# Syntheses of High-Performance Biopolyamides Derived from Itaconic Acid and Their Environmental Corrosion

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S *Supporting Information*

ABSTRACT: A new synthetic route for high-performance biopolyamides with a rigid N-substituted pyrrolidone ring was developed from the biomonomer itaconic acid (IA), which was mass-produced by the fermentation of *Aspergillus terreus*. We used salt-type monomers composed of diacidic IA and diamines. These salts thermally converted into polyamides in the presence of sodium dihydrogen phosphate through the aza-Michael addition, followed by intramolecular cyclization to create a pyrrolidone ring in the polymer main chain. Polyamides with molecular weights ranging over 28 000 showed T_g values over 87 °C, which were higher than conventional polyamides (around 57 °C). The Young's modulus and mechanical strength of these polyamides also showed high values of 430−2800 MPa and 90−165 MPa, respectively. In addition, the polyamides became soluble in water by ring-opening reaction of the pyrrolidone, which led to environmental corrosion by landfill or ultraviolet irradiation.
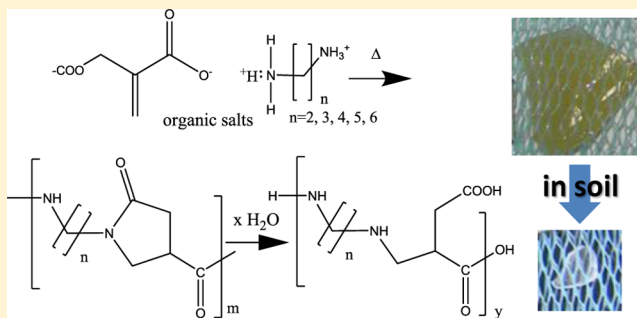
INTRODUCTION

The development of high-performance, environmentally degradable polymers usable as engineering plastics from renewable resources is important for the establishment of a sustainable society.[1] Biodegradable resins provide a solution for overcoming the plastic waste problem.[2,3] Conventional polyamides such as nylon account for a substantial percentage of engineering plastics,[4] and thus bioderived polyamide development is desirable in various fields from automobile parts to medical materials. In addition, it is quite significant to develop a high-performance biopolyamide by utilizing the structural characteristics of biomolecules. The performance characteristics such as the glass transition temperature (T_g) were enhanced by the incorporation of rigid rings such as alicycles and benzenes into the polymer backbone.[4] However, reactive alicycles or benzene derivatives do not exist very widely as biomolecules, and the toxicity of these rigid compounds renders their biological availability particularly low. In this study, we selected the widely used biomolecule "itaconic acid" (IA) in order to meet the above-mentioned requirements based on cyclic amide formation by chemical reactions. IA is a diacidic biomonomer mass-produced by the fermentation of *Aspergillus terreus*[5] and contains a reactive vinylidene group.[6] The polyamides from IA have not been reported in the scientific literature but were shown only in an old patent[7] where structural analyses in the solution state such as the molecular weight determination were not performed and the concept of bioderivative or degradability was not mentioned. This is why the two carboxylic acids and one vinylidene group of IA were

able to react to generate three-way branching points, which make it difficult to control the polymerization. If this difficulty can be solved by reacting IA another way with diamides, then IA-derived polyamides could extend the field of green sustainable polymers.[8] Here, we report the syntheses of polyamides containing a pyrrolidone ring derived from IA salts with aliphatic diamines via the aza-Michael addition,[9] followed by amidation. The polyamides synthesized using IA and bioavailable diamines showed high heat resistance and good environmental degradability. Additionally, we observed their in-soil corrosion and photoinduced dissolution in water, based on the ring-opening reaction of the pyrrolidone groups in the main backbones.

METHODS

Materials. Bio-derived itaconic acid (IA), which was kindly dedicated from Iwata Chemical Co. Ltd. (Iwata, Japan), was used as received. Aliphatic diamines (TCI) which were used as monomers were used as received without purification. NaH_2PO_4 (Sigma-Aldrich) which was used as a catalyst for polymerization of IA was used as received without purification. *N,N*-Dimethylformamide (DMF), trifluoroacetic acid (TFA), ethanol (EtOH), dichloromethane (DCM), tetrahydrofuran (THF), acetonitrile, *m*-cresol, NMP (*N*-methylpyrrolidone), dimethyl sulfoxide (DMSO), and acetone were purchased from Wako Pure Chemical Industries Ltd. and used as solvents as received.

