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Description	

Syntheses of rigid-rod but degradable biopolyamides from itaconic acid with aromatic diamines

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Abstract

Highly-thermostable but degradable polyamides have been synthesized by a polycondensation of bio-derived itaconic acid salts with aromatic diamines to form heterocyclic pyrrolidone ring in the polymer backbone. The molecular weight was greater than 33600 g/mol. Glass transition temperatures, T_g, and 10 % weight loss temperatures, T_{10}, ranged 156-242 ^{o}C and 370-400 ^{o}C, respectively, which were higher than those of conventional bio-based plastics. However their processability was too low to process the fiber as specimens of mechanical tests. We then incorporated an appropriate amount of aliphatic moiety into the aromatic backbones to prepare the high-performance and processable polyamides with T_g over 115 ^{o}C and T_{10} over 355 ^{o}C. The processed fibers showed tensile strength and Young's modulus ranged 20-58 MPa and 0.2-2.3 GPa, respectively. The degradation behaviors inside soil and under ultraviolet-irradiation in water were additionally found.

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1. Introduction:

Production of environmental friendly materials could enhance to develop a sustainable low-carbon society, and then bio-derived polymers such as biopolyesters [1] and biopolyamides [2] are widely developed. However their thermomechanical performances are not very high, and then their wide spread use is very difficult under the severe competition with commodity plastics [3, 4]. A rigid polyamide containing aromatic and heterocyclic rings has high strength, good fatigue resistance, wearing durability due to the existence of strong intermolecular hydrogen bonding and π-electron stacking based on the rings [5-7]. Itaconic acid (IA) is a bio-based monomer which has been used for various polymers [8-9], is obtained by a thermal conversion of citric acid [10] or as a fermented product of *Aspergillus terreus* in the presence of carbohydrate-containing matters such as potato, jatropha seed cake, and corn starch [11]. IA reacted readily with the diamine to form a heterocycle N-substituted 3-carboxy-2-pyrolidines via the aza-Michael addition followed by amidation [2, 12] by a melt-polycondensation of corresponding nylon salt-type monomers to create a high molecular weight polyamide, as we reported previously [13]. In order to apply them in advance fields, the investigation of structure-property relationships of the IA-derived polyamides containing pyrrolidone rings is very important [14].

Here we extend our research to develop a series of various IA-derived polyamides with higher thermomechanical performances than those of the former aliphatic polyamides. Additionally they show the corrosion behavior in soil and photo-induced solubilization in water under UV light, which can be applied for the plastic decomposition [15-16] leading to overcome a disposal problem around the landfill [16-17].

2. Materials and Methods

2.1.Materials: Itaconic acid (IA) was dedicated as a bio-derived diacid from Iwata chemical co.ltd. *p*-Phenylenediamine (Sigma Aldrich), *p*-xylenediamine (TCI), *m*-xylyenediamine (TCI), and oxydianiline (TCI) as aromatic diamine 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. Ethylenediamine (TCI) as aliphatic diamine monomer was used after distillation. Solvents such as dichloromethane (DCM), methanol (MeOH), ethanol (EtOH), isopropanol (iPrOH), acetone, acetonitrile, hexane, *N,N*-dimethylformamide (DMF), dimethylacetamide (DMAc), trifluoroacetic acid (TFA), dimethyl sulfoxide (DMSO), *N*-methylpyrrolidone (NMP), and tetrahydrofuran (THF) were purchased from Wako Pure Chemical Industries Ltd. (Osaka Japan) used as received.

2.2. 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 NaH_2PO_4 (0.1 wt%) to be polymerized in bulk, where the reaction temperature was set at 5 ^oC higher than onset weight loss temperature of the thermogravimetry (TGA) curve of individual salt monomers. For instance, the salt of *m*-xylenediamine with IA was put in a sealed tube equipped with a mechanical stirrer bar and temperature controller, and heated around 230 ^oC under slow agitation and kept for 6-8 hours. The condensed water was removed by vacuum. The product was purified by re-precipitation 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 ^oC for 1 day *in vacuo* (yields, 82 wt %). The aromatic-aliphatic copolymers were prepared by an analogous procedure with the homopolymer while total amount of diamines was adjusted to 1 mol.

