceptable, convenient method for catalytically copolymerizing aspartic acid and other polyfunctional monomer to succinimide copolymers with high yield, purity and desired high molecular weight. The present method described in this paper satisfies this need, provides a useful product and overcomes the disadvantage of the previous methods. The Asp-Glu copolymer (modified PASP) is produced under microwave irradiation. As a result, the conversion ratio of product is increased and the inhibiting capability of copolymer is enhanced, which is new start for the study on modified PASP.

2 MATERIALS AND METHODS
2.1 Materials

L-aspartic acid and L-glutamic acid used are generally of food-grade from commercial source. The powdered L-aspartic acid with purity of 99.29% was obtained from Beijing Jianli Pharmaceutical Factory (China). The powdered L-glutamic acid with purity of 99.8% was purchased from Wuxi Jinghai Amino Acid Co. Ltd (China). The PASP solution (40%) was obtained from Changmao Biochemical Engineering Co. Ltd (Changzhou, China). Standard polyglycol (M_w: 400, 600, 2000, 6000 and 10000) was purchased from Sigma (St. Louis, MO). Other chemicals were commercially available and were used without further purification. Deionized water was used in this work.

2.2 Instruments and measurements

A 2450 MHz microwave oven made by Nanjing Sanle Microwave Technology Development Co.,

(China), available on several power settings (0.5, 0.9, 1.0, 1.5, 2.0, 2.5, 3.0 kW), was used.

For the measurement of Infra-red (IR) spectrum, the powdered samples were mixed with KBr and pressed into disk. IR spectrum of copolymer was measured by means of a Perkin Elmer Infrared Spectrometer (Foster City, CA).

^{13}C nuclear magnetic resonance (^{13}CNMR) and ^{1}H nuclear magnetic resonance (^{1}HNMR) spectra were recorded on a Bruker ARX400 NMR spectrometer (Fallanden, Switzerland). 5mg of sample and 1ml of D$_2$O was used for measurement. The operation parameter for ^{13}CNMR spectra was SI＝32768, SF＝100.61MHz, WDW＝EM, SSB＝0, LB＝1.0Hz, GB＝0 and PC＝1.40. The operation condition for ^{1}HNMR spectra was SI＝32768, SF＝400.13MHz, WDW＝EM, SSB＝0, LB＝0.3Hz, GB＝0 and PC＝1.0.

Average molecular weight of copolymer was measured on a Perkin Elmer Series 200 LC system (St. Louis, MO) equipped with a gel permeation chromatography column. The mobile phase was 0.1mol·L^{-1} Na$_2$SO$_4$ solution. Polyglycol was used as a standard with pH of 6.5.

2.3 Synthesis method

A small amount of catalyst was added in the mixture of aspartic acid and glutamic acid and the mixture was triturated adequately. Certain volume of dimethylformamide (DMF) was used to soak the reactant. The fully mingled reactant with catalyst and solvent in a 500ml closed beaker was irradiated under microwave. After a few minutes, the beaker was taken out and the fulvous resultant was obtained. 20ml of solution NaOH was added in the break. The pH was adjusted to 9.5 so that resultant succinimide copolymer was hydrolyzed to modified polyaspartic or Asp-Glu copolymer, and the hydrolysis process lasted 12h. The pH was adjusted to 3.86 with 6mol·L^{-1} HCl. The solution was filtrated and the filtrate was dehydrated with ethanol to form sediment. And the deposit was dried at 70℃ under vacuum and the powder product was obtained. The reaction course was described in Fig.1.

2.4 Determination of yield

Certain amount of the fulvous resultant was dissolved in a certain volume of dimethylformamide (DMF). The dissolution was allowed to proceed for 4 to 6h until all of the polymers dissolved in the DMF, leaving unreacted L-Asp or L-Glu to be filtered out. The yield (ϕ) was determined by using Eq.(1):
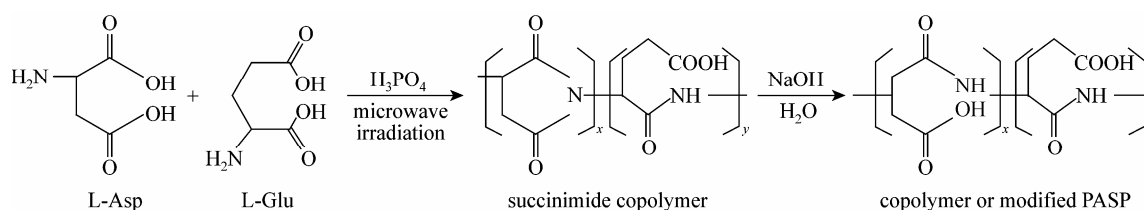
$$\varphi = \frac{A_0 - A_1}{A_0} \times 100\% \qquad (1)$$

where A_0 is the mass of the fulvous resultant sample (mg) and A_1 the mass of the unreacted L-Asp and L-Glu (mg).

