# Microwave-assisted Synthesis of Polyaspartic Acid and its Effect on Calcium Carbonate Precipitate

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**ABSTRACT:** Without organic solvent or catalyst, polyaspartic acid (PASP) was synthesized from maleic anhydride (MA) and ammonia (AN) under microwave irradiation. The influences of the molar ratio of maleic anhydride to ammonia and the microwave output power and irradiation time on product yield were investigated. Also, the function of microwave in the process was simply addressed. The results showed that when the molar ratio of MA/AN was 1.2, the output power was 900 W, the irradiation time was 3.5 min, and the product yield was highest and its inhibition performance on calcium carbonate was as good as the polymer synthesized by conventional pyrocondensation polymerization. The main function of microwave was its heat effect. Characterization of the product was carried out by IR, ^{1}HNMR, and ^{13}CNMR spectra and the results showed that the product was PASP. The microwave-assisted synthesis process of PASP has many advantages, including quicker reaction rate, high purity, lower cost, and little pollution. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 358–364, 2007

**Key words:** polyaspartic acid; microwave irradiation; inhibition performance

## INTRODUCTION

Polyaspartic acid is considered to be an environmentally friendly chemical. Its biodegradability makes it particularly valuable from the point of view of environmental acceptability and waste disposal. PASP having a weight average molecular weight of 1000 to 5000 exhibits a high degree of inhibition on calcium carbonate, calcium phosphate, calcium sulfate, and barium sulfate.[1,2] Carbon dioxide corrosion of mild steel in brine substantially free of dissolved oxygen can be effectively inhibited under mild to moderate dynamic-flow use conditions by relatively low concentrations of PASP.[3]

PASP is obtained by base hydrolysis of polysuccinimide (PSI) synthesized by some raw materials. According to the difference of the raw materials, synthesis methods of PSI can be categorized into two kinds. Firstly, aspartic acid is directly polymerized into PSI with or without solvent and catalyst.[1,2] Secondly, dicarboxylic acid or anhydride having four carbon atoms, such as maleic anhydride and fumaric acid, reacts with ammonia or amine salt to produce D,L-aspartic acid, then PSI can be obtained by polymerizing D,L-aspartic acid. With regard to the latter, solvent and catalyst are usually used.

There has been much research on the synthesis of PASP. It was reported that the direct polymerization of aspartic acid in the absence of catalyst or solvent required a long reaction time,[4,5] and the yield[6,7] and molecular weight[8] of the product were low. In order to increase the weight average molecular weight, orthophosphoric acid, sodium bisulfate and sodium sulfate were used as catalysts[9,10] in the process. Polysuccinimide having a relatively broad range of weight average molecular weights can be obtained by the thermal polymerization of aspartic acid in the presence of sulfur trioxide or heat decomposable sulfur trioxide precursor.[11] Using a cyclic carbonate solvent such as propylene carbonate and ethylene carbonate, the catalytic polymerization of aspartic acid can produce polysuccinimide with a relatively high weight average molecular weight, high purity, and relatively high yields while employing a relatively low catalyst loading.[11,12] Similarly, the product having relatively high weight average molecular weight and yield from aspartic acid is obtained using a mixed solvent of mesitylene and sulfolane (W/W, 7/3) and phosphoric acid catalyst.[14] All of the above processes suffer from relatively expensive starting materials.

Methods for the preparation of polysuccinimide from maleic acid or anhydride and ammonia are known for having inexpensive starting material. The reaction steps and material state directly affect the molecular weight and product yield. The directly thermal polymerization of maleic acid and ammonia makes the molecular weight and yield of polysuccinimide low.[15] The product from maleic anhydride and ammonia has high molecular weight by two reaction steps,[16,17] but the yield is low. Increasing the length of the reaction

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and the amount of ammonia relative to the amount of maleic anhydride can increase yield. Thus, the reaction time becomes long.[18,19] By reacting ammonia gas with liquid maleic anhydride to produce polysuccinimide, the reaction time can be shortened.[20] In another process polysuccinimide was prepared by reaction of fumaric acid, maleic acid, or a derivative thereof with urea, isourea, carbamic acid, ammonium carbonate, ammonium bicarbonate, ammonium sulfate, or mixtures of the abovementioned substances.[21,22] The molecular weight of the product was low, but the yield was high.