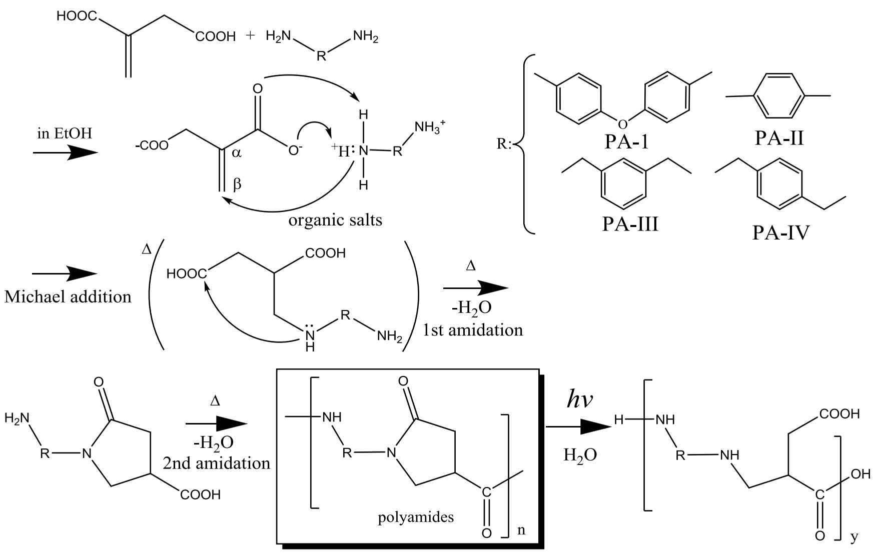
2.3. Measurements

The molecular weights of the polyamides were determined by gel permeation chromatography (GPC; Shodex GPC101 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 ^1H NMR. A deuterated solvent of DMSO-d_6 was used. Fourier transformed 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. DSC (differential scanning calorimetry) measurements were carried out under a nitrogen gas atmosphere, and dried polymer samples (5-8 mg) were measured at a scanning rate of 10 ^oC/min between 0 and 200 ^oC (EXSTAE6100; Seiko Instruments Inc., Chiba, Japan). Thermogravimetry (TGA; SSC/5200 SII Seiko Instruments Inc.) was carried out to determine 10% weight-loss temperature by heating from 30 to 800 °C at a rate of 10 °C/min under a nitrogen atmosphere. Stress-strain analyses were performed with crosshead speed at 1 mm/s at 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, The results of five specimen were averaged to obtain a mean value for Young's moduli, E, tensile strength, σ, and elongation at break, ε, calculated with stress-strain curve.

3. Results and Discussion:

3.1. Aromatic IA-derived polyamides

IA-derived aromatic polyamides were prepared by heating the corresponding monomers of nylon salts which were obtained as white powers by 1:1 mixing IA with aromatic diamines at the molecular level in ethanol (Scheme 1). In the salt state, the diamines were adjacent to every IA to give the monomers and yields were 94-98 wt %. The salt formation between the itaconate dianions and the aliphatic diamino dications was confirmed by FT-IR (representative spectrogram: Fig. S1b top) and ^{1}H NMR (representative spectrogram: Fig. S1a) spectroscopy with referring the literature [2]. The powders 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: Fig. 1). Additionally TG curve of the salts gave important information of their structure and reactivity; Fig. 1 is a representative TG curve of *m*-xylenediamine/IA salt showing a weight loss with ca.17.3 wt%, and the loss shows the water elimination at the threshold temperature of 193 ^{o}C.



Scheme 1. Synthetic route of bio-based polyamides derived from itaconic acid salts with aromatic diamines. Abbreviations of polyamides are shown right.

