NEW OPTICALLY ACTIVE ORGANO-SOLUBLE POLY(AMIDE-IMIDE)FS FROM [N,N′-(4,4’-DIPHTALOYL)-BIS-L-AMINO DIACID]S AND 1,2-BIS[4,4’-AMINOPHENOXY] ETHANE: SYNTHESIS AND CHARACTERIZATION

AKRAM FEYZI, KHALIL FAGHIHI*, AHAMD RAEISI, MARYAM KOUSHKI, MANSOURE FARAHANI

Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, Arak University, Arak, 38156-8-8349, Iran
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ABSTRACT

Six new dicarboxylic acids 3a-f were synthesized by the reaction of 3,3’,4,4’-biphenyltetraarylcarboxylic dihydride (BPDA) 1 with L-amino acids 2a-f in a solution of glacial acetic acid/pyridine (Py) at refluxing temperature. Then six new optically active poly(amide-imide)s (PAI)s with good inherent viscosities were synthesized by direct polycondensation reaction of [N,N’-(4,4’-diphtaloyl)-bis-L-amino diacid]s with 1,2-bis[4,4’-aminophenoxy] ethane (APE) 4 in a medium of N-methyl-2-pyrrrolidone (NMP)/ triphenyl phosphite (TPP)/ calcium chloride (CaCl₂)/pyridine. Not only PAIs are optically active but also soluble in various organic solvents. These resulting new polymers can be used in column chromatography for the separation of enantiomeric mixtures. The resulted polymers were fully characterized by means of FTIR, H-NMR spectroscopy, elemental analyses, inherent viscosity, specific rotation, solubility tests and UV-Vis spectroscopy. Also thermal properties of the PAIs 3a-f were investigated using thermal gravimetric analysis (TGA).

Keywords: Poly(amide-imide); Thermal properties; Organo-soluble polymer; Inherent viscosity.

INTRODUCTION

Since their development in the 1960s, polyimides have become an important class of polymers, finding a wide range of applications in the aerospace and microelectronics industries. Aromatic polyimides are well known high-performance polymers because of their excellent thermal stability, mechanical and electrical properties and chemical resistance [1, 2]. However, polyimides are often insoluble and intractable characteristics resulting in processing difficulties which limit their applications [3].

Modification of high performance polymers by increasing the solubility and lowering the transition temperatures while maintaining thermal stability are of particular interest. Copolycondensation is one of the possible ways for modification of polymer properties. Thus, processing of polyimides many copolymides, such as poly(amide-imide)s, poly(ester-imide)s, and other copolymides have been prepared [4-9]. The synthesis of poly(amide-imide)s is more attractive than the other methods of copolymerization, because solubility and processability can be improved without significantly sacrificing the thermal and mechanical properties, they are useful in numerous applications in electrical wire enamel, adhesives, and injection-molding and extrusion products [10-12]. These polymers are a type of chemicals materials, which could become one of the new sources of a family of environmentally friendly. We use amino acids as chiral agents which are often naturally occurring compounds therefore synthetic polymers based on amino acids are expected to be biodegradable and biocompatible.

This paper reports the preparation and basic characterization of photosensitive and thermally stable poly(amide-imide)s (PAI)s 5a-f by the direct polycondensation reaction of [N,N’-(4,4’-diphtaloyl)-bis-L-amino diacid]s with 1,2-bis[4,4’-aminophenoxy] ethane (APE) 4 in a medium consisting of N-methyl-2-pyrrrolidone (NMP), triphenyl phosphite (TPP), calcium chloride (CaCl₂) and pyridine (Py). As reported previously, APE has been synthesized through a two step reaction starting from 4-nitro phenol and 1,2- dibromo ethane in the presence of potassium carbonate, followed by catalytic reduction with hydrazine monohydrate 10% Pd/C [13-15].

EXPERIMENTAL

Materials

3’, 3’, 4, 4’-Biphenyltetraarylcarboxylic dihydride (1; Aldrich), L-alanine 2a, L-valine 2b, L-leucine 2c, L-2-amino-2-phensalicyclic acid 2d, L-phenylalanine 2e and L-2-amino-butyrinic acid 2f (Merek) were used without previous purification. Diamine APE 4 (mp = 115-117°C) was prepared according to our previous work [16]. NMP (Fluka), Py (Acros) and TPP (Merek) were used as received. Commercially available CaCl₂ (Merek) was dried under vacuum at 150 °C for 6 h.

Techniques

1H-NMR and 13C-NMR spectra were recorded on a Bruker 300 MHz instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solid were performed by using KBr pellets. Vibration transition frequencies were reported in wave numbers (cm⁻¹). Band intensities were assigned as weak (w), medium (m), shoulder (sh), strong (s) and broad (br). Inherent viscosities were measured by a standard procedure by using a Technico Regd Trad Mark Viscometer. UV-Vis absorptions were recorded at 25°C in the 270–790 nm spectral regions with a Perkin-Elmer Lambda 15 spectrophotometer on DMP solution by using cell lengths of 1 cm. Specific Rotations were measured by an A-Kruss polarimeter. Thermal Gravimetric Analysis (TGA and DTG) data of polymers were taken on a Mettler TA4000 System under N₂ atmosphere at rate of 10°C/min. Elemental analyses were performed by Vario EL equipments.