In the above-listed synthesis processes, conventional heating methods were used. In order to obtain the required product, catalyst and organic solvent were used. Thus, there were various disadvantages, including complicated operation, long reaction time, low yield and purity, difficulty of product separation from organic solvent, and damage to the environment.

It is well known that microwave-assisted organic synthesis has become an available technique for the generation of polymer, which usually leads to shorter reaction times and higher yields and purity. Many solvent-free reactions using microwaves have been developed since this reduces the risks of hazard due to pressure build-up in the reaction vessel and the scale-up is easier. We report herein a reaction in which a new polymer is produced without organic solvent or catalyst.

Considering the progress of synthesis of polyaspartic acid and the characteristic of microwave-assisted organic synthesis, polyaspartic acid was synthesized from maleic anhydride and ammonia without organic solvent or catalyst under microwave irradiation in this article. And the influence of polyaspartic acid on calcium carbonate precipitate was investigated.

## MATERIALS AND METHOD

### Reagents

Maleic anhydride was obtained from Shijiazhuang Chemical Factory (Shijiazhuang, China). Standard polyglycol (400, 600, 2000, 6000, and 10,000 MW) was purchased from Sigma Company (St. Louis, MO). The other chemicals were commercially available and used without further purification. Deionized water was used in this work.

### Instruments and measurements

A 2450-MHz microwave oven made by Nanjing Sanle Microwave Technology Development Co., Ltd. (Nanjing, 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 the IR spectrum, the powdered samples were mixed with KBr and pressed onto disk. The IR spectrum was measured by means of a Perkin Elmer Spectrum One spectrometer (Foster City, CA).

^{13}CNMR and ^{1}HNMR spectra were measured on a Bruker ARX400 NMR spectrometer (Fallanden, Switzerland). A 5 mg sample and 1 mL $D_2O$ were used in the measurements. The operation parameters for ^{13}CNMR spectra were SI = 32768, SF = 100.61 MHz, WDW = EM, SSB = 0, LB = 1.0 Hz, GB = 0. PC = 1.40. SI = 32768, SF = 400.13 MHz, WDW = EM, SSB = 0, LB = 0.3 Hz, and GB = 0. PC = 1.0 was the operation parameter for ^{1}HNMR spectra.

The average molecular weight of PASP was measured on a Perkin Elmer Series 200 LC system (St. Louis, MO) equipped with a gel permeation chromatography column. The mobile phase was 0.3 mol/L NaCl–$H_3PO_4$ solution. And polyglycol was used as a standard with pH of 6.5.

### Synthesis method of PASP

The general procedure (Scheme 1) was as follows. A suspension of maleic anhydride (14.7 g, 0.15 mol) and water (10 mL) was formed in a 500-ml beaker. A determinate amount of ammonia was added in the above suspension when aspartic acid was produced. The new suspension was irradiated via microwave with a frequency of 2450 MHz and a certain output power. After a few minutes, the beaker was taken out and suitable NaOH solution was added in the beaker. The pH was adjusted to 9.5 so that the resultant polysuccinimide (PSI) was hydrolyzed to PASP. The hydrolysis process lasted 12 h. Then the pH was adjusted to 3.86 with 6 mol/L HCl. The solution was filtrated and the filtrate was dehydrated with ethanol to form sediment. And the deposit was dried at 70°C under low pressure and powder product was obtained. The yield (φ) of the product was calculated following the listed formula

$$\phi = \frac{m_p}{x m_m} \times 100\%$$
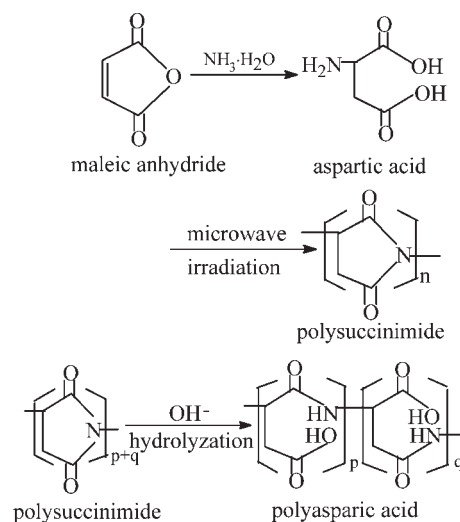