Syntheses of Monomers and Polymers. A solution of IA (1 mol) in EtOH (300 mL) was mixed with the solution of diamines (1 mol) in EtOH (200 mL) to give the homogeneous mixture. The mixture was kept for 30 min at room temperature to appear salts as white solid (94−98% yield). The salts were heated at a certain temperature in vacuo and were agitated in the presence of catalyst NaH₂PO₄ (0.1 wt %) to be polymerized in bulk, where the reaction temperature was set at 5 °C higher than onset weight loss temperature of the thermogravimetry (TGA) curve of individual salt monomers. For instance, the salt of ethylenediamine with IA was put in a sealed tube equipped with a mechanical stirrer bar and temperature controller and heated around 230 °C under slow agitation and kept for 6−8 h. The condensed water was removed by vacuum. The product was purified by reprecipitation over *N,N*-dimethylformamide (DMF) solution into acetone in the volume ratio of DMF:acetone 10:90 for removal of catalyst and some impurity and were dried at 120 °C for 1 day *in vacuo* (yields 87−92 wt %).

Measurements. The molecular weights of the polyamides were determined by gel permeation chromatography (GPC; Shodex GPC-101 with a connection column system of 803 and 807) that was calibrated with pullulan standards (eluent: dimethylformamide). The NMR spectra were obtained on a Bruker DRX 500 spectrometer operating at 400.13 MHz for ^{1}H NMR. A deuterated solvent of DMSO-d_6 was used. Fourier transform infrared spectra (FT-IR) of the polyamides and salt monomers were recorded on a PerkinElmer Spectrum One spectrometer using a diamond-attenuated total reflection (ATR) accessory. The thermotropic behavior was confirmed by differential scanning calorimetry (DSC) measurement (EX-STAE6100; Seiko Instruments Inc., Chiba, Japan) at a scanning ratio of 10 °C/min from 30 to 200 °C in nitrogen. Thermogravimetric analysis (TGA; SSC/5200 SII Seiko Instruments Inc.) was made for determine 10% weight-loss temperature by heating from 30 to 800 °C at a rate of 10 °C/min under a nitrogen atmosphere. The tensile test was performed at a 1 mm/s movement in a room temperature using a tensile testing machine (INSTRON, Canton City, MA, 3365-L5). The fibrous samples with a length over 10 mm were set and elongated. Young's moduli were defined as the initial inclination of the stress−strain curve.

■ RESULTS AND DISCUSSION

Polyamide Synthesis from Organic Salts of Itaconic Acid with Aliphatic Diamines. We used organic salts of IA with aliphatic diamines because a 1:1 mixing of the diacid and diamine at the molecular level was performed. Furthermore, the aliphatic diamines were adjacent to every IA to give the monomers almost even reaction conditions. Salt formation was important to control the reaction in order to prohibit the generation of three-way branching points from the vinylidene group and two carboxylic acids of IA. We prepared organic IA salts by carefully mixing the monomers in ethanol to obtain a white powder (yield: 75−93 wt %). The salt formation between the itaconate dianions and the aliphatic diamino dications was confirmed by FT-IR (representative spectrogram: Figure 1, top) and ^{1}H NMR (representative spectrogram: Figure S1) spectroscopy. The crystals melted upon heating to a certain temperature as detected by differential thermal analyses (DTA), accompanied by a weight loss corresponding to the weight percent of two water molecules (thermogravimetry; TGA) (representative curves: Figure 2).

Moreover, this weight loss can be considered as two-step water elimination at the threshold of 187 °C. Thus, the condensation reaction might be a two-step process: the first step is water elimination during pyrrolidone ring formation, and the second step is the polymerization illustrated in the last reaction of Scheme 1. The shape of the DTA curve was very complex, and we can discuss it by dividing it into two regions
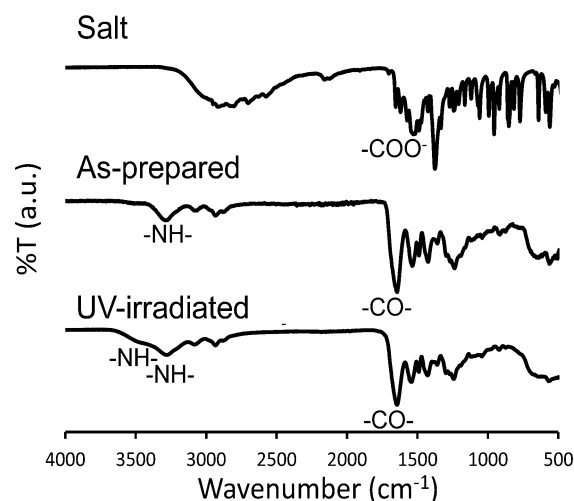