Monomer synthesis

[N, N’-(4,4’-diphtaloyl)-bis-L-amino diacid]s 3a-f, 2.942 g (10.00 mmol) of 3, 3’, 4, 4’-biphenyltetraarylcarboxylic dihydride 1, 2.00 mmol of L-amino acids 2a-f, 80 mL of mixture of acetic acid/pyridine (3:2) and a stirring bar were placed into a 250-mL round-bottomed flask. The mixture was stirred at room temperature overnight and refluxed for 4-10 h. The solvent was removed under reduced pressure, and the residue was dissolved in 100 mL of cold acetic water. A white to cream precipitate was formed, filtered off, and dried to give compounds [N, N’-(4,4’-diphtaloyl)-bis-L-amino diacid] 5a-f.

Polymer synthesis

A mixture of di carboxylic acid 3a-f (1 mmol), di amine APE 4 (1 mmol), calcium chloride (0.350 g), TPP (0.8 ml), pyridine (1.2 ml) and NMP (4.0 ml) was refluxed for 10 h. After cooling, the reaction mixture was poured into methanol (50 ml) to precipitate the corresponding polymer. The precipitated polymer was then separated by vacuum filtration and washed with methanol (30 ml) and hot water (100 ml) and dried at 120°C under vacuum for 24 h. IR and NMR spectroscopic results of the obtained polymers will be discussed in the Results and Discussion section.

RESULTS AND DISCUSSION

Monomer synthesis

Asymmetric di carboxylic acids 3a-f were synthesized by the condensation reaction of 3,3’,4,4’-biphenyltetraarylcarboxylic dihydride 1 with two equimolars of L-alanine 2a, L-valine 2b, L-leucine 2c, L-2-amino-2-phenylacetic acid 2d, L-phenyl alanine 2e and L-2-amino-butyrinic acid 2f in an acetic acid/pyridine solution. In this work, we used six diacids 3a-f for direct polycondensation (Scheme 1). Di acid 3e was synthesized previously [17]. The yields and some physical properties of these compounds are shown in Table 1. Chemical structure and purity of the optically active di carboxylic acids 3a-f were proved by using elemental analysis, FTIR, H-NMR and 13C-NMR spectroscopic techniques. These data are shown in Table 2.
Yields and some physical properties of chiral di carboxylic acids 3a-f.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Amino acid</th>
<th>Yield (%)</th>
<th>Mp (°C)</th>
<th>$[\alpha]_D^{20}$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>L-Alanine</td>
<td>94</td>
<td>287-289</td>
<td>-7.5</td>
</tr>
<tr>
<td>3b</td>
<td>L-Valine</td>
<td>92</td>
<td>270-271</td>
<td>+4.5</td>
</tr>
<tr>
<td>3c</td>
<td>L-Leucine</td>
<td>83</td>
<td>275-277</td>
<td>+2.1</td>
</tr>
<tr>
<td>3d</td>
<td>L-2-amino-2-phenyl acetic acid</td>
<td>91</td>
<td>245-246</td>
<td>-8.2</td>
</tr>
<tr>
<td>3e</td>
<td>L-Phenyl alanine</td>
<td>94</td>
<td>295-297</td>
<td>-6.5</td>
</tr>
<tr>
<td>3f</td>
<td>L-2-Aminobutyric acid</td>
<td>88</td>
<td>263-265</td>
<td>+14.6</td>
</tr>
</tbody>
</table>

(a) Measured at a concentration of 0.5 g/dl in DMF at 25°C.

These FTIR data showed absorption around 2500 and 3400 cm$^{-1}$, which was assigned to the COOH groups. Peaks appearing at around 1700-1770 cm$^{-1}$ (acid C=O and symmetric imide stretching), 1390-700 cm$^{-1}$ imide characteristic ring vibration) confirmed the presence of imide ring and carboxylic groups in these compounds. Also $^1$H-NMR data showed carboxylic acid and imide carbons and aromatic carbons in related signals.

As an example, the $^1$H-NMR spectrum of diacid 3f showed peaks between 0.84 and 0.89 ppm as a triplet, which was assigned for two CH$_2$ group (d) peak between 2.04 and 2.18 ppm as a multiplet, which was assigned to the CH (b) protons, which are chiral centers. The peaks at 8.04-8.35 ppm were assigned to aromatic protons (e, f and g). Also a broad peak in 12.95 ppm was assigned to COOH groups (Fig. 1). The measured results in elemental analyses of these compounds were closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained.

**Polymer synthesis**

The direct polycondensation of a diacylic acid and the diamine is one of the well-known methods for (PAI)s synthesis. In this work, we synthesized (PAI)s 5a-f containing ether and methylene moieties by direct polycondensation reactions of six chiral [N,N'-(4,4'-diphtaloyl)-bis-L-amino diacid3-f with 1,2-bis[4,4'-aminophenoxyl] ethane 4 by using triphenyl phosphate (TPP) and pyridine as condensing agents (Scheme 2).