**Scheme 1**

where $m_p$ is the amount of polymer (in grams), $m_m$ is the amount of maleic anhydride added (in grams), and $x$ is theoretic conversion coefficient from maleic anhydride to PASP, which is obtained according to the reaction described in Scheme 1. Given that 1 mol of maleic anhydride weighs 98 g, if 98 g of maleic anhydride are completely converted into polyaspartic acid, then 115 g of polyaspartic acid are produced; therefore, $x$ is 115/98.

## RESULTS AND DISCUSSIONS

### Choice of reaction system

According to different raw materials and reaction systems, a series of tests was carried out. Carboxylic acid or anhydride having four carbon atoms, such as L-Asp, maleic anhydride, and fumaric acid, was used as a kind of raw material. The nitrogen source was chosen from familiar chemicals, such as ammonia, carbamide, and salvolatile. The molar ratio of carboxylic acid or anhydride to nitrogen source was 1 : 1. The other reaction conditions were the same: the containing reaction vessel, the frequency of microwave, output power, and irradiation time. The results are listed in Table I.

As can be seen from Table I, five of the 12 reaction systems have new product, which indicates that a polymerization reaction occurred. In the first experiment, four in five reactions proceeded in liquid phase, while the reaction in solid phase had the lowest yield. The above conditions indicate that microwave is hardly absorbed by carboxylic acid, amino acid, and amine salt in solid phase. When water is added into the reactant, the electromagnetic energy of microwave can be rapidly changed into heat energy in order to make polymerization reactions take place. In the second experiment, aspartic acid was firstly obtained by reacting maleic anhydride or fumaric acid with ammonia. Then polyaspartic acid was synthesized by aspartic acid.

Just because two of the raw materials (maleic anhydride and fumaric acid) are different chiral reagents, aspartic acid obtained falls into D-aspartic acid and L-aspartic acid. Maleic anhydride as raw material was present in the four reaction systems having chemical changes; only one in all the systems containing fumaric acid had new product appearance. The above phenomena suggest that the absorbing microwave ability of reactants is correlative with their levorotation or dextrorotation. In the third experiment, the yields of the two-liquid phase reaction systems using carbamide as nitrogen source are 43.63% and 44.48%, respectively. This result shows that the reaction between carbamide and maleic anhydride or fumaric acid is following 1 : 1 of carbamide: C4 instead of 1 : 1 of N: C4. Thus, 1 mol of N is wasted when 1 mol of carbamide is consumed. It was observed that the conversion of the third and seventh tests was high and the products were homogeneous in the experiments. In the reaction process, salvolatile in the seventh test not only provided nitrogen but also released $CO_2$ when it was heated. The results of the third test are more advantageous as compared with those of the seventh test. So the third test was chosen as the best method to product polyaspartic acid.

### Ratio of raw materials

Maleic anhydride (MA) and ammonia (AN) were chosen as raw materials. 14.7 g of MA were mixed with 10 ml water. According to the different molar ratio of MA/AN, the required amount of ammonia was determined. Microwave irradiation lasted 3 min with 900 W of output power. The yield of PASP is shown in Figure 1.

