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Convenient synthesis of high molecular weight poly(succinimide) by acid-catalysed polycondensation of L-aspartic acid

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Poly(succinimide) (PSI) was synthesized by acid-catalysed polycondensation of L-aspartic acid. Polycondensation proceeded at a reaction temperarture of above *ca.* 160°C, and a PSI with the highest weight-average molecular weigh, 64 300, was obtained using a mixed solvent of mesitylene and sulfolane (w/w, 7/3) and phosphoric acid. Poly(aspartic acid), which was produced by alkali-hydrolysis of PSI, exhibited higher biodegradability than that originated from thermally polycondensed aspartic acid. After 28 days, biochemical oxygen demand/theoretical oxygen demand (BOD/TOD) and dissolved organic carbon for catalytic PASP were 82 and 89%, respectively, and 26 and 46% for thermal PASP. © 1997 Elsevier Science Ltd.

(Keywords: L-aspartic acid; poly(succinimide); poly(aspartic acid))

INTRODUCTION

Poly(acrylic acid) and poly(acrylamide) are often used as water-soluble polymeric materials with anti-scale and dispersion properties, but they do not exhibit biodegradability[1]. Thus they are widely scattered and left to pollute the natural world, with grave environmental consequences. Therefore, a biodegradable, water-soluble polymer has been needed and has been actively studied in recent years. Poly(amino acid), which has an amide linkage as well as a peptide, is completely biodegradable[2–4], and that with carboxylic acid groups has attracted a great deal of attention as a candidate for a biodegradable, water-soluble polymer.

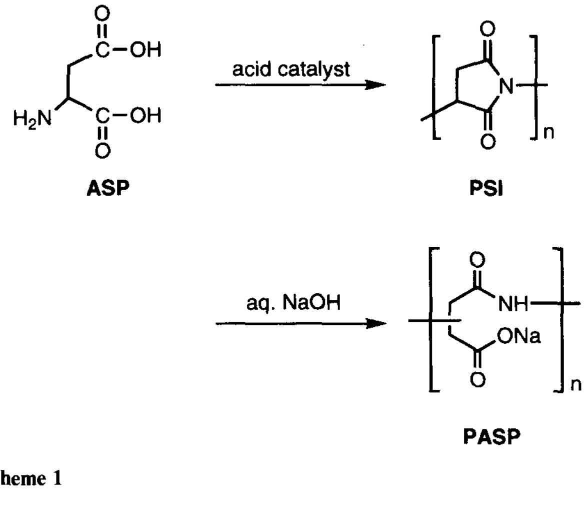
Among poly(amino acid) with carboxylic acid groups, poly(aspartic acid) has been synthesized by thermal polycondensation of aspartic acid (ASP) and ammonium salts of maleic acid and malic acid to form poly(succinimide) (PSI) with relatively low molecular weight, followed by hydrolysis[5,6]. On the other hand, high molecular weight PSI was prepared by the polycondensation of ASP in a large amount of phosphoric acid as the catalyst and solvent under reduced pressure. However, this synthetic method has the disadvantage of isolating PSI from the reaction mixture, because the remaining phosphoric acid is difficult to remove. Thus improvement of the synthetic procedure was desired in order to produce PSI on a commercial scale. Recently, we preliminarily reported that PSI and its copolymeric derivative were synthesized by the polycondensations of ASP alone and ASP with ω-amino acid, respectively, using a catalytic amount of acid[7,8]. The present study aims to elucidate the polycondensations of ASP in detail.

In this article, we report that PSI of various molecular weights is prepared by the polycondensation of ASP by changing reaction conditions, e.g. temperature, solvent, and acid catalyst. In addition, the biodegradability of poly(aspartic acid) (PASP) prepared by alkali-hydrolysis of PSI was examined using activated sludge (*Scheme 1*).