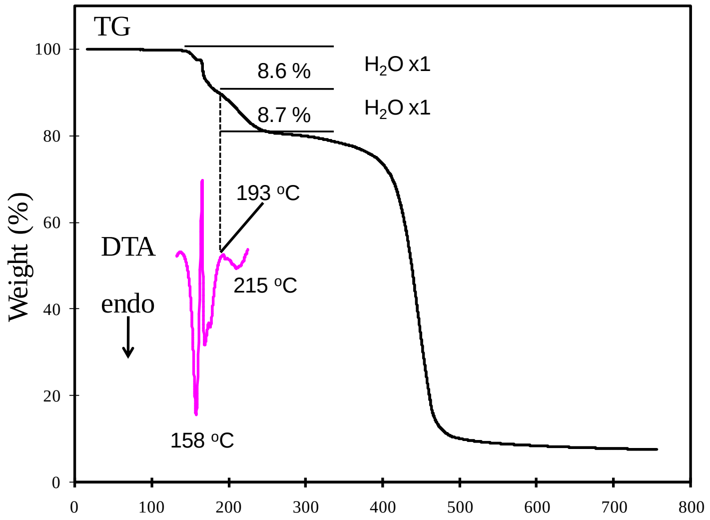


Figure1. Representative thermogravimetric (TG) and differential thermal analysis (DTA) curves of salt monomer of itaconic acid with *m*-xylenediamine.

Then the condensation reaction can be considered to proceed by two-step: the first step is water elimination during pyrrolidone ring formation and the second step is the polymerization as confirmed previously [2]. The shape of DTA dividing-into two regions below and above 193°C (dotted line in Fig.1); above 193°C, a DTA endotherm with a peak of 215 °C accompanied by an 8.7 wt % loss (one mol water), while the aza-Micheal addition and the amidation occurred over narrow range of temperature accompanied by an 8.6 wt % loss (one mol water) below 187 °C. The two overlapped reactions made the DTA peaks too complex to find the exact melting temperatures (T_m) of the salt monomers. Other salts showed the similar behavior to the IA/*m*-xylenediamine and previous IA/aliphatic diamine salt monomers [2], which suggest the reaction process (Scheme 1) was independent on the diamine structure. The polymerization temperatures were adjusted between 200-235 °C which were 20 °C higher than the on-set weight-loss temperature (T_mo; 160-235 °C.) of the individual salts. Salt monomers were polymerized by a melt polycondensation in vacuo in the presence of NaH_2PO_4 catalyst (0.1 wt%) by heating gradually and mechanically agitated for 10-12 hrs. The viscosity of the melting reactants gradually increased finally to solidify and not allow further agitation. The obtained polymers were purified by re-precipitation over DMF solution into isopropyl alcohol or acetone and washed with a few times with hot acetone to remove the impurity as well as DMF, and then dried at 120 °C for 24 hr in vacuo (collection yield, 81-92 wt%). The prepared polyamides were insoluble in water, acetone, THF, MeOH EtOH, iPrOH, hexane, and DCM while were soluble in polar solvents such as DMF, TFA, and NMP. In DMSO and DMAc, the polymer became soluble only after heating to 50 °C. The solubility of the IA-derived polyamides with aromatic diamines was kept high although the heating was required in DMSO and DMAc. M_w and M_n ranges between 57100-105000 and 27500-61000 which were higher than M_w and M_n of the polyamide prepared without catalyst, 21200-24700 and 12800-26500, respectively. Polydispersity range M_w/M_n ranged between 1.4 and 2.0. Thermal behaviors such as the glass transition temperature (T_g) measured by differential scanning calorimetry and 10 % weight loss temperature (T_{10}) by TGA (representative curve, Fig. S2) of the polymers are summarized in Table 1. The T_g values of the polyamides ranged between 156-242 °C (DSC; representative curves, Fig. 2) while T_{10} ranged between 370-400 °C. The prepared IA-derived polyamides showed excellent thermal properties, owing to rigidity of the pyrrolidone and aromatic rings. PA-II showed the highest thermostability in spite of the lowest molecular weights of all the polyamides prepared here because of para-substitution, no ether linkage, and no methylene group.