All the polycondensations proceeded readily in a homogeneous solution. Tough and stringy precipitates formed when the viscous polymer solutions were trickled into the stirring methanol.

Yields and some physical properties of these new (PAI)s 5a-f are given in Table 3. All the polymers were obtained in high yields (82-94%), and the inherent viscosities (0.30-0.45 d/l)g was measured in DMF solutions. Due to the presence of chiral amino acid moieties 2a-f in the polymer backbone, the polymers 5a-f are optically active and the specific rotations are given in Table 3. Also the resulting polymers have a range of color between cream and light brown.
The absorption bands of amide groups appeared at 3340 cm\(^{-1}\) (N-H stretching). All of these PAIs exhibited strong absorption at 1675 (m), 1638 (w), 1587 (m), 1465 (m), 1385 (s), 1321 (w), 1245 (m), 1140 (m), 1052 (m), 922 (m), 743 (m). The polymer showed the C=O asymmetric stretching at 1714 cm\(^{-1}\) and C-N stretching at 1375 cm\(^{-1}\). The FT-IR peaks of PAIs 5a-f were in agreement with the calculated values for the proposed structure (Table 5).

### Solubility of the PAIs
Solubility of (PAIs) 5a-f was investigated as 0.01 g of polymeric sample in 2 mL of solvent. These poly(amide-imide)s have good solubility in aprotic organic solvents. Remarkably, all of these PAIs were easily soluble at room temperature in aprotic polar solvents such as NMP, N, N’-dimethylacetamide (DMAc), N,N’-dimethylformamide (DMF), and insoluble in solvents such as chloroform, ethanol and methanol. It is due to the flexibility effect of the etheric structure of the diamine (Table 6).

### UV-Vis Absorption characteristics
Photo-sensitive property of the new poly(amide-imide)s 5a-f in the DMF solution was studied by a UV spectrophotometer. All polymer solutions exhibit...
the same two positions of absorption maximum in UV-Vis spectra at 330–337 nm. The absorption maximum at around 340 nm corresponds to $n \rightarrow \pi^*$ transition of the nonbonding electrons which is present in nitrogen and oxygen atoms in the polymer backbone. The UV-Vis absorption spectrum of PAI 5f in DMF is shown in Fig. 4. The spectrum of PAI 5f exhibited a typical peak around 330 nm ($n \rightarrow \pi^*$ transition).

**Fig. 4.** UV-Vis absorption spectrum of PAI 5f in DMF solution

**Thermal properties**

TGA and derivative of thermogravimetric (DTG) analysis at a rate of 10 °C/min in a nitrogen atmosphere were utilized to examine the thermal properties of the PAIs. Obtained results are summarized in Table 7. Figure 5 shows TGA results of the PAIs 5b and 5d, respectively.

The thermal stability of the polymers was studied on the basis of 5% and 10% weight losses ($T_{5\%}$ and $T_{10\%}$, respectively) of the polymers and the residue at 800 °C (char yield). The results revealed that the PAIs were thermally stable up to 400 °C (Table 7).

The char yield can be applied as a decisive factor for estimating the limited oxygen index (LOI) of polymers using Van Krevelen and Hoftyzer's equation [18]:

$$\text{LOI} = 17.5 + 0.4CR$$

Where CR is the char yield.

PAIs 5b and 5d had LOI values around 35, which were calculated from their char yield. On the basis of the LOI values, such macromolecules can be classified as self-extinguishing polymers.

**Table 7.** Thermal behavior of PAIs 5b and 5d.

<table>
<thead>
<tr>
<th>polymer</th>
<th>$T_{5%}$ (°C)</th>
<th>$T_{10%}$ (°C)</th>
<th>Char yield (%)</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>5b</td>
<td>420</td>
<td>460</td>
<td>45</td>
<td>35.5</td>
</tr>
<tr>
<td>5d</td>
<td>412</td>
<td>450</td>
<td>46</td>
<td>35.9</td>
</tr>
</tbody>
</table>

$^a$ Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10 °C/min under N₂.

$^b$ Weight percentage of material left after TGA analysis at a maximum temperature of 800 °C under N₂.

$^c$ Limiting Oxygen Index (LOI).

**CONCLUSIONS**

In this article, we have successfully synthesized 6 dicarboxylic acid 3a-f containing amino acidic moieties. A series of new thermally stable PAIs 5a-f were prepared from chiral [N, N’-(4, 4’-diphtaloyl)-bis-L-amino diacid]s 3a-f with 1,2-bis[4,4’-aminophenoxy] ethane 4 by direct polycondensation method. The results presented here also clearly demonstrate that incorporating the imide group into the polymer main chain as well as combination of the wholly aromatic backbone and several functional groups enhanced the thermal stability of the new polymers. These polymers are expected to have high solubility due to the presence of the alkyl groups in the polymer chain. These properties could make these PAIs attractive for practical applications such as processable high-performance engineering plastics, column chromatography for the separation of the enantiomeric mixtures.

**REFERENCES**