Figure 1 shows that the yield of PASP reaches 95.77% or above when the molar ratio of MA/AN is not less than 1.2. A little excessive ammonia increases the yield of PASP. When the molar ratio of MA/AN reaches a certain number, the yield can no longer be

**TABLE 1**
**Results of the Synthetic Experiment**

| No. | Material | Phase | Reaction | Yield (%) | Appearance of product |
|---|---|---|---|---|---|
| 1 | L-aspartic acid | S | N | — | — |
| 2 | L-aspartic acid solution | L | N | — | — |
| 3 | Maleic anhydride, ammonia | L | Y | 88.32 | Brown yellow fluffy solid |
| 4 | Maleic anhydride, carbamide | S | N | — | — |
| 5 | Maleic anhydride, carbamide solution | L | Y | 43.63 | Buff fluffy solid |
| 6 | Maleic anhydride, salvolatile | S | Y | 12.7 | Partial reaction |
| 7 | Maleic anhydride, salvolatile solution | L | Y | 87.65 | Buff fluffy solid |
| 8 | Fumaric acid, ammonia | L | N | — | — |
| 9 | Fumaric acid, carbamide | S | N | — | — |
| 10 | Fumaric acid, carbamide solution | L | Y | 44.48 | Brown yellow fluffy solid |
| 11 | Fumaric acid, salvolatile | S | N | — | — |
| 12 | Fumaric acid, carbamide solution | L | N | — | — |

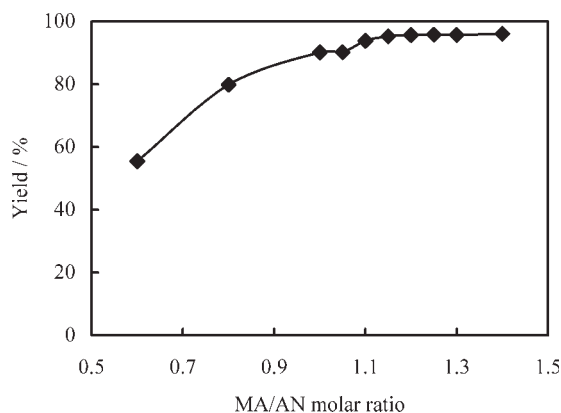S, solid phase; L, liquid phase; N, no reaction; Y, reaction.

**Figure 1** Effect of the ratio of raw materials on yield.

increased. According to the results described in Figure 1, a molar ratio of 1.2 for MA/AN was determined as the appropriate condition for producing polysuccinimide. Superabundant ammonia is wasteful and uneconomical, so the overflowing ammonia needs to be recycled on the spot.

## Output power of microwave

14.7 g of MA was mixed with 10 ml water. According to an MA/AN molar ratio of 1.2, the required amount of ammonia was put into the slurry of MA. When the microwave output powers were 500, 900, 1000, 1500, and 2000 W with an irradiation time of 3.5 min, yields of PASP were obtained as shown in Figure 2.

It is seen from Figure 2 that the yields of PASP can be increased with increasing output power in certain range. When the output power is 900 W, the yield of PASP reaches 95.76%. Figure 2 also shows that there is an optimal microwave range for quantitative reactant. If output power is lower, the reactant cannot be completely converted into polymer. Another reaction— not polymerization—will take place when output power is higher than the optimal. Thus the yield of PASP will be lower.
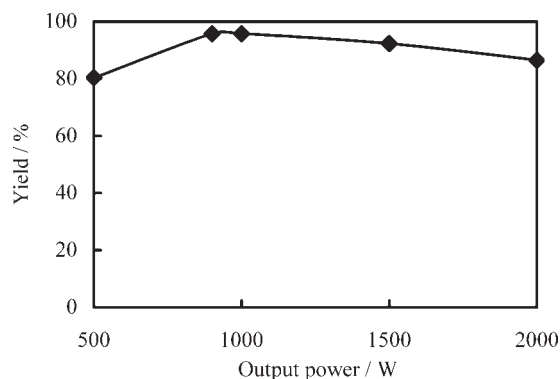
## Irradiation time

10 ml water was added to 14.7 g of MA to form slurry before ammonia dripped according an MA/AN molar ratio of 1.2. The yield of PASP with different microwave irradiation times and 900 W of output power is depicted in Figure 3.

It can be seen from Figure 3 that the whole irradiation time is divided into two periods. The former period is prereaction time while the latter is reaction time. The prereaction time is about 1.0 min, which is the warm-up process for the reactant. When the irradiation time is 3.5 min, the yield arrives at 95.76%. If the irradiation time lasts longer, the yield increases insignificantly. Once polymerization takes place, the reaction is very quick and completed in short time. All the abovementioned results are the characteristics of this polymerization reaction.