2.5 Determination of scale inhibition

All of the copolymers were tested in a modified version of method for calcium carbonate scale inhibition reported in the Ref.[11]. The copolymer to be tested was added to bottles (150ml) containing 50ml of CaCl$_2$ solution at specified concentrations and the test bottles and controls (without inhibitor) were incubated at 70℃ for 0.5h. Then 50ml of NaHCO$_3$ solution was added to the bottles and the bottles were incubated at 70℃ for 25h. After cooling to room temperature, the solutions were filtered through 0.45μm filter and the calcium concentrations in the percolate were measured by EDTA titration. The inhibiting ability of a test copolymer was expressed by the percentage inhibition η:

$$\eta = \frac{V_i - V_0}{V_t - V_0} \times 100\% \qquad (2)$$

where V_0 is the consumed volume of EDTA for titrating the percolate sample without inhibitor (control) (ml), V_t the consumption of EDTA for the original sample (ml) and V_i the consumption volume of EDTA for the percolate in the sample with inhibitor (ml).

3 RESULTS AND DISCUSSION
3.1 Choice of reaction system

Glu is the chosen copolymerizable monomer containing two functional groups (carboxyl, amido). Caboxyl and amido groups on the unit of Asp-Glu copolymer are both thought to be responsible for inhibition of mineral scale precipitation. According to different systems, a series of experiments were conducted. The total amount of reactant is 20g, containing 10g of Asp and 10g of Glu. The volume of solvent is 10ml and the molar ratio of catalyst to reactant is 0.01. Irradiation of microwave was at 900W. Table 1 show that experimental conditions and results.

It is seen from tests 1 and 2 in Table 1 that copolymerization of L-Asp and L-Glu could not occur without solvent, which shows L-Asp and L-Glu cannot absorb microwave energy. Tests using water as solvent (tests 3 and 4) show that very little amount of reactant was polymerized, which indicates the temperature required for copolymerization of L-Asp and L-Glu is above the boiling point of water. It is shown by tests 5—7 that succinimide copolymer was obtained using DMF as solvent. The increase in conversion of reactant is due to catalyst added in tests 5,6. The conversion of reactant and scale inhibiting capability of

Figure 1　Synthetic route of modified PASP

Table 1   Results of the synthetic experiments

No.	Catalyst	Solvent	t, min	Test result
1	—	—	9	no reaction
2	NaH_2PO_4	—	9	no reaction
3	—	H_2O	8	little new material appeared, white substance spilled
4	NaH_2PO_4	H_2O	8	a little reacted, product having no obvious scale inhibition
5	—	DMF	4	partly reacted
6	NaH_2PO_4	DMF	4	entirely reacted, 98.82% of yield, inhibition above 70%
7	$NH_4H_2PO_4$	DMF	4	entirely reacted, 99.32% of yield, inhibition $\geqslant 70\%$

copolymer obtained from test 1 are almost the same as those obtained from test 2, which shows that $H_2PO_4^-$ is primarily responsible for catalysis. The results in all tests show that using DMF as solvent, the copolymerization of L-Asp and L-Glu occur easily under microwave irradiation, and a small amount of catalyst can increase reaction rate and shorten reaction time.

3.2   Influence of the reaction conditions

In the microwave-assisted copolymerization process, various organic solvents can be used. Different solvents have different dielectric constants that determine the efficiency of transform of electromagnetic energy to heat energy. The results in Table 1 suggest that using DMF as solvent, the high conversion and the relatively good scale inhibiting ability of copolymer were obtained. Thus, DMF was used as solvent in the subsequent study. Since $H_2PO_4^-$ has good catalysis for copolymerization of L-Asp and

L-Glu, phosphatic acid (H_3PO_4) was chosen as catalyst in the copolymerization process.

To investigate the influences of the reaction conditions on yield, molecular weight and inhibition of copolymer, an orthogonal test of 4 factors with 4 levels was designed and the appropriate copolymerization parameters were determined. The results of orthogonal test were shown in Table 2. The total amount of glutamic acid and aspartic acid was 25g. The analysis of margin of yield, molecular weight and inhibition of copolymer were recorded in Table 3, Table 4 and Table 5 respectively.