Figure 1. IR spectra of salt monomer and the corresponding polyamides (as-prepared and UV-irradiated) prepared from itaconic acid salt with ethylenediamine.
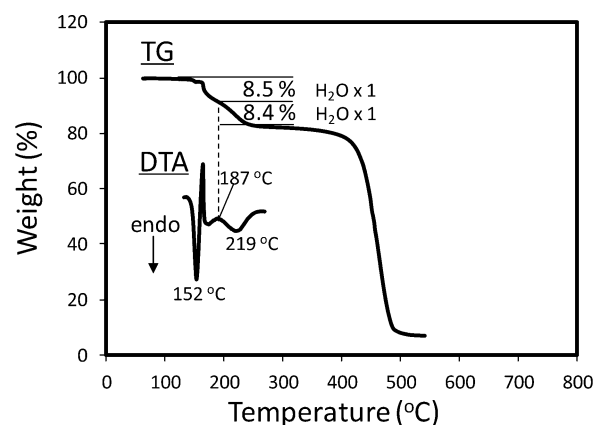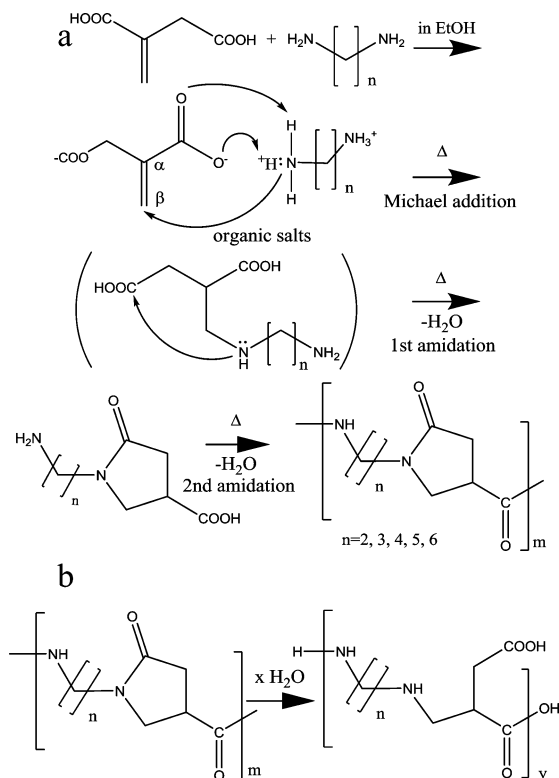

Figure 2. Thermogravimetric (TG) and differential thermal analysis (DTA) curves of the salt monomer of itaconic acid with 1,6-diaminohexane.

below and above 187 °C (dotted line in Figure 2). Above 187 °C, a DTA endotherm with a peak of 219 °C accompanied by an 8.4 wt % loss (by TG) was detected. Below 187 °C, the melting point, the aza-Michael addition, and the amidation occurred over a narrow temperature range, and thus the DTA curve became too complex to find the exact melting temperatures (T_m) of the salt monomers. This reaction will be discussed after NMR analyses. The onset temperature of melting ($T_{m,o}$) for the salts was estimated to range between 155 and 225 °C independent of the carbon number of the aliphatic amines, *n*.

The salt was polymerized by a melt polycondensation *in vacuo* in the presence of NaH₂PO₄ catalyst (0.1 wt %) by heating gradually to a specific temperature between 160 and 230 °C, which was set at 5 °C higher than the $T_{m,o}$ of the individual organic salt.[7] The obtained polymers were purified by reprecipitation over *N,N*-dimethylformamide (DMF) solution into acetone and then dried at 120 °C for 1 day *in vacuo* (collection yield 87−92 wt %).