## Factors affected by irradiation time

Irradiation time is the main factor in the synthesis process. Research on the relation between irradiation time and other conditions contributes to the analysis of the microwave-operation mechanism. In the microwave chemical-synthesis process, it is considered that microwave has two functions: one is heat effect and the other is catalysis. The primary result was obtained by the following research wok.

### Relation between the amounts of MA and irradiation time

Difference amounts of MA were mixed with appropriate volumes of water to slurry before adding ammonia according to an MA/AN molar ratio of 1.2. When the reactant was irradiated by 900 W microwave, the starting time of the resultant appearance were recorded. The relation between amount of MA and the starting time is depicted in Figure 4.

A nearly linear relation of the two factors can be observed from Figure 4. This reaction characteristic is close to the thermal polycondensation, which indi-
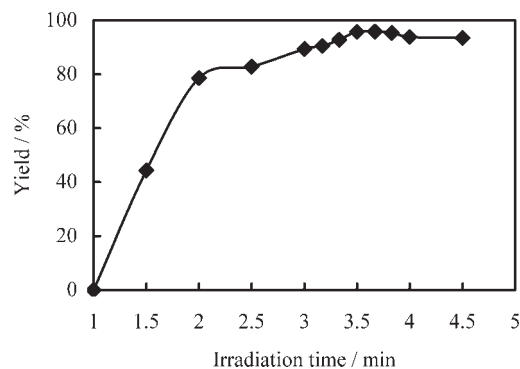


**Figure 2** Effect of the output power on product yield.



**Figure 3** Effect of irradiation time on product yield.
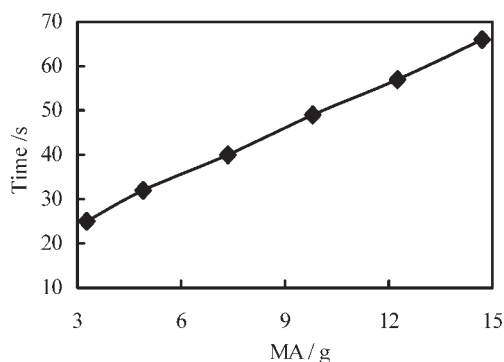
**Figure 4** Effect of the amount of MA on the initiative reaction time.

cates that here the main microwave function is heating and catalysis is hardly existent.

Relation between output power and irradiation time

The microwave output power not only significantly affects the yield of polymer, but also is the crucial factor with regard to the required irradiation time. Research on the relation between output power and irradiation time can make the microwave-operation mechanism effective with regard to the converstion of energy. 10 mL of water was mixed into 14.7 g of maleic anhydride, and then ammonia was added in the mixture according to an MA/AN molar ratio of 1.2. With the different powers, the starting time of copolymerization was also different, and the results are listed in Table II.

From the data in Table II, the product of output power and the time of each test are very close to each other (about 60 kJ), which indicates that the required energy is determinate for a certain amount of reactant in spite of different output power. If catalysis occurs in the synthesis, the required energy would drop slightly with an increase of output power. The results show that the main function of microwave is the heat effect in the polymerization process.

**Characterization of polymer**

The structure of polymer was analyzed using infrared spectra (Fig. 5), $^1$H NMR spectra (Fig. 6), and $^{13}$C NMR spectra (Fig. 7). The infrared spectra of PASP exhibit a remarkable band at 3000–3700 cm$^{-1}$, indicating the NH characteristic absorption peak, which makes clear