EXPERIMENTAL

Materials and instruments

L-Aspartic acid (ASP) was obtained from Mitsubishi



Scheme 1

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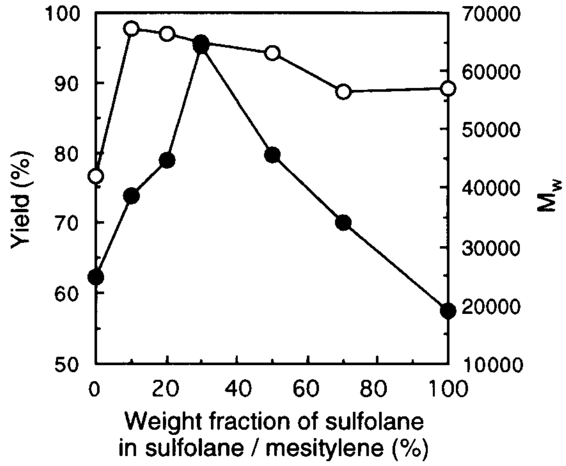


Figure 1 Yields and M_ws of PSI prepared by polycondensation of L-ASP using phosphoric acid in various ratio of mixed solvent of sulfolane and mesitylene

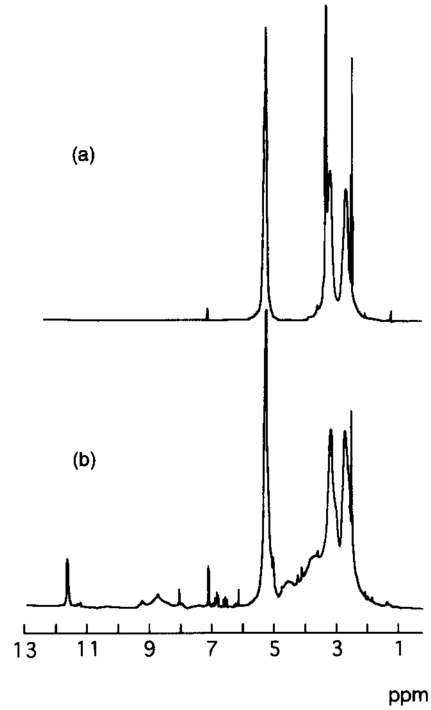


Figure 2 ^{1}H n.m.r. spectra of PSIs prepared by acid-catalysed (a) and thermal (b) polycondensations of L-ASP

Chemical Corporation (Tokyo, Japan). Phosphoric acid (85%), sulfuric acid, *p*-toluenesulfonic acid, trichloroacetic acid, toluene, mesitylene, diethylbenzene, *N*-methylpyrrolidone (NMP), *N,N*-dimethylformamide (DMF), and sulfolane were commercially available and were used without further purification. The molecular weight of the obtained polymer was estimated in DMF containing 20 mmol l^{-1} of LiBr by gel permeation chromatography (g.p.c.) (column: Plgel 5 mm MIXED-C × 2, detector: RI, standard: polystyrene). ^{1}H n.m.r. spectra were measured with a Bruker ASX300 NMR spectrometer.

Acid-catalysed polycondensation of ASP

The general procedure is as follows: A suspension of ASP (25 g, 0.188 mol) and acid catalyst (9.4 mmol) in the solvent (80 g) was refluxed under N_2 atmosphere. Water formed in a reaction mixture was removed using a Dean–Stark trap with a reflux condenser. After 4.5 h, the solvent was removed, the precipitate was washed with MeOH (200 ml) and then with water (200 ml) several times until it was neutral. The residue was washed with MeOH (200 ml) and dried at 85°C under reduced pressure.

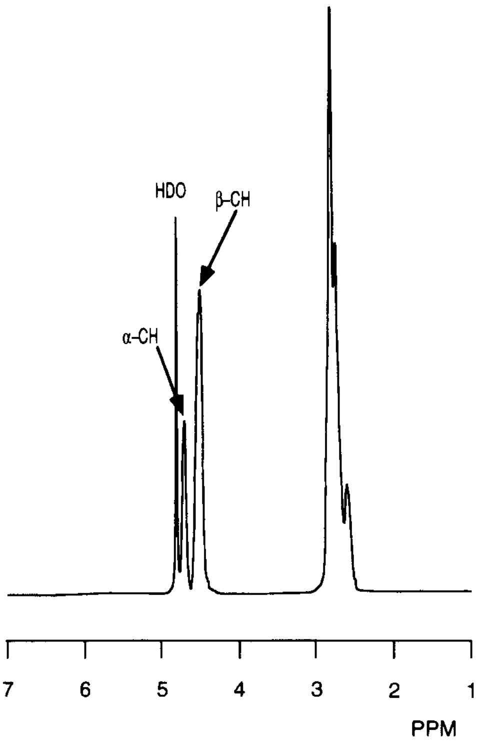


Figure 3 ^{1}H n.m.r. spectrum of PASP produced by alkali-hydrolysis of acid-catalytic prepared PSI (solvent, D_2O; internal standard, 3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid, sodium salt)