The polyamide structures containing the pyrrolidone ring were confirmed by their FT-IR spectra (Figure 1, middle), showing the vibration of the amides and alkyls; the ^{1}H NMR spectra showed one (not two) N−H proton signal plus alkyl

Scheme 1. (a) Syntheses of Itaconic Acid-Derived Polyamides from Its Salt with Aliphatic Diamines; (b) Ring-Opening Conversion of Pyrrolidone in Polymer Backbone

31000−67200 g/mol, respectively. The polydispersity index ranged between 1.2 and 2.8 depending on the structure, which in turn affects the solubility an efficiency of reprecipitation made before the GPC measurement (Table 1). One can confirm the acceleration effects of the catalyst on the polymerization, since the M_w and M_n of the polymers prepared without the catalyst showed much lower values, ranging between 15300−34500 g/mol and 7900−16000 g/mol, respectively, as compared to those prepared with the catalyst. In the direct method using NaH_2PO_4 not via the organic salt, the M_w and M_n of the polymers ranged between 16500−37500 g/mol and 9200−15600 g/mol, respectively, which were lower than those of the polymers prepared by the organic salt method. This was presumably due to the branch formation of the three-way reactions, which rendered the one-to-one ratio of the two monomers imbalanced. The synthesized polymers were insoluble in water, tetrahydrofuran, acetone, ethanol, *m*-cresol, glycerin, and hexane but were soluble in some polar solvents such as DMF, *N,N*-dimethylacetamide (DMAc), *N*-methyl-pyrrolidone (NMP), trifluoroacetic acid (TFA), and dimethyl sulfoxide (DMSO). Using pulsed field gradient NMR (DMSO-d_6) of the oligoamide, prepared by sampling the polymerizing liquid of the organic salt of IA with ethylenediamine, the pyrrolidone ring formation process was proven. In the $^1H-^{13}C$ HSQC (heteronuclear single quantum coherence, Figure 3) spectrum, three specific $^1H-^{13}C$ couplings of two protons with one carbon were detected, which supported the formation of the pyrrolidone ring in/around the three geminal proton pairs at H^a, H^c, and H^d, which were nonequivalent. In the $^1H-^1H$ COSY (correlation spectroscopy, Figure 4a) spectrum, all of the geminal and vicinal proton−proton couplings in the pyrrolidone and alkylenes were detected. Furthermore, the N−H proton coupled with only the H^e signal. Using $^1H-^{13}C$ HMBC (heteronuclear multiple-bond connectivity, Figure 4b), all of the $^2J_{CH}$ and $^3J_{CH}$ couplings in the pyrrolidone and alkylenes were detected. In addition, two signals at 178 and 183 ppm in the ^{13}C NMR spectrum appeared separately, which supported the presence of two nonequivalent carbonyls. As a

protons (see Figure 7). The detailed procedures regarding the pulsed field gradient NMR method will be discussed later. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the polyamides were estimated by GPC using pullulan standards (eluant DMF, flow rate 1 mL/min). The M_w and M_n of the polymers prepared in the presence of NaH_2PO_4 ranged between 66200−86700 g/mol and

Table 1. Molecular Weights and Characters of Itaconic Acid-Bioderived Polyamides[a]

n	$M_w^{[b]}$ (g mol^{-1})	$M_n^{[b]}$ (g mol^{-1})	$M_w/M_n^{[b]}$	$T_g^{[c]}$ (°C)	$T_{10}^{[d]}$ (°C)	yield (wt %)	$\sigma^{[e]}$ (MPa)	$E^{[e]}$ (MPa)	$\varepsilon^{[e]}$
2	86 700	31 000	2.8	154	365	87	165	2800	0.018
	(33 200)	(15 800)	(2.1)	(118)	(365)	(78)	(105)	(1300)	(0.020)
3	66 200	46 000	1.4	83	370	86	90	450	0.023
	(34 500)	(16 000)	(2.1)	(73)	(360)	(57)	(65)	(420)	(0.026)
4	88 500	62 600	1.4	93	380	89	90	430	0.024
	(15 300)	(7 900)	(1.9)	(62)	(390)	(69)	(70)	(360)	(0.021)
5	80 600	67 200	1.2	87	390	92	90	550	0.049
	(16 700)	(11 800)	(1.4)	(63)	(375)	(70)	(75)	(450)	(0.052)
6	84 400	36 500	2.3	97	400	89	95	580	0.025
	(24 800)	(14 000)	(1.8)	(73)	(415)	(72)	(80)	(490)	(0.026)
PA66				57	390		65−68	590−1700	0.06
PA6				53	400		41−60	440−1400	0.18