Table 1. Molecular weights and thermal properties of itaconic acid-derived biopolyamides with aromatic diamines.

Polyamides[a]	M_w[b] (g mol^{-1})	M_n[b] (g mol^{-1})	$M_\mathrm{w}/M_\mathrm{n}$[b]	T_g[c] (°C)	T_{10}[d] (°C)	Yields (wt %)
PA-I	105000	61000	1.7	199	400	81
PA-II	57100	27500	2.0	242	400	78
PA-III	62200	46700	1.4	156	370	82
PA-IV	65400	41200	1.6	173	390	89

[a] The polyamides were prepared by an in-bulk polymerization of the corresponding salt monomers in the presence of NaH_2PO_4 as a catalyst. M_w and M_n of the polymers without the catalyst showed much lower values ranging between 21200-38000 g/mol and 12800-26500 g/mol, respectively. The abbreviations of PA-I, PA-II, PA-III, PA-IV refer to IA-derived polyamides with 4,4'-diaminodiphenylether, *p*-phenylenediamine *m*-xylenediamine, and *p*-xylenediamine, respectively. [b] Weight-average, M_w, number-average molecular weights, M_n, and polydispersity index ($M_\mathrm{w}/M_\mathrm{n}$) were measured by gel permeation chromatography with pullulan standards. [c] Glass transition temperatures, T_g, were measured by differential scanning calorimetry under nitrogen at a scanning rate of 10 °C min^{-1}. [d] 10 % weight-loss temperatures, $T_{10,}$ were measured by thermogravimetry under nitrogen at a heating rate of 10 °C min^{-1}.

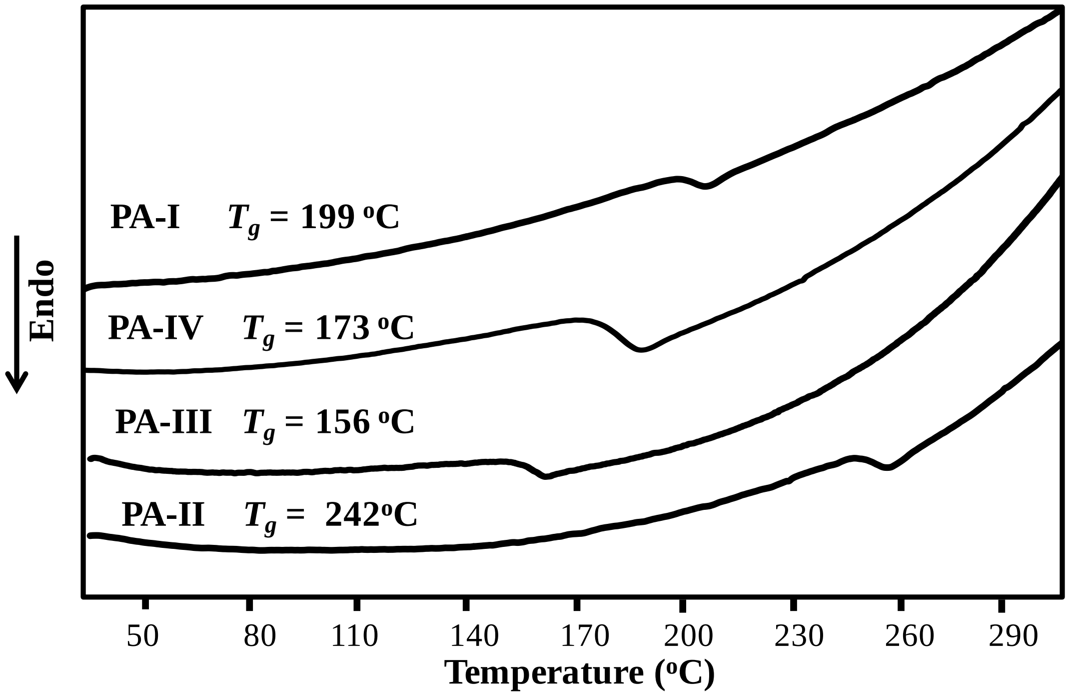


Figure 2. Differential scanning calorimetry thermograms for itaconic acid-derived biopolyamides with aromatic diamines

