S0032-3861(96)00267-4

Polymer Vol. 37 No. 19, pp. 4435–4437, 1996
Copyright © 1996 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/96/$15.00 + 0.00

Novel method of synthesizing poly(succinimide) and its copolymeric derivatives by acid-catalysed polycondensation of L-aspartic acid

Masayuki Tomida, Takeshi Nakato and Mayumi Kuramochi
Tsukuba Research Centre, Mitsubishi Chemical Corporation, Chuo 8-3-1, Ami-machi, Inashiki-gun, Ibaraki 300-03, Japan

and Minako Shibata, Shigeyuki Matsunami and Toyoji Kakuchi*
Graduate School of Environmental Earth Science, Hokkaido University, Sapporo 060, Japan
(Received 8 January 1996; revised 23 January 1996)

High molecular weight poly(succinimide) was quantitatively synthesized by polycondensation of L-aspartic acid using a catalytic amount of *o*-phosphoric acid in the mixed solvent of mesitylene and sulfolane. In addition, under similar conditions, L-aspartic acid and ω-amino acid produced an organic solvent-soluble poly(succinimide-*co*-ω-amino acid), which melted below the decomposition temperature. Copyright © 1996 Elsevier Science Ltd.

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

Introduction

Poly(acrylic acid) and poly(acrylamide) are generally used as water-soluble polymeric materials, but they do not exhibit biodegradability[1]. Therefore, they are rarely incinerated, collected and reused, and thus are widely scattered and left to pollute the natural world, with grave environmental consequences. On the other hand, poly(amino acid) is biodegradable and is used as a medical, cosmetic, fabric and metal-absorbent material[2–4]. In particular, poly(glutamic acid) and poly(aspartic acid) have been studied in terms of their methods of synthesis and polymer characterization[5,6]. For example, poly(aspartic acid) has been synthesized by thermal polycondensations of aspartic acid and the ammonium salts of maleic and malic acids[7], followed by hydrolysis, to form poly(succinimide) (**2**) with a relatively low molecular weight. On the other hand, high molecular weight **2** was prepared by the polycondensation of L-aspartic acid (**1**) in a large amount of phosphoric acid as the catalyst and solvent under reduced pressure (see *Scheme 1*)[5]. However, this synthetic method has the disadvantage of isolating **2** from the reaction mixture, because the remaining phosphoric acid is difficult to remove. A more sophisticated method is therefore required with regard to controlling the molecular weight and instigating a commercial production process. In addition, a polymer based on **1**, such as the copolymer, is of interest in terms of expanding its potential for biodegradable materials.

Here we report the convenient synthesis of **2** by the polycondensation of **1**, using a catalytic amount of acid in an appropriate solvent. Moreover, acid-catalysed polycondensation of **1** with ω-amino acid (**3**) proceeds without gelation to yield organic solvent-soluble poly(succinimide-*co*-ω-amino acid) (**4**).

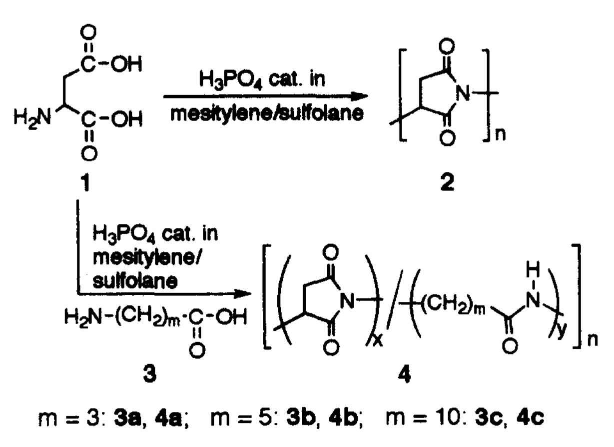
Experimental

Materials. L-Aspartic acid (**1**) was obtained from Mitsubishi Chemical Corporation. *o*-Phosphoric acid (85%), 4-aminobutylic acid (**3a**), 6-aminocaproic acid (**3b**) and 11-aminoundecanoic acid (**3c**) were commercially available and used without further purification.