[a]The polymers were prepared by an in-bulk polycondensation of the corresponding salt-type monomers of IA and aliphatic diamines with different carbon numbers in the presence of NaH_2PO_4 as a catalyst. The values in the parentheses are the data from polymers prepared without the catalyst. The mark *n* refers to the carbon number of the diamine monomers. PA66 refers to poly(hexamethylene adipamide) whose data were from refs 10 11, and 13, and PA6 refers to poly(ε-caprolactam) whose data were from refs 10, 12, and 13. [b]Number-average molecular weights, M_n, weight-average molecular weight, M_w, and polydispersity index (M_w/M_n) were measured by GPC (gel permeation chromatography, Pullulan standard). [c]Glass transition temperatures, T_g, of the polymers were measured by DSC (differential scanning calorimetry) under nitrogen at a scanning rate of 10 °C min^{-1}. [d]The 10% weight-loss temperatures, T_{10}, were measured by TG (thermogravimetry) under nitrogen at a heating rate of 10 °C min^{-1}. [e]The mechanical properties were measured by a stress−strain tensile test. Marks σ, E, and ε refer to mechanical strength, Young's modulus, and strain at break, respectively.
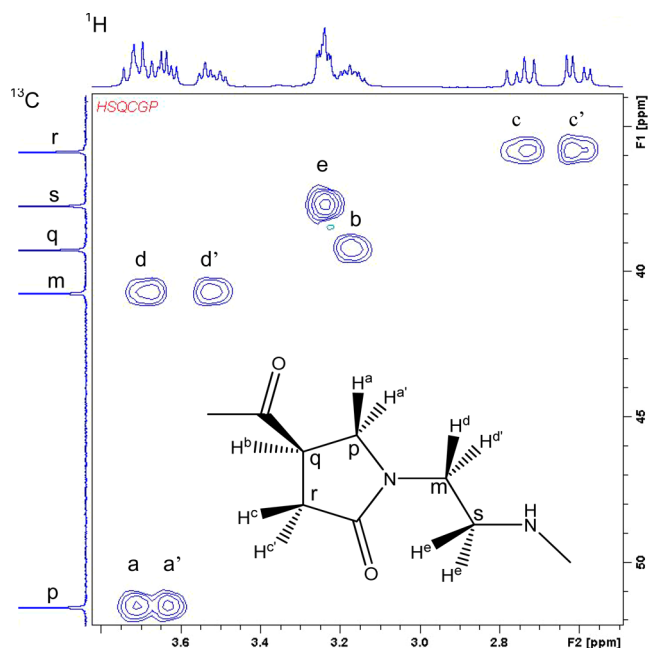
Figure 3. $^1H-^{13}C$ HSQC spectrum of the oligoamide taken from the polymerizing liquid from the salt-type monomer of itaconic acid and ethylenediamine.

consequence, the desired pyrrolidone structure in the polymer backbone was formed via organic salts in the presence of NaH_2PO_4 with water loss. We hypothesized the following reaction mechanism: the amino group could be drawn close the carboxylate group in the solid salt and upon melting can react nucleophilically with the double bond.

Although the hydrogen ion was drawn to the carboxylate ion, a lone pair of amino groups was added to the relatively positive β-carbon of the double bond connected to the carbonyl group, and a proton was added to the oxygen of the carbonyl (1,4-addition). This formed a resonantly stabilized intermediate enolate with an electronegative oxygen, which was again protonated to convert it into a ketone. As a result, an imino group was formed, which immediately reacted with the distal carboxylic acid to form a five-membered cyclic amide (pyrrolidone). The carboxylic acid adjacent to the double bond would not react with this imine, because an unstable four-membered ring is formed as a result of this reaction. In the final stage, an ordinal polycondensation of the unreacted carboxylic acid with the amine occurred to generate the bioderived polyamide (Scheme 1a). Using ^1H NMR analyses, we confirmed in a model reaction of IA with benzylamine that the amidation did not occur before the aza-Michael addition.

On the other hand, the normal melt reaction of IA with an amino compound is less homogeneous than the reaction via an organic salt. In this case, some side reactions yielding three-way branching should occur, such as (1) a primary amidation of the distal carboxylic acid with the amine before the aza-Michael addition and (2) a secondary amine formed as a result of the aza-Michael addition, which behaved as a donor for another Michael addition.