3.2. Aromatic/aliphatic IA-derived polyamides

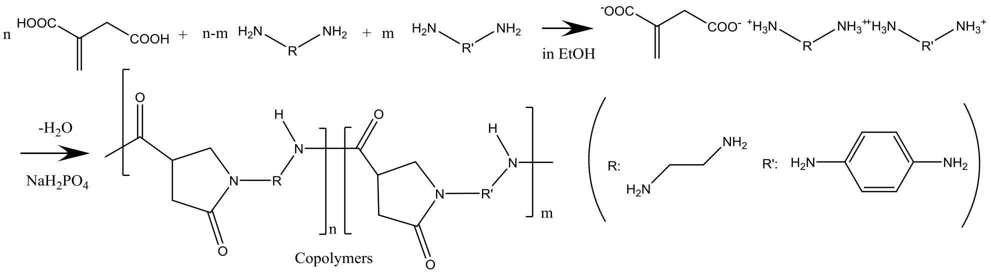
Although the aromatic polyamides showed the high thermostability, it was too difficult to spin their robust fibers which can be used as mechanical test specimens. The aromatic polyamide materials seemed too hard and then we tried to incorporate aliphatic moiety to aromatic backbone, which we expected to provide flexibility to the polymer chains with maintaining the high thermal properties. We selected *p*-phenylenediamine as aromatic monomer because of the highest thermal stability of the corresponding polyamide as related above and ethylene diamine as aliphatic one because we previously demonstrated that the IA-derived aliphatic polyamides with ethylene diamine showed the highest thermal stability of all the used diamines with the alkylene carbon number from 2 to 8 [2]. The salt monomer method similarly to the procedure of the IA-derived polyamides with only aromatic diamines was performed to create the aromatic/aliphatic polyamide successfully. N, N-dimethylformamide (DMF) solution into iPrOH (DMF: iPrOH 5/95) with 2-3 times washing with acetone to remove impurity and catalyst. Even if two different diamines were mixed with IA, the salt monomers in any compositions were obtained as white powders. As a result, the aromatic/aliphatic copolyamides were expectedly prepared (Table 2); M_w and M_n ranges 33600-78400 and 15500-28300, respectively, which were comparable with those of aromatic polyamides. Polydispersity values ranged M_w/M_n ranged between 2.0-2.7, and were narrow enough to study further. T_g and T_{10} of the copolyamides Incorporation of aliphatic moiety into the aromatic polyamide backbone make the fibers softer and tougher than the aromatic polyamide ones, which make use to investigate the mechanical behavior of the IA-derived polyamides. The results of the tensile test of the fibers of the copolymers with different molar ratios of diamine monomers are shown in Table 2. E and σ ranged between 0.2-2.3 GPa and 20-72 MPa, respectively, showing maximal values at an aromatic composition of 0.05 in polyamides while ε ranged between 0.04-0.07 independent on the composition and not very high. Overall the IA-derived polyamide fibers were hard and ductile even if the aliphatic ethylene moiety was incorporated into the aromatic backbones, and the aromatic composition of 0.05 mol% gave the mechanically strongest fiber, presumably owing to the best structural balance of the aromatic/aliphatic moiety of all the samples prepared here.

Table 2. Molecular weights and thermomechanical properties of itaconic acid-derived co-biopolyamides with aromatic/aliphatic diamines

Composition[a]	M_w[b] (g/mol)	M_n[b] (g/mol)	M_w/M_n[b]	T_g[c] (°C)	T_{10}[d] (°C)	E[e] (GPa)	σ[e] (MPa)	ε[e]	Yield (wt%)
0.30/0.70	33600	15500	2.1	148	397	-	-	-	78
0.25/0.75	46200	20100	2.2	147	394	0.2	20	0.04	82
0.20/0.80	45700	16400	2.7	145	375	0.5	42	0.04	85
0.15/0.85	54100	22900	2.3	142	374	0.9	31	0.06	89
0.10/0.90	58700	22600	2.5	133	376	1.2	62	0.05	81
0.05/0.95	78200	28300	2.7	132	374	2.3	72	0.05	92
0.03/0.97	62900	23700	2.6	129	370	1.5	61	0.06	88
0.01/0.99	48300	21300	2.2	119	353	1.4	47	0.07	84