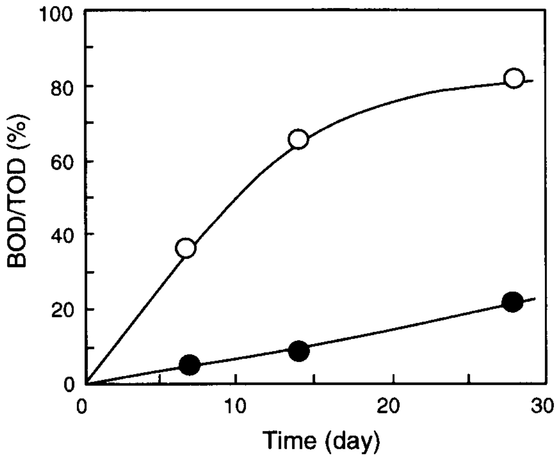


Figure 4 The values of the BOD/TOD for PSIs prepared by acid-catalysed (○) and thermal (●) polycondensations of L-ASP using activated sludge (JIS K 6950-1994) at 25°C

Alkali hydrolysis of PSI

To a solution of NaOH (8.24 g, 0.206 mol) in water (160 ml), PSI (20 g, 0.206 mol) was added portionwise with stirring in an ice-bath. After stirring for 3 h at room temperature, the reaction mixture was poured in MeOH (2 l) over a 1-h period and the entire mixture was stirred

Table 1 Polycondensation of L-aspartic acid (ASP) with acid catalyst in various solvent system[a]

Run	Solvent	Acid catalyst	Reaction temp.	Yield (%)	M_w (M_w/M_n)
1	Toluene	85% phosphoric acid	110–111	0	–
2	Mesitylene	85% phosphoric acid	164–166	77	24 800 (1.5)
3	DMF	85% phosphoric acid	152–153	0	–
4	Sulfolane	85% phosphoric acid	158–159	89	19 000 (1.5)
5	Toluene/sulfolane	85% phosphoric acid	110–111	0	–
6	Mesitylene/DMF	85% phosphoric acid	150–152	59	12 900 (1.2)
7	Mesitylene/NMP	85% phosphoric acid	160–162	96	24 500 (1.6)
8	Diethylbenzene/sulfolane	85% phosphoric acid	176–178	96	49 300 (1.9)
9	Mesitylene/sulfolane	85% phosphoric acid	160–162	96	64 300 (1.9)
10		Trichloroacetic acid	164–166	0	–
11		*p*-Toluenesulfonic acid	160–162	89	27 000 (1.5)
12		Sulfuric acid	160–162	96	27 900 (1.6)

[a] ASP, 25 g (0.188 mol); acid catalyst, 0.019 mol; solvent, 80 g or 56 g/24 g; time, 4.5 h; under N_2

for 1 h. The precipitate was filtered, washed with MeOH, and then dried in vacuum at 50°C for 24 h. Yield, 26 g (95%).

Biodegradability of PASP

Biodegradability was examined by the JIS testing method using activated sludge (JIS K 6950-1994) and was estimated by the values of the BOD/TOD and dissolved organic carbon.

RESULTS AND DISCUSSION

Table 1 lists the results of the acid-catalysed polycondensation of ASP. Azeotropic removal of water from the reaction mixture was carried out throughout the reaction except for the sulfolane alone system in which water was removed by flashing dry nitrogen gas through the reaction mixture at 160°C. When 85% phosphoric acid was used as a catalyst, no polymer was obtained and ASP was recovered using toluene (b.p. 110.6°C, run 1) and DMF (b.p. 153°C, run 3), indicating that the boiling points of toluene and DMF were at low temperature to produce polycondensation. On the other hand, the yield and weight average molecular weight (M_w) were 77% and 24 800 for mesitylene (b.p. 162–164°C, run 2) and 89% and 19 000 for sulfolane (run 4) at 160°C. These results indicate that the reaction temperature had to exceed *ca.* 160°C.