Thermal and Mechanical Performance of the Polyamides. We summarized the thermal properties of the polyamides prepared from IA in Table 1. The glass transition temperature (T_g) and 10% weight loss temperature (T_{10}) of the polymers were measured by differential scanning calorimetry

(DSC; representative curve, Figure S2a) and TGA (representative curve, Figure S2b), respectively. TGA was performed under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} and revealed excellent thermal stability for this bioderived polyamide containing a pyrrolidone ring; the T_{10} ranged between 300 and 410 °C, and the T_g ranged between 80 and 97 °C. The T_{10} values were comparable to those of conventional polyamides such as PA66 [poly(hexamethylene adipamide)] and PA6 [poly(ε-caprolactam)], showing T_{10} values of 390 and 400 °C, respectively. In contrast, the T_g values were much higher than those of PA66 and PA6 with T_g values of 57 and 53 °C, respectively.[10] The good thermal performance of the polyamides prepared here may be attributed to not only strong interchain interactions via amide linkages but also the rigid main chains containing pyrrolidone rings, although steric hindrance against interchain hydrogen bonding by the nonplanar pyrrolidone rings might be considered. The mechanical properties of the polyamides are also summarized in Table 1, which showed that the mechanical strength (σ) and the Young's modulus (E) ranged between 90−65 MPa and 430−2800 MPa, respectively, which were higher than those of PA66 (σ: 65−68 MPa, E: 590−1700 MPa)[11,13] and PA6 (σ: 41−60 MPa, E: 440−1400 MPa).[12,13] The strain values at mechanical failure, ε, ranged between 0.018 and 0.049, meaning that the polyamide specimens did not elongate very much. As a consequence, the biopolyamides prepared here were stiffer and stronger than conventional polyamides, owing to the rigidity of the pyrrolidone ring.

Environmental Corrosion Behavior of the Polyamides. We next tested the corrosion capability of the synthesized biopolyamides containing a pyrrolidone ring. Prior to the environmental-corrosion tests, we confirmed the water solubility of the polyamides by immersing the polyamide resins into an alkaline solution of pH >10 due to the ring-opening hydrolysis of the pyrrolidone shown in Scheme 1b. The as-prepared resins were all insoluble in water, and the water-absorption ratio to thoroughly dried resins was only around 4 wt %. However, the polyamide powders dispersed in an alkaline solution after stirring at 60 °C for more than 2 h. Next, we used environmental soil with pH values ranging from 7.5 to 7.9. The resins with sizes ranging from 2 to 4 cm held by polyethylene nets were buried. After one year, the nets were recovered, and the shapes and weights of the samples were checked. As one can see from Figure 5, most of the polyamide samples shrank, indicating the corrosion in the soil. In particular, polyamides derived from IA with 1,3-diaminopropane, 1,4-diaminobutane, and 1,6-diaminohexane disappeared due to in-soil corrosion. Similarly, the polyamides composed of IA with 1,5-diaminopentane (cadaverine) and 1,2-diaminoethylene showed weight loss values of 96 and 98 wt %, respectively. However, poly(lactic acid) coburied with the polyamides showed only 16 wt % weight loss. The weight loss of the polymers due to soil corrosion can result from the cumulative effects of physical, chemical, and biological processes.[14] Judging from their water solubility as a result of the pilot test using an alkaline solution, the large weight loss of the present IA-derived polyamides in environmental soil may be attributed to hydrophilization of the polymer chains by a ring-opening conversion of pyrrolidones to the carboxylates by water and some biological functions, as shown in Scheme 1b.