[a] Composition refers to in fed molar ratio of *p*-phenylenediamine/ethylenediamine in IA-derived copolyamides [b] Weight-average, M_w, number-average molecular weights, M_n, and polydispersity index (M_w/M_n) were measured by gel permeation chromatography with pullulan standards. [c] Glass transition temperatures, T_g, were measured by differential scanning calorimetry under nitrogen at a scanning rate of 10 °C min^{-1}. [d] 10 % weight-loss temperatures, T_{10}, were measured by thermogravimetry under nitrogen at a heating rate of 10 °C min^{-1}. [e] Mechanical properties such as E (young moduli), σ (tensile strength), and ε (elongation at break) were measured by a tensile test at a stretching rate of 1 mm/s at a room temperature.

T_g and T_{10} of the polymer decreased from 148 to 119 °C (DSC; representative curves, Fig. 3) and from 397 to 353, respectively, with a decrease in an aromatic monomer composition from 0.30 to 0.01. The tendency suggests the successful incorporation of aliphatic moiety into aromatic backbones. T_g of the copolyamides kept much higher values than those of conventional nylons (6,6-nylon: 57 °C) [19] while T_{10} was comparable with those of 6,6-nylon (390 °C) [20]



Scheme 2. Syntheses of copolyamides via salt monomers of itaconic acid with *p*-phenylenediamine and 1,2-ethylenediamine with itaconic acid

The moisture absorption for the polyamides is generally a serious problem decreasing stability, T_g, and elastic modulus. The aromatic/aliphatic IA-derived copolyamide showed the moisture absorption around 1.5-2.1 wt % less than those of the conventional polyamides 6-nylons or 6,6-nylons (8-10%) [18], Conventional polyamides should have stronger amide interaction with water molecules than IA-derived polyamide without NH hydrogen in the pyrrolidone ring. In addition, the moisture absorption values of aromatic/aliphatic copolyamides were lower than those of aromatic or aliphatic polymers (ca.3 wt% and 4 wt%, respectively), which might be related with the abovementioned good structural balance in the aromatic/aliphatic moiety.