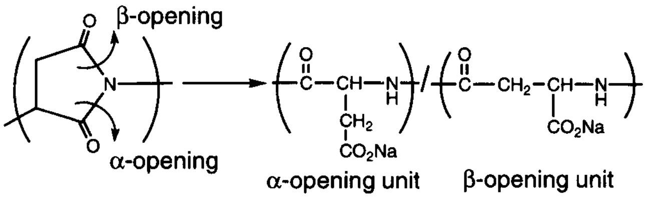
The two-solvent system consisting of a water-inmiscible (toluene, mesitylene, and diethylbenzene) and a water-miscible solvent (DMF, NMP, and sulfolane) apparently affected the polycondensation results. For the toluene/sulfolane system (run 5), no polymer was obtained, which should be caused by the insufficient reaction temperature. The yield and M_w were as low as 59% and 12 900 for mesitylene/DMF (run 6), but mesitylene/NMP (run 7), diethylbenzene/sulfolane (run 8), and mesitylene/sulfolane (run 9) were effective for the polymer yield (96%), and the M_w increased in the order of the mesitylene/NMP < diethylbenzene/sulfolane < mesitylene/sulfolane. For mesitylene/sulfolane, the effect of the solvent composition on the polycondensation was examined, and *Figure 1* shows the results of the yields and M_ws for the polymers obtained. The polymer yield increased with an increasing amount of mesitylene but remarkably decreased for only mesitylene. The highest M_w, 64 300, was obtained for the mesitylene/sulfolane ratio of 7/3.

The type of acidic catalyst apparently affected the yield and M_w of the resulting polymers as listed in *Table 1*. Every polycondensation was carried out in a mixed solvent of mesitylene and sulfolane (7/3). Trichloroacetic acid (run 10) did not exhibit catalytic activity, and no polymer was obtained. On the other hand, *p*-toluenesulfonic acid (run 11) and sulfuric acid (run 12) were effective for producing PSI in high yield, and the M_w was 27 000 and 27 900 for *p*-toluenesulfonic acid and sulfuric acid, respectively. These results indicate that 85% phosphoric acid is the most suitable as an acid catalyst.

Figure 2 shows the ^{1}H n.m.r. spectra of PSIs prepared by acid-catalysed and thermal polycondensations of ASP. For PSI prepared using an acid catalyst, only the signals at 2.7 and 3.2 ppm and 5.3 ppm, which were assigned to the methine and methylene protons of the succinimide unit, respectively, were observed. On the other hand, thermally prepared PSI showed absorption in the region of 8–10 ppm, which was attributable to branched and/or opened amide groups. These results mean that the acid-catalytically prepared PSI contained little amount of irregular units, which was very different from the result for the thermally prepared PSI consisting of succinimide and many other units.

POLY(ASPARTIC ACID) AND ITS BIODEGRADABILITY

PSI was easily hydrolysed in alkali medium for conversion into poly(aspartic acid) (PASP). *Figure 3* shows the ^{1}H n.m.r. spectrum of the sodium salt of poly(aspartic acid) in deuterium oxide. Because the signals due to the methine and methylene protons of the succinimide unit disappeared, the hydrolysis of poly(imide amide) completely proceeded. The signals at 4.5 and 4.7 ppm and at 2.5–2.9 ppm were assigned to the methine and methylene protons of the aspartic acid unit, respectively. The two chemical shift values of the methine proton were caused by the different ring-opening manner, i.e. α- and β-openings (*Scheme 2*). The ratio of α- and β-openings, which was determined by the area ratio of the ^{1}H n.m.r. spectrum, was 26/74, indicating that the β-opening predominantly occurred rather than the α-opening.



Scheme 2

The biodegradability of the sodium salt of PASP was evaluated by the value based on biochemical measurement using activated sludge at 25 ± 1°C. PASP originated from PSI prepared using an acid catalyst was biodegraded at a faster rate than that from a thermally prepared polymer, as shown in *Figure 4*. After 28 days, the BOD/TOD and dissolved organic carbon for catalytic PASP were 82 and 89%, respectively, and 26 and 46% for thermal PASP.

CONCLUSION

A high molecular weight polymer consisting essentially of succinimide units, poly(succinimide), was produced in high yield by polycondensation of L-aspartic acid, using a catalytic amount of phosphoric acid in a mixed solvent of mesitylene and sulfolane. In addition, poly(succinimide) was easily hydrolysed for conversion into poly(aspartic acid) whose biodegradability was higher than that originated from thermally prepared poly(succinimide).

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