3.2.1   *Influence of the reaction conditions on yield*

It is seen from Table 3 that the microwave power is the main factor influencing the yield of copolymer, which indicates that there is an optimal range of microwave power for certain amount of reactant. If output power is lower, the reactant couldn't be completely converted into product. If output power is high

Table 2   Results of orthogonal test

No.	Glu/(Asp+Glu) molar ratio	Cat/(Asp+Glu) molar ratio	Solvent vol., ml	Irradiation time, min	Output power, W	Yield, %	M_w	Inhibition, %
1	0.1	0.02	13	3	360	5.57	317	5.21
2	0.1	0.03	16	4	540	42.89	2241	43.84
3	0.1	0.04	19	5	720	76.65	1932	54.79
4	0.1	0.05	22	6	900	96.23	2277	41.10
5	0.2	0.02	16	5	900	92.89	1783	67.12
6	0.2	0.03	13	6	720	91.32	1439	56.16
7	0.2	0.04	22	3	540	28.24	578	21.63
8	0.2	0.05	19	4	360	37.22	1334	42.47
9	0.3	0.02	19	6	540	96.62	1917	57.5
10	0.3	0.03	22	5	360	44.18	769	32.21
11	0.3	0.04	13	4	900	75.57	1918	57.3
12	0.3	0.05	16	3	720	98.05	2709	97.75
13	0.4	0.02	22	4	720	91.34	1733	66.29
14	0.4	0.03	19	3	900	94.42	1054	41.57
15	0.4	0.04	16	6	360	73.14	899	56.18
16	0.4	0.05	13	5	540	98.54	936	49.44

Table 3   Margin analysis for yield

Level	Factor				
	Glu/(Asp+Glu)	Cat/(Asp+Glu)	Solvent	Irradiation time	Output power
1	55.335	70.605	67.750	56.570	40.028
2	62.417	68.203	76.742	61.755	65.573
3	77.605	63.400	75.228	78.065	89.340
4	89.360	82.510	64.998	88.328	89.778
margin	34.025	19.110	11.744	31.758	49.750

Table 4 Margin analysis for molecular weight

Level	Factor				
	Glu/(Asp+Glu)	Cat/(Asp+Glu)	Solvent	Irradiation time	Output power
1	1703.25	1449.00	1164.00	1176.00	841.25
2	1283.50	1375.75	1908.00	1806.50	1418.00
3	1828.25	1331.75	1559.25	1355.00	1953.25
4	1155.50	1814.00	1396.25	1633.00	1758.00
margin	672.75	484.25	744.00	630.50	1112.00

Table 5 Margin analysis for inhibition on $CaCO_3$

Level	Factor				
	Glu/(Asp+Glu)	Cat/(Asp+Glu)	Solvent	Irradiation time	Output power
1	36.235	49.030	42.027	41.540	34.017
2	46.845	43.445	66.222	52.475	43.102
3	61.190	47.475	49.082	50.890	68.748
4	53.370	57.690	40.082	52.735	51.772
margin	24.955	14.245	25.914	11.195	34.731

than the optimal, charred reactant will appear in short time, thus the yield of product is lower.

3.2.2 *Influence of the reaction condition on molecular weight of copolymer*

It is seen from Table 4 the most important factors influencing molecular weight of copolymer are microwave power and amount of organic solvent. The copolymerization process could be divided into two steps. The first step was solution copolymerization of L-Asp and L-Glu to obtain Asp-Glu oligomer, during which DMF was all converted into vapor. The later step was melt polymerization of Asp-Glu oligomer to produce large copolymer. The microwave power is a key factor for driving of the copolymerizatin process.

3.2.3 *Influence of the reaction condition on inhibiting capability of copolymer*

Table 5 shows that three main factors on inhibition are output power of microwave, the amount of solvent and molar ratio of Glu/(Asp+Glu) in turn. It is seen from Table 2 that the copolymer has good inhibition for calcium carbonate when molar ratio of Glu/(Asp+Glu) is 0.3 and its weight average molecular weight is 2709, which was made by the given con-

ditions: 0.05 of molar ratio of catalyst to reactant, 16ml of solvent, 720W of microwave power and 3min of irradiation time. Here inhibiting ratio of the optimal copolymer arrived at 97.75% under following conditions: 1500 $mg \cdot L^{-1}$ of Ca^{2+}, 2300 $mg \cdot L^{-1}$ of HCO_3^- and 10 $mg \cdot L^{-1}$ of inhibitor, which is higher than of that of PASP (91.5%)[11].

