Polymer Bulletin 40, 647–650 (1998)

Polymer Bulletin

Synthesis of poly(succinimide-amide) by acid-catalyzed polycondensation of L-aspartic acid and aromatic aminocarboxylic acid

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Received: 24 February 1998/Revised version: 3 April 1998/Accepted: 13 April 1998

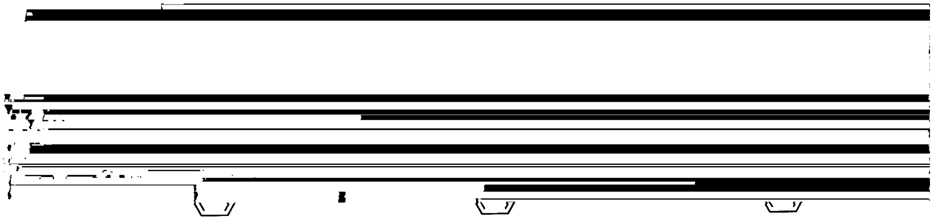
Summary

The polycondensations of L-aspartic acid (**1**) with aromatic aminocarboxylic acid, 4-aminobenzoic acid (**2a**), 4-aminophenylacetic acid (**2b**), 4-aminomethylbenzoic acid (**2c**), 4-(4-aminophenyl)butyric acid (**2d**), and 4-aminocinnamic acid (**2e**) were carried out using phosphoric acid as a catalyst. The obtained copolymers consiting of the succinimide and amide units, poly(succinimide-co-amide) (**3**), were soluble in DMF and DMSO except for that with **2e**. The thermal properties differed with varying the **2** unit in **3**, i.e., the T_gs of **3a-c** (99 ~ 138 °C) were higher than those of **3d** (81 ~ 1 01 °C), the apparent difference in the T_m between **3a-d** did not observed, and the T_d decreased in the order of **3a**, **3c** > **3d** > **3b**.

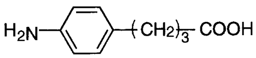
Introduction

Plastic waste is one of the serious problems concerning the earth's environment, because it is not degraded in landfill and some of them produce toxic gases when they are burned. In addition, plastics scattered in nature also hurt the wildlife. Therefore, in order to reduce the environmental pollution due to plastic waste, several proposals, e.g., chemical, material, and thermal recycling and the development of biodegradable polymers [1-6], have been attempted.

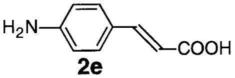
Recently, we reported that the polycondensation of L-aspartic acid (**1**) using an acid catalyst in a mixed solvent produced high molecular weight poly(succinimide), which is an important precursor for biodegradable poly-aspartic acid [7]. In addition, the method was found to be applicable to the synthesis of a copolymer, i.e., poly(succinimide-*co*-amide) was obtained by the reaction of **1** and aliphatic ω-aminocarboxylic acid, which was easily hydrolyzed for conversion into biodegradable poly(aspartic acid-*co*-ω-aminocarboxylic acid) with a high Ca^{2+}-chelating ability [8, 9]. We are interested in poly(succinimide) and its copolymeric derivatives as novel thermoplastics, because they are biodegradable after hydrolysis in the earth's environment. However, poly(succinimide) could not be thermally processed, because it decomposes without melting. Thus the introduction of aromatic units into the polymer is expected to improve the thermal property of poly(succinimide).



2a **2b** **2c**



2d



2e

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In this study, we report the synthesis of poly(succinimide-*co*-amide) (**3**) by the acid-catalyzed polycondensation of **1** with aromatic aminocarboxylic acid, such as 4-aminobenzoic acid (**2a**), 4-aminophenylacetic acid (**2b**), 4-aminomethylbenzoic acid (**2c**), 4-(4-aminophenyl)butyric acid (**2d**), and 4-aminocinnamic acid (**2e**). In addition, the thermal properties of **3** are characterized as thermally processable materials.

Experimental

Materials and Measurements. All reagents were used without further purification. **1** was obtained from Mitsubishi Chemical Corporation. Aminocarboxylic acids **2a** from the Kanto Chemical Co., Inc, and **2b**, **2c**, and **2e** were purchased from the Tokyo Chemical Industry Co., Ltd.. The ^{1}H and ^{13}C NMR spectra were obtained in DMSO-d_6 using a Bruker ASX-300 NMR spectrometer. Molecular weights of the polymers were estimated in DMF using 10 mM LiBr by gel permeation chromatography (GPC) (column, PLgel 5m-MIXED-C; detector, RI; standard, polystyrene). Decomposition temperatures were measured using a Seiko SSC-5200 TG/DTA220 under a nitrogen flow with heating rates of 10 ºC/min. Glass transition temperatures, taken as the midpoint of the change in slope of the baseline, and melting temperatures were measured with a Seiko SSC-5200 DSC220 under the same conditions as the TG/DTA measurement.

