

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



Mohammad Asif Ali, Seiji Tateyama, Tatsuo Kaneko^{*}

School of Materials Science, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Nomi, Ishikawa 923-1292 Japan

ARTICLE INFO

Article history:

Received 20 January 2014

Received in revised form

28 April 2014

Accepted 13 May 2014

Available online 11 June 2014

Keywords:

Itaconic acid

Bioplastics

Polyamides

Heterocycles

Biodegradation

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 33,600 g/mol. Glass transition temperatures, T_g , and 10% weight loss temperatures, T_{10} , ranged 156–242 °C and 370–400 °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 °C and T_{10} over 355 °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.

© 2014 Elsevier Ltd. All rights reserved.

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-pyrrolidines 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*-xylenediamine (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

^{*} Corresponding author. Tel.: +81 761 51 1631; fax: +81 761 51 1635.

E-mail address: kaneko@jaist.ac.jp (T. Kaneko).

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 °C 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 °C under slow agitation and kept for 6–8 h. 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 °C 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 $\text{DMSO}-d_6$ 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 °C/min between 0 and 200 °C (EXSTAE6100; Seiko Instruments Inc., Chiba, Japan). Thermogravimetry (TGA; SSC/5200

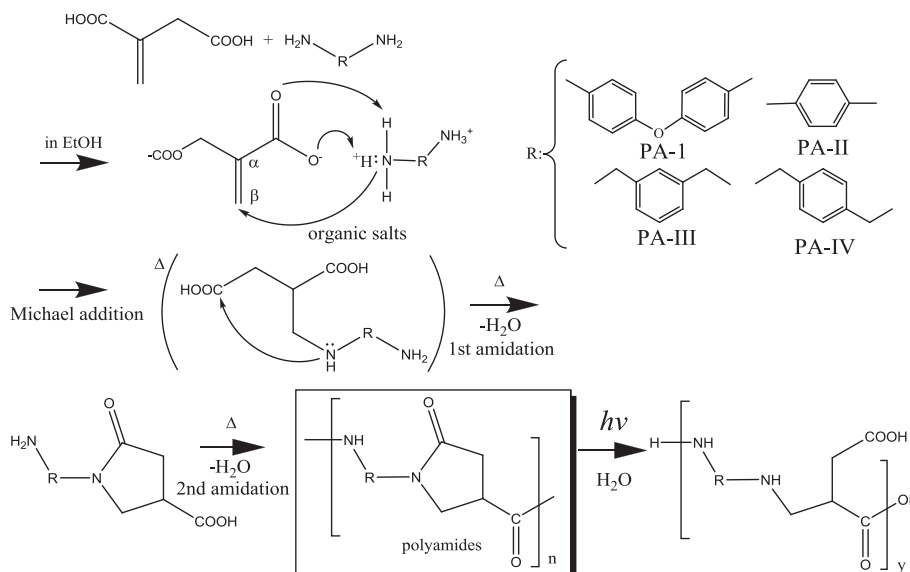
SII Seiko Instruments Inc.) was carried out to determine 10% weight-loss temperature by heating from 30 to 800 °C at a rate of 10 °C/min under a nitrogen atmosphere. Stress-strain analyses were performed with crosshead speed at 1 mm/s at a room temperature using a tensile testing machine (INSTRON, Canton 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 ^1H 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 °C.

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-Michael 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



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

Download English Version:

<https://daneshyari.com/en/article/5201695>

Download Persian Version:

<https://daneshyari.com/article/5201695>

[Daneshyari.com](https://daneshyari.com)