In addition, we confirmed the ring-opening reaction of the polyamide pyrrolidone by photoirradiation. Photoinduced solubilization of the polyamides in water upon UV-irradiation
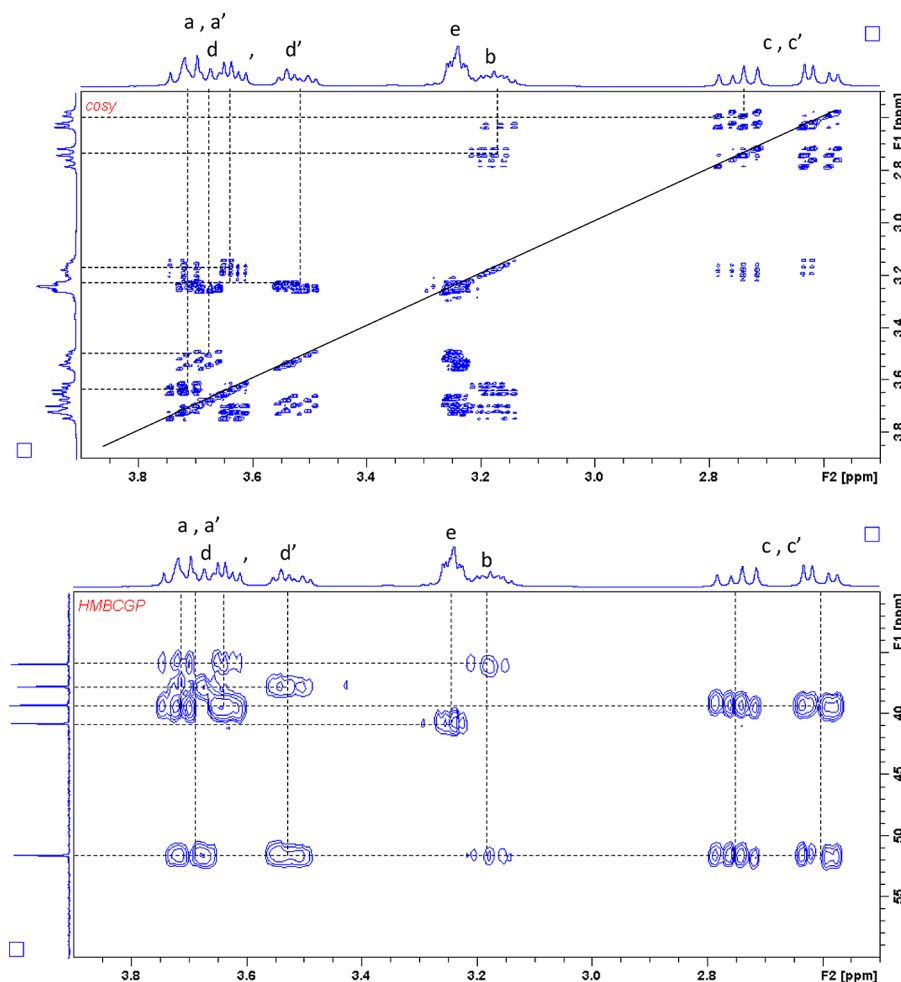
Figure 4. $^1H-^1H$ COSY (a) and $^1H-^{13}C$ HMBC (b) spectra of the oligoamide taken from a polymerizing liquid for the salt-type monomer of itaconic acid with ethylenediamine. In (b), transverse spectrum is ^1H NMR, and the vertical spectrum is ^{13}C NMR. Chemical structures in Figure 3 were used for assignment indications.
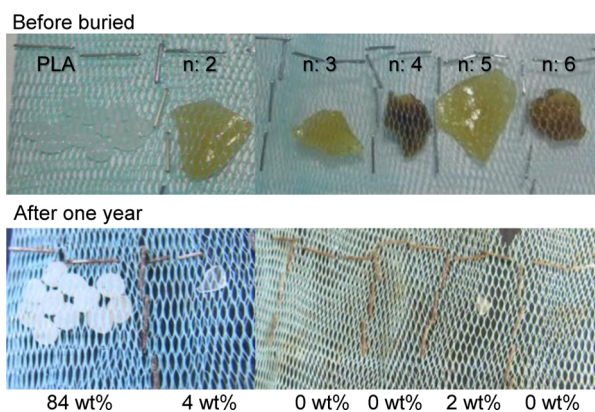

Figure 5. In-soil corrosion behavior of polyamides by keeping them in soil for one year. PLA refers to poly(lactic acid). Others were polyamides derived from itaconic acid with aliphatic diamines with different carbon numbers, n. Residual weight percentages after keeping polyamide resins for one year are shown at the bottom.

with a high-pressure mercury lamp at a wavelength range of 250−450 nm was observed (Figure 6). Although the as-prepared polyamides showed only one IR peak of a NH vibration around 3300 cm^{-1}, the samples which were water-dissolved by UV-irradiation and then freeze-dried showed a

new peak around 3500 cm^{-1} as shown in the bottom of Figure 1. This new peak can be assigned to the vibration of the NH group formed as a result of the ring-opening reaction of pyrrolidone. This NH signal also appeared in the ^1H NMR spectrum at 5.08 ppm as a result of UV-irradiation (inset, Figure 7). If the present polyamides were floating on the sea and became water-soluble due to a photoreaction under sunlight, which includes the wavelength range 280−400 nm, then the plastic waste may be corroded. Although it will take a long time to perform a corrosion test using only direct use sunlight, we plan to study the photoinduced corrosion of polyamides containing a photosensitizer in the near future.