Polycondensation. A typical procedure for the polycondensation of **1** with **2** is as follows: A mixture of **1** (2.5 g, 19 mmol), **2b** (1.23 g, 8.1 mmol), and 85 % phosphoric acid (0.18 ml, 2.7 mmol) in mesithylene/sulfolane (16 ml/5 ml) were placed in a 100 ml flask equipped with a Dean-Stark trap. The reactants were refluxed with stirring at 180 ºC for 4.5 h. Mesithylene was evaporated under reduced pressure from the reaction mixture. The residual crude product was purified by reprecipitation with DMSO-MeOH and then dried in a vacuum. The M_w and M_w/M_n were 15100 and 1.23, respectively. Yield, 2.13 g (70 %).

Results and Discussion

For the polycondensation of **1** and **2**, *o*-phosphoric acid was used as a catalyst and mesithylene/sulfolane as a mixed solvent. Azeotropic removal of water from the reaction mixture was carried out throughout the reaction. Table 1 lists the results of the polycondensation of **1** with various aromatic aminocarboxylic acids. Copolymer yields significantly decreased with increasing mole fractions of **2a, 2c,** and **2d** in the monomer feeds, i.e., from 80 to 35 % for **3a,** from 91 to 44 % for **3c,** and from 85 ~ 49 % for **3d.** On the other hand, The copolymer yields of **3b** were as high as 70 ~ 90 % for every monomer feed ratio. The yield for **3d** and **3e** were 62 and 51 % at the monomer ratio of 7/3, respectively. The copolymers obtained except for **3e** were soluble in DMF and DMSO but insoluble in $CHCl_3$ and THF. The weight-average molecular weight (M_w), which was determined by GPC in DMF using as a polystyrene calibration curve, tended to decrease as the succinimide unit in copolymer decreased, i.e., the M_ws were 15,600 ~ 9,200 for **3a**, 20,900 ~ 13,400 for **3b**, 18,900 ~ 9,700 for **3c**, and 29,000 ~ 11,400 for **3d**.

Figure 1 shows the ^{1}H NMR spectrum of **3b** (x/y = 0.79/0.21). The signals at 2.7 and 3.2 ppm and at 4.7 and 5.3 ppm were assigned to the methylene and methine protons of the succinimide units, respectively. In addition, the signals at 8.5, 8.6, 9.8, and 9.9 ppm, at 7.1 - 7.7 ppm, and at 3.4 - 3.8 ppm were assigned to the amide, aromatic, and methylene protons due to the **2b** units, respectively. A few signals due to the amide and methine protons were also observed, which were caused by the difference in the copolymer sequence, such as the succinimide and succinimide unit, the succinimide-**2b** unit, and the **2b-2b** unit. A similar result was observed in the ^{1}H NMR spectra of **3a, 3c,** and **3d**. Thus, the **2a-d** units were randomly introduced into the copolymer.

Table 1. Polycondensation of L-aspartic acid (**1**) and aromatic aminocarboxylic acids (**2**) with *o*-phosphoric acid [a] and thermal properties of poly(succinimide-*co*-amide) (**3**)

2	Mole flaction of **1** in monomer feed	Yield (%)	Mole flaction of succinimide unit in copolymer **3** [b]	M_w (M_w/M_n) [c]	T_g [d] (°C)	T_m [e] (°C)	T_d [f] (°C)
2a	0.9	80	0.88	15600 (1.27)	-	314	419
	0.8	70	0.78	8500 (1.34)	112	288	410
	0.7	74	0.75	12000 (1.17)	99	281	380
	0.6	41	0.71	9500 (1.12)	112	278	401
	0.5	35	0.70	9200 (1.17)	122	269	392
2b	0.9	80	0.89	17800 (1.81)	128	306	392
	0.8	90	0.79	20900 (1.35)	-	323	388
	0.7	70	0.66	15100 (1.23)	128	306	370
	0.6	75	0.56	14900 (1.20)	112	284	361
	0.5	76	0.48	13400 (1.50)	116	289	363
2c	0.9	91	0.91	18900 (1.66)	138	316	428
	0.8	44	0.83	9700 (1.20)	107	257	408
	0.7	0	-	-	-	-	-
2d	0.9	80	0.87	25200 (1.06)	97	299	403
	0.8	85	0.80	29000 (1.05)	91	282	393
	0.7	57	0.71	12100 (1.10)	83	264	379
	0.6	57	0.64	11700 (1.10)	101	266	376
	0.5	49	0.56	11400 (1.10)	81	261	375
2e	0.7	51	-	-	-	-	-

a) Solvent, mesitylene/sulfolane (7/ 3 wt ratio); [*o*-phosphoric acid] / [**1** + **2**] = 0.1; temp., 180 °C; time, 4.5 h.
b) Determined by ^{1}H and ^{13}C-NMR spectra in DMSO-d_6.
c) Determined by GPC in DMF using polystyrene as a standard.
d) Glass transition temperature.
e) Melting temperature.
f) Decomposition temperature.