**TABLE 2**
**Influence of Output Power on Irradiation Time**

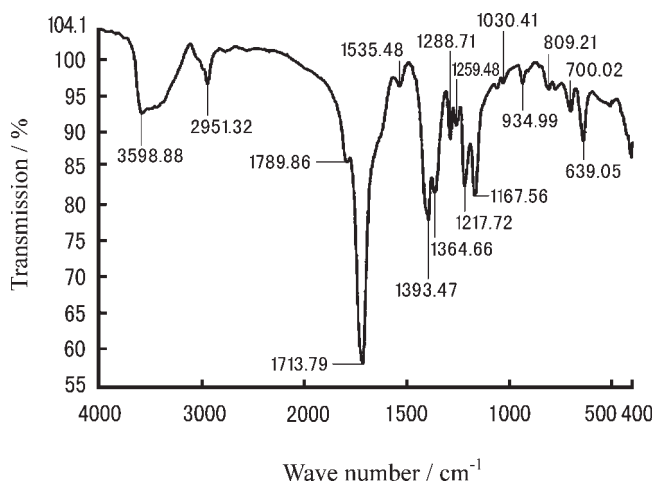| Output Power (kW) | 0.5 | 0.9 | 1.0 | 1.5 | 2.0 |
|---|---|---|---|---|---|
| Time (s) | 119 | 67 | 59 | 40 | 29 |
| Product of the above projects (kJ) | 59.5 | 60.3 | 59.0 | 60.0 | 58.0 |

**Figure 5** IR spectra of the product.

polymerization in the synthesis. Infrared spectra exhibit a strong band at 1713 cm$^{-1}$ assigned to the C=O vibration of the carboxyl group (—COOH). The above two bands show that there are plenty in the amido group (—CONH). The wide band at 3000 cm$^{-1}$, the sharp band at 1790cm$^{-1}$, the two bands in the 1450–1650cm$^{-1}$ range, and the band at 935 cm$^{-1}$ are characteristic spectra of the carboxyl group (—COOH). The fingerprint band at 935 cm$^{-1}$ explains that —COOH exists in polymer, not in monomer. The IR analysis results show that the function group of the product has the same characteristic as that of PASP.

In Figure 6, the first spectrum shows the $^1$H MRH spectrum of PASP made by L-aspartic acid thermal polycondensation via conventional heating (230°C, 5 h). Maleic anhydride reacted with ammonia to produce PASP under the condition of conventional heating, 5 h of reaction time, and 230°C, which is the second spectrum (Fig. 6). The third spectrum is that of the product
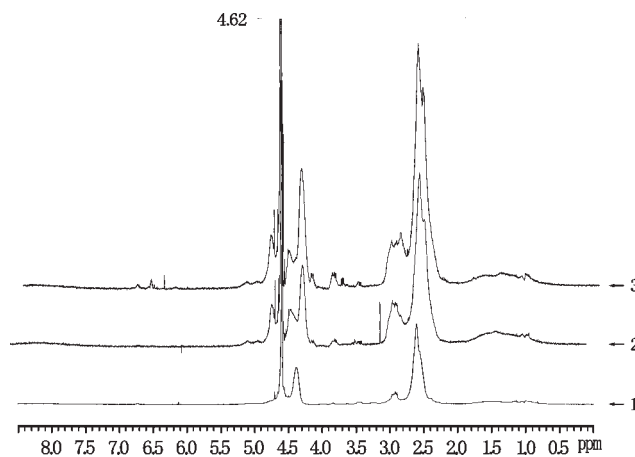


**Figure 6** $^1$H NMR spectra of the products in pD7.4 D$_2$O: (1) L-asp via conventional heating (230°C, 5 h); (2) maleic anhydride via conventional heating; (3) maleic anhydride via microwave irradiation.

studied in this article (2450 MHz microwave, 900 W of power, and 3.5 min of irradiation time). The characteristics of the three spectra are almost the same, which indicates that the products from two manufactured methods, conventional heating up and microwave irradiation, are the same kind of substance. At the chemical shift from 2.4 to 3.0 ppm, the proton magnetic resonance (PMR) peak of methene ($=CH_2$) appears. The proton resonance peak of methenyl ($\equiv CH$) is seen at the chemical shift from 4.3 to 4.8 ppm. Any acid or amide protons would have exchanged with the bulk solvent ($D_2O$), and peaks for these species are not observed.

