

# The degradability and thermal properties of chiral polyamide-imides synthesized from several L-amino acids: Side group effects

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## ARTICLE INFO

### Keywords:

Chiral polyamide-imides (PAIs)  
Glass transition temperature (T<sub>g</sub>)  
Degradability  
Hydrophilicity

## ABSTRACT

A series of chiral optically active monomers were prepared from L-amino acids with different structures. These monomers were polymerized to chiral polyamide-imides (PAIs) via an eco-friendly direct polycondensation process. The glass transition temperature (T<sub>g</sub>) values were obtained by differential scanning calorimetry (DSC), and showed that the rigid and bulk effect of the substituents will co-affect the T<sub>g</sub> values of the polymers. Their degradability were studied via soil degradation experiments, and the variations of water contact angles, molecular weights, structure and appearance during degradation were characterized by contact angle tester, gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM) respectively. The results revealed that the damages of polymer chains started with the amide bonds, and then proceed to the imide rings. With degradation, PAI films' hydrophilicity raised, and when introduced amino acids with longer carbon chain or bulky ring into the polymers' backbone, their degradability decreased.

## 1. Introduction

Nowadays, polymer materials play an increasingly important role in people's lives. They have changed our life greatly. While polymer materials bring convenience to us, their difficult degradability brought multiple potential hazards on ecological security and human survival, so it has been a hot trend to develop green materials and biomaterials, especially degradable materials [1–6].

Polyamides and polyimides are well-known materials that exhibit excellent thermal, mechanical and outstanding chemical resistance. However, its use in some fields is limited by their low solubility, high glass-transition temperatures (T<sub>g</sub>) and stiffness [7]. Polyamide-imides derived from amino acids are a kind of high-performance material, which have overcome these shortcoming and combine the thermal resistance properties of polyimides and easy machinability of polyamides [8,9], moreover, the incorporation of amino acids give PAIs better solubility, biocompatibility and degradability [10–12]. Tian et al. [13,14] have committed to the synthesis of the PAIs. Zou et al. [15] synthesized a degradable and hydrophilic PAI through incorporating L-amino acids unit into the polymer backbone, which solve the PEEK non-degradable and surface hydrophobic issues in bone repairing implants. Along with the materials performance requirements increasingly strict, it is important to develop controllable degradation rate polymers that with the

capacity of thermal stability and other good performance. And these properties could be affected by the sequence or structure of the monomers in a multi block polymers, but there are very few reports on it [16–18].

The main purpose of this paper is to understand the effect of side group structures on thermal properties and degradation rate of obtained PAIs. The side group effect is easy to achieve by controlling the sorts of amino acids that incorporated to PAIs. So six kinds of PAIs derived from L-amino acids that with different rigidities and side chain lengths were prepared by direct polycondensation process at 120 °C. The effects of amino acids' structure on PAIs' thermal properties and degradability were evaluated by thermal tests and soil degradation experiments respectively.

## 2. Experimental

### 2.1. Materials

L-alanine, L-phenylalanine, L-2-aminobutyric acid, L-norvaline, L-methionine, L-tryptophan and 4,4'-diaminodiphenyl ether (ODA) were provided by Shanghai Darui Fine Chemical Co. Triphenyl phosphite (TPP) was purchased from Macklin Biochemical Co. (Shanghai). Pyromellitic dianhydride (PMDA) was purchased from Shijiazhuang

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Haili Fine Chemicals Co. (China). N-methyl-2-pyrrolidone (NMP) was purchased from Tianjin Chemical Reagent Mao (Business). Pyridine (Py) was purchased from Tianjin Guangfu Fine Chemical Research Institute. Anhydrous calcium chloride ( $\text{CaCl}_2$ ) was purchased from Tianjin Baishi Chemical Research Institute. All chemicals were used directly without further purification. N,N-dimethylformamide (DMF) and Anhydrous ethanol were purchased from Tianjin Fuyu Fine Chemical Co. Dimethyl sulfoxide (DMSO).

## 2.2. General characterization

Proton nuclear magnetic resonance  $^1\text{H}$  NMR were carried out on a Bruker AVANCE II 400 MHz spectrometer (Swiss) in deuterated dimethyl sulfoxide ( $\text{DMSO}-d_6$ ) as solvent. Fourier transform infrared (FTIR) spectra were done by a Thermo Fisher IS10 spectrophotometer (America) in KBr. Specific rotations were determined with concentration of 0.2020 g/100 mL in DMF at 25 °C by a MCP-200 polarimeter (Anton Par, Austria). Elemental analyses were recorded using Elementar Vario EL model element analyses equipment (Germany). The gravimetric analysis (TGA) was performed using a TGA 1 SF/1100 instrument (Germany) under nitrogen ( $\text{N}_2$ ) atmosphere with a flow rate of 10 °C/min. The glass transition temperatures of polymers were recorded by Q-100 differential scanning calorimetry (DSC; TA instruments, America) instrument at a heating rate of 10 °C/min. The molecular weights of polymers were analyzed with gel permeation chromatography (GPC) and multi-angle laser light scattering (MALLS, Dawn Heleos), using a linear MZGel SD Plus GPC column set (two columns, 5  $\mu\text{m}$  particles, 300  $\times$  8 mm) with DMF as eluent at room temperature with a flow rate of 1 mL/min and a concentration of the polymer of ca. 1 mg/mL. The calibration was based on polystyrene standard. A UV-Vis detector at  $\lambda = 254$  nm and a RI detector were used for the signal recording. The water contact angles of polymers were characterized in SL200B type contact angle tester (Kenuo, USA).