3.3 Characterization of copolymer

The structure of copolymer is analyzed by infrared spectra (Fig.2), ^{13}C NMR spectra (Fig.3) and ^{1}H NMR spectra (Fig.4). Infrared spectra of copolymer exhibit two remarkable bands at 3000—3700 cm^{-1} indicating absorption peaks of imino-($=NH$), but infrared spectra of PASP exhibit a remarkable band[12], which shows there is unit of Glu in copolymer. Infrared spectra exhibits a strong band at 1610 cm^{-1} assigned to the vibration of the carbonyl group ($C=O$), which show there are plenty of —CONH. The bands at about 1385 cm^{-1} exists bending vibration of $=CH_2$ and $\equiv CH$. The IR analysis results indicate that the structure of copolymer is similar to that of PASP synthesized by
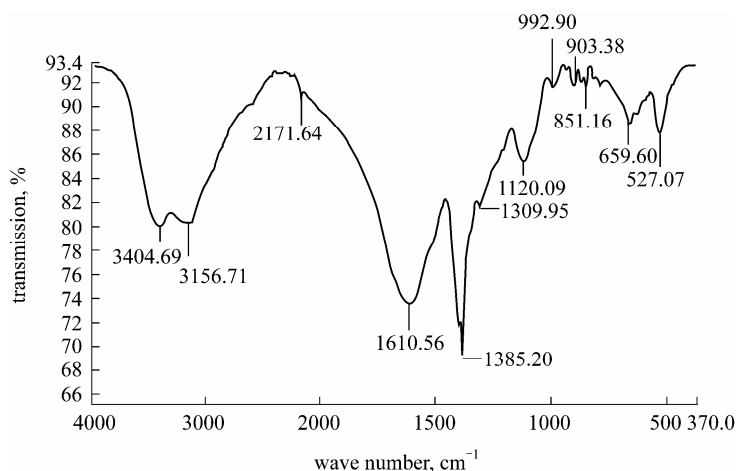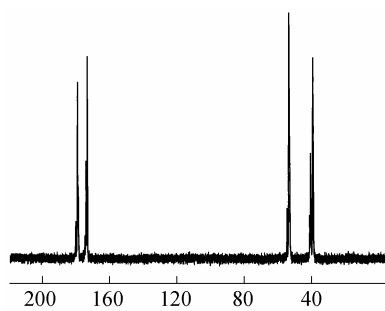
Figure 2 IR spectra of the product

Figure 3 ^{13}C NMR spectra of the
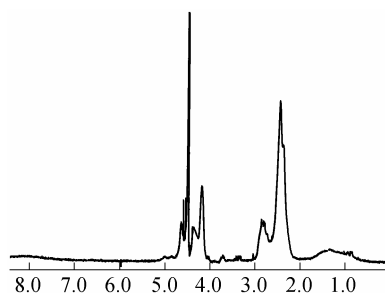product in D_2O (pD7.4)

Figure 4 ^1H NMR spectra of the
product in D_2O (pD7.4)

thermal polymerization of aspartic acid[12], which suggest that the copolymer is polyaspartic acid derivative.

^{13}C NMR and ^1H NMR spectra of the copolymer in heavy water (D_2O) are shown in Figs.3 and 4. It is seen from Fig.3 there are two chemical shifts at 170—180. The chemical shift in downfield represents COOH and the chemical shift in upfield appears CONH. The methine ($\equiv CH$, 53—57) and methylene ($\equiv CH_2$, 35—40) carbons are observed from ^{13}C NMR spectra of the product. Fig.4 shows the chemical shift at 2.0—3.0 represented methylene. The chemical shift at 4.1—4.8 indicate methine proton. Any acid or amide protons would have exchanged with the bulk solvent (D_2O), and peaks for these species were not observed. ^1H NMR and ^{13}C NMR spectra of the product in this study are homologous with ^1H NMR and ^{13}C NMR spectra of PASP prepared by thermal polymerization of L-aspartic acid reported in the Ref.[13,14], which further indicates the product in the study is polyaspartic acid derivative.

3.4   Scale inhibiting performance of copolymer

Using the optimal copolymer in the paper and commercial PASP as inhibitors, their inhibition for $CaCO_3$ was investigated. The inhibiting ratios were depicted in Fig.5 under the given conditions: Ca^{2+} concentration was different in solution, the molar ratio of Ca^{2+}/HCO_3^- was 1 : 1 and the inhibitor concentration was $10mg \cdot L^{-1}$. Fig.5 shows that the inhibition performance of copolymer is superior to that of PASP. With Ca^{2+} concentration increased, inhibiting ratio of two inhibitors is descending. And the descending trend of PASP is more remarkable. This indicates the copolymer is more suitable for water treatment system with high Ca^{2+} concentration.
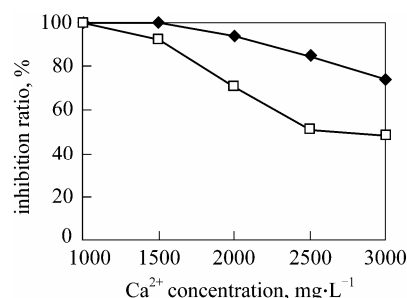
Figure 5   Influence of Ca^{2+} concentration on inhibition
◆ copolymer; □ PASP

NOMENCLATURE

EM   exponential motion
GB   Gaussian broadening factor
LB   Line broadening factor
PC   peak picking sensitivity
SF   proton resonance frequency
SI   the number of data point
SSB   sine bell shift
WDW   window multiplication mode

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