From Figure 7, carbonyl carbon is seen in the 170–180 ppm region. There are two distinct groups of resonance, corresponding to the acid (downfield) and amide (upfield) carbonyls. The methenyl ($\equiv CH$; 53–57 ppm) and methylene ($=CH_2$, 35–40 ppm) carbons are observed from the $^{13}C$ NMR spectra of the product.

The $^1H$ NMR and $^{13}C$ NMR spectra of the product in this study are in accordance with the $^1H$ NMR and $^{13}C$ NMR spectra of PASP prepared by thermal polymerization of L-aspartic acid reported in the literature,[22] which further indicates that the product in the study is polyaspartic acid.

The weight average molecular weight of the product was estimated as 1460 by gel permeation chromatography with polyglycol as the standard sample.

### Inhibition performance of polymer on $CaCO_3$ precipitation

Using GB/T16632-1996 (General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China, Beijing) for the determination of the scale-inhibition performance of water treatment agents — the Calcium carbonate precipitation method, with the polymer in this article and commercial PASP as inhibitors, their inhibition on $CaCO_3$ was investigated when the $Ca^{2+}$ concentration was different in solution. The results are depicted in Figure 8.
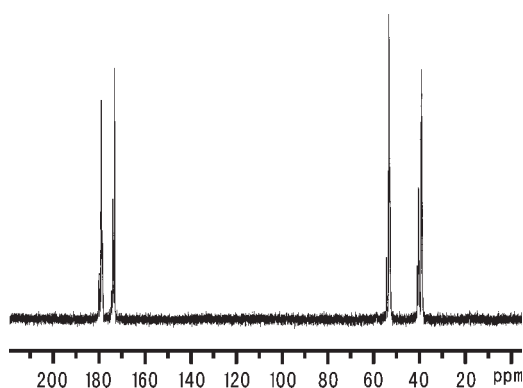


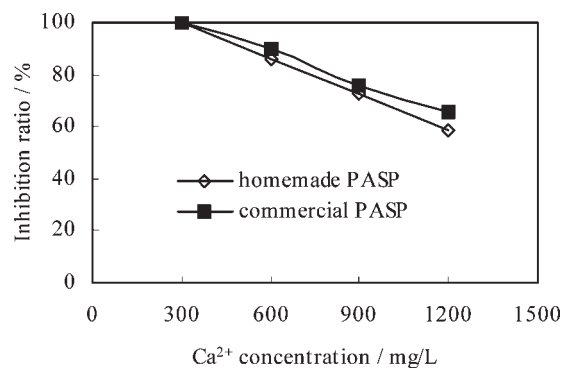**Figure 7** $^{13}C$ NMR spectra of the product in pD7.4 $D_2O$.



**Figure 8** Calcium carbonate inhibition test (pH = 7, [PASP] = 3 mg/L, 80°C, $t$ = 10 h).

The inhibition effect of two kinds of inhibitors on $CaCO_3$ reduces with increasing $Ca^{2+}$ concentration. From Figure 8, it can be seen that the polyaspartic acid made by microwave irradiation has the same scale-inhibition performance as commercial polyaspartic acid. This indicates that microwave-assisted synthesis is an effective way to produce PASP. The method not only provides high yield, but also enables a good scale-inhibition performance to be achieved by the product.

## CONCLUSIONS

Using microwave irradiation as a new heating method, polyaspartic acid was synthesized from maleic anhydride and ammonia in solution without organic solvent or catalyst. This method not only gives a faster reaction rate, but also reduces the difficulty of separating the product from the solvent. The effect of reaction conditions on the yield of polyaspartic acid was investigated and the optimal reaction condition was obtained: a molar ratio of maleic anhydride to ammonia of 1.2, output power of 900 W, and irradiation time of 3.5 min. The absorption of microwave energy by materials is relevant to their chirality. The polyaspartic acid having 1460 molecular weight has the same scale-inhibition performance and chemical structure as the commercial polyaspartic acid. The research on factors affected by irradiation time suggests that the main function of microwave is heating in this process. Compared with conventional heating methods, microwave irradiation gives the synthesis process more advantages such as high yield, energy conservation, and pollution reduction. This research result provides the basis for microwave chemistry technology application to the synthesis of PASP.

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