The copolymer composition was determined using the area ratio between the methine proton of the succinimide unit and the aromatic protons of the comonomer unit. The mole fractions of the **2a** unit in copolymer **3a** were smaller than those of **2a** in the monomer feed ratios of 0.7 and 0.6, whereas the copolymer compositions for **3b** and **3d** were in fair agreement with the monomer feed ratios. For **3c**, the copolymer compositions of succinimide and the **2c** units were similar to the monomer feed ratio of 9/1 and 8/2, but no copolymer was obtained for the monomer ratio of 7/3 or below. These results indicate that the reactivity of the amino group in aminocarboxylic acid apparently affected the polycondensation.

In order to clarify the copolymerization characteristics, the polycondensation of **1** was carried out in the presence of aniline or benzylamine at the **1**/amine molar ratio of 7/3 under the same conditions as in Table 1. The polycondensation of **1** in the presence of aniline proceeded to yield poly(succinimide) though its M_w was extremely low, whereas benzylamine inhibited the polycodensation of **1** and almost the amount of **1** was recovered. These results suggest that the amino methyl group in **2c** tends to disturb the polycondensation of **1** as well as benzylamine, resulting in no copolymer being obtained for the monomer ratio of 7/3 or below. Previously, we reported that an aliphatic ω-aminocarboxylic acid such as 6-aminocaproic acid was copolymerized with **1** to form poly(succinimide-*co*-amide) [9]. The basicity of the amino group in the amino carboxylic acid should play an important role in the

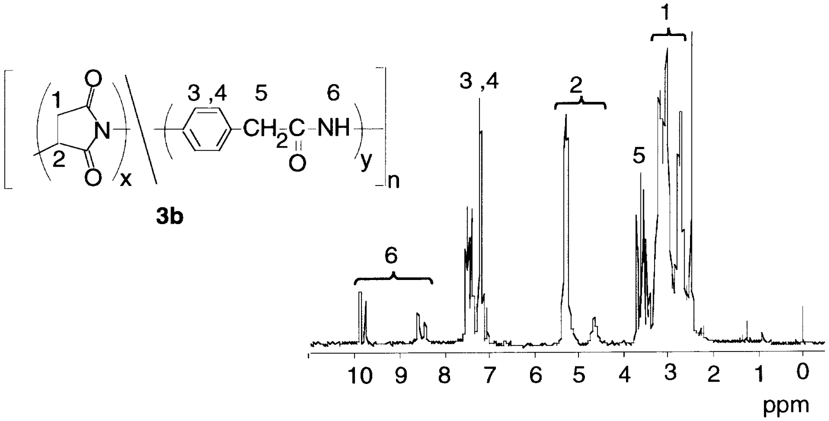

Figure 1. ^{1}H NMR spectrum of copolymer 3b

acid-catalyzed polycondensation, but it is obscure and thus further studies are needed.

The thermal properties of poly(succinimide-*co*-amide) are listed in Table 1. Poly(succinimide) did not exhibit a glass transition temperature (T_g) and decomposed at 424 °C without melting. In contrast, the copolymers had a T_g, a melting temperature (T_m), and a decomposition temperature (T_d) though the T_d of the copolymer was lower than that of poly(succinimide). The thermal properties differed with varying the **2** unit in **3**, i.e., the T_gs of **3a-c** (99 ~ 138 °C) were higher than those of **3d** (81 ~ 1 01 °C), the apparent difference in the T_m between **3a-d** did not observed, and the T_d decreased in the order of **3a, 3c** > **3d** > **3b**. In addition, the T_g, T_m, and T_d tended to decrease with the increase in the **2** unit for **3**. The T_g, T_m, and T_d of **3a-d** were higher than those for the aliphatic copolymer from 6-aminocaproic acid whose T_g, T_m, and T_d were 97,227, and 374 °C, respectively [9]. These results indicate that the thermal property of poly(succinimide) was improved by introducing aromatic units into the poly(succinimide), and thus the poly(succinimide-*co*-amide)s should be a new thermoplastic material.

Conclusion

The acid- catalized polycondensation of L-aspartic acid with various aromatic aminocarboxylic acids has been studied in order to improve the thermal property of poly(succinimide). The copolymer consisting of succinimide and amide units, i.e., poly(succinimide-*co*-amide), were obtained using 4-aminobenzoic acid, 4-aminophenylacetic acid, 4-aminobenzoic acid, and 4-(4-aminophenyl)butyric acid. For the thermal property, the copolymer melted before decomposition, which differed from poly(succinimide).

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