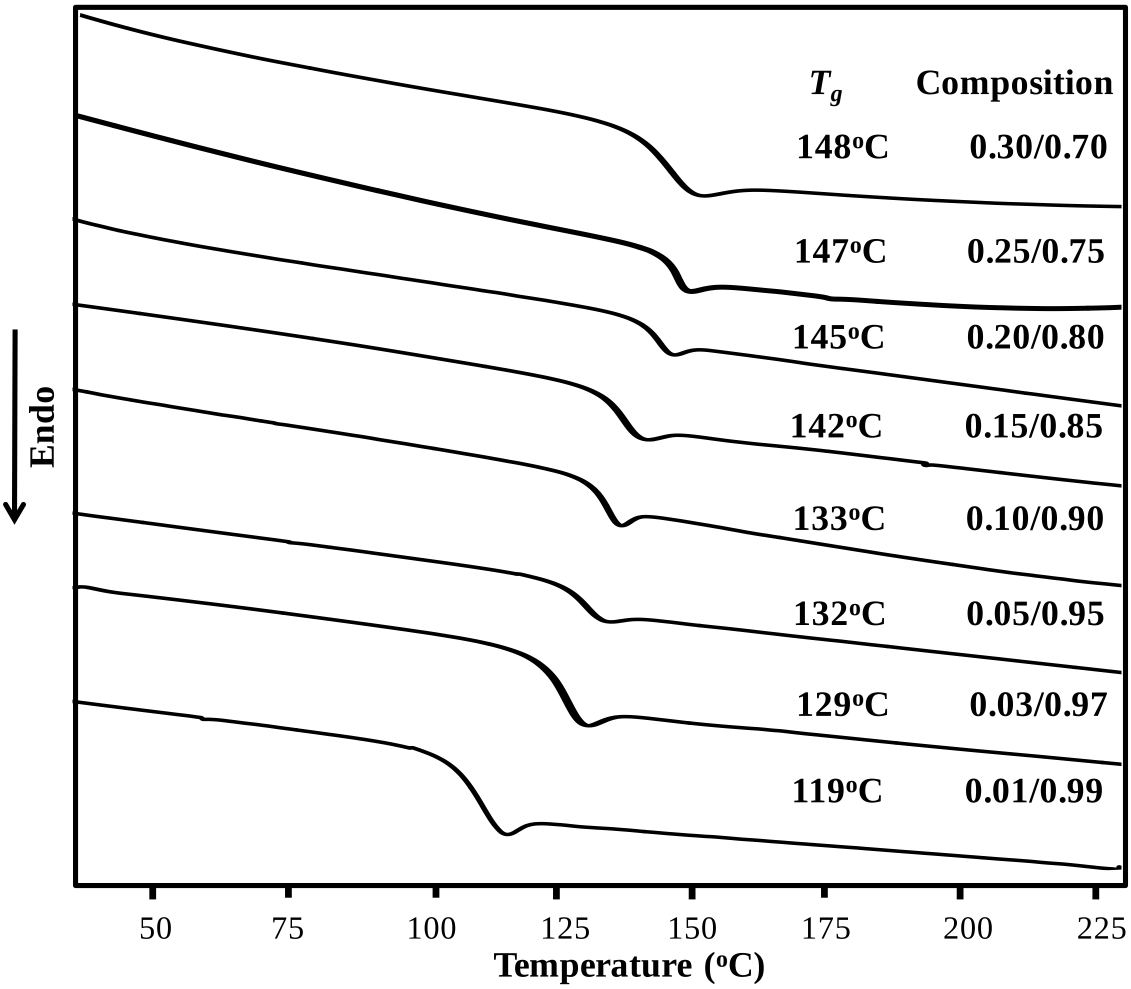


Figure 3. Differential scanning calorimetry thermograms for aromatic/aliphatic IA-derived polyamides

4. Polyamide degradation

We previously found photo-induced solubilization of IA-derived aliphatic polyamides under the irradiation of high pressure mercury-lamp with a wavelength of 250-450nm [2]. In the present IA-derived polyamides, the photo-induced dissolution was also confirmed in both of the aromatic polyamide and aromatic/aliphatic copolyamides under the 48 hrs irradiation of UV lamp with a wavelength of 280-400 nm that are in the range of sun light, due to ring-opening reaction of pyrrolidone instead of amide lysis of general polyamide backbones as shown in the final step of Scheme 1 [2]. If the polyamides such as Nylon^{TM} fish lines floating on the sea became water-soluble by photoreaction under the sunlight, the present phenomenon might induce to overcome the plastic waste problems to marine creatures. Sunlight UV-A and UV-B rays corresponding with the wavelength of the used UV-lamp can reach to the earth's atmospheres and can induce the degradation for sensitive functionality of the pyrrolidone rings shown in Fig 4.

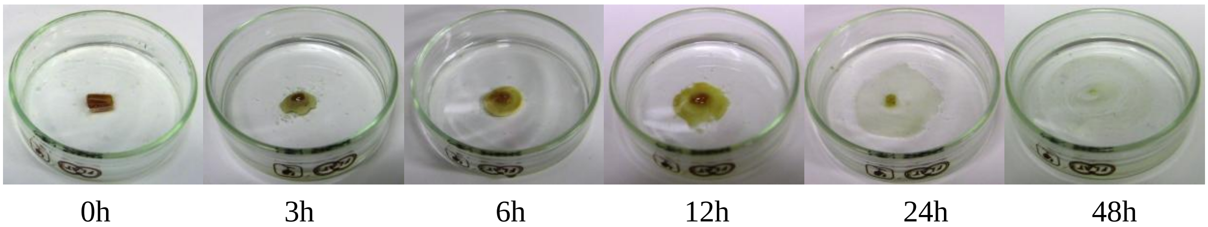


Figure 4. Time course of water-solubilization behavior of polyamide resin derived from itaco itaconic acid with *m*-xylenediamine by high-pressure mercury lamp irradiation with wave-length ranging 250-450 nm.