## 2.3. Synthesis of chiral diacid monomers

Chiral diacid monomers (2a-2f) were obtained by the condensation of pyromellitic dianhydride and various amino acids according to our previous works (see **step 1** in **Scheme 1**) [19]. Yields and physical properties of the diacid monomers are described in **Table 1**.

## 2.4. Synthesis of chiral polyamide-imides (PAI3a-PAI3f)

Chiral polyamide-imides (PAI3a-PAI3f) were synthesized by direct polycondensation of diacid monomers with 4,4'-diaminodiphenyl ether

under the reported procedure (see **step 2** in **Scheme 1**) [12,20]. Yields and physical properties of polymers are showed in **Table 2**.

## 2.5. Preparation of PAI films

The prepared 0.25 g of PAI was putted into beaker with 10 mL DMF under sufficient stirring until dissolved completely. Then the solution was added into a Teflon mold with the diameter of 5 cm. After that, by removing the solvent under intensive vacuum drying oven of 50 °C, the pieces of clear yellow flexible PAI films was obtained.

## 2.6. Soil degradation of PAI films

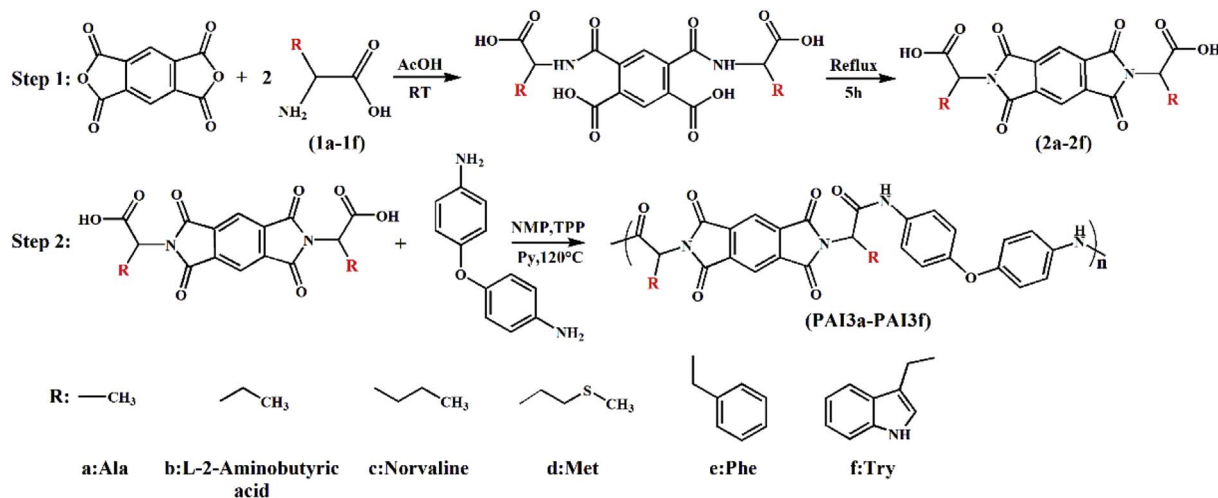
The moist soil was collected from outdoor covered by lush vegetation. After sieving out the bulky grain and the remaining vegetation, the obtained soil with uniform particles was placed into six crystallizing dishes in reserve. Then, each PAI film was divided into four units and buried in a petri dish with 200 g of moist soil as shown in **Fig. 1**. Throughout the experiment, the water-holding ratio of the soil was maintained at 30% by weighting and adding water if necessary periodically. The PAI films were picked out at certain time intervals (weeks 4, 6, 8, 12) and then washed and dried at room temperature to a constant weight [21].

## 3. Results and discussion

### 3.1. Characterization on polymers

**Fig. S3** displays FTIR spectra of chiral PAI3a-PAI3f. In the IR spectra, the polymers show characteristic carbonyl absorptions resulting in imide ring at 1773 ( $\text{C}=\text{O}$  asymmetric stretching vibration) and 1711  $\text{cm}^{-1}$  ( $\text{C}=\text{O}$  symmetric stretching vibration), while the amide  $\text{C}=\text{O}$  stretching appears at 1654  $\text{cm}^{-1}$  (amide  $\text{C}=\text{O}$  asymmetric stretching vibration) and 1608  $\text{cm}^{-1}$  (amide  $\text{C}=\text{O}$  symmetric stretching vibration). The specific absorption peak of C-C stretching vibration on benzene ring exists in 1494  $\text{cm}^{-1}$ . The typical C-N stretching of aromatic-imide observed at 1383  $\text{cm}^{-1}$ , and the absorption peak of C-O-C asymmetric vibration on aromatic nucleus appears at 1211  $\text{cm}^{-1}$ . A strong peak at 834  $\text{cm}^{-1}$  is corresponded to the C-H outside bending vibration on benzene ring. In addition, a broad bands between 3300 and 2500  $\text{cm}^{-1}$  are ascribed to amide N-H and  $-\text{CH}_2$ -stretches. The absorption peak at 721  $\text{cm}^{-1}$  may be attributed to the  $\text{C}=\text{O}$  bending vibration on imide five-membered ring [22].

The  $^1\text{H}$  NMR spectrum of PAI3a is showed in **Fig. 2**, and  $^1\text{H}$  NMR spectra of PAI3b-PAI3f are displayed in **Fig. S4**. A distinct response for



**Scheme 1.** Polymerization scheme of PAI3a-PAI3f.

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