Polycondensation of 1. A typical procedure was as follows. While a mixture of **1** (25 g, 0.188 mol), mesitylene/sulfolane (14 g/6 g) and 85% phosphoric acid (9.4 mmol) was refluxed under a nitrogen atmosphere for 4.5 h, water was removed from the reaction mixture using a Dean–Stark trap. After removal of the solvent, the precipitate was washed with MeOH (200 ml) and then with water (200 ml) several times until it was of neutral pH. The residue was washed with MeOH (200 ml) and dried at 85°C under reduced pressure to yield **2** (17.5 g, 96%).

Results and discussion

For polycondensation of **1**, *o*-phosphoric acid was



m = 3: **3a**, **4a**; m = 5: **3b**, **4b**; m = 10: **3c**, **4c**

Scheme 1

---

* To whom correspondence should be addressed

Table 1 Polycondensations of L-aspartic acid (**1**) and of **1** with ω-amino acid (**3**) using *o*-phosphoric acid[a]

Monomer[b] (molar ratio)	Solvent[c]	Yield (%)	Mole fraction of **3** unit in copolymer[d]	M_w (M_w/M_n)[e]
1	toluene	0		
1	mesitylene	77	—	24 800 (1.50)
1	sulfolane	96		19 000 (1.45)
1	mesitylene/sulfolane	96	—	64 300 (1.91)
1/3a (7/3)	mesitylene/sulfolane	92	0.12	21 300 (2.12)
1/3b (7/3)	mesitylene/sulfolane	75	0.24	16 500 (1.40)
1/3c (7/3)	mesitylene/sulfolane	50	0.21	14 400 (1.70)

[a] Reflux for 4.5 h; molar ratio of monomer(s)/phosphoric acid (85%) = 20/1
[b] **3a**, 4-aminobutylic acid; **3b**, 6-aminocaproic acid, **3c**, 11-aminoundecanoic acid
[c] Weight ratio of mesitylene/sulfolane = 7/3
[d] Determined by ^{1}H n.m.r. spectra
[e] Determined by g.p.c. in DMF using polystyrene as standard

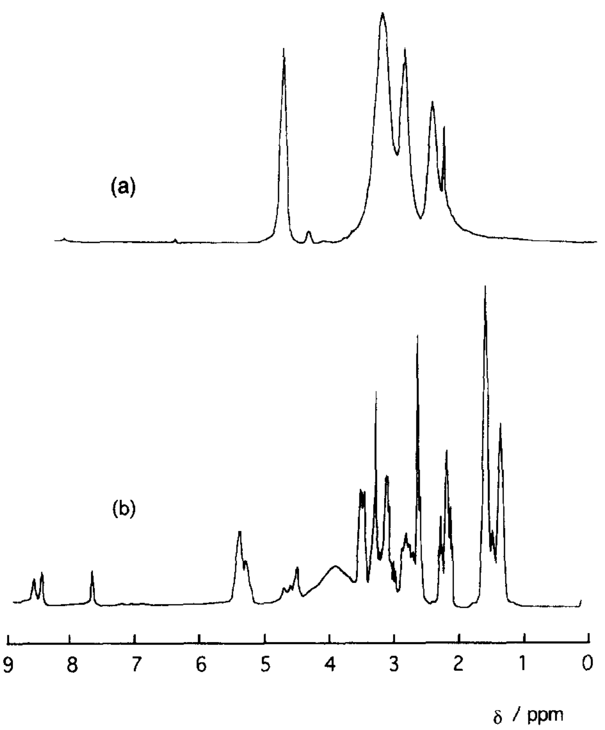


Figure 1 ^{1}H n.m.r. spectra of poly(succinimide) (a) and poly(succinimide-*co*-6-aminocaproic acid) (b) in DMSO-d_6

used as a catalyst and toluene, mesitylene and sulfolane as the reaction solvent. Azeotropic removal of water from the reaction mixture was carried out throughout the reaction. A few results are listed in *Table 1*. For the water-immiscible solvents, toluene and mesitylene, no polymer was formed using toluene, because the boiling point of toluene is too low a temperature to produce polycondensation. On the other hand, the polymer with a weight-averaged molecular weight (M_w) of 24 800 was obtained in 77% yield using mesitylene. Monomer **1** and the resulting polymer were scarcely soluble in mesitylene, i.e. the reaction system proceeded heterogeneously, which was expected to produce a lower yield. For sulfolane, a water-miscible solvent which dissolves **1** and **2**, the polymer yield was higher than that for mesitylene, but the M_w decreased to 19 000. When a mixture of mesitylene and sulfolane was used, the M_w varied as the ratio of the solvents was changed. The polymer with the highest M_w of 64 300 was obtained in 96% yield at a mesitylene/sulfolane ratio of 7/3.