We finally examined the degradation under the soil at pH 7.5-7.9. The polyamide resines were buried and kept over one year. After picking up, the polyamides showed weight loss values of 34 wt %, 100 wt %, 76 wt% and 23 wt% for PA-I, PA-III, PA-IV, and PA-II, respectively. The in-soil degradations of the aromatic polyamides were more efficient than the well-known degradable polymer of poly(lactic acid), PLA, showing 16 wt% weight loss as shown in Fig. 5 although the thermal performances of the polyamides were much higher than those of PLA (T_g 60°C) [21], which may be also attributed by the ring-opening hydrolysis of the pyrollidone ring by rain water or other environmental functions inducing the water-solubilization. The weight loss of the polyamides due to soil corrosion was accompanied with the changes in shape and colors resulted from not only chemical factors but also physical and biological processes [2, 22-23].

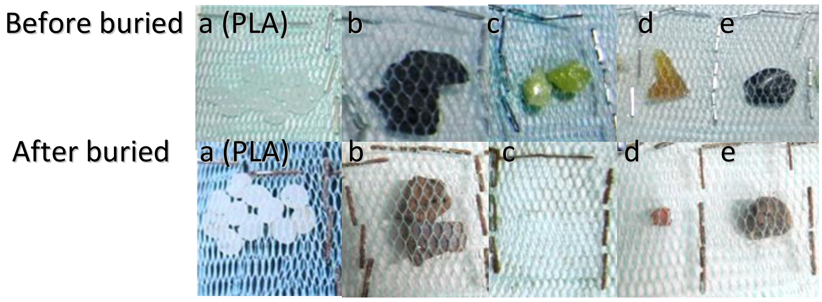


Figure 5. In-soil degradation behavior of IA-derived polyamides Top pictures are samples just before bury while bottom pictures are samples taken after keeping them in soil one year. a) poly(lactic acid) (PLA), b) PA-I (4,4’-diaminodiphenylether), c) PA-III (*m*-xylenediamine) d) PA-IV (*p*-xylenediamine), e) PA-II (*p*-phenylenediamine).

5. Conclusion:

We have prepared itaconic acid-derived polyamides with aromatic diamines by melt-polycondensation of the corresponding salt monomers where the acid moiety adjacent to the amine moiety avoiding side reactions. The molecular weight was greater than 33600 g/mol. Glass transition temperatures, T_g, and 10 % weight loss temperatures, T_{10}, ranged 156-242 ^oC and 370-400 ^oC, respectively, which were much higher than those of conventional bio-based plastics such as poly(lactic acid) (T_g 60 ^oC) and polyamide 11 (T_g 29 ^oC) [24]. However their processability was very low to give too brittle fiber to use as specimens of mechanical tests. We then incorporated an appropriate amount (0.05 mol% to total diamines) of aliphatic moiety into the aromatic backbones to prepare the high-performance and processable polyamides with T_g of 132 ^oC, T_{10} of 374 ^oC, E of 2.3 GPa, and σ of 72 MPa, respectively. Moreover moisture absorption ratio of the aliphatic/aromatic polyamides were very low 1.5-2.1 wt % and less than those of the conventional polyamides 6-nylons or 6,6-nylons. The degradation behaviors of IA-derived polyamides were shown under ultra-violet light irradiation whose wavelengths were contained in sunlight and in the soil. The present polyamides with high thermomechanical performance but degradability were very important to overcome the plastic waste problem and reduce threat for the life of marine creatures.

Notes

The authors declare no competing financial interest.

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