■ CONCLUSIONS

A new synthetic route to generate bioderived polyamides with a N-substituted pyrrolidone ring was established by a melt polycondensation of salt monomers composed of itaconic acid and aliphatic diamines in the presence of NaH$_2$PO$_4$. The molecular weights of these polyamides were over 27 000, and their thermal and mechanical properties were superior to conventional aliphatic polyamides such as PA66 and PA6. The hydrolysis of polyamides was deduced to be a ring-opening reacion of the pyrollidone to generate hydrophilic carboxyl side chains. This ring-opening reaction occurred not only in alkaline solution but also in environmental soil and under UV-
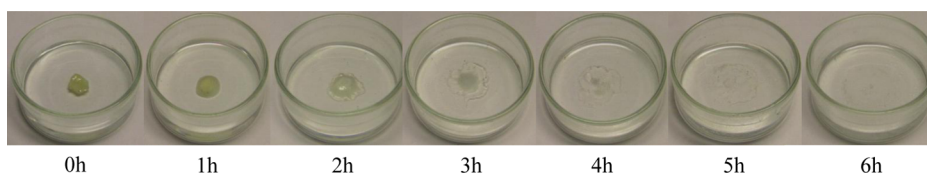
Figure 6. Time course of water-solubilization behavior of polyamide resin derived from itaconic acid with 1,5-diaminopentane by high-pressure mercury lamp irradiation with a wavelength range 250−450 nm.
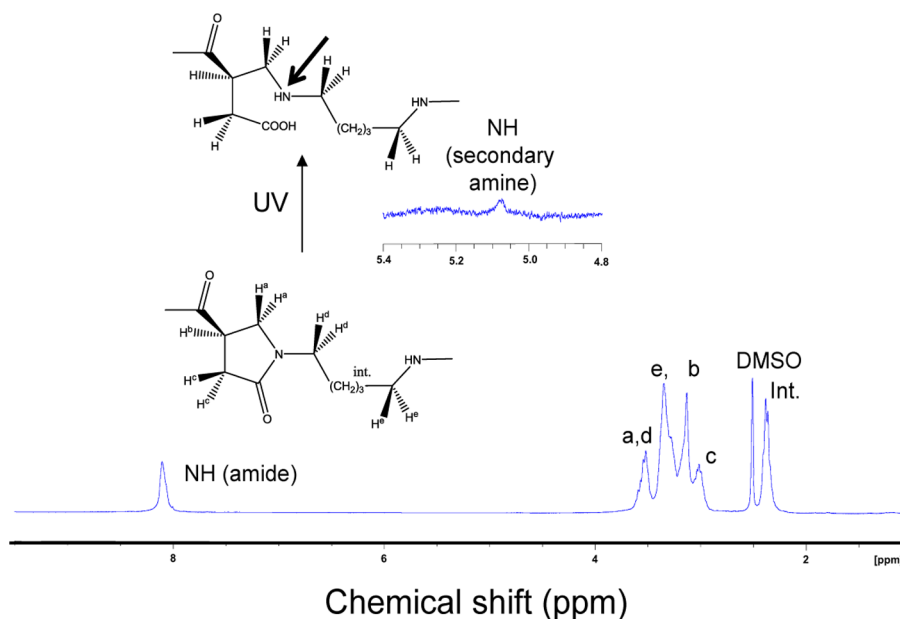

Figure 7. ¹H NMR spectra (400 MHz, DMSO-d_6) of the polyamide derived from itaconic acid with propylenediamine, where inset is UV-irradiated polyamide spectrum showing the appearance of a secondary amine.

irradiation. As a result, the polyamides became water-soluble and were corroded. This corrosion was important in terms of overcoming plastic waste problems and especially the endangerment of marine creatures by polyamides such as fish lines. Sunlight includes these UV wavelengths, and UV-A and UV-B rays penetrate through the earth's atmospheres to irradiate these plastics to make them corrosive in seawater.

■ ASSOCIATED CONTENT

ⓈSupporting Information
¹H NMR of salt monomer, DSC and TGA of polyamides. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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