Polycondensations of **1** and ω-amino acid (**3**), 4-aminobutylic acid (**3a**), 6-aminocaproic acid (**3b**) and 11-aminoundecanoic acid (**3c**), were carried out under conditions similar to that for **1** alone. The polymer yield and M_w increased with a decreasing number of methylene groups in ω-amino acids in the order **3a** > **3b** > **3c**. For the **1** and **3a** system, a polymer with $M_w = 21\,300$ was obtained in 92% yield. All of the copolymer (**4**) was soluble in DMF, DMSO and sulfolane, as well as **2**.

The ^{1}H n.m.r. spectra of **2** and **4b** are shown in *Figure 1*. For **2**, the signals at 2.7 and 3.2 ppm and at 5.3 ppm were assigned to the methylene and methine groups, respectively. In addition, no absorption in the region of 8–10 ppm, which is attributable to branched and/or opened amide protons, was observed. This means that **2**, obtained by the acid-catalysed polycondensation of **1**, contained only a slight proportion of irregular units, which was very different from the result for polymer thermally prepared from **1**.

For the ^{1}H n.m.r. spectrum of **4b**, signals at 4.5–4.8 and 5.2–5.6 ppm, due to the methine protons of the succinimide units, were observed. In addition, signals at 7.7, 8.4 and 8.5 ppm and at 1.2–1.8 and 2.0–2.2 ppm were respectively assigned to the amide and methylene protons due to the **3b** units. Many chemical shift values were observed for the methine and amide protons, believed to be caused by the difference in the copolymer sequence. The **3** unit in copolymer **4**, determined using the area ratio of the methine and methylene protons, was 0.12 for **4a**, 0.24 for **4b** and 0.21 for **4c**.

Poly(imide) (**2**) did not exhibit a glass transition property and decomposed at 424°C (T_d, 5% weight loss) without melting. In contrast, poly(imide-amide) (**4**) had a glass transition temperature of 92°C for **4a**, 97°C for **4b** and 126°C for **4c**, and melting points of 227°C for **4b** and 255°C for **4c**, though the T_d of **4** was lower than that of **2**, i.e., 390°C for **4a**, 354°C for **4b** and 375°C for **4c**. These thermal properties indicate that poly(imide-amide)s **4b** and **4c** can be expected to be used as a new thermoplastic material. In addition, poly(succinimide) and poly(succinimide-amide) were easily hydrolysed for conversion into poly(aspartic acid) and its copolymeric derivatives, and exhibited biodegradability. Further investigations are currently being undertaken.

In summary, high molecular weight poly(succinimide) was quantitatively synthesized by polycondensation of L-aspartic acid, using a catalytic amount of *o*-phosphoric acid in a mixed solvent of mesitylene and sulfolane. Moreover, under similar conditions, L-aspartic acid and ω-amino acid produced organic solvent-soluble poly-(succinimide-*co*-ω-amino acid), which melted below the decomposition temperature.

References

1 Matsumura, S., Maeda, S. and Yoshikawa, S. *Polym. Mater. Sci. Eng.* 1990, **62,** 984
2 Ouchi, T., Shiratani, M., Jinno, M., Hirao, M. and Ohya, Y. *Macromol. Chem., Rapid Commun.* 1993, **14,** 825
3 Hayashi, T. and Iwatsuki, M. *Biopolymers* 1990, **29,** 549
4 Jain, G. L. and Ray, A. R. *Macromol. Chem.* 1981, **182,** 2557
5 Neri, P., Antoni, G., Benvenuti, F., Cocoda, F. and Gazze, G. *J. Med. Chem.* 1973, **16,** 893
6 Walk, S. K., Swift, G., Paik, Y. H., Yocom, K. M., Smith, R. L. and Simon, E. S. *Macromolecules* 1994, **27,** 7613
7 Harada, K. *J. Org. Chem.* 1